AIR POLLUTANT
EMISSION FACTORS

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TRW
SYSTEMS GROUP OF TRW INC.

This report contains an updating of selected existing emission factors in addition to twenty new factors compiled for the National Air Pollution Control Administration, Division of Air Quality and Emission Data, under contract CPA-22-69-119.

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I. INTRODUCTION

1. INTRODUCTION

This report represents a compilation of the latest atmospheric emission data available for a wide variety of selected processes. One-half of the 40 processes discussed in this report involve an updating or review of existing emission factors presented in Public Health Service Publication 999-AP-42, "A Compilation of Air Pollutant Emission Factors" by R.L. Duprey. The remaining factors represent new processes for which emission factors were not previously reported. All emission factors refer to uncontrolled processes unless otherwise stated.

Information for emission factors was gathered primarily from the technical literature up to November 1969, state and local air pollution control agencies, trade and professional associations, releasable portions of data obtained by TRW in various past studies, and individual companies and persons within the various industries under study. In all cases, attempts were made to obtain some idea of the validity of the information obtained, and thus place each bit of data relative to other data in the same area. Greatest weight was given to actual measured emission data, i.e., source tests, especially when the measuring technique was known. Estimates of emissions were also made when feasible by making material balances and process loss or yield calculations.

In general, it was found that except for the combustion and incineration fields, very little new emission factor data has been made public since Duprey's work in 1967. In the metallurgical and mineral industries, additional emission data has been obtained by various companies and control equipment manufacturers. This information has not been made public, however. Some emission data was available for most of the new factors developed in this report. Frequently, however, these data were in the form of concentrations only, not quantitative emission rates. Process weight rates were also frequently not given or reported. Considerable engineering calculations were thus required in order to put these data into a form usable for emission factors. These calculations, based on material balances, combustion reactions, humidity balances, and comparisons with similar processes with available emission data, allowed one to relate the reported data with process throughputs and develop a factor which is usable until better data are made available.

Detailed information used to obtain the emission factors is generally presented in an appendix to each section. Selection of a final emission factor depended on the amount and range of data available. Where considerable data existed a direct arithmetic average was used. Values on order of magnitude greater or less than the bulk of the data were not considered in determining the arithmetic average. Where limited data were available (1 to 5 values) and the values covered a wide range, the selected factor was based on our best judgment considering the factors affecting emissions. Whenever possible, the range or variation in emission factors was reported and shown in parenthesis following the factor. This range represents the range of values used in obtaining the factor and represents the expected variation in emissions. A lack of information sometimes prevented the reporting of a reasonable factor range.

Standard statistical deviations of the emission factors were not generally reported since insufficient or only widely scattered data were available and a significant deviation could not be calculated.

All emission factors in this report were ranked according to the available data upon which they were based. A system which weighted various information categories was used to rank the final factors. These categories were: measured emission data with a total possible weight of 20, process data with a weight of 10, and engineering analysis with a weight of 10. The highest possible score for any factor was thus 40. Any factor ranking less than 20 was considered questionable and those ranked 20 or greater were considered reliable.

The emission data category rated the amount of measured emission data, i.e., stack test data available with which to develop an emission factor.

The process data category included such factors as the variability of the process and its effect on emissions, and available data on the variables. The engineering analysis category included the data available upon which a material balance or related emission calculation could be based.

The range of values for many emission factors is large. However, when the factors are applied to a large number of sources, the calculated overall emissions should approximate the true value. When applied to a single isolated source, an emission factor may yield emissions that differ considerably from the true value. Measured emission data should therefore be used, if possible, for single sources.

2. STATIONARY FUEL COMBUSTION

Particulate emissions from most types of stationary fuel combustion sources have been the subject of considerable research. However, emissions from the combustion of some of the less common fuels have not been determined to any great extent, nor have gaseous emissions been studied in any great depth. This section concentrates on some of these areas, and further quantifies some of these emissions.

Emissions from all types of fuel combustion are highly dependent on the efficiency of combustion and type of fuel. The resulting emission factors therefore cover a wide range.

Data used to determine the emission factors presented in this section were largely based on measured values or by comparison with similar combustion processes.

Anthracite coal combustion yielded the following approximate particle size breakdown (% by weight, size by microns).

Particle Size	>44	20-44	10-20	5-10	<5
% in Range	45	7	8	5	35

No particle size data was found for wood combustion emissions, the only other particulate source investigated in this section.

2.1 ANTHRACITE COAL COMBUSTION

General Information

The combustion of anthracite coal is characterized by the type of firing methods used for this fuel, and by the fuel's composition and properties. As shown in Table 2.1-1, anthracite coal contains very little volatile matter and sulfur, and has a relatively high ignition temperature and ash fusion temperature as compared to bituminous coal.

Consumption of anthracite coal has declined in recent years . It is mainly consumed in Pennsylvania, New York, and New Jersey.

Table 2.1-1. Anthracite Coal Characteristics[1]

Characteristic[a]	Pea, Buckwheat, Rice, and Barley Sizes	Egg, Stove, & Chestnut Sizes
Average Composition, Weight Percent		
Water	6.2	4.4
Volatile Matter	4.2	4.3
Fixed Carbon	78.1	82.4
Ash	11.5	8.9
Sulfur	0.7	0.7
Heating Value, Btu/Pound	12,300	13,015
Average Ash Fusion Temperature	2890°F	
Average Ignition Temperature	925°F	

a) As received basis.

[illegible]

non-clinkering

Firing Practice

Due to its low volatile content, and the non-clinking characteristics of the ash, anthracite coal is largely used in medium sized industrial and institutional boilers using stationary or traveling grates. Anthracite coal is not used in spreader stokers because of its low volatile content and relatively high ignition temperature. This fuel may be burned in pulverized coal-fired units, but due to ignition difficulties, this practice is limited to only a few plants in Eastern Pennsylvania. This fuel has also been widely used in hand-fired furnaces.

Combustion of anthracite coal on a traveling grate is characterized by a coal bed depth of 3 to 5 inches (bituminous coal is usually 5 to 7 inches deep), and a high blast of underfire air at the rear or dumping end of the grate. This high blast of air lifts incandescent fuel particles and gases from the grate and reflects them from a long rear arch over the grate toward the front of the fuel bed where fresh or "green" fuel is entering. This special furnace arch design is required to assist in the ignition of the green fuel.[2] Additional underfire air passes up through the grate through manually adjusted air boxes. Fuel feed rates are controlled by a manually adjusted leveling gate at the front of the grate which regulates the bed depth. Combustion rates are controlled by the speed of the grate and by the underfire air rates. When automatic controls are used, the grate speed and air rates are regulated by steam pressure. Some of the smaller traveling grate and hand-fired units use only natural draft to supply combustion air.

Fly ash collectors are not usually installed. However, for some of the larger units, burning smaller sizes of coal such as Buckwheat 4 or 5, ash carryover may be high due to the large blast of underfire air at the rear of the grate. These units sometimes install mechanical type collectors and then reinject the fly ash.[2]

Factors Affecting Emissions

Particulate emissions are greatly affected by the rate of firing and by the fuel's ash content. Due to the low volatile content of the anthracite coal, smoke emissions are rarely a problem. High grate heat release loadings result in excessive emissions since greater quantities of underfire air are required to burn the fuel. Hand-fired and some small natural draft units have lower particulate emissions since underfire air rates cannot be increased very much. However, larger units equipped with forced draft fans may produce high rates of particulate emissions, especially when operating at or near rated capacity.

Multicyclones may be used on anthracite coal-fired units, and very large units may use electrostatic precipitators to reduce particulate emissions.

Emissions

Based on stack test data, literature references, comparisons to bituminous coal combustion, and judgments , the emission data in Table 2.1-2 were compiled. The appendix contains more detailed data and calculations upon which these factors were based. Figure 2.1-1 presents limited particle size data.[4]

As is the case with other fuels, sulfur dioxide emissions are directly related to the sulfur content of the coal. Nitrogen oxides and carbon monoxide emissions can be expected to be similar to those found in bituminous coal-fired units since excess air rates and combustion temperatures are similar. No emission data on these pollutants was found in the literature.

Due to the lower volatile matter content of anthracite, hydrocarbon emissions are probably somewhat lower than those from bituminous coal combustion. Again no quantitative data were available.

Table 2.1-2. Uncontrolled Emissions From Anthracite Coal Combustion, lbs/ton of coal burned

Type of Furnace	Particulate	SO_2	SO_3	HC[d]	CO	NO_x[e]
Pulverized (dry-bottom) no fly ash reinjection	17A[b]	38S[c]	0.5S[c]	0.03 (0.01 to 0.04)	1	18
Overfeed Stokers[a] no fly ash reinjection	1.7A (1.1A-2.3A)	38S	0.5S	0.2 (0.1 to 0.3)	1.5 to 10 [f]	6 to 15[g]
Hand-fired Units	10~~A~~(6-15~~A~~)	36S	0.8S	2.5	90	3

a) Based on data obtained from traveling grate stokers in the 12 to 180 Btu/hr heat input range. Anthracite is not burned in spreader stokers.

b) A is the ash content expressed as weight %. For units with a multicyclone collector use 20% of this value.

c) S is the sulfur content expressed as weight %.

d) Expressed as methane.

e) Emitted as NO but expressed as NO_2.

f) Use high side of range for smaller sized units (less than 10×10^6 Btu/hr heat input).

g) Use low side of range for smaller sized units (less than 10×10^6 Btu/hr heat input).

h) Efficiency of control devices used for anthracite are approximately - Cyclone - 75-85% Electrostatic precipitator - 85%.

NOTE: Higher range of particulate emissions should be used for grate loadings, see Figure 2.1-2.

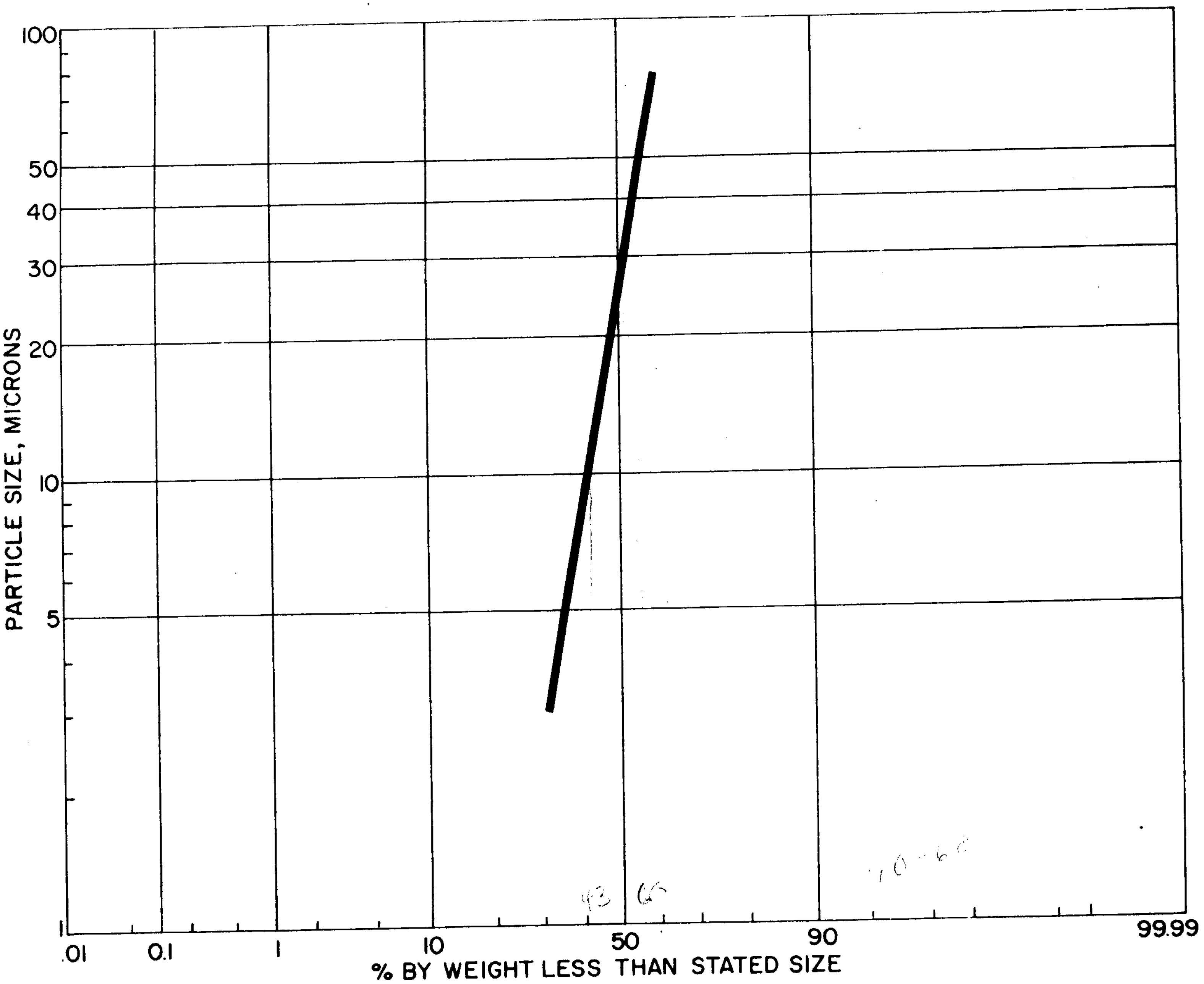

Figure No. 2.1-1. Particulate particle size from anthracite coal combustion in stokers[4]

Reliability of Emission Factors

Rankings based on the various factors which affect the accuracy of emission factors are presented in Table 2.1-3.

Table 2.1-3. Ranking of Anthracite Coal Combustion Emission Factors

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	10	8	5	23
SO_x	5	8	8	21
HC	0	8	8	16
CO	0	5	8	13
NO_x	0	5	8	13

Based on these rankings and arbitrarily using a mid-point of 20 as a dividing line between good and questionable factors, it is seen that only the particulate and SO_x factors are good and the remaining factors are questionable.

Particulate samples were gathered by methods outlined in ASME PTC 27 and Western Precipitation Company's Bulletin WP-50. Particulate data obtained by the State of New Jersey for traveling grate stokers was largely obtained by the Null Balance Method and by a modified U.S. Public Health Service Method. In almost all cases particulate represents that material collected on an alundum thimble at stack temperatures of about 300°F.

Further emission research work in this area is not warranted since the consumption of anthracite is decreasing every year, and considerable particulate emission data already exists for the traveling grate units which are the largest single type of unit in common use for this fuel.

The only major assumptions made in obtaining these factors were that hydrocarbons would approximate one-eighth of the bituminous coal emissions and that carbon monoxide and nitrogen oxide emissions would be similar to those found in bituminous coal combustion (see Appendix).

A. PARTICULATE EMISSIONS

1. Pulverized coal-fired unit - dry bottom; based on data from a single stack test made by the State of Pennsylvania.

Coal Composition:
12.1% - Water
14.2% - Ash
6.1% - Volatile Matter
79.7% - Fixed Carbon
11,066 - Btu/lb

Coal rate 31,300 lbs/hr. Units equipped with cyclone and electrostatic precipitator collection system - efficiency not known. Measured particulate emissions were 805 lbs/hr (0.91 grs/scf, 103,200 scfm)

Based on an <u>assumed</u> particulate collection efficiency of 80% the inlet particulate loading was:

$$\frac{805}{0.20} = 4025 \text{ lbs ash/hr}$$

Amount of ash entering furnace in coal was:

$$31{,}300 \text{ lbs coal/hr} \times 0.142 \text{ ash} = 4450 \text{ lbs ash/hr}$$

$$\% \text{ ash emitted} = \frac{4025}{4450} \times 100 = 90\%$$

A 90% ash emission rate yields an emission factor of 18A lbs particulate/ton

The State of Pennsylvania had used a factor of 15A.[5] The factor for bituminous coal, dry-bottom, pulverized coal-fired units is 17A. Since the anthracite value is close to this, but based on only one test and on an assumed fly ash collection efficiency, use the bituminous coal factor of 17A.

2. Traveling Grate Stokers

Considerable stack test data from the State of New Jersey is shown in the Table 2.1-4 and plotted in Figure 2.1-2. Considerable variations in these data are evident. The arithmetic mean values of percent ash emitted in various ranges of grate heat release rates, and their variances are shown in Table 2.1-5.

Table 2.1-5. Average Particulate Emission From Anthracite Coal Combustion in Traveling Grate Stokers

Operating Mode	Grate Heat Release Rate 10^6 Btu/ft^2 - hour	Emissions % of Inlet Ash	Emissions lb/10^6 Btu[a]	Factor[6]
Normal (40-70% of Capacity)	0.12 to 0.24	5.6 ± 5.6	--	1.1A
	0.25 to 0.31	11.6 ± 3.9	--	2.3A
	General	8.3 ± 5.9	0.685	1.7A
Soot Blowing	General	26.8 ± 18.2	2.2	5A

a) Based on average ash content of 10.4% and heating value of 12,600 Btu/lb.
b) A is the percent ash in the coal

The State of New York uses 15 lb/ton as particulates emission from anthracite coal combustion.[6] This is equivalent to an emission factor of 1.5A for a coal containing 10% ash. Their factor was based on bituminous coals combustion.

The State of Pennsylvania used the same factors for anthracite and bituminous coals combustion, namely:[5]

Underfeed Stoker	3A lbs/ton (A=% ash in coal)
Traveling Grate	3A lbs/ton

The State of Pennsylvania has, however, now accepted the factors used by the National Air Pollution Control Administration for bituminous fuel combustion; namely 5A.

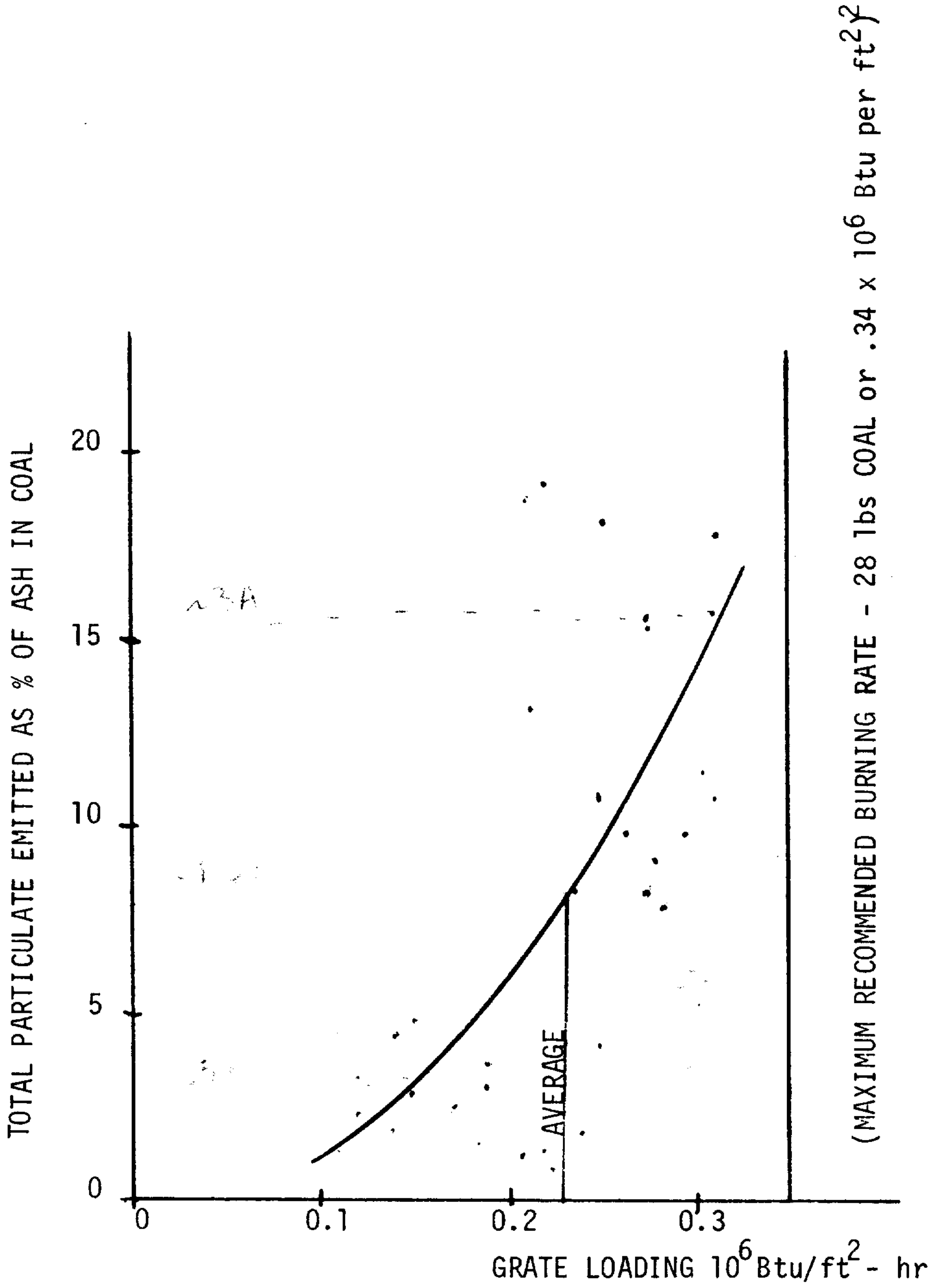

FIGURE 2.1-2. EFFECT OF FIRING RATE ON EMISSIONS FROM TRAVELING GRATE STOKERS BURNING ANTHRACITE COAL DURING NORMAL OPERATION

TABLE 2.1-4. ANTHRACITE COAL EMISSION DATA

COMPANY	RUN	FUEL			Btu/hr 10⁶	lbs Ash/hr	GRATE		EMISSION			COMMENTS
		lb/hr	% Ash	Btu/lb			Area ft^2	Btu/ft^2-hr 10^6	lbs/hr	$lb/10^6$Btu	% of Inlet Ash	
Plant A	1	5150	12.5	13,300	68.1	645	482.5	.14	11.8	.17	1.8	Natural Draft
	2	4566	12.5	12,533	57.2	570	482.5	.12	13.3	.23	2.3	for all Runs in A
	3	6181	12.5	13,052	80.7	770	482.5	.168	81.7	1.0	10.2	Soot Blow
	4	4446	12.5	13,123	58.3	555	482.5	.121	17.4	.30	3.1	Soot Blow
	5	4434	12.5	13,055	57.9	555	482.5	.12	50.2	.81	9.1	
Plant B	1	2265	7.2	14,337	32.5	163			56.9	1.75	35	Soot Blow
	2	2201	7.2	14,337	31.5	159			17.6	.56	11	
	3	2076	7.2	14,337	29.7	149			27.5	.93	18.2	Soot Blow
	4	2332	9.8	14,089	32.85	228			150.7	4.5	66	Unusually High (omit)
	5	2580	9.8	14,089	36.3	253			103.2	2.8	41	
Plant C	1	3132	11	12,855	40.3	344	141	.285	27.2	.67	7.9	66% of Full Load
	2	2765	12.1	12,733	35.2	334	141	.25	13.5	.38	4.1	
	3	2100	12.1	12,733	26.7	254	141	.188	107.5	4.0	42.4	Soot Blow
Plant D	1	3000	10.5	13,000	39.0	315	141	.276	48.7	1.2	15.5	
	2	3050	10.5	13,000	39.65	320	141	.28	159.1	4.0	49.7	Soot Blow
	3	3395	10.5	13,000	44.1	356	141	.25	64	1.45	18.0	
Plant E	1	1140	11.5	12,895	14.7	131	100	.15	3.7	.25	2.8	Forced Draft
	2	1045	11.0	12,991	13.6	115	100	.14	54.4	4.0	47.3	Soot Blow
	3	1190	9.9	13,198	15.7	118	100	.16	55.9	3.5	47.6	Soot Blow
	4	1280	11.2	13,023	16.7	143	100	.17	7.2	0.43	5	
	5	1150	10.9	13,059	15.0	125	100	.15	5.76	0.36	4.6	

COMPANY	RUN	FUEL			Btu/hr 10^6	lbs Ash/hr	GRATE		EMISSION			COMMENTS
		lb/hr	% Ash	Btu/lb			Area Ft^2	Btu/ft^2-hr 10^6	lbs/hr	lb/10^{6}Btu	% of Inlet Ash	
Plant F	1	11,682	14.3	12,300	143.7	1670	344	.42	163.7	1.13	9.8	No Soot Blown in F,G,H
	2	8,805	14.3	12,300	108.3	1260	344	.31	169.0	1.56	15.6	Appear High
	3	5,704	14.3	12,300	70.16	815	344	.204	213.3	3.03	28.8	
Plant G	1	5,940	12	12,874	76.5	712	348	.22	135.6	1.77	19.0	Appears High
	2	3,963	12	12,874	51.0	476	348	.147	136.5	2.68	28.7	
	3	5,634	12	12,874	72.5	675	348	.21	126.3	1.74	18.7	
Plant H	1	9,259	12.7	12,212	113.1	1180	372	.31	128.5	1.13	10.9	
	2	5,480	12.7	12,212	66.9	696	372	.18	78.5	1.17	11.2	
	3	8,958	12.7	12,687	113.6	1140	372	.304	200.7	1.76	17.6	
	4	8,355	12.7	12,687	106.	1060	372	.28	95.7	.90	9.0	
Plant I	1	14,195	11.3	12,845	182.3	1600	672	.27	252	1.38	15.7	
	2	14,265	11.3	12,845	183.2	1610	672	.27	337.3	1.84	21	Soot Blow
	3	12,891	11.3	12,677	163.4	1460	672	.245	182.3	1.15	10.9	
	4	12,417	11.3	12,677	157.4	1408	672	.234	153.9	0.98	9.5	Soot Blow
	5	11,357	11.3	12,677	143.9	1285	672	.214	193.3	1.34	13.1	
Plant J	1	13,900	10	12,800±	178	1390	582	.306	160	0.9	11.5	
	2	13,400	10	12,800±	172	1340	582	.295	130	0.75	9.7	76% of Load
	3	10,600	10	12,800±	135.5	1060	582	.232	330	2.44	31	Scot Blow

COMPANY	RUN	FUEL			Btu/hr 10^6	lbs Ash/hr	GRATE		EMISSION			COMMENTS
		lb/hr	% Ash	Btu/lb			Area Ft^2	Btu/ft^2-hr 10^6	lbs/hr	lb/10^{6}Btu	% of Inlet Ash	
Plant K	1 a & b	3,394	11.3	12,848	43.6	384	196	.222	5.6	.13	1.4	
	2	3,910	9.4	13,104	51.2	367	196	.261	26.7	.52	7.3	Fly Ash Reinjected
	3	3,580	9.4	13,104	46.9	336	196	.24	6.6	.14	1.9	
Plant L	1	1,308	10.9	13,256	17.3	142	120	.14	6.35	.37	4.45	50% ± Load
	4	1,090	10.5	13,237	14.4	114	120	.12	2.76	.19	2.4	Forced Draft
	5	2,050	10.5	13,145	26.9	211	120	.224	1.93	.072	0.9	Appears Low
	6	2,265	10.5	13,145	29.8	238	120	.248	32.3	1.09	13.5	Soot Blow
	7	1,894	10.5	13,145	24.9	199	120	.208	2.5	0.1	1.2	
Plant M	1	6,989	11.4	13,127	91.7	800	348	.264	79.2	.86	9.9	80% Load, Forced Draft
	2	7,300	11.4	13,127	96	830	348	.275	67.7	.705	8.1	Soot Blown forl min. (No Effect)
Plant N	1	960	13.3	12,779	12.3	127	64	.19	3.83	0.32	3.0	
Boiler #2	-2	920	13.3	12,779	11.7	122	64	.185	1.83	0.16	1.5	51% Load ±, Natural Draft
	3	960	13.9	12,556	12.05	133	64	.189	4.83	0.4	3.6	
	4	1,040	13.9	12,556	13.1	145	64	.204	13.9	1.07	9.6	Soot Blow
	5	1,340	11.6	12,987	17.3	156	64	.27	23.4	1.3	15.0	" "
	6	955	11.6	12,987	12.4	111	64	.195	15.8	1.27	14.3	" "

3. Hand-Fired Units:

The State of Pennsylvania used 24-54 lbs/ton of coal for both anthracite and bituminous.[5] These figures appear high because they include smoke and tars, and these substances are not as prevalent with anthracite.

The State of New York used 15 lb/ton for all anthracite combustion.[6] Blackie reports particulate emissions from domestic hand-fired units with anthracite to be 6 lbs per ton of coal.[3] Smith reports values from 6-10 lbs/ton for anthracite combustion in hand-fired equipment;[7] these data are, however, rather old. Hand-fired units burn the larger sized coals such as egg and stove which contain about 9% ash.

Based on the above information, an emission factor of 10 lbs per ton of coal was selected.

B. GASEOUS EMISSIONS

1. Sulfur Oxides

A stack test performed by the State of Pennsylvania on a traveling grate stoker burning anthracite coal with a sulfur content of 0.65% yielded emissions of 117 lbs/hr of SO_2 at a fuel rate of about 11,400 lbs/hr.

$$\% \text{ S emitted} = 100 \times \frac{117}{11{,}400 \times .0065 \times 2} = \frac{11700}{148} = 79\%$$

Based on earlier work on bituminous coal presented in the literature, approximately 95% of the sulfur in the fuel appears as SO_2 and about 1% appears as SO_3 in the flue gas.[5,7] There is no large body of evidence to show that this value should be different for anthracite coal fired in large units. Limited data indicates that for hand-fired units the amount of sulfur emitted amounts to 90% as SO_2 and 1.5% as SO_3.[8,9]

3.2.3.3 Emission factors for oil-fired boilers. The emission factors for oil-fired boilers are summarized in Table 3-15. These factors are typical of firetube as well as watertube oil-fired boilers in the given size ranges.

As noted earlier, particulate emissions from residual oil-fired boilers are expressed as a function of the sulfur content of the fuel. Assuming a fuel sulfur content of 3 percent (see Table 3-14), particulate emissions from residual oil-fired units are greater by roughly a factor of 15 than for distillate oil-fired boilers. This is due, in part, to the lower carbon residue content of distillate oil.

Figure 3-10 shows particulate emissions as a function of fuel oil carbon residue and illustrates the range of values that have been measured. As can be seen from Figure 3-10, industrial boilers firing oil containing little or no carbon residue emit from 5 to 20 ng/J of particulate matter.

The type of atomization has been shown to affect the amount of particulate matter emitted. One study on residual oil-fired units has shown that a mechanically atomized unit produces 20 times the particulate matter that a comparable air-atomized unit does (9.9 ng/J to 186.2 ng/J), and that steam atomization produces roughly three times as much particulate matter as air atomization (25.2 ng/J to 9.0 ng/J).[69] The same study indicates that mechanical atomization is the most common method of atomization, thus accounting for the fact that the emission factor in Table 3-15, which represents the current mix of installed atomization techniques, is 96.0 ng/J, a factor close to the high end of the range. This is based on a fuel sulfur content of 3 percent.

As noted in Table 3-15, NO_x emissions from oil-fired boilers are subject to a wide variety of influences which can interact to affect emission rates. In general, boilers firing residual oil emit more NO_x than equivalent boilers firing distillate oil. Furthermore, the range of NO_x emissions is wider for boilers firing residual oil. Both these trends are accounted for by the larger amount and higher variability of fuel nitrogen in residual oil.

3. Nitrogen Oxides and Carbon Monoxide

The emission of these compounds is affected by the firing method used and not by the type of coal. Since no quantitative emission data were found, the factors used for bituminous coal were selected as shown in Table 2.1-2 and based on data developed in Section 2.2.

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2.2 BITUMINOUS COAL COMBUSTION - GASEOUS EMISSIONS

General

Coal is the most plentiful fuel in the United States, and is burned in a wide variety of furnaces to produce heat and steam. Coal-fired furnaces range in size from small hand-fired units with capacities of 10-20 pounds of coal per hour to large pulverized coal-fired units which burn 300-400 tons of coal per hour.

Although predominantly carbon, coal contains many compounds in varying amounts. The exact nature and quantity of these compounds is determined by the source of the coal and will usually affect the final use of the coal.

Particulate and sulfur oxide emissions from coal combustion have received considerable attention, but the other gaseous emissions which are less noticeable have not been the subject of intensive investigations.

Emissions of gaseous hydrocarbons, carbon monoxide and nitrogen oxides are currently not reduced by using control equipment. They can, however, be reduced by optimum adjustment of combustion conditions as discussed in the next section.

Factors Affecting Emissions

The carbon monoxide and hydrocarbon content of the gases emitted from bituminous coal combustion depend mainly on the efficiency of combustion. Complete combustion and a low level of gaseous carbon and organic emissions involves a high degree of turbulence, high temperatures, and sufficient time for the combustion reaction to take place. Thus, careful control of excess air rates, high combustion temperature, and intimate fuel-air contact will minimize these emissions.

Since the larger furnaces are usually better equipped to control air and fuel feed rates, they have lower gaseous emission rates. Smaller furnaces, both manual and stoker-fired, have less control over air and fuel rates and combustion temperatures, and produce higher emissions. Composition of the bituminous coal does not apparently have any significant effect on these emissions.

Emissions of nitrogen oxides result primarily from the high temperature reaction of atmospheric nitrogen and oxygen in the combustion zone. The main factors affecting these emissions are furnace temperature, residence time in the furnace, and the rate of gas cooling. Generally, larger more efficient combustion units yield higher nitrogen oxide emissions. The practice of preheating combustion air at large boilers is considered a significant reason for the resultant higher NO_x release.

Since some of the factors affecting gaseous emissions such as combustion temperatures or excess air rates are frequently not readily apparent to the operator, the emissions of these compounds tend to vary over a wide range. Reported CO and hydrocarbon emissions vary 3 to 4 orders of magnitude among smaller combustion sources. (See Appendix).

Emissions

Selected gaseous emissions from bituminous coal combustion are presented in Table 2.2-1. The size range in Btu per hour for the various categories is shown only as a guide in applying these factors and cannot be used as a clear demarcation between furnace applications. The actual values selected are based on engineering judgment and on knowledge and involvement with most of the tests.

Due to their higher firebox temperatures, cyclone-fired furnaces and other types of wet bottom burnaces produce greater concentrations of nitrogen oxides. However, longer residence time in the conventional wet bottom furnace appears to reduce concentrations again by causing decomposition of the oxide.[4]

Table 2.2-1. Selected Gaseous Emissions from Bituminous Coal Combustion.

Lbs/ton of Coal Burned

Furnace Size, 10^6 Btu/hr heat input	NO_x[a]	CO	HC[b]
1. Greater than 100 - utility and large industrial boilers			
General-dry bottom	18	1 (0.1-3)	0.25 (.11-1)
Cyclone Furnaces	55	1 (0.1-3)	0.25 (.11-1)
2. 10 to 100			
large commercial and general industrial boilers, stoker-fired	15	1.5 (1-3)	1 (0.2-20)
3. Less than 10			
stoker-fired commercial and domestic furnaces	6	10 (4.5-31)	2.5 (1-3.3)
4. Hand-fired Units	3	90	20

a) Expressed as NO_2. The equation, $\log NO_x = 1.165 \log$ (hourly heat input) - 7.6081, represents NO_x emissions from dry bottom pulverized and stoker fired units and can be used to estimate hourly NO_x emissions.

b) Expressed as methane.

Carbon monoxide and hydrocarbons are generally emitted at concentrations of 5-50 ppm under normal combustion conditions in stoker-fired units.

Nitrogen oxides are mainly emitted as nitric oxide (NO) at concentrations of about 100 to 500 ppm, except for the large cyclone-fired units which emit concentrations in the range of 700 to 1200 ppm.[4] Relationships between Btu input and hourly emission of NO_x may be found in the literature.[9, 10] For larger combustion sources, an empirical relationship which expresses NO_x emissions in terms of heat input would probably be more accurate than using a general emission factor. Based on emission data available for this review (excluding cyclone furnaces), the equation:

$$\log NO_x = 1.165 \ (\log \text{heat input}) - 7.608$$

was derived. This equation gives the NO_x emissions in lbs/hr when the hourly heat input is known. Figure 2.2-1 shows this relationship.

Reliability of Emission Factors

Gaseous emissions from bituminous coal combustion vary widely since they are affected by many variables some of which are not easily controlled. Thus, emissions even from the same furnace will vary from day to day since only a small change in the efficiency of combustion can greatly affect carbon monoxide and hydrocarbon emissions. It must be realized, that these pollutants are only emitted in ppm quantities, and they are not easily measured with a great degree of accuracy.

Nitrogen oxide emissions are also affected by many variables and thus cover a wide range. However, these emission data correlate well with furnace size and are representative of the true emission.

Table 2.2-2 ranks the emission factors and indicates that they are fairly reliable.

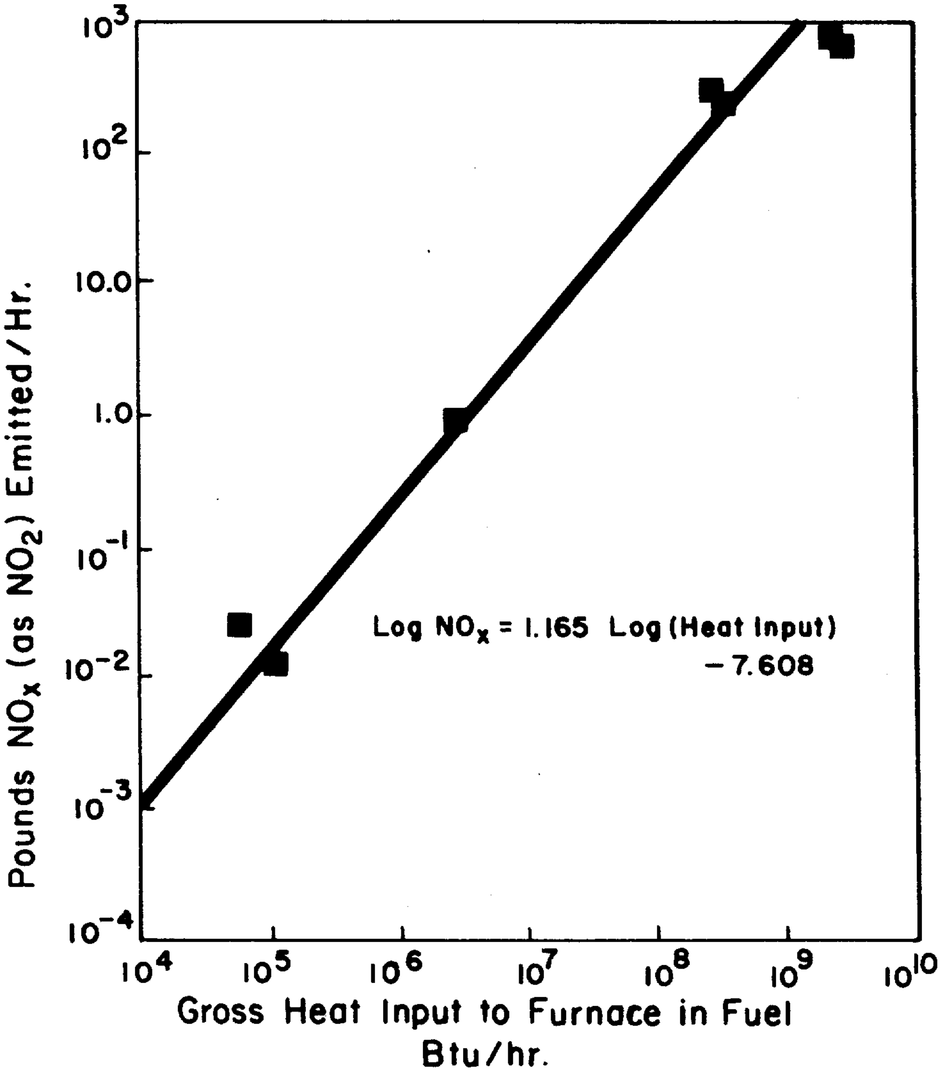

Figure 2.2-1. Nitrogen Oxide Emissions from Dry Bottom Pulverized, and Stoker-Fired Bituminous Coal Burning Furnaces.

Table 2.2-2. Gaseous Emission Factor Ranking for Bituminous Coal

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
NO_x	12	7	8	27
CO	10	7	5	22
HC	10	7	5	22

APPENDIX 2.2

A. NITROGEN OXIDE EMISSIONS

1. Furnaces larger than 100 x 10^6 Btu/hr heat input
Large Industrial and Public Utility Sizes

Full Load Tests

Pulverized Coal - Dry bottom

	lbs/10^6Btu	lbs/ton Coal	Reference
	0.55	13.0	4
	0.71	17.1	4
	0.95	24.8	4
Avg.	0.74	18.3	

Cyclone-Fired

2.2	61	4

Other Firing Methods, Stokers, etc.

0.76	19.2	4
0.59	15.6 - wet bottom furnace	4

Partial Load Tests

Pulverized Coal - Dry bottom

	lbs/10^6Btu	lbs/ton Coal	
	0.31	7.3	4
	0.51	13.7	4
	0.74	19.3	4
Avg.	0.52	13.4	

lbs/10^6 Btu	lbs/ton	Reference
Cyclone-Fired		
1.8	55	4
Other Firing Methods		
0.68	17.2	4
0.56	14.8 - wet bottom furnace	4
Data not designating load or type of unit		
0.17 to 2.5	4.1 - 60	5
0.12 to 2.4[a]	3 - 20	1
2.3[a]	19.2	2,3

A value of 18 lbs/ton was chosen for dry bottom units, and 55 for cyclone units.

2. Furnaces in the 10 to 100 x 10^6 Btu/hr heat input range.
   Large Commercial and General Industrial Sizes; Underfeed or Overfeed Stokers

lb/10^6Btu	lbs/ton	Reference
-	20 (estimate)	6,7
0.8	19.2	2,3

Note, Oil-fired units in this size range emit 12-17 lbs NO_x/ton.

Factor chosen based on data for both larger and smaller sized units and on relationship in Figure 2.2-1, was 15 lbs. NO_x/ton coal.

---

a) Based on 25 million Btu per ton of coal.

3. Furnaces less than 10 x 10^6 Btu/hr heat input stoker-fired including residential.

lbs/10^6Btu	lbs/ton fuel	Reference
0.30	8.3	9
0.36	9.8	9
	0.4	7
	0.5	8
Hand-Fired Units		
0.11	3.2	9

Factor chosen was 6 and 3 lbs/ton of fuel respectively for small stokers and hand-fired units.

B. CARBON MONOXIDE AND HYDROCARBON EMISSIONS

1. Furnaces larger than 100 x 10^6 Btu/hr heat input

	CO		HC[a]		Reference
	lbs/10^6Btu	lbs/ton	lbs/10^6Btu	lbs/ton	
PULVERIZED COAL					
	0.017	0.41	0.013	0.32	3,4
	0.011	0.26	0.005	0.13	3,4
	0.005	0.13	0.013	0.35	3,4
	0.10	2.8	0.004	0.11	9
	0.044	1.16	0.001	0.35	3,4
Avg.	0.035	0.95	0.007	0.25	
Other Data	-	0.1 - 0.6	-	0.34 - 1.25	1[c]
STOKER-FIRED					
	0.029	0.73	0.012	0.31	3,4
	0.51	12	0.005	0.11	9[b]
Value chosen for factor		1		0.25	

---

a) Expressed as methane. Data from reference 3 & 4 converted from carbon to methane by multiplying by 16/12.

b) Old unit without modern combustion controls.

c) Data from reference one converted from hexane to methane.

2. Furnaces in the 10 x 10^6 to 100 x 10^6 Btu/hr heat input range.

CO		HC		Reference
lbs/10^6Btu	lbs/ton	lbs/10^6Btu	lbs/ton	
0.1	3	0.0045	0.16	9
-	1	-	20	6
-		-	14 - 26	7

Since very limited and scattered data are available for furnaces in the 10 x 10^6 to 100 x 10^6 Btu/hr heat input range, the final CO and HC factor was chosen by picking values between the factors for the larger and smaller stoker-fired units and not on the values reported above. Values chosen were 1.5 lbs/ton for CO and 1 for HC.

3. Furnaces less than 10 x 10^6 Btu/hr heat input.

	CO		HC		Reference
	lbs/10^6Btu	lbs/ton	lbs/10^6Btu	lbs/ton	
	STOKER-FIRED				
	0.16	4.5	0.116	3.2	9
	0.14	3.9	0.036	1.0	9
	1.1	31	0.12	3.3	9
Avg.	0.47	13.1	0.095	2.5	
Value chosen		10		2.5	
	HAND-FIRED				
	3.5	99	0.73	21	9

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2.3 HYDROCARBON EMISSIONS FROM FUEL OIL COMBUSTION IN POWER PLANTS

General Information

Residual or Grade 6 fuel oil is the major liquid fuel used by electric power generating stations and accounts for approximately 8.5% of all fuel burned at power stations.[a] This fuel oil is a component of the higher boiling residue resulting from the distillation of crude petroleum. Its viscosity is high and it requires heating for efficient transfer and injection into the boiler. The average analysis of #6 or residual oil is 86% carbon, 10% hydrogen, 1.0% water, 0.5% nitrogen, 1.6% sulfur, and the remainder ash.[2] However, wide variations in composition may occur depending on the crude oil and refining practices used to produce the residual fuel. Grade 6 oil has a heating value of about 18,300 Btu/pound.[b] Many boilers use coal, oil, and natural gas interchangeably and sometimes simultaneously.

Factors Affecting Emissions

The major factors affecting hydrocarbon emissions at oil fired power plants are the quantity of oil used and the efficiency of combustion within the furnace. This efficiency is affected in turn by the temperature of the injected oil, the composition of the oil, the pressure and temperature of the fuel at the burner, and the excess air rates. "The key to optimum oil burner operation is careful control of fuel viscosity."[3] Viscosity of the fuel entering the burner should be less than 150 Saybolt Seconds Universal (SSU).

In order to burn properly, oil must be atomized as it enters the combustion chamber. This atomization provides a high degree

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a) On a Btu basis, Reference 1.

b) Approximately 147,000 Btu/gallon.

of air/fuel mixing and exposes a large amount of droplet surface area to the heat of the combustion zone. There are three basic types of oil atomizers; namely, air, steam,and mechanical (rotary cup). However, steam atomizers are most commonly used at power plants. In this type of atomizer, steam at a pressure greater than 100 psi and hot oil (170 - 260°F) are mixed in the burner nozzle and then sprayed into the combustion chamber. The oil mixture is this atomized as it passes out through the burner's nozzles.

Oil burners are usually mounted in banks inside the boiler's firebox. As many as 24 burners may be mounted in a large furnace, either all in a single side in rows (front-wall fired) or in sets in the four corners of the boiler (tangentially or corner fired). Excess air rates on the order of 15 to 30% are usually used. Under ideal firing and combustion conditions the hydrocarbon emissions are very low.

Emissions

Based on data presented in Appendix 2.3, the hydrocarbon emission factor for oil-fired power plants shown below was determined:

0.25 lbs/1000 lbs of oil burned or 2 lbs/1000 gallons of oil burned, when the hydrocarbons are expressed as methane.

The range of values reported in the literature was 0.1 to 0.4 lbs per 1000 pounds of fuel oil.

Reliability of Emission Factor

Only references to actual source tests based mainly on work conducted by the Los Angeles County Air Pollution Control District in the late 1950's were used to determine these emission factors. However, due to the limited number of these data, the complicated techniques required to measure rather low concentrations, and the limited geographical area in which tests were made, further work in this area should be done. Data on the composition of these hydrocarbons would also be useful. The numerical ranking for this factor is presented in Table 2.3-1.

Table 2.3-1. Emission Factor Ranking for Hydrocarbons

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	8	2	15

APPENDIX 2.3

Emission Data from the Literature

Data	Reference
0.4 lbs methane/1000 lbs of oil	4
0.097 lbs hexane/1000 lbs of oil	5,6 (same data)
0.19 lbs hexane/ton of oil	7 (1 ton oil = 244 gals)
0.56 lbs hexane/ton of oil	7
13 ppm (0.324 lbs propane/1000 lbs of oil)	8

Converting these values to methane[a], and putting them on a common basis of lbs/1000, we have:

0.40 lbs methane/1000 lbs oil
0.11 lbs methane/1000 lbs oil
0.11 lbs methane/1000 lbs oil
0.31 lbs methane/1000 lbs oil
0.35 lbs methane/1000 lbs oil

Total = 1.28   Avg = 0.256

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a) Pounds of hexane are converted to equivalent pounds of methane by multiplying by 96/86. Pounds of propane are converted to methane by multiplying by 48/44.

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2.4 LIQUEFIED PETROLEUM GAS COMBUSTION

General Information

Liquefied petroleum gas, commonly referred to as LPG, consists mainly of butane, propane, or a mixture of the two, and trace amounts of propylene and butylene. This gas, obtained from oil or gas wells, or as a by-product of gasoline refining is sold as a liquid in metal cylinders under pressure. It is therefore often called bottled gas.

Butane, C_7H_{10}, boils at 31.1°F and propane, C_3H_8, boils at -43.8°F. The use of these gases is therefore limited to those areas with ambient temperatures generally higher than these, since vaporization is greatly impaired at temperatures approaching the boiling point. LP gases are graded according to maximum vapor pressure with Grade A being predominantly butane, Grade F being predominantly propane, and Grades B thru E consisting of various mixtures of butane and propane. Generally, sulfur content is less than one grain per hundred cubic feet of vapor, although variance is not uncommon. The heating value of LPG ranges from 3200 $\frac{\text{Btu}}{\text{cf}}$ for Grade A to 2500 $\frac{\text{Btu}}{\text{cf}}$[b] for Grade F.

The use of LPG has grown from 77 million gallons in 1935 to 14,466 million gallons in 1967 and is expected to top 43,500 million gallons in 1978. The largest market for LPG is presently the domestic-commercial heating market which consumed 43.0% of the 1967 total. The chemical industry and internal combustion engines consumed 37.6% and 8.0% of the 1967 total respectively. Annual utility use accounted for 97 million gallons or only 0.67% of the 1967 total, registering a decline for two straight years (1966 and 1967).[1]

This fuel is considered a "clean" fuel because of the lack of visible emissions. Gaseous pollutants such as carbon monoxide, hydrocarbons, and nitrogen oxides do occur, however.

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a) Equal to ~~337,000~~ Btu per gallon.

b) Equal to ~~308,000~~ Btu per gallon.

Factors Affecting Emissions

The most significant factor affecting emissions is the burner design, adjustment, and venting.[2] Improper design, blocking and clogging of the flue vent, and lack of combustion air will result in improper combustion causing the emission of aldehydes, carbon monoxide, hydrocarbons, and other organics.

Nitrogen oxide emissions are a function of a number of variables including temperature, excess air, and residence time in the combustion zone. These variables in turn are a function of hydrogen to carbon ratio in the fuel and to furnace design. Since the hydrogen to carbon ratio for LPG is similar to fuel oil,[3] and combustion chamber designs are similar to natural gas fired units, a nitrogen oxide emission between that of fuel oil and natural gas combustion is probable.

The amount of SO_2 emitted is directly proportional to the amount of sulfur in the fuel.

Emissions

There have been no published results of source testing of stationary sources using LPG nor have any unpublished results been found. However, due to the similarities between LPG and natural gas, it is felt that for most emissions, the data used to compute emission factors for natural gas combustion when put on a Btu basis may be reasonably used when considering LPG. For nitrogen oxides a factor based on both fuel oil and natural gas was used. Factors based on these data as shown in the Appendix are presented in Table 2.4-1. In some instances, the sulfur content in LPG may be different than that normally found in natural gases thus affecting the amount of SO_2 produced. Therefore, a separate factor for SO_2 is presented.

Table 2.4-1. Emissions From LPG Combustion, pounds per 1000 gallons

Pollutant	Industrial Processes Furnaces		Domestic and Commercial Furnaces	
	Butane	Propane	Butane	Propane
Aldehydes (HCHO)	0.70	0.64	Neg.	Neg.
Carbon Monoxide	0.14	0.13	0.14	0.12
Hydrocarbons (CH_4)	Neg.	Neg.	Neg.	Neg.
Oxides of Nitrogen[a]	120	110	30-100[c]	30-90[c]
Oxides of Sulfur[b]	0.300S	0.335S	0.300S	0.335S
Other Organics	1.76	1.6	Neg.	Neg.
Particulate	6.3	5.8	6.7	6.1

a) Expressed as NO_2.

b) S equals sulfur content expressed in grains per 100 CF gas vapor, e.g., if the sulfur content is 0.16 grains per 100 CF vapor, the SO_2 emission would be 0.300 (for butane) x 0.16 or 0.048 lb SO_2 per 1000 gallon butane burned.

c) Use values of 30-50 for domestic units 50-100 for commercial units.
Neg. = negligible.

Reliability of Emission Factors

While there is a lack of measured emission data from LPG combustion in stationary sources, this fuel does have many of the characteristics of natural gas and the emissions are therefore similar. The factors listed in Table 2.4-1 are based on an engineering analysis of similar processes and fuels (LPG, natural gas combustion, and fuel oil combustion) and on measured emissions from natural gas and oil combustion.

An overall ranking of questionable is assigned to these factors based on the ranking in Table 2.4-2, and on the fact that the natural gas emission data itself is about 10 years old. Los Angeles County Air Pollution Control District sampling techniques were used. Further work in this area is warranted due to the lack of data, and the increased use of this fuel.

Table 2.4-2. LPG Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
2	8	8	18

The major assumptions made in deriving these factors were that particulate and gaseous carbon compounds were the same as those from natural gas combustion, and nitrogen oxide emissions were between those for oil and gas combustion.

APPENDIX 2.4

Particulate, Carbon Monoxide, Hydrocarbons, and Aldehydes

The factors found in Table 4, Reference 4, are based upon pounds per million cubic feet of natural gas burned. That table was derived from the figures given in Reference 5 which assumed that 6000 cubic feet of gas is equivalent to one barrel of fuel oil. One barrel of fuel oil contains 312 lb at 18,500 Btu/lb, or 5.76 x 10^6 Btu.[5] Therefore, Duprey's emission factors are based upon pounds per 960 x 10^6 Btu.

Using the values given in Table 2.4-3; the heating value of LPG can be found on a gallon basis.

Table 2.4-3. Properties of LPG[5]

	Column				
	A	B	C	D liq. fuel	E
Gas	Avg. Gross Btu/CF	CF/LB	Avg. Specific Gravity w.r.t. air	LB/GAL	Btu/1000 GAL (AxBxDx1000)
Butane	3200	6.29	2.02	~4.3 ~~16.75~~	~97 ~~337~~ x 10^6
Propane	2525	8.45	1.66	13.85 ~4.5	308 x 10^6 ~90

The emission factors shown by Duprey therefore can be converted to relate gallonage (pounds per 1000 gallons LPG burned) by multiplying each of Duprey's factors (excluding SO_2 which is treated separately herein) as follows:

GAS	MULTIPLIER
Butane	$\frac{337}{960} = 0.351$
Propane	$\frac{308}{960} = 0.321$

Duprey's table is shown below, with his column for emissions from power plants omitted:

Table 2.4-4. Emission Factors For Natural Gas Combustion
(Pounds million cubic feet of natural gas burned)[4]

	Type of Unit	
Pollutant	Industrial Process Boilers	Domestic and Commercial Heating Units
Aldehydes (HCHO)	2	Neg.
Carbon Monoxide	0.4	0.4
Hydrocarbons (CH_4)	Neg.	Neg.
Oxides of Sulfur (SO_2)	0.4	0.4
Other Organics	5	Neg.
Particulate	18	19

Table 2.4-1 in the main text is based upon the values given in Table 2.4-4, with each value multiplied by 0.351 and 0.321 for butane and propane, respectively.

Sulfur Oxides

When the sulfur content, S, is expressed in grains per 100 cf of gas fuel, the weight of SO_2 given off upon complete combustion of the 100 cf is:

$$S \times \left[\frac{\text{mole. wt. } SO_2}{\text{mole. wt. } S} \times \frac{1 \text{ lb.}}{7000 \text{ grains}}\right] = S\left[\frac{32}{16} \times \frac{1}{7000}\right] = 0.000286 \text{ S lb.}$$

To determine the pounds SO_2 emitted from 1000 gal. of LPG, find the number of 100 ft.^{3} units in 100 gallons of butane and propane. Using the values shown in Table 2.4-3:

$$\text{Butane:}\quad 6.29\,\frac{ft^3}{lb} \times \overset{4.3}{16.75}\,\frac{lb}{gal} \times \frac{1000\ gal}{100\ ft^3} = \overset{270}{\cancel{1050}},\ 100\ ft.^3 \text{ in 1000 gal.}$$

$$\text{Propane:}\quad 8.45 \times \overset{4.8}{13.85} \times \frac{1000}{100} = 1170,\ 100\ ft.^3 \text{ units in 1000 gal.}$$

Thus the weight of SO_2 emitted from combustion of 1000 gal is:

Butane: 1050 x 0.000286 S = 0.300 S

0.005

Propane: 1170 x 0.000286 S = 0.335 S

Nitrogen Oxides

For natural gas combustion in industrial furnaces, Duprey reports 214 lbs $NO_x/10^6$ ft^3 or .214 per 10^6 Btu of fuel (1000 Btu/ft^3), and 72 lbs NO_x/1000 gallons of oil or 0.5 lbs per 10^6 Btu of fuel (142,000 Btu/gal). An average factor for LPG assuming NO_x emissions lie mid-way between oil and gas, would be 0.35 lbs per 10^6 Btu.

For domestic and commercial units, the natural gas NO_x factor is 0.116 NO_x per 10^6 Btu and the oil factor varies from 0.5 to 0.083 lbs per 10^6 Btu. LPG factors are therefore 0.3 to 0.1 lbs per 10^6 Btu depending on size of unit.

Butane contains 337 x 10^6 Btu per 1000 gals. and propane contains 308 x 10^6 Btu per 1000 gals. (Table 2.4-3). NO_x emissions are therefore:

	Propane lbs/1000 gal.	Butane lbs/1000 gal.
Industrial	0.35 x 308=108	0.35 x 337=118
Commercial - Domestic	0.1 x 308=30.8	0.1 x 337= 33.7

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2.5 WOOD WASTE COMBUSTION IN BOILERS

General Information

Wood is no longer a primary source of heat energy as it was before the latter part of the nineteenth century. However, there are situations today where the availability of wood as a by-product or waste makes it a desirable fuel for steam generation. Industries such as lumber, furniture, plywood, and pulp, use wood in the form of hogged chips, shavings, and sawdust as fuel. It is sometimes burned in combination with oil, gas, or pulverized coal. This technique is used where the available wood waste is substantial enough to utilize, but the quantity is not always sufficient to meet the power requirements of the plant.

Firing Practices

In general, furnaces designed for the burning of wood waste fall into three types: 1) pile, 2) thin-bed, and 3) cyclonic. All three of these furnaces are usually water-cooled and can be modified to burn supplemental fuel with the wood.

In pile burning, the wood is fed through the furnace roof and burned in a cone shaped pile on the grate. Most of the combustion air enters under the grate around the edge of the pile. Excess air at the boiler outlet is maintained at about 30-40%, but accurate control is difficult.

Thin-bed burning is accomplished on a moving grate similar to a spreader stoker. In a cyclone furnace, wood (especially bark) is usually burned with coal.

Wood refuse from some processes contains more than 75% moisture. Since it is not practical to burn wood with more than 60 or 65% moisture, the excessive water is often extracted by means of mechanical presses.

Excessive water content is particularly common to pulping processes where wood is frequently floated to the plant.

Unless the furnace is properly designed and operated, a smoke problem will develop. The particulate matter resulting from the combustion of hog fuel can be seen over a wide area depending on weather conditions.[1] In addition, gaseous emissions common to all combustion processes will occur.

It is common practice to reinject the collected fly ash from wood boilers. A study of 15 bark boilers indicated that each of these had a mechanical collector which collected 80% of the fly ash and then reinjected half of the collected portion.[4] NCASI - OAP SURVEY

Factors Affecting Emissions

Unless the furnace is properly designed and maintained, incomplete combustion will result. The design of wood burning furnaces should differ from that for coal furnaces as follows:[2]

1. Larger area of refractory surface in the primary fuel-drying zone
2. Higher proportion of overfire secondary air above the grate to primary air through the grate
3. Larger combustion space, or secondary air space, to burn the volatile matter

Excessive smoking will result from improper grate maintenance, especially where coal is burned simultaneously with the wood. When mixed and burned in common, the resulting ash will cause furnace slagging and adversely affect grate performance.

Another major factor is the water content of the wood refuse. This is not only a function of the absorptive property of the wood but also a function of the process which produces the waste. Thus wet bark will generally produce more emissions than kiln-dried lumber.

Of minor importance, except as it reflects on the factor noted above, is the species of wood. Table 2.5-3. (see Appendix 2.5) shows the ultimate analysis of various wood fuels on a dry basis. However, the composition of bark is significantly different than wood. As shown in Table 2.5-4., bark contains less carbon and nitrogen, but more sulfur than wood. This difference coupled with a high moisture content is thought to account for more severe dust and smoke problems when burning bark.

Emissions

Emissions factors for the combustion of wood and bark in boilers are shown in Table 2.5-1. These factors are based on the information in Appendix 2.5.

Table 2.5-1. Emission Factors for Wood and Bark Combustion in Boilers, lb/ton of fuel-fired (approximately 50% moisture content)

Emissions	Conditions of Operation		
	no reinject.	50% reinject.[a]	100% reinject.[a]
Particulate	25-30	30-35	40-45
CO	1.5 (1 to 3)		
HC[c]	2.0 (0.2 to 20)		
NO_x[d]	10 (6 to 15)		
SO_2[b]	0-3		
Carbonyls[e]	0.5 (0.4 to 0.9)[f]		

a) This is not an emission factor. Value represents the loading reaching the control equipment usually used on this type of furnace, and is based on the percentage of fly ash reinjection indicated.
b) Use zero for most wood and higher values for bark.
c) HC expressed as methane.
d) NO_x expressed as NO_2.
e) As formaldehyde.
f) Trench incinerator emission (see Reference 6).
g) Particulate emissions are frequently reduced by using cyclone collectors with efficiencies in the 75-85% range.

Reliability of Emission Factors

A variety of data was used to arrive at emissions from wood waste combustion in boilers. Particulate emissions are based on measured data from 15 separate bark boilers and are believed to be reliable. However, gaseous emission data are lacking and were based on other related processes. The factor rankings are presented in Table 2.5-2.

Table 2.5-2. Emission Factor Ranking for Wood Combustion in Boilers

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	15	5	5	25
Gases	5	5	4	14

The following assumptions were made in determining the emission factors listed in this section:

1. Particulate emissions from wood burning is slightly less than that for bark.
2. Gaseous emissions (CO, HC, and NO_x) from wood and bark are similar to that from the combustion of coal in industrial boilers.
3. Carbonyls emitted from wood and bark are similar to that from the combustion of wood in trench incinerators.

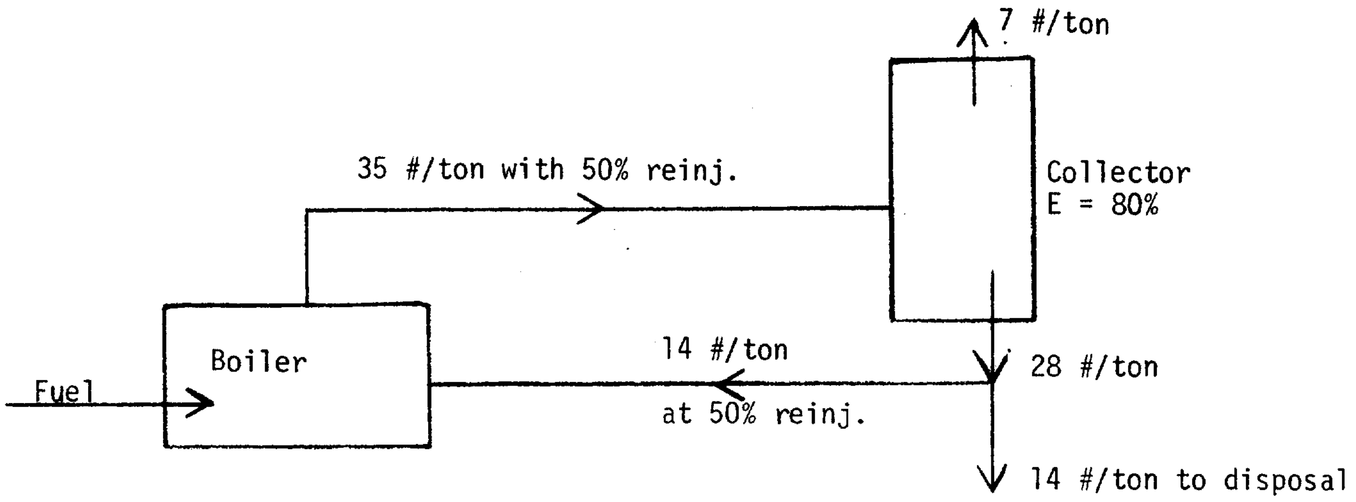
Further work on obtaining quantitative gaseous emission data appears justified.

APPENDIX 2.5

ATA

Results of source testing of wood boilers have not been published nor have unpublished tests results been found (with the exception of bark boilers). Emissions from bark boilers may be substantial in the form of particulate matter. Even some odorous gases have been reported[1], although no indication was made as to gas type and quantity. While Hough and Gross[1] reported particulate emissions of 35 pounds per ton of pulp produced, they are not clear as to the amount of wood burned. It is generally expected that one half ton of burnable wood is generated per ton of air dried pulp. On that basis, the reported 35 pound figure might well be expressed in terms of 70 pounds per ton (based on 50% moisture content). Since that figure is at great variance with 15 other reported figures[4] and its origin is not stated, it will not be considered.

Based on a fly ash collector efficiency of 80%, the amount of particulate that would be emitted from a boiler without fly ash reinjection is about 25 to 30 pounds/ton of wood, depending on the combustible content of the reinjected material. The process is shown below:



At 100% reinjection the particulate entering the collector would increase to about 40-45 #/ton of wood.

Table 2.5-5 is a compilation of known emission data for the burning of bark in boilers with comparable figures for coal combustion. In the absence of data for gaseous emissions for wood boilers the known emission figures for coal boilers may be considered reasonably similar to that expected from the combustion of wood.

Table 2.5-3. Ultimate Analysis of Wood Refuse Burned,[3] percent by weight

	Jack Pine	Birch	Maple	Eastern Hemlock	Dry Average	Wet Average
Carbon	53.4	57.4	50.4	53.6	53.7	26.8
Hydrogen	5.9	6.7	5.9	5.8	6.1	3.0
Sulfur	0.0	0.0	0.0	0.0	0.0	0.0
Nitrogen	0.1	0.3	0.5	0.2	0.3	0.2
Ash	2.0	1.8	4.1	2.5	2.6	1.3
Oxygen (by difference)	38.6	33.8	39.1	37.9	37.3	18.6
Water	-	-	-	-	-	50.0

Table 2.5-4. Ultimate Analysis of Wood and Bark, percent by weight

	Dry Average		Wet Average	
	Wood[a]	Bark[b]	Wood[a]	Bark
Carbon	53.7	26.5	26.8	13.2
Hydrogen	6.1	8.2	3.0	4.1
Sulfur	0.0	0.1	0.0	0.05
Nitrogen	0.3	0.0	0.2	0.0
Ash	2.6	1.7	1.3	0.8
Oxygen	37.3	62.0	18.6	31.0
Water	-	-	50.0	50.0

a) See Table 2,5-3.

b) Reference No. 4.

Table 2.5-5. Comparable Emission Data for Wood, Bark, and Coal Combustion

Fuel Type and Equipment Type	Emissions, lbs/ton of fuel fired[c]						Ref. No.
	Part.	CO	HC[a]	NO_x[b]	SO_2	Carbonyls[f]	
Bark Boilers	30[d]	--	--	--	2.3	--	4
Coal-fired Industrial Boiler-Stoker	5 A[e]	1.5	1 to 2.5	6 to 15			5,7
Open Pit Burning	4.6 to 12.8	--	--	4	--	0.4 to 0.9	6

a) HC expressed as methane.

b) NO_x expressed as NO_2.

c) Wood weighed on an as-fired basis of 45-50% moisture content.

d) Value represents the loading reaching the control equipment used on this type of furnace, and is an average of 15 reported installations. The range of emissions was 21-36 lb/ton of wood, based on 50% reinjection of flyash.

e) Percent ash in coal; See Reference 5.

f) Expressed as formaldehyde.

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[illegible] PROPOSAL

3. REFUSE DISPOSAL

While incineration from an air pollution viewpoint is not a recommended form of solid waste disposal, it does occur in almost every part of the country and forms a significant part of the air pollution problem. More than five pounds per day of solid waste are currently collected from every person in this country, and this value is increasing by 2-3% per year.

Process	Approximate Particle size, microns - % by weight				
	>44	20-44	10-20	5-10	<5
Municipal Incineration	45	18	15	10	12

Atmospheric emissions, both gaseous and particulate, result from refuse disposal operations which utilize combustion to reduce the quantity of refuse. Many types of solid waste are currently disposed of by a wide variety of combustion methods including both enclosed and open burning. Emissions from these combustion processes cover a wide range because of their dependence on the refuse burned, the method of combustion or incineration, and the efficiency of combustion. Many of these variables are not well controlled during incineration.

Reported factors were largely based on measured emission data. These data were found to vary considerably. The number chosen as the emission factor represented our best judgment based on the available data.

3.1 REFUSE INCINERATION

Process Description

Refuse incineration is the process of reducing combustible wastes to inert residue by the use of high temperature combustion. A wide variety of incinerators presently in existence. Due to the variations in incinerator design, the types of waste, and the methods of operation, incinerator emissions vary widely. The most common type of incinerators consists of a refractory lined chamber with a grate upon which refuse is burned. This primary chamber may be followed by a secondary combustion chamber to promote more complete combustion of the particulate and gaseous material which is carried over from the primary chamber. Many small size incinerators are single chamber units which vent the gases from the primary combustion chamber directly into the exhaust stack.

No exact definitions of incinerator size categories exist. However, for this report the following general categories and descriptions have been selected.

- °Municipal incinerator - A multiple chamber unit with capacities greater than 50 tons per day usually equipped with automatic charging mechanisms and temperature controls. Municipal incinerators are usually equipped with some type of particulate control device such as a spray chamber.
- °Industrial/commercial incinerators - These units cover a wide size range and are generally in the 50-4000 lbs per hour range. They are frequently manually charged, operate intermittently, and may be either single or multiple chamber designs. Emission control systems

among the better designs include gas-fired afterburners and/or particulate scrubbing systems.

°Domestic incinerators - This category includes incinerators marketed for residential use. They are fairly simple in design (with single or multiple chamber) and usually are equipped with an auxiliary burner to aid combustion.

°Flue-fed incinerators - These units, commonly found in large apartment houses, are characterized by the charging method which consists of dropping refuse down the incinerator flue and into the combustion chamber. Modified flue-fed incinerators utilize afterburners and draft controls to improve combustion efficiency and reduce emissions.

°Pathological incinerators - These are incinerators used to dispose of animal remains and other high moisture content organic material. Generally, these units are in a size range of 50-100 pounds per hour. They are equipped with combustion controls and afterburners to insure good combustion and minimum emission.

Factors Affecting Emissions

Operating conditions, refuse composition, and basic incinerator design have a great effect on emissions. The manner in which air is supplied to the combustion chamber or chambers has the greatest effect on the quantity of particulate emission. Air may be introduced from beneath the chamber, from the side or from the top of the combustion area. As underfire air is increased, an increase in fly ash emission is noted. The way in which refuse is charged has a great effect on the particulate emissions. Improper charging causes a disruption of the combustion bed with the subsequent release of large quantities of particulate. Emission of oxides of sulfur dependent on the sulfur content of the refuse. Nitrogen oxide emissions depend on the temperature of the combustion gases, residence time in the combustion zone, and the excess air rate. Carbon monoxide and hydrocarbon emissions also depend on the quantity of air supplied to the combustion chamber and the efficiency of combustion.

Emissions

Table 3.1-1 lists the particulate and gaseous emission factors for various incinerator types and classes based on data in the Appendix. Properly operated multiple chamber incinerators promote more complete combustion and subsequently produce less emission than those of the simple single chamber design. The single chamber high temperature regulated air ("starved air") incinerator is not included as a simple single chamber design in this summary. The high temperature incinerators employ a burner, at the base of the stack, to achieve low particulate emission rates.

Table 3.1-2 lists the relative collection efficiencies of various types of control equipment for incinerators. This control equipment has little effect on gaseous pollutant emissions. Table 3.1-3 lists a chemical analysis of particulate emissions from a municipal incinerator, and Figure 3.1-1 shows the particle size distribution of particulate emissions from a municipal incinerator.[11, 12]

Table 3.1-1. Emission Factors for Refuse Incineration

Incinerator Type	Emissions, lbs/ton of refuse charged				
	Particulate	SO_x[a]	HC[b]	NO_x[c]	CO
Municipal					
Multiple Chamber Uncontrolled	30(3 to 35)	1.5 (1 to 1.8)	1.5 (0.1 to 1.8)	2 (0.1 to 3.3)	0.8 (0.3 to 4)
With Settling Chamber & baffled water spray system	17[d](2.6 to 20)	(Gaseous emissions same as above)			
Industrial/Commercial					
Multiple Chamber	5(3 to 6)[d]	1.5[e]	3(0.3 to 20)	3 (2.5 to 3.5)	10 (1 to 25)
Single Chamber	15(4 to 31)	1.5[e]	15(0.5 to 50)	2 (0.1 to 2)	20 (4 to 200)
Flue Fed	30(7 to 76)	0.5	15(2.2 to 40)	3 (1.3-6)	20[f]
Flue Fed (Modified)[i]	6(1 to 10.2)	0.5	3[g]	10(7-16)	neg[h]
Domestic Single Chamber					
Without primary burner	35	0.5	100	2[f]	300
With primary burner	7	0.5	2	2	neg.[h]
Pathological	5(2.3 to 8)	neg.	neg.	3(1.2-8.8)	neg.

a) Expressed as SO_2.

b) Expressed as methane.

c) Expressed as NO_2.

d) Cyclones and scrubbers can reduce this factor by 70-80%.

e) Based on municipal incinerator.

f) Based on single chamber commercial incinerator.

g) Estimated factor, based on commercial units.

h) Neg. = negligible.

i) With afterburner and draft controls.

<u>Note</u>: Use high side of particulate, HC, and CO emission range when operation is intermittent, and combustion conditions are not good.

Table 3.1-2. Particulate Control Efficiencies of Various Types of Control Equipment Applied to Municipal Incinerators[a]

System Type	Efficiency, %
Settling Chamber	0 to 30
Settling Chamber and Water Spray	30 to 60
Mechanical Collector	30 to 80
Scrubber	80 to 95
Electrostatic Precipitator	90 to 96
Fabric Filter	97 to 99

a) Based on Reference 1.

Table 3.1-3. Chemical Analysis of Fly Ash Samples From Typical Municipal Incinerator

Component	Percent of Particulate Emitted
Organic	10.4
Inorganic	89.6
Silica as SiO_2	36.1
Iron as Fe_2O	4.2
Alumina as Al_2O_3	22.4
Calcium as CaO	8.6
Magnesium as MgO	2.1
Sulfur as SO_3	7.6
Sodium and potassium oxides	19.0

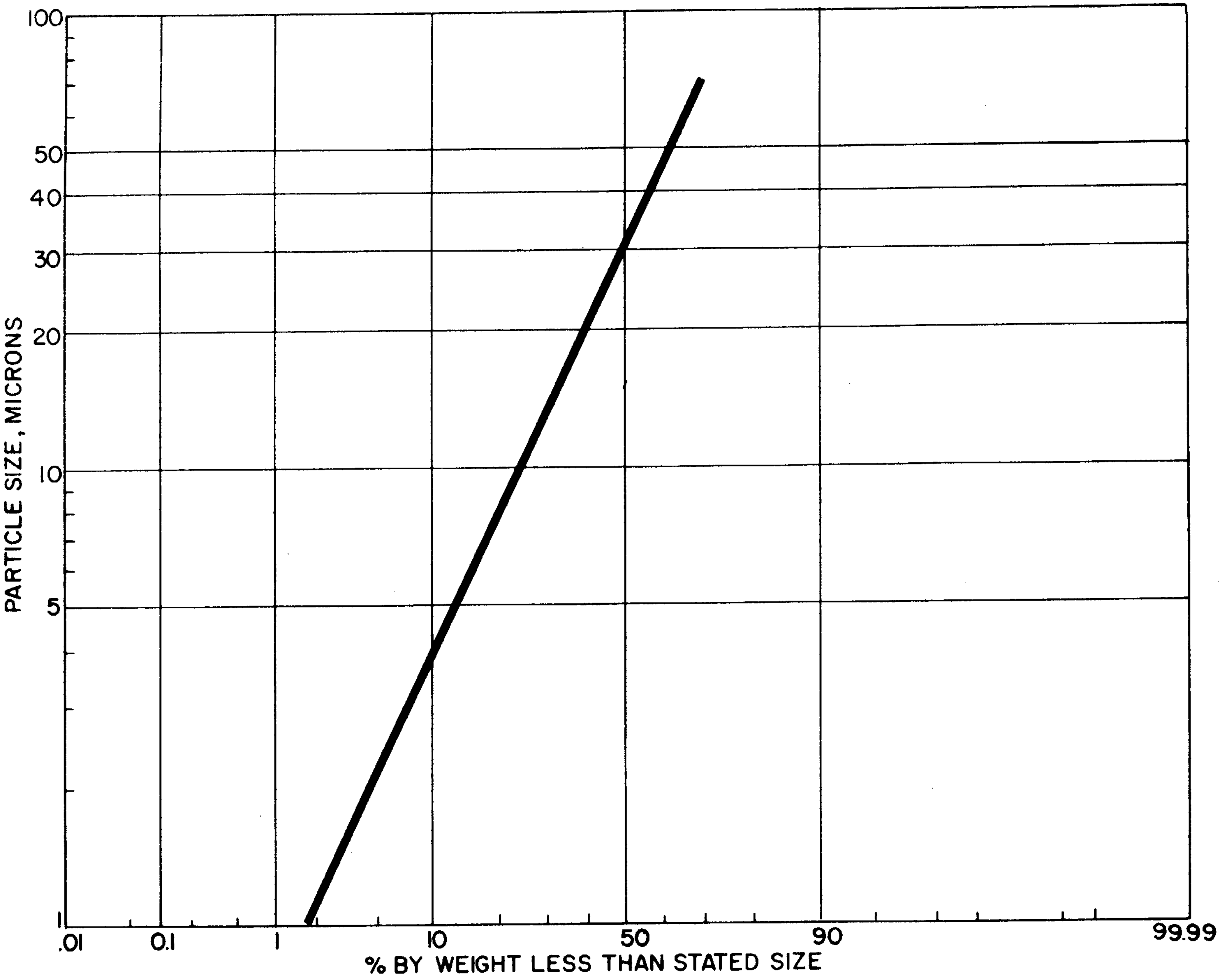

Figure 3.1-1 Particulate particle size distribution from municipal incinerators

Reliability of Emission Factors

Emission factors for particulates from multiple chamber municipal incinerators was largely based on data obtained by various Bureaus of the Public Health Service. The sampling techniques are set forth in "Specifications for Incinerator Testing at Federal Facilities".

Substantial particulate emission data on small sized incinerators was obtained from Resources Research, Inc. (RRI), source sampling information and from literature sources. Most of the RRI data was obtained using the PHS procedures or a modification of these procedures.

Gaseous emission data were not as readily available as particulate emission data. Considerable variation was found due to the difference in incinerator operation.

The emission factor information in this section incorporates much previously unpublished information obtained from RRI's source tests and various Bureaus of the Public Health Service. RRI data, PHS data and Los Angeles County data have been considered as more reliable than other data found.

Table 3.1-4. Emission Factor Ranking for Incinerators

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Municipal Incinerators				
Particulate	15	8	5	28
Gases	8	8	5	21
Commercial/Industrial				
Particulate	15	5	5	25
Gases	8	5	5	18
Domestic				
Particulate	5	5	3	13
Gases	5	5	3	13
Flue Fed				
Particulate	15	5	5	25
Gases	3	5	5	13
Pathological				
Particulate	10	5	8	23
Gases	8	5	8	21

Table 3.1-4 indicates that most of the particulate emission factors are considered good, while most of the gaseous factors are considered questionable.

No major assumptions were made in obtaining these data since they are mainly based on actual emission measurements.

APPENDIX 3.1

Table 3.1-5. Emissions from Municipal Multiple Chamber Incinerators, lbs/ton of Refuse Charged

Particulate	SO_x[a]	HC[b]	NO_x[c]	CO	Reference
35					1
8.1		<0.08	2.4	4	2
18[d]		1	2.5	0.67	2
9	1.8	0.34	2.4	0.3	3
12.4		1.8	1.4-3.3	0.7	4
25.1					4
9.1					4
30.8					4
11.8					4
			0.8		5
			2.3		5
			3.1		5
			1.2		5
			2.8		5
			0.1		6
20.4[e]					7
14.5[e]					7
14.8[e]					7
17.2[e]					7
13.6[e]					7
3	1.0		3.0		8
2.6[e]					2
17[d,e] or 30	1.5	1.5	2	0.8	Factor
(2.6-20) (3-35)	(1.0- 1.8)	(0.1-1.8)	(0.1-3.3)	(0.3-4)	Range

a) SO_x expressed as SO_2.

b) Hydrocarbons expressed as methane. When the referenced data was reported as hexane, it was converted to methane by multiplying by 96/86.

c) NO_x expressed as NO_2.

d) After settling chamber.

e) After water spray system.

Table 3.1-6. Emissions from Industrial and Commercial Multiple Chamber Incinerators, lbs/ton of Refuse Charged

Particulate	HC[a]	NO_x[b]	CO	Reference
6.2[c]	3.6		25	2
3.7				3
3.4				3
	0.28		0.05	4
4.7[d]				9
4.6[d]				9
4.8[d]	16(6 to 20)	3.5	7(4 to 9)	9
4.2[d]				9
3.5	1[e]	2.5	2.9	5
	0.3			8
5 (with water sprays)	3	3	10	Factor
3.4-6.2	0.3-20	2.5-3.5	0.05-25	Range

a) HC expressed as methane.

b) NO_x expressed as NO_2.

c) With auxiliary burner in primary chamber.

d) With low efficiency scrubber or spray system, average of three tests.

e) Originally reported by Williamson as < 1 expressed as hexane.

Table 3.1-7. Emissions from Industrial and Commercial Single Chamber Incinerators, lbs/ton of Refuse Charged

Particulate	HC[a]	NO_x[b]	CO	Reference
4.1[c]	0.45	1.6	4.3	2
31.0				3
	20-50		84	4
23.8		0.1	197-991	5
6.3[d]	8	2	5.6(2 to 8)	9
6.9[d]	19	2	2.5	9
14.2[d]	9	2	8	9
15	15	2	20	Factor
4.1-31.0	0.45-50	0.1-2	4.3-991	Range

a) HC expressed as methane.

b) NO_x expressed as NO_2.

c) No underfire air.

d) With water sprays.

Table 3.1-8. Emissions from Flue Fed Incinerators, lbs/ton of Refuse Charged.

Particulate	SO_x[a]	HC[b]	NO_x[c]	Reference
		40	1.3-4.4	4
	0.5			8
76		2.2	6	5
52				5
48				5
37				5
37				5
34				5
25				5
23				5
23				5
19				5
17				5
7				5
26.2	0.5		0.07	6
		13.4		10
		3.9		10
11.7(with scrubber)				9
14.5(with scrubber)				9
33(no scrubber)	0.5	14	2.9	Average
7-76		2.2-40	1.3-6	Range Used

a) SO_x expressed as SO_2.

b) HC expressed as methane.

c) NO_x expressed as NO_2.

Table 3.1-9. Emissions from Modified Flue Fed Incinerators[f], lbs/ton of Refuse Charged

Particulate	SO_x[a]	HC[b]	NO_x[c]	CO	Reference
6.1	0.5		16		5
6.5			4.2		5
5.9			7		5
5.2					5
5.6					5
1.2					5
10.2			0.14		6
5.9(1.3 after water spray)					9
5.3					9
6	0.5	3[d]	10		Factor
1.2 to 10.2			7 to 16		Range

a) SO_x expressed as SO_2.

b) HC expressed as methane.

c) NO_x expressed as NO_2.

d) Estimate based on commercial units.

e) Chute fed unit, average of 3 tests.

f) With afterburners and draft controls.

Table 3.1-10. Emissions from Domestic Incinerators (Without Gas-Fired Primary Burner), lbs/ton of Refuse Charged.

Particulate	SO_x[a]	HC[b]	NO_x[c]	CO	Reference
39	0.4	100	7[d]	300	3
		100		300-600	4

a) SO_x expressed as SO_2.

b) HC expressed as methane.

c) NO_x expressed as NO_2

d) Final factor was based on single chamber incinerator.

Table 3.1-11. Emissions from Domestic Incinerators (With Gas Afterburner), lbs/ton of Refuse Charged

Particulate	SO_x[a]	HC[b]	NO_x[c]	CO	Reference
6.3	0.4	1.5	2.0		3

a) SO_x expressed as SO_2.

b) HC expressed as methane.

c) NO_x expressed as NO_2

Table 3.1-12. Emissions from Pathological Incinerators, lbs/ton of Refuse Charged

Particulate	HC[a]	NO_x[b]	Reference
2.3	neg.	1.2	5
8.0	neg.	1.6	5
3.1	neg.	8.8	5
7.3	neg.	2.0	5
5	neg.	3	Factor
2.3-8.0		1.2-8.8	Range

a) HC expressed as methane.

b) NO_x expressed as NO_2.

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3.2 AUTOMOBILE BODY INCINERATION

Process Description

Approximately 10 million automobiles are scrapped each year in the United States,[1] and the accumulation and eventual disposal of these discarded bodies presents an increasing problem in urban areas. For many years open burning of automobile bodies to prepare them for use in the steel industry has been practiced, but the heavy black smoke resulting from this practice has led to regulations banning this form of open burning in many areas.

However, burning is still a practical way to prepare scrapped cars for steel processing if the air pollution problems resulting from the incomplete combustion of paint, upholstery, insulation, floor mats, hoses, etc., can be solved. In an attempt to reduce the various air pollutants produced by this burning, automobile incinerators have been developed which are equipped with emission control devices. Both afterburners and/or low voltage electrostatic precipitators have been used to reduce particulate emissions[2,3], with the former also reducing some of the gaseous emissions. Afterburner particulate removal efficiencies of about 40% have been reported.[3]

Automobile incinerators consist of a primary combustion chamber into which the partially stripped car(s) is placed. The car is then ignited, and the incinerator doors are closed. Approximately 30-40 minutes are required to burn two bodies simultaneously.[4] Up to 50 cars per day can be burned in this batch type operation depending on the size of the incinerator, that is, the number of cars burned simultaneously. Continuous operations in which cars are placed on a conveyor belt and passed through a tunnel type of incinerator have capacities of more than 50 cars per 8 hour day.

Factors Affecting Emissions

Both the degree of combustion as determined by the incinerator design, and the amount of combustible material left on the car greatly affect combustion.

Temperatures on the order of 1200°F are reached during automobile body incineration.[4] This relatively low combustion temperature is caused by the large incinerator volume needed to contain the bodies as compared to the small quantity of combustible material. The use of overfire air jets in the primary combustion chamber will increase combustion efficiency by providing air and increased turbulence.

Normally tires are removed from the cars before incineration. Incineration with tires would tend to increase the particulate emissions.

When afterburners are used to control emissions, the temperature in the secondary combustion chamber should be at least 1500°F. Lower temperatures will result in higher emissions.

Emissions

Particulates in the form of smoke, aldehydes, hydrocarbons, organic acids, and nitrogen oxides are emitted from the combustion of junked automobiles. Particulate is composed of approximately 67% combustible matter, largely carbon.[4]

Table 3.2-1 presents a summary of emission data reported in the literature. More detailed data and related calculations are provided in the Appendix 3.2.

Table 3.2.-1. Emissions from Automobile Body Incineration, lbs/Car Burned

	Uncontrolled	With Afterburner
Particulates	2 (1.6 - 2.1)	1.5 (1 - 1.9)
CO	2.5 (2 - 3)	negligible
HC (as methane)	0.5 (0.3 - 0.7)	negligible
Aldehydes (as HCOH)	0.1 (0 - 0.2)	0.02
Organic Acids (as Acetic)	0.2 (0 - 0.4)	0.06
Nitrogen Oxides (as NO_2)	0.3 (0.2 - 0.4)	0.4

Reliability of Emission Factor

Limited emission testing has been done on automobile body incineration. However, the reported data agree fairly well considering the process variables inherent in any type of incineration.

Table 3.2-2 presents the factor ranking.

Table 3.2-2. Automobile-Body Incineration Emission Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
10	5	5	20

The trend toward automobile shredders and pulverizers will probably reduce the amount of automobile body incineration in the future. Further work in this area does not appear warranted.

The only major assumption made in obtaining these factors was that CO and hydrocarbon emissions approximated one-sixth of the factors obtained in open burning of automobile components.

APPENDIX 3.2

Emission Data Calculations

A. Particulate

<u>Uncontrolled</u> - burning 3 cars per hour (Ref. 3)

1. $0.63 \text{ grs/ft}^3 \text{ at } 12\% \text{ CO}_2 \times \frac{4\% \text{ CO}_2}{12\% \text{ CO}_2} \times \frac{3500 \text{ ft}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{1 \text{ lb}}{7000 \text{ gr}} = 6.3 \text{ lbs/hr}$

2. $\text{At } 0.45 \text{ grs/ft}^3 \times \frac{4.5\% \text{ CO}_2}{12} \times 3500 \times 60 \times \frac{1}{7000} = \underline{5.1 \text{ lbs/hr}}$
Avg. = 5.7 lbs/hr or
1.9 lbs/car

<u>Controlled</u> - with gas-fired afterburners - 3 cars/hour (Ref. 3)

1. $0.26 \text{ grs/ft}^3 \text{ at } 12\% \text{ CO}_2 \times \frac{5.5\%}{12} \times \frac{3400 \text{ ft}^3}{\text{min}} \times 60 \times \frac{1}{7000} = 3.5 \text{ lbs/hr}$ or
1.2 lbs/car

2. $0.16 \times \frac{6.3}{12} \times 3200 \times 60 \times \frac{1}{7000} = \underline{2.3 \text{ lbs/hr}}$
Avg. = 2.9 lbs/hr or 1 lb/car

<u>Controlled</u> with oil-fired afterburner, $3^1/_2$ cars/hour

$0.27 \times \frac{7.3}{12} \times 4200 \times 60 \times \frac{1}{7000} = 5.9 \text{ lbs/hour}$

At $3^1/_2$ cars/hour, emissions = 1.7 lbs/car

<u>Controlled</u> with afterburner - 4 cars/hour (Ref. 4, pg. 70 and 71.)

$$2170 \text{ ft/min} \times \frac{\pi \times 39^2}{4 \times 144} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{520°\text{R}}{1960°\text{R}} \times \frac{29 \text{ lb/lb mol}}{379 \text{ ft}^3\text{/mol}} \times \frac{0.357 \text{ lb}}{1000 \text{ lb gas}}$$

= 7.84 lbs/hour
= 1.9 lbs/car

B. Gaseous Emissions (Ref. 3) - 3 cars/hour burning rate

NO_x as NO_2

<u>Uncontrolled</u>

Avg. = 32 ppm ± 25%

$32 \times 10^{-6} \times \frac{3500 \text{ ft}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hour}} \times \frac{46 \text{ lbs/lb-mol}}{379 \text{ ft}^3\text{/lb-mol}} = 0.815 \text{ lb NO}_2\text{/hour}$ or
0.27 lbs/car

With gas-fired afterburner

Avg. = 46.5 ppm

$46.5 \times 10^{-6} \times \frac{3300 \text{ ft}^3}{\text{min}} \times 60 \times \frac{46}{379} = 1.2 \text{ lbs NO}_2\text{/hour}$ or
0.4 lbs/car

Aldehydes as HCOH (formaldehyde)

Uncontrolled - 16 ppm

$$16 \times 10^{-6} \times \frac{3500\ \text{ft}^3}{\text{min}} \times \frac{60\ \text{min}}{\text{hour}} \times \frac{30\ \text{lbs/lb-mol}}{379\ \text{ft}^3\text{/lb-mol}} = \begin{array}{l}0.27\ \text{lbs/hour or}\\ 0.1\ \text{lbs/car}\end{array}$$

With gas-fired afterburner - 3 ppm
Emission = 0.05 lbs/hour pr 0.02 lbs/car
Estimated range for aldehyde emission was assumed ± 100%.

Organic Acids[3]

Uncontrolled 0.62 lbs/hour - 0.2 lbs/car (± 100% estimated)
With gas-fired afterburner 0.2 lbs/hour = 0.06 lbs/car

CO and Hydrocarbons

Open burning emissions (Reference 5) which are reported on a lbs/ton automobile components, and the fact that there are about 250 lbs of combustible material on a stripped car body (one without tires)[4] yields the following emission rates.

$$\text{Open burning data, lbs/ton} \times \frac{250}{2000} = \text{lbs/car body}$$

	LBS/TON[5,6]	LBS/CAR
Particulate	100	12.5
NO_x	2-5	0.25 - 0.62
Formaldehyde	0.03	0.38
CO	125	15
HC (as methane)	30	3.7

It is seen that uncontrolled emissions of particulate and formaldehyde from automobile incineration are approximately 1/6 to 1/4 of the open burning values. An estimate of CO and gaseous hydrocarbons based on 1/6 of the open burning values should give some idea of the incineration emission. These values are 2.5 lbs CO per car and 0.5 lb. HC per car.

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3.3 MUNICIPAL REFUSE AND WOOD DISPOSAL IN CONICAL BURNERS

Process Description

Conical burners are generally a truncated sheet metal cone with a screened top vent. The charge is placed on a raised grate by conveyor or bulldozer, the former method resulting in more efficient burning. No supplemental fuel is used but limited control of combustion air is often effected by means of a blower which supplies underfire air below the grate and peripheral openings in the shell which provide overfire air. For best results, each of these supply air systems is designed to create a cyclonic action. Excessive combustion air prevents good control of the combustion process and results in excessive smoke and other air contaminants.

The cylindrical or silo incinerator consists of a steel silo lined with refractory materials. Air is admitted through openings near the base of the incinerator. It is generally held that more efficient combustion can be attained in a cylindrical incinerator since the refractory-lined chamber maintains higher operating temperatures than the standard conical burner. However, emission test data does not indicate any significant reduction in contaminants emitted and, for the purpose of this study, no distinction is made between these two types of incinerators.

Factors Affecting Emissions

Many factors affect combustion within conical and cylindrical type incinerators. Quantity and types of pollutants are dependent on the makeup and moisture content of the charged material, control of combustion air, type of charging system used, and the condition in which the incinerator is maintained. It is difficult to establish what effect each of these factors has on the emission of contaminants. The most critical single factor seems to be the lack of maintenance on the incinerators. It is not uncommon for conical incinerators to have doors missing and a multiplicity of holes in the shell, all resulting in excessive combustion air, low temperatures, and therefore high emission rates.[1]

Particulate control systems have been adapted to conical burners with some success. These control systems include water curtains (wet caps) and water scrubbers.

Emissions

Published emission data for waste combustion in conical burners are very limited. Regarding municipal waste, some particulate data were available, but gaseous emission factors were estimated based on open burning and incineration test data. Detailed emission data are presented in the Appendix and summarized in Table 3.3-1.

Table 3.3-1. Emission Factors for Waste Incineration in Conical and Cylindrical Burners

Type of Waste	Emissions, lb/ton of waste as fired[d]				
	Particulate	CO	HC[e]	NO_x[f]	SO_2
Municipal Refuse	30 (10 to 60)	60	20	5	3
Wood	1[a] 10[b] 20[c]	130(30 to 360)	10(0.8 to 43)	1.2	0.15

a) Properly maintained burner with adjustable underfire air supply and adjustable, tangential overfire air inlets; approximately 500% excess air and 700°F exit gas temperature.

b) Properly maintained burner with radial overfire air supply near bottom of shell; approximately 1200% excess air and 400°F exit gas temperature.

c) Improperly maintained burner with radial overfire air supply near bottom of shell and many gaping holes in shell; approximately 1500% excess air and 400°F exit gas temperature.

d) Moisture content as-fired is approximately 50% for wood waste.

e) HC expressed as methane.

f) Expressed as NO_2.

Note: Use high side of range for intermittent operations charged with a bulldozer.

Reliability of Emission Factors

Particulate emission factors for combustion of municipal refuse or wood waste in conical burners are good even though they cover a range of values. However, gaseous emission data are very scarce and difficult to estimate. Emission factor rankings are presented in Table 3.3-2.

Table 3.3-2. Emission Factor Ranking for Conical Burners

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	14	5	5	24
Gases	7	5	3	15

No major assumptions were made in obtaining the factors presented in this section, except that inferences were drawn from incineration emission data to determine gaseous emissions from conical burners.

APPENDIX 3.3

Municipal Waste

There are no published results of incineration of municipal waste in conical or cylindrical burners. The results of one unpublished test for particulate emissions made on a conical burner by the Bureau of Solid Waste Management[2] are shown in Table 3.3-3. Note that there is no correlation between the rate of feed and the particulate emissions. For instance, while the feed rate of test No. 1 was 50% greater than test No. 4, the emissions were substantially less. Comparing tests 4, 5, and 6, we find there is no correlation. Since all tests were made under identical conditions on the same burner it can only be concluded that the particulate emissions are greatly affected by the composition of the charged material. Due to the limited sample size, a statistical evaluation of the data has not been made. Under the circumstances, it seems more reasonable to assign a range (10-60) to the particulate emission factor.

Table 3.3-3. Particulate Emissions From a Pilot Scale Conical Burner

Test No.	Feed Rate, lbs/hr	Particulate Emission, lb/hr	lb/ton	% of feed
1	1670	8.65	10.3	0.5
2	1670	8.70	10.5	0.5
3	1460	13.26	18.2	0.9
4	1190	32.44	54.6	2.7
5	1190	17.46	29.4	1.5
6	1190	4.41	7.4	0.4

Values for gaseous emissions must be approximated from the values found for other types of incinerators. These values are shown in

Table 3.3-4. Incineration in conical and cylindrical burners tends to resemble open burning in that the fire must support itself, no auxiliary fuel being used. Unlike open burning, however, outside wind conditions do not appreciably affect the combustion and the combustion air supply can be regulated. The ambient temperature is a factor since the metal skin has no significant insulation value. Except for size, the backyard incinerators are seemingly most similar to the conical burners, but the data from Reference No. 6, shown in Table 3.3-4, are so high, relatively speaking, as to preclude full consideration. More complete combustion may generally be expected from flue fed and single chamber incinerators since they control the overfire and underfire air rates to a greater extent.

Analyzing the above, it must be concluded that the incineration of municipal waste in conical and cylindrical burners is more efficient than open burning and less efficient than single chamber incinerators.

Table 3.3-4. Gaseous Emissions From Municipal Waste Incineration

Type of Incineration	Emissions, lb/ton of waste				Reference
	SO_2	CO	HC^a	$NO_x{}^b$	Number
Open Burning and Single Chamber	3	40	8	4	3
Open Burning	-	85	30	4-9	4
Single-Chamber (Commercial)	1.5	20	15	2	5
Backyard Incinerator		600	115^c	1	6

a) HC expressed as methane.

b) NO_x expressed as NO_2.

c) Reported values for saturated HC (30) and methane (85) were assumed to be expressed as methane.

Wood Waste

Very little testing has been done to measure emissions from the incineration of wood waste in conical and cylindrical burners. Almost all the reported figures are confined to particulate emissions. Table 3.3-5 compares the available test data with the open burning figures developed by Gerstle and Kemnitz.[4]

There is no correlation between the particulate emission figures which range from 1 to 20 lb/ton of wood waste. The highest figure was obtained from a conical burner having radial air openings and many gaping holes all over the shell. The exit gas temperature averaged about 400°F with approximately 1500% excess air while the burner which emitted only 2 lb. particulate matter/ton of wood waste, averaged approximately 700°F exit gas temperature with 500% excess air. Thus three particulate emission factors are given in Table 3.3-1 based on the condition and operation of the equipment.

Table 3.3-5. Emissions From Wood Waste Incineration

Type of Incineration	Emissions, lb/ton of waste as-fired[b]					Reference
	Part.	SO_2	CO	HC[a]	NO_x	Number
Open Burning	17		50	3	1	4
Cylindrical (Silo)	20	0.15			1.3	7
Cylindrical (Silo)	2	0.16		20	1.2	8
Conical - Satisfactory Operation	0.2-2.8					9
Conical - Unsatisfactory	7.3					9
Conical - Very Unsatisfactory	20.2					9
Cylindrical (Silo)	12					10
Conical			130(30-360)	11(0.8-43)		11
Conical	10.7(0.2-19.9)					12

a) Hydrocarbons expressed as methane.

b) Moisture content as-fired is approximately 50%.

Carbon monoxide emissions from conical burners have been measured by Droege and Lee.[11] These measurements are the basis for carbon monoxide emission factors. The emission factors for hydrocarbon and oxides of nitrogen are based on measured data.[8]

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3.4 OPEN BURNING

General Information

Open burning can be carried out in open drums or baskets and in large scale open dumps or pits. Materials commonly disposed of in this manner are municipal waste, automobile body components, landscape refuse, agricultural field refuse, wood refuse, and bulky industrial waste.

While open burning of waste is not desirable from an air pollution point of view, exemptions from control are often applied to right-of-way clearing, field burning of agricultural wastes, logging debris and bulky materials, since it is frequently the cheapest method for disposing of such refuse.[1]

Disposal of agricultural wastes is imperative because the refuse piles act as reservoirs of horticultural diseases and agricultural pests. As agricultural activities grow more intensive, the danger of horticultural debris carrying diseases and pests to succeeding crops increases. Thus, until a non-chemical means of disease control can be found, open burning of residues will continue to be common practice.

A similar problem exists regarding lumbering activities. On the average, 25 million tons of logging debris are left in the woods each year. As with horticultural wastes, this debris harbors tree diseases and harmful insects and, in addition, poses an exceedingly serious fire hazard. It has been reported that the average size of forest fires originating in logging waste is more than seven times the average size of fires originating in uncut areas.[1]

Factors Affecting Emissions

Ground level, open burning is affected by many variables including wind, ambient temperature, moisture content of the debris burned, size and shape of the debris, and compactness of the pile. To what degree each of these variables affects the burning is not known. Additional research is required in this area if refinement of the emission factors is desired.

In general, the relatively low temperatures associated with open burning increase the emissions of particulate, carbon monoxide, and hydrocarbons, while suppressing the emission of nitrogen oxides and sulfur oxides. The sulfur oxides are also a direct function of the sulfur content of the refuse.

Emissions

Emission factors are presented for the open burning of three broad categories: 1) municipal refuse, 2) automobile components, and 3) horticultural refuse. The factors are listed in Table 3.4-1. See Appendix 3.4 for a discussion of these factors.

Table 3.4-1. Emission Factors for Open Burning

Type of Waste	Emissions, lb/ton of waste as fired				
	Particulate	CO	HC[a]	NO_x[b]	SO_2
Municipal Refuse	15 (14 to 59)	85 (80 to 90)	30	6 (4 to 9)	1
Automobile Components[c]	100	125	30	4 (2 to 5)	neg.
Horticultural Refuse					
1) Agricultural Field Burning	17 (12 to 23)	100 (36 to 175)	20 (3 to 50)	1 to 4	neg.
2) Landscape Refuse and Pruning	17 (12 to 23)	60 (45 to 87)	20 (5 to 35)	1 to 4	neg.
3) Wood	17 (12 to 23)	50	4	1 to 4	neg.

Table 3.4-1. Continued

a) HC expressed as methane.
b) NO_x expressed as NO_2.
c) Upholstery, belts, hoses, and tires burned in-common.

Reliability of Emission Factors

The factors for open burning are limited by the fact that accurate source testing on large scale burning dumps is extremely difficult. Factors thus must be based on simulated open burns carried out under controlled conditions in the laboratory or on information collected at actual open burns which is subject to considerable variation. The documented laboratory studies plus actual testing do however give information which is fairly complete and should serve to categorize the emissions from open burning within satisfactory limits. The factors here are thus considered to be good and no further work is indicated,except a more detailed analysis of gaseous hydrocarbon emissions is warranted. Emission factor rankings are presented in Table 3.4-2.

Table 3.4-2. Emission Factor Ranking for Open Burning

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
10	8	6	24

No major assumptions were made in obtaining the factors presented in this section except that the determination of SO_2 emissions from the open burning of municipal refuse was based on information obtained from incinerator emissions.

APPENDIX 3.4

Little testing has been done regarding the open burning of municipal waste. Table 3.4-3 compiles all the figures found in the literature for such burning. In general, the average figures reported by Gerstle and Kemnitz[2] are adopted as emission factors since none of the other reported numbers is based on actual testing of open burns. The figures reported by Feldstein, et al[7] are at such great variance with the other figures that little or no weight has been given them.

Since the open burn test data for municipal refuse does not include sulfur oxides, and the reported estimated figures (See Table 3.4-3.) do not agree with incineration test data, a comparative analysis is warranted. The formation of sulfur oxides is dependent on two factors: 1) sulfur content of refuse and 2) efficiency of the combustion operation. The sulfur content of municipal waste is, generally speaking, constant. Open burning differs from multiple chamber incineration only as regards efficiency of combustion. Less sulfur is oxidized in the less efficient open burn. Thus the sulfur oxides emitted from open burning must be less than that emitted from incinerators. Incinerators emit approximately 1.5 lb/ton (see Section 3.1 supra.). Estimating an open burn combustion efficiency of 60-70% relative to multiple chamber incineration, it is expected that the former operation will emit 1.0 lb/ton of sulfur oxides. This figure is between the 3.0 and 0.3 reported in Table 3.4-3.

Only one data source has been found for emissions from the open burning of automobile components These figures are shown in Table 3.4-4.

Table 3.4-5 lists all the reported data for emissions from open burning of horticultural wastes.

There are no reported particulate emission figures for the open burning of purely wood wastes. The data reported for hydrocarbon and carbon monoxide emissions are for fruit tree prunings and do not directly relate to wood wastes due to lumbering and saw mill activities. The composition of the fruit prunings necessarily included small branches, leaves, and twigs.

Only one study has expressed nitrogen oxide emissions in terms of pounds per ton of material burned.[2] Even these readings are not conclusive, as they are instantaneous determinations of a rate. The reported figure is low since, in open burning, temperatures are generally relatively low. The temperature of the test fires reached its peak at approximately four minutes after burning was started and then diminished at a rapid rate. Thus the high-intensity burning required for the oxidation of atmospheric nitrogen exists only for a short period of time. The studies made by Gerstle and Kemnitz[2] and Darley, et al,[6] indicate that the mean rate of NO_x production would yield approximately 1 lb/ton of material initially present. Burkle, et al,[4] determined that 4 lb of NO_x per ton of cord wood was produced when burned in a trench incinerator. This higher rate is due, no doubt, to the extended residence time at the peak temperature achieved in a trench type incinerator.

The data shown in Table 3.4-5 indicates that as the wood content of the fuel increases, the emissions of hydrocarbon and carbon monoxide decrease.

Note that the reported figures for particulate emissions are essentially similar. What effect the wood content of the waste would have on the particulate emission is not known. For the purposes of this study, the figure found for landscape refuse will be used.

While moisture content will affect the emissions, no data has been reported in this regard with the exception of two of the brush and prunings tests.[2] However, there is no agreement in those figures that emissions increase as moisture content increases and, indeed, the magnitudes of emission remain the same.

Table 3.4-3. Emissions From Open Burning of Municipal Refuse

Emissions, lb/ton of waste					Reference
Particulate	CO	HC[a]	NO_x[b]	SO_2	Number
16 (14 to 18)	85 (80 to 90)	30	4 to 9	-	2
-	40	8	4	3	3[c]
30	0	80	0.6	0.3	5[e]
20 - 59	-	-	-	-	4[d]
	600	115[f]	1	-	7[g]

a) HC expressed as methane.

b) NO_x expressed as NO_2.

c) Whether figures are based on actual testing is not stated.

d) Measured emission from pilot-scale trench incinerator varied directly in proportion to the amount of combustion air admitted.

e) Figures based on estimate only.

f) Reported values for saturated HC (30) and methane (85) were assumed to be expressed as methane.

g) Figures are result of testing backyard incinerators.

Table 3.4-4. Emissions From Open Burning of Automobile Components

Emissions, lb/ton of Waste					Reference
Particulate	CO	HC[a]	NO_x[b]	SO_2	Number
100	125	30	2 to 5	-	2[c]

a) HC expressed as methane.

b) NO_x expressed as NO_2.

c) Figures based on tests of upholstery, belts, hoses, and tires burned in-common.

Table 3.4-5. Emissions From Open Burning of Horticultural Refuse

Type of Refuse Burned	Emissions, lb/ton of waste					Reference Number
	Particulate	CO	HC[a,b]	NO_x	SO_2	
Fruit Prunings	-	45 to 87	3.9 to 18.5	-	-	6
Landscape Refuse	17 (12 to 23)	65 (50 to 80)	30 (25 to 35)	1 to 4	-	2
	0	0	415	0.6	-	5
Grass Stubble and Straw	15.6 (9 to 26)	101 (56 to 147)	16 (5 to 25)	-	-	8
Rice Straw	-	56 to 90	11.5 to 15.4	-	-	6
Barley Straw	-	60 to 106	14.5 to 24.3	-	-	6
Native Brush	-	36 to 175	2.9 to 48.2	-	-	6
Redwood Chips	-	70	2.9	-	-	6
Fir Chips	-	35	3.7	-	-	6

a) HC expressed as methane.

b) Where HC was reported as carbon, figures were converted to methane.

c) NO_x expressed as NO_2.

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4. CHEMICAL MANUFACTURING INDUSTRIES

This section deals with the emissions from the manufacture and/or use of chemicals or chemical products. Potential emissions from many of these processes are high, but due to the nature of these compounds, they are, in general, recovered as an economic necessity to the profitable operation of the process. In still other cases, the manufacturing operation is run as a closed system allowing little or no escape to the atmosphere of any of the reactants or by-products.

In general, the emission which can reach the atmosphere from these processes is primarily gaseous and is controlled by incineration, adsorption, or absorption. In some cases, however, particulate emissions are also a problem from the manufacturing processes. When these occur, they are generally particles of extremely small size and require very efficient treatment for removal.

In a few cases, such as carbon black, charcoal, and rayon manufacture, emission of various noxious gases is a major problem which could be controlled, but control is apparently not economically attractive.

For many chemical processes emission data is extremely sparse, or non existent. Emissions were therefore frequently estimated based on material balances, yields, or similar processes. These factors are,of course,not as reliable as measured emission data.

Since the major emissions from the processes presented in this section are gases, no particle size summary is presented.

4.1 AMMONIA

Process Description[1,2,3]

The manufacture of ammonia (NH_3) is accomplished primarily by the catalytic reaction of hydrogen and nitrogen at high temperatures and pressures. In a typical modern plant as shown in Figure 4.1-1 a hydrocarbon feed stream (usually natural gas) is desulfurized to less than 2 ppm of sulfur, mixed with steam and catalytically reformed to carbon monoxide and hydrogen. A nickel-base catalyst is used in this high temperature (1400-1500°F) step. Air is introduced into the secondary reformer to supply oxygen and provide a nitrogen to hydrogen ratio of 1:3. The gases then enter a two-stage shift converter which reacts the carbon monoxide with water vapor to form carbon dioxide and hydrogen. The gas stream is then scrubbed with either monoethanolamine (MEA), hot potassium carbonate or other CO_2 absorbing solutions to yield a gas containing less than 1% CO_2. A methanator may then be used to convert quantities of unreacted CO to inert CH_4 before the gases, now largely nitrogen and hydrogen in a ratio of 1:3, are compressed to 150 to 300 atmospheres and passed to the converter. Alternatively, the gases leaving the CO_2 scrubber may pass through a CO scrubber where they are scrubbed with an ammoniacal solution of copper formate and then passed to the converter.

Most converters in the United States operate at about 150 atmospheres of pressure (2200 psi) and 1000°F with a once-through yield of 15%. The synthesis gases react in the converter to form ammonia in the presence of an iron oxide catalyst whose activity is increased by adding other trace metal oxides. Since CO greatly reduces the activity of the catalyst, its concentration must be reduced to a level of 10 ppm or less.

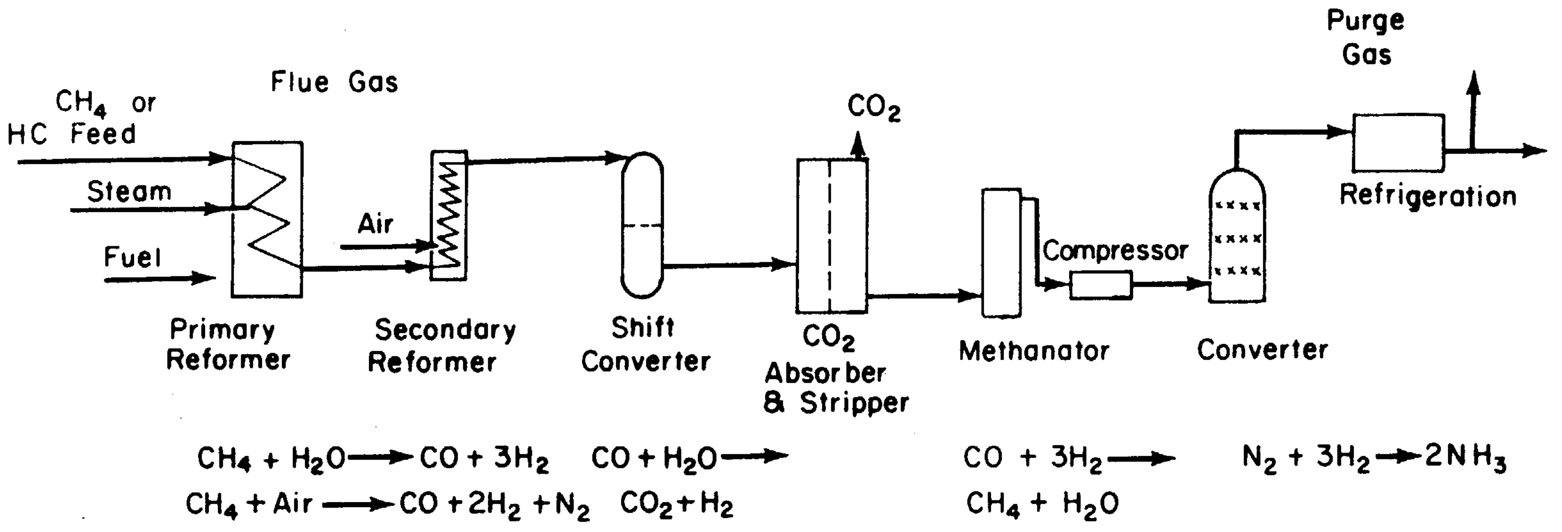

Figure 4.1-1 Typical Ammonia Manufacturing Process

The converted ammonia gases are partially recycled, and the balance is cooled and compressed to liquefy the ammonia. The non-condensable portion of the gas stream consisting of unreacted nitrogen, hydrogen, and traces of inerts such as methane, carbon monoxide, and argon, is largely recycled to the converter. However, to prevent accumulation of the inerts, some of the non-condensable gases must be purged from the system.

When a carbon monoxide scrubber is used in the synthesis gas preparation system, the scrubber solution (copper formate) regenerator off-gases contain significant amounts of carbon monoxide (73%) and ammonia (4%) in addition to hydrogen, nitrogen, and carbon dioxide. This gas may be scrubbed to recover ammonia and then burned to utilize the CO fuel value.[4]

Emissions of ammonia also occur from the storage and loading area.

Factors Affecting Emissions

The major factor affecting emissions from the synthesis of ammonia is the general operating condition of the plant such as the condition of compressor and valve seals, relief valve settings, product loading operations, etc. Plants equipped with a methanator will have much lower CO emissions as compared to plants using a CO scrubbing system.

Emissions

Since a portion of the uncondensed exit gases are recycled, all ammonia plants must bleed-off or purge some of these gases in order to prevent the accumulation of inerts in the system. These gases contain about 15% ammonia.[4] Gases from the loading and storage operations contain 60-100% ammonia.[4] These gases may be scrubbed with water to reduce the atmospheric emissions. In addition, emissions of CO and ammonia can occur from those plants equipped with copper formate CO scrubbing systems.

Emission factors based on data in the Appendix are presented in Table 4.1-1.

Table 4.1-1 Uncontrolled Emissions from Ammonia Manufacturing, lbs/ton

	NH_3	CO	CH_4
Plants with Methanator			
Purge Gas[a]	3(2 to 4)	Neg.	90(40 to 130)
Storage and Loading[a]	200(150 to 250)	0	0
Total	203(152 to 254)	Neg.	90
Plants with CO Absorber and Regeneration System			
Regenerator Exit[b]	7	200	0
Purge Gas[a]	3(2 to 4)	Neg.	90(40 to 130)
Storage and Loading[a]	200(150 to 250)	0	0
Total	210(152 to 254)	200	90(40 to 130)

a) NH_3 emissions can be reduced by 99% by passing through a 3 stage packed tower water scrubber. CH_4 is not reduced.

b) A two stage water scrubber and incineration system can reduce these emissions to a negligible amount.

Note: Ranges in emissions are due to variations in gas flows and concentrations, and not any specific factor.

Reliability of Emission Factors

Though based on limited emission data, the ammonia processes used today are well defined, and data based on only one plant should represent emissions from all plants of similar design. The emission factors presented here are considered reliable, but would benefit from additional emission data. Table 4.1-2 presents the factor ranking.

Table 4.1-2. Ammonia Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	8	8	21

No assumptions were made in determining these emission factors. Additional detailed emission test data for ammonia manufacture appear desirable.

APPENDIX 4.1

Emission Calculations for a 450 ton per day Ammonia Plant. (Reference 4)

Purge Gas

100-200 cfm, 15% NH_3

$$150\ \frac{ft^3}{min} \times .15\ NH_3 \times 1440\ \frac{min}{day} \times \frac{17\ lb/lb\ mol}{380\ ft^3/lb\ mol} = 1450\ lbs/day \pm 33\%$$

or 3.2 ± 33% lbs/ton product

CO at about 10 ppm in this gas stream would produce a negligible emission. CH_4 at 1% (± 50%) in this gas stream would produce an emission of 91 lbs/ton.[a]

Loading and Storage

Approximately 1800 cfm @ 60-100% NH_3

$$1800\ \frac{ft^3}{min} \times .80\ NH_3 \times 1440\ \frac{min}{day} \times \frac{17}{380} = 93{,}000 \pm 25\%\ lbs/day$$

or 208 ± 25% lbs/ton product

Combined purge and storage emissions after water scrubber

600 cfm 0.2% NH_3, CH_4 is not changed.

$$600\ \frac{ft^3}{min} \times 0.0020\ NH_3 \times 1440\ \frac{min}{day} \times \frac{17}{380} = 77.5\ lbs/day$$

or 0.17 lbs/ton product

Emissions from CO Scrubber when used in system:

1200 cfm, 73% CO, 4% NH_3

$$1200\ \frac{ft^3}{min} \times .73\ CO \times 1440\ \frac{min}{day} \times \frac{28}{380} = 93{,}000\ lbs\ CO/day$$

or 206 lbs CO/ton product

$$1200\ \frac{ft^3}{min} \times 0.04\ NH_3 \times 1440\ \frac{min}{day} \times \frac{17}{380} = 3110\ lbs\ NH_3/day$$

or 6.9 lbs NH_3/ton product

These emissions can be virtually eliminated by a water scrubber and final combustion of the gases in a boiler.

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a) CH_4 based on very limited gas concentration data in Reference 3, page 18.

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4.2 ASPHALT ROOFING

Process Description

The manufacture of asphalt roofing felts and shingles involves saturating a fiber media with asphalt by means of dipping and/or spraying.

While not always done at the same site, an integral part of the operation is the preparation of the asphalt saturant. This preparation consists of oxidizing the asphalt and is accomplished by bubbling air through liquid (430-500°F) asphalt for 8 to 16 hours. The industry refers to this operation as "blowing". The time required for blowing depends on the desired properties of the saturant. It had been the practice to blow the asphalt in horizontal stills where the material loss ranges from 3 to 5%.[1] Most of this material is recovered by venting the exhaust gases through oil knock-out tanks which are an integral part of the process. The recaptured mist is not reintroduced into the saturant but is used for other products such as cut-back asphalt. Thus, in horizontal stills, it requires approximately 1.05 tons of asphalt to produce 1.00 ton of saturant. However, most roofing manufacturing firms are currently using vertical stills from which the material loss is 1 to 2% over a 1 1/2 to 5 hour cycle.[1] The ameliorating effect of these stills, regarding emissions, is significant.

After blowing, the saturant is transported to the saturation tank or spray area. The saturation of the felts is accomplished at temperatures of 400-500°F by dipping, by high pressure sprays, or both. Where both methods are used, the spray is preliminary to the dipping. This spray, applied to one side of the felt only, drives the moisture out the other side. The felts must contain less than 7% moisture to prevent subsequent blistering of the asphalt.

The entire saturation process is limited by the properties of the felt and the speed at which the felt can be fed to the saturator. Maximum speeds of 600 fpm are obtained for 15 to 30 lb. felt and 400-500 fpm for the heavier weights. However, the speed on the average installation is more like 250-275 fpm. Normally, felts are 3 or 4 ft. wide. On rare occasions however, 6 ft. wide felts are run.

Felts are made in varying weights: 15, 30, and 55 lb/100 sq. ft. (1 square). Often granules of gravel or mica are applied to the 55 lb. felt making it suitable for use as shingles. Dust generation may accompany this procedure. Regardless of the weight of the final product, the makeup is approximately 40% dry felt and 60% asphalt saturant.

Common methods of air pollution control at asphalt saturating plants include complete enclosure of the spray area and saturator followed by good ventilation through one or more collection devices including combinations of wet scrubbers, and two-stage low voltage electrical precipitators, or cyclones and fabric filters. A low voltage electrical precipitator preceded by a wet scrubber has been reported to provide a collection efficiency of about 85%.[2]

Factors Affecting Emissions

Factors affecting emissions include the temperature of the asphalts, the amount of volatiles in the asphalt, the amount of spray air used initially, the feed rate, width, and weight of the felt, the moisture content of the felt, the amount of asphalt applied to felts by spraying, the rate of ventilation of the system, and the efficiency and degree of maintenance of control equipment used.

Emissions

Table 4.2-1 lists the emission factors derived for the asphalt blowing and felt saturation processes. Limited test data is available and the factors are based on the information obtained from industry as well as published works. Appendix 4.2 contains a compilation of available data. Gaseous emissions from the saturation process are unknown. It is likely that such emissions are slight due to the initial driving off of these contaminants during the blowing process. Likewise, no data has been found for emissions from saturation processes which employ the use of sprays. The spray will increase emissions due to the entrainment of asphalt in the water particles which are driven through and out the lee side of the felt. Factors given for such operation in Table 4.2-1 are engineering estimates which comport with previously used hourly emission rates. (See Appendix 4.2 for this correlation.) Ranges in emissions were not given since the reported information did not provide a basis for estimation.

Table 4.2-1. Emission Factors for Asphalt Roofing

	Uncontrolled Emissions, lb/ton of saturated felt		
Operation	Particulate[b]	HC[a]	CO
Asphalt Blowing	2.5	1.5	0.9
Felt Saturation			
a) Dipping only	1	-	-
b) Dipping and spraying	2	-	-
c) Spraying only	3	-	-

a) HC expressed as methane.

b) Low voltage precipitator can reduce emissions by about 60%; when used in combination with a scrubber, overall efficiency is about 85%.

Reliability of Emission Factors

The factors listed in Table 4.2-1 are based on limited data, and gaseous data were not available for the saturation process. The factors for asphalt blowing and the dipping-only saturation process are based on test data and are felt to be representative. The factors developed for the dipping-and-spraying and the spraying-only saturation processes are based on engineering judgment and are therefore to be considered questionable. Further work in this area is justified, especially regarding the gaseous emissions from the various saturation processes. Emission factor rankings are presented in Table 4.2-2.

Table 4.2-2. Emission Factor Ranking for Asphalt Roofing

Process	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Asphalt Blowing	10	8	3	21
Saturation				
a) Dipping only	10	8	3	21
b) Spraying and dipping	0	8	3	11
c) Spraying only	0	8	3	11

No major assumptions were made except that the factors for the spraying-and-dipping and the spraying-only saturation processes were assumed to be 200% and 300%, respectively, of that found for the dipping-only process.

APPENDIX 4.2

A. Reported Emissions from Asphalt Blowing

The test reported in Reference 2 provides emission information for a 24 tons per hour asphalt blowing operation. This information is compiled in Table 4.2-3.

Table 4.2-3. Test Data from Asphalt Blowing Operation[2]

Exhaust gas, scfm	Temp. °F	Particulate grains/scf	HC[a], ppm	CO, ppm	Input tons/hr
8400	210	1.30[b]	2500	900	24

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a) HC expressed as methane [Note: original text is in conflict whether HC is expressed as carbon or methane.]

b) Reading taken in exhaust stack after steam spray-baffle arrangement was higher (1.45). However, since the baffles are not an integral part of the process, the reading taken ahead of the baffles is used.

The emissions given in Table 4.2-3 are converted to lb/ton and reported in Table 4.2-4.

Table 4.2-4. Emissions from Asphalt Blowing Operation, lb/ton of input[a]

Particulate	HC[b]	CO
3.9	2.25	1.38

---

a) Conversion of data given in Table 4.2-3.

b) HC expressed as methane.

However, the figures in Table 4.2-4 are based on lb/ton of asphalt input. It should be noted that approximately 5% of the initial material is lost in the blowing process (See main text, Process Description). Further, only 61.5% of the final product (asphalt saturated felts) is asphalt. All emissions for this section will be based on the final product, viz., lb/ton of asphalt saturated felts. Thus it requires 0.65 tons (105% x 61.5% x 1 ton) of unoxidized asphalt to produce 1 ton of saturated felts. The factors reported in Table 4.2-1 are 65% of those reported in Table 4.2-4 and are rounded off for ease of use.

B. Emissions from Felt Saturation

No gaseous emissions have been reported from this process and very little information is available regarding particulate emissions. The published emissions are based on a lb/hr basis and are shown in Table 4.2-5.

Table 4.2-5. Reported Uncontrolled Particulate Emissions from Felt Saturation

Emissions, lb/hr	Reference Number
67.7	3
55.0	3
71.4	3
20[a]	4

a) Emission after control device.

An unpublished test reported 24 lb/hr uncontrolled particulate emissions from a process operating at the rate of 22.5 tons finished product/hr.[1] (Approximately 1.0 lb/ton of saturated felt). This process did not utilize sprays. This fact seems to account for the relatively low emission rate. The highest reported rate shown in Table 4.2-5 is approximately three time the above figure. Since spraying increases the potential particulate emissions, the factors are arbitrarily weighted as follows:

a)	Dipping only	100%
b)	Dipping and Spraying	200%
c)	Spraying only	300%

That is to say, the factor for Spraying-Only is 300% greater than for Dipping-Only.

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4.3 CARBON BLACK

Process Description

Carbon black is produced by reacting a hydrocarbon fuel such as oil and/or gas with a limited supply of air at temperatures of 2500°F - 3000°F. Part of the fuel is burned to CO_2, CO, and water thus generating heat for the combustion of fresh feed. The unburnt carbon is collected as a black fluffy particle. Three basic processes currently exist in the United States for producing this compound. They are: The furnace process accounting for about 83% of production; the older channel process which accounts for about 6% of production; and the thermal process. Atmospheric pollutants from the thermal process are negligible since the exit gases which are rich in hydrogen are used as fuel in the process. In contrast, the pollutants emitted from the channel process are excessive and characterized by copious amounts of highly visible black smoke. Emissions from the furnace process consist of carbon dioxide, nitrogen, carbon monoxide, hydrogen, hydrocarbons, some particulate matter, and some sulfur compounds.

In the channel black process, natural gas is burned with a limited air supply in long low buildings containing 3000 to 4000 small burners. The flame impinges on long steel channel sections that swing continuously over the flame. Carbon black, deposited on the channels, is scraped off and falls into collecting hoppers. The combustion gases containing solid carbon not collected on the channels, in addition to carbon monoxide and other combustion products, are then vented directly from the building. Approximately 1 to 1.5 pounds of carbon black are produced from the 32 pounds of carbon available in 1000 ft^3 of natural gas.[1,2,3] The balance of the carbon is lost as CO, CO_2, hydrocarbons, and particulate.

The furnace process is sub-divided into either the gas or oil process depending on the primary fuel used to produce the carbon black. In either case, gas (gas process) or gas and oil (oil process) are injected into a reactor with a limited supply of combustion air. Common practice currently consists of also feeding some oil to the reactor in the gas process. This enrichment is on the order of 5.65 gallons of oil per 1000 ft^3 gas.[1] Part of the feed is burned with the combustion air to provide heat for decomposing the balance of the feed at a temperature of about 2600 - 2900°F. The combustion gases containing the hot carbon are then rapidly cooled to a temperature of about 500°F by water sprays and by radiant cooling. Yields of 10 to 30% are obtained in the gas process (i.e., 10 to 30% of the carbon in the feed is recovered as carbon black). Approximately 55% of the oil feed is recovered as carbon in the oil process.

The largest and most important portion of the furnace process consists of the particulate or carbon black removal equipment. While many combinations of control equipment exist, common practice as shown in Figure 4.3-1 is to provide an electrostatic precipitator, a cyclone, and a fabric filter system in series to collect the carbon black. In newer plants, the electrostatic precipitator may be omitted. In some older plants the final fabric filter system is not used, or a scrubber may be used in its place. Control of gaseous emissions of carbon monoxide and hydrocarbons is not practiced in the United States. Incineration of these gases is feasible, however, and is practiced in Great Britain.

In thermal black plants, natural gas is decomposed by heat in the absence of air or flame. In this cyclic operation, methane is pyrolyzed or decomposed by passing it over a heated brick checkerwork at a temperature of about 3000°F. ($CH_4 \rightarrow C + 2H_2$).

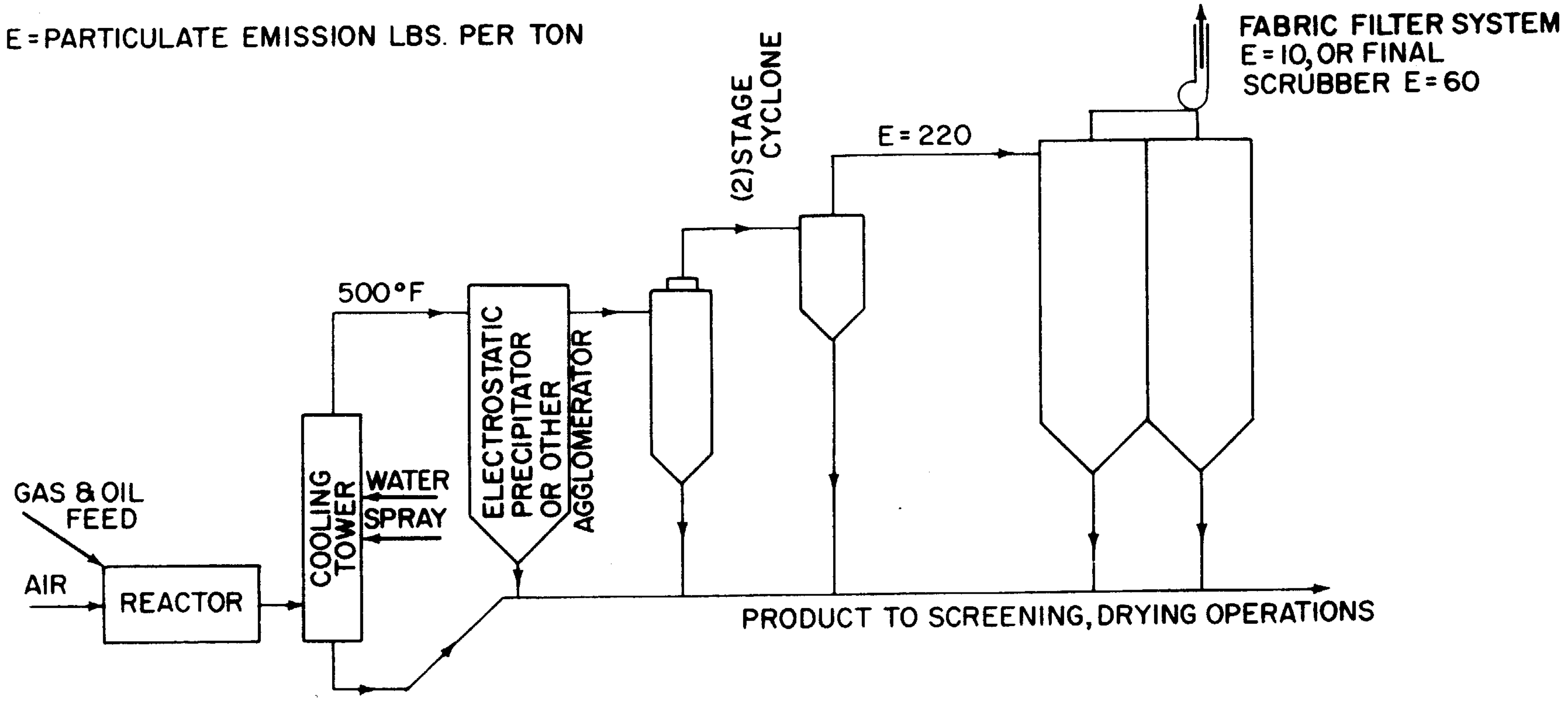


Figure 4.3-1. General process flow of furnace process carbon black manufacturing 1, 3.

This checkerwork is first heated by burning hydrogen generated in the decomposition reaction and/or by additional gas fuel. While one set of checkerwork is decomposing gas to produce carbon black, the other set is being heated. The gas flows are then switched and the heating/decomposition cycle is repeated. The decomposed gas is then cooled and the carbon black removed by a series of cyclones and fabric filters. The exit gas consisting largely of hydrogen (85%), methane (5%), and nitrogen is then recycled to the process burners or used to generate steam in a boiler. Due to the recycling of the effluent gases, there are essentially no atmospheric emissions from this process. Particulate emissions can, of course, occur from product handling.

Factors Affecting Emissions

The most important factor affecting emissions is the basic manufacturing process and its inherent efficiency. Thus, emissions from the channel black process are excessive, while those from the thermal process are negligible. Particulate emissions from the furnace process are affected by the type of control equipment used. Gaseous emissions are largely determined by the overall yield, type of fuel (that is, liquid or gas), the reaction time and temperature, the ratio of gas to oil in the feed, and the amount of combustion air.

Emissions

Table 4.3-1 presents the calculated emissions from the various carbon black processes. Nitrogen oxide emissions are not included since data are not available and they are believed to be low due to the lack of available oxygen in the reaction.

Table 4.3-1. Emissions From Carbon Black Manufacturing Processes, lbs/ton of product

Process	Particulate	CO	H_2S	HC[a]
Channel[f]	2300(2000 to 5000)	33,500(26,000 to 44,000)	-	11,500(5000 to 15,000)
Thermal	neg.	neg.	neg.	neg.
Furnace				
Gas	220[b] 60[c] 10[d]	5,300(4200 to 6400)	neg.	1,800
Oil		4,500(3600 to 5400)	38S[e]	400

a) As methane.

b) 90% overall collection efficiency, that is, no collection after cyclone.

c) 97% overall collection efficiency, that is, cyclones followed by scrubber.

d) 99.5% overall collection efficiency, that is, fabric filter system.

e) S = weight % sulfur in feed.

f) Based on yield of 1.5 pounds of carbon black per 1000 ft.^{3} of gas feed.

Note: Emission ranges are due to variations in operating conditions and not any specific factors.

Trace quantities of carbonyl sulfide, thiophene and carbon disulfide have also been reported when oil is used in the feed. Most of the gas used in the carbon black industry is scrubbed to remove sulfur compounds. Oil feeds may, however, contain more than 1% of sulfur. When sulfur contents increase beyond about 1.2% by weight, additional H_2S is not produced and free sulfur is formed.

Additional emissions may occur from the grinding, screening, and drying operations at a carbon black plant. These emissions are usually controlled by a pneumatic system which exhausts into a bag filter system. However, poorly designed or maintained equipment can result in spills and leaks. Due to the variability of these emissions, no emission estimate is possible.

Reliability of Emission Factors

Factors for the channel black process are questionable due to a complete absence of emission data. Factors for furnace black plants are considered good since exit gas concentrations and considerable process throughput data were available. Table 4.3-2 presents the factor ranking.

Table 4.3-2. Carbon Black Emission Factor Ranking

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Channel Process	0	5	5	10
Furnace Process	7	8	8	23

No major assumptions were made in determining the emissions from the furnace process. For the channel black process, gaseous emissions were assumed to be similar in composition to those from the gas furnace process. Product yield was based on reported data, and the balance of the feed was lost to the atmosphere. Variations in emissions due to these assumptions are shown in Table 4.3-1.

APPENDIX 4.3

A. CARBON BALANCE TO ESTIMATE EXIT GAS VOLUMES - FURNACE PROCESS

1. Oil Furnace Process Input[1] (Intermediate super abrasion grade)

220 gal oil/hr
12,200 ft^3 gas/hr
190,000 ft^3 air/hr

220 gal oil/hr x 7.1 lb/gal x .90 C = 1408 lbC/hr entering reactor in oil

12,200 ft^3 gas/hr x $\frac{12}{380}$ x .97 C = 374 lbC/hr entering reactor in gas

55% of oil feed is converted to carbon black.[1]

0.55 x 1408 = 774 lb carbon black produced

0.45 x 1408 = 634 lb carbon not converted to carbon black

634 lbs C from oil + 374 lbs C from gas = 1008 lbs C in exit gas

Exit gas carbon composition is:[1,4,5]

4.9% CO_2
11.4% CO
0.8% CH_4
0.5% C_2H_2

Exit gas rate may be calculated from carbon mass balance, namely:

$$(\%\ \text{Carbon})(\text{exit gas rate}) \times \frac{12\ \text{lbs/lb mol}}{380\ \text{ft}^3\text{/lb mol}} = \text{lbs carbon in exit gas}$$

Let Q = exit gas rate

$$\left[\left(\underset{CO_2}{0.049\ Q} + \underset{CO}{0.114\ Q} + \underset{CH_4}{0.008\ Q}\right)\frac{12}{380}\right] +$$

$$\left[0.005\ Q\frac{(24\text{ lbs C/lb mol }C_2H_2)}{380\text{ ft}^3\text{/lb mol}}\right]$$

$$= 1008\text{ lbs carbon/hr}$$

$$0.00534\ Q + 0.00032\ Q = 1008$$

$Q = 180{,}000\text{ ft}^3\text{/hr}$ (dry basis rounded off)

= 3000 SCFM @ 60°F, dry basis

or 3000 SCFM per 774 lbs carbon black produced/hr

$\frac{3000}{0.774}$ = 3900 SCFM per 1000 lbs carbon black/hr dry basis (calculated).

Calculations based on data in article by Reinke and Ruble[4] gives 25,700 SCFM (wet) per 3000 lbs of product/hr, or

$$\frac{25{,}700 \times .60\ H_2O \times 10^{-3}}{3000} = 5140\text{ SCFM/1000 lb C/hr (dry)}$$

Therefore use an average value of 4500 SCFM (dry basis) per 1000 lbs of carbon black produced or 9000 SCFM per ton of carbon black.

2. <u>Gas Furnace Process</u>[1]

560 ft^3/min of gas[a]

2520 ft^3/min of air

$$560\text{ ft}^3\text{/min} \times \frac{12}{380} \times .97 \times 60\text{ min/hr} = 1030\text{ lb C/hr entering}$$

---

a) Oil is sometimes added at the rate of 5.5 gallons per 1000 ft^3 of gas. This has very little effect on the overall emission rate per ton of product.

25% conversion to carbon black = 258 lb carbon black/hr product.

Lbs gaseous carbon in exit gas = (1030 - 258) = 772 lb/hr.

Exit gas carbon composition is (dry basis):

CO_2	5%
CO	5%
CH_4	1%
C_2H_2	1%

Let Q = ft^3/hr of exit gas flow

$$[(.05 + .05 + .01) \times \frac{12}{380}]\ Q + [.01 \times \frac{24}{380}]\ Q = 772 \text{ lbs carbon in exit gas}$$

$$.00348\ Q + .00063\ Q = 772$$

$$.00411\ Q = 772$$

$$Q = 187{,}000\ ft^3/hr \text{ (dry basis)}$$

$$= 3130 \text{ SCFM dry basis for 258 lb/hr of product}$$

For 1000 lbs of product, $\frac{3130}{.258}$ = 12,100 SCFM dry basis at 60°F.

Use 24,000 SCFM/ton of carbon black.

B. GASEOUS EMISSIONS - FURNACE PROCESSES

Average Exit Gas Composition, percent by volume, dry basis.

	Oil Process[1,4,5]	Gas Process[1]
CO_2	4.9	5 ± 20%
CO	11.4	5 ± 20% (The range was estimated.)
CH_4	0.8	1
C_2H_2	0.5	1
H_2	13.5	17 - 18
H_2S	0.035	-
N_2	Balance	Balance

1. Oil Process - per ton of product

CO: $9000\ \frac{ft^3}{min}$ (dry basis) x 60 min/hr x .114 x $\frac{28\ lb/mol}{380\ ft^3/mol}$

= 4550 lbs/ton

CH_4: 540,000 ft^3/hr x .008 x $\frac{16}{380}$ = 181 lbs/ton

C_2H_2: (expressed as CH_4): 540,000 ft^3/hr x .005 x $\frac{32}{380}$

= 228 lbs/ton

H_2S: 540,000 ft^3/hr x 0.00035 x $\frac{34}{380}$ = 16.9 lbs/ton

(See later calculation for H_2S emissions).

2. Gas Process - per ton of product

CO: 24,000 ft^3/min x 60 min/hr x .05 x $\frac{28}{380}$ = 5300 lbs/ton[a] ± 20%

CH_4: 1,440,000 ft^3/hr x .01 x $\frac{16}{380}$ = 606 lbs/ton[b]

C_2H_2: (as CH_4): 1,440,000 ft^3/hr x .01 x $\frac{32}{380}$ = 1212 lbs/ton[c]

---

a) Represents 2280 lbs of carbon (5300 x 12/28), CO_2 also represents 2280 lbs of carbon

b) Represents 460 lbs of carbon

c) Represents 910 lbs of carbon

Nitrogen Oxide Emissions

Due to lack of oxygen in the high temperature zones, very little nitric oxide will form. No emission data are available.

Sulfur Emissions

Drogin reports 90% of S goes to effluent gas.[1] For low sulfur feeds this sulfur appears largely as H_2S, not SO_2. Free sulfur could also be formed but this would be collected as a particulate.

Based on 90% S emitted as H_2S, emission factor for oil process is:

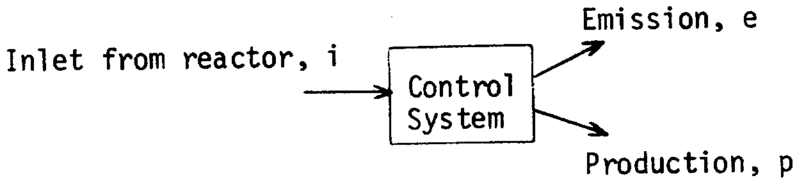
$$\frac{34\ H_2S}{32\ S} \times .90 \times \frac{S}{100} \times \frac{570\ \text{gal oil}}{\text{ton prod}} \times \frac{7.1\ \text{lb}}{\text{gal}} = 38.6S$$

Where S is weight % in feed

$$\frac{570\ \text{gal of oil}}{\text{ton}} = 220 \times \frac{2000\ \text{lbs/ton}}{774\ \text{lbs/220 gal}}$$

C. PARTICULATE EMISSIONS - FURNACE PROCESS - (either gas or oil)

Since production is the amount collected in the particulate control system, the efficiency of the control system can be mathematically related to the production:



$$i = e + p$$

$$E = \text{Collector Efficiency} = \frac{i - e}{i} = \frac{p}{i}$$

$$iE = i-e$$

$$i\,(1-E) = e$$

$$\text{and } i = \frac{p}{E}$$

$$\text{Therefore } \; e = \frac{p}{E}\,(1-E)$$

Particulate Emissions per ton of production are therefore:

@ 90% collection efficiency, that is, no collection after cyclone[1,4,5]

$$e = \frac{2000}{.90}\;(1 - .90) = 220 \text{ lbs/ton}$$

@ 97% collection efficiency, that is, with a scrubber following cyclone

$$e = \frac{2000}{.97}\;(1- .97) = 61.9 \text{ lbs/ton}$$

@ 99.5% (good fabric filter system)

$$e = \frac{2000}{.995}\;(1- .995) = 10.05 \text{ lbs/ton}$$

D. CHANNEL PROCESS

Yield is 1 to 1.5 lb per 1000 ft^3 of gas.[1,2]

1000 ft^3 gas contains about 32 lb of available carbon $(1000 \times \frac{12}{380} = 32 \text{ lb})$

Therefore 30.5 lbs of carbon are lost as particulate, CO_2, CO and hydrocarbons for each 1.5 lb of product (32-1.5 = 30.5).

Due to the higher excess air (open flame) less particulate is initially formed as compared to the furnace process, and more CO and CO_2 are formed.

In the gas furnace process about 25% of the feed (by weight) is converted to solid carbon. Assume in channel black process that about 10% of feed is converted to solid carbon and balance is split between CO, CO_2, and HC. For 1000 ft^3 of gas entering (32 lb carbon), 1.5 lb is product, and 1.7 lb is lost in smoke (3.2-1.5). This could vary up to 3-4 lbs, depending on amount of feed converted to solid carbon. Remaining 28.2 lb carbon (32-3.2) appears as a gas with the following assumed composition, based on gas furnace process:

38.4% of carbon appeared as CO_2 in the exit gas (probably varies from 30 to 50%)

38.4% of carbon appeared as CO in the exit gas (probably varies from 30 to 50%)

23.2% of carbon appeared as HC in the exit gas (probably varies from 10 to 30%)

on a lbs per ton basis:

$$1.7 \text{ lb part} \times \frac{2000 \text{ lb/ton}}{1.5 \text{ lb/product}} = 2{,}260 \text{ lb part/ton of product (2000 to 5000)}$$

$$28.2 \times \frac{2000}{1.5} \times 0.384 \times \frac{28}{12} = 33{,}600 \text{ lb CO/ton (Varies from 26,000 to 44,000)}$$

$$28.2 \times \frac{2000}{1.5} \times 0.232 \times \frac{16}{12} = 11{,}500 \text{ lb } CH_4\text{/ton (Varies from 5,000 to 15,000)}$$

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2. Cox, J.T. High Quality - High Yield Carbon Black. Chem. Eng. 57:116-117, June 1950.
3. Shreve, R.N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill Book Co. 1967, p. 124-130.
4. Reinke, R.A. and T.A. Ruble. Oil Black. Industrial and Engineering Chemistry. 44:685-694, April 1952.
5. Allan, D.L. The Prevention of Atmospheric Pollution in the Carbon Black Industry. Chemistry and Industry. p. 1320-1324, October 15, 1955.

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4.4 CHARCOAL

General Information

Charcoal is generally manufactured by means of pyrolysis, or destructive distillation of wood waste from members of the deciduous hardwood species. In 1958, approximately 214,000 tons of charcoal were manufactured and shipments of that product totaled $14.7 million.[1] The production figures for 1963 had nearly doubled to 379,000 tons and $28.4 million.[2] This increase was registered in spite of the decrease in profits due to the more economical production of synthetic methanol, acetic acid, and acetone by methods other than wood distillation.

Using maple as a typical hardwood, the composition is found to be 50.64% carbon, 6.02% hydrogen, 41.74% oxygen, 0.25% nitrogen, and 1.35% ash.[3] All percentages are based on dry weight. In the pyrolysis of wood, all the gases, tars, oils, acids, and water are driven off leaving virtually pure carbon. All but the gas is a useful by-product if recovered. The gas itself contains methane, carbon monoxide, carbon dioxide, nitrogen oxides, and aldehydes. By weight, two-thirds of the gas is carbon dioxide and therefore the thermal value of the gaseous effluent is low. Table 4.4-1 lists the products of wood distillation.

Other by-products of the pyrolysis may be refined to produce methanol, acetic acid, methyl acetone, tar and oil. All of these can, however be manufactured more economically by other means; and wood is distilled only for charcoal manufacture; there being no synthetic counterpart for that product. Unfortunately,economics has rendered the recovery of the distillate by-products unprofitable and they are generally permitted to be discharged to the atmosphere. This is evidenced by a bluish plume similar to that resulting from open burning of wood. The plume is very irritating to the eyes and throat.[5]

Table 4.4.1. Products From Hardwood Distillation, percent by weight[4]

Charcoal	25.2
Water	46.7
Tar, Oil	5.0
Acetic Acid	2.9
Crude Methanol	1.9
Carbon Monoxide	4.0[a]
Carbon Dioxide	12.3[a]
Methane	1.3[a]
Other Gases	0.7[a]

a) See Appendix 4.4 for calculations

Process Description

In manufacturing charcoal by destructive distillation or pyrolysis, the wood is placed in a retort where it is externally heated for about 20 hours at 500 - 700°F. While the retort has air intakes at the bottom, these are only used during startup and thereafter are closed. The entire distillation cycle takes approximately 24 hours, the last 4 hours being an exothermic reaction with no external heat being applied. A white plume is observed during the early stages of the process, due to the water being boiled off. Thereafter the plume, if recovery of the by-products is not employed, is irritating and bluish in color. If a recovery plant is utilized, the vapors formed by the heat-treatment are passed through water-cooled condensers. The condensate then refined while the remaining cool non-condensable gas is discharged to the atmosphere as shown in Figure 4.4-1. Four tons of hardwood are required to produce one ton of charcoal.

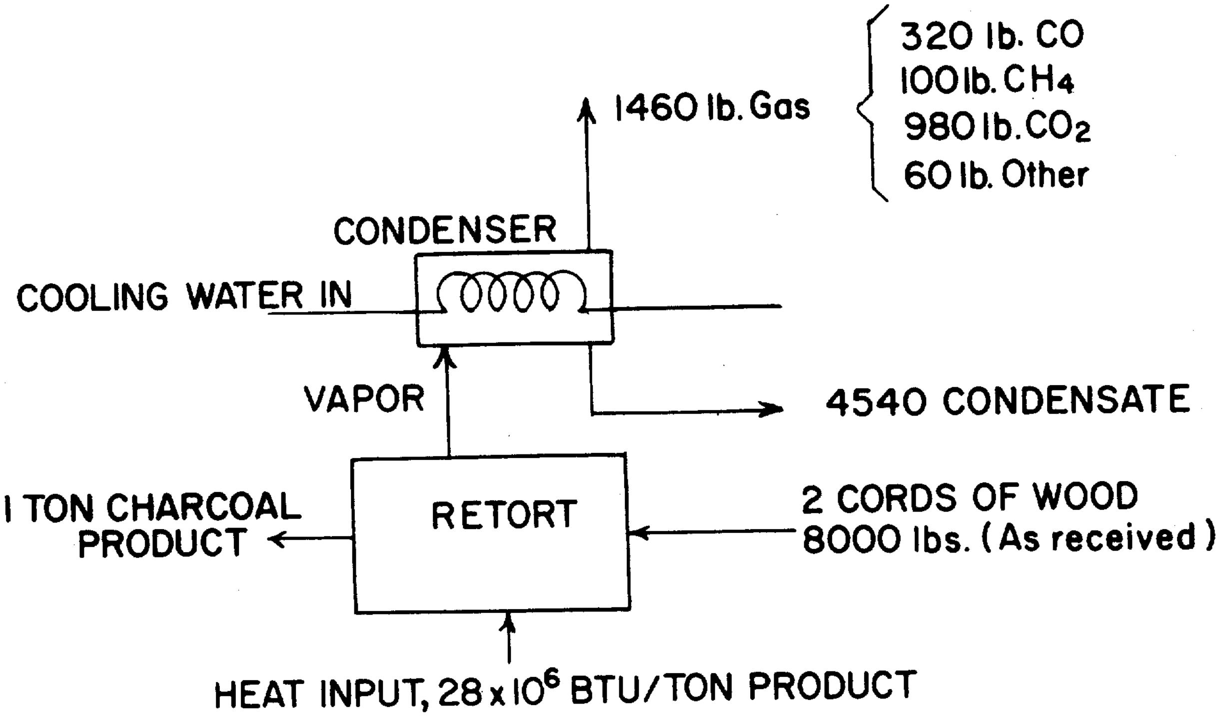

Figure 4.4-1. Charcoal manufacturing processes with condenser.

Factors Affecting Emissions

The nature of pyrolysis is to produce copious quantities of potential pollutants, a full three-fourths of the charged material being driven off.

The most obvious factor affecting the composition and quantity of the emissions is the recovery plant condenser. If the cooling medium (chilled water, etc.) temperature is too high or the heat transfer area is inadequate, complete condensation will not occur. The most common situation, however, is the complete absence of a condenser, the recovery of the condensable by-product being unprofitable.

The emission is also increased by the introduction of outside air. However, the intakes are normally closed as soon as possible since further injections of outside air, above that needed for start-up, diminish the finished product.

Notwithstanding the absence of a recovery plant, the emission can be controlled by means of an afterburner, since the unrecovered by-products are combustible. Some charcoal plants presently control emissions with this device.[5] If the afterburner operates efficiently no organic pollutants should escape into the atmosphere.

Emissions

Results of source testing of charcoal plants have not been published nor have any unpublished results been found. However, an engineering analysis of the by-products of the pyrolysis of hardwood provides a reasonably accurate estimate of the kinds and quantities of emission. The quantity of pollutants resulting from the manufacture of one ton of charcoal (distillation of 4 tons of hardwood) is shown in Table 4.4-2.

Table 4.4-2. Emission Factors for the Manufacture of Charcoal, lb/ton of product

Pollutant	Type of Manufacturing Operation With Chemical Recovery Plant	Without Chemical Recovery Plant
CO	320[a]	320[a]
HC[b]	100[a]	100[a]
Other Gases (HCHO, N_2, NO)	60	60[a]
Crude Methanol	-	152
Acetic Acid	-	232
Particulate (Tar, Oil)	-	400

a) Emissions are negligible if afterburner is used.

b) HC expressed as methane.

Reliability of Emission Factors

The factors presented in Table 4.4-2 were based on limited data and were arrived at by material balance calculations. As shown in Table 4.4-3 these factors are all ranked as questionable due to the lack of emission data.

Table 4.4-3. Emission Factor Ranking for Charcoal Manufacturing

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
0	6	8	14

Further work in this area appears to be justified due to the potential health hazards from these fumes and the growth rate of this industry. To date, charcoal operations have been located in rural areas and have not received much attention from an air pollution standpoint.

The lack of emission data and the variance in the composition of the raw product required the assumption that the reported products of distillation are correct and relatively constant between the various species of wood. Only a slight variance in the figures reported in Table 4.4-1 will greatly vary the emission factor.

APPENDIX 4.4

It has been reported that the weight of gas driven off in the pyrolysis of hardwood is 18.3% of the weight of the wood and the weight of the resulting charcoal is 25.2% of the raw product.[4] Thus approximately 8000 lb wood is required for the production of one ton of charcoal and the gas thereby liberated weighs approximately 1460 lb. The volumetric make up of this gas is 53% carbon dioxide, 27% carbon monoxide, and 15% methane.[4] The remaining 5% shall be designated "other"herein. To determine the weight of these constituents (P_x), find the weight a pound mole of the constituent gas (W_x), multiply that by the total weight of flue gas (1460 lb), multiply by the volumetric percentage of the constituent (R_x) and divide by the weight of a pound mole of the flue gas (W_t). Expressed in equation form

$$P_x = \frac{W_x \times 1460 \times R_x}{W_t} \qquad \text{Eq (2)}$$

for values of W_x see Table 4.4-4
for values of R_x see Table 4.4-4
for values of W_t see Table 4.4-5

Table 4.4-4 Gaseous Constituents of Wood, Percent by Volume

	CO	CO_2	CH_4	Other
Mole Wt., W_x	28	44	16	28[a]
Percent by Volume R_x	27	53	15	5

a) Estimated average based on HCHO being 30, N_2 being 28, and NO being 30.

Table 4.4-5 Gaseous Constituents of Wood, Percent by Weight

Constituent Gas	% By Volume	x Mole Wt.	= Partial Mole Wt. of Flue Gas
CO	27	28	7.6
CO_2	53	44	23.3
CH_4	15	16	2.4
Others	5	28	1.4
W_t, Total Weight of 1 mole of flue gas			34.7 lb.

Applying eq (2) to each constituent gas:

$$CO \quad P_x = \frac{28 \times 1460 \times .27}{34.7} = 320 \text{ lb.}$$

$$CO_2 \quad P_x = \frac{44 \times 1460 \times .53}{34.7} = 980 \text{ lb.}$$

$$CH_4 \quad P_x = \frac{16 \times 1460 \times .15}{34.7} = 100 \text{ lb.}$$

$$\text{Other} \quad P_x = \frac{28 \times 1460 \times .05}{34.7} = \underline{60 \text{ lb.}}$$

$$1460 \text{ lb.}$$

Dividing the weights found above by the total weight of the 8000 lb. charge in the retort, we find that the percentages are as shown in Table 4.4-1.

REFERENCES 4.4

1. Census of Manufacturers 1958: V2, Part 2. U.S. Bureau of Census. Washington, D.C. 1961.
2. Census of Manufacturers 1963: V2, Part 2. U.S. Bureau of Census. Washington, D.C. 1966.
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4.5 HYDROFLUORIC ACID

Process Description

All hydrofluoric acid in the United States is currently produced by reacting acid-grade fluorspar with sulfuric acid for 30-60 minutes in externally fired rotary kilns at a temperature of 400-500°F according to the following reaction:[1,2,3]

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

The resulting gas is then cleaned, cooled, and absorbed in water and weak hydrofluoric acid to form a strong acid solution. Anhydrous hydrofluoric acid is formed by distilling 80% hydrofluoric acid and condensing the gaseous HF which is driven off. The by-product, calcium sulfate or anhydrite is recoverable. Figure 4.5-1 illustrates a typical process for producing 80% acid and anhydrous acid; however, many variations in scrubber and absorber arrangements may be used.

The fluorspar used to prepare hydrofluoric acid is a specially prepared finely ground (approximately 95% through a 170 mesh screen) acid grade material with a minimum purity of about 97-98% calcium fluoride as marketed. It also contains some silicon dioxide and calcium carbonate in addition to trace amounts of sulfur (less than 0.05%) and water. Process yields vary from 85 to 92% depending on the purity of the reactants.

Air pollutant emissions are minimized by the scrubbing and absorption systems used to purify and recover the HF. The initial scrubber utilizes concentrated sulfuric acid as a scrubbing medium and is designed to remove dust, SO_2, and SO_3, sulfuric acid mist, and water vapor present in the gas stream leaving the primary dust collector. The HF recovery system utilizes water and hydrofluoric acid of increasing strengths to countercurrently cool and absorb the HF. Anhydrous hydrofluoric acid 99.9% HF is produced by distilling the 80% acid. Uncondensed gases from the distillation process may be scrubbed by sulfuric acid to recover additional HF and followed by a water scrubber to remove any silicon tetrafluoride in the exit gases.

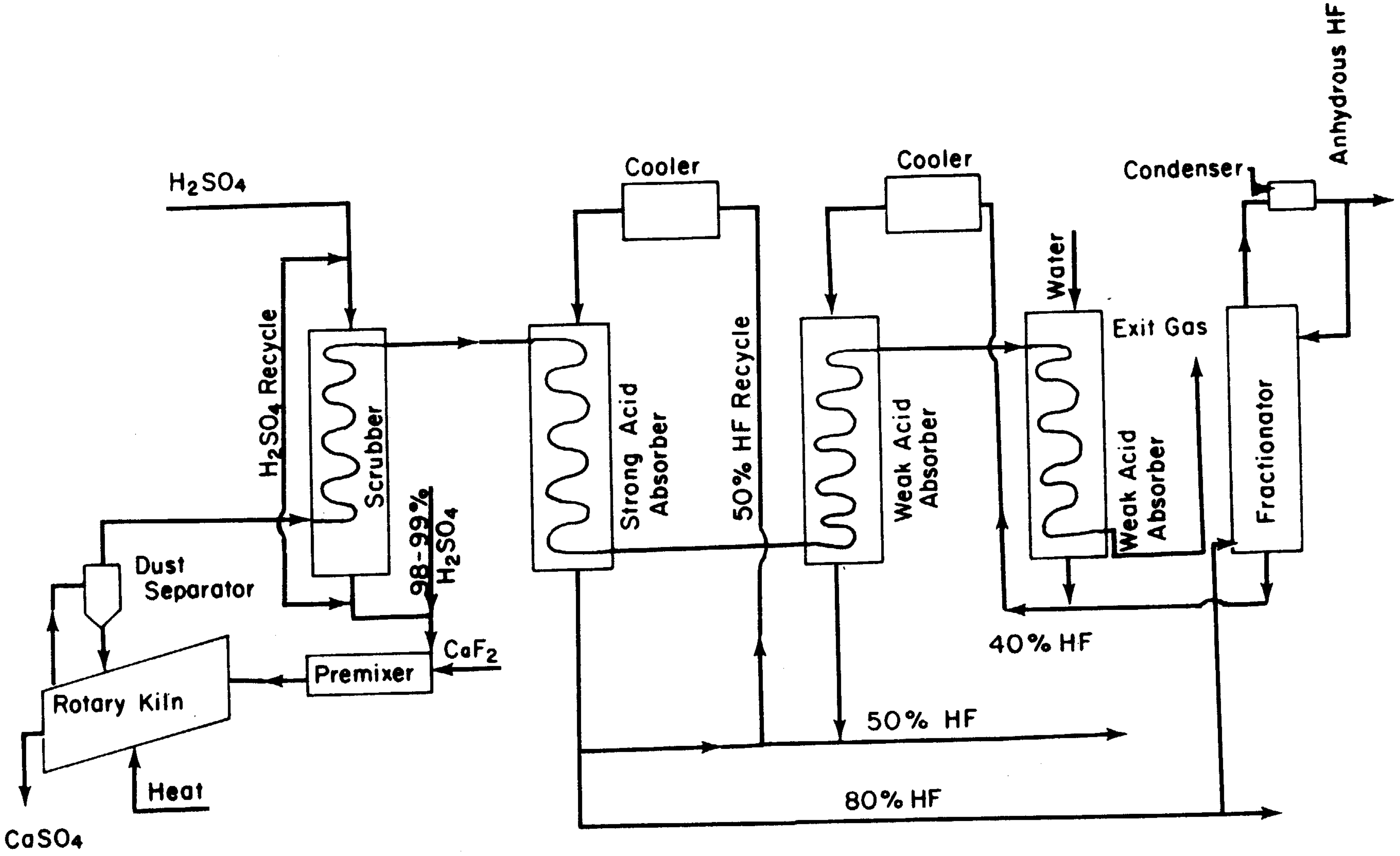

Figure 4.5-1 Example Hydrofluoric Acid Manufacturing Process[2]

Factors Affecting Emissions

The main factor affecting emissions is the general operating condition of the plant and the equipment maintenance. Plants operating in excess of rated capacity will have emissions many times those of a plant operated within limits. Maintenance problems exist due to the corrosive nature of hydrofluoric acid. Badly corroded scrubbers and/or dust collectors will not operate at optimum efficiency.

Emissions

The exit gases from the final absorber contain small amounts of HF, silicon tetrafluoride (SiF_4), CO_2, and SO_2 and may be scrubbed with a caustic solution to further reduce emissions. A final water ejector, sometimes used to draw the gases through the absorption system, will also reduce fluoride emissions. Emissions of non-condensable gases from the anhydrous acid condenser consisting mainly of CO_2, SiF_4, and HF may also occur.

Table 4.5.1 Emissions from Hydrofluoric Acid Manufacturing lbs/ton

Particulate	20[a]	From raw material processing.
HF	50[b]	From manufacturing process.

a) Based on Reference 1. Reported value is a maximum with dust control system installed (Probably fabric filter, but reference was not specific).
b) A high efficiency water scrubber will reduce these emissions by 99.6%, or down to 0.2 lbs/ton. Based on Reference 4.

Reliability of Emission Factor

Due to the very limited emission data available for this process, and the variability in emissions caused by only small changes in scrubber efficiency, these emission factors must be considered questionable. Additional emission measurements for this process are warranted. Table 4.5.2 presents the factor ranking.

Table 4.5.2 Emission Factor Ranking for Hydrofluoric Acid

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
3	5	3	11

REFERENCES 4.5

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4.6 PAINT AND VARNISH

Process Description[1,2]

The manufacture of paint involves the dispersion of a colored oil or pigment in a vehicle, usually an oil or resin, followed by the addition of an organic solvent for viscosity adjustment. Only physical processes of weighing, mixing, grinding, tinting, thinning and packaging are involved; there are no chemical reactions. These processes take place in large mixing tanks at approximately room temperature. Higher temperatures are also occasionally used depending on the product. Tinting pigments include lead and titanium oxides, and carbon black. Thinners and solvents include mineral spirits, turpentine, naphtha, xylol, etc.

The manufacture of varnish also involves the mixing and blending of various ingredients to produce a wide range of products. However, in this case chemical reactions are initiated by heating, to produce the desired product. Varnish cooking is accomplished in either open or enclosed gas-fired kettles for periods of 4 to 16 hours at a temperature of 200-650°F. The exact cooking time and temperature vary widely and depend on the ingredients and desired product.

Emissions, largely in the form of organic compounds, escape during the cooking process while the chemical reactions, such as polymerization, esterification and isomerization, and distillation occur.

Factors Affecting Emissions

The primary factors affecting emissions from paint manufacture are care in handling dry pigments, type of solvents used, and mixing temperature. Varnish cooking emissions depend on the cooking temperatures and time, solvent used, degree of tank enclosure, and type of air pollution controls used.

Emissions

In the manufacture of paint, about 1 to 2% of the solvents are lost even under well controlled conditions.[2,3] Particulate emissions amount to 0.5 to 1% of the pigment handled.[4]

Emissions from varnish cooking amount to 1 to 6% of the raw material and consist of both gaseous and condensed organic compounds.[1] Particle sizes in the 8 to 10 micron size range have been measured.[1] Table 4.6-1 lists the types of compounds which may be emitted from various varnish manufacturing operations.

Table 4.6-1. Typical Varnish Raw Materials and Emissions During Cooking[2]

RAW MATERIAL			
Bodying Oils	Running Natural Gums	Manufacturing Oleoresinous Varnish	Manufacturing Alkyd Varnish
EMISSIONS			
Water Vapor	Water Vapor	Water Vapor	Water Vapor
Fatty Acids	Fatty Acids	Fatty Acids	Fatty Acids
Glycerine	Terpenes	Glycerine	Glycerine
Acrolein	Terpene Oils	Acrolein	Phthalic Anhydride
Aldehydes	Tar	Phenols	Carbon Dioxide
Ketones		Aldehydes	
Carbon Dioxide		Ketones	
		Terpene Oils	
		Terpenes	
		Carbon Dioxide	

Based on information summarized in Appendix 4.6, the emission factors in Table 4.6-2 were developed.

Table 4.6-2. Uncontrolled Emission Factors for Paint and Varnish Manufacturing[b]

PAINT

Particulates	2 (1-4)	lbs/ton of pigment
Hydrocarbons[a]	30 (10-40)	lbs/ton of paint

VARNISH

Type of Varnish	Emission, lbs/ton of varnish[a]
Bodying Oil	40 (20-60)
Oleoresinous	150 (60-240)
Alkyd	160 (80-240)
Acrylic	20

a) Expressed as undefined organic compounds whose composition depends on the type of varnish or paint.

b) Control techniques used to reduce hydrocarbons include condensers and/or adsorbers on solvent handling operations, and scrubbers and afterburners on cooking operations. Afterburners can reduce gaseous hydrocarbon emissions by 99% and particulates by about 90%.[1] A water spray and oil filter system reduce particulate emissions from paint blending by 90%.

Reliability of Emission Factors

These factors are questionable due to lack of new data or source tests. The reported emissions are based on estimates or measurements of process weight loss and are considered to be all atmospheric losses. Table 4.6-3 presents the factor ranking.

The major assumption inherent in these factors is that the emissions as determined by process weight losses are essentially all atmospheric losses.

Table 4.6-3. Emission Factor Ranking for Paint and Varnish Manufacture

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
8	5	5	18

APPENDIX 4.6

Emission Data from literature:

Paint Mixing and Blending

Type of Emission	Quantity	Reference
Particulates	1-4 lbs/ton of pigment	3, 4
	0.5-1.7 lbs/ton after a water spray and filter	6
Hydrocarbons	20-40 lbs/ton of paint	4
	36 lbs/ton of paint	5
	1-2% of solvent (20-40 lbs/ton)	2
	10 lbs/ton of paint	7

Varnish (Reference 2)

Hydrocarbons, lbs/ton of varnish		Type of Varnish
range	average	
20-60	40	Bodying Oils
60-240	150	Oleoresinous
80-240	160	Alkyd
20	-	Acrylic
1-5%	3% or 60 lbs/ton	- (Reference 1)

Note: Paints weigh 10-15 pounds/gallon; varnish weighs about 7 pounds/gallon.

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The model plant boiler house consists of four boilers, with a total heat input capacity of 381 MW (1,300 MMBtu/hr). Each boiler has a firing capacity of 95 MW (325 MMBtu/hr) and is used at 75 percent of heat input capacity. Three of the boilers are existing units, firing refinery and natural gas. The fourth unit, firing a mixture of petroleum coke and residual oil, will be replaced by a new coal-firing boiler in 1990. Approximately 25 percent of boiler steam generation for this plant will be provided by the new coal-firing boiler.

9.2.3.7.2 Financial analysis. The petroleum refining industry historically has been able to recoup increased crude import costs and refinery costs through higher product prices charged to retail establishments. Since 1973, retail gasoline and fuel oil prices have kept pace with the nominal cost increases in crude imports. Federal price regulations create ceiling prices at the pump but have interfered minimally with the trend of higher retail fuel prices to maintain profit levels. The demand for refinery products has, in general, surpassed the supply capabilities of domestic refineries, causing price levels to rise in response to a tight market.

If the petroleum refining industry does face increased steam costs, it is not likely to adjust its production process to reduce the level of steam use in its production equipment. Steam is an integral input to most of the individual process elements in a refinery; thus, increased steam costs cannot be mitigated by process changes. Because steam is such an important input, new or replacement boiler investments are not likely to be cancelled due to an increase in steam costs. Product demand is healthy and sufficiently inelastic to cover these additional costs without having the refinery experience decreased profits.

Table 9-38 delineates the financial indicators of the petroleum refining industry. Because petroleum-derived products exhibited strong sales during 1974-1978, the profitability indicators for the industry have been high and stable. Profits were extremely healthy, especially in 1974, during the oil embargo. Since 1975, net profits ranged from $658 million to $868 million per year and averaged $775 million per firm between 1974 and 1978. Return on total assets was between 5.8 and 10.1 percent, with the 5-year average at 6.93 percent.

Capital availability appears to be stable for the petroleum refining industry. Although the coverage ratio has fallen in recent years, as of

4.7 PLASTICS

Process Description

The manufacture of most resins or plastics begins with the polymerization or linking of the basic compound (monomer) usually a gas or liquid, into high molecular weight non-crystalline solids. The manufacture of the basic monomer is not considered part of the plastics industry and is usually accomplished at a chemical or petrochemical plant.

The three largest selling plastics are currently polyethylene, polystyrene, and polyvinyl chloride. Consumption of some of the major plastics in 1967 were:[1]

Polyethylene	3632 million lbs/year
Polyvinyl Chloride	2167
Polystyrene	2110
Phenolics	800
Polypropylene	641

Plastic manufacture of most compounds involves an enclosed reaction or polymerization step in the presence of a catalyst, a drying step, and a final treating and forming step. Two principal types of polymerization reactions occur in the manufacture of resins or plastics, namely, condensation and addition reactions. Condensation polymerization occurs when single molecules or monomers combine to form larger functional groups with a resulting loss of simple molecules such as water or alcohol. Addition reactions involve the joining of bonds between like molecules without the formation of any side products.

Phenolic and polyester resins such as phenol-formaldehyde are made via condensation reactions while polyolefins such as polyethylene, polyvinyl chlorides, and polystyrene are made by addition reactions.

Most plastics are polymerized or otherwise reacted in stainless steel or glass-lined vessels, which are completely enclosed, equipped with a stirring mechanism, and generally contain an integral reflux condenser. Since most of the reactions are exothermic, cooling coils are usually required. Some resins, especially those formed by condensation reactions, require that the kettle be under vacuum during part of the cycle. This can be supplied either by a vacuum pump or by a steam or water jet ejector. Alternatively, the addition reactions usually occur at elevated temperatures and pressures.

The following process description for polyvinyl chloride (PVC) also shown in Figure 4.7-1, will illustrate the steps involved in making many types of plastics.[2,3]

> The vinyl chloride monomer is purified by scrubbing and distillation, (the monomer is shipped with an inhibitor such as phenol to prevent polymerization). The purified monomer is then stored at 60°F at 50 psig before charging to the reactor. The polymerization addition reaction is carried out in a 3000 - 4000 gallon batch reaction at a temperature of 100 - 160°F and a pressure of 80 - 180 psig in the presence of organic peroxide, persulfate, or metallic chloride catalysts. Reaction time varies from 12 to 72 hours depending on the reaction conditions, desired product, and yield. The reactor contents are then stripped of unreacted monomer by applying a vacuum, and the polymerized slurry is dried in a spray dryer or dewatered and dried in a rotary dryer. Unreacted monomer is recycled. Particle size of the finished product varies from 0.1 to 1 micron and is further processed by adding plasticizers, stabilizers, etc.

Treatment of the resin after polymerization varies with the proposed use. Resins for moldings are dried and crushed or ground into molding powder. Resins, such as the alkyd resins, to be used for protective coatings are normally transferred to an agitated thinning tank, where they are thinned with some type of solvent and then stored in large steel tanks equipped with water-cooled condensers to prevent loss of solvent to the atmosphere. Still other resins are stored in latex form as they come from the kettle.

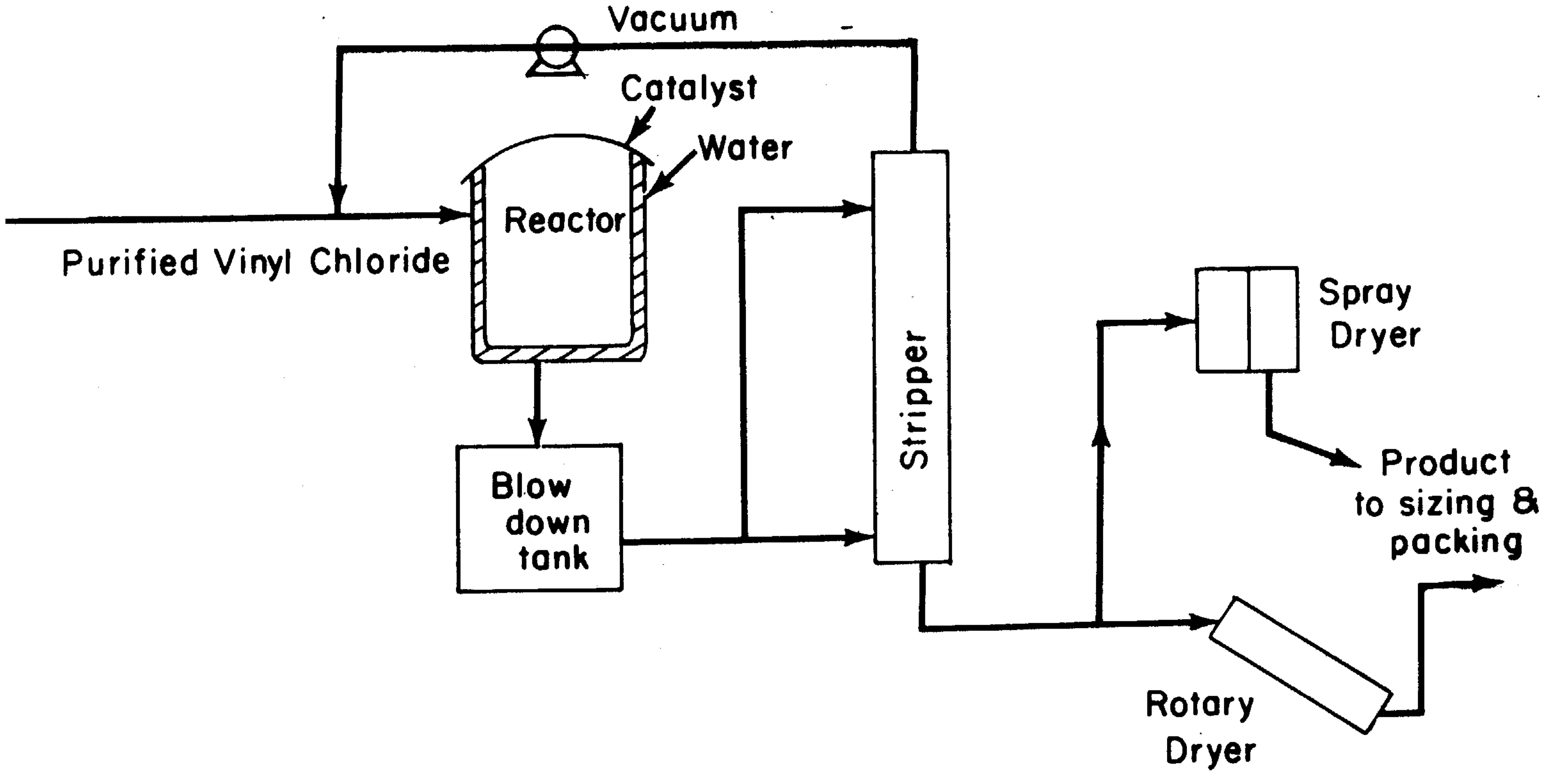

Figure 4.7-1. Typical Flow Diagram for Polyvinyl Chloride Manufacture

Because of the many types of raw materials, ranging from gases to solids, storage facilities vary accordingly. Ethylene is handled under pressure; vinyl chloride, a gas at standard conditions, is liquefied easily under pressure and is stored as a liquid in a pressurized vessel. Most of the other liquid monomers do not present any particular storage problems. Some, such as styrene, must be stored under an inert atmosphere to prevent premature polymerization. Some of the more volatile materials are stored in cooled tanks to prevent excessive vapor loss. Some of the materials have strong odors, and care must be taken to prevent emission odors to the atmosphere. Solids, such as phthalic anhydride, are usually packaged and stored in bags or fiber drums.

The major sources of possible air contamination in plastic manufacturing are the emissions of raw materials or monomer to the atmosphere, emissions of solvent or other volatile liquids during the reaction, emissions of sublimed solids such as phthalic anhydride in alykd production, emissions of solvents during storage and handling of thinned resins. Table 4.7-1 lists the most probable types and sources of air contaminants from various plastic manufacturing operations.

Table 4.7-1. Plastic Manufacturing Emissions and Sources[4]

Plastic	Emission	Source
Phenolic Resins	Aldehydes	Storage, leaks, condenser outlets
Amino Resins	Aldehydes	Storage and leaks
Polyesters	Oil cooking odors, phthalic anhydride, solvents	Cooker discharge, condenser discharge
Polyvinyl Acetate	Odors, solvents	Storage, condenser outlets
Polyvinyl Chloride	Odors	Leaks
Polystyrene	Odors	Leaks
Polyurethane	Toluene, Odor	Product

Much of the emission control equipment used in this industry is really a basic part of the system and serves to recover a reactant or product. These controls include: floating roof tanks or vapor recovery systems on volatile material storage units, vapor recovery systems (adsorption or condensers), purge lines and relief valves which vent to a flare system; and recovery systems on vacuum exhaust lines.

Factors Affecting Emissions

The major factor affecting atmospheric emissions is the basic design of the plant, its maintenance, and the amount of control equipment included in the basic plant. Greater emissions may be expected from those processes operating at atmospheric pressure since condensers then vent directly to the atmosphere, and care in sealing the reactor is not generally as great.

Emissions

Quantitative emission data from plastics manufacturing are not readily available. In the manufacture of ethylene gas (a high pressure process) hydrocarbon emissions amounted to 0.21% (4.2 lbs/ton) of the feed.[5] Other reported data, from manufacturing plant estimates based largely on material balance estimates, are shown in Table 4.7-2.[6,7]

Table 4.7-2. Estimated Emissions From Plastics Manufacturing, lbs/ton

Plastic	Gases[b]	Particulate
Polyvinyl Chloride	17	35[a]
Polypropylene	0.7	3
General	5 to 10	-

a) Usually controlled with a fabric filter, efficiency of 98-99%.
b) Reported as the monomer (vinyl chloride, or propylene, etc.).

This wide range in emission data is due to the difficulty in accurately performing material balance estimates, and to actual emission differences.

Based on the reported emissions from ethylene manufacture and the two estimates in Table 4.7-2, a general gaseous emission factor of about 5 - 10 lbs/ton of feed may be used until better data are available.

Reliability of Emission Factor

Due to the limited data available and the wide variation in processing methods and products, the emission factor for plastics manufacturing must be classified as questionable. Table 4.7-3 presents the factor ranking.

Table 4.7-3. Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	2	2	9

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4.8 PRINTING INK

Process Description

Ink is a fluid or viscous material of various colors, but most often black, used for writing and printing. Printing inks as supplied to the graphic arts industry are used in much greater volume as compared to writing inks. There are approximately 350 printing-ink manufacturing establishments in the United States today with a production value of over $300 million in 1968.[1]

Printing ink is a mixture of coloring matter, dispersed or dissolved in a vehicle or carrier, which forms a fluid or paste which can then be printed on a substrate and dried. The coloring agents used are most often pigments, toners and dyes, or combinations of these materials. These agents are selected to provide color contrast with the background on which the ink is printed. The vehicle used acts as a carrier for the colorant during the printing operation. In most cases the vehicle serves to bind the colorant to the substrate.[2] Drying oils, petroleum oils, and resins are usually employed as vehicles. However, newer synthetic-resins are becoming increasingly popular because they are quick-drying and have better working properties.[1]

There are four major classes of printing ink. These vary considerably in physical appearance, composition, method of application, and drying mechanism. The four classes are letterpress and lithographic inks, commonly called oil or paste inks; and flexographic and rotogravure inks, which are referred to as solvent inks.

Flexographic and rotogravure inks have many elements in common with the paste inks, but differ in that they are of very low viscosity, and they almost always dry by evaporation of highly volatile solvents.[3]

There are three general processes in the manufacture of printing inks, namely:

1) Cooking the vehicle and adding dyes
2) Grinding of a pigment in a vehicle using a roller mill
3) Replacing water in the wet pigment pulp by an ink vehicle (commonly known as the flushing process).[1]

The ink "varnish" or vehicle consists of resins, drying oils, and/or petroleum oils. This varnish is generally cooked in large kettles at 200-600°F for an average of 8-12 hours in much the same way that regular varnish is made.[7] Most modern kettles are totally enclosed stationary vessels; however, there are still a number of mobile, open kettles being used. Cooking the varnish performs many functions, depending upon the raw materials used and the formulation cycle. These functions include:[4]

1) Polymerization of the oil
2) Depolymerization of the high molecular weight resins at 600 to 650°F
3) Melting and accelerated solution of any solids
4) Esterfication at 450° - 525°F
5) Isomerization
6) Distillation and evaporation

Letterpress, litho, and dry-offset inks are produced in two ways:

1) By mixing preground or flushed pigment concentrates with vehicles, solvents, oils, and compounds.
2) By mixing dry pigments with vehicles and compounds and then grinding them on ink mills.

Some typical ink formulas are given in Table 4.8-1.

Table 4.8-1 Typical Ink Formulas[2]

Letterpress Newsprint Black

10 or 15[a]	carbon black
2 or 3	induline toner
85 or 67	mineral oil
3 or 15	mineral oil (low viscosity)

Quick-Set Litho Black

16 or 18	carbon black
4 or 6	alkali blue toner
65 or 58	phenolic resin/oil (hydrocarbon solvent, 530°F)
10 or 6	bodied linseed oil
2 or 2	cobalt linoleate
5 or 10	aliphatic hydrocarbon solvent (530°F)

Heat-Set Publication Blue

10	phthalocyanine blue
15	alumina hydrate
65	pentaerythritol resin ester/hydrocarbon solvent
5	polyethylene wax compound
5	aliphatic hydrocarbon solvent (470°F)

Gloss Letterpress Oleoresinous Red

25	permanent 2B red
5	clay or alumina hydrate
50	phenolic resin/China wood oil
15.5	ester gum/linseed oil
2	cobalt naphthenate
2	lead naphthenate
0.5	eugenol

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a) Numbers refer to proportions by weight in mixture.

Mixing of the pigment and vehicle is done in dough mixers of various sizes, or in large agitated tanks which may hold up to 1000 pounds. Grinding is most often carried out in three-roller or five-roller horizontal or vertical mills. Softer, more fluid inks can be ground in colloid mills, sand mills, or ball mills. Dispersion of the pigment in the roller mills is accomplished by shearing forces generated by the differential speed of the rollers as well as by the closeness of roller setting.

Flexographic and rotogravure printing processes require the use of volatile solvents such as low boiling point alcohols, esters, aliphatic and aromatic hydrocarbons, ketones, and water.

Factors Affecting Emission

The quantity, composition, and rate of emissions depend upon the ingredients in the cook, the cooking temperature and time, the method of introducing additives, the degree of stirring, and the extent of air or inert gas blowing.[4]

Particulate emissions resulting from the addition of pigments to the vehicle are affected by the type of pigment and its particle size. Carbon black handling generally causes the biggest particulate problem, and efforts are always made to control this emission with fabric filters.

Emissions

Varnish or vehicle preparation by heating is by far the largest source of ink manufacturing emissions. Cooling the varnish components--resins, drying oils, petroleum oils, and solvents--produces odorous emissions which are very objectionable. At about 350°F the products begin to decompose, resulting in the emission of decomposition products from the cooking vessel. Emissions continue throughout the cooking process with the maximum rate of emissions occurring just after the maximum temperature has been reached.[4]

Compounds emitted from cooking of oleoresinous (resin plus varnish) varnish include water vapor, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils, terpenes, and carbon dioxide.[4] Some highly offensive sulfur compounds such as hydrogen sulfide, allyl sulfide, butyl mercaptan, and thiphene are formed when tall oil is used in the ink vehicle.

Emissions of thinning solvents used in flexographic and rotogravure inks may also occur. In most of the newer installations, the cooked varnish is pumped to a thinning tank that is equipped with integral condensers and emissions are kept to a minimum. In the older open-kettle operations, however, the thinning operation is carried out near the boiling point of the solvent, and emissions of vapor can be considerable.

Quantitative emission data from ink manufacturing were not found. However, based on published emissions from similar processes such as paint and varnish manufacturing, and discussions with a manufacturer,[5] the factors in Table 4.8-2 were derived. This information is based on information in Chapter 4.6, and no appendix is included in this chapter.

Table 4.8-2. Emissions From Printing Ink Manufacturing

Process	Gaseous Organics[a] lbs/ton	Particulate[b] lbs/ton
Vehicle Cooking		
General	120	
Oils	40 (20-60)	
Oleoresinous	150 (60-240)	
Alkyds	160 (80-240)	
Pigment Mixing		2 (1-4)

a) Emitted as a gas, but rapidly condense as the effluent is cooled, see Reference 6 and 7.

b) Based on Reference 7.

Emissions from the cooking phase can be reduced by more than 90% with the use of scrubbers or condensers, followed by afterburners.[4,5]

Reliability of Emission Factors

Due to a lack of measured emission data, these factors for ink manufacture must be considered questionable. Table 4.8-3 presents the factor ranking.

Table 4.8-3. Emission Factor Ranking for Printing Ink Manufacture

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
0	5	3	8

The current National Air Pollution Control Administration study on printing processes will cover the manufacture of ink, and should provide more quantitative data when it is completed in 1970.[8]

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4.9 SOAP AND DETERGENTS

Process Description

The manufacture of detergents generally begins with the sulfonation by sulfuric acid of a fatty alcohol or linear alkylate. The sulfonated compound is then neutralized with caustic solution (NaOH), and various dyes, perfumes, and other compounds are added.[1,2] The resulting paste or slurry containing 40 - 60% water is then sprayed under pressure into a vertical drying tower where it is dried with a stream of hot (400 - 500°F) air passing upward through the falling droplets, as shown in Figure 4.9-1. The dried detergent is then cooled and packaged. The main source of particulate emission is the spray drying tower, since the exit gases contain entrained particles. Odors may also be emitted from this source and from storage and mixing tanks.

The manufacture of soap entails the catalytic hydrolysis of various fatty acids or glycerides, such as stearic, oleic, palmitic, etc., with sodium or potassium hydroxide to form a glycerol-soap mixture. This mixture is separated by distillation, neutralized and blended to produce soap. The finished soap may be in a bar, flake, or powder form. The main atmospheric pollution problem in the manufacture of soap is odor, and if a spray drier is used a particulate emission problem may also occur. Vent lines, vacuum exhausts, product and raw material storage, and waste streams are all potential odor sources.

Depending on the type of soap or fatty acid used and the required pretreatment of the raw materials, a variety of odors could be emitted. Nitrogen containing compounds such as soya bean, soap stock, or cottonseed stock produce amine compounds which have an objectionable fishy odor.[3] Control of these compounds may be achieved by scrubbing all exhaust fumes and if necessary incinerating the remaining compounds. Odors emanating from the spray drier may be scrubbed with an acid solution to control odors.[3]

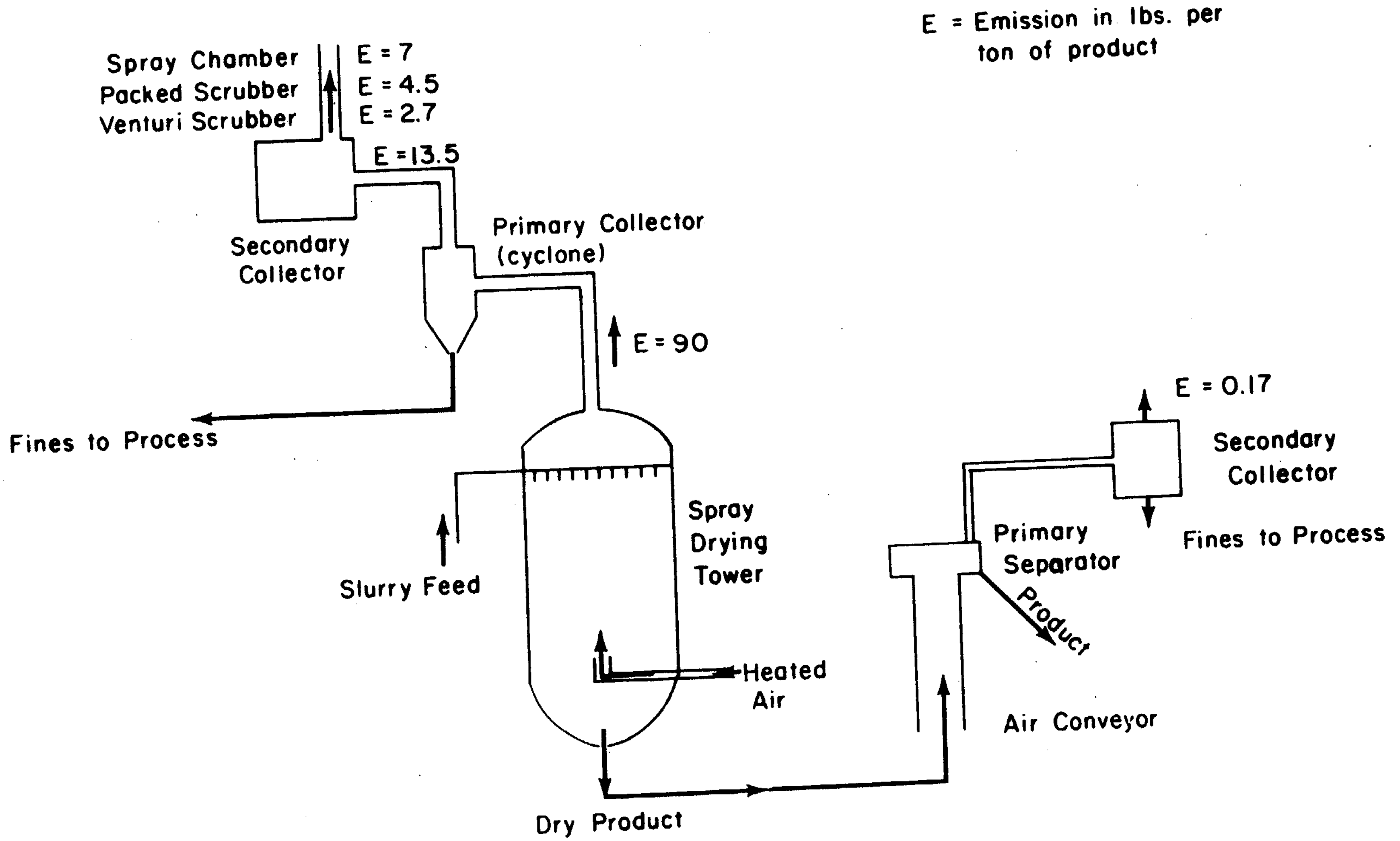

Figure 4.9-1 Process Flow and Particulate Emissions from Detergent Manufacturing.

Factors Affecting Emissions

In the manufacture of soap and detergents, particulate emissions from the spray dryer are affected by the basic design of the unit, the desired product (especially its size), and the type of control equipment and process throughput. Odor emissions are affected by the type of raw materials used, the basic equipment design such as reactor volume and condenser capacity, and product throughput.

Emissions

Particulate emissions from spray drying operations are shown in Figure 4.9-1 and summarized in Table 4.9-1. More detailed emission information is presented in the Appendix.

Table 4.9-1. Particulate Emissions From Detergent Spray Drying.

Control Device	Overall Efficiency, %	Emissions, lbs/ton of Product
None	-	90 (72-108)
Cyclone [a]	85	13.5
Cyclone Followed By:		
1. Spray Chamber	92	7
2. Packed Scrubber	95	4.5
3. Venturi Scrubber	97	2.7

[a] Some type of primary collector such as a cyclone is considered an integral part of the spray drying system.

Other dust emissions from cooling and packaging amount to about 0.17 lb per ton of product.

The size distribution of the particulate emissions leaving the spray dryers before any collection equipment is shown in Figure 4.9-2.

While the above data were obtained for detergent manufacturing operations, they can, if no other data are available, be used for soap manufacturing operations which use spray dryers.

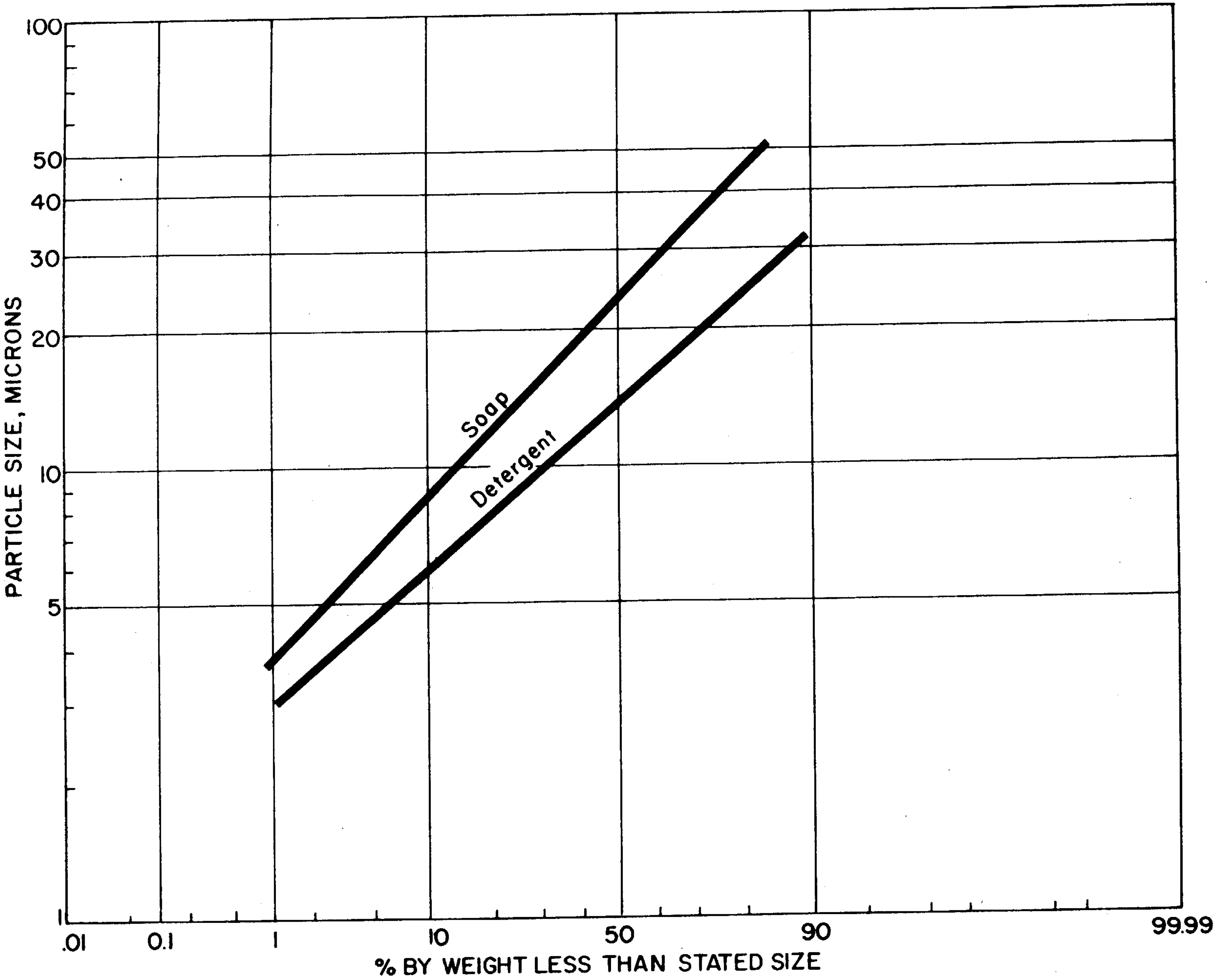

Figure 4.9-2 Particle size distribution of spray dryer emissions[4]

Emissions of odorous organic compounds also occur, but no emission information is available and the emissions cannot be estimated because of the many variables involved. Carbon monoxide emissions do not occur from these manufacturing processes.

Reliability of Factor

Fair agreement between calculated values and the single reported field measurement for particulate matter was obtained. Based on the ranking procedure in Table 4.9-2, the particulate emission factor is felt to be good. However, there is room for improvement; and additional emission data, especially for gases, are required.

Table 4.9-2. Detergent Manufacturing Emission Factor Ranking

Emission Data	Process Data	Engineering Analysis	Total
0-20	0-10	0-10	
8	8	8	24

No major assumptions were involved in determining these emission factors. Minor assumptions required to use various reported bits of information were:

1) 10% of air in leakage around dryer outlet (this increased emission from 70 to 77 lbs/ton).
2) 15% organic content in emission (this could affect the calculated value of 10.4 lbs/ton after a cyclone by ± 10%).

These assumptions give estimated emissions well within the overall range of final results.

APPENDIX 4.9

A. Calculation of Gas Volumes From Spray Dryer[1,5]

1) Air entering at 70°F and 50% relative humidity contains about 40 grains H_2O per lb dry air or 0.0057/lb dry air, and is heated to about 450°F.
2) Exit air is at 250°F and 140°F Wet Bulb Temp. and contains 0.13 lb H_2O/lb dry air (from high temperatures psychrometric chart). Therefore, each lb of dry air entering system picks up 0.13 lbs of H_2O. The exit gas temperature may be as low as 200°F. This would increase the moisture content by about 10%.
3) Pounds of dry air required per 1000# of finished product based on 40% water in detergent slurry (1667 lbs of slurry) is:

$$\frac{667\ \text{lb}\ H_2O}{0.13\ \text{lb}\ H_2O/\text{lb dry air}} = \underline{5120}\ \text{lb dry air required}$$

4) Exit volume in SCF @70°F 29.92 "H_g is:

$$5120\ \text{lb air} \times \frac{387\ \text{ft}^3/\text{lb mol}}{29\ \text{lb/mol}} = 68{,}325\ \text{ft}^3\ \text{dry air}$$

$$667\ \text{lb}\ H_2O \times \frac{387}{18} = \underline{14{,}340}\ \text{ft}^3\ \text{water vapor}$$

$$\text{TOTAL} = 82{,}665^{a}\ \text{ft}^3\ \text{moist air per 1000 lb product at 70°F.}$$

Assume 10% in leakage of outside air, or 90,000 ft^3 total air per 1000 lb of product. This is the same as 180,000 ft^3 per ton of product.

5) Based on grain loadings reported by Phelps[1], the lbs of particulate emitted <u>per ton of product</u> may be calculated as follows:

Leaving dryer - $3\ \text{grs/ft}^3 \times 180{,}000\ \frac{\text{ft}^3}{\text{ton}} \times \frac{1}{7000\ \text{grs/lb}} = 77\ \text{lbs/ton}$

Larson reported an emission of 8.8 lbs/ton of product of non-ether soluble particulate following a cyclone collector on a detergent spray dryer.[6] Heavy duty detergents with controlled sudsers contain 8 - 20% organic surfactants.[2] Using 15% as the average organic fraction, the total particulate emission would be 8.8/.85 or 10.4 lbs/ton after a cyclone collector.

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a) Based on humid volume of 21.5 ft^3/lb dry air at 250°F, 5120 lb dry air $\times \frac{21.5\ \text{ft}^3}{\text{lb dry air}} \times \frac{530°\text{R}}{710°\text{R}} = 82{,}000\ \text{ft}^3$ moist volume at 70°F.

A 90% efficient cyclone would mean the inlet loading was 104 lbs/ton $\frac{(10.4)}{(\ .10)}$; an 80% cyclone would give 52 lbs/ton.

Data from Reference 7 showed uncontrolled emission rates of 125 lbs/ton of product each from two installations with emissions reduced by cyclone-scrubber combinations to 5 lb/ton and 1.5 lb/ton, respectively.

An average of these sources of data yields an uncontrolled particulate emission rate of from about 75 to 125 with a most probable value of about 90 lbs/ton. This figure is always reduced by at least a cyclone type collector, and usually by other more efficient secondary collectors.

Based on Phelps' data[1] and knowing efficiencies of various types of collectors, the following emission data were computed:

COLLECTOR	EFFICIENCY, %		FACTOR
	Increment	Overall	lbs/ton,
Uncontrolled (right from tower)	0	-	90 (75-125)
Primary Cyclone	85	85	13.5
Secondary Device In Series Spray Chamber	50	92.5	6.7
Secondary Scrubber	65	94.7	4.7
Venturi Scrubber	80	97	2.7

From Conveying of Dry Product

One cfm of air is used for each lb/hr of product.[1] For 1 ton of product/hr., 2000 cfm are therefore required. Exit loss after primary inertial device (cyclone) and a bag collector is 0.01 grs/ft.^{3} or less.[1]

$$2000\ \frac{ft.^3}{min.} \times 60\ \frac{min.}{hr.} \times \frac{0.01\ grs}{ft.^3} \times \frac{1}{7000\ grs/lb} = 0.171\ lbs/hr$$

or 0.17 lbs/ton or less

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4.10 SYNTHETIC RUBBER

Process Description[1,2]

Copolymers of butadiene and styrene commonly known as SBR account for more than 70% of all synthetic rubber produced in the United States.

The manufacture of synthetic rubber and plastics (Section 4.7) are similar. In a typical SBR manufacturing process, the monomers of butadiene and styrene are mixed in a ratio of about 3:1; various additives such as soaps and mercaptans are added, and the mixture is polymerized to approximately a 60% conversion point. A cumene peroxide which acts as a polymerization catalyst is also added. Approximatley 680 pounds of butadiene and 212 pounds of styrene are required to produce 1,000 pounds of product. This mixture is cooled before being charged to the reactor. The polymerization reaction takes place at about 40°F and at essentially atmospheric pressure for 8-16 hours. When conversion reaches about 60%, the reactor contents are dumped into flash drums or blow-down tanks. Unreacted butadiene is evolved from the latex mixture in the flashing process and returned to the process. Unreacted styrene is removed in a stripping column operated under vacuum and also returned to the process. The latex product is then mixed with various ingredients such as oil, carbon black, etc.; coagulated and precipitated from the latex emulsion. The rubber particles are then dried and baled. Drying operations may take many forms depending on the desired product. Spray dryers, vacuum dryers, and tunnel or conveyor dryers have been used.

Emissions from synthetic rubber manufacturing process consist of organic compounds, largely the monomers used, emitted from the reactor and blow-down tanks, and particulate matter and odors from the drying operations.

Drying operations are frequently controlled with fabric filter systems to recover any particulate emissions since this emission represents a product loss. Potential gaseous emissions are largely controlled by recycling the gas stream back to the process.

Factors Affecting Emissions

The overall condition and equipment maintenance at the plant, the overall yield, the degree of monomer recovery, and the degree of control applied to vacuum vents and dryer operations all affect emissions. The largest single factor is the degree of control used on the blow-down tank vents and on the stripping tower.

Emissions

Gaseous emissions consisting mainly of the monomer compounds used to make the rubber, account for the largest portion of emissions. Table 4.10-1 presents the emissions from a butadiene-acrylonitrile and butadiene-styrene rubber manufacturing plant.[3]

Table 4.10-1 Emissions from Synthetic Rubber Plant (Butadiene-Acrylonitrile and Butadiene-Styrene)[3]

Compound		Quantity Emitted, tons per year
1, 3 - Butadiene		500[a]
2 - Methyl Propene		180
1 - Butyne		36
1, 4 - Pentadiene		15
	Total Alkenes	753
3, 4 - Dimethylheptane		15
Cis - 2 - Pentane		29
	Total Alkanes	44
Ethanenitrile (Alaphatic)		10
Acrylonitrile		210
Aerolein (Propenal)		31
	Total Carbonyls	241

a) The butadiene emission is not continuous and is greatest right after a batch of partially polymerized latex enters the blowdown tanks.

While the data in Table 4.10-1 were based on measured emission rates, no relationship to plant production was made and a usable emission factor based on pounds per ton is thus not obtainable. The table does, however, show the types of compounds that are emitted.

Reported emissions from another rubber plant showed 0.55 pound of particulate, 40 pounds of butadiene, and 17 pounds acrylonitrile per ton of product.[4] These emissions are comparable to those reported in Table 4.10-1 for a 25,000 ton per year plant.

Reliability of Emission Factor

Due to the many variables in the synthetic rubber manufacturing process and the limited emission data available, the emission factor is questionable. Table 4.10-2 presents the factor ranking.

Table 4.10-2. Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
4	5	2	11

Additional emission measurements are required to assess the quantity and composition of emissions from synthetic rubber manufacturing processes.

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4.11 SYNTHETIC FIBERS

Process Description

Fibers are either natural, semi-synthetic, or "true" synthetic. Natural fibers are produced from naturally found materials such as cotton or wool. Semi-synthetics (e.g.,viscose rayon and acetate fibers) result when natural polymeric materials such as cellulose are brought into a dissolved or dispersed state and then spun into fine filaments. True synthetic polymers, such as nylon, orlon and dacron result from two methods of forming long chain molecules: addition polymerization and condensation polymerization. United States annual production of synthetic and semi-synthetic fibers is now more than 3 billion pounds.[1]

Some of the major synthetic (true and semi-synthetic) fibers are classified chemically and by method of spinning in Table 4.11-1.[1] All true synthetic fibers begin with the preparation of extremely long, chainlike molecules. The polymer is spun in one of four ways:[3] 1) melt spinning - involves pumping molten polymer through spinneret jets. The polymer solidifies into filaments as it strikes the cool air. 2) dry spinning - the polymer is dissolved in a suitable organic solvent, and the resulting solution is forced through spinnerets. Dry filaments result upon the evaporation of the solvent in warm air. 3) wet spinning - the solution is coagulated in a chemical bath as it emerges from the spinneret.[1] 4) core spinning - newest method - a continuous filament yarn together with short-length "hard" fibers are introduced onto a spinning frame in such a way that a composite yarn is formed in which the continuous filament is a core and the stable fibers are a sheath.[2]

Table 4.11-1. Types of Fibers and Films[1]

Classification	Spinning Method
Polyamides, or nylon fibers	
Nylon 66, nylon 6	Melt
HT-1, or Nomex	Dry
Polyesters	
Fibers: Dacron, Vycron, Kodel, Fortrel	Melt
Films: Mylar, Gronar, Kodar, Estar	Melt
Acrylics and modacrylics	
Orlon fiber	Dry
Acrilan fiber	Wet
Creslan fiber	Wet
Dynel fiber (vinyl-acrylic)	Dry
Verel fiber	Dry
Vinyls and Vinylidines	
Saran fiber and film	Melt
Vinyon N fiber (vinyl and acrylonitrile)	Dry
Spandex	
Lycra fiber (DuPont)	Core
Vyrene fiber (U.S. Rubber)	Core
Blue C fiber or film (Chemstrand)	Core
Olefins	
Polyethylene films	
Polypropylene fibers and films: Avisun, Herculon	
Fluorocarbons	
Teflon	
Regenerated cellulose	
Fibers: Rayon (viscose), Cordura, cuprammonium	Wet
Film: Cellophane	Wet
Cellulose Esters	
Acetate fibers and films: Acele, Estron	Dry
Triacetate fiber: Arnel	Dry

In order to illustrate in more detail the processes involved in the manufacturing of synthetic fibers,simplified flow charts for the manufacture of nylon yarn (true synthetic) and viscose rayon yarn (semi-synthetic) are shown in Figures 4.11-1 [1] and 4.11-2[2], respectively. In addition, a brief description of each of these particular manufacturing processes follows:

Nylon(66): This fiber is made from basically two chemicals--hexamethylene diamine ($H_2N(CH_2)_6NH_2$) and adipic acid ($HOOC(CH_2)_4COOH$). These compounds are combined to form nylon salt, hexamethylene diamonium adipate and polymerized to polyhexamethylene adipamide or nylon.[1] Emissions of gaseous hydrocarbons may occur, especially from drying of the finished fiber. Emission controls are not generally used.

Viscose Rayon: Wood chips or cotton fibers are treated to produce sheets of purified cellulose. The cellulose sheets are then soaked in caustic soda, producing sheets of alkali cellulose, which is broken up into grains called "cellulose crumbs." The "cellulose crumbs" are aged for two or three days under controlled temperature and humidity. Liquid carbon disulfide is then added, which combines with the cellulose crumbs to form cellulose xanthate.[1] The cellulose xanthate crumbs are dissolved in a weak solution of caustic soda and transformed into a thick viscous solution called viscose. The viscose is aged, filtered, and vacuum-treated to remove air bubbles. It is then forced through the holes of a spinneret into sulfuric acid, which coagulates the cellulose of the soluble cellulose xanthate to form pure generated cellulose filaments.[2] The filament is stretched, treated, dried, and wound. Sodium sulfate is a by-product while carbon disulfide is a major gaseous emission. Hydrogen sulfide is also emitted.

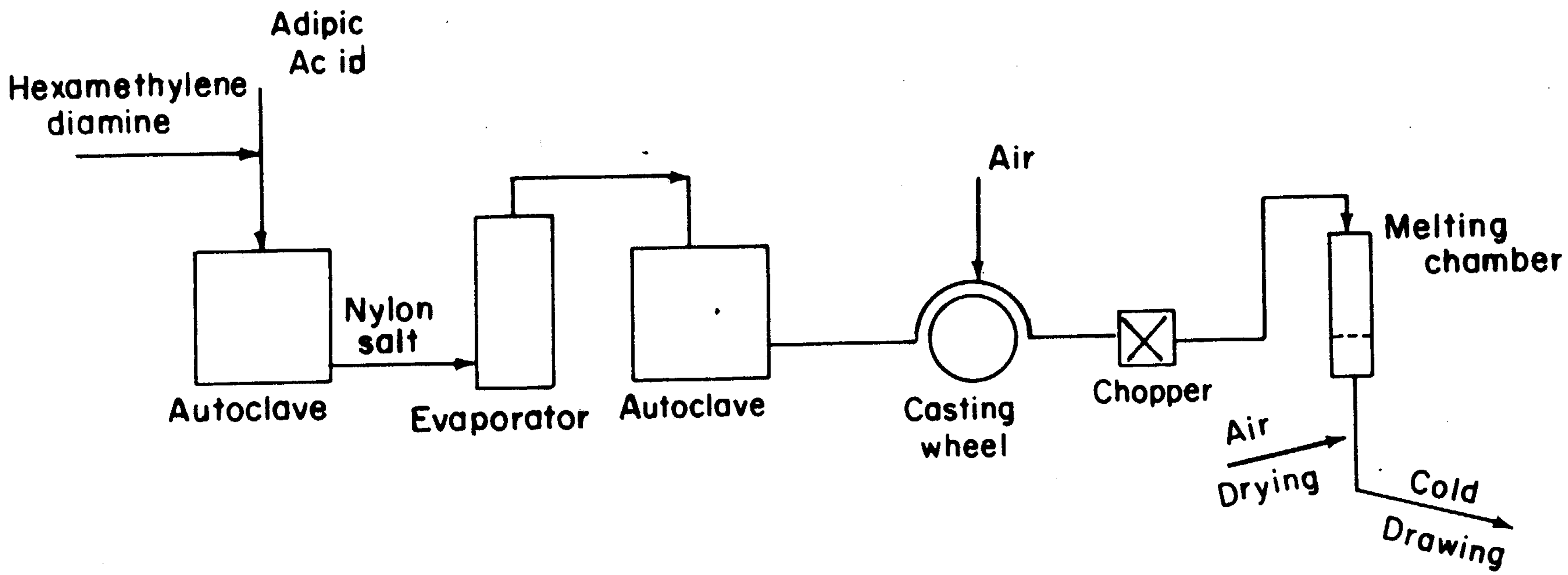

Figure 4.11-1 Nylon Manufacturing process

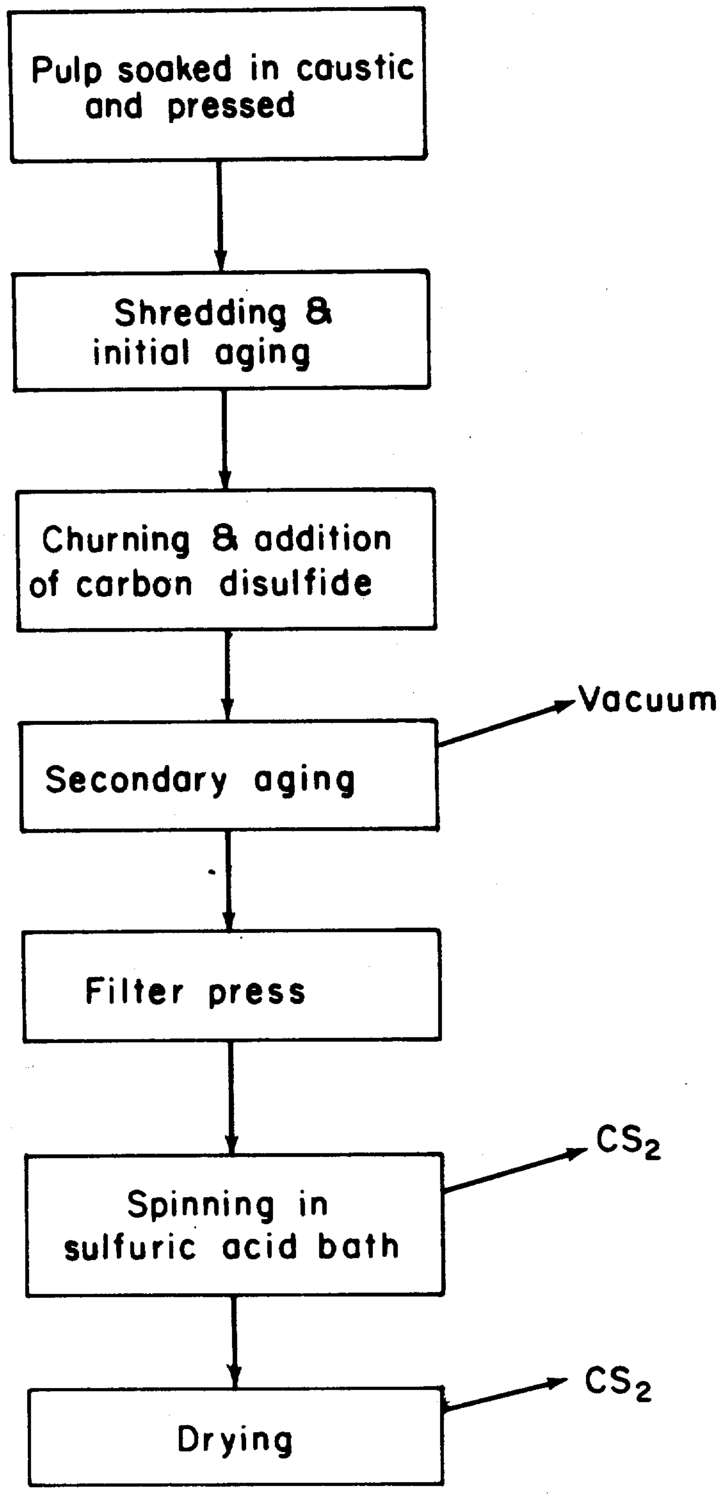

Figure 4.11-2 Viscose Rayon Manufacturing

Air pollution controls are not used to reduce CS_2 or H_2S emissions in the United States. However, an activated fixed bed carbon absorber has been successfully used in England.[4]

Factors Affecting Emissions

The major factors affecting emissions from synthetic fiber manufacturing is the type of fiber produced and the manufacturing process involved, and the volatility of any binder used on the fibers.

Emissions

Very limited emission data are available from synthetic fiber manufacturing plants. Exit gas stream concentrations of 1000 ppm CS_2 and 30 ppm H_2S have been reported for rayon plants.[4]

Table 4.11-2 Emission Factors for Synthetic Fiber Manufacturing

Type of Fiber	Emission	Quantity, lbs per ton of Fiber
Rayon	CS_2 H_2S	55[a] 6[a]
Nylon	Oil Vapor or Mist Gaseous Hydrocarbons	10 to 20[b] 4 to 10[b]
Dacron	Oil Vapor or Mist	4 to 10[b]

a) May be reduced by 80-95% by adsorption in activated charcoal.[4] Emission Data Based on Reference 5.

b) Emissions vary with type and volatility of binder - Reference 6.

Reliability of Emission Factor

Due to the very limited data available on fiber manufacturing, the emission factors must be considered questionable. Further work in obtaining both quantity and composition of gaseous emissions is required and appears warranted due to the growth of this industry. Table 4.11-3 presents the emission factor ranking.

Table 4.11-3 Emission Factor Ranking for Synthetic Fibers

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Rayon	5	5	2	12
Nylon	5	2	2	9

Due to the limited amount of information available for synthetic fiber manufacturing, no Appendix is included in this section.

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5. FOOD AND AGRICULTURAL INDUSTRY

Atmospheric emissions from feed and grain handling, meat smoking, and fermentation processes are reviewed in this section. In general, these industries are characterized by a lack of available emission information.

Grain handling is largely based in the midwestern area of the country. Due to the tremendous quantities of grain handled and the dry, dusty nature of the material handled, grain handling is a significant source of particulate emissions.

Continued improvements in meat smoking processes have reduced the smoke problem from this source.

Quantitative emission data from fermentation processes was not found. Due to the alternate methods of processing, a wide range in the emissions can be expected.

5.1 FEED AND GRAIN MILLS AND ELEVATORS

Process Description

Grain elevators are primarily transfer and storage units and are classified into two categories. These are the smaller more numerous country elevators and the larger terminal elevators. In addition, many elevator locations also contain feed manufacturing facilities. Particulate emissions occur due to the dry, light nature of most grains and the way they are handled via pneumatic and mechanical conveyors. A wide variety of grain handling configurations are possible at elevator sites depending on the number and quantity of grains handled, and the amount of processing required to produce feeds. At grain elevator locations any or all of the following operations can occur:

Receiving, transfer and storage
Cleaning
Drying
Milling or grinding

Receiving and transfer operations are accomplished by unloading the grain usually by dumping into a bin followed by conveyor belt or pneumatic transfer. Cleaning operations are designed to eliminate impurities such as sticks, stones, and other foreign matter. Both screening and air classifiers are used to separate grain and foreign matter.

Drying is usually accomplished in rotary, column, or shelf dryers using heated air as the drying medium.

Grinding may be done in a variety of devices in either a wet or dry state. Common devices used include hammer mills and rollers.

Dust control at elevator operations is most commonly accomplished by cyclones or baghouses. Hooding and ventilation of such dust generation points as shipping and receiving, conveyor drop, cleaning, drying, and elevating points accomplishes dust pickup at the source, with the cyclone and bag filter used to remove dust from the exhausted air. Cyclones are the most commonly used collectors due to their low cost and durability under conditions of high temperature and moisture. Combinations of the two types of collectors are often used for high efficiency of air cleaning.

Many of the large terminal elevators also process grain at the same location. The grain processes may include wet and dry milling (cereals), flour milling, oil seed crushing, and distilling. Wet milling by its nature is not conducive to major dust formation, although dust may escape from dryer cyclones. Dry milling, however, is somewhat more dusty in its operation. Most handling and transfer in these operations is pneumatic, allowing good dust control. Small particle size makes dust control a much greater problem. Oil seed crushing generally is not conducive to major dust generation, but losses can occur from extracting and drying operations and from cyclone collectors used on these operations. Grain distilling operations also are not conducive to major dust formation although particulates can escape during unloading of grains and be entrained in the gaseous discharge from cooling operations. The major problem at these operations remains that of odor emissions.

Feed manufacturing involves the receiving, conditioning (drying, sizing, cleaning) and blending of grains and various nutritional supplements and their subsequent bagging or bulk loading. Emissions may occur during receiving and loading operations and from dust collection systems which are generally applied to most phases of the operation to reduce product and component losses. Pneumatic conveying is widely used in these processes for transfer and loading.

Factors Affecting Emissions

Factors affecting emissions from grain elevator operations include the types of grain, the moisture content of the grain (usually 10-30%), amount of foreign material in the grain (usually 5% or less), the amount of moisture in the grain at the time of harvest (hardness), the amount of dirt harvested with the grain, the degree of enclosure at loading and unloading areas, the type of cleaning and conveying, and the amount and type of control equipment used, if any.

Factors affecting emission from grain processing operations include the type of processing (wet or dry), the amount of grain processed, the amount of cleaning, the degree of drying or heating, the amount of grinding, the temperature of the process, plus the degree of control applied to the particulates generated.

Factors affecting emissions from feed manufacturing operations include the type and amount of grain handled, the degree of drying, the amount of additive or water blended into the feed, the type of handling (conveyor or pneumatic), and the degree to which control equipment is applied to the process.

Emissions

Emissions from feed and grain operations may be separated into those occurring at all elevators involving transfer losses, and those emissions occurring at other grain processing operations such as cleaning, drying, and grinding.

Emissions are greatest at the loading and unloading areas, especially when these operations are carried out in the open. Most of the particulate emission is 50μ or smaller in size. A particle size distribution for grain dust emissions is shown in Table 5.1-1. Beeswings or corn chaff, although a small weight percent of the emitted particulate, cause a major air pollution problem. This material is of low specific gravity (1.5) and can be carried great distances by moderate winds. Emission data are presented in Table 5.1-2.

Table 5.1-1. Size of Particulate Matter Generated From Dust Conveyor System[a]

	% By Weight	
Particle Size (μ)	Before Cyclone	After Cyclone
0 - 44	6.4	58
44 - 74	19.2	11
74 - 104	17.4	10
104+	57	21

a) System serves soybeans, wheat, milo and yellow corn, and corn cleaning. From Reference 7.

Table 5.1-2. Particulate Emissions From Grain Handling and Processing

(pounds/ton of grain processed)

Emission Source	lbs/ton processed	range of emissions (lbs/ton)
1. Terminal Elevators		
Shipping or Receiving		
Rail	1	(1 - 3)
Truck	1.4	(0.8 - 3.5)
Barge	1.2	(1 - 3.5)
Transferring, Conveying, etc.	2.0	(2 - 2.5)
Screening and Cleaning	5.0	(5 - 7)
Drying	5.5	(4 - 8)
2. Country Elevators		
Shipping or Receiving		
Rail	4	(3 - 8)
Truck	4.5	(2 - 8)
Barge	5.5	(3 - 8)
Transferring, Conveying, etc.	3.5	(2 - 4)
Screening and Cleaning	8.5	(7 - 10)
Drying	7.5	(4 - 8)

Emission Source	lbs/ton processed	range of emissions (lbs/ton)
3. Grain Processing		
Alfalfa Dehydrating (overall plant)[a]	4.5	20 - 70
Alfalfa Meal Milling	0.2	-
Corn Meal (based on process weight loss)	5	1 - 27[b]
Soybean Processing (based on process weight loss)	7	4 - 10[b]
Malted Barley Cleaner or Wheat Cleaner	0.2[b]	
Milo Cleaner	0.35[b]	
Barley Flour Milling	3[b]	
4. Feed Manufacturing		
Barley	3.2[b]	

---

a) Not a true grain operation per se.
b) At cyclone exit (only non-ether soluble).

Reliability of Emission Factor

The factors for grain elevators are good due to a fair amount of data and engineering evaluation of the available data.

Factors for grain processing and feed mills are questionable due to lack of data.

Further work is indicated in the area of emission data from grain processes and feed blending operations. The limited data in this area are old and very incomplete. The factor ranking is shown in Table 5.1-3.

Table 5.1-3. Emission Factor Ranking for Grain Handling and Processing

Emission Data 0-20	Process Data 0-10	Engineering Analysis[a] 0-10	Total
Elevators			
10	7	9	26
Grain Processing			
5	6	8	19
Feed Mills			
4	7	8	19

---

a) Engineering Analysis performed by industry personnel.

APPENDIX 5.1

Terminal Elevators Emission Source	Emission lbs/ton Processed	Ref.	Country Elevators % Lost During Processing	Ref.
Shipping & Receiving				
Rail	1.0 1.1	3 4	0.2 - 0.5%	4
Truck	2.0 .8	3 4	0.2 - 0.5%	4
Barge	1.0 1.2	3 4	0.2 - 0.5%	4
Transferring & Conveying	2.0	3	0.1 - 0.25%	4
Screening & Cleaning	5 2-10	3 4	0.1 - 0.5%	4
Grain Drying	4 8	3 4	0.1 - 0.5%	4

Grain Processing

Type	lb/ton	Ref. No.
Alfalfa Dehydrating	20-70	5
Alfalfa Meal Milling	0.2[b]	6
Barley Flour Milling	3.1[b]	6
Corn Meal	26.7	2
Corn Meal	1-10	4
Soybean Processing	4-10	4
Wheat Cleaning	0.2[b]	6
Malted Barley Cleaner	0.2[a]	1
Milo Cleaner	0.35[a]	1

Feed Manufacture

Type	lb/ton	Ref. No.
Barley Feed	3.2[a]	1

a) At cyclone exit

b) At cyclone exit - but only includes non-ether soluble particulate.

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5.2 MEAT SMOKEHOUSES

Process Description

Meat smoking has been employed for centuries for the preservation of meat and fish products. Today, however, with the influx of more efficient and more economical methods of curing and preserving meat, smoking is primarily used to impart flavor and color to the meat for better "customer appeal". While some smoking of fish and poultry products is done, the vast majority of smoked products are meats of bovine and porcine origin. In addition, a token amount of vegetable products are smoked as gourmet items.[1]

Smoking is a diffusion process in which food products are exposed to an atmosphere of hardwood smoke. This exposure causes various organic compounds to be absorbed by the food. Smoke is produced commercially in the United States by three major methods: 1) burning dampened sawdust (20-40% moisture); 2) burning dry (5-9% moisture) sawdust continuously, and 3) by friction. Today, burning dampened sawdust and kiln-dried sawdust are the most widely used methods. Smoke production by friction--by pressing the end grain of hardwood block against a rotating carbide-tipped disk--is in use to some extent with relatively small production units.

The smoke production takes place at temperatures from 700 - 1000°F.[2] Most large, modern, production meat smokehouses are the recirculating type, in which smoke is circulated at reasonably high temperatures throughout the smokehouse. There are some atmospheric smokehouses still in operation, but these outmoded systems are rapidly giving way to the modern recirculating type. Recirculation smokehouses usually include automatic temperature and humidity controls, and thus the opacity and make up of exhaust gases are more constant than those from atmospheric units.[1]

The actual smoking of the meat is an absorption or scrubbing process, rather than a settling process,[2] and it has been found that the rate of deposition of phenols from the smoke is about 20 times as high for wet surfaces as for dry surfaces.[3] Furthermore, the percentage loss of the smoke particles is a linear function of temperature.[2]

Liquid smoke materials prepared by burning hardwood or hardwood sawdust in a manner similar to that used in meat smoking are available. There are many potential advantages to liquid smoking; however, the fear that this process might deposit lethal quantities of toxic materials from the smoke onto the meat has restricted its development and use in many states. From an air pollution standpoint, liquid smoking is ideal, since the scrubbing process which produces the liquid smoke simultaneously removes the air pollutants.

Another rather new smoking method is electrical precipitation, in which the smoke particles are electrically charged and precipitated on the meat. This process, though not widely used, has the advantages of faster smoking and greater use of generated smoke. Air pollutants from the process are considerably less than those from conventional methods. Spacing problems and difficulty with irregularly shaped smoked products have severely curtailed the development of the electrical smoke precipitator as a major smoking process.

Both low voltage electrostatic precipitators and direct-fired afterburners may be used to reduce particulate and organic emissions. Aldehydes may be decreased by 35-40% and particulates by about 65% with either device.[1]

Factors Affecting Emissions

The composition of smoke is dependent on several factors, including 1) type of wood, 2) type of smoke-generator, 3) moisture content of the wood, 4) temperature of combustion, 5) air supply, 6) rate and quantity of smoke deposition, and 7) amount of smoke recirculated.

Emissions

While the smoking process is widely used in meat packing plants, very little work has been done to estimate the smoking industry's contribution to air pollution. There have been some studies made on the chemical composition of smoke from smokehouses, and this information coupled with production data was used to determine the emission factors in Table 5.2-1.

Table 5.2-1. Emissions From Meat Smoking, lbs/ton of Meat[a]

Pollutant	Uncontrolled		Controlled[b]
	Range	Avergae	Average
Particulate	0.04 to 0.5	0.27	0.09
CO	0.4 to 0.7	0.6	Neg.[f]
HC[c]	0.03 to 0.16	0.07	Neg.[f]
Aldehydes[d]	0.065 to 1.1	0.08	0.05
Organic Acids[e]	0.23 to 0.25	0.24	0.13

---

a) Based on 110 lbs of meat smoked per pound of wood burned.

b) Controls consist of a wet collector and low voltage precipitator in series, or direct-fired afterburner.

c) As methane.

d) As formaldehyde.

e) As acetic acid.

f) With afterburner.

Reliability of Emission Factors

Concentrations of particulate emissions and some gaseous emissions have been reported in the literature. However, little data exists which relates the volume of exit gases to the amount of wood burned, or to the amount of food smoked. The overall emission factor must therefore be considered questionable as shown by the ranking in Table 5.2-2.

Table 5.2-2. Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
8	2	2	12

APPENDIX 5.2

Emission Data

1. Grain loading range and average particulate emissions from smokehouses.[1]
    a. range: 0.016 to 0.234 gr/scf
    b. average: 0.116 gr/scf ± 86%
2. Production figures - meat smoking process.[5]
    a. 20 lbs. sawdust burned per hour
    b. 2200 lbs. meat smoked per hour
    c. 300 cfm exhaust gases
3. Particulate emission.

    $$300 \text{ cfm} \times 0.116 \text{ gr/scf} \times 60 \text{ min/hr} \times \frac{1 \text{ lb}}{7000 \text{ gr.}}$$

    $$\times 1 \text{ hr}/2200 \text{ lbs} \times 2000 \text{ lbs/ton} =$$

    0.272 lbs particulates/ton of meat
    or 29.8 lbs particulates/ton of sawdust
4. Carbon monoxide and hydrocarbons.

    These pollutants were estimated from similar processes, namely charcoal and open wood burning. Since 29.8 lbs particulates/ton of sawdust is within the range of particulate emissions for charcoal manufacturing and open wood burning (see Table 5.2-3), the CO and HC emission factors for smokehouses were assumed to fall within these respective ranges by about the same ratio. Thus the CO emission factor is about 55 lbs/ton of sawdust or about 0.55 lbs/ton of meat. Similarly, HC emissions should be about 7 lbs/ton of sawdust or about 0.07 lbs/ton of meat.

Table 5.2-3. Wood Smoke Emissions[4]

Charcoal	Pollutant, lbs/ton of Wood	Open Burning of Wood
80	CO	50
25	HC	3
100	Particulates	17

5. Aldehydes and organic acids.

   a. Aldehydes (as formaldehyde)

      Molecular weight = 30

      Average concentration = 57 ppm[1] ± 30%

      $57 \times 10^{-6} \times 300 \text{ cfm} \times 60 \text{ min/hr} = 1.025 \text{ cf/hr.}$

      $1.025 \text{ cf/hr} \times 2000 \text{ lbs/ton} \times 1 \text{ hr/2200 lbs} \times \frac{30 \text{ lbs/lb mol}}{387 \text{ ft}^3\text{/lb mol}} = 0.0725 \text{ lbs/ton meat}$

   b. Organic acids (as acetic acid)

      Molecular weight = 60

      Average concentration = 89 ppm[1] ± 2%

      $89 \times 10^{-6} \times 300 \text{ cfm} \times 60 \text{ min/hr} = 1.60 \text{ cf/hr}$

      $1.60 \text{ cf/hr} \times 2000 \text{ lbs/ton} \times 1 \text{ hr/2200 lbs} \times \frac{60}{387} = 0.225 \text{ lbs organic acids/ton of meat}$

Average control efficiencies of 65% for particulates, 37% for aldehydes, and 55% for organic acids for either a scrubber-precipitator combination or an afterburner, were used.[1]

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5.3 FERMENTATION

General

A wide spectrum of product materials are derived from various fermentation processes. All fermentation industries employ one common element, the biochemical action of microorganisms to convert one substance to another. Fermentation industries can be divided into three subgroups according to their manufactured products. Table 5.3-1 lists the predominant fermentation products:

Table 5.3-1. Fermentation Products

Food	Pharmaceuticals	Chemical
Beer	Antibiotics	Organic Acids
Wine	Hormones	
Whiskey	Enzymes	
	Vitamins	
	Penicillin	

The U. S. production of beers, liquors, and wines (116.5, 7.3, and 5.0 million barrels, respectively in 1967) completely dwarfs the production of the other fermentation products, and emissions from the production of these beverages also dwarfs the emissions from the remaining fermentation processes. For this reason, only emissions from the production of beers, liquors, and wines will be considered in this report.

Process Descriptions

Beer and allied products are beverages of low alcoholic content (2 to 7%) made by brewing various cereals with hops, usually

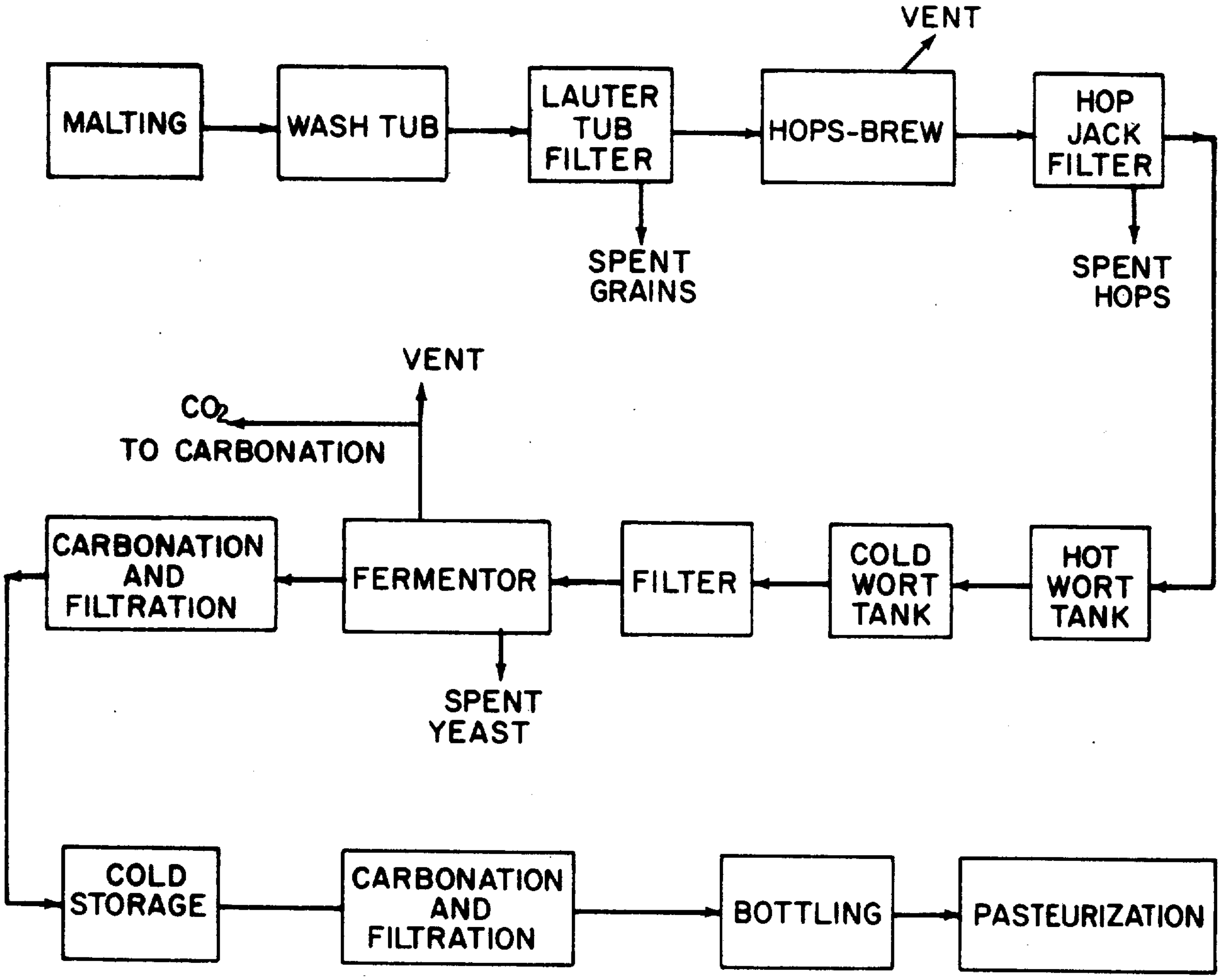

Figure No. 5.3-1 Beer manufacturing flow diagram

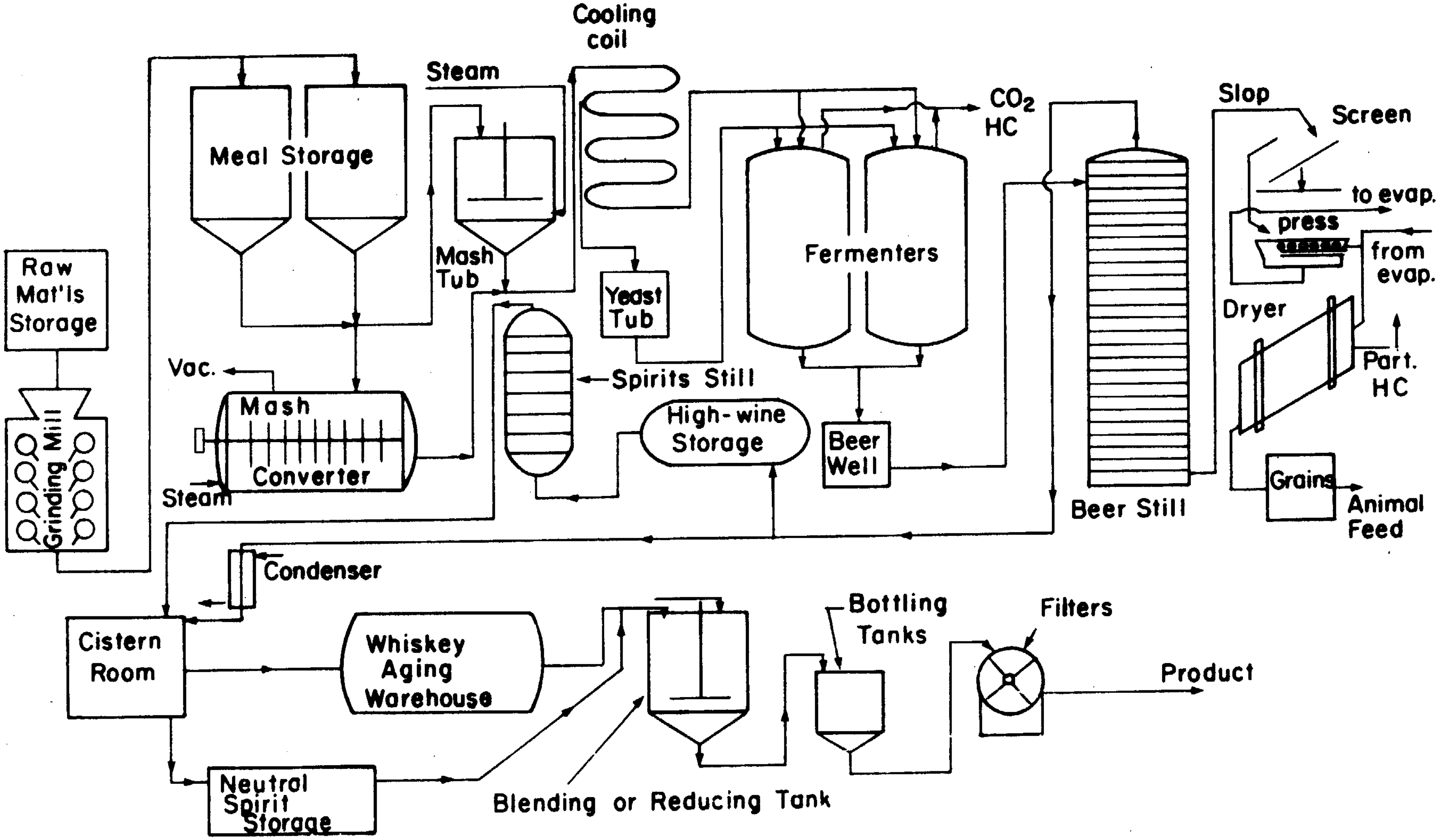

Figure 5.3-2 Typical Distilled Whiskey Flow Diagram

added to impart a more or less bitter taste and to control the fermentation that follows. The cereals employed are malted barley and malt adjuncts: flaked rice, oats, and corn. Brewing sugars, syrups, and yeast complete the raw materials. A flow diagram of the brewery operations describes the beer making process as shown in Figure 5.3-1. The four main brewing production stages and their respective sub-stages are: [1] BREWHOUSE OPERATIONS, which includes a) malting of the barley; b) addition of adjuncts (corn, grits, and rice) to barley mash; c) conversion of starch in barley and adjuncts to maltose sugar by enzymatic processes; d) separation of wort from grain by straining; and e) hopping and boiling of the wort. [2] FERMENTATION, which includes a) cooling of the wort; b) additional yeast cultures; c) fermentation for 7-10 days; d) removal of settled yeast; and e) filtration and carbonation. [3] AGING, which lasts from 1-2 months under refrigeration . [4] PACKAGING PROCESS, which includes a) bottling-pasteurization, and b) racking-draft beer.

The spent hops, spent grains, and spent yeast (see Figure 5.3-1), which have been separated from the liquid which ultimately is beer, are generally drained and then dried. The dried spent products are then either sold as by-products or wasted.

Particulate control systems or grain handling systems are generally the only type of air pollution controls used. These systems consist of cyclones.

Various fermented products, upon distillation and aging, yield the <u>distilled liquors</u>. Figure 5.3-2 shows the flow chart for whiskey. There are a multitude of distilled liquors, differing in raw materials and distillation processes. By law, the aging of bourbon or rye whiskey of claimed age must take place in charred new white-oak barrels of approximately 50 gallons. These are kept in bonded warehouses at 65° to 85°F and at a preferred humidity of 65 to 70 percent for 1 to 5 years. During this time, an evaporation of the contents takes place, largely through the ends of the barrel staves. By reason of a more rapid capillary travel and osmosis of the smaller water molecules in comparison to alcohol molecules, an increase in the percentage of alcohol is found in the barrel contents. The government shrinkage allowance is approximately 8 percent in the first year, 4 percent in the second year, 4 percent in the third, and 3 percent in the fourth year. The distillate from the spirit is still under 160 proof and is subsequently diluted upon barreling to about 100 proof. Packaging of the finished liquor is the last manufacturing process in the production of distilled spirits.

As shown in Figure 5.3-2, the discharge liquor, known as slop or spillage is treated to separate the solids from the liquid slop. After vacuum evaporation of the liquid portion, it is added to the solids and the mixture dried in rotating steam-heated driers to produce cattle feed. Particulates and odors are emitted from this drying process.

Wines are classified as natural (alcohol 7 to 14%), fortified (alcohol 14 to 30%) sweet or dry, stillas sparkling. The fortified wines have alcohol or brandy added. In the sweet wines, some of the sugar remains.

The manufacturing processes for most wines are generally the same. For example in the manufacture of dry red wine, red or black grapes are run through a crusher which macerates them but does not crush the seeds, and also removes part of the stems. The resulting pulp, or "must", is pumped into 3,000-10,000 gallon tanks, where sulfurous acid is added to check the growth of wild yeast. An active culture of selected and cultivated yeast equal to 3-5 percent of the volume is then added. During fermentation, the temperature rises, so that cooling coils are necessary to maintain a temperature of 85°F. When the fermentation process slows, the juice is pumped out of the bottom of the vat and back over the top. The wine is run into closed tanks in the storage cellar where, during a period of 2 to 3 weeks, the yeast ferments the remainder of the sugar. By quick aging methods, it is possible to put out a good sweet wine in 4 months. These methods include pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation, and aeration. The wine is finally racked, clarified, and bottled.

Factors Affecting Emissions

The general factors affecting atmospheric emissions in addition to type and throughput of the process are general plant operation and maintenance, and degree of control on solids (grain) handling systems. Gaseous control systems are rarely used on fermentation processes; however, particulate controls in the form of cyclones are commonly used on the grain handling systems.

Emissions

Emissions from fermentation processes are nearly all gases and primarily consist of carbon dioxide, hydrogen, oxygen, and water vapor, none of which presents an air pollution problem. Purification and concentration of the fermentation product and by-products are generally carried out by distillation, drying, and filtration, and it is in this area that gaseous emissions occur. These emissions are mainly hydrocarbons and are emitted from the condensers, dryer vents, and mash cooker vents.

Origin of emissions from the individual processes involved in beer, liquor, and wine production are: [1] BEER a) grain handling - particulates; b) drying of spent grains, hops, and yeast - gaseous hydrocarbons; c) vent gases from brew kettle - primarily H_2, CO_2, O_2, and H_2O vapor. [2] DISTILLED LIQUORS a) grain handling; b) drying spent grains and yeast - gaseous hydrocarbons; and c) whiskey aging warehouse - gaseous hydrocarbons. [3] WINE - no significant emissions.

Neither emission data nor sufficient process data are available from which emissions can be calculated.

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[illegible] METALLURGICAL INDUSTRIES

6. METALLURGICAL INDUSTRIES

The metallurgical industries can be broadly divided into primary and secondary metal production operations. The primary metal industries produce metal from ore. The secondary metal industries recover metal from scrap and salvaged metal.

The secondary metallurgical industries, discussed in this section, are steel foundries, lead smelting, magnesium smelting and zinc processing. The major air contaminants from these operations are particulates in the forms of metallic fumes, smoke and dust. The small particle sizes of the emissions require high efficiency collectors such as electrostatic precipitators, baghouses and high energy scrubbers (e.g., venturi scrubbers).

The metallurgical processes, except the coking process, discussed in this section are limited to processes which utilize metal scrap and salvaged metal to produce a metal or metal alloy.

Coking, while not a metallurgical process, is an essential step to the production of a fuel and reducing agent required by many metallurgical processes. Coke is used in blast furnaces and smelters to generate the heat and reducing atmosphere vital to the production of iron, lead, zinc, copper, and other metals from their ores.

In general, emission data for these processes are sparse. Some of the data cited are for processes of a similar type rather than for the listed process itself.

Typical Particle Size Distribution,
Weight Percents Metallurgical Industries

Coking Process	0-5μ	5-10μ	10-20μ	7-20μ
Steel Foundries	-	5	5	90
Electic Arc	68	7	10	15
Oxygen Lanced Open Hearth	46	22	17	15
Secondary Lead Smelting	95	4.8	0.2	-
Secondary Magnesium Smelting		No Information		
Secondary Zinc Processing	100	-	-	-

a) Magnesium fume is quite fine; the fume is probably all less than 5 microns in diameter.

6.1 METALLURGICAL COKE MANUFACTURE

Process Description

Coking is the process of heating coal in an atmosphere of low oxygen content, i.e., destructive distillation. During this process organic compounds in the coal break down to yield gases and a residue of relatively non-volatile nature. Two processes are used for the manufacture of metallurgical coke, the beehive process and the by-product process. The by-product process, however, accounts for about 98% of coke produced.

The beehive oven is a refractory lined enclosure with a dome-shaped roof. The coal charge is deposited onto the floor of the beehive and leveled to give a uniform depth of material. Openings to the beehive oven are then restricted to control the amount of air reaching the coal. The carbonization process begins in the coal at the top of the pile and works down through the pile. The volatile matter being distilled escapes to the atmosphere through a hole in the roof. Although some attempts have been made at capturing the gases from beehive ovens for waste heat recovery or by-product recovery, most have been unsatisfactory. At the completion of the coking time, the coke is "watered out" or quenched.

The by-product process, as the name suggests, is oriented toward the recovery of the gases produced during the coking cycle. The coking chamber is a rectangular oven 6 to 14 feet high, 30 to 43 feet in length, and 12 to 22 inches in width. These ovens are grouped together in a series called a coke battery. Coal is charged to the oven through ports in the top and then sealed. Heat is supplied to the ovens by burning some of the coke gas produced. Upon completion of the coking period, the coke is pushed from the oven by a ram and quenched with water. Coking is largely accomplished at temperatures of 1650°F to 2150°F for a period of 16 to 20 hours.

Visible smoke, hydrocarbons, CO, and other emissions originate from the following by-product coking operations: (1) charging of coal into the red-hot ovens, (2) oven leakage during the coking or carbonization period, (3) pushing the coke out of the ovens, and (4) quenching the hot coke.

Associated with both coking processes are the material handling operations. These include: unloading coal, storage of coal, grinding and sizing of coal, screening and crushing coke, and coke storage and loading. All of these material handling operations are potential particulate emission sources. In addition, the operations of oven-charging, coke pushing, and quenching produce particulate emissions. For the most part, the latter three operations go uncontrolled at the present time.

Virtually no attempts are being made to prevent gaseous emissions from beehive ovens. Gaseous emissions from the by-product ovens are drawn off to a collecting main and are subjected to various operations for separating ammonia, coke oven gas, tar,phenol, light oil (benzene, toluene, and xylene), and pyridine. These unit operations are potential sources of hydrocarbon emissions.

Oven charging operations and leakage around poorly sealed coke oven doors and lids are major sources of gaseous emissions from by-product ovens. Sulfur is present in the coke oven gas in the form of hydrogen sulfide and carbon disulfide. Some plants desulfurize the coke oven gas before consuming it. If the gas is not desulfurized, the combustion process will produce sulfur dioxide which is, in turn, emitted to the atmosphere.

Factors Affecting Emissions

Factors affecting emissions include the amount of fines in the coal used and the degree of dust control practiced on the material handling phases. The manner and speed of charging the oven affects the particulate and the gaseous emissions from the oven. Routine maintenance practices on the coke oven doors affect the amount of leakage around the doors. Most coking coals are low sulfur coals; however, a variation in the sulfur content of the coal will vary the amount of sulfur-bearing compounds in the emissions.

Upsets in coking operations can cause significant amounts of gaseous pollutants to be discharged. If suction is lost on the collecting mains of a by-product battery, hydrocarbons, ammonia, carbon monoxide, and sulfur-bearing compounds will be released to the atmosphere.

The water used for coke quenching can affect the emissions from the quenching process. In some plants contaminated waste water, containing phenol and clorides from other portions of the coking operations, is used as quench water. Since quenching causes sudden, violent evaporation, liquid mist as well as coke particles are entrained in the rising vapor. A substantial portion of this material does, however, fall out in the immediate area of the quenching water.

Emissions

Data concerning emissions from the coking process are sparse. Most of the data are limited to the composition and concentration of the by-product gases and particulates. Table 6.1-1 contains a list of by-product substances which are normally recovered during by-product coking operations, but would be emitted in the case of beehive coking.

Table 6.1-1.[1] Recovered Coking By-Products

Material	Quantity Recovered (lbs/ton of coal charged)
Coke Gas	105
Tar Mist	104
Light Oil	8
Ammonia	1.6
Hydrogen Sulfide	1.7

Some data on coking emissions were published recently in a United Nations report. These data were obtained from European operations, and no judgments on their comparability to United States operations or their accuracy have been made. Table 6.1-2 lists emission factors based on European data.

Reliability of Emission Factors

Limited data are available for both gaseous and particulate emissions from coking operations. Much of the reported data was based on European measurements and estimates which frequently combined measured concentrations with estimated total gas flows to obtain total emissions. Table 6.1-3 presents the factor ranking.

Further emission research is indicated in this area.

Table 6.1-3. Emission Factor Ranking for Metallurgical Coke

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	7	6	3	16
Gases	4	6	3	13

Table 6.1-2. Emission Factors for By-product Coking, lbs/ton of Coal Charged

Operation	Particulate	CO	CH_4	C_xH_x[a]	Tar	H_2S	NO_x	NH_3	SO_2
Unloading	0.4 (0.07-0.96)								
Charging	1.5 (0.11-4.3)	0.6 (0.08-1.2)	1.9 (0.23-3.5)	0.6	1.3 (0.23-2.0)	0.03	0.03	0.02	0.02
Coking Cycle	0.1	0.6	1.5		0.8	0.1	0.01	0.06	0.002
Discharging	0.6 (0.14-1.37)	0.07 (0.01-0.13)	0.2 (0.04-0.40)		0.06 (0.01-0.10)	0.08[b]		0.12[b]	
Quenching	0.9 (0.5-1.40)								
TOTALS	3.5	1.27	3.6	0.6	2.16	0.21	0.04	0.20	0.022

[a] Aromatic Hydrocarbons, e. g., benzene (C_6H_6) - reported as methane.

[b] Emission reported from discharging and quenching combined.

APPENDIX 6.1

Table 6.1-4. Coke Plant Emission Data

	Emissions, lb/ton of coal charged				
	Particulate	CO	CH_4	C_xH_x	Tar
Plant 1[2]					
Unloading	0.96				
Charging	4.30	1.2	3.5	0.6 as CH_4	1.7-2
Discharging	0.14-1.37	0.01-0.13	0.04-0.4		
Quenching	0.55-1.40 (lb/ton coke)				
Plant 2[2]					
Unloading	0.07-0.11				
Charging	0.11-0.15				
Discharging	0.29-0.44 (lb/ton coke)				
Other data[4]					
Quenching	0.5				

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a) Aromatic hydrocarbons, e.g., benzene (C_6H_6).

Table 6.1-5. Polish Estimates of Coke Plant Emissions [3]

Pollutant	Formula	Charging*	Coking Cycle*	Discharging* & Quenching
Coal Dust	-------	1.366	0.130	0.400
Tar	-------	0.229	0.768	0.022
Methane & homologues	$C_nH_{2n}+2$	0.227	1.487	-----
Ethylene & homologues	C_nH_{2n}	0.033	0.224	-----
Acetylene	C_2H_2	0.002	0.013	-----
Carbon Monoxide	CO	0.081	0.554	0.011
Benzene	C_6H_6	0.033	0.019	-----
Napthalene	$C_{10}H_8$	0.011	0.075	0.031
Phenol	C_6H_5OH	0.013	0.022	0.174
Pyridine	C_5H_5N	0.134	0.013	-----
Ammonia	NH_3	0.018	0.059	0.125
Hydrogen Sulfide	H_2S	0.026	0.103	0.084
Hydrocyanic acid	HCN	0.002	0.007	0.011
Oxides of Nitrogen	NO_x	0.029	0.013	-----
Sulfur Dioxide	SO_2	0.024	0.002	-----
Carbon Disulfide	CS_2	-----	0.002	-----
Chlorine	Cl_2	0.002	0.007	-----
Chlorides	Cl^-	-----	-----	0.062
Sulfates	SO_4	-----	-----	0.158

*lbs/ton charged

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6.2 STEEL FOUNDRIES

Process Description

Steel foundries produce steel castings by melting steel metal and pouring it into molds. Castings of nearly any desired shape or size can be made in this manner.

The melting of steel for castings is accomplished in one of five types of furnaces. These various types are direct electric arc, electric induction, open hearth, crucible, and pneumatic converter. The first three types are most frequently used since the older crucible and pneumatic types are being replaced by electric furnaces. Raw materials supplied to the various melting furnaces include: steel scrap of all types, pig iron, ferroalloys and limestone. The basic melting process operations are furnace charging, melting, tapping the furnace into a ladle and pouring the steel into molds.

The direct electric arc furnace is a refractory-lined, cylindrical basin. The roof is a flat dome with openings for the electrodes. The furnace is charged either through a door in the side of the furnace or through the top of the furnace after the roof is swung aside. Heat for the melting process is supplied by applying low voltage, high current electrical power to carbon or graphite electrodes positioned just above the level of the metal or bath. Arcs are formed between the electrodes and the bath, and current travels through the bath. Thus, heat is supplied to the bath by radiation from the arcs and by the electrical resistance of the bath to the current. Steel is tapped from the furnace after the electrodes are raised by tilting the furnace and allowing the metal to run out the tap hole into a ladle. Capacities of direct electric arc furnaces range from 3 to 200 tons per heat. Heat times vary from one to four hours. Oxygen lancing may be used.

Fume control is achieved by placing a canopy hood above the furnace or by having an exhaust takeoff in the furnace roof or sidewall. While the overhead canopy hood could, possibly, catch particulate emitted from the charge or tap operations, the roof hood and sidewall tap do not have this potential.

Open hearth furnaces range in size from 10 to 600 tons capacity. Most open hearths in the United States are basic furnaces, i.e., utilize basic refractory brick and a basic process. The furnaces have a long, relatively shallow hearth and a low roof. Heat for steel melting is supplied by combustion of natural gas, coke oven gas, heavy fuel oil or tar. These heat sources may be augmented by oxygen enrichment of combustion air or oxygen lancing. Combustion air is preheated in a regenerative chamber system consisting of brick checker-work heated by the exhaust gases. Raw materials are charged to the furnace through doors in the front of the furnace. The furnace is tapped through a hole in the rear of the furnace. Oxygen lancing is frequently used.

Fume control may be achieved by processing the waste gases downstream of the regenerative chambers. Gas temperatures may require the use of a waste heat boiler or other cooling apparatus upstream of the air pollution control equipment.

Electric induction furnaces are generally small in capacity, usually 1/4 to 1 ton in size. These furnaces are generally used for melting with little or no refining of the charged materials.

The charge is introduced into the top of the furnace. Energy is supplied to the furnace by activating the induction coil around the furnace. The electrical resistance to secondary currents in the charged material generates heat which, in turn, melts the charged material. The completed heat is tapped either directly into molds or into a ladle in the case of larger furnaces.

Fume emissions from the electric induction process can be captured by use of a canopy hood. This type of hood can potentially control emissions generated during charging and tapping.

An integral part of the steel foundry operation is the preparation of casting molds and the shakeout and cleaning of these castings. Molds can be made from many materials. The choice of molding material is dependent upon variables such as size of castings, metal temperature, and the pouring method. Some common materials used in molds and cores for hollow casting include sand, oil, clay, and resin. Shakeout is the operation in which the cool casting is separated from the mold. The castings are commonly cleaned by shotblasting, and surface defects such as fins may be removed by burning and grinding.

Factors Affecting Emissions

Factors affecting emissions from the melting process include quality and cleanliness of the scrap and increased oxygen lancing. Additional particulate is generated due to the oxidation of iron, zinc, lead and other metals which depend upon the source of scrap metal in the furnace charge. If the scrap metal is quite dirty or oily or increased oxygen lancing is employed, the emission factor should be chosen from the high side of the factor range. The concentrations of oxides of nitrogen will be dependent upon operating conditions in the melting unit such as temperature and the rate of cooling of the exhaust gases. The concentration of carbon monoxide in the exhaust gases is dependent on the amount of draft on the melting furnace. Sulfur oxide emissions depend mainly on the sulfur content of the fuel when used. Emissions from the shakeout and cleaning operations, being mostly particulate, will vary according to the type and efficiency of dust collection and air cleaning systems used.

Gaseous emissions from the mold and baking operations are dependent upon the fuel used by the ovens and the temperature reached in these ovens. Odorous emissions may be produced by baking operations, depending on the resins, oils and other mold ingredients used by the foundries.

Emissions

Particulate emissions from steel foundry operations include iron oxide fume, sand fines, graphite and metal dust. These particulates range in size from 0.1 microns to 1000 microns or larger. The smaller particles are the oxide fumes from melting operations, and the larger are typical of grinding operations

Table 6.2-1. Typical Particle Size Distribution for Melting Operations in Weight Percent

	0-5μ	5-10μ	10-20μ	>20μ
Electric Arc Furnace[1]	68	7	10	15
Oxygen Lanced Open Hearth[2]	46	22	17	15

Table 6.2-2[3]. Foundry Operations Emissions

Operation	Grain Loading (grains/SCF)
Shakeout	0.5 - 1.0
Sand Cooler	1.0 - 20.0
Airless Abrasive Cleaning	0.5 - 5.0
Grinders	0.5 - 2.0
Dry Sand Reclaimer	10.0 - 40.0
Screens and Transfer Points	0.5 - 3.0

Gaseous emissions from foundry operations include oxides of nitrogen, oxides of sulfur, and hydrocarbons.

6.2-3. Emission Factors for Steel Foundries

	Uncontrolled Emissions - lb/ton processed			
Type of Process	Particulate	Range	NO_x	Range
Electric Arc Furnace[a]	13	3.5-40	0.2	0.07-0.4
Open Hearth[b]	11	1.5-20	0.013	
Oxygen Lanced Open Hearth[c]	10	9.3-10		
Induction Electric[d]	0.1			

a)	Electrostatic precipitator	92-98% control efficiency
	Baghouse (Fabric filter)	98-99% control efficiency
	Venturi scrubber and other high energy scrubbers	94-98% control efficiency
b)	Electrostatic precipitator	95-98.5% control efficiency
	Baghouse	99.9% control efficiency
	Venturi scrubber and other high energy scrubbers	96-99% control efficiency
c)	Electrostatic precipitator	95-98% control efficiency
	Baghouse	99% control efficiency
	Venturi scrubber and other high energy scrubbers	95-98% control efficiency
d)	Usually not controlled	

Reliability of Emission Factors

Particulate emission data are generally available for the various steel melting operations, and these emission factors are considered to be reliable. Gaseous emission data is not available, and the factors cited are questionable. Additional experimental work is recommended to determine NOx, CO, and hydrocarbon emission from the various steel melting and casting processes.

Table 6.2-4 presents the factor rankings.

Table 6.2-4. Steel Foundry Emission Factor Ranking

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	16	9	5	30
Gases	2	4	2	8

APPENDIX 6.2

Electric Arc Furnace - Particulate Emissions Data

Factor, lbs/ton	Reference
10.0	5
3.5-4.0	5
40.0	5
12.7	5
30.0	5
10.7	5
6.8	6
12.0	6
9.3	7,8
18.6	7,8
7.6	9
10.4	9
5.5	9
5.2	9
13.4	9
4.5	10
5.8	10
15.3	10
12.8	10
6.1	11
37.8	12
29.4	12,13
7.0	14
4.5	19
10.6	19

$$\text{Average} = \frac{335.9}{26} = 12.9$$

Open Hearth Data (no oxygen lances)

Factor, lbs/ton	Reference
17.50	15
12.90	15
7.95	16
5-10.00	17
1.50	19
7.50	19
20.00	19

Average = $\frac{74.85}{7}$ = 10.7

Open Hearth Data (oxygen lanced)

Factor, lbs/ton	Reference
10.2	18
9.3	10

Although emission rates for oxygen lanced open hearths are generally believed to be higher than those for non-lanced furnaces, the emission factors determined for this report do not indicate that such is the case. No explanation for this discrepancy is evident.

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6.3 SECONDARY LEAD SMELTING

Process Description

There are three types of furnaces used to produce the common types of lead. These are the pot furnace for the production of soft or high purity lead, the reverberatory furnace for the production of semi-soft lead, and the blast furnace or cupola for hard lead containing antimony and other metallic impurities. The pot furnaces are used for the production of the purest of the lead products. They are usually gas-fired and they operate under more closely controlled temperature conditions using charges of better quality lead. Pot furnace air polluting emissions are, therefore, of a lesser magnitude.

Reverberatory furnaces are used for the production of semi-soft lead from lead scrap, oxides and drosses. These furnaces maintain temperatures around 2300°F which favor the production of sulfur oxides from the sulfur content of the charge and nitrogen oxides from the fixation of atmospheric nitrogen at these temperatures. In addition, particulate emissions of lead, tin, copper, and antimony with a particle size averaging 0.3 microns usually occur.[3]

The third common type of furnace, the blast furnace, is used to produce hard lead (typically averaging 8% antimony and up to 2% additional metallic impurity).[1] The charge to these furnaces consists of rerun, slag, and reverberatory slags. Emission problems are greatest with this type of furnace with particulate matter, oil vapors, and carbon monoxide being emitted.

Factors Affecting Emissions

Factors affecting emissions from the pot furnace include the composition of the charge, temperature of the pot, and the degree of control, usually hooding followed by a baghouse applied to the system. Emission from the reverberatory furnace is affected by the content of sulfur in the charge, the temperature in the furnace (typically around 2300°F) and the amount of air pulled across the furnace. The off gases here are much hotter than those from the pot furnace and require cooling before a baghouse can be employed. Lead blast furnace emissions are dependent on the amount of air passed through the charge, the temperature of the furnace, and the amount of sulfur and other impurities contained in the charge. In addition, significant quantities of carbon monoxide are released due to the reduction of the lead oxides in the charge by the coke included in the charge. These emissions, as well as those of oil vapors and hydrocarbons, must be controlled by incineration. Blast furnace stack gases, thus, range from 1200-1350°F and must be cooled before a baghouse can be employed to remove particulates from the gas stream.

Emissions

Emissions are primarily of particulates consisting of lead, lead oxides, and contaminants in the lead charged. A particle size distribution of lead smelting emissions is given in Figure 6.3-1. Emissions from battery lead reclaiming and other reclaiming of dirty lead scrap can consist of sulfur oxides, hydrocarbons, and particulates. Carbon monoxide is also released by the reduction of lead oxide by carbon in the cupola. Nitrogen oxides are formed by fixation of atmospheric nitrogen due to the high temperatures associated with the smelting. Control of emissions is directed primarily toward particulates with the bag filter the most common control device.

Reliability of Emission Factors

Only limited information on smelting emissions was found to be available at this time. Some information does exist, but is not available for release at this time. Further information on smelting emissions should be published as it becomes available.

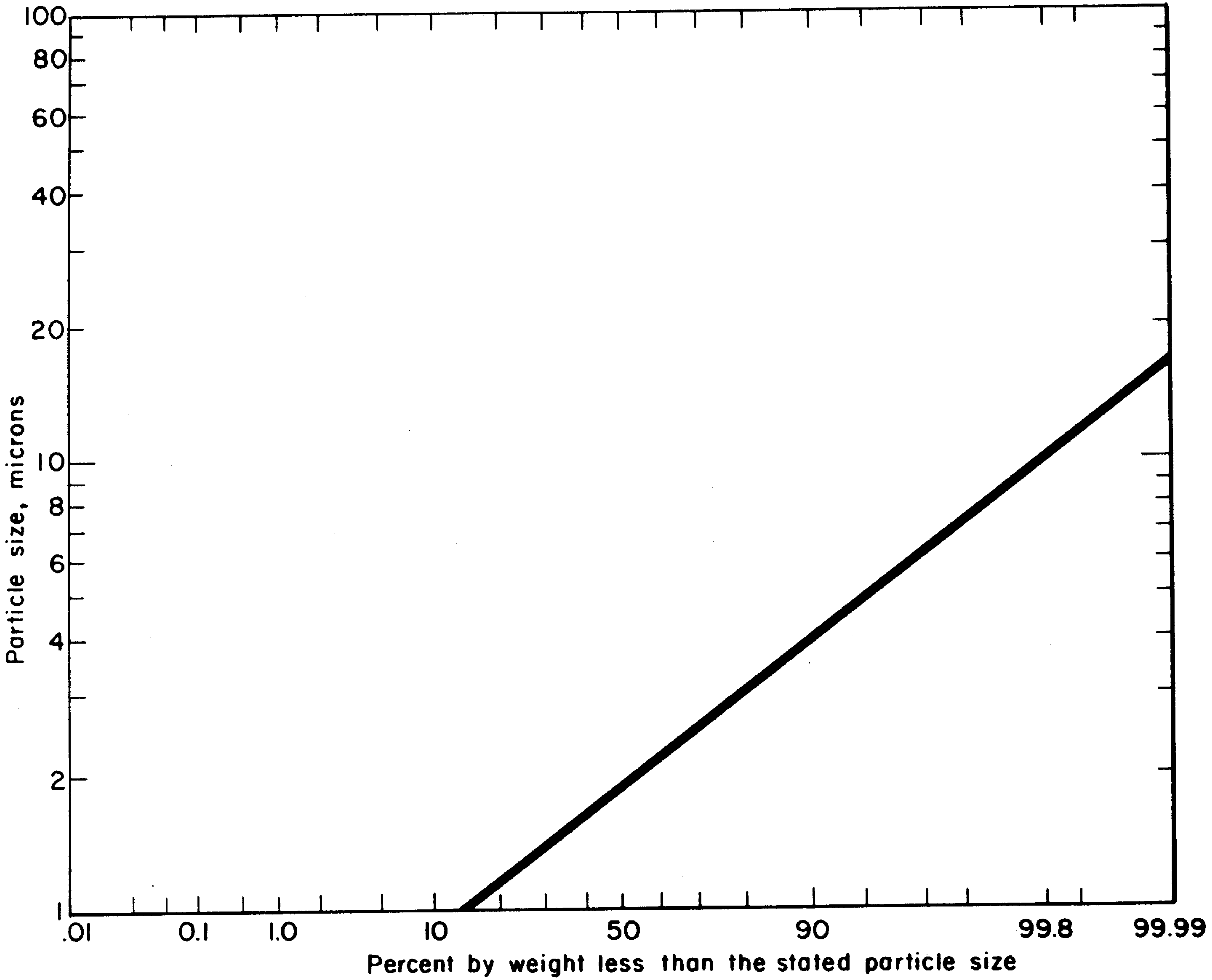

Figure 6.3-1. Approximate particle size distribution of particulate from secondary lead smelting[6]

Table 6.3-1 Lead Smelting Emissions, lbs/ton Processes

	Particulate				SO_x[a]			
Furnace Type	Uncontrolled	Range	Controlled	Range	Uncontrolled	Range	Controlled	Range
Pot Furnace	0.8	0.23-1.36	Neg					
Reverberatory Furnace	130	106-154	1.6	0.96-2.33	85			
Blast (cupola) Furnace	190	80-181	2.3	0.80-5.1	90	64-116	0.8,[b] 46.2[c]	
Rotary Reverberatory	70	6.6-132						

a) SO_x expressed as SO_2

b) With NaOH scrubber

c) With water spray chamber

Table 6.3-2 Emission Factor Ranking for Lead Smelting Operations

Emission Data 0-20	Process Data 0-10	Engineering Evaluation 0-10	Total
8	5	5	18

This factor must be considered questionable due to lack of emission data.

APPENDIX 6.3

Emission Data from the Literature

(pounds/ton processed)

BEFORE CONTROL

Furnace Type	Particulate	Ref.	SO_x[b]	Ref.
Pot Furnaces	0.1	6		
	0.34	3		
	1.36	4		
	0.34	4		
	0.68	4		
	0.23	4		
	0.25-11	5		
Average	0.77[a]			
Reverberatory Furnaces	106.00	1	26	1
	149-154	6	149	6
Rotary Furnace	6.60-132	5		
Blast (cupola)	181	1	116	1
	80[c]	2	95.5	2
	300	6	58-64	6
Average	187		91	

---

a) High value of 11 was not included in average.
b) As SO_2.
c) Assuming baghouse control 99% efficient for particulate emissions.

Emission Data from the Literature

(pounds/ton processed)

Furnace Type	AFTER CONTROL Particulate	Ref	SO_x	Ref
Pot Furnaces	Neg.			
Reverberatory Furnaces	1.4	6		
	0.96	1		
	2.33	3		
Average	1.56			
Blast (cupola) Furnaces	3.04	1		
	0.80	2	0.79	2[b]
	5.1[c]		46.20	2[a]
Average	2.33			

---

a) Spray tower and cyclone control.

b) NaOH scrubbing venturi scrubber.

c) With fabric filter.

No data was available on CO or NO_x emissions for secondary lead smelting.

REFERENCES 6.3

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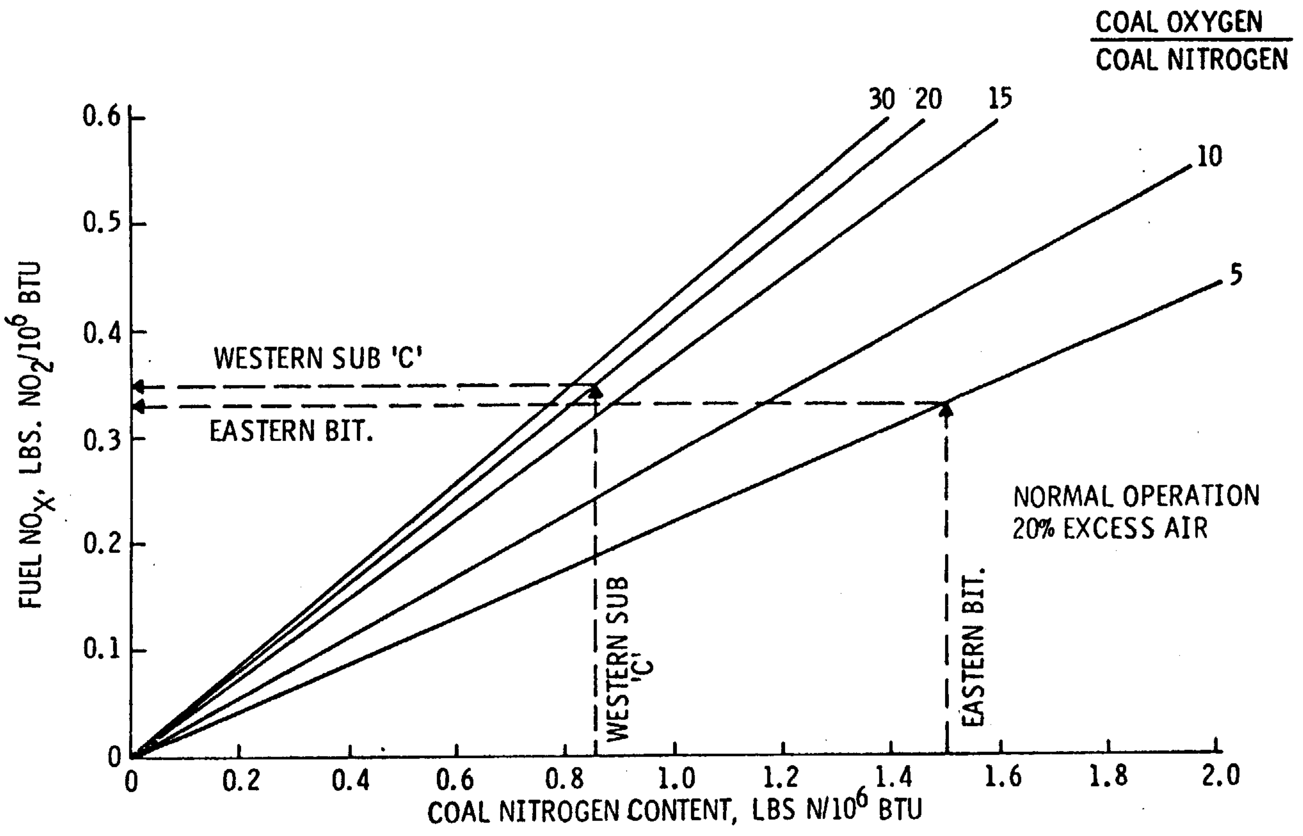

Figure 4.3-11 Fuel NO$_x$ formation as a function of the coal oxygen to nitrogen ratio and the coal nitrogen content.

lancing. Carbon monoxide emissions may occur in magnesium reduction furnaces where magnesium oxide is reduced to magnesium metal by coke (carbon).

Table 6.4-1 Magnesium Smelting Emissions

	Emissions, pounds per ton processed	
Furnace Type	Particulate	Range
Pot	0.4	0.38-0.46

Reliability of Emission Factors

Emission data from magnesium smelting are extremely limited, and the factor must be considered questionable.

Table 6.4-2 Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Evaluation 0-10	Total
5	3	5	13

Due to the very limited data available, additional work on determining both particulate and gaseous emissions is warranted.

APPENDIX 6.4

Emission Data from the Literature

(pounds/ton processed)

	Particulate	Ref.
POT Furnace	0.38	1 With Control
	0.46	1 With Control
	4.4	3

No data were available on CO and NO_x emissions from secondary magnesium smelting operations.

REFERENCES 6.4

1. Allen, G. L., F. H. Viets, and L. C. McCabe. Control of Metallurgical and Mineral Duct and Fumes in Los Angeles County, U. S. Bureau of Mines, Washington, D. C. Information Circular 7627. April 1952.
2. The Non-Ferrous Scrap Metal Industry, by the National Association of Secondary Material Industries, Inc. 1967.
3. Hammond - See Reference 6 previous chapter.

6.5 SECONDARY ZINC PROCESSING

Process Description

Zinc processing includes zinc reclaiming carried out by zinc melting or zinc vaporization, zinc oxide manufacturing typically by zinc vaporization furnaces, and zinc galvanizing done by dipping the material to be galvanized in a molten zinc bath. Separations of zinc from scrap containing lead, copper, aluminum, and iron are made by careful control of temperature in the furnace allowing each metal to be removed at its melting range. The furnaces typically employed are the pot, muffle, reverberatory or electric induction. These furnaces are oil-, gas- or electrically-fired and must allow for careful temperature control. Further refining of the zinc can be done in retort distilling or vaporization furnaces where the vaporized zinc is condensed to the pure metallic form. Zinc oxide is produced by distilling metallic zinc into a dry air stream and capture of the subsequently formed oxide in a baghouse. Fluxing is used to clean molten zinc and prevent oxidation when zinc metal is desired as a final product. Most fluxes do not fume appreciably if careful temperature control is applied to the furnace. Zinc fuming can occur if the furnace temperature is allowed to exceed 1100°F. Zinc galvanizing is carried out in vat or bath type dip tanks utilizing a flux cover. Iron and steel pieces to be coated are cleaned and dipped into the vat through the covering flux. Temperatures in the vat are held between 840°F - 860°F.[3]

Factors Affecting Emissions

Factors affecting emissions from zinc melting include the type of flux used, temperature in the furnace, amount of organic material in the charge and the degree to which control of the generated fume and particulate is practiced. Factors affecting zinc vaporization furnaces include the use of carbon as a reducing agent causing the emission of CO, the amount of organic material in the charge, the temperature of the furnace residue upon removal, and the degree to which control is applied to the charging, distilling, removal of residue and screening of the residue from the zinc vaporization operations. Factors affecting emissions from zinc galvanizing include the temperature of the bath, the type of flux and method of flux charging on the bath, the amount of disruption of the flux upon charging of parts to be galvanized, the amount of dusting of finished pieces with ammonium chloride, and the amount of control applied to generated emissions from the bath.

Emissions

A potential for emission of particulates, mainly zinc oxide, occurs if the temperature of the furnace exceeds 1100°F. Zinc oxide (ZnO) may escape from condensers or distilling furnaces, and due to its extremely small particle size (0.5 to 0.03 microns), may pass through even the most efficient collection systems. Some loss of zinc oxides occurs during the galvanizing processes but these losses are small due to the flux cover on the bath and the relatively low temperature maintained in the bath. Some emissions of particulate ammonium chloride occur when galvanized parts are dusted after coating to improve their finish. Average particle size of emissions from galvanizing vats is approximately 2 microns.

Another source of potential emission of particulates and gaseous zinc is in the tapping of zinc vaporizing muffle furnaces to remove accumulated slag residue. This slag is hot enough to generate some zinc fume, and when screened to separate drosses from solid metal, considerable dust is generated. Emissions of carbon monoxide occur when reduction of zinc oxide by carbon is done. The potential for emission depends on the amount of charge.

Nitrogen oxide emissions are also possible due to the high temperatures associated with the smelting and the resulting fixation of atmospheric nitrogen. Typical pollution control systems include cyclones, gas cooling units followed by bag-type filters or electrostatic precipitators where oil mist is a problem.[3]

Table 6.5-1 lists the emissions from zinc processing. It relies on information obtained some years ago because very little new emission data are available at this time.

Table 6.5-1. Emissions from Zinc Smelting

	Emissions - lbs/ton of product	
Furnace Type	Particulate	Range
Retort Reduction Furnace	47	20-71.6
Horizontal Muffle Furnace	45	30-60
Galvanizing Kettles	5	
Calcining Kiln	89	
Pot Furnace	0.1	
Sweat Furnace	11	

Reliability of Emission Factors

Very little data were available on emissions from secondary zinc smelting operations. Table 6.5-2 presents the factor ranking.

Table 6.5-2. Emission Factor Ranking

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	5	4	5	14

Futher work on determining particulate and gaseous emission is warranted.

APPENDIX 6.5

Emission Data from the Literature

(pounds/ton processed)

Furnace Type	Particulate	Reference Number
Retort Reduction Furnace	20-50 71.6	1 4
Horizontal Muffle Furnace	30-60	4

REFERENCES 6.5

1. McCabe, L. C., et al. Control of Metallurgical and Mineral Dusts and Fumes in Los Angeles County, California. U. S. Bureau of Mines. Washington, D. C. Information Circular 7627. April 1952
2. The Nonferrous Scrap Metal Industry. National Association of Secondary Materials Industries, Inc. 1967.
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MINERAL PRODUCTS INDUSTRY

7. MINERAL PRODUCTS INDUSTRY

Mineral processing is characterized by particulate emissions in the form of dust. Frequently, as in the case of crushing and screening, this dust is identical to the material being handled. Emissions also occur through handling and storage of the finished product since this material is often a dry fine material. Particulate emissions from some of the processes such as quarrying, yard storage, and road dust are difficult to control. However, most of the emissions from the manufacturing processes discussed in this Section, with the exception of fiber glass, can be reduced by conventional particulate control equipment such as cyclones, scrubbers, and fabric filters. Because of the wide variety in processing equipment and final product, emissions cover a wide range.

Gaseous emissions may occur when the minerals are subjected to high temperatures such as in calcining or sintering operations. Fluorides are among the more common gaseous emissions. Gaseous emissions from fuel combustion also occur when heat is generated on site.

Particle size data is summarized for those processes in this section for which such information was available.

7.1 CERAMIC CLAY MANUFACTURING

Process Description

The manufacture of ceramic clay involves the conditioning of the basic ores by several methods. These include the separation and concentration of the minerals by screening, floating, wet and dry grinding and blending of the desired ore varieties. The basic raw materials in ceramic clay manufacture are kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)and montmorillonite ($(Mg, Ca)\ O \cdot Al_2O_3 \cdot 5SiO_2 \cdot \underline{n}H_2O$) clays. These clays are refined by separation and bleaching, blended and after kiln drying are formed into such items as whiteware, heavy clay products (brick, etc.) and various stoneware and other products such as diatomaceous earth used as a filter aid.

New processes such as halide bleaching for preparation of kaolinite present an additional potential for air pollution. This process utilizes the reactivity of the halide to remove the chemically active and unwanted constituents of the clay ore leaving behind a purified white product suitable for ceramics manufacture. See Figure 7.1-1 for a schematic diagram of this process.

The manufacture of filter and activated clays includes grinding and wet or acid treating followed by drying and regrinding. The drying is accomplished in rotary kilns, which reduce moisture content from 15-20% to 10%, and the discharge gases contain high particulate concentrations (4-6 gr/ft^3) as well as some acid gases and fluorine when this is present in the ores.[1]

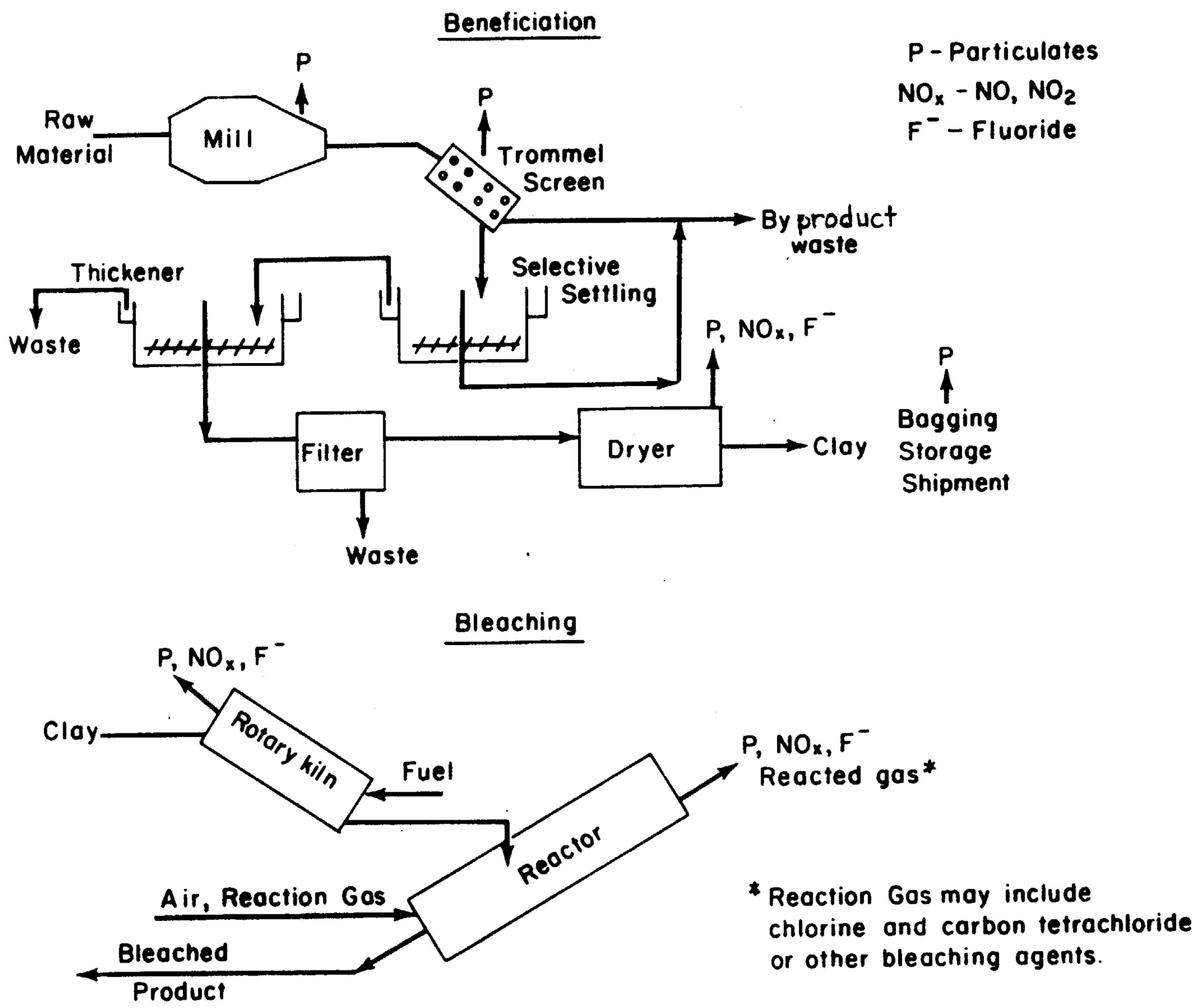

Figure 7.1-1. Ceramic Clay Manufacturing Processes

Ceramic clay is manufactured from a mixture of wet talc, whiting, silica clay, and other ceramic materials. This mixture is dried in an instant spray dryer.

Factors Affecting Emissions

Factors affecting emissions include the amount of material processed, the type of grinding (wet or dry), the temperature of the drying kilns, the gas types velocities and flow direction in the kilns, the amount of fluorine in the ores, and the type and extent of pollution control equipment applied to the processes.

Common control techniques include settling chambers, cyclones, wet scrubbers, electrostatic precipitators and bag filters. Cyclones for the coarser material followed by wet scrubbers, bag filters or electrostatic precipitators for dry dust are the most effective control techniques.

There is no correlation between the various drying processes and reported emissions. See Appendix 7.1, Table 7.1-3.

Emissions

Emissions consist primarily of particles but some fluorides and acid gases are also emitted in the drying process. The high temperatures of the firing kilns are also conducive to the fixation of atmospheric nitrogen and the subsequent release of NO . Acid and halide gases from the bleaching of ceramic clays and the activating of bentonite clays are also emitted depending on both the amount of acid and excess gas used in the process and the exit gas velocities. No published information has been found regarding gaseous emissions from ceramic clay manufacture.

Particulate emissions also occur from the grinding process and storage of the ground product. There is no emission data in the literature. The emission factors for these operations are based on limited unpublished test data.[2] See Appendix 7.1 for this data. These readings were taken after the dust collector on the grinding mill exhaust. Whether a collector was used in the storage area ventilation exhaust is not known. However, the test results indicate that the readings were taken after a collector since less than 2.5% of the emissions are greater than 44 μ. The percentage of coarse particles (> 44μ) downstream of the dust collector was found to be as follows:[2]

Drying operation - 13.0%
Grinding operation - 0.6%
Storage bins - 2.3%

Table 7.1-1 lists the factor ranges for particulate emissions from ceramic clay manufacturing processes.

Table 7.1-1. Emission Factors for Ceramic Clay Manufacture

	Particulate Emissions, lb/ton of input to process		
Process	No Controls	Cyclone[a]	Multiple-unit cyclones & scrubber[b]
Drying	70(14 to 110)	18(4 to 27)	7 (2 to 11)
Grinding	76(64 to 88)	19(16 to 22)	-
Storage	34(16 to 52)	8(4 to 13)	-

a) Approximate collection efficiency 75%; b) Approximate collection efficiency 90%.

Reliability of Emission Factors

No test data was found to exist for uncontrolled emissions and the controlled emission data is sparse. Broad ranges are found to exist even within the same installation. Due to the scarcity of particulate emission data and the absence of gaseous emission data, further testing is warranted. Emission factor rankings are presented in Table 7.1-2.

Table 7.1-2. Emission Factor Ranking for Ceramic Clay Manufacture

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Drying	12	8	8	28
Grinding	10	8	8	26
Storage	4	8	5	17

The factors presented herein for uncontrolled emissions are based on the major assumption that the collection devices on which the source tests were made had the following efficiencies:

Cyclone	75%
Cyclone and sprays	80%
Multiple-unit cyclone and scrubber	90%

APPENDIX 7.1

A. Emissions from Drying Process

The results of nine tests of dryer exhaust gases are shown in Table 7.1-3. In all cases the readings were taken downstream of the particulate collection device. Using the test data, Table 7.1-4 presents uncontrolled emission rates based on estimated collection device efficiencies and estimated grain loading of 6 grains/ft.^{3} upstream of the control device.

Table 7.1-3. Clay Dryer Particulate Emissions Test Data

Test No.	Process Equipment	Collection Device	Gas Temp.,°F	Gas Volume, scfm	Process Wt. lb/hr	Particulate lb/hr	Reference Number
1	Dryer	Cyclone & sprays	66	23800	15000	20.7	1
2	Rotary dryer	Multiple-unit	109	17600	29300	56.1	1
3	Kiln & cooler	cyclone & wet scrubber	159	23900	31000	127.0	1
4	"	"	160	27300	31000	92.4	1
5	Instant spray dryer	Cyclones	244	10500	3300	24.8	1
6	Rotary dryer	Cyclones	-	-	10000	28.8	2
7	"	"	-	-	10000	128	2
8	"	"	-	-	10000	135	2
9	"	"	-	-	10000	85.1	2

Table 7.1-4. Estimated Uncontrolled Particulate Emissions from the Clay Drying Process

Test No.	Estimated eff. of collector, %	Controlled Emissions lb/ton of input	Uncontrolled Emissions, lb/ton of input	
			Based on Collector Efficiency	Based on 4-6 gr/ft.^{3} loading
1	80	2.8	14	107 to 160
2	90	3.9	39	43 to 66
3	90	8.2	82	63 to 94
4	90	6.0	60	71 to 106
5	75	15.0	60	290 to 430
6	75	5.8	23	-
7	75	25.6	102	-
8	75	27.0	108	-
9	75	17.0	68	-
Average			61.8	74
Range		3 to 27	14 to 110	43 - 110[a]

a) Not including Tests No. 1 and 5

[illegible] 2
[illegible] 32

Particulate loss on drying has been estimated to be 13.8 lb/ton[3] and 14.4 lb/ton[4]. These figures tend to agree with estimated emissions for Tests No. 1 and 6 above. Note, however, that the emissions based on estimated grain loadings do not correlate well for Tests No. 1 and 5.

Based on the above data, an uncontrolled factor of 70 lbs/ton was chosen.

B. Emissions from Grinding Process

Table 7.1-5 presents test data taken from a clay grinding mill.[2] Three separate tests were run on the same facility. The test port was located downstream of the cyclone collector.

Table 7.1-5. Particulate Emissions from a Clay Grinding Mill[2]

Feed Rate, tons/hr	Controlled Emissions[a] lb/hr	Controlled Emissions[a] lb/ton
5	111.3	22.2
5	81.8	16.3
5	81.5	16.3
Range		16-22

a) Measured after cyclone collector.

Assuming a collection efficiency of 75%, the uncontrolled emissions would range from 64 to 88 lb/ton with an average of 76.

C. Emissions from Storage Bin

Table 7.1-6 presents test data taken from a storage bin area of the ceramic clay manufacturing installation tested above. The operating production rate was 5 tons/hr. A collector having a 75% efficiency was assumed to be in use with the test readings taken downstream of such collector.

Table 7.1-6. Particulate Emissions from Ground Clay Storage Bin Area[2]

Feed Rate, tons/hr	Controlled[a] Emissions lb/hr	Controlled[a] Emissions lb/ton
5	65.1	13.0
5	20.4	4.1
5	27.2	5.4
Range		4 to 13

a) Assumed.

Based on a collector efficiency of 75%, the uncontrolled emissions would range from 16 to 52 lb/ton with an average of 34.

REFERENCES 7.1

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7.2 BRICKS AND RELATED CLAY PRODUCTS MANUFACTURING

Process Description[1,2,3]

The manufacture of brick and related products such as clay pipe, pottery and some types of refractory brick involves the grinding, screening, blending of the raw materials; forming, drying or curing, firing, and final cutting or shaping. Particulate emissions occur during handling of raw materials, grinding, screening and blending, and during cutting and shaping operations. Gaseous emissions occur from the curing and firing operations.

Refractory brick may be formed by pressing at high pressure, after the raw material is blended and mixed with various binders. The formed brick is then fired at temperatures in excess of 3000°F in long tunnel ovens. Most of the refractory brick manufactured in the United States is either silica (acid) or fire-clay (neutral). Silica brick contains 95-96% silicon dioxide and about 2% lime, and is formed by high pressure pressing. Fire clays are made from clay and vary in composition from those with high silica content to those with high alumina content. The relatively small amount of basic refractories manufactured include magnesia, chromite, and mixtures of magnesia and silicon dioxide.

The drying and firing of pressed bricks, both common and refractory, is accomplished in many types of ovens. The most popular type is the long tunnel oven in which the bricks, loaded on steel carts, pass counter-currently against the heat flow. Total heating time varies, but is usually 50-100 hours for 9 inch refractory bricks. Normally gas or oil fuel is used for heating, but coal may be used. Temperatures up to about 2000°F are used in firing common brick.

Common brick or building brick is prepared by molding a wet mix (20-25% water, 75-80% clay) followed by baking in chamber kilns at 1600-1800°F. Common brick is also prepared by extrusion of a stiff mix (10-12% water), followed by pressing and baking of the sections cut from the extrusion. These operations using large quantities of water are not major sources of dust.

Factors Affecting Emissions

The extent of raw material handling and processing, and the degree of control on these operations greatly affect the dust emissions from this part of the manufacturing process. Emissions when firing and/or curing the formed bricks are affected by the temperature in the ovens and the type and quantity of trace components in the brick. Thus, sulfur and/or fluoride compounds may be emitted when the bricks are subjected to high temperatures. The type of fuel used to heat the ovens also has a direct bearing on the combustion emissions.

Emissions

Particulate emissions, similar to those obtained in clay processing (Section 7.1) are emitted from the materials handling process in refractory and brick manufacturing.

Combustion products from the fuel consumed in the curing, drying, and firing portion of this process are also emitted. Approximately 3-4 x 10^6 Btu of heat are required per ton of brick produced.[3] Nitrogen oxide emissions were therefore estimated based on emission factors available for fuel combustion in boilers (See Appendix 7.2).

Fluorides, largely in a gaseous form, are also emitted from brick manufacturing operations.[4] Sulfur dioxide may also be emitted from the bricks when firing temperatures of 2500°F or more occur, or when the fuel contains sulfur.

A variety of control systems may be used to reduce both particulate and gaseous emissions. Almost any type of particulate control system will reduce emissions from the material handling process. However, good design and hooding are required to keep emissions to a minimum. Fluoride emissions can be reduced to very low levels by using a water scrubber.

Table 7.2-1 presents the emission factors for brick manufacturing.

Table 7.3-1. Uncontrolled Emissions From Brick Manufacturing, lbs per ton of product

Process		Particulate	Fluoride[a]	NO_x[b]
Raw Material			-	-
Handling[c] -	Drying	70 (14 to 110)		
	Grinding	76 (64 to 88)		
	Storage	34 (16 to 52)		
Curing and Firing				
	Gas Fired	Neg.	0.8	0.6
	Oil Fired	Neg.	0.8	1.3
	Coal Fired	5A to 10A[d]	0.8	1.5

a) Expressed as HF and based on a raw material content of 0.05 weight percent fluoride.

b) Expressed as NO_2.

c) Based on Reference 8.

d) A is the percent ash in the coal and gives the emission on a lbs per ton of fuel used basis. This is an estimate based on coal-fired furnaces.

Reliability of Emission Factor

Limited data are available on gaseous emissions from brick and related clay product manufacturing processes. The raw material handling processes used at any particular installation could vary widely. Emission factors for these processes are, however, considered reliable (Section 7.1). Emissions from curing and firing of clay products are based on very limited data and are considered questionable as shown in Table 7.2-2.

Table 7.2-2. Emission Factor Ranking for Bricks

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
2	5	5	12

Nitrogen oxide emissions were based on the fuel consumption used in firing bricks and on emission factors used for boilers.

APPENDIX 7.2

Nitrogen oxide emissions may be estimated based on a heat consumption of 10 - 12 x 10^6 Btu per 1000 bricks,[3] and on existing emission factors for fuel combustion. Combustion chamber temperatures in brick ovens and boilers are similar, but excess air rates are usually lower in the ovens. Therefore, use 0.75 of existing NO_x emission factor for industrial boilers. One thousand bricks weigh about 3 tons,[a] therefore, 3 - 4 x 10^6 Btu are required to treat 1 ton of brick.

NO_x emission factors for Industrial Boilers[5,6]

Gas-Fired	214 lbs/10^6 ft^3	=	0.214 lbs/10^6 Btu
Oil-Fired	72 lbs/1000 gal	=	0.5 lbs/10^6 Btu
Coal-Fired	15 lbs/ton	=	0.58 lbs/10^6 Btu

Emissions from brick firing ovens may be estimated as follows:

Gas-Fired	0.214 lbs/10^6 Btu x 3.5 x 10^6 Btu/ton x .75 = 0.56 lbs/ton
Oil-Fired	0.5 lbs/10^6 Btu x 3.5 x 10^6 Btu/ton x .75 = 1.3 lbs/ton
Coal-Fired	0.58 lbs/10^6 Btu x 3.5 x 10^6 Btu/ton x .75 = 1.5 lbs/ton

HF emissions from brick baking[7]: based on 500 ppm F^- by weight in the clay and 80% evolved at a temperature of 1800°F of higher, the emission would be:

$$1 \text{ ton clay} \times 2000 \text{ lbs/ton} \times \frac{500}{10^6} \times .80 = 0.8 \text{ lbs } F^-/\text{ton of brick.}$$

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a) Bricks weigh about 110 lbs/ft^3 and each brick occupies 0.058 ft^3, one brick thus weighs about 6.45 lbs (Reference 4).

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7. Semrau, K.T. Emission of Fluorides from Industrial Processes. A Review. J. Air Pollution Control Association. 7(2):105, August 1957.
8. Supra, 7.1.

7.3 CASTABLE REFRACTORIES MANUFACTURING

Process Description[1,2]

Castable or fused-cast refractories are manufactured by carefully blending such components as alumina, zirconia, silica, chrome, and magnesia, melting the mixture in an electric arc furnace at temperatures of 3200-4500°F, pouring into molds, and slowly cooling to the solid state.

Fused refractories are less porous, and more dense than kiln-fired refractories.

Particulate emissions occur from the drying, crushing, handling, and blending phases of this process; the actual melting process; and in the molding phase. Fluoride emissions largely in the gaseous form may also occur during the melting operations.

The general types of particulate controls may be used on the materials handling aspects of refractory manufacturing. However, emissions from the electric arc furnace are largely condensed fume and consist of very fine particles, largely 2 microns or smaller.[3] Fluoride emissions can be effectively controlled with a scrubber.

Factors Affecting Emissions

Particulate emissions are affected by the amount of material handling and pre-treatment required before melting, and by the components in the melt. Generally, increasing concentrations of silicon will cause increased particulate emissions. The effectiveness of hooding and control equipment will, of course, have a direct bearing on emissions.

Fluoride emissions are a direct function of the feed's fluoride content. Dry type particulate collectors will have little effect on fluorides.

Emissions

Emission factors based on the data presented in Appendix 7.3 are shown in Table 7.3-1 for the various processes involved in cast refractories manufacturing.

Table 7.3-1. Particulate Emissions from Castable Refractories Manufacturing

Process	Emissions, lbs/ton of feed material		
	Uncontrolled	Controlled	Type of Control
Raw Material Dryer	30	0.3	Baghouse
Raw Material Crushing and Processing	120 (100-190)	7 45	Scrubber Cyclone
Electric Arc Melting	50 (10-88)	0.8 10	Baghouse Scrubber
Curing Oven	Neg.		
Molding and Shakeout	25	0.3	Baghouse

Fluoride emissions from the melting operation averaged 1.3 pounds of HF per ton of melt with a range of 0.7 to 1.9 pounds per ton.

Reliability of Emission Factors

Emission factors for cast refractories are based on limited data and cover a wide range. Variations in processes and at the various plants, and in the composition of the product account for some of this variation. Table 7.3-2 presents the factor rankings and shows the factors to be questionable.

Table 7.3-2. Emission Factor Ranking for Cast Refractories

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	7	4	3	14
Fluoride	5	3	3	11

Additional work appears warranted in this area because of the large amount and small particle size of particulate emissions, and the possibility of fluoride emissions.

APPENDIX 7.3

Table 7.3-3. Particulate Emission Data for Castable Refractories

Process	Emission, lbs/ton of feed Uncontrolled	Type of Control	Controlled	Reference
Raw Material Dryer	30	Baghouse	0.3	4
Raw Material Crushing, Screening, Blending	102	Rotoclone	6	4
	189	Cyclone	76	5
Electric Arc Furnace Melting	88	Baghouse	0.9	4
	10-70			5
	11[a]	Scrubber	9[a]	3
	55[a]	Baghouse	0.5[a]	3
	Avg. 47			
Molding and Shakeout	25	Baghouse	0.25	4
Curing Oven (if used)	0.2	-	-	5

a) Emissions were measured, but process weight was estimated based on furnace size.

Fluoride Emission Data[3]

From electric arc melting process, pounds of HF/ton

Uncontrolled	Type of Control	Controlled
0.7	Scrubber	0.005
1.9	Baghouse	1.7
Avg. 1.3		

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7.4 STONE QUARRYING AND PROCESSING

Process Description

Rock and gravel products are loosened by drilling and blasting from their deposit beds and removed with the use of heavy earth moving equipment. This mining of rock is done primarily in open pits. The use of pneumatic drilling and cutting as well as the blasting and transferring cause considerable dust formation. Further processing includes crushing, screening, regrinding, and removal of fines.[1] Dust emissions can occur from all of these operations as well as from quarrying, transferring, loading, and storage operations. Drying operations, when used,can also be a source of dust emissions.

An additional major source of air pollution at these plants is the traffic of heavy equipment over unpaved dusty surfaces. The control of this dust is very difficult and is usually handled by wetting of traveled areas with oil or water. Paving has had limited success in dust control in that dust accumulates on the paving and is thus recirculated to the atmosphere by the traffic over the pavement. Common controls of these operations include cyclones and fabric filters or scrubbers on processing machinery, and dust suppression through cleaning and wetting traveled surfaces. Cyclones can achieve an efficiency of about 80% while fabric filter systems can collect 99% of the dust vented from the process equipment. Approximately 10-15% of dust generally escapes the hooding and ventilation systems.[2]

Factors Affecting Emissions

Factors affecting emissions include the amount of rock processed, the method of transfer of the rock, the moisture content of the raw material, the degree of enclosure of the transferring, processing or storage areas, and the degree to which control equipment is used on the processes. The amount of vehicular traffic and the method and degree of control of dust generated by traffic in the plant also affect emissions.

Emissions

Limited particulate emission data are presented in Table 7.4-1. These data are based on the amount of particulate collected in a baghouse control system. While individual process emissions are only crude estimates, the overall plant emission is representative of these variable emissions. Particle size data are presented in Figure 7.4-1.

The data presented in Table 7.4-1 based on reference 2 is based on the dust collected at processes controlled by fabric filter systems. The quantity of dust collected was then correlated with the process throughput. These factors have an estimated range of about ±25%.

Table 7.4-1. Uncontrolled Emissions From Rock Handling Processes[2]

Process	Estimated Atmospheric Emission, lbs/ton[a] From Process	% Settled Out in Plant	Suspended Emission
Primary Crushing	0.5	80	0.1
Secondary Crushing & Screening	1.5	60	0.6
Tertiary Crushing & Screening (if used)	6.0	40	3.6
Recrushing & Screening	5	50	2.5
Fines Mill	6	25	4.5
TOTAL	19.0		11.3

a) All values are based on raw materials entering primary crusher except for recrushing and screening which is based on throughput for that operation. Typical collection efficiencies: Cyclone 70-85%; Fabric Filter 99%.

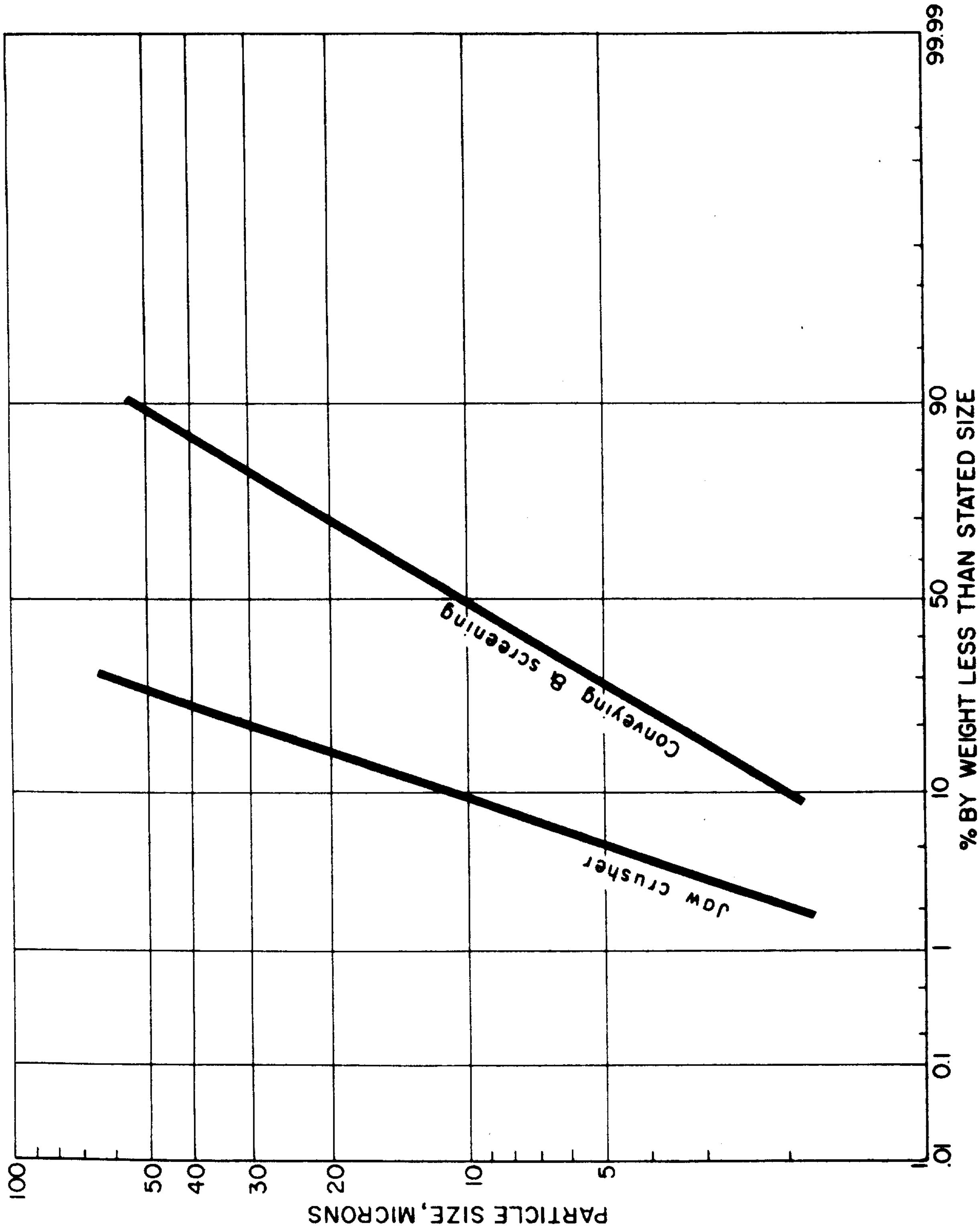

Figure 7.4-1. Particulate size from rock processing operations[3]

Storage pile losses due to wind erosion have been estimated at about 1% of product.[4] While this figure is probably representative of sand and other finer material, it is thought to be too high for rock and gravel storage.[1] A value of about 0.5% of the finished product is probably closer to the wind losses from rock and gravel storage piles.

Particulate emissions from dryer operations also occur. Normally dryers are not used, but for some minerals such as dolomite they are required. These units are usually direct fired, either parallel or counter flow, rotary dryers. Particulate emissions from a dolomite dryer have been reported in the 2 - 50 lb/ton of product range after a cyclone type collector.[5]

General screening, conveying, and handling losses have been estimated to be 1.7 pounds per ton.[6]

Ambient air data around rock processing plants have been reported and are summarized in Table 7.4-2.

Table 7.4-2. Ambient Air Particulate Concentrations Around a Rock Quarrying and Processing Plant[1] - Production Rate of 600 - 700 tons/hr

Distance From Center of Plant, Feet	Average Dustfall Tons/Mile^2/Month	Average Daily Suspended Particulate μgm/M^3
0	225	
1,000	78	
2,500	15	50 - 130*
4,000	13	
5,000	8	

* During plant shut-down, a value of 35 μgm/M^3 was obtained and during periods of inversions, values as high as 954 were obtained.

Reliability of Emission Factors

Actual source test data is limited and would vary widely depending on plant design and operation. Ambient air conditions around this type of operation have been monitored, and information is available. Further work in this area must include source testing and engineering analysis. The factors given here must be considered questionable. Factor ranking is presented in Table 7.4-3.

Table 7.4-3. Emission Factor Ranking for Stone Processing

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	7	5	17

Appendix was not included in this Section, since large quantities of emission data were not found, and no calculations were involved.

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7.5 GYPSUM MANUFACTURING

General Information

Gypsum or hydrated calcium sulfate is a naturally occurring mineral which is found in large deposits throughout the world. With its fire resistance, structural strength, adaptability to design, ease of handling and ready availability, gypsum has been an important building material for nearly four thousand years. When heated, gypsum loses its water of hydration and becomes what is commonly known as plaster of paris, which is used for casts and stucco work. When blended with fillers such as lignin or starch, the calcined gypsum serves as wall plaster. In both cases the material hardens as water reacts with it to form the solid crystalline hydrate.[1,2]

Gypsum is very widely distributed in the United States. The largest producing states are Michigan, New York, Iowa, and California, but there are also extensive deposits in Kansas, Ohio, Wyoming, New Mexico, Virginia, Texas, Nevada, and Montana.[3] In 1967, there were 76 active gypsum calcining plants in the United States, and nearly 8 million short tons of calcined gypsum were produced with a value of over 115 million dollars.[4]

Process Description[1,5]

Calcination of gypsum to first-settle plaster (plaster of paris) occurs according to the following reactions:

$$2\left(CaSO_4 \cdot 2\ H_2O\right) \rightarrow (CaSO_4)_2 \cdot H_2C + 3\ H_2O \qquad \Delta H_{25} = +33.0\ \text{Kcal}$$

The usual method of calcination of gypsum consists of grinding the mineral to about 90% minus 100 mesh and placing it in large externally heated calciners holding 10 to 25 tons. The calciners are usually large kettles, but rotary kilns are sometimes used. In the kettle process, the pulverized gypsum is placed in a vertical cylindrical kettle which is 8 to 10 feet in diameter and depth. The center of the bottom is about one foot higher than the sides. The temperature is raised to 120 to 150°C (250 - 300°F) and the material is stirred with a heavy blade closely conforming to the bottom of the kettle. External heat is applied directly to the kettle bottom, and hot gases rise around the sides and also pass through flues higher up in the kettle. Complete calcination takes about 3 hours. The material in the kettle, known as plaster of paris or first-settle plaster, may be heated further to 190°C (375°F) to produce a material known as second-settle plaster. First settle plaster is approximately the half-hydrate, $CaSO_4 \cdot {}^1/_2\ H_2O$, while second-settle plaster is anhydrous.

The more modern rotary kiln method involves heating crushed gypsum rock in rotary kilns and dropping the hot material into concrete bins lined with firebrick, where calcination reaches the hemihydrate stage, $CaSO_4 \cdot {}^1/_2\ H_2O$.

The finished product may be passed through mechanical air separators (cyclone) to segregate the material before packaging.

Approximately 1.0 million Btu are required to calcine 1 ton of plaster.[5,9]

Factors Affecting Emissions

The major factor affecting particulate emissions from the actual calcining process is the calcination rate which in turn determines the emission rate of the escaping gases. Particle size of the gypsum and degree of agitation are other factors affecting particulate emissions during calcination. In general, emissions from a direct-fired rotary kiln are greater due to the added agitation in the kiln caused by the fuel's combustion products.

Dust emissions resulting from the grinding of the gypsum before or after calcining and from the mixing of the calcined gypsum with filler are also affected by particle size and degree of agitation.

Emissions

Calcining gypsum appears at first glance to be devoid of any air pollutants, since the process involved is simply the relatively low temperature removal of the water of hydration. However, the resultant gases created by the release of the water of crystallization carry gypsum rock dust and partially calcined gypsum dust into the atmosphere in a steamy, dusty condition.[6] For each ton of gypsum calcined, there are 314 pounds of water vapor liberated (6600 ft^3). In addition, dust emissions from the grinding of the gypsum before calcining, and from the mixing of the calcined gypsum with filler also occur.

Ninety-five percent of gypsum dust particles emitted from the calcining process are smaller than ten microns in diameter and grain loadings from handling and conveying range from 1.5 - 5.0 grains per cubic foot of exhaust.[7]

Table 7.5-1 presents limited emission data based on actual plant estimates and measurements. This table incorporates all the data found, and no appendix is included in this chapter.

Table 7.5-1. Particulate Emissions From Gypsum Processing, lbs/ton throughput[8]

	Emission
1. Raw Material Dryer (if used)	
a. Uncontrolled	40 (4 to 80)
b. Fabric Filter	Negligible to 0.3
c. Cyclone and Electrostatic Precipitator	0.4
2. Primary Grinder (if used)	
a. Uncontrolled	1
b. Fabric Filter	0.001
3. Calciner	
a. Uncontrolled	90 (87 to 93)
b. Fabric Filter	0.13
4. Conveying	
a. Uncontrolled	0.7
b. Fabric Filter	0.001

Total uncontrolled emissions thus vary from about 93 to 175 lbs/ton with controlled emissions of about 0.15 lbs/ton. An average uncontrolled factor of about 130 lbs/ton of raw material input for a large integrated plant can be used for general estimating purposes with a range of ± 30%.

Reliability of Emission Factor

Due to limited emission data and the lack of process information required to perform engineering analysis, the emission factors for gypsum processing must be classified as questionable as ranked in Table 7.5-2.

Table 7.5-2. Gypsum Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	2	2	9

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7.6 CLAY AND FLY ASH SINTERING

General Information

The use of sintered fly ash in the manufacture of lightweight masonry products has been a potential solution to the difficult disposal problem facing large coal-burning operations. Fly ash cannot simply be dumped. Due to its extreme lightness it must be covered with soil and vegetation, or treated and disposed of in a subterranean site. Conventional fly ash disposal costs range from $0.60 to $2.00 per ton. However, sintered fly ash may be sold for more than $5.00 per ton.[1]

Clay, on the other hand, does not present a disposal problem, but its natural characteristics render it desirable for sintering purposes.

The predominant use of sintered clay is for concrete building products. Sintering drives off the volatile matter within the pellet thereby creating macroscopic voids and creating a strong bond between clay particles. This process reduces the weight of the clay material by approximately 20 to 30%, and the sintered product weighs 1200 lbs per cubic yard.[2]

Process Description

While the processes for sintering fly ash and clay are generally similar, some distinctions exist which justify a separate discussion of each process.

Fly ash sintering plants are generally located near the source - the fly ash being delivered to a storage silo at the plant by a closed pneumatic system. The storage silos generally have bag-type filters to control dust. The dry fly ash is moistened with a 1% water solution of lignin or other binding agent and agglomerated into pellets, balls, or other convenient shapes generally less than 1 inch in circumference. The material then goes to a traveling grate sintering machine, where direct contact with hot combustion gases at 2300°F sinters the individual particles of the pellet and completely burns off the residual carbon in the fly ash. After sintering, the product is crushed since the individual pellets normally fuse together into clusters. Finally, the material is screened, further crushed as required, graded and stored in yard piles. The typical aggregate grades are $^3/_4$ - $^1/_4$ inch, $^1/_4$ - $^1/_8$ inch, and less than $^1/_8$ inch. Figure 7.6-1 illustrates a typical fly ash sintering operation.

As was previously stated, clay sintering involves the driving off of entrained volatile matter.

It is desirable that the clay contain a sufficient amount of volatile matter in its natural state. Should the sintered clay not contain enough volatile matter, the resultant aggregate will be too heavy. Thus, in areas where the natural clay contains insufficient amounts of volatile matter, it is necessary to mix the clay with finely pulverized coke. Some sources require that up to 10% coke by weight be added.[2,3] To sinter clay, it is first mixed with pulverized coke, if necessary, and then pelletized. After pelletizing, the clay is sintered in a rotating kiln, or on a traveling grate by direct contact with hot combustion gases at 1950 - 2200°F. The sintered pellets are then crushed, screened, and stored, similar to fly ash pellets.

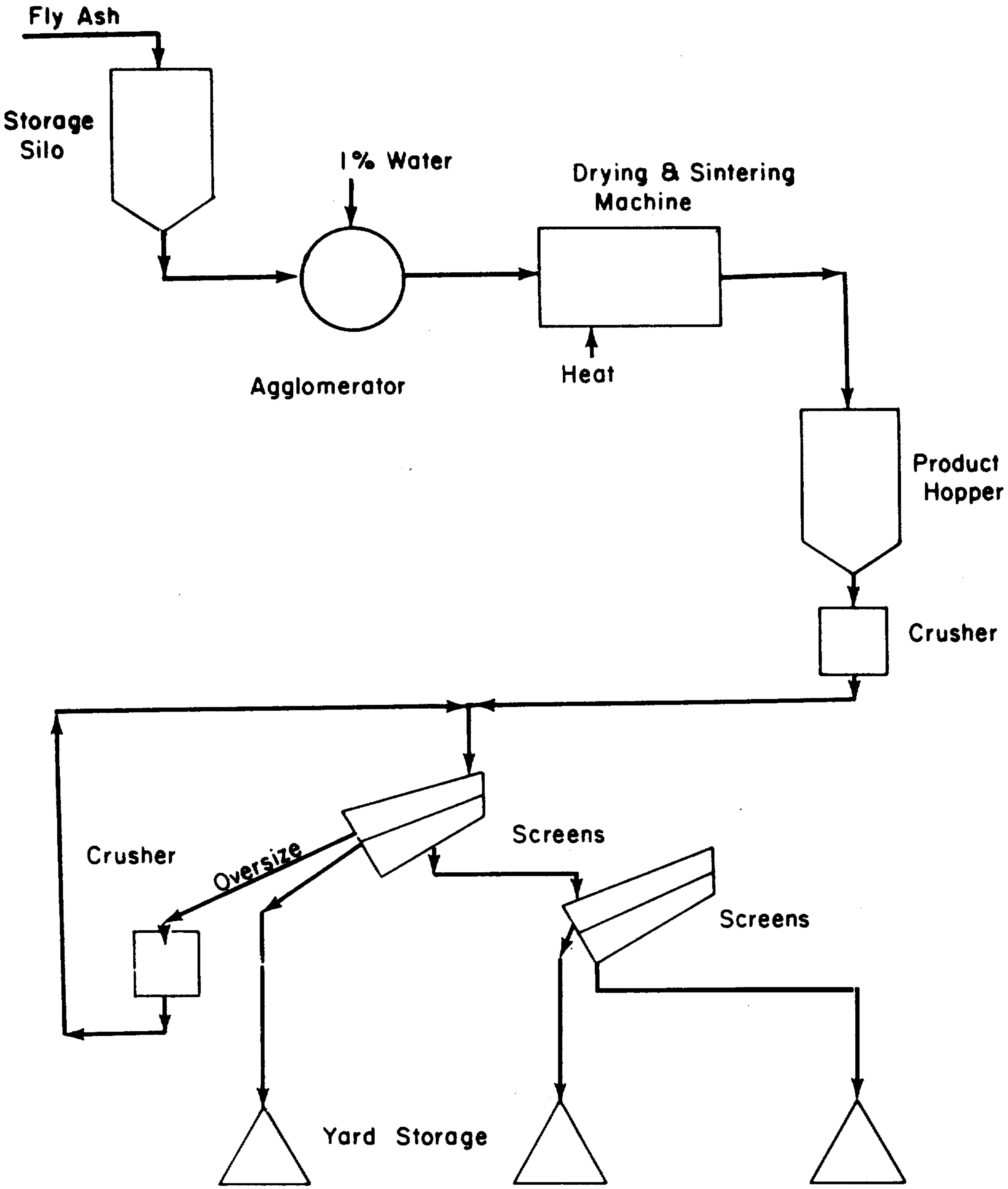

Figure 7.6-1. Fly Ash Sintering

Factors Affecting Emissions

For both fly ash and clay sintering, the major factor affecting particulate emissions, in addition to plant throughput, is plant design and maintenance. Each process will be discussed separately.

Fly ash will, if improperly handled, create an air pollution problem. Adequate design features including fly ash wetting systems, and particulate collection systems on all exit stack-conveyor belt transfer points and on crushing and screening operations will greatly reduce emissions.

Normally fabric bag filters are used to control emissions from the storage silo. The absence or malfunction of this dust collection system would create a major emission problem.

Upon discharge from the silo to the agglomerator, moisture is added and very little emission occurs between the storage silo and the sintering machine. However, emissions do vary with the type of conveying system used. If an open belt is used between these points, efficient water sprays must be utilized at the silo discharge.

Normally, there is little emission in the sintering machine. However, it is important that the traveling grate be properly maintained. If the grate is defective, dried pellets will drop through the grate. These pellets will then break and create dust particles which are carried along in the exit gas stream. The speed of grate travel is also important since drying too rapidly or raising the temperature too quickly will cause the pellets to crumble. Downdraft sintering machines inherently produce less emissions due to the basic design feature which directs the hot gas stream downward. Continuity of operation also affects emissions since the low temperatures experienced during start-up will result in a brittle pellet which crumbles and drops through the grate.

After sintering, the crushing, screening, handling, and storage of the sintered product creates dust problems. These emissions are usually controlled with scrubbers on the crushers and water sprays as required at the various handling points and in the yard.

In general, a dust problem arises at points of transfer where sufficient hoods and venting are not provided or where skirts are inadequately designed. While strategically placed water sprays will help keep the dust down, it is important that all dry fly ash handling be done by means of enclosed conveyors.

Scrubbing systems on the crushing and screening operations, proper conveyor belt design, and liberal use of water sprays can reduce these emissions an estimated 90%.

Emissions from the combustion process also occur. The fuel is usually light oil or gas and the gaseous emissions may be estimated from available factors.[4] No correlation between fuel use and finished product is available.

The addition of pulverized coke, when sintering clay, presents an emission problem. If the coke pulverizing system is improperly maintained, it can be a major source of particulate emission. Also, the sintering of coke impregnated dry pellets produces more particulate emissions than the natural clay. In a traveling grate sintering machine, the direction of the hot process gases also affects emissions. For example, if the gas flows downward through the grate, particulate emissions will be less than from an updraft unit which discharges after one pass.

The crushing, screening, handling, and storage of the sintered clay pellets creates dust problems similar to those encountered in fly ash sintering.

Emissions

Results of source testing of fly ash sintering operations have not been reported. However, a yield of 90% has been reported in the literature.[1] Another plant has estimated an 83% yield based on a fly ash carbon content of approximately 7%.[5] Assuming that about half of the difference may be airborne, the potential particulate emission may range from about 4 to 5% of input, or 5 to 6% of finished product (100 to 120 lb/ton). These losses include yard losses of the finished product due to wind.

Limited source test data and engineering analysis have been found for clay sintering processes. From this information, emission factors have been calculated. (See Appendix 7.6 for detailed calculations). In addition to the actual sintering operation, particulate losses occur from crushing, screening, and storing the sintered product.

Table 7.6-1 lists the emission factors for sintering of fly ash and clay.

Table 7.6-1. Emission Factors for Sintering Operations

Type of Sintering Operation	Particulate Emissions, lb/ton of finished product Sintering Operation[e]	 Crushing, Screening and Yard Storage[c]
Fly Ash	110 (100 to 120)	d
Clay Mixed with Coke[a]	40 (25 to 65)	15
Natural Clay[b]	12 (10 to 14)	12

a) 90% clay, 10% pulverized coke; traveling grate, single-pass up-draft sintering machine.

b) Rotary dryer sinterer.

c) Estimated, based on data in Reference 6.

d) Included in sintering losses.

e) Cyclones would reduce this emission by about 80%, Scrubbers would reduce this emission by about 90%.

Reliability of Emission Factors

Due to the limited process data and emission data available and the general lack of source testing data, the emission factors for fly ash and clay sintering are questionable. Emission factor rankings are presented in Table 7.6-2. Further work in this area is necessary to provide more realistic factors. The reported factors are felt to be correct ± 50%.

Table 7.6-2. Emission Factor Rankings for Sintering Processes

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Fly Ash	0	8	5	13
Clay Mixed with Coke	5	5	5	15
Natural Clay	5	5	8	18

The emission factor developed for fly ash sintering is based on the assumption that only half the reported losses (viz. 10% of input) are actually airborne. This is an engineering judgment If all the reported losses became airborne, the factor for fly ash would be 240 lb/ton instead of the 100 to 120 shown in Table 7.6-1.

APPENDIX 7.6

Clay Sintering Emission Data

A. Data Obtained from Reference 2.

Sintered Material	Natural Clay
Input Rate	560 tons/day
Finished Product Rate	420 tons/day
Particulate Removed by Dust Collector	2 tons/day

Thus assuming the dust collector is only 80% efficient, the sintering process dispels 2.5 tons of particulate per 420 tons of finished product, or 12 lb/ton of finished product. A variation from about 10 to 14 lbs/ton could be expected

B. Data Obtained from Reference 3.

Sintered Material	90% Clay, 10% Pulverized Coke
Input Rate	35 tons/hr
Finished Product Rate	26 tons/hr
Particulate in Exhaust Gas After Collector	0.74 lb/1000 lb Exhaust Gas
Collector Type	Cyclone
Quantity and Temperature of Exhaust Gas	94,200 cfm at 175°F

The above information yields particulate emissions as follows:

94,200 cfm at 175°F is equivalent to 78,600 scfm or 4,720,000 scfh. This amount of gas weighs 355,000 lb.

$$\text{Thus } \frac{355{,}000 \text{ lb gas}}{\text{hr}} \times \frac{0.74 \text{ lb part}}{1000 \text{ lb gas}} = 263 \text{ lb part/hr}$$

Assuming the collection equipment (cyclone) has an efficiency of 75%, the 263 lb represents 25% of the total emission. Total emissions therefore are 1050 lb/hr$(\frac{263}{0.25})$.

This amount of particulate represents 40 lb/ton of finished product ($\frac{1050\ \text{lb}}{26\ \text{tons/hr}}$). An assumed collection efficiency of 85% would give a factor of 67.5 lbs/ton while an efficiency of 60% would give 25 lbs/ton.

Table 7.6-3 presents a summary of the emission data derived from the above calculation and the data found in References 7 and 8.

Table 7.6-3. Particulate Emissions From Sintering Operations

Sintered Material, Operation, and Qualifying Conditions	Particulate Emissions lb/ton of Finished Product	Reference Number
Based on estimate of particulate collected from sintering of natural clay in rotary kiln.	12 (10 to 14)	2
Based on material-balance for sintering clay mixed with limestone.	20	7 and 8
Based on stack sample after collection equipment; 90% clay, 10% pulverized coke pellets sintered on traveling grate, updraft sintering machine.	40 (25 to 65)	3

The emissions reported in References 7 and 8 are not the result of actual tests but of an engineering analysis. Further, the analysis is based on clay-mixed-with-limestone. While the analyzed process is unrelated to sintering of clay for the purposes of producing lightweight aggregate, it is presented herein as a model to lend reliability to figures based on scant data. That these emissions are between the figure calculated in A and B, indicates the calculated emission factors are in a ± 50% range.

Crushing, screening and storage losses were estimated from the data presented in Chapter 7-4 for rock crushing.

waste solids (both sludge and dry scrubbing products) from the control of SO_2 emissions. No incremental solid waste results from NO_x emission control by combustion modification. In this section, the impacts of the incremental solid wastes produced from PM and SO_2 controls are discussed by considering the following:

- solid waste quantities and characteristics,
- waste treatment and disposal, and
- applicable regulations.

7.3.1 Solid Waste Quantities and Characteristics

The primary constituents of coal fly ash are silicon, aluminum, iron, and calcium, with lesser quantities of magnesium, titanium, sodium, potassium, sulfur, and phosphorus. In addition, fly ash contains trace concentrations of from 20 to 50 elements (depending on the specific coal), including lead, arsenic, and cadmium, and radionuclides of several elements.[9]

Dual alkali scrubber sludges are composed primarily of calcium sulfite/sulfate solids. Also present are dissolved sodium salts and trace elements (e.g., lead, arsenic and cadmium), which may contaminate the groundwaters and surface waters due to runoff and leaching from sludge disposal sites (see Section 7.2.3). The chemical composition and concentration of FGD sludge varies with the different coal types used in industrial boilers. When a particulate collection device is not used upstream of the FGD system and the FGD system is being used to control both SO_2 and PM emissions, the trace element concentrations in the scrubber sludge are increased due to the addition of fly ash to the sludge.

The dry solid waste produced from dry scrubbing FGD processes consists primarily of calcium or sodium salts, depending upon the type of alkali used as the SO_2 sorbent. Significant quantities of fly ash will also be present, because the PM collection device is located downstream of the spray dryer and removes fly ash along with the spray dried solids.

7.7 LIME MANUFACTURING

Process Description

Lime (CaO) is the high temperature product of the calcination of limestone which is calcium carbonate ($CaCO_3$). Lime is manufactured in vertical or rotary kilns fired by coal, oil, or natural gas. Figure 7.7-1 presents a schematic process diagram of lime manufacturing. Kiln temperatures approaching 950°C decompose the limestone with the loss of CO_2 by the following reaction:

$$\overset{100}{CaCO_3} \rightarrow \overset{56}{CaO}+\overset{44}{CO_2}$$

The charge to the kiln ranges in size from stones of 6-8 inches diameter for the vertical kiln to 1/4 to 1/2 inch diameter for the rotary kiln. Somewhat more than 50% of the lime produced in the United States is from rotary kilns.[1] Several modifications of the vertical and rotary kilns have been introduced. However, the standard vertical and rotary kilns are, by far, the most common types of lime manufacturing equipment. Typical exhaust rates for vertical kilns, averaging approximately 3.5 tons per hour, are 8000-10,000 SCFM. For rotary kilns, averaging 14-16 tons per hour, the exhaust rate is approximately 75,000-80,000 SCFM.[3] Other types of kilns currently in use are fluidized bed, modified vertical, and traveling grate kilns. Their typical features are good fuel economy and lower emission rates. These types are used for the minor portion of the production in the United States.[1]

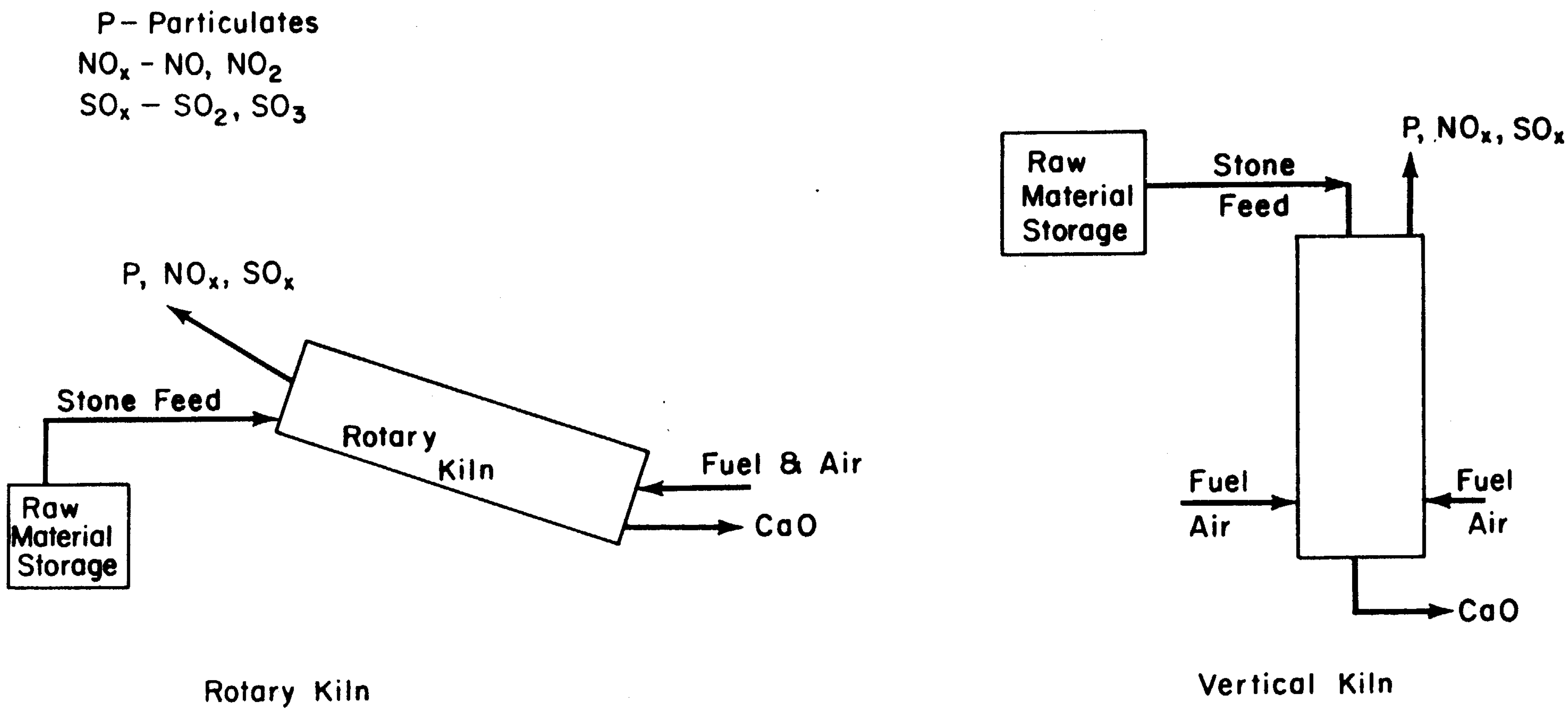

Figure 7.7-1. **LIME MANUFACTURING**

Factors Affecting Emissions

Factors affecting emissions from lime manufacturing kilns are: (1) the type and capacity of the kiln, (2) the type of fuel used to fire the kiln, (3) the rate of air flow through the kiln, (4) the particle size of the charge, (5) the amount of agitation of the charge, and (6) the type and extent of control equipment used to reduce the emissions from the kiln.

Emissions

Atmospheric emissions in the lime manufacturing industry include the particulate emissions from the mining, handling, crushing, screening and calcining of the limestone and the combustion products from the kilns. The lime emitted from the kilns (referred to as quicklime) is a fine particulate which may be 15% of the total weight of limestone charged to the rotary kiln.[1] The vertical kilns, because of the use of larger size of charge material, lower air velocities and less agitation, have considerably less particulate emission. Emission of fly ash and smoke may be a greater problem in the vertical kilns which are fired by coal or heavy fuel oil. Control of emissions from vertical kilns is accomplished by sealing the exit of the kiln and exhausting the gases through various control equipment or through other processes, i.e., alkali and sugar industry where the CO_2 content of the exhaust is utilized.[1]

535 lb/hr/[illegible]

230 lb/[illegible]

Particulate emission problems are much greater on the rotary kilns due to a smaller size of charge material (1/2" - 1/4"), higher fuel consumption, and greater air velocities.

through the rotary chamber. The rotary kilns are becoming more popular for new installations due to their average capacity. Methods of control on rotary kiln plants include simple and multiple cyclones, wet scrubbers, baghouses and electrostatic precipitators.[1] The most common control is the cyclone. A cyclone's collection efficiency is approximately 70%, with better efficiency for particles greater than 10 microns.[2] Bag filtration and venturi scrubbers are often used to obtain 99% + collection efficiencies.[1] Exit grain loadings of 0.05 to 0.6 have been measured after various scrubbing devices.[4]

Typical analyses of the particulate emission from a lime kiln showed lime (CaO) dust to constitute two thirds of the material with $CaCO_3$ being the remainder.[1] Products of fuel combustion are also emitted. For coal these are primarily sulfur oxides and fly ash. The amounts of these emissions are inconsequential compared to the lime dust emission. Table 7.7-1 lists the particulate emissions from lime manufacture.

Table 7.7-1. Particulate Emissions from Lime Manufacturing

Operation	Emissions, lbs /ton processed - uncontrolled[a]
Crushing	
primary	31 (2.4 to 78)
secondary	2 -
Calcining	
vertical	8 (2.5 to 15.4)
rotary	315 (100 to 430)

---

a) Cyclones could reduce this factor by about 70%
Venturi scrubbers could reduce this factor by about 95-99%
Fabric filters could reduce this factor by about 99%.

Reliability of Emission Factor

Emission factors from primary crushing, vertical and rotary kilns are considered reliable, and no further work is indicated in these areas at this time. Factors for secondary crushing are questionable due to lack of data. These emissions do not appear to be major. Thus it is felt no further work is necessary in this area at this time. Table 7.7-2 presents the factor ranking.

Table 7.7-2. Emission Factor Ranking for Lime Manufacturing

Operation	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Crushing				
primary	10	5	5	20
secondary	5	2	2	9
Kilns				
vertical	10	8	5	23
rotary	7	8	5	20

APPENDIX 7.7

Table 7.7-3. Particulate Emissions from Lime Manufacturing

Operation	Emission, lbs/ton processed	Reference
LIMESTONE CRUSHING		
Primary	5.0	3
	8.0	3
	18.3	3
	9.4	3
	2.4	3
	36.0	3
	78.3	3
	371.0[a]	3
	374.0[a]	3
Average	31.5	
Secondary	2.1	3
LIME KILNS		
Vertical	7.4	1
	5.3	2
	15.4	2
	8.6	2
	2.5	
Average	7.8	
Rotary	100-300	1
	430	2

a) Not used in determining average.

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7.8 CONCRETE BATCHING

Process Description[1,2]

Concrete batching involves the proportioning of sand, gravel, and cement by means of weight hoppers and conveyors into a mixing receiver such as a transit mix truck. The required amount of water is also discharged into the receiver along with the dry materials. In some cases, the concrete is prepared for on-site building construction work or the manufacture of concrete products such as pipe and prefabricated construction parts. Particulate emissions consist primarily of cement dust, but some sand and aggregate gravel dust emissions do occur during batching operations. There is also a potential for dust emissions during the unloading and conveying of concrete and aggregates at these plants and during the loading of dry batched concrete mix. Another source of dust emissions is the traffic of heavy equipment over unpaved or dusty surfaces in and around the concrete batching plant.

Factors Affecting Emissions

Factors affecting emissions include the amount and particle size of materials handled and the type of handling methods used. Enclosure of dumping and loading areas, and of conveyors and elevators, filters on storage bin vents and liberal use of water sprays will reduce particulate emissions. The degree to which dust control of traveled surfaces, and general plant housekeeping is practiced will also affect emissions.

Emissions

Very limited particulate emissions data were found in the literature. These data estimated emissions at 0.04 to 0.05 lbs of dust per ton of concrete.[3] This is equivalent to 0.08 to 0.1 lbs of dust per cubic yard while using good dust control procedures. Emissions of 0.2 lbs/cubic yard could probably be expected for some dusty operations.*

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* 1 yard^3 of concrete = 4000 pounds

Reliability of Emission Factors

No actual source test data are available. Engineering estimates were the only references to emissions. Data and references to emissions are old and based on engineering estimates. Further work must include source test information. Lack of new work in the field causes this factor to be questionable. Table 7.8 presents the factor ranking.

TABLE 7.8-1 Ranking of Emission Factors

Emission Data 0-40	Process Data 0-10	Engineering Analysis 0-10	Total
2	5	5	12

No appendix is included in this section due to a lack of data.

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7.9 FIBER GLASS MANUFACTURING

Process Description

Fiber glass is manufactured by melting various raw materials to form glass, drawing the molten glass into fibers, and coating the fibers with an organic material. Figure 7.9.1 is a simplified flow diagram of the fiber glass manufacturing process. The basic ingredients for continuous-filament glass fiber are:[1]

Silicon dioxide	52 - 56%
Calcium oxide	16 - 25%
Aluminum oxide	12 - 16%
Boron oxide	8 - 13%
Sodium and Potassium oxides	0 - 1%
Magnesium oxide	0 - 6%

The glass-forming reaction takes place at 2800°F (about 100°F higher than that required for normal plate glass) in a large rectangular, gas-or-oil-fired reverberatory furnace. The melting furnaces are equipped with either regenerative or recuperative heat recovery systems.

After refining, the molten glass passes to a forehearth where temperatures are kept between 2,300 and 2,400°F. At this point, the glass is either formed into marbles for subsequent remelting, or passed directly through orifices (bushings) to form a filament. The older method of producing continuous filament fiber glass is to form the molten glass into marbles, inspect the marbles for quality, and then remelt them for final filament drawing. This method is still required for very fine fibers (less than 0.00025 inch diameter).

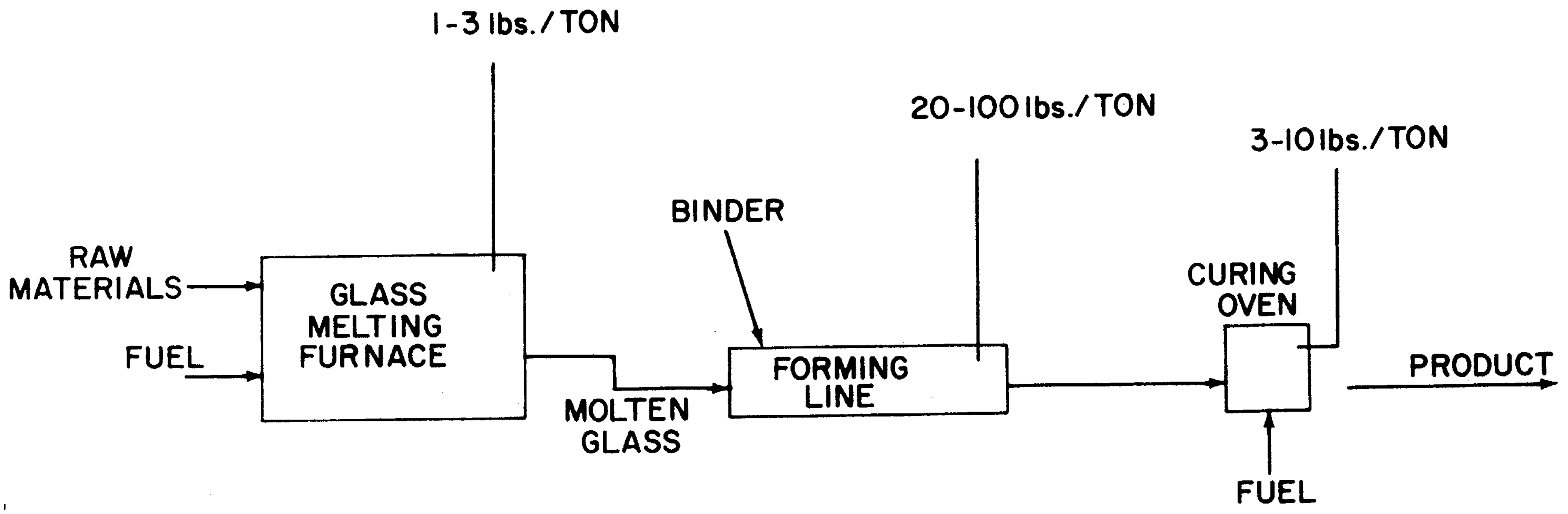

Figure 7.9-1. Fiber glass manufacturing process

However, for larger fibers, the marble producing stage may be bypassed and the glass filaments drawn directly from the forehearth through orifices in platinum-rhodium bushings.

After forming, the continuous filaments are treated with organic binder material, wound, spooled, and sent to a high-humidity curing area where the binder sets. Retention time in the curing area varies from 1 to 10 hours and depends on the type of binder used and the desired product. The product is then cooled by blowing air over it.

In the manufacture of glass wool as used in insulation, the molten borosilicate glass is also drawn through orifices. However, in this case, the filament is dropped onto a moving bed conveyor or forming line and sprayed with a binder. This stringy mass is then cured by heat treating at temperatures in the 300 - 600°F range in a curing oven.[2,3,4] Phenolic base organic binders have been used in this operation.

The major emissions from fiber glass manufacturing processes are particulates from the glass melting furnace, the forming line, the curing oven, and the product cooling line. In addition, gaseous organic emissions occur from the forming line and curing oven. Combustion products from the natural gas or oil burned in the melting furnace and curing oven are also emitted. The emissions from the forming line are the largest single source of emissions and are characterized by a dense light-colored cloud.

Factors Affecting Emissions

Particulate emissions from the glass melting furnace are affected by basic furnace design, type of fuel (oil or gas), raw material size and composition, and type and volume of furnace heat recovery system.[5] Regenerative heat recovery systems generally allow more particulate matter to escape than do recuperative systems. Particulate control systems are not generally used on the glass furnace.

Organic and particulate emissions from the forming line are most affected by the composition and quantity of the binder, and the spraying techniques used to coat the fibers.[6] Very fine spray and volatile binders increase emissions. Pollutant control systems are not generally used.

Emissions from the curing oven are affected by the oven temperature and binder composition. Direct-fired afterburners with heat exchangers may be used to control emissions.

Emissions

Particulate emissions from fiber glass manufacturing based on data in the Appendix are summarized in Table 7.9-1.

Table 7.9-1. Uncontrolled Particulate Emissions From Fiber Glass Manufacturing

Process	Emissions, lbs/ton of material processed
Glass Furnace[a]	
Regenerative Heat Exchanger	3 (2 to 4)
Recuperative Heat Exchanger	1 (0.5 to 1)
Electric Induction Furnace	0
Forming Line	50 (20 to 100)
Curing Oven	7 (3 to 10)
TOTAL	57 to 60 (25-114)

a) Only one type is usually used at any one plant.

Overall emissions may be reduced approximately 50% by using:

1) An afterburner on the curing oven.
2) A filtration system on the product cooling and handling processes.
3) Process modifications for the forming line.

Hydrocarbon emission data were not available and due to the extreme variability of these emissions depending on binder composition and operating temperatures, no reliable estimate could be made.

Reliability of Emission Factors

The forming line emissions account for the major portion of the plant emissions. However, quantitative emission data from this process were limited to one stack test. Due to this lack of emission data and the variability in emissions due to process variables, the overall factor is questionable. Table 7.9-2 presents the factor ranking.

Table 7.9-2. Emission Factor Ranking for Fiber Glass Manufacturing

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
6	2	5	13

APPENDIX 7.9

Table 7.9-3. Particulate Emissions From Fiber Glass Manufacturing

Operational Source	Uncontrolled Emissions, lb/ton of Product	Reference
1. Glass Melting Furnace (Regenerative)	3.4	7
	2.0-4.	8
	3.	9
	1.0-2	6
Glass Melting (Recuperative)	0.5-1.	6
2. Forming Line	23.5	4
	100.	6
3. Curing Oven	3.4, 14	4
	3.6, 6.4	4
	10.	4
(Curing Mineral Wool)	4.	3

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7.10 PULPBOARD MANUFACTURING

General Information

Pulpboard manufacturing includes the manufacture of fibrous boards from a pulp slurry. This encompasses two distinct types of product, paperboard and fiberboard.

Paperboard is a general term which describes a sheet 0.012 inches or more in thickness made of fibrous material on a paper machine.[1] It is commonly made from wood pulp, straw, or paper stock. In short, paperboard is merely heavy paper, manufactured on a cylinder machine or a Fourdrineir machine in the same manner as paper less than 0.012 inches thick.

Fiberboard, also referred to as particle board, is much thicker than paperboard and is made somewhat differently. This general product is used extensively by the construction industry and includes both cellular fiber and hard pressed composition board (containing no gypsum). Resins are often used in fiberboard to impart the characteristics of strength and stability.

Process Description

There are two distinct phases in the conversion of wood to pulpboard. These are (1) the manufacture of pulp from the raw wood and (2) the manufacture of pulpboard from the pulp. This investigation concerns itself only with the latter phase, the former having been the subject of earlier reviews.[2]

Paperboard is manufactured on a cylinder machine or a Fourdrineir machine. Whether the board is formed on a cylinder machine or a Fourdrineir machine does not appreciably affect emissions since each machine utilizes the same principle. For the purposes of this report, the Fourdrineir machine will be discussed.

First the stock is sent through screens into the head box from which it flows through the sluice onto a moving bronze-wire screen. Approximately 15% of the water is removed by suction boxes located under the screen. From the wire screen, the paperboard is transferred to the first felt blanket and enters the drying section of the machine with a moisture content of 60 to 70 percent. The drying section is vented and consists of steam-heated drying rolls and felt-drying blankets. Water content of the board upon leaving the dryer is between 6 and 10 percent. After drying, the board enters the calender stack which imparts the final surface to the product.

Unlike paperboard, fiberboard is often made from fibrous by-products such as bagasse. After pulping, the slurry is pumped to a shredder and washed in rotary washers to remove dirt, pith, and soluble compounds. The slurry next enters half stock chests where the sizing is added.

A typical fiberboard composition is:

100 lbs.	shredded fiber
3 lbs.	sawdust
1 - 2 lbs.	wax, resins, or other binders
150 lbs.	water
Trace -	alum
Trace -	aluminate

throughput at the plants. For air pollution calculations virtually all solvent loss was considered as loss to the atmosphere. Due to good evaluation of conditions at dry cleaning operations and reliable estimates of solvent usage, the factor is considered good. Table 8.1-2 shows the factor ranking.

Table 8.1-2 Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	8	8	21

Reliability of Emission Factor

Emissions from the drying operations of paperboard manufacturing do not appear to be a major problem, and the factors reported in this review are believed to be good. Additional work is, however, required to obtain emission data from the product trimming, cutting, and other finishing operations.

The reported factor for particulate emissions from fiberboard drying is also believed to be accurate. However, in addition to determining emissions from the cutting and fabricating operations, additional work is warranted to determine the gaseous emissions from the dryer due to the various resins and binders used in the stock. Emission factor rankings are presented in Table 7.10-2.

Table 7.10-2. Emission Factor Ranking for Pulpboard Manufacture

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Paperboard	10	8	8	26
Fiberboard	5	8	3	16

One major assumption was made in obtaining the factors presented in this section in that the particle emissions from the drying of fiberboard are assumed to be identical for all fiberboards regardless of the type of pulp and binder used.

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I[illegible]ORGANIC SOLVENTS

8. ORGANIC SOLVENTS

Organic solvent emissions from dry cleaning and surface coating operations are presented in this section. The solvent emissions from these processes represent a wide range of hydrocarbon compounds. Some dry cleaning plants recover the solvent which evaporates during operations when a substantial savings in operating costs can be effected. Nearly all solvents from surface coating operations escape to the atmosphere. Control techniques such as adsorption or incineration are used to reduce the emissions of organic compounds.

8.1 DRY CLEANING

Process Description

Clothing and other textiles may be cleaned by treating them with organic solvents. This treatment process involves agitating the clothing in a solvent bath, rinsing with clean solvent, and drying with warm air.

There are basically two types of dry cleaning installations: those using petroleum solvents (Stoddard and 140°F), and those using chlorinated synthetic solvents (perchloroethylene). All of the older dry cleaning plants used petroleum solvents. Because of the inherent fire hazard, most zoning restrictions prohibit the operation of petroleum cleaning plants in residential and commercial areas. This led to the development of non-flammable, chlorinated solvents which can be used in residential installations.

In a petroleum solvent dry cleaning plant, the equipment generally consists of a washer, centrifuge (extractor), tumbler, filter, and often a batch still. The centrifuge is used to recover solvent by spinning it from the clothes. The clothes then enter a tumbler where they are dried with warm air. The tumbler is usually vented through a lint trap to the atmosphere in this type of plant.

In synthetic solvent plants, the washer and extractor are a single unit. The tumbler is vented through a closed system with a condenser for vapor recovery while in operation. The tumbler is vented to the atmosphere only during short deodorizing periods.

Both adsorption and condensation systems may be used to control hydrocarbon emissions from dry cleaning plants. Solvent recovery systems are not only commercially available as part of a synthetic solvent cleaning plant, but they are also economically attractive. The primary control element is a water cooled condenser which is an integral part of the closed cycle in the tumbler or drying system. Up to 95% of the solvent that is evaporated from the clothing is recovered here. About half of the remaining solvent is then recovered in an activated-carbon adsorber giving an overall control efficiency of 97-98%. About half of the synthetic dry cleaning plants in the country use carbon adsorbers.[4]

There are no commercially available control units for solvent recovery in petroleum based plants because it is less economical to recover the vapors. The vaporized solvent is not condensable at the temperatures employed and thus the whole solvent recovery burden would fall on an adsorption system, necessitating equipment up to 20 times larger than that used in a comparable synthetic solvent plant.

Factors Affecting Emissions

Factors affecting hydrocarbon emissions from dry cleaning operations include the amount of solvent used, the amount of fabric cleaned, the temperature of the wash, the degree of enclosure of the washers, the maintenance of the washers, the amount of ventilation throughout the operation, the amount of open handling of wet fabric, the aromatic content of the solvent, the degree to which control equipment is applied to the exhaust system of the plant and the amount of the generated solvent reaching the control equipment.

Emissions

The major source of hydrocarbon emissions in dry cleaning is the tumbler through which hot air is circulated to dry the clothes. Drying leads to vaporization of the solvent and emissions to the atmosphere unless control equipment is used. Because of the volatility of the solvents used, additional emissions occur when storage tanks are loaded, equipment doors are opened, ductwork or equipment leaks and textiles soaked in solvent are removed from equipment. These latter sources are more of a problem in petroleum plants because the low cost of the solvent does not give much economic incentive for conserving the solvent during handling operations.

Since dry cleaning is only a physical process, hydrocarbon emissions consist of the respective evaporated solvents. Chemical composition of petroleum solvents was about 46% paraffins, 42% naphthenes, and 12% aromatic compounds. The advent of Los Angeles Rule 66 has led to some reformulations so that in many parts of the country the solvent's aromatic content now is at or below 8 percent.

Table 8.1-1 presents the emissions from dry cleaning operations based on data in the Appendix.

The trend in dry cleaning operations today is toward the smaller package operations located in shopping centers and suburban business districts. These operations typically handle less than 2,000 lbs. of clothes per week with 1500 lbs. being an average weekly production. These plants almost exclusively use perchloroethylene and have recovery systems for the solvent built into the process. It has been estimated that perchloroethylene is used on 50% of the weight of clothes dry cleaned in the United States today and that 70% of the dry cleaning plants use perchloroethylene.[3] The remaining plants use the common petroleum solvents but in cases where air pollution potential is high, i.e., Los Angeles, regulations are requiring the use of petroleum solvents with a low initial concentration of aromatics.

Table 8.1-1 Total Hydrocarbon Emissions from Dry Cleaning Operations, lbs/ton clothes cleaned[a]

	Petroleum Solvents	Chlorinated Solvents
Uncontrolled	305 lbs (22.7 gal)	210 lbs (15.6 gal)
	Range 125 lbs to 500 lbs	Range 70 to 280 lbs
Average Control	-	95
Good Control	-	35

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[a] Approximately 18-25 lbs of clothes are cleaned per person per year.[4]

Reliability of Emission Factor

Little emission data on source tests at dry cleaning plants are available. Most emission calculations are based on solvent usage and throughput at the plants. For air pollution calculations virtually all solvent loss was considered as loss to the atmosphere. Due to good evaluation of conditions at dry cleaning operations and reliable estimates of solvent usage, the factor is considered good. Table 8.1-2 shows the factor ranking.

Table 8.1-2 Emission Factor Ranking

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	8	8	21

APPENDIX 8.1

Emission Data

Lbs Hydrocarbon Solvent Released/Ton Clothes Cleaned

Uncontrolled Perchloroethylene	Reference	After Control with Activated-Carbon Adsorber	Reference
270	1	95	1
230	5	New Plant	
481	5	30-40	7
128	6		
70	3		
280	3		

Data in Reference 1 are 10 gallons emitted per 1000 lbs clothes for uncontrolled, 3.5 gallons per 1000 lb for controlled plants. Density of perchloroethylene is about 13.5 lbs/gallon (s.g. = 1.623).

$$\frac{10\ \text{gal}}{1000\ \text{lbs}} \times \frac{13.5\ \text{lb}}{\text{gal}} \times \frac{2000\ \text{lbs}}{\text{ton}} = 270\ \text{lbs/ton clothes}$$

Average quantity of clothes cleaned is about 18 lbs/capita/year in moderate climates[8] and about 25 lbs/capita/year in colder areas.[5] An average emission factor on a per capita basis may be estimated as follows. Since 50% of all plants use petroleum solvents,[3] and 25% of synthetic solvent plants are controlled:[4]

$$\left[\frac{305\ \text{lbs}}{\text{ton clothes}} \times \frac{18\ \text{lbs/capita/year}}{2000\ \text{lbs/ton}} \times 0.50\right] + \left[210 \times \frac{18}{2000} \times 0.25\right]$$

$$+ \left[\frac{95 + 35}{2}\ \text{Avg. controlled factor} \times \frac{18}{2000} \times 0.25\right] = 2\ \text{lbs/capita/year in}$$

moderate climates, and,
by a similar calculation,
using 25 lbs/capita,
2.7 lbs/capita/year in
colder areas.

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1. Chass, R. L., C. V. Kanter, and J. H. Elliot. Contribution of Solvents to Air Pollution and Methods for Controlling Their Emissions. J. Air Pollution Control Association, 13:64-72, February, 1963.
2. Bailor, W.C., Dry Cleaning Equipment, In: Air Pollution Engineering Manual, J.A. Danielson, (ed.) National Air Pollution Control Administration, Raleigh, N.C., Public Health Service 999-AP-40, p. 393-397, 1967.
3. Personal Communication, The National Institute of Dry Cleaning, 1969.
4. Personal Communication, S. Landon, Washer Machinery Corp., June, 1968.
5. Dry Cleaning Plant Survey, Kent County, Michigan, 1965, Michigan Dept. of Public Health.
6. Bi-State Study of Air Pollution in the Chicago Metropolitan Area, 1957-1959.
7. Personal Communication, A. Netzley, Los Angeles County Air Pollution Control District, July, 1968.
8. Los Angeles and San Francisco Area Data as reported In: Compilation of Air Pollutant Emission Factors, Duprey, R.L., National Air Pollution Control Administration, Public Health Service Publication 999-AP-42, p. 46.

8.2 SURFACE COATING

Process Description[1,2]

Surface coating operations are primarily involved with the application of paint, varnish, lacquer, or paint primer for decorative or protective purposes. This is accomplished by brushing, rolling, spraying, flow coating and dipping. Electro-dipping is also used. Spraying is generally carried out in booths. Other coating techniques such as dip tanks, flow coaters, and roller coaters are often operated without hooding or ventilation. Hooding is used on most operations where some ventilation is required.

Control of the gaseous emissions can be accomplished by the use of adsorbers (activated carbon) or by afterburners. The collection efficiency of activated carbon has been reported at 90% or greater. Water curtains or filter pads have little or no effect on escaping solvent vapors. These are widely used, however, to stop paint particulate emissions.

Factors Affecting Emissions

The major factor affecting emissions from surface coating operations is the amount of volatile matter contained in the coating. The type of operation (spraying, dipping, rolling, etc.) and the extent to which control equipment is used will also affect emissions for those applications which occur in an enclosed area.

Emissions of hydrocarbons occur due to the evaporation of the paint vehicles, thinners, and solvents used to facilitate the application of the coatings. This evaporation is very rapid in high pressure spraying where as much as 80% of the spray does not contact the part to be coated and is called overspray. In brush and roller applications the evaporation occurs more slowly and the total evaporation time depends on the coating thickness.

The volatile portion of most common surface coatings averages approximately 50% and most, if not all, of this is emitted upon applying and drying of the coating. The compounds released include aliphatic and aromatic hydrocarbons, alcohols, ketones, esters, alkyl and aryl hydrocarbon solvents and mineral spirits. Table 8.2-1 presents emission factors for surface coatings.

Table 8.2-1 Gaseous Emissions from Surface Coating Applications

Coating Type	Emission, lbs/ton[a]
Paint	1120
Varnish and Shellac	1000
Lacquer	1540
Enamel	840
Primer (Zinc Chromate)	1320

[a] Reported as undefined hydrocarbons, usually organic solvents both aryl and alkyl. Paints weigh 10-15 pounds per gallon, varnishes weigh about 7 pounds per gallon.

The emission factor is based on the composition of the coating and assumes that all of the solvent eventually evaporates from the applied coating.

Reliability of Emission Factor

While no total emission data are available, solvent content does provide a fairly accurate estimate of total organic emissions. The ranking in Table 8.2-1 indicates these factors are reliable.

Table 8.2-2 Emission Factor Ranking for Surface Coating

Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
5	9	9	23

APPENDIX 8.2

Emission Data from the Literature[1]

Coating	Composition % Volatile	Emission Factor[b] lbs/ton of coating applied
Paint	56	1120
Varnish	50	1000
Lacquer	77	1540
Enamel	42	840
Primer	66	1320

[b] Reported as undefined hydrocarbons, usually organic solvents both aryl and alkyl.

REFERENCES 8.2

1. Weiss, S.F., Surface Coating Operations, In: Air Pollution Engineering Manual, Danielson, J.A. (ed.), National Air Pollution Control Administration, Raleigh, N.C., Public Health Service Publication 999 AP-40, p. 387-390.
2. Control Techniques for Hydrocarbon Air Pollutants, National Air Pollution Control Administration, Raleigh, N.C., First Draft, Oct., 1969, Chap. 7.6.

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Martens, C.R., Technology of Paints, Varnishes and Lacquers, Rheinhold Book Corp., New York, N.Y., 1968.

Elliot, J. H., et. al., Experimental Program for the Control of Organic Emissions for Protective Coating Operations, Los Angeles Air Pollution Control District, June, 1962.