CHEMICAL PROCESS INDUSTRY

MALAYSIA

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Department of Environment

MALAYSIA

5. CHEMICAL PROCESS INDUSTRY

This section deals with emissions from the manufacture and use of chemicals or chemical products. Potential emissions from many of these processes are high, but because of the nature of the compounds they are usually recovered as an economic necessity. In other cases, the manufacturing operation is run as a closed system allowing little or no escape to the atmosphere.

In general, the emissions that reach the atmosphere from chemical processes are primarily gaseous and are controlled by incineration, adsorption, or absorption. In some cases, particulate emissions may also be a problem. The particulates emitted are generally extremely small and require very efficient treatment for removal. Emission data from chemical processes are sparse. It was therefore frequently necessary to make estimates of emission factors on the basis of material balances, yields, or similar processes.

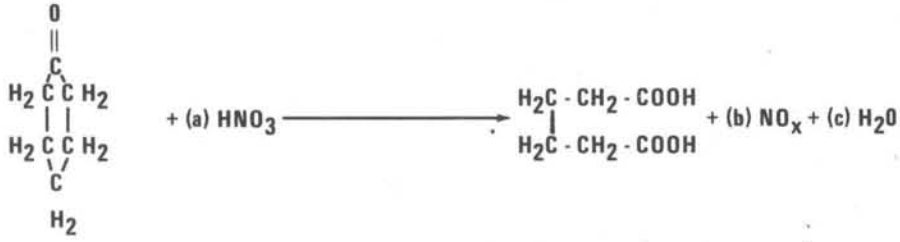
5.1 ADIPIC ACID

by Pam Canova

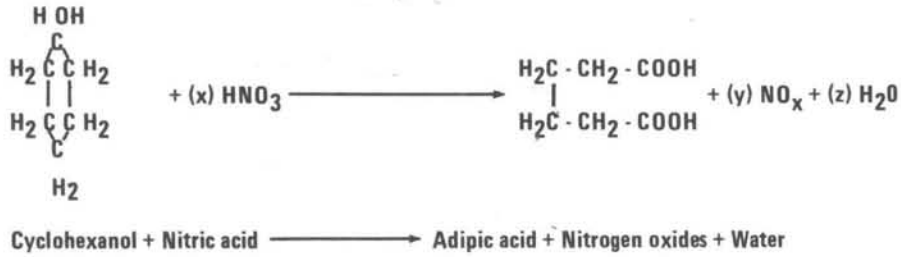
5.1.1 General[1,2]

Adipic acid, $HOOC(CH_2)_4COOH$, is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Ninety percent of all adipic acid produced in the United States is used in manufacturing Nylon 6,6. Cyclohexane is generally the basic raw material used to produce adipic acid; however, one plant uses cyclohexanone, which is a by-product of another process. Phenol has also been utilized, but has proved to be more expensive and less readily available than cyclohexane.

During adipic acid production, the raw material, cyclohexane or cyclohexanone, is transferred to a reactor, where it is oxidized at 260 to 330°F (130 to 170°C) to form a cyclohexanol/cyclohexanone mixture. The mixture is then transferred to a second reactor and oxidized with nitric acid and a catalyst (usually a mixture of cupric nitrate and ammonium vanadate) at 160 to 220°F (70 to 100°C) to form adipic acid. The chemistry of these reactions is shown below.



Cyclohexanone + Nitric acid ⟶ Adipic acid + Nitrogen oxides + Water



Cyclohexanol + Nitric acid ⟶ Adipic acid + Nitrogen oxides + Water

Dissolved NO_x gas plus any light hydrocarbon by-products are stripped from the adipic acid/nitric acid solution with air and steam. Various organic acid by-products, namely acetic acid, glutaric acid, and succinic acid, are also formed and may be recovered and sold by some plants.

The adipic acid/nitric acid solution is then chilled, and sent to a crystallizer where adipic acid crystals are formed. The solution is centrifuged to separate the crystals. The remaining solution is sent to another crystallizer, where any residual adipic acid is crystallized and centrifugally separated. The crystals from the two centrifuges are combined, dried, and stored. The remaining solution is distilled to recover nitric acid, which is routed back to the second reactor for re-use. Figure 5.1-1 presents a general schematic of the adipic acid manufacturing process.

5.1.2 Emissions and Controls

Nitrogen oxides, hydrocarbons, and carbon monoxide are the major pollutants produced in adipic acid production. The cyclohexane reactor is the largest source of CO and HC, and the nitric acid reactor is the predominant source of NO_x. Particulate emissions are low because baghouses are generally employed for maximum product recovery and air pollution control. Figure 5.1-1 shows the points of emission of these pollutants.

The most significant emissions of HC and CO come from the cyclohexane oxidation unit, which is equipped with high- and low-pressure scrubbers. Scrubbers have a 90 percent collection efficiency of HC and are used for economic reasons to recover expensive hydrocarbons as well as for pollution control. Thermal incinerators, flaring, and carbon absorbers can all be used to limit HC emissions from the cyclohexane oxidation unit with greater than 90 percent efficiency. CO boilers control CO emissions with 99.99 percent efficiency and HC emissions with practically 100 percent efficiency. The combined use of a CO boiler and a pressure scrubber results in essentially complete HC and CO control.

Three methods are presently used to control emissions from the NO_x absorber: water scrubbing, thermal reduction, and flaring or combustion in a powerhouse boiler. Water scrubbers have a low collection efficiency of approximately 70 percent because of the extended length of time needed to remove insoluble NO in the absorber offgas stream. Thermal reduction, in which offgases containing NO_x are heated to high temperatures and reacted with excess fuel in a reducing atmosphere, operates at up to 97.5 percent efficiency and is believed to be the most effective system of control. Burning offgas in a powerhouse or flaring has an estimated efficiency of 70 percent.

Emission factors for adipic acid manufacture are listed in Table 5.1-1.

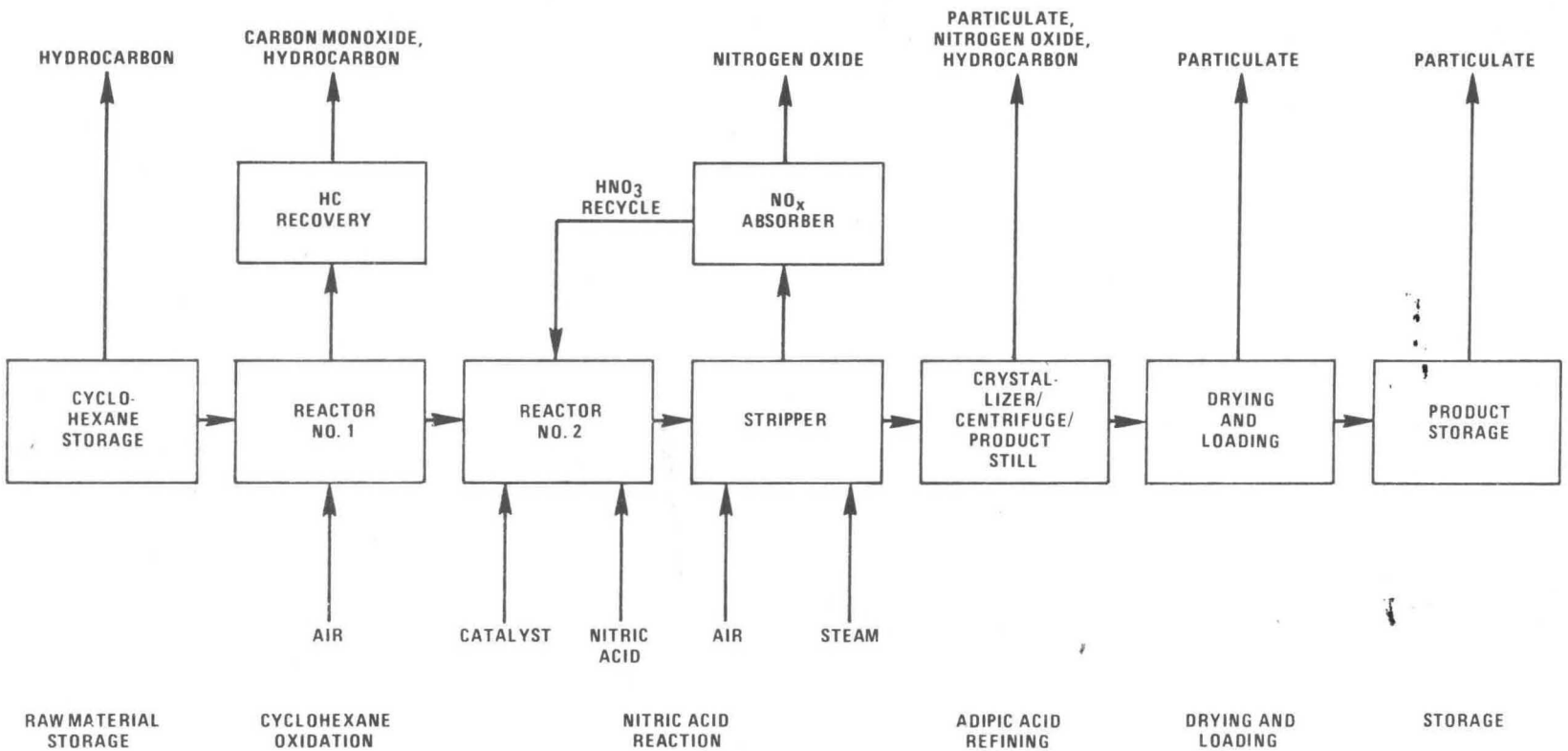


Figure 5.1-1. General flow diagram of adipic acid manufacturing process.

Table 5.1-1. EMISSION FACTORS FOR ADIPIC ACID MANUFACTURE[1,a]
EMISSION FACTOR RATING: B

Process	Particulate		Nitrogen oxides[b]		Hydrocarbon		Carbon monoxide	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Raw material storage								
Uncontrolled	0	0	0	0	2.2	1.1	0	0
Cyclohexane oxidation								
Uncontrolled[c]	0	0	0	0	40	20	115	58
W/boiler	0	0	0	0	Neg[l]	Neg	1	0.5
W/thermal incinerator[d]	0	0	0	0	Neg	Neg	Neg	Neg
W/flaring[e]	0	0	0	0	4	2	12	6
W/carbon absorber[f]	0	0	0	0	2	1	115	58
W/scrubber plus boiler	0	0	0	0	Neg	Neg	Neg	Neg
Nitric acid reaction								
Uncontrolled[g]	0	0	53	27	0	0	0	0
W/water scrubber[h]	0	0	16	8	0	0	0	0
W/thermal reduction[i]	0	0	1	0.5	0	0	0	0
W/flaring or combustion[h]	0	0	16	8	0	0	0	0
Adipic acid refining[j]								
Uncontrolled[k]	<0.1	<0.1	0.6	0.3	0.5	0.3	0	0
Adipic acid drying, loading, and storage								
Uncontrolled[k]	0.8	0.4	0	0	0	0	0	0

[a]Emission factors are in units of pounds of pollutant per ton and kilograms of pollutant per metric ton of adipic acid produced.

[b]NO_x is in the form of NO and NO_2. Although large quantities of N_2O are also produced, N_2O is not considered a criteria pollutant and is not, therefore, included in these factors.

[c]Uncontrolled emission factors are after scrubber processing since hydrocarbon recovery using scrubbers is an integral part of adipic acid manufacturing.

[d]A thermal incinerator is assumed to reduce HC and CO emissions by approximately 99.99%.

[e]A flaring system is assumed to reduce HC and CO emissions by 90%.

[f]A carbon absorber is assumed to reduce HC emissions by 94% and to be ineffective in reducing CO emissions.

[g]Uncontrolled emission factors are after NO_x absorber since nitric acid recovery is an integral part of adipic acid manufacturing.

[h]Based on estimated 70% control.

[i]Based on estimated 97.5% control.

[j]Refining includes chilling, crystallization, centrifuging, and purification.

[k]Particulate emission factors are after baghouse control device.

[l]Negligible.

References for Section 5.1

1. Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants. GCA/Technology Division, Bedford, Mass. Prepared for Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-1316. July 1976.

2. Kirk-Othmer Encyclopedia of Chemical Technology. Adipic Acid. Vol. 1, 2nd Ed. New York, Interscience Encyclopedia, Inc. 1967. pp. 405-420.

5.2 SYNTHETIC AMMONIA

Frank Noonan

5.2.1 General

Anhydrous ammonia is synthesized by reacting hydrogen with nitrogen at a molar ratio of 3:1, then compressing the gas and cooling it to −33°C. Nitrogen is obtained from the air, while hydrogen is obtained from either the catalytic steam reforming of natural gas (methane) or naphtha, or the electrolysis of brine at chlorine plants. In the United States, about 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas (Figure 5.2-1).

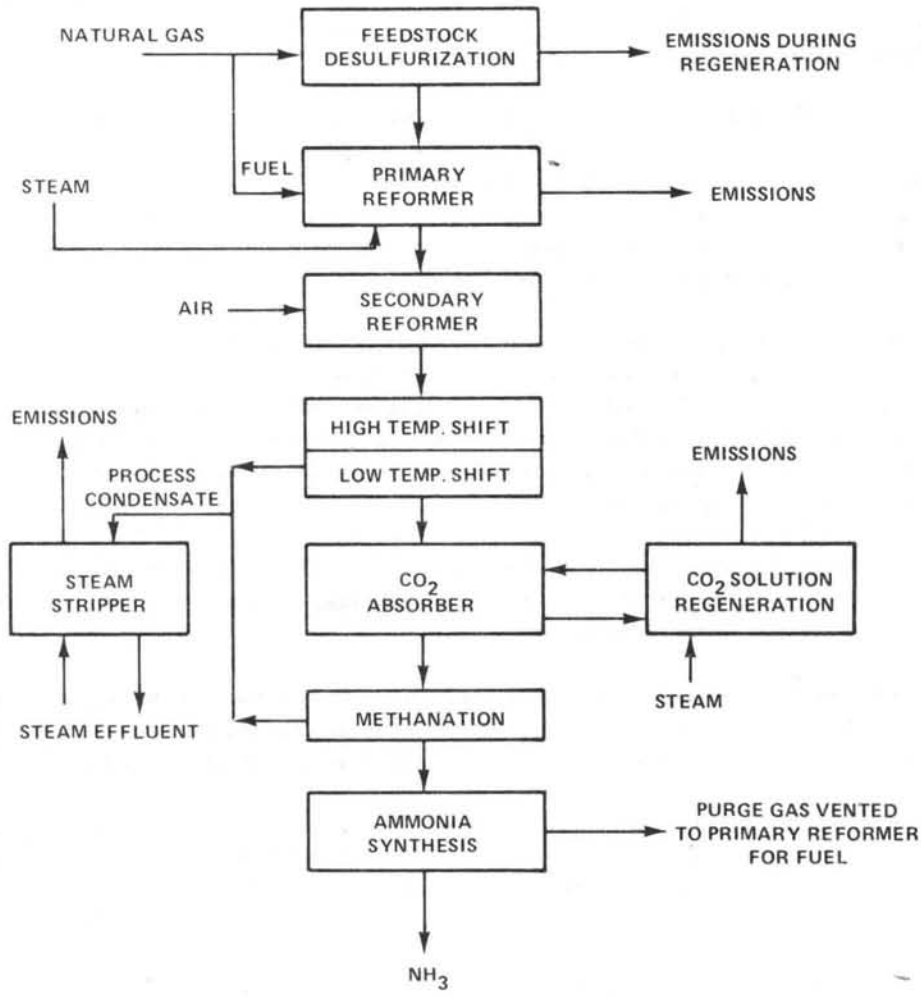


Figure 5.2-1. General process flow diagram of a typical ammonia plant.

Seven process steps are required to produce synthetic ammonia by the catalytic steam reforming method:

Natural gas desulfurization
Primary reforming with steam

Secondary reforming with air
Carbon monoxide shift
Carbon dioxide removal
Methanation
Ammonia synthesis

The first, fourth, fifth and sixth steps are to remove impurities such as sulfur, CO, CO_2 and water from the feedstock, hydrogen and synthesis gas streams. In the second step, hydrogen is manufactured, and in the third step, additional hydrogen is manufactured and nitrogen is introduced into the process. The seventh step produces anhydrous ammonia from the synthetic gas. While all ammonia plants use this basic process, details such as pressures, temperatures and quantities of feedstock will vary from plant to plant.

5.2.2 Emissions

Pollutants from the manufacture of synthetic anhydrous ammonia are emitted from four process steps:

Regeneration of the desulfurization bed
Heating of the primary reformer
Regeneration of carbon dioxide scrubbing solution
Steam stripping of process condensate

More than 95 percent of the ammonia plants in the U. S. use activated carbon fortified with metallic oxide additives for feedstock desulfurization. The desulfurization bed must be regenerated about once every 30 days for a 10 hour period. Vented regeneration steam contains sulfur oxides and/or hydrogen sulfide, depending on the amount of oxygen in the steam. Regeneration also emits hydrocarbons and carbon monoxide. The primary reformer, heated with natural gas or fuel oil, emits the combustion products NO_x, CO, SO_x, HC and particulates.

Carbon dioxide is removed from the synthesis gas by scrubbing with monoethanolamine or hot potassium carbonate solution. Regeneration of this CO_2 scrubbing solution with steam produces emissions of HC, NH_3, CO, CO_2 and monoethanolamine.

Cooling the synthesis gas after low temperature shift conversion forms a condensate containing quantities of NH_3, CO_2, methanol and trace metals. Condensate steam strippers are used to remove NH_3 and methanol from the water, and steam from this is vented to the atmosphere, emitting NH_3, CO_2 and methanol.

Table 5.2-1 presents emission factors for the typical ammonia plant. Control devices are not used at such plants, so the values in Table 5.2-1 represent uncontrolled emissions.

5.2.3 Controls

Add-on air pollution control devices are not used at synthetic ammonia plants, because their emissions are below state standards. Some processes have been modified to reduce emissions and to improve utility of raw materials and energy. Some plants are considering techniques to eliminate emissions from the condensate steam stripper, one such being the injection of the overheads into the reformer stack along with the combustion gases.

Table 5.2-1. UNCONTROLLED EMISSION FACTORS FOR TYPICAL AMMONIA PLANT
EMISSION FACTOR RATING: A

Emission point	Emission species	lb/ton	kg/MT
Desulfurization[a]	Total sulfur[b,c]	0.019	0.0096
	CO[c]	13.8	6.9
	HC[c]	7.2	3.6
Primary reformer			
Natural gas	NO_X	5.8	2.9
	SO_X	0.0048	0.0024
	CO	0.136	0.068
	TSP	0.144	0.072
	HC[d]	0.024	0.012
Fuel oil	NO_X	5.4	2.7
	SO_X	2.6	1.3
	CO	0.24	0.12
	TSP	0.90	0.45
	HC	0.30	0.15
Carbon dioxide regenerator	Ammonia	2.0	1.0
	CO	2.0	1.0
	CO_2	2440.0	1220.0
	HC	0.94	0.47
	Monoethanolamine	0.1	0.05
Condensate stripper	Ammonia	2.2	1.1
	CO_2	6.8	3.4
	Methanol	1.2	0.6

[a]Intermittent source, average 10 hours once every 30 days.

[b]Worst case assumption, that all sulfur entering tank is emitted during regeneration.

[c]Normalized to a 24 hour emission factor.

[d]Total HC in methane equivalents, species undetermined. Expected emissions are methane (Reference 1, p. 13).

Reference for Section 5.2

1. G. D. Rawlings and R. B. Reznik, *Source Assessment: Synthetic Ammonia Production*, EPA-600/2-77-107m, U. S. Environmental Protection Agency, Research Triangle Park, NC, November 1977.

5.3 CARBON BLACK

Audrey McBath

5.3.1 Process Description

Carbon black is produced by the reaction of a hydrocarbon fuel such as oil or gas with a limited supply of combustion air at temperatures of 2400 to 2800°F (1320 to 1540°C). The unburned carbon is collected as an extremely fine, black, fluffy particle, 10 to 500 nm diameter. The principal uses of carbon black are as a reinforcing agent in rubber compounds (especially tires) and as a black pigment in printing inks, surface coatings, paper and plastics. Two major processes are presently used in the United States to manufacture carbon black—the oil furnace process and the thermal process. The oil furnace process accounts for about 90 percent of production, and the thermal about 10 percent. Two others, the lamp process for production of lamp black and the cracking of acetylene to produce acetylene black, are each used at one plant in the U. S. However, these are small volume specialty black operations which constitute less than 1 percent of total production in this country. The gas furnace process is being phased out, and the last channel black plant in the U. S. was closed in 1976.

5.3.1.1 Oil Furnace Process – In the oil furnace process (Figure 5.3-1 and Table 5.3-1), an aromatic liquid hydrocarbon feedstock is preheated and injected continuously into the combustion zone of a natural gas fired furnace, where it is decomposed to form carbon black. Primary quench water cools the gases to 1000°F (540°C) to stop the cracking. The exhaust gases entraining the carbon particles are further cooled to about 450°F (230°C) by passage through heat exchangers and direct water sprays. The black is then separated from the gas stream, usually by a fabric filter. A cyclone for primary collection and particle agglomeration may precede the filter. A single collection system often serves several manifolded furnaces.

The recovered carbon black is finished to a marketable product by pulverizing and wet pelletizing to increase bulk density. Water from the wet pelletizer is driven off in a gas fired rotary dryer. Oil or process gas can be used. From 35 to 70 percent of the dryer combustion gas is charged directly to the interior of the dryer, and the remainder acts as an indirect heat source for the dryer. The dried pellets are then conveyed to bulk storage. Process yields range from 35 to 65 percent, depending on the feed composition and the grade of black produced. Furnace designs and operating conditions determine the particle size and the other physical and chemical properties of the black. Generally, yields are highest for large particle blacks and lowest for small particle blacks.

5.3.1.2 Thermal Process – The thermal process is a cyclic operation in which natural gas is thermally decomposed (cracked) into carbon particles, hydrogen and a mixture of other organics. Two furnaces are used in normal operation. The first cracks natural gas and makes carbon black and hydrogen. The effluent gas from the first reactor is cooled by water sprays to about 250°F (125°C), and the black is collected in a fabric filter. The filtered gas (90 percent hydrogen, 6 percent methane and 4 percent higher hydrocarbons) is used as a fuel to heat a second reactor. When the first reactor becomes too cool to crack the natural gas feed, the positions of the reactors are reversed, and the second reactor is used to crack the gas while the first is heated. Normally, more than enough hydrogen is produced to make the thermal black process self-sustaining, and the surplus hydrogen is used to fire boilers that supply process steam and electric power.

The collected thermal black is pulverized and pelletized to a final product in much the same manner as is furnace black. Thermal process yields are generally high (35 to 60 percent), but the relatively coarse particles produced, 180 to 470 nm, do not have the strong reinforcing properties required for rubber products.

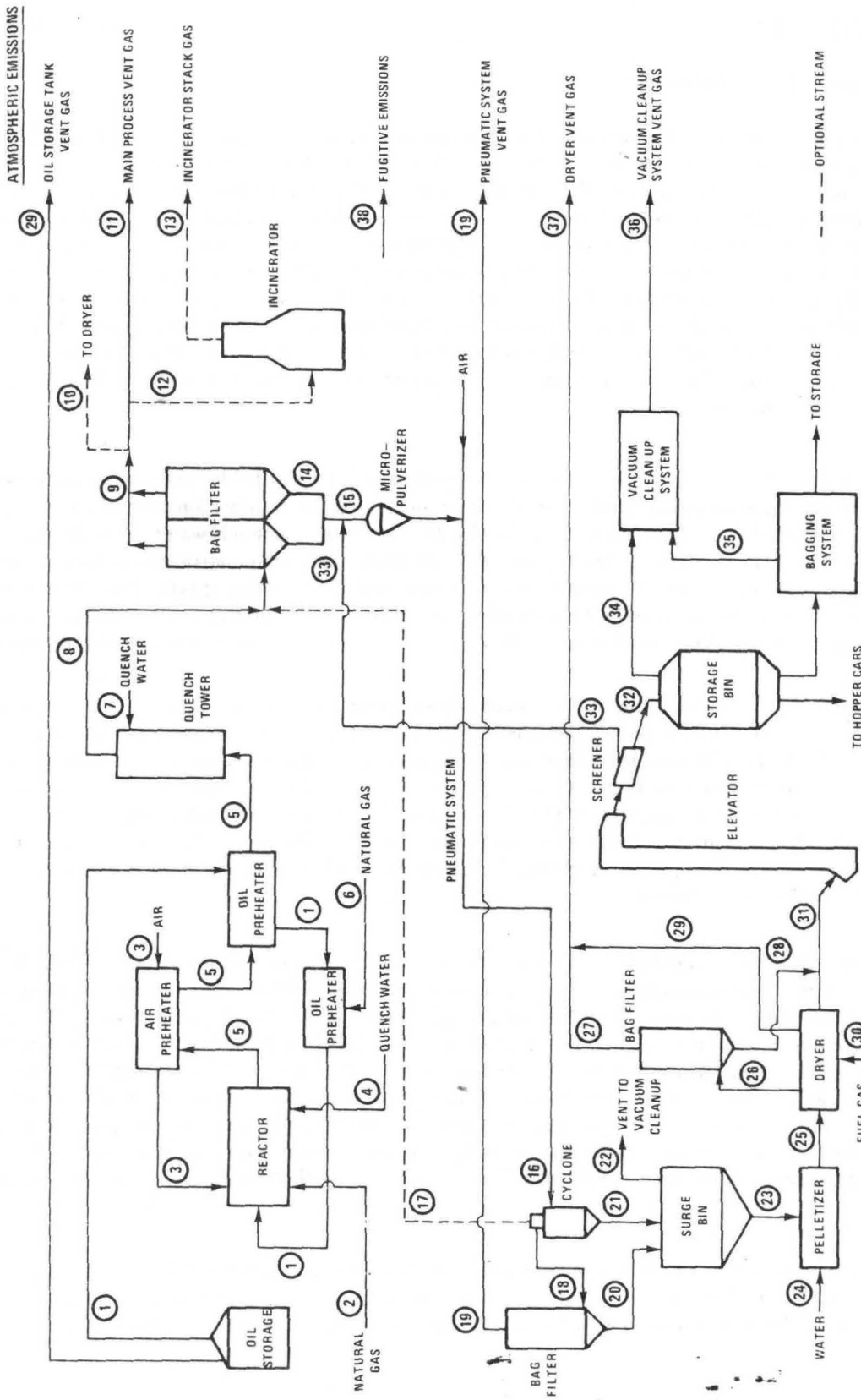


Figure 5.3-1. Flow diagram for the oil furnace carbon black process.

Table 5.3-1 STREAM CODE FOR THE OIL FURNACE PROCESS (Figure 5.3-1)

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

5.3.2 Emissions and Controls

5.3.2.1 Oil Furnace Process – Emissions from carbon black manufacture include particulate matter, carbon monoxide, organics, nitrogen oxides, sulfur compounds, polycyclic organic matter (POM) and trace elements.

The principal source of emissions in the oil furnace process is the main process vent. The vent stream consists of the reactor effluent and the quench water vapor vented from the carbon black recovery system. Gaseous emissions may vary considerably, according to the grade of carbon black being produced. Organic and CO emissions tend to be higher for small particle production, corresponding with the lower yields obtained. Sulfur compound emissions are a function of the feed sulfur content. Tables 5.3-2 and 5.3-3 show the normal emission ranges to be expected, with typical average values.

Particulates, sulfur oxides and nitrogen oxides are also emitted from the dryer vent. The oil feedstock storage tanks are a source of organic emissions. Carbon black emissions also occur from the pneumatic transport system vent, the plantwide vacuum cleanup system vent, and from cleaning, spills and leaks (fugitive emissions).

Gaseous emissions from the main process vent may be controlled with CO boilers, incinerators or flares. The pellet dryer combustion furnace, which is, in essence, a thermal incinerator, may also be employed in a control system. CO boilers, thermal incinerators or combinations of these devices can achieve essentially complete oxidation of organics and can oxidize sulfur compounds in the process flue gas. Combustion efficiencies of 99.6 percent for hydrogen sulfide and 99.8 percent for carbon monoxide have been measured for a flare on a carbon black plant. Particulate emissions may also be reduced by combustion of some of the carbon black particles, but emissions of sulfur dioxide and nitrogen oxides are thereby increased.

5.3.2.2 Thermal Process – A comparison between the thermal and oil furnace processes reveals that emissions from the former are less severe. Nitrogen oxides and particulates are emitted from the furnaces during the heating part of the cycle. Particulate matter is emitted when carbon black deposited on the furnace checkerbrick is released to the atmosphere in puffs, which occur when a furnace is switched from carbon black production to the heating part of the cycle.

Emissions from the dryer vent, the pneumatic transport system vent, the vacuum cleanup system vent, and fugitive sources are similar to those for the oil furnace process, since the operations which give rise to these emissions in the two processes are similar. There is no emission point in the thermal process which corresponds to the oil storage tank vents in the oil furnace process. Also in the thermal process, sulfur compounds, POM, trace elements and organic compound emissions are minimal, because low sulfur natural gas is used, and the process off-gas is burned as fuel.

Table 5.3-2. EMISSION FACTORS FOR CARBON BLACK MANUFACTURE
EMISSION FACTOR RATING: B [OIL FURNACE PROCESS]
C [THERMAL PROCESS]

Process	Particulate[a]		Carbon monoxide		Hydrocarbons[b]		Nitrogen oxides		Sulfur oxides		Hydrogen sulfide	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Oil furnace process[c]												
Main process vent	6.53[d] (0.2-10)	3.27[d] (0.1-5)	2,800[e] (1,400-4,400)	1,400[e] (700-2,200)	100[e] (20-300)	50[e] (10-159)	0.56[e] (2-5.6)	0.28[e] (1-2.8)	0[e,f] (0-24)	0[e,f] (0-12)	60[e] 10S-26S	30[e] 5S-13S[g]
Flare[h]	2.70 (2.4-3)	1.35 (1.2-1.5)	245 (216-274)	122 (108-137)	3.7 (3.4-4)	1.85 (1.7-2)	NA[i]	NA	50 (44-56)	25 (21.9-28)	2	1
CO boiler and incinerator[d]	2.07	1.04	1.75	0.88	1.98	0.99	9.3	4.65	35.2	17.5	0.22	0.11
Dryer vent												
Uncontrolled[h]	0.45 (0.10-0.80)	0.23 (0.05-0.40)							0.10	0.05		
Bag filter[h]	0.24 (0.02-0.80)	0.12 (0.01-0.40)					0.73 (0.24-1.22)	0.36 (0.12-0.61)	0.52 (0.06-1.08)	0.26 (0.03-0.54)		
Scrubber[h]	0.71 (0.02-1.40)	0.36 (0.01-0.70)					2.20	1.10	0.40	0.20		
Pneumatic system vent[h]												
Bag filter	0.58 (0.12-1.40)	0.29 (0.06-0.70)										
Oil storage tank vent[j]												
Uncontrolled					1.44	0.72						
Vacuum cleanup system vent[h]												
Bag filter	0.06 (0.02-0.10)	0.03 (0.01-0.05)										
Fugitive emissions[h]	0.20	0.10										
Solid waste incinerator[k]	0.24	0.12	0.02	0.01	0.02	0.01	0.08	0.04	0.02	0.01		
Thermal process[l]	Neg	Neg	Neg	Neg	Neg	Neg	Unknown	Unknown	Neg	Neg	Neg	Neg

Table 5.3-2 (continued). EMISSION FACTORS FOR CARBON BLACK MANUFACTURE
EMISSION FACTOR RATING: B [OIL FURNACE PROCESS]
C [THERMAL PROCESS]

[a]The particulate matter is carbon black.

[b]Total nonmethane hydrocarbons. Individual organic species are included in Table 5.3-3.

[c]Blanks indicate no emissions. All plants use bag filters on all process trains for product recovery except solid waste incineration.

[d]Average values based on surveys of plants in References 4 and 5. Uncontrolled.

[e]Average values are based on results of six sampling runs conducted by Monsanto Research Corporation at a representative plant with the industry mean production rate of 5.1×10^4 MT/yr (5.6×10^4 ton/yr). The ranges of values are based on a survey of fifteen plants in Reference 4. Controlled by bag filter.

[f]Not detected at detection limit of 1 ppm.

[g]S is the weight percent sulfur in the feed.

[h]Average values and the corresponding ranges of values are based on a survey of plants in Reference 4 and on the public files of Louisiana Air Control Commissiom.

[i]Not available.

[j]Emission factor calculated using empirical correlations for petrochemical losses from storage tanks (vapor pressure = 0.7 kPa).

[k]Based on emission rates obtained from the National Emissions Data System. All plants do not use solid waste incineration. See Section 2.1.

[l]Emissions data are not available, but all emissions are believed to be negligible.

Table 5.3-3. EMISSION FACTORS FOR CHEMICAL SUBSTANCES FOR OIL FURNACE CARBON BLACK MANUFACTURE

Chemical substance	Main process vent gas[a]	
	lb/ton	kg/MT
Carbon disulfide	60	30
Carbonyl sulfide	20	10
Methane	50 (20–120)	25 (10–60)
Acetylene	90 (10–260)	45 (5-130)
Ethane	0[b]	0[b]
Ethylene	3.2	1.6
Propylene	0[b]	0[b]
Propane	0.46	0.23
Isobutane	0.20	0.10
n-Butane	0.54	0.27
n-Pentane	0[b]	0[b]
POM	0.004	0.002
Trace elements[c]	<0.50	<0.25

[a]These chemical substances are emitted only from the main process vent. Average values are based on six sampling runs made at a representative plant given in Reference 1. The ranges given in parentheses are based on results of a survey of operating plants given in Reference 4.

[b]Not detected at detection limit of 1 ppm.

[c]Included are beryllium, lead, and mercury, among several others.

References for Section 5.3

1. R. W. Serth and T. W. Hughes, *Source Assessment: Carbon Black Manufacture*, EPA-600/2-77-107k, U. S. Environmental Protection Agency, Research Triangle Park, NC, October 1977.

2. *Air Pollutant Emission Factors*, NAPCA Contract No. CPA-22-69-119, Resources Research, Inc., Reston, VA, April 1970.

3. I. Drogin, "Carbon Black", *Journal of the Air Pollution Control Association*, *18*:216-228, April 1968.

4. *Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Vol. 1: Carbon Black Manufacture by the Furnace Process*, EPA-450/3-73-006a, U. S. Environmental Protection Agency, Research Triangle Park, NC, June 1974.

5. Kent C. Hustvedt and Leslie B. Evans, *Standards Support and Emission Impact Statement: An Investigation of the Best Systems of Emission Reduction for Furnace Process Carbon Black Plants in the Carbon Black Industry (Draft)*, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1976.

6. *Source Testing of a Waste Heat Boiler*, EPA-75-CBK-3, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1975.

5.4 CHARCOAL

5.4.1 Process Description[1]

Charcoal is generally manufactured by means of pyrolysis, or destructive distillation, of wood waste from members of the deciduous hardwood species. In this process, the wood is placed in a retort where it is externally heated for about 20 hours at 500 to 700°F (260 to 370°C). Although the retort has air intakes at the bottom, these are only used during start-up and thereafter are closed. The entire distillation cycle takes approximately 24 hours, the last 4 hours being an exothermic reaction. Four units of hardwood are required to produce one unit of charcoal.

5.4.2 Emissions and Controls[1]

In the pyrolysis of wood, all the gases, tars, oils, acids, and water are driven off, leaving virtually pure carbon. All of these except the gas, which contains methane, carbon monoxide, carbon dioxide, nitrogen oxides, and aldehydes, are useful by-products if recovered. Unfortunately, economics has rendered the recovery of the distillate by-products unprofitable, and they are generally permitted to be discharged to the atmosphere. If a recovery plant is utilized, the gas is passed through water-cooled condensers. The condensate is then refined while the remaining cool, noncondensable gas is discharged to the atmosphere. Gaseous emissions can be controlled by means of an afterburner because the unrecovered by-products are combustible. If the afterburner operates efficiently, no organic pollutants should escape into the atmosphere. Emission factors for the manufacture of charcoal are shown in Table 5.4-1.

Table 5.4-1. EMISSION FACTORS FOR CHARCOAL MANUFACTURING[a,d]
EMISSION FACTOR RATING: C

Pollutant	Type of operation			
	With chemical recovery plant		Without chemical recovery plant	
	lb/ton	kg/MT	lb/ton	kg/MT
Particulate (tar, oil)	–	–	400	200
Carbon monoxide	320[b]	160[b]	320[b]	160[b]
Hydrocarbons[c]	100[b]	50[b]	100[b]	50[b]
Crude methanol	–	–	152	76
Acetic acid	–	–	232	116
Other gases (HCHO, N_2 NO)	60	30	60[b]	30[b]

[a]Calculated values based on data in Reference 2.
[b]Emissions are negligible if afterburner is used.
[c]Expressed as methane.
[d]Emission factors expressed in units of tons of charcoal produced.

References for Section 5.4

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Shreve, R.N. Chemical Process Industries, 3rd Ed. New York, McGraw-Hill Book Company. 1967. p. 619.

5.5 CHLOR–ALKALI

5.5.1 Process Description[1]

Chlorine and caustic are produced concurrently by the electrolysis of brine in either the diaphragm or mercury cell. In the diaphragm cell, hydrogen is liberated at the cathode and a diaphragm is used to prevent contact of the chlorine produced at the anode with either the alkali hydroxide formed or the hydrogen. In the mercury cell, liquid mercury is used as the cathode and forms an amalgam with the alkali metal. The amalgam is removed from the cell and is allowed to react with water in a separate chamber, called a denuder, to form the alkali hydroxide and hydrogen.

Chlorine gas leaving the cells is saturated with water vapor and then cooled to condense some of the water. The gas is further dried by direct contact with strong sulfuric acid. The dry chlorine gas is then compressed for in-plant use or is cooled further by refrigeration to liquefy the chlorine.

Caustic as produced in a diaphragm-cell plant leaves the cell as a dilute solution along with unreacted brine. The solution is evaporated to increase the concentration to a range of 50 to 73 percent; evaporation also precipitates most of the residual salt, which is then removed by filtration. In mercury-cell plants, high-purity caustic can be produced in any desired strength and needs no concentration.

5.5.2 Emissions and Controls[1]

Emissions from diaphragm- and mercury-cell chlorine plants include chlorine gas, carbon dioxide, carbon monoxide, and hydrogen. Gaseous chlorine is present in the blow gas from liquefaction, from vents in tank cars and tank containers during loading and unloading, and from storage tanks and process transfer tanks. Other emissions include mercury vapor from mercury cathode cells and chlorine from compressor seals, header seals, and the air blowing of depleted brine in mercury-cell plants.

Chlorine emissions from chlor-alkali plants may be controlled by one of three general methods: (1) use of the gas in other plant processes, (2) neutralization in alkaline scrubbers, and (3) recovery of chlorine from effluent gas streams. The effect of specific control practices is shown to some extent in the table on emission factors (Table 5.5-1).

References for Section 5.5

1. Atmospheric Emissions from Chlor-Alkali Manufacture. U.S. EPA, Air Pollution Control Office. Research Triangle Park, N.C. Publication Number AP-80. January 1971.

2. Duprey, R.L. Compilation of Air Pollutant Emission Factors. U.S. DHEW, PHS, National Center for Air Pollution Control. Durham, N.C. PHS Publication Number 999-AP-42. 1968. p. 49.

Table 5.5-1. EMISSION FACTORS FOR CHLOR-ALKALI PLANTS[a]
EMISSION FACTOR RATING: B

Type of source	Chlorine gas	
	lb/100 tons	kg/100 MT
Liquefaction blow gases		
Diaphragm cell	2,000 to 10,000	1,000 to 5,000
Mercury cell[b]	4,000 to 16,000	2,000 to 8,000
Water absorber[c]	25 to 1,000	12.5 to 500
Caustic or lime scrubber[c]	1	0.5
Loading of chlorine		
Tank car vents	450	225
Storage tank vents	1,200	600
Air blowing of mercury cell brine	500	250

[a]References 1 and 2.
[b]Mercury cells lose about 1.5 pounds mercury per 100 tons (0.75 kg/100 MT) of chlorine liquefied.
[c]Control devices.

5.6 EXPLOSIVES

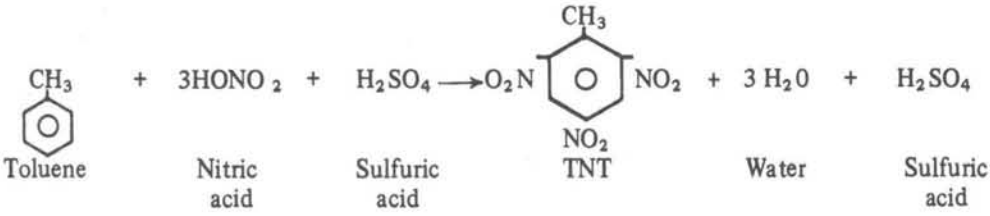
by Charles Mann

5.6.1 General[1]

An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of large amounts of heat and gas. Explosives fall into two major categories: high explosives and low explosives. High explosives are further subdivided into initiating or primary high explosives and secondary high explosives. Initiating high explosives are very sensitive and are generally used in small quantities in detonators and percussion caps to set off larger quantities of secondary high explosives. Secondary high explosives, chiefly nitrates, nitro compounds, and nitramines, are much less sensitive to mechanical or thermal shock, but explode with great violence when set off by an initiating explosive. The chief secondary high explosives manufactured for commercial and military use are ammonium nitrate blasting agents and 2.4. 6,-trinitrotoluene (TNT). Low explosives, such as black powder and nitrocellulose, undergo relatively slow autocombustion when set off and evolve large volumes of gas in a definite and controllable manner. A multitude of different types of explosives are manufactured. As examples of the production of a high explosive and a low explosive, the production of TNT and nitrocellulose are discussed in this section.

5.6.2 TNT Production [1-3]

TNT may be prepared by either a continuous process or a batch, three-stage nitration process using toluene, nitric acid, and sulfuric acid as raw materials. In the batch process, a mixture of oleum (fuming sulfuric acid) and nitric acid that has been concentrated to a 97 percent solution is used as the nitrating agent. The overall reaction may be expressed as:



Spent acid from the nitration vessels is fortified with make-up 60 percent nitric acid before entering the next nitrator. Fumes from the nitration vessels are collected and removed from the exhaust by an oxidation-absorption system. Spent acid from the primary nitrator is sent to the acid recovery system in which the sulfuric and nitric acid are separated. The nitric acid is recovered as a 60 percent solution, which is used for refortification of spent acid from the second and third nitrators. Sulfuric acid is concentrated in a drum concentrator by boiling water out of the dilute acid. The product from the third nitration vessel is sent to the wash house at which point asymmetrical isomers and incompletely nitrated compounds are removed by washing with a solution of sodium sulfite and sodium hydrogen sulfite (Sellite). The wash waste (commonly called red water) from the purification process is discharged directly as a liquid waste stream, is collected and sold, or is concentrated to a slurry and incinerated in rotary kilns. The purified TNT is solidified, granulated, and moved to the packing house for shipment or storage. A schematic diagram of TNT production by the batch process is shown in Figure 5.6-1.

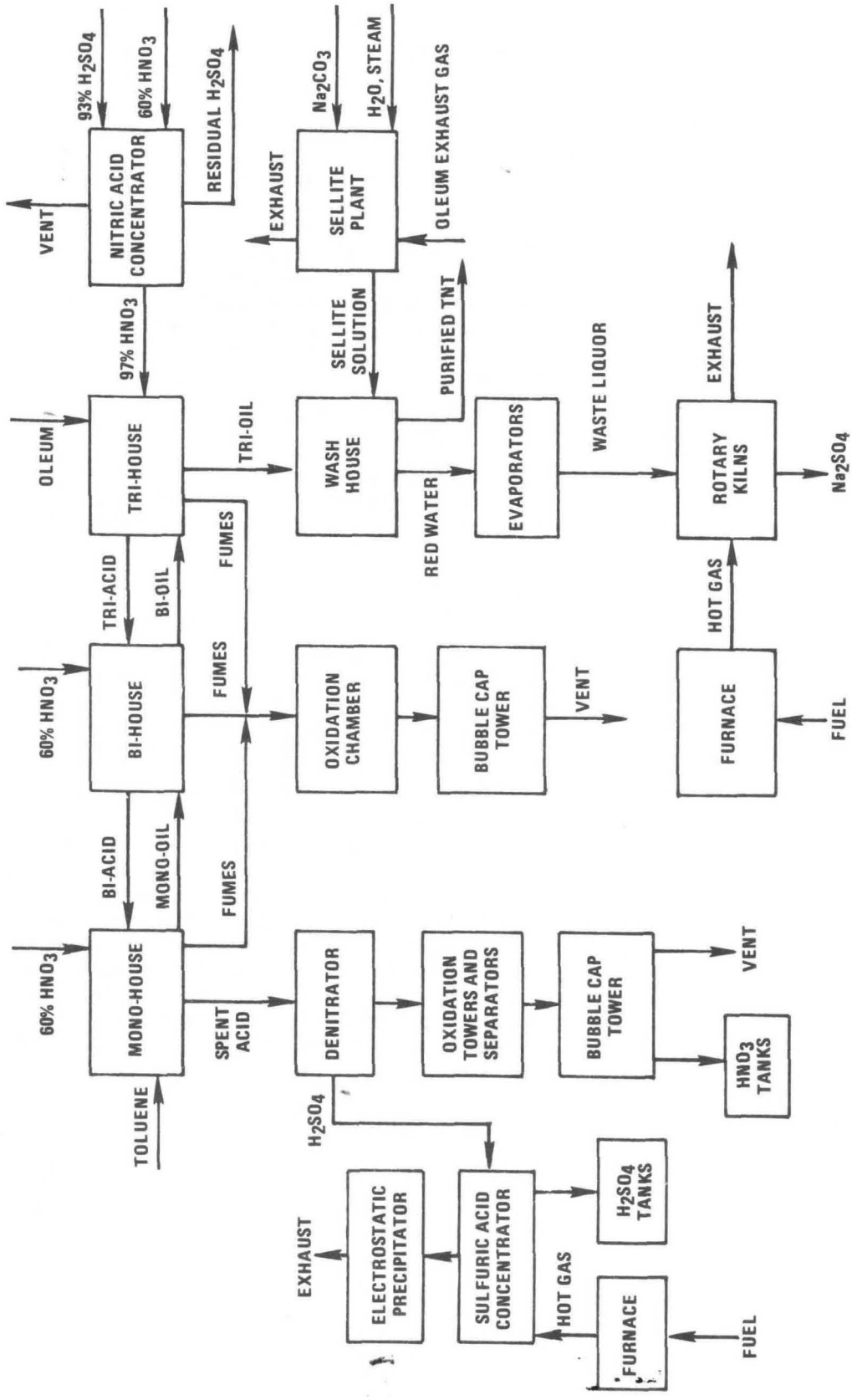


Figure 5.6-1. Flow diagram of typical batch process TNT plant.

5.6.3 Nitrocellulose Production [1]

Nitrocellulose is prepared by the batch-type "mechanical dipper" process. Cellulose, in the form of cotton linters, fibers, or specially prepared wood pulp, is purified, bleached, dried, and sent to a reactor (niter pot) containing a mixture of concentrated nitric acid and a dehydrating agent such as sulfuric acid, phosphoric acid, or magnesium nitrate. The overall reaction may be expressed as:

$$C_6H_7O_2(OH)_3 + 3HONO_2 + H_2SO_4 \longrightarrow C_6H_7O_2(ONO_2)_3 + 3H_2O + H_2SO_4 \quad (2)$$

Cellulose	Nitric acid	Sulfuric acid	Nitrocellulose	Water	Sulfuric acid

When nitration is complete, the reaction mixtures are centrifuged to remove most of the spent acid. The spent acid is fortified and reused or otherwise disposed of. The centrifuged nitrocellulose undergoes a series of water washings and boiling treatments for purification of the final product.

5.6.4 Emissions and Controls [2,3,5]

The major emissions from the manufacture of explosives are nitrogen oxides and acid mists, but smaller amounts of sulfuric oxides and particulates may also be emitted. Emissions of nitrobodies (nitrated organic compounds) may also occur from many of the TNT process units. These compounds cause objectionable odor problems and act to increase the concentration of acid mists. Emissions of sulfur oxides and nitrogen oxides from the production of nitric acid and sulfuric acid used for explosives manufacturing can be considerable. It is imperative to identify all processes that may take place at an explosives plant in order to account for all sources of emissions. Emissions from the manufacture of nitric and sulfuric acid are discussed in other sections of this publication.

In the manufacture of TNT, vents from the fume recovery system, sulfuric acid concentrators, and nitric acid concentrators are the principal sources of emissions. If open burning or incineration of waste explosives is practiced, considerable emissions may result. Emissions may also result from the production of Sellite solution and the incineration of red water. Many plants, however, now sell the red water to the paper industry where it is of economic importance.

Principal sources of emissions from nitrocellulose manufacture are from the reactor pots and centrifuges, spent acid concentrators, and boiling tubs used for purification.

The most important factor affecting emissions from explosives manufacture is the type and efficiency of the manufacturing process. The efficiency of the acid and fume recovery systems for TNT manufacture will directly affect the atmospheric emissions. In addition, the degree to which acids are exposed to the atmosphere during the manufacturing process affects the NO_X and SO_X emissions. For nitrocellulose production, emissions are influenced by the nitrogen content and the desired quality of the final product. Operating conditions will also affect emissions. Both TNT and nitrocellulose are produced in batch processes. Consequently, the processes may never reach steady state and emission concentrations may vary considerably with time. Such fluctuations in emissions will influence the efficiency of control methods. Several measures may be taken to reduce emissions from explosives manufacturing. The effects of various control devices and process changes upon emissions, along with emission factors for explosives manufacturing, are shown in Table 5.6-1. The emission factors are all related to the amount of product produced and are appropriate for estimating long-term emissions or for evaluating plant operation at full production conditions. For short time periods or for plants with intermittent operating schedules, the emission factors in Table 5.6-1 should be used with caution, because processes not associated with the nitration step are often not in operation at the same time as the nitration reactor.

Table 5.6-1. EMISSION FACTORS FOR
EMISSION FACTOR

Type of process	Particulates		Sulfur oxides (SO_2)	
	lb/ton	kg/MT	lb/ton	kg/MT
TNT - batch process[b]				
Nitration reactors				
Fume recovery	–	–	–	–
Acid recovery	–	–	–	–
Nitric acid concentrators	–	–	–	–
Sulfuric acid concentrators[c]				
Electrostatic precipitator (exit)	–	–	14(4-40)	7(2-20)
Electrostatic precipitator with scrubber[d]	–	–	Neg.	Neg.
Red water incinerator				
Uncontrolled[e]	25(0.03-126)	12.5(0.015-63)	2(0.05-3.5)	1(0.025-1.75)
Wet scrubber[f]	1	0.5	2(0.05-3.5)	1(0.025-1.75)
Sellite exhaust	–	–	59(0.01-177)	29.5(0.005-88)
TNT - continuous process[g]				
Nitration reactors				
Fume recovery	–	–	–	–
Acid recovery	–	–	–	–
Red water incinerator	0.25(0.03-0.05)	0.13(0.015-0.025)	0.24(0.05-0.43)	0.12(0.025-0.22)
Nitrocellulose[g]				
Nitration reactors[h]	–	–	1.4(0.8-2)	0.7(0.4-1)
Nitric acid concentrator	–	–	–	–
Sulfuric acid concentrator	–	–	68(0.4-135)	34(0.2-67)
Boiling tubs	–	–	–	–

[a] For some processes considerable variations in emissions have been reported. The average of the values reported is shown first, with the ranges given in parentheses. Where only one number is given, only one source test was available.
[b] Reference 5.
[c] Acid mist emissions influenced by nitrobody levels and type of fuel used in furnace.
[d] No data available for NO_x emissions after the scrubber. It is assumed that NO_x emissions are unaffected by the scrubber.

EXPLOSIVES MANUFACTURING[a]
RATING: C

Nitrogen oxides (NO_2)		Nitric acid mist (100% HNO_3)		Sulfuric acid mist (100% H_2SO_4)	
lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
25(6-38)	12.5(3-19)	1(0.3-1.9)	0.5(0.5-0.95)	–	–
55(1-136)	27.5(0.5-68)	92(0.01-275)	46(0.005-137)	–	–
37(16-72)	18.5(8-36)	–	–	9(0.3-27)	4.5(0.15-13.5)
40(2-80)	20(1-40)	–	–	65(1-188)	32.5(0.5-94)
40(2-80)	20(1-40)	–	–	5(4-6)	2.5(2-3)
26(1.5-101)	13(0.75-50)	–	–	–	–
5	2.5	–	–	–	–
–	–	–	–	6(0.6-16)	3(0.3-8)
8(6.7-10)	4(3.35-5)	1(0.3-1.9)	0.5(0.15-0.95)	–	–
3(1-4.5)	1.5(0.5-2.25)	0.02(0.01-0.03)	0.01(0.005-0.015)	–	–
7(6.1-8.4)	3.5(3-4.2)	–	–	–	–
14(3.7-34)	7(1.85-17)	19(0.5-36)	9.5(0.25-18)	–	–
14(10-18)	7(5-9)	–	–	–	–
		–	–	0.3	0.3
2	1	–	–	–	–

[e] Use low end of range for modern, efficient units and high end of range for older, less efficient units.
[f] Apparent reductions in NO_x and particulate after control may not be significant because these values are based on only one test result.
[g] Reference 4.
[h] For product with low nitrogen content (12 percent), use high end of range. For products with higher nitrogen content, use lower end of range.

References for Section 5.6

1. Shreve, R.N. Chemical Process Industries, 3rd Ed. New York, McGraw-Hill Book Company, 1967. p. 383-395.

2. Unpublished data on emissions from explosives manufacturing, National Air Pollution Control Administration, Office of Criteria and Standards, Durham, N.C. June 1970.

3. Higgins, F.B., Jr., et al. Control of Air Pollution From TNT Manufacturing. (Presented at 60th annual meeting of Air Pollution Control Association. Cleveland. June 1967. Paper 67-111.)

4. Air Pollution Engineering Source Sampling Surveys, Radford Army Ammunition Plant. U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Md.

5. Air Pollution Engineering Source Sampling Surveys, Volunteer Army Ammunition Plant and Joliet Army Ammunition Plant. U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Md.

5.7 HYDROCHLORIC ACID

Hydrochloric acid is manufactured by a number of different chemical processes. Approximately 80 percent of the hydrochloric acid, however, is produced by the by-product hydrogen chloride process, which will be the only process discussed in this section. The synthesis process and the Mannheim process are of secondary importance.

5.7.1 Process Description[1]

By-product hydrogen chloride is produced when chlorine is added to an organic compound such as benzene, toluene, and vinyl chloride. Hydrochloric acid is produced as a by-product of this reaction. An example of a process that generates hydrochloric acid as a by-product is the direct chlorination of benzene. In this process benzene, chlorine, hydrogen, air, and some trace catalysts are the raw materials that produce chlorobenzene. The gases from the reaction of benzene and chlorine consist of hydrogen chloride, benzene, chlorobenzenes, and air. These gases are first scrubbed in a packed tower with a chilled mixture of monochlorobenzene and dichlorobenzene to condense and recover any benzene or chlorobenzene. The hydrogen chloride is then absorbed in a falling film absorption plant.

5.7.2 Emissions

The recovery of the hydrogen chloride from the chlorination of an organic compound is the major source of hydrogen chloride emissions. The exit gas from the absorption or scrubbing system is the actual source of the hydrogen chloride emitted. Emission factors for hydrochloric acid produced as by-product hydrogen chloride are presented in Table 5.7-1.

Table 5.7-1. EMISSION FACTORS FOR HYDROCHLORIC ACID MANUFACTURING[a]
EMISSION FACTOR RATING: B

Type of process	Hydrogen chloride emissions	
	lb/ton	kg/MT
By-product hydrogen chloride		
With final scrubber	0.2	0.1
Without final scrubber	3	1.5

[a]Reference 1.

Reference for Section 5.7

1. Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes. U.S. DHEW, PHS, CPEHS, National Air Pollution Control Administration. Durham, N.C. Publication Number AP-54. September 1969.

5.8 HYDROFLUORIC ACID

5.8.1 Process Description[1-3]

Nearly all of the hydrofluoric acid, or hydrogen fluoride, currently produced in the United States is manufactured by the reaction of acid-grade fluorospar with sulfuric acid in the reaction:

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

CaF_2	H_2SO_4	$CaSO_4$	HF
Calcium Fluoride (Fluorospar)	Sulfuric Acid	Calcium Sulfate (Anhydrite)	Hydrogen Fluoride (Hydrofluoric Acid)

The fluorospar typically contains 97.5 percent or more calcium fluoride, 1 percent or less silicon dioxide (SiO_2), and 0.05 percent or less sulfur, with calcium carbonate ($CaCO_3$) as the principal remainder. See Figure 5.8-1 for a typical process flow diagram.

The reaction to produce the acid is endothermic and is usually carried out in externally heated horizontal rotary kilns for 30 to 60 minutes at 390 to 480°F (200-250°C). Dry fluorospar and a slight excess of sulfuric acid are fed continuously to the front end of the kiln. Anhydrite is removed through an air lock at the opposite end. The gaseous reaction products - hydrogen fluoride, excess sulfuric acid from the primary reaction, silicon tetrafluoride, sulfur dioxide, carbon dioxide, and water produced in secondary reactions - are removed from the front end of the kiln with entrained particulate materials. The particulates are removed from the gas stream by a dust separator, and the sulfuric acid and water are removed by a precondenser. The hydrogen fluoride vapors are condensed in refrigerant condensers and are delivered to an intermediate storage tank. The uncondensed gases are passed through a sulfuric acid absorption tower to remove most of the remaining hydrogen fluoride, which is also delivered with the residual sulfuric acid to the intermediate storage tank. The remaining gases are passed through water scrubbers, where the silicon tetrafluoride and remaining hydrogen fluoride are recovered as fluosilicic acid (H_2SiF_6). The hydrogen fluoride and sulfuric acid are delivered to distillation columns, where the hydrofluoric acid is extracted at 99.98 percent purity. Weaker concentrations (typically 70-80 percent) are prepared by dilution with water.

5.8.2 Emissions and Controls[1,2,4]

Air polluting emissions are suppressed to a great extent by the condensing, scrubbing and absorption equipment used in the recovery and purification of the hydrofluoric and fluosilicic acid products. Particulate material in the process gas stream is controlled by a dust separator near the outlet of the kiln and is recycled to the kiln for further

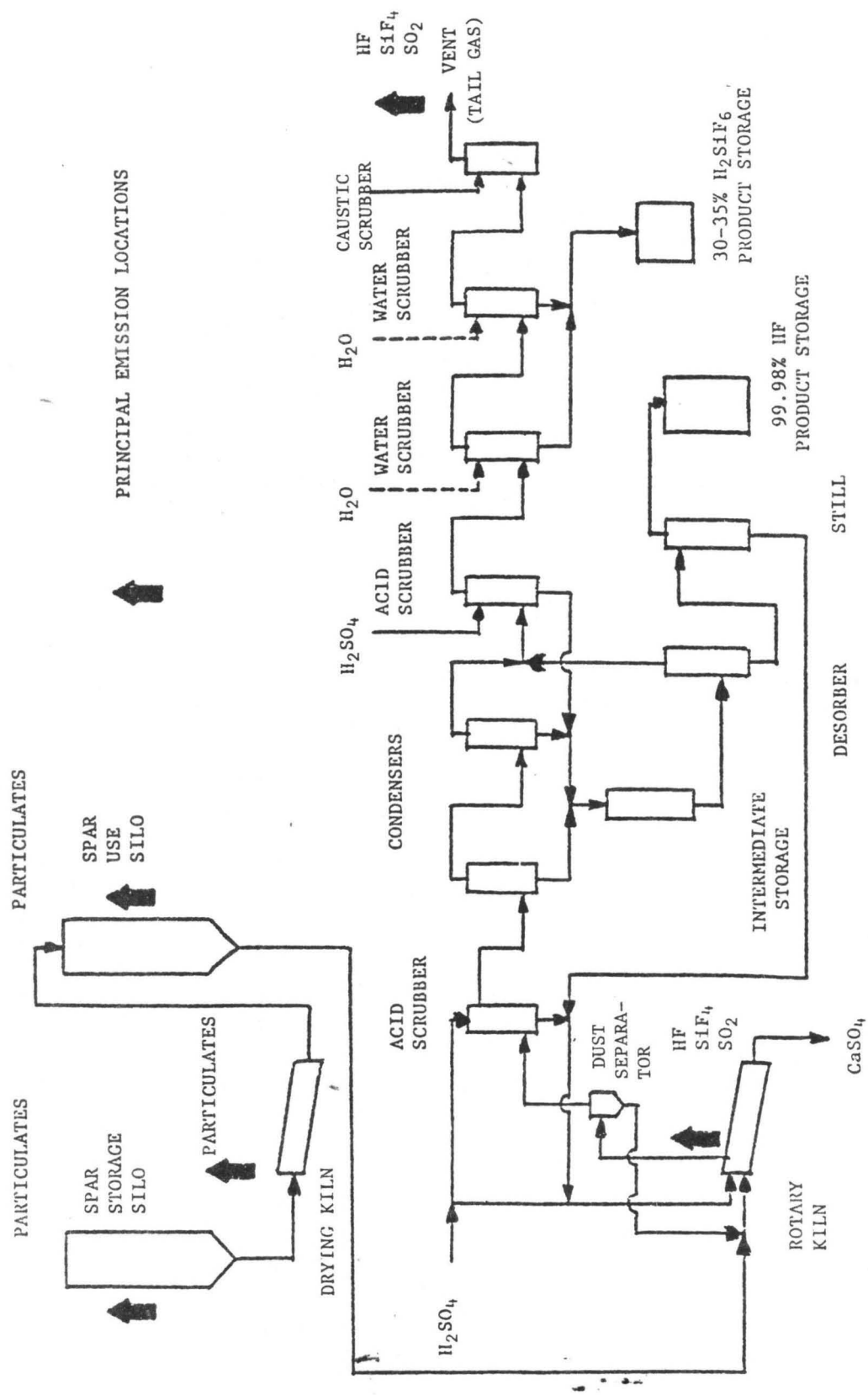


Figure 5.8-1. Process flow diagram of a typical hydrofluoric acid plant.

Table 5.8-1. EMISSION FACTORS FOR HYDROFLUORIC ACID MANUFACTURE

Type of Operation and Control	Control efficiency (%)	Emissions				Emission Factor Rating
		Gases		Particulates (Spar)		
		lb/ton acid	kg/MT acid	lb/ton Fluorospar	kg/MT Fluorospar	
Spar drying[a]						
Uncontrolled	0			75.0	37.5	C
Fabric filter	99			0.8	0.4	
Spar handling silos[b]						
Uncontrolled	0			60.0	30.0	D
Fabric filter	99			0.6	0.3	
Transfer operations						
Uncontrolled	0			6.0	3.0	E
Covers, additives	80			1.2	0.6	
Tail gas[c]						
Uncontrolled	0	25.0 (HF) 30.0 (SiF_4) 45.0 (SO_2)	12.5 (HF) 15.0 (SiF_4) 22.5 (SO_2)			D
Caustic scrubber	99	0.2 (HF) 0.3 (SiF_4) 0.5 (SO_2)	0.1 (HF) 0.2 (SiF_4) 0.3 (SO_2)			

[a] Reference 1. Averaged from information provided by four plants. Hourly fluorospar input calculated from reported 1975 year capacity, assuming stoichiometric amount of calcium fluoride and 97.5% content in fluorospar. Hourly emission rates calculated from reported baghouse controlled rates. Values averaged were:

Plant	1975 capacity	Emissions lb/Ton Fluorospar
1	15,000 ton HF	106
2	20,000 ton HF	130
3	50,000 ton HF	42
4	11,000 ton HF	30

[b] Information as in Note a. Four plants averaged for silo emissions, two plants for transfer operations emissions.

[c] Information as in Note a. Three plants averaged. HF and SiF_4 emission factors verified by information in Reference 4.

processing. The precondenser removes water vapor and sulfuric acid mist, and the condenser, acid scrubber and water scrubbers remove all but small amounts of hydrogen fluoride, silicon tetrafluoride, sulfur dioxide and carbon dioxide from the tail gas. A caustic scrubber is employed to reduce further the levels of these pollutants in the tail gas.

Dust emissions result from the handling and drying of the fluorospar, and they are controlled with bag filters at the spar storage silos and drying kilns, their principal emission points.

Hydrogen fluoride emissions are minimized by maintaining a slight negative pressure in the kiln during normal operations. Under upset conditions, a standby caustic scrubber or a bypass to the tail gas caustic scrubber are used to control hydrogen fluoride emissions from the kiln.

Fugitive dust emissions from spar handling and storage are controlled with flexible coverings and chemical additives.

Table 5.8-1 lists the emission factors for the various process operations. The principal emission locations are shown in the process flow diagram, Figure 5.8-1.

References for Section 5.8

1. Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture, EPA-450/3-78-109, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1978.

2. "Hydrofluoric Acid", Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 9, Interscience Publishers, New York, 1965.

3. W. R. Rogers and K. Muller, "Hydrofluoric Acid Manufacture", Chemical Engineering Progress, 59:5:85-8, May 1963.

4. J. M. Robinson, et al., Engineering and Cost Effectiveness Study of Fluoride Emissions Control, Vol. 1, PB 207 506, National Technical Information Service, Springfield, VA, 1972.

5.9 NITRIC ACID

5.9.1 Process Description

Weak Acid Production[1] - Nearly all the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (Figure 5.9-1). This process typically consists of three steps, each of which corresponds to a distinct chemical reaction. First, a 1:9 ammonia/air mixture is oxidized at high temperature (1380 - 1470°F or 750 - 800°C) as it passes through a platinum/rhodium catalyst, according to the reaction:

$$\underset{\text{Ammonia}}{4NH_3} + \underset{\text{Oxygen}}{5O_2} \rightarrow \underset{\text{Nitric oxide}}{4NO} + \underset{\text{Water}}{6H_2O} \qquad (1)$$

After the process stream is cooled to 100°F (38°C) or less by passage through a cooler/condenser, the nitric oxide reacts with residual oxygen to form nitrogen dioxide:

$$2NO + O_2 \rightarrow \underset{\text{Nitrogen dioxide}}{2NO_2} \rightleftarrows \underset{\text{Nitrogen tetroxide}}{N_2O_4} \qquad (2)$$

Finally, the gases are introduced into a bubble cap plate absorption column for contact with a countercurrent stream of water. The exothermic reation that occurs is:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

The production of nitric oxide in Reaction 3 necessitates the introduction of a secondary air stream into the column to oxidize it into nitrogen dioxide, thereby perpetuating the absorption operation.

In the past, nitric acid plants have been operated at a single pressure, ranging from 14.7 to 176 pounds per square inch (100 - 1200 kPa). However, since Reaction 1 is favored by low pressures and Reactions 2 and 3 are favored by higher pressures, newer plants tend to be operating two pressure systems, incorporating a compressor between the oxidizer and the condenser.

The spent gas flows from the top of the absorption tower to an entrainment separator for acid mist removal, through a heat exchanger in the ammonia oxidation unit for energy absorption by the ammonia stream, through an expander for energy recovery, and finally to the stack. In most plants, however, the tail gas is treated to remove residual nitrogen oxides before release to the atmosphere.

High Strength Acid Production[1] - The nitric acid concentration process consists of feeding strong sulfuric acid and 50 - 70 percent nitric acid to the top of a packed dehydrating column at approximately atmospheric pressure. The acid mixture flows downward counter to ascending vapors. Concentrated nitric acid leaves the top of the column as 98

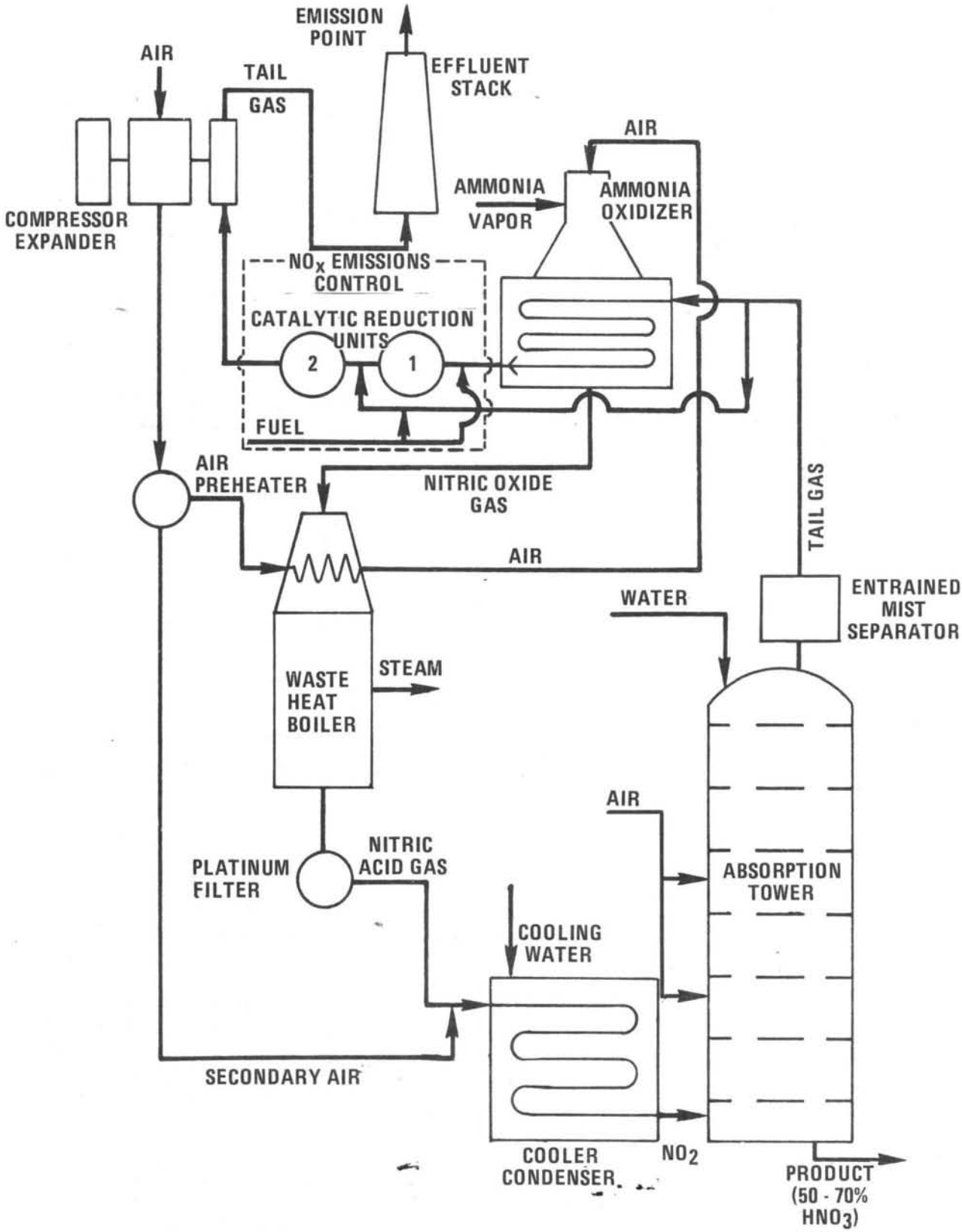


Figure 5.9-1. Flow diagram of typical nitric acid plant using pressure process (high strength acid unit not shown).

percent vapor, containing a small amount of NO_2 and O_2 from dissociation of nitric acid. The concentrated acid vapor leaves the column and goes to a bleacher and countercurrent condenser system to effect the condensation of strong nitric acid and the separation of oxygen and nitrogen oxide byproducts. These byproducts then flow to an absorption column where the nitric oxide mixes with auxiliary air to form NO_2, which is recovered as weak nitric acid. Unreacted gases are vented to the atmosphere from the top of the absorption column.

TABLE 5.9-1. NITROGEN OXIDE EMISSIONS FROM NITRIC ACID PLANTS[a]

EMISSION FACTOR RATING: B

Source	Control Efficiency, %	Emissions lb/ton Acid	Emissions kg/MT Acid
Weak Acid Plant Tail Gas			
Uncontrolled[b]	0	43 (14 - 86)	22 (7 - 43)
Catalytic reduction			
Natural gas[b]	99.1	0.4 (0.05 - 1.2)	0.2 (0.03 - 0.6)
Hydrogen[c]	97 - 99.8	0.8 (0 - 1.5)	0.4 (0 - 0.8)
Natural gas/hydrogen (25%/75%)[d]	98 - 98.5	1.0 (0.8 - 1.1)	0.5 (0.4 - 0.6)
Extended absorption[b]	95.8	1.8 (0.8 - 2.7)	0.9 (0.4 - 1.4)
High Strength Acid Plant[e]	NA[f]	10	5

[a]Based on 100% acid. Production rates are in terms of total weight of product (water and acid). A plant producing 500 tons (454 MT)/day of 55 wt. % nitric acid is calculated as producing 275 tons (250 MT)/day of 100% acid. Ranges in parentheses. NA: Not Applicable.

[b]Reference 3. Based on a study of 18 plants.

[c]References 1 and 2. Based on data from 2 plants with these process conditions: production rate, 130 tons (118 MT)/day at 100% rated capacity; absorber exit temperature, 90°F (32°C); absorber exit pressure, 87 psig (600 kPa); acid strength, 57%.

[d]References 1 and 2. Based on data from 2 plants with these process conditions: production rate, 208 tons (188 MT)/day at 100% rated capacity; absorber exit temperature, 90°F (32°C); absorber exit presure, 80 psig (550 kPa); acid strength, 57%.

[e]References 1 and 2. Based on a unit that produces 3000 lb/hr (6615 kg/hr) at 100% rated capacity, of 98% nitric acid.

The two most common techniques used to control absorption tower tail gas emissions are extended absorption and catalytic reduction. The extended absorption technique reduces emissions by increasing the efficiency of the absorption tower. This efficiency increase is achieved by increasing the number of absorber trays, operating the absorber at higher pressures, or cooling the weak acid liquid in the absorber.

In the catalytic reduction process (often termed catalytic oxidation), tail gases are heated to ignition temperature, mixed with fuel (natural gas, hydrogen, carbon monoxide or ammonia) and passed over a catalyst. In the presence of the catalyst, the fuels are oxidized, and the nitrogen oxides are reduced to N_2. The extent of reduction of NO_2 and NO to N_2 is a function of plant design, fuel type operating temperature and pressure, space velocity through the reduction catalytic reactor, type of catalyst, and reactant concentration. See Table 5.9-1.

Two seldom used alternative control devices for absorber tail gas are molecular sieves and wet scrubbers. In the molecular sieve technique, tail gas is contacted with an active molecular sieve which catalyticly oxidizes NO to NO_2 and selectively adsorbs the NO_2. The NO_2 is then thermally stripped from the molecular sieve and returned to the absorber. In the scrubbing technique, absorber tail gas is scrubbed with an aqueous solution of alkali hydroxides or carbonates, ammonia, urea or potassium permanganate. The NO and NO_2 are absorbed and recovered as nitrate or nitrite salts.

Comparatively small amounts of nitrogen oxides are also lost from acid concentrating plants. These losses (mostly NO_2) are from the condenser system, but the emissions are small enough to be controlled easily by inexpensive absorbers.

Acid mist emissions do not occur from the tail gas of a properly operated plant. The small amounts that may be present in the absorber exit gas streams are removed by a separator or collector prior to entering the catalytic reduction unit or expander.

Emissions from acid storage tanks may occur during tank filling. The displaced gases are equal in volume to the quantity of acid added to the tanks.

Nitrogen oxide emissions (expressed as NO_2) are presented for weak nitric acid plants in Table 5.9-1. The emission factors vary considerably with the type of control employed and with process conditions. For comparison purposes, the EPA New Source Performance Standard for both new and modified plants is 3.0 pounds per ton (1.5 kg/MT) of 100 percent acid produced, maximum 3 hour average, expressed as NO_2.

5.9.2 Emissions and Controls[1]

Emissions from nitric acid manufacture consist primarily of nitric oxide, nitrogen dioxide (which accounts for visible emissions) and trace amounts of nitric acid mist. By far, the major source of nitrogen oxides is the tail gas from the acid absorption tower (Table 5.9-1). In general, the quantity of NO_x emissions is directly related to the kinetics of the nitric acid formation reaction and absorption tower design.

The two most common techniques used to control absorption tower tail gas emissions are extended absorption and catalytic reduction. The extended absorption technique reduces emissions by increasing the efficiency of the absorption tower. This efficiency increase is achieved by increasing the number of absorber trays, operating the absorber at higher pressures, or cooling the weak acid liquid in the absorber.

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new and modified plants is 3.0 pounds per ton (1.5 kg/MT) of 100 percent acid produced, maximum 3 hour average, expressed as NO_2.

References for Section 5.9

1. Control of Air Pollution from Nitric Acid Plants, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1971. Unpublished.

2. Atmospheric Emissions from Nitric Acid Manufacturing Processes, 999-AP-27, U.S. Department of Health, Education and Welfare, Cincinnati, OH, 1966.

3. Marvin Drabkin, A Review of Standards of Performance for New Stationary Sources - Nitric Acid Plants, EPA-450/3-79-013, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1979.

4. "Standards of Performance for Nitric Acid Plants", 40 CFR 60. G.

5.10 PAINT AND VARNISH

5.10.1 Paint Manufacturing[1]

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 the physical processes of weighing, mixing, grinding, tinting, thinning, and packaging take place; no chemical reactions are involved.

These processes take place in large mixing tanks at approximately room temperature.

The primary factors affecting emissions from paint manufacture are care in handling dry pigments, types of solvents used, and mixing temperature.[2,3] About 1 or 2 percent of the solvents is lost even under well-controlled conditions. Particulate emissions amount to 0.5 to 1.0 percent of the pigment handled.[4]

5.10.2 Varnish Manufacturing[1-3]

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. Varnish is cooked in either open or enclosed gas-fired kettles for periods of 4 to 16 hours at temperatures of 200 to 650°F (93 to 340°C).

Varnish cooking emissions, largely in the form or organic compounds, depend on the cooking temperatures and times, the solvent used, the degree of tank enclosure, and the type of air pollution controls used. Emissions from varnish cooking range from 1 to 6 percent of the raw material.

To reduce hydrocarbons from the manufacture of paint and varnish, control techniques include condensers and/or adsorbers on solvent-handling operations, and scrubbers and afterburners on cooking operations. Emission factors for paint and varnish are shown in Table 5.10-1.

Table 5.10-1. EMISSION FACTORS FOR PAINT AND VARNISH MANUFACTURING WITHOUT CONTROL EQUIPMENT[a,b]
EMISSION FACTOR RATING: C

Type of product	Particulate		Hydrocarbons[c]	
	lb/ton pigment	kg/MT pigment	lb/ton of product	kg/MT pigment
Paint	2	1	30	15
Varnish				
Bodying oil	–	–	40	20
Oleoresinous	–	–	150	75
Alkyd	–	–	160	80
Acrylic	–	–	20	10

[a]References 2 and 4 through 8.
[b]Afterburners can reduce gaseous hydrocarbon emissions by 99 percent and particulates by about 90 percent. A water spray and oil filter system can reduce particulates by about 90 percent.[5]
[c]Expressed as undefined organic compounds whose composition depends upon the type of varnish or paint.

References for Section 5.10

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Stenburg, R.L. Atmospheric Emissions from Paint and Varnish Operations. Paint Varn. Prod. p. 61-65 and 111-114, September 1959.

3. Private Communication between Resources Research, Incorporated, and National Paint, Varnish and Lacquer Association. September 1969.

4. Unpublished engineering estimates based on plant visits in Washington, D.C. Resources Research, Incorporated. Reston, Va. October 1969.

5. Chatfield, H.E. Varnish Cookers. In: Air Pollution Engineering Manual. Danielson, J. A. (ed.). U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. Publication Number 999-AP-40. 1967. p. 688-695.

6. Lunche, E.G. et al. Distribution Survey of Products Emitting Organic Vapors in Los Angeles County. Chem. Eng. Progr. *53*. August 1957.

7. Communication on emissions from paint and varnish operations with G. Sallee, Midwest Research Institute. December 17, 1969.

8. Communication with Roger Higgins, Benjamin Moore Paint Company. June 25, 1968 .

5.11 PHOSPHORIC ACID

Phosphoric acid is produced by two principal methods, the wet process and the thermal process. The wet process is employed when the acid is to be used for fertilizer production. Thermal process phosphoric acid is of higher purity and is used in the manufacture of high grade chemical and food products.

5.11.1 Process Description[1,2]

5.11.1.1 Wet Process Acid Production - In modern wet process phosphoric acid plants, as shown in Figure 5.11-1, finely ground phosphate rock, which contains 31 to 35.5 percent phosphorus pentoxide (P_2O_5), is continuously fed into a reactor with sulfuric acid which decomposes the phosphate rock. In order to make the strongest phosphoric acid possible and to decrease later evaporation costs, 93 or 98 percent sulfuric acids are normally used. Because the proper ratio of acid to rock in the reactor must be maintained as closely as possible, precise automatic process control equipment is employed in the regulation of these two feed streams.

Gypsum crystals ($CaSO_4 \cdot 2H_2O$) are precipitated by the phosphate rock and sulfuric acid reaction. There is little market for the gypsum, so it is handled as waste, filtered out of the acid and sent to settling ponds. Approximately 0.7 acres of cooling and settling pond are required for every ton of daily P_2O_5 production.

Considerable heat is generated in the reactor, which must be removed. In older plants, this is done by blowing air over the hot slurry surface. Modern plants use vacuum flash cooling of part of the slurry, then sending it back into the reactor.

The reaction slurry is held in the reactor for periods of up to eight hours, depending on the rock and reactor design, and is then sent to be filtered. This produces a 32 percent acid solution, which generally needs concentrating for further use. Current practice is to concentrate it in two or three vacuum evaporators to about 54 percent P_2O_5.

5.11.1.2 Thermal Process Acid Production - Raw materials for the production of phosphoric acid by the thermal process are elemental (yellow) phosphorus, air and water. Thermal process phosphoric acid manufacture, as shown in Figure 5.11-2, typically involves three steps.

First, the liquid elemental phosphorus is burned (oxidized) in a combustion chamber at temperatures of 3000 to 5000°F (1650 - 2760°C) to form phosphorus pentoxide. Then, the phosphorus pentoxide is hydrated with dilute acid or water to produce phosphoric acid liquid and mist. The final step is to remove the phosphoric acid mist from the gas stream.

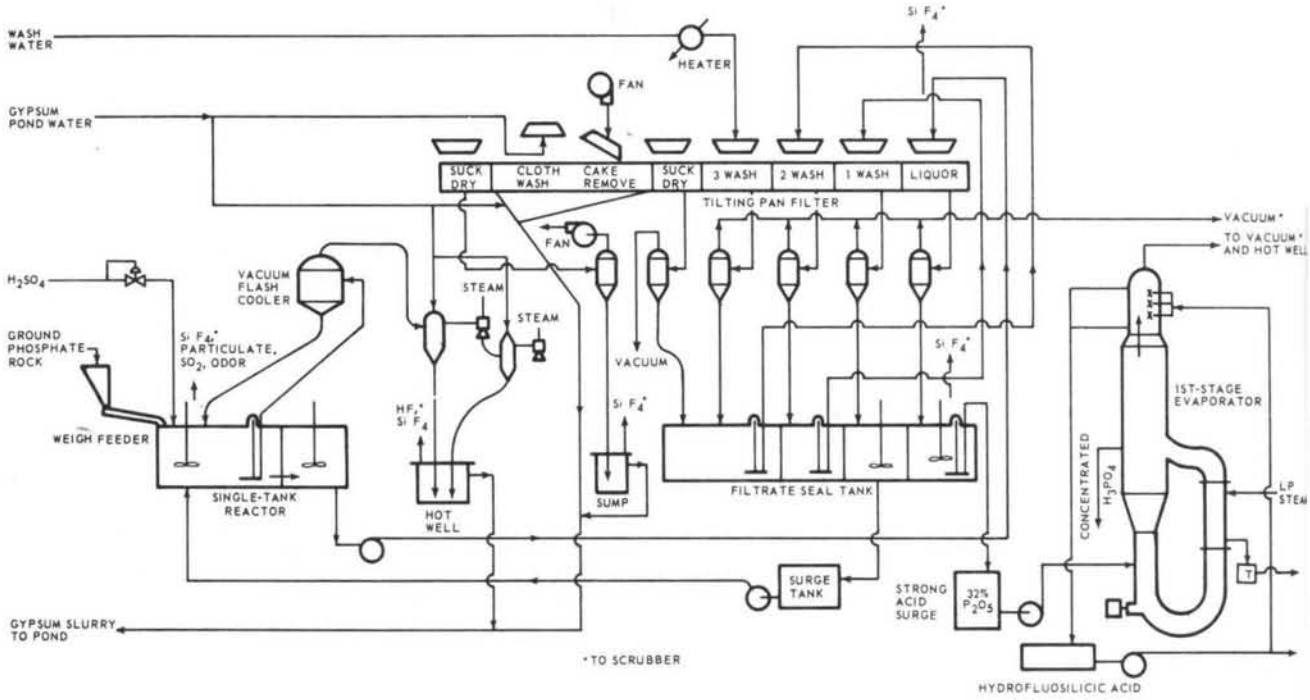


Figure 5.11-1. Flow diagram of wet process phosphoric acid plant.

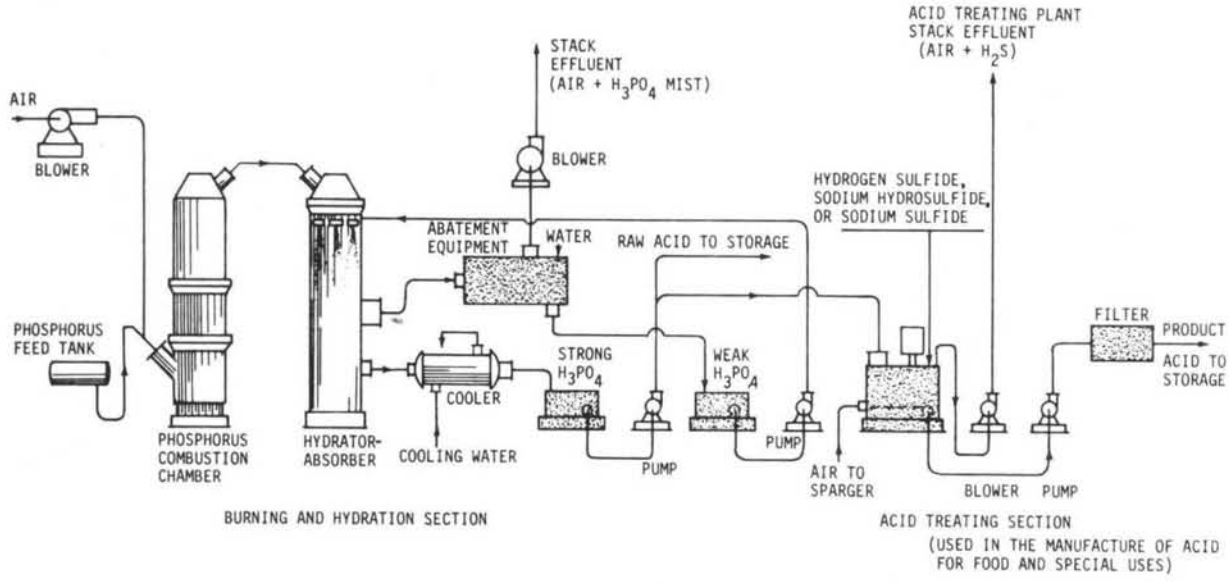


Figure 5.11-2. Flow diagram of thermal process phosphoric acid plant.

The reactions involved are:

$$P_4 + 5\ O_2 \rightarrow P_4O_{10}$$

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$$

Thermal process acid normally contains 75 to 85 percent phosphoric acid (H_3PO_4). In efficient plants, about 99.9 percent of the phosphorus burned is recovered as acid.

5.11.2 Emissions and Controls[1-3]

5.11.2.1 Wet Process Emissions and Controls - Gaseous fluorides, mostly silicon tetrafluoride and hydrogen fluoride, are the major emissions from wet process acid. Phosphate rock contains 3.5 to 4.0 percent fluorine, and the final distribution of this fluorine in wet process acid manufacture varies widely. In general, part of the fluorine goes with the gypsum, part with the phosphoric acid product, and the rest is vaporized in the reactor or evaporator. The proportions and amounts going with the gypsum and acid depend on the nature of the rock and process conditions. Disposition of the volatilized fluorine depends on the design and operation of the plant. Substantial amounts can pass off into the air, unless effective scrubbers are used. Some of the fluorine which is carried to the settling ponds with the gypsum will get into the atmosphere, once the pond water is saturated with fluorides.

The reactor, where phosphate rock is decomposed by sulfuric acid, is the main source of atmospheric contaminants. Fluoride emissions accompany the air used to cool the reactor slurry. Vacuum flash cooling has replaced the air cooling method to a large extent, since emissions are minimized in the closed system.

Acid concentration by evaporation provides another source of fluoride emissions. It has been estimated that 20 to 40 percent of the fluorine originally present in the rock vaporizes in this operation.

Total particulate emissions directly from process equipment were measured for one digester and for one filter. As much as 11 pounds of particulates per ton of P_2O_5 were produced by the digester, and approximately 0.2 pounds per ton of P_2O_5 were released by the filter. Of this particulate, 3 to 6 percent was fluorides.

Particulate emissions occurring from phosphate rock handling are covered in Section 8.18.

5.11.2.2 Thermal Process Emissions and Controls - The principal atmospheric emission from the thermal process is phosphoric acid mist (H_3PO_4) contained in the gas stream from the hydrator. The particle size of the acid mist ranges from 0.4 to 2.6 micrometers. It is not uncommon for as much as half of the total phosphorus pentoxide to be present as liquid phosphoric acid particles suspended in the gas stream.

Economical operation of the process demands that this potential loss be controlled, so all plants are equipped with some type of emission control equipment.

Control equipment commonly used in thermal process phosphoric acid plants includes venturi scrubbers, cyclonic separators with wire mesh mist eliminators, fiber mist eliminators, high energy wire mesh contactors, and electrostatic precipitators.

Table 5.11-1. EMISSION FACTORS FOR PHOSPHORIC ACID PRODUCTION

EMISSION FACTOR RATING: B

Source	Particulates[a]		Fluorine[b]	
	lb/ton	kg/MT	lb/ton	kg/MT
Wet Process				
Reactor, uncontrolled	-	-	56.4	28.2
Gypsum settling and cooling ponds[c]	-	-	1.12	0.56
Condenser, uncontrolled	-	-	61.2	30.6
Typical controlled emissions[d]	-	-	.02-.07	.01-.04
Thermal Process[e,f]				
Packed tower (95.5%)	2.14	1.07	-	-
Venturi scrubber (97.5%)	2.53	1.27	-	-
Glass fiber mist eliminator (96.0 - 99.9%)	0.69	0.35	-	-
Wire mesh mist eliminator (95.0%)	5.46	2.73	-	-
High pressure drop mist eliminator (99.9%)	0.11	0.06	-	-
Electrostatic precipitator (98 - 99%)	1.66	0.83	-	-

[a] Acid mist particulates (0.4 - 2.6 μm).
[b] References 1 and 3. Pounds of fluorine (as gaseous fluorides) per ton of P_2O_5 produced. Based on a material balance of fluorine from phosphate rock of 3.9% fluorine and 33% P_2O_5.
[c] Approximately 0.7 acres (0.3 hectares) of cooling and settling pond are required to produce 1 ton of P_2O_5 daily. Emissions in terms of pond area would be 1.60 lb/acre per day (1.79 kg/hectare per day).
[d] Reference 5.
[e] Reference 3. Pounds of particulate per ton of P_2O_5.
[f] Numbers in parentheses indicate the control efficiency associated with each device.

References for Section 5.11

1. Atmospheric Emissions from Wet Process Phosphoric Acid Manufacture, AP-57, National Air Pollution Control Administration, Raleigh, NC, April 1970.

2. Atmospheric Emissions from Thermal Process Phosphoric Acid Manufacture, AP-48, National Air Pollution Control Administration, Durham, NC, October 1968.

3. Control Techniques for Fluoride Emissions, Unpublished, U.S. Public Health Service, Research Triangle Park, NC, September 1970.

4. W.R. King, "Fluorine Air Pollution from Wet Process Phosphoric Acid Plants - Water Ponds", Doctoral Thesis, Supported by EPA Research Grant No. R-800950, North Carolina State University, Raleigh, NC, 1974.

5. Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1977.

5.12 PHTHALIC ANHYDRIDE

by Pam Canova

5.12.1 General[1]

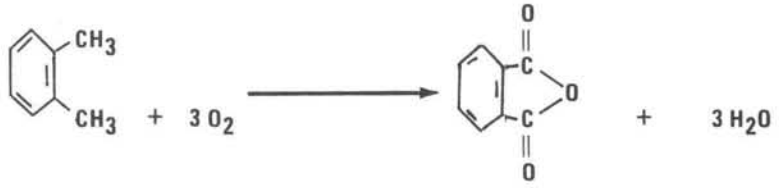
Phthalic anhydride (PAN) production in the United States in 1972 was 0.9 billion pounds per year; this total is estimated to increase to 2.2 billion pounds per year by 1985. Of the current production, 50 percent is used for plasticizers, 25 percent for alkyd resins, 20 percent for unsaturated polyester resins, and 5 percent for miscellaneous and exports. PAN is produced by catalytic oxidation of either ortho-xylene or naphthalene. Since naphthalene is a higher priced feedstock and has a lower feed utilization (about 1.0 lb PAN/lb o-xylene versus 0.97 lb PAN/lb naphthalene), future production growth is predicted to utilize o-xylene. Because emission factors are intended for future as well as present application, this report will focus mainly on PAN production utilizing o-xylene as the main feedstock.

The processes for producing PAN by o-xylene or naphthalene are the same except for reactors, catalyst handling, and recovery facilities required for fluid bed reactors.

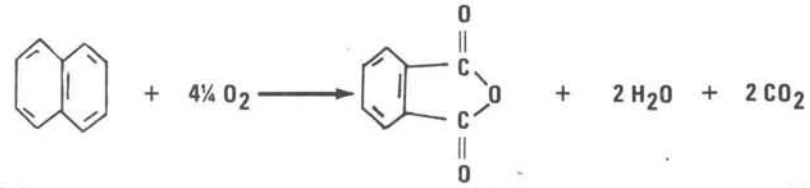
In PAN production using o-xylene as the basic feedstock, filtered air is preheated, compressed, and mixed with vaporized o-xylene and fed into the fixed-bed tubular reactors. The reactors contain the catalyst, vanadium pentoxide, and are operated at 650 to 725°F (340 to 385°C). Small amounts of sulfur dioxide are added to the reactor feed to maintain catalyst activity. Exothermic heat is removed by a molten salt bath circulated around the reactor tubes and transferred to a steam generation system.

Naphthalene-based feedstock is made up of vaporized naphthalene and compressed air. It is transferred to the fluidized bed reactor and oxidized in the presence of a catalyst, vanadium pentoxide, at 650 to 725°F (340 to 385°C). Cooling tubes located in the catalyst bed remove the exothermic heat which is used to produce high-pressure steam. The reactor effluent consists of PAN vapors, entrained catalyst, and various by-products and non-reactant gas. The catalyst is removed by filtering and returned to the reactor.

The chemical reactions for air oxidation of o-xylene and naphthalene are as follows.



o-xylene + oxygen → phthalic anhydride + water



naphthalene + oxygen → phthalic anhydride + water + carbon dioxide

The reactor effluent containing crude PAN plus products from side reactions and excess oxygen passes to a series of switch condensers where the crude PAN cools and crystallizes. The condensers are alternately cooled and then heated, allowing PAN crystals to form and then melt from the condenser tube fins.

The crude liquid is transferred to a pretreatment section in which phthalic acid is dehydrated to anhydride. Water, maleic anhydride, and benzoic acid are partially evaporated. The liquid then goes to a vacuum distillation section where pure PAN (99.8 wt. percent pure) is recovered. The product can be stored and shipped either as a liquid or a solid (in which case it is dried, flaked, and packaged in multi-wall paper bags). Tanks for holding liquid PAN are kept at 300°F (150°C) and blanketed with dry nitrogen to prevent the entry of oxygen (fire) or water vapor (hydrolysis to phthalic acid).

Maleic anhydride is currently the only by-product being recovered.

Figures 1 and 2 show the process flow for air oxidation of o-xylene and naphthalene, respectively.

5.12.2 Emissions and Controls[1]

Emissions from o-xylene and naphthalene storage are small and presently are not controlled.

The major contributor of emissions is the reactor and condenser effluent which is vented from the condenser unit. Particulate, sulfur oxides (for o-xylene-based production), and carbon monoxide make up the emissions, with carbon monoxide comprising over half the total. The most efficient (96 percent) system of control is the combined usage of a water scrubber and thermal incinerator. A thermal incinerator alone is approximately 95 percent efficient in combustion of pollutants for o-xylene-based production, and 80 percent efficient for naphthalene-based production. Thermal incinerators with steam generation show the same efficiencies as thermal incinerators alone. Scrubbers have a 99 percent efficiency in collecting particulates, but are practically ineffective in reducing carbon monoxide emissions. In naphthalene-based production, cyclones can be used to control catalyst dust emissions with 90 to 98 percent efficiency.

Pretreatment and distillation emissions—particulates and hydrocarbons—are normally processed through the water scrubber and/or incinerator used for the main process stream (reactor and condenser) or scrubbers alone, with the same efficiency percentages applying.

Product storage in the liquid phase results in small amounts of gaseous emissions. These gas streams can either be sent to the main process vent gas control devices or first processed through sublimation boxes or devices used to recover escaped PAN. Flaking and bagging emissions are negligible, but can be sent to a cyclone for recovery of PAN dust. Exhaust from the cyclone presents no problem.

Table 5.12-1 gives emission factors for controlled and uncontrolled emissions from the production of PAN.

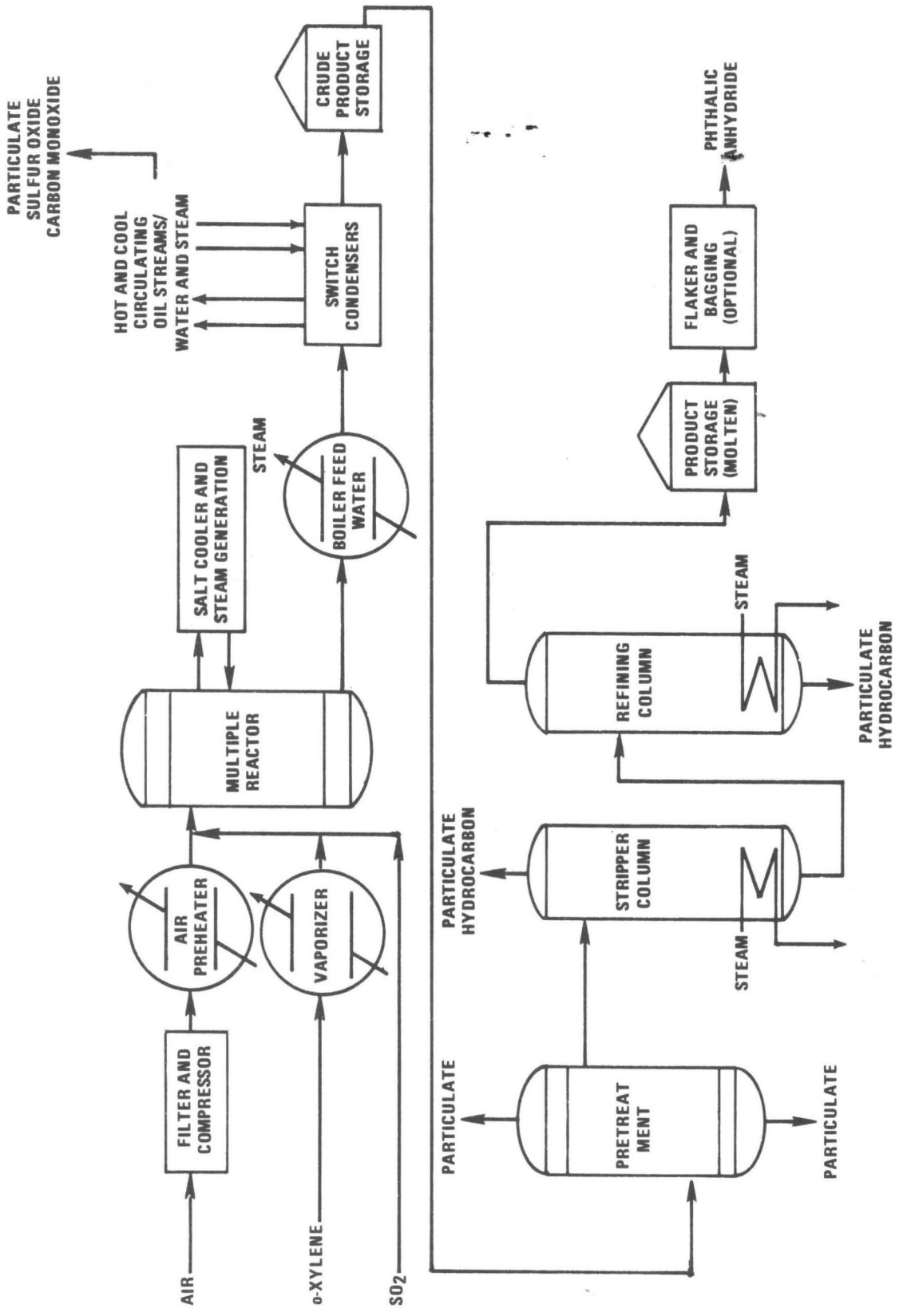


Figure 5.12-1. Flow diagram for phthalic anhydride using o-xylene as basic feedstock.[1]

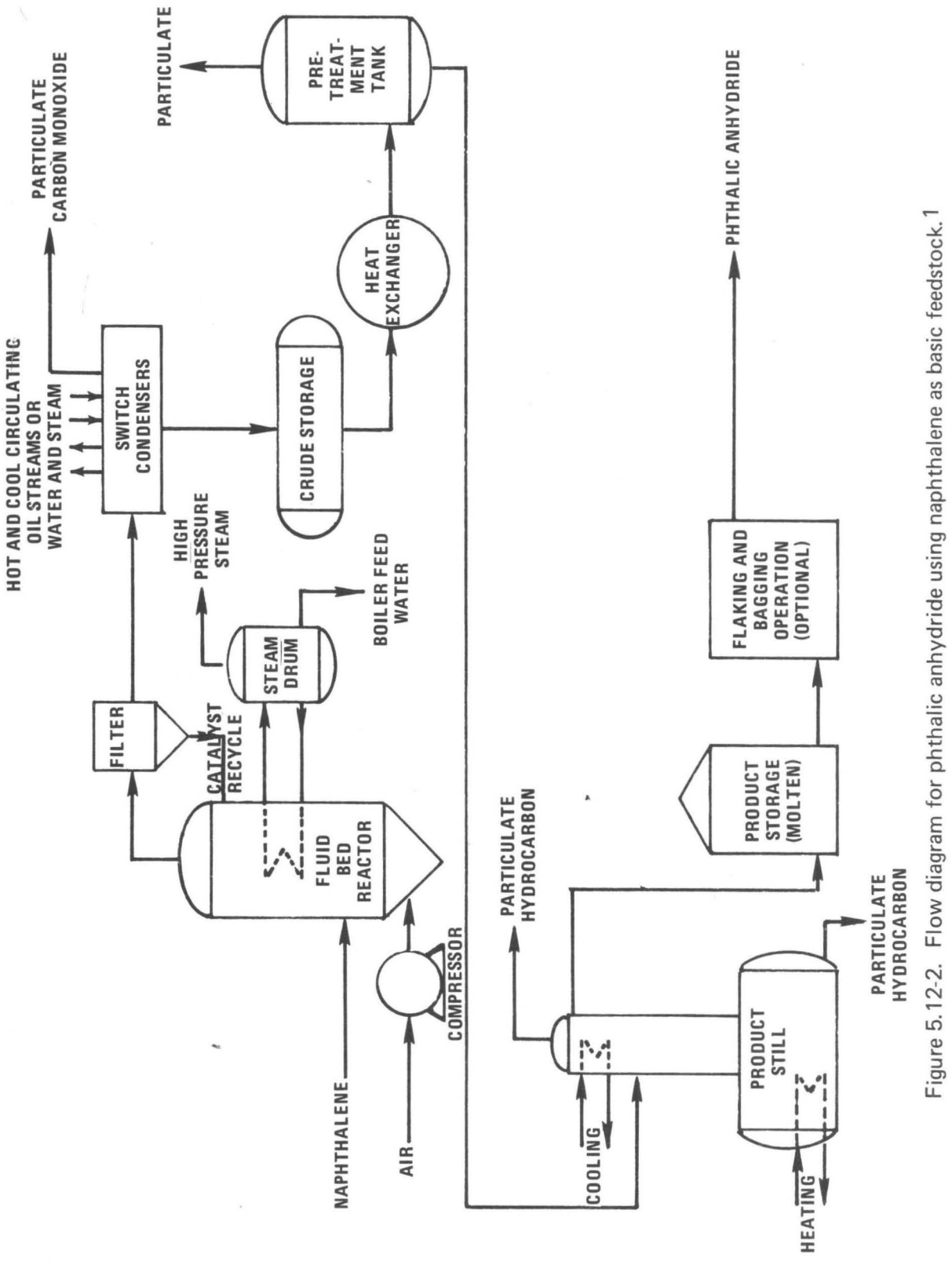


Figure 5.12-2. Flow diagram for phthalic anhydride using naphthalene as basic feedstock.[1]

Table 5.12-1. EMISSION FACTORS FOR PHTHALIC ANHYDRIDE[1,a]
EMISSION FACTOR RATING: B

Process	Particulate		SO_x		HC		CO	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Oxidation of o-xylene[b]								
Main process stream[c]								
Uncontrolled	138[d]	69[d]	9.4[e]	4.7[e]	0	0	301	151
W/scrubber and thermal incinerator	6	3	9.4	4.7	0	0	12	6
W/thermal incinerator	7	4	9.4	4.7	0	0	15	8
W/incinerator with steam generator	7	4	9.4	4.7	0	0	15	8
Pretreatment								
Uncontrolled	13[f]	6.4[f]	0	0	0	0	0	0
W/scrubber and thermal incinerator	0.5	0.3	0	0	0	0	0	0
W/thermal incinerator	0.7	0.4	0	0	0	0	0	0
Distillation								
Uncontrolled	89[d]	45[d]	0	0	2.4	1.2	0	0
W/scrubber and thermal incinerator	4	2	0	0	<0.1	<0.1	0	0
W/thermal incinerator	4	2	0	0	0.1	<0.1	0	0
Oxidation of naphthalene[b]								
Main process stream[c]								
Uncontrolled	569[i]	289[i]	0	0	0	0	100	50
W/thermal incinerator	11	6	0	0	0	0	20	10
W/scrubber	0.6	0.3	0	0	0	0	100	50
Pretreatment								
Uncontrolled	5[h]	2.5[h]	0	0	0	0	0	0
W/thermal incinerator	1	0.5	0	0	0	0	0	0
W/scrubber	<0.1	<0.1	0	0	0	0	0	0
Distillation								
Uncontrolled	389	199	0	0	10	5	0	0
W/thermal incinerator	8	4	0	0	2	1	0	0
W/scrubber	0.4	0.2	0	0	0.1	<0.1	0	0

[a]Emission factors are in units of pounds of pollutant per ton (kilogram of pollutant per metric ton) of phthalic anhydride produced.

[b]Control devices listed are those currently being used by phthalic anhydride plants.

[c]Main process stream includes the reactor and multiple switch condensers as vented through the condenser unit.

[d]Particulate consists of phthalic anhydride, maleic anhydride, and benzoic acid.

[e]Emissions change with catalyst age. Value shown corresponds to relatively fresh catalyst. Can be 19 to 25 lb/ton (9.5 to 13 kg/MT) for aged catalyst.

[f]Particulate consists of phthalic anhydride and maleic anhydride.

[g]Particulate consists of phthalic anhydride, maleic anhydride, and naphthaquinone.

[h]Particulate is phthalic anhydride.

[i]Particulate does not include catalyst dust which is controlled by cyclones with an efficiency of 90 to 98 percent.

Reference for Section 5.12

1. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Vol 7: Phthalic Anhydride Manufacture from Ortho-Xylene. Houdry Division, Air Products and Chemicals, Inc., Marcus Hook, Pa. Prepared for Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-450/3-73-006-g. July 1975.

5.13 PLASTICS

5.13.1 Process Description[1]

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 noncrystalline solids. The manufacture of the basic monomer is not considered part of the plastics industry and is usually accomplished at a chemical or petroleum plant.

The manufacture of most plastics involves an enclosed reaction or polymerization step, a drying step, and a final treating and forming step. These plastics are polymerized or otherwise combined in completely enclosed stainless steel or glass-lined vessels. Treatment of the resin after polmerization varies with the proposed use. Resins for moldings are dried and crushed or ground into molding powder. Resins such as the alkyd resins that are 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.

5.13.2 Emissions and Controls[1]

The major sources of air contamination in plastics manufacturing are the emissions of raw materials or monomers, emissions of solvents or other volatile liquids during the reaction, emissions of sublimed solids such as phthalic anhydride in alkyd production, and emissions of solvents during storage and handling of thinned resins. Emission factors for the manufacture of plastics are shown in Table 5.13-1.

Table 5.13-1. EMISSION FACTORS FOR PLASTICS MANUFACTURING WITHOUT CONTROLS[a]
EMISSION FACTOR RATING: E

Type of plastic	Particulate		Gases	
	lb/ton	kg/MT	lb/ton	kg/MT
Polyvinyl chloride	35[b]	17.5[b]	17[c]	8.5[c]
Polypropylene	3	1.5	0.7[d]	0.35[d]
General	5 to 10	2.5 to 5	–	–

[a]References 2 and 3.
[b]Usually controlled with a fabric filter efficiency of 98 to 99 percent.
[c]As vinyl chloride.
[d]As propylene.

Much of the control equipment used in this industry is 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 that vent to a flare system, and recovery systems on vacuum exhaust lines.

References for Section 5.13

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Unpublished data from industrial questionnaire. U.S. DHEW, PHS, National Air Pollution Control Administration, Division of Air Quality and Emissions Data. Durham, N.C. 1969.

3. Private Communication between Resources Research, Incorporated, and Maryland State Department of Health, Baltimore, Md. November 1969.

5.14 PRINTING INK

5.14.1 Process Description[1]

There are four major classes of printing ink: letterpress and lithographic inks, commonly called oil or paste inks; and flexographic and rotogravure inks, which are referred to as solvent inks. These inks vary considerably in physical appearance, composition, method of application, and drying mechanism. 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.[2]

There are three general processes in the manufacture of printing inks: (1) cooking the vehicle and adding dyes, (2) grinding of a pigment into the vehicle using a roller mill, and (3) replacing water in the wet pigment pulp by an ink vehicle (commonly known as the flushing process).[3] The ink "varnish" or vehicle is generally cooked in large kettles at 200° to 600°F (93° to 315°C) for an average of 8 to 12 hours in much the same way that regular varnish is made. Mixing of the pigment and vehicle is done in dough mixers or in large agitated tanks. Grinding is most often carried out in three-roller or five-roller horizontal or vertical mills.

5.14.2 Emissions and Controls[1,4]

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. At about 350°F (175°C) 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 occuring just after the maximum temperature has been reached. Emissions from the cooking phase can be reduced by more than 90 percent with the use of scrubbers or condensers followed by afterburners.[4,5]

Compounds emitted from the cooking of oleoresinous varnish (resin plus varnish) include water vapor, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils, terpenes, and carbon dioxide. Emissions of thinning solvents used in flexographic and rotogravure inks may also occur.

The quantity, composition, and rate of emissions from ink manufacturing depend upon the cooking temperature and time, the ingredients, the method of introducing additives, the degree of stirring, and the extent of air or inert gas blowing. Particulate emissions resulting from the addition of pigments to the vehicle are affected by the type of pigment and its particle size. Emission factors for the manufacture of printing ink are presented in Table 5.14-1.

Table 5.14-1. EMISSION FACTORS FOR PRINTING INK MANUFACTURING[a]
EMISSION FACTOR RATING: E

Type of process	Gaseous organic[b]		Particulates	
	lb/ton of product	kg/MT of product	lb/ton of pigment	kg/MT of pigment
Vehicle cooking				
General	120	60	–	–
Oils	40	20	–	–
Oleoresinous	150	75	–	–
Alkyds	160	80	–	–
Pigment mixing	–	–	2	1

[a]Based on data from section on paint and varnish.
[b]Emitted as gas, but rapidly condense as the effluent is cooled.

References for Section 5.14

1. Air Pollutant Emission Factors. Final Report. Resources Research Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Shreve, R. N. Chemical Process Industries, 3rd Ed. New York, McGraw Hill Book Co. 1967. p. 454-455.

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5. Private communication with Interchemical Corporation, Ink Division. Cincinnati, Ohio. November 10, 1969.

5.15 SOAP AND DETERGENTS

5.15.1 Soap Manufacture[1]

The manufacture of soap entails the catalytic hydrolysis of various fatty acids with sodium or potassium hydroxide to form a glycerol-soap mixture. This mixture is separated by distillation, then neutralized and blended to produce soap. 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. Control of these odors may be achieved by scrubbing all exhaust fumes and, if necessary, incinerating the remaining compounds. Odors emanating from the spray drier may be controlled by scrubbing with an acid solution.

5.15.2 Detergent Manufacture[1]

The manufacture of detergents generally begins with the sulfuration by sulfuric acid of a fatty alcohol or linear alkylate. The sulfurated compound is then neutralized with caustic solution (NaOH), and various dyes, perfumes, and other compounds are added.[2,3] The resulting paste or slurry is then sprayed under pressure into a vertical drying tower where it is dried with a stream of hot air (400° to 500°F or 204° to 260°C). The dried detergent is then cooled and packaged. The main source of particulate emissions is the spray-drying tower. Odors may also be emitted from the spray-drying operation and from storage and mixing tanks. Particulate emissions from spray-drying operations are shown in Table 5.15-1.

Table 5.15-1. PARTICULATE EMISSION FACTORS FOR SPRAY-DRYING DETERGENTS[a]
EMISSION FACTOR RATING: B

Control device	Overall efficiency, %	Particulate emissions	
		lb/ton of product	kg/MT of product
Uncontrolled	–	90	45
Cyclone[b]	85	14	7
Cyclone followed by:			
Spray chamber	92	7	3.5
Packed scrubber	95	5	2.5
Venturi scrubber	97	3	1.5

[a]Based on analysis of data in References 2 through 6.
[b]Some type of primary collector, such as a cyclone, is considered an integral part of the spray-drying system.

References for Section 5.15

1. Air Pollutant Emission Factors. Final Report. Resources Research Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Phelps, A.H. Air Pollution Aspects of Soap and Detergent Manufacture. J. Air Pol. Control Assoc. *17*(8):505-507, August 1967.

3. Shreve, R.N. Chemical Process Industries. 3rd Ed. New York, McGraw-Hill Book Company. 1967. p. 544-563.

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5. McCormick, P.Y., R.L. Lucas, and D.R. Wells. Gas-Solid Systems. In: Chemical Engineer's Handbook. Perry, J.H. (ed.). New York, McGraw-Hill Book Company. 1963. p. 59.

6. Private communication with Maryland State Department of Health, Baltimore, Md. November 1969.

5.16 SODIUM CARBONATE (Soda Ash)

5.16.1 Process Description[1]

Soda ash is manufactured by three processes: (1) the natural or Lake Brine process, (2) the Solvay process (ammonia-soda), and (3) the electrolytic soda-ash process. Because the Solvay process accounts for over 80 percent of the total production of soda ash, it will be the only one discussed in this section.

In the Solvay process, the basic raw materials are ammonia, coke, limestone (calcium carbonate), and salt (sodium chloride). The salt, usually in the unpurified form of a brine, is first purified in a series of absorbers by precipitation of the heavy metal ions with ammonia and carbon dioxide. In this process sodium bicarbonate is formed. This bicarbonate coke is heated in a rotary kiln, and the resultant soda ash is cooled and conveyed to storage.

5.16.2 Emissions

The major source of emissions from the manufacture of soda ash is the release of ammonia. Small amounts of ammonia are emitted in the gases vented from the brine purification system. Intermittent losses of ammonia can also occur during the unloading of tank trucks into storage tanks. The major sources of dust emissions include rotary dryers, dry solids handling, and processing of lime. Dust emissions of fine soda ash also occur from conveyor transfer points and air classification systems, as well as during tank-car loading and packaging. Emission factors are summarized in Table 5.16-1.

Table 5.16-1. EMISSION FACTORS FOR SODA-ASH PLANTS WITHOUT CONTROLS
EMISSION FACTOR RATING: D

Type of source	Particulates		Ammonia	
	lb/ton	kg/MT	lb/ton	kg/MT
Ammonia recovery[a,b]	–	–	7	3.5
Conveying, transferring, loading, etc.[c]	6	3	–	–

[a] Reference 2.
[b] Represents ammonia loss following the recovery system.
[c] Based on data in References 3 through 5.

References for Section 5.16

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Shreve, R.N. Chemical Process Industries, 3rd Ed. New York, McGraw-Hill Book Company. 1967. p. 225-230.

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5.17 SULFURIC ACID

5.17.1 General

All sulfuric acid is made by either the lead chamber process or the contact process. Because the contact process accounts for more than 97 percent of the total sulfuric acid production in the United States, it is the only process discussed in this Section. Contact plants are generally classified according to the raw materials charged to them - (1) elemental sulfur burning, (2) spent acid and hydrogen sulfide burning, and (3) sulfide ores and smelter gas burning. The contributions from these plants to the total acid production are 68, 18.5 and 13.5 percent respectively.

All contact processes incorporate three basic operations, each of which corresponds to a distinct chemical reaction. First, the sulfur in the feedstock is burned to sulfur dioxide:

$$\underset{\text{Sulfur}}{S} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Sulfur dioxide}}{SO_2} \qquad (1)$$

Then, the sulfur dioxide is catalytically oxidized to sulfur trioxide:

$$\underset{\text{Sulfur dioxide}}{2SO_2} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Sulfur trioxide}}{2SO_3} \qquad (2)$$

Finally, the sulfur trioxide is absorbed in a strong aqueous solution of sulfuric acid:

$$\underset{\text{Sulfur trioxide}}{SO_3} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Sulfuric acid}}{H_2SO_4} \qquad (3)$$

Elemental Sulfur Burning Plants[1,2] - Elemental sulfur, such as Frasch process sulfur from oil refineries, is melted, settled or filtered to remove ash and is fed into a combustion chamber. The sulfur is burned in clean air that has been dried by scrubbing with 93 - 99 percent sulfuric acid. The gases from the combustion chamber cool and then enter the solid catalyst (vanadium pentoxide) converter. Usually, 95 - 98 percent of the sulfur dioxide from the combustion chamber is converted to sulfur trioxide, with an accompanying large evolution of heat. After being cooled, the converter exit gas enters an absorption tower, where the sulfur trioxide is absorbed with 98 - 99 percent sulfuric acid. The sulfur trioxide combines with the water in the acid and forms more sulfuric acid.

If oleum, a solution of uncombined SO_3 in H_2SO_4, is produced, SO_3 from the converter is first passed to an oleum tower that is fed with 98 percent acid from the absorption system. The gases

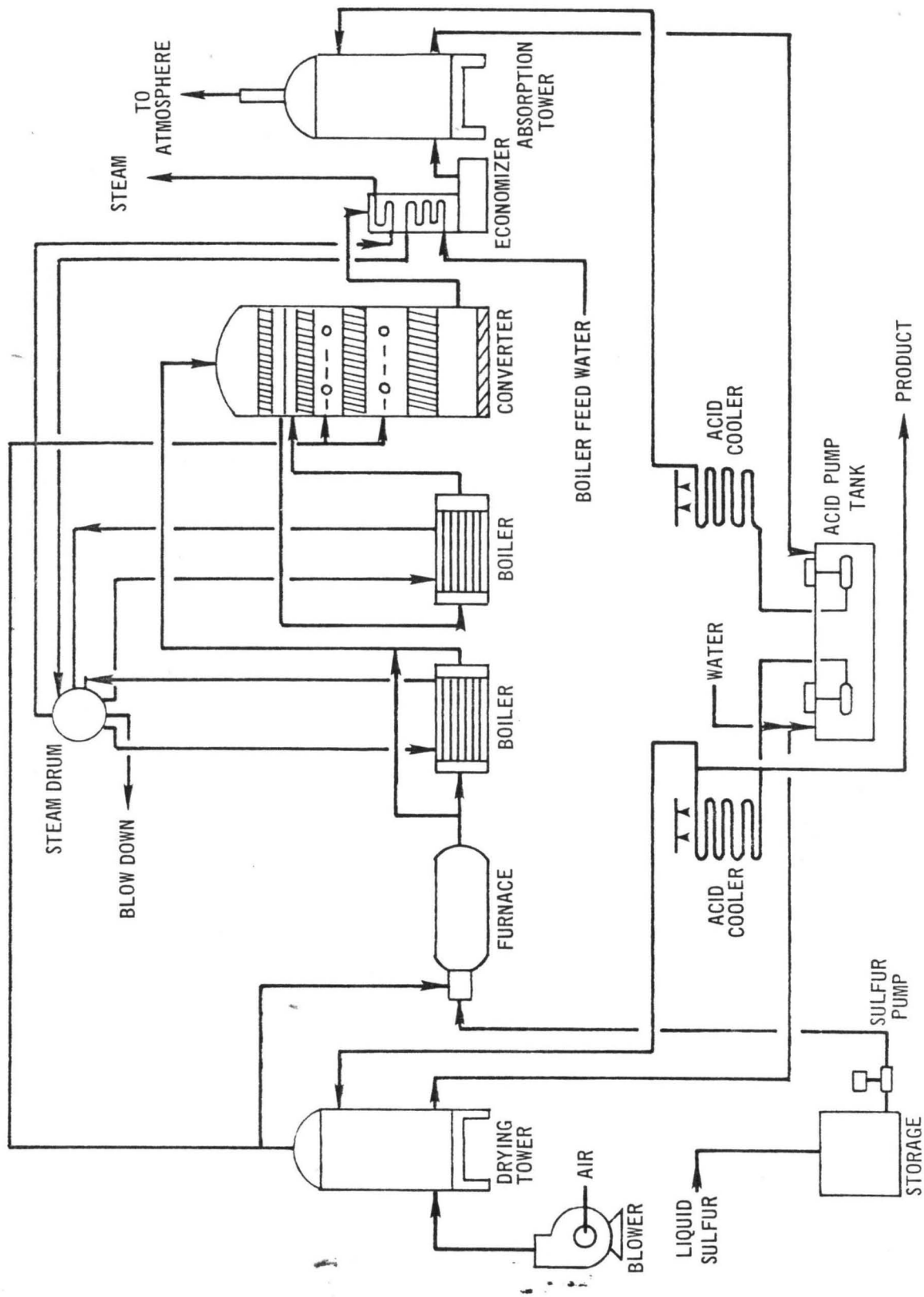

Figure 5.17-1. Basic flow diagram of contact process sulfuric acid plant burning elemental sulfur.

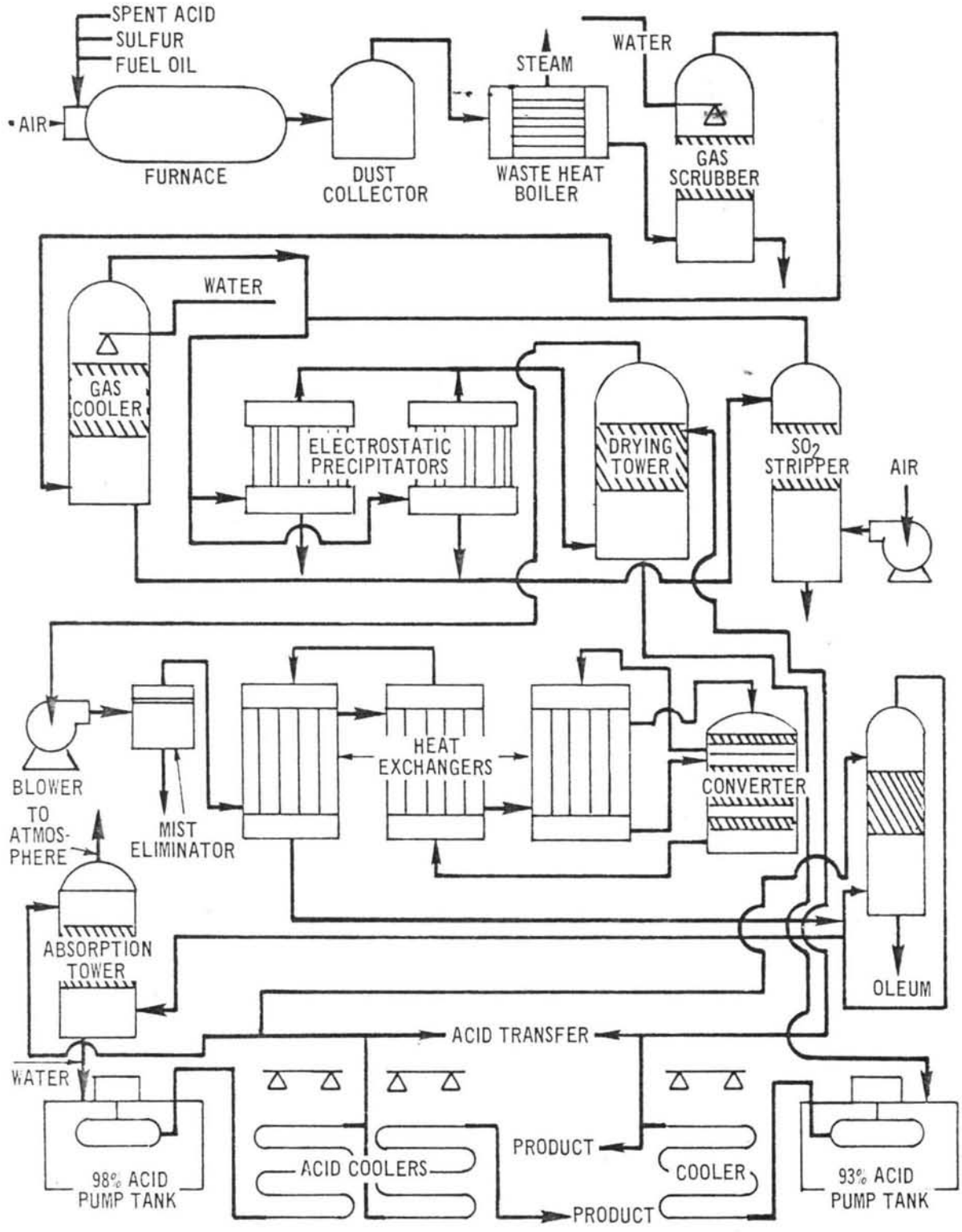

Figure 5.17-2. Basic flow diagram of contact process sulfuric acid plant burning spent acid.

from the oleum tower are then pumped to the absorption column where the residual sulfur trioxide is removed.

A schematic diagram of a contact process sulfuric acid plant that burns elemental sulfur is shown in Figure 5.17-1.

Spent Acid and Hydrogen Sulfide Burning Plants[1,2] - Two types of plants are used to process this type of sulfuric acid. In one, the sulfur dioxide and other combustion products from the combustion of spent acid and/or hydrogen sulfide with undried atmospheric air are passed through gas cleaning and mist removal equipment. The gas stream next passes through a drying tower. A blower draws the gas from the drying tower and discharges the sulfur dioxide gas to the sulfur trioxide converter. A schematic diagram of a contact process sulfuric acid plant that burns spent acid is shown in Figure 5.17-2.

In a "wet gas plant", the wet gases from the combustion chamber are charged directly to the converter with no intermediate treatment. The gas from the converter flows to the absorber, through which 93 - 98 percent sulfuric acid is circulating.

Sulfide Ores and Smelter Gas Plants - The configuration of this type of plant is essentially the same as that of a spent acid plant (Figure 5.17-2), with the primary exception that a roaster is used in place of the combustion furnace.

The feed used in these plants is smelter gas, available from such equipment as copper converters, reverberatory furnaces, roasters and flash smelters. The sulfur dioxide in the gas is contaminated with dust, acid mist and gaseous impurities. To remove the impurities, the gases must be cooled and passed through purification equipment consisting of cyclone dust collectors, electrostatic dust and mist precipitators, and scrubbing and gas cooling towers. After the gases are cleaned and the excess water vapor is removed, they are scrubbed with 98 percent acid in a drying tower. Beginning with the drying tower stage, these plants are nearly identical to the elemental sulfur plants shown in Figure 5.17-1.

5.17.2 Emissions and Controls

Sulfur Dioxide[1-3] - Nearly all sulfur dioxide emissions from sulfuric acid plants are found in the exit gases. Extensive testing has shown that the mass of these SO_2 emissions is an inverse function of the sulfur conversion efficiency (SO_2 oxidized to SO_3). This conversion is always incomplete, and is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentrations of the reactants (sulfur dioxide and oxygen). For example, if the inlet SO_2 concentration to the converter were 8 percent by volume (a representative value), and the conversion temperature were 473°C (883°F), the conversion efficiency would be 96 percent. At this conversion, the

uncontrolled emission factor for SO_2 would be 27.5 kg/Mg (55 pounds per ton) of 100 percent sulfuric acid produced, as shown in Table 5.17-1. For purposes of comparison, note that the Environmental Protection Agency performance standard for new and modified plants is 2 kg/Mg (4 pounds per ton) of 100 percent acid produced, maximum 2 hour average.[3] As Table 5.17-1 and Figure 5.17-3 indicate, achieving this standard requires a conversion efficiency of 99.7 percent in an uncontrolled plant or the equivalent SO_2 collection mechanism in a controlled facility. Most single absorption plants have SO_2 conversion efficiencies ranging from 95 - 98 percent.

In addition to exit gases, small quantities of sulfur oxides are emitted from storage tank vents and tank car and tank truck vents during loading operations, from sulfuric acid concentrators, and through leaks in process equipment. Few data are available on the quantity of emissions from these sources.

Of the many chemical and physical means for removing SO_2 from gas streams, only the dual absorption and the sodium sulfite/bisulfite scrubbing processes have been found to increase acid production without yielding unwanted byproducts.

TABLE 5.17-1. EMISSION FACTORS FOR SULFURIC ACID PLANTS[a]

EMISSION FACTOR RATING: A

Conversion of SO_2 to SO_3 (%)	SO_2 Emissions	
	kg/Mg of 100% H_2SO_4	lb/ton of 100% H_2SO_4
93	48.0	96
94	41.0	82
95	35.0	70
96	27.5	55
97	20.0	40
98	13.0	26
99	7.0	14
99.5	3.5	7
99.7	2.0	4
100	0.0	0

[a] Reference 1.
[b] This linear interpolation formula can be used for calculating emission factors for conversion efficiencies between 93 and 100%: emission factor = 13.65 (% conversion efficiency) + 1365.

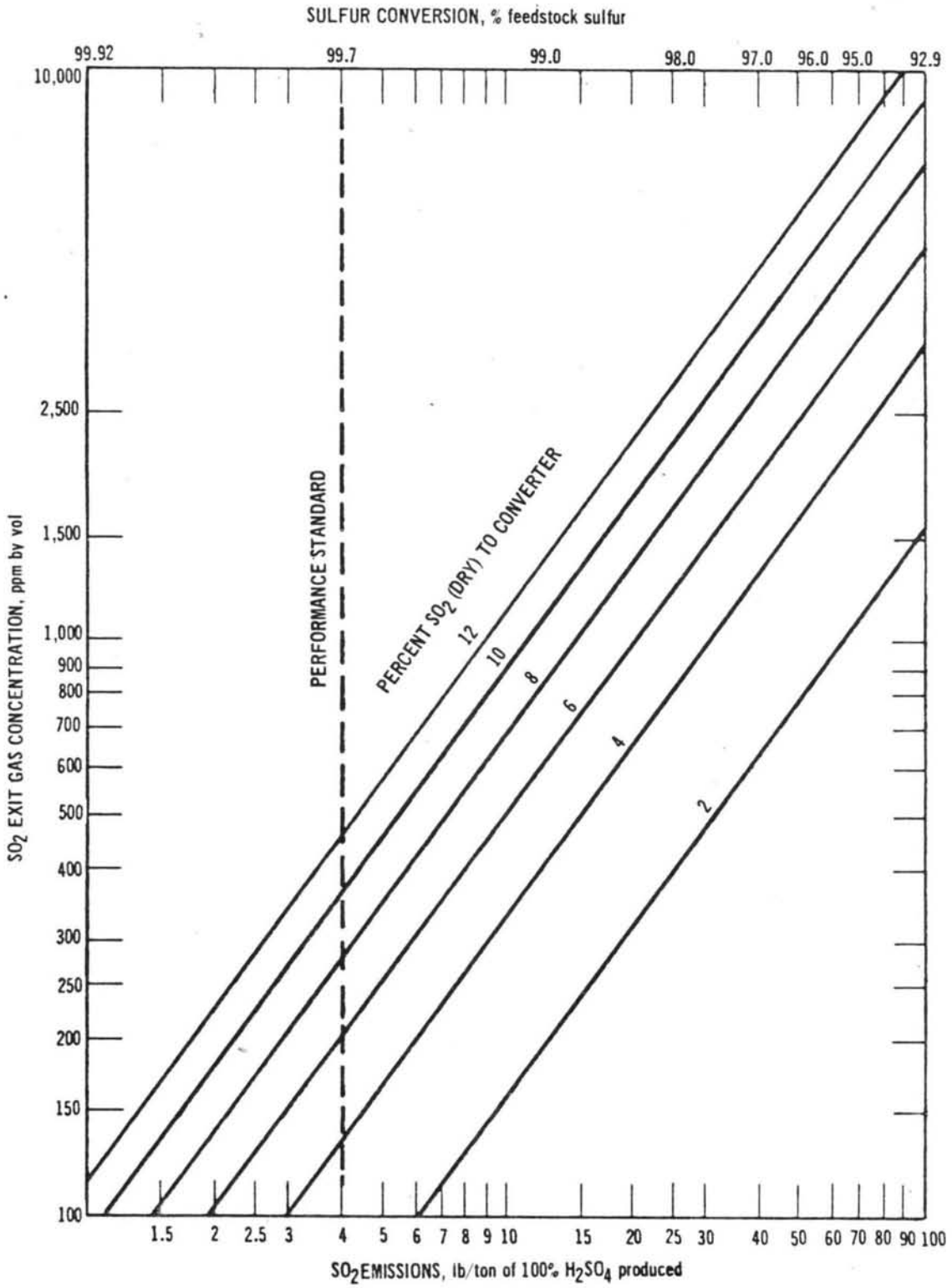

Figure 5.17-3. Sulfuric acid plant feedstock sulfur conversion versus volumetric and mass SO_2 emissions at various inlet SO_2 concentrations by volume.

In the dual absorption process, the SO_3 gas formed in the primary converter stages is sent to a primary absorption tower where most of the SO_3 is removed to form H_2SO_4. The remaining unconverted sulfur dioxide is forwarded to the final stages in the converter to remove much of the remaining SO_2 by oxidation to SO_3, from whence it is sent to the secondary absorber for final sulfur trioxide removal. The result is the conversion of a much higher fraction of SO_2 to SO_3 (a conversion of 99.7 percent or higher, on the average, which meets the performance standard). Furthermore, dual absorption permits higher converter inlet sulfur dioxide concentrations than are used in single absorption plants, because the secondary conversion stages effectively remove any residual sulfur dioxide from the primary absorber.

Where dual absorption reduces sulfur dioxide emissions by increasing the overall conversion efficiency, the sodium sulfite/bisulfite scrubbing process removes sulfur dioxide directly from the absorber exit gases. In one version of this process, the sulfer dioxide in the waste gas is absorbed in a sodium sulfite solution, is separated, and is recycled to the plant. Test results from a 680 Mg (750 ton per day) plant equipped with a sulfite scrubbing system indicated an average SO_2 emission factor of 1.35 kg/Mg (2.7 pounds per ton) of 100 percent acid.

Acid Mist[1-3] - Nearly all the acid mist emitted from sulfuric acid manufacturing can be traced to the absorber exit gases. Acid mist is created when sulfur trioxide combines with water vapor at a temperature below the dew point of sulfur trioxide. Once formed within the process system, this mist is so stable that only a small quantity can be removed in the absorber.

In general, the quantity and particle size distribution of acid mist are dependent on the type of sulfur feedstock used, the strength of acid produced, and the conditions in the absorber. Because it contains virtually no water vapor, bright elemental sulfur produces little acid mist when burned. However, the hydrocarbon impurities in other feedstocks - dark sulfur, spent acid and hydrogen sulfide - oxidize to water vapor during combustion. The water vapor, in turn, combines with sulfur trioxide as the gas cools in the system.

The strength of acid produced - whether oleum or 99 percent sulfuric acid - also affects mist emissions. Oleum plants produce greater quantities of finer more stable mist. For example, uncontrolled mist emissions from oleum plants burning spent acid range from 0.5 to 5.0 kg/Mg (1.0 to 10.0 pounds per ton), while those from 98 percent acid plants burning elemental sulfur range from 0.2 to 2.0 kg/Mg (0.4 to 4.0 pounds per ton). Furthermore, 85 - 95 weight percent of the mist particles from oleum plants are less than 2 microns in diameter, compared with only 30 weight percent that are less than 2 microns in diameter from 98 percent acid plants.

The operating temperature of the absorption column directly affects sulfur trioxide absorption and, accordingly, the quality of acid mist formed after exit gases leave the stack. The optimum absorber operating temperature depends on the strength of the acid produced, throughput rates, inlet sulfur trioxide concentrations, and other variables peculiar to each individual plant. Finally, it should be emphasized that the percentage conversion of sulfur trioxide has no direct effect on acid mist emissions. In Table 5.17-2, uncontrolled acid mist emissions are presented for various sulfuric acid plants.

TABLE 5.17-2. ACID MIST EMISSION FACTORS[a] FOR SULFURIC ACID PLANTS WITHOUT CONTROLS[a]

EMISSIONS FACTOR RATING: B

Raw material	Oleum produced, % total output	Emissions[b]	
		kg/Mg acid	lb/ton acid
Recovered sulfur	0 to 43	0.175 - 0.4	0.35 - 0.8
Bright virgin sulfur	0	0.85	1.7
Dark virgin sulfur	33 to 100	0.16 - 3.15	0.32 - 6.3
Sulfide ores	0 to 25	0.6 - 3.7	1.2 - 7.4
Spent acid	0 to 77	1.1 - 1.2	2.2 - 2.4

[a] Reference 1.

[b] Emissions are proportional to the percentage of oleum in the total product. Use low end of ranges for low oleum percentage and high end of ranges for high oleum percentage.

Two basic types of devices, electrostatic precipitators and fiber mist eliminators, effectively reduce the acid mist concentration from contact plants to less than the EPA New Source Performance Standard, which is 0.075 kg/Mg (0.15 pound per ton) of acid. Precipitators, if properly maintained, are effective in collecting the mist particles at efficiencies up to 99 percent (see Table 5.17-3).

The three most commonly used fiber mist eliminators are the vertical tube, vertical panel, and horizontal dual pad types. They differ from one another in the arrangement of the fiber elements, which are composed of either chemically resistant glass or fluorocarbon, and in the means employed to collect the trapped liquid. The operating characteristics of these three types are compared with electrostatic precipitators in Table 5.17-3.

TABLE 5.17-3. EMISSION COMPARISON AND COLLECTION EFFICIENCY OF TYPICAL ELECTROSTATIC PRECIPITATOR AND FIBER MIST ELIMINATORS[a]

	Particle size collection efficiency, %		Acid mist emissions			
			98% acid plants[b]		Oleum plants	
Control device	>3 μm	≤3μm	kg/Mg	lb/ton	kg/Mg	lb/ton
Electrostatic precipitator	99	100	0.05	0.10	0.06	0.12
Fiber mist eliminator						
Tabular	100	95-99	0.01	0.02	0.01	0.02
Panel	100	90-98	0.05	0.10	0.05	0.10
Dual pad	100	93-99	0.055	0.11	0.055	0.11

[a] Reference 2.
[b] Based on manufacturers' generally expected results. Calculated for 8% SO_2 concentration in gas converter.

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2. Unpublished report on control of air pollution from sulfuric acid plants, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1971.

3. Standards of Performance for New Stationary Sources, 36 FR 24875, December 23, 1971.

4. M. Drabkin and Kathryn J. Brooks, A Review of Standards of Performance for New Stationary Sources - Sulfuric Acid Plants, EPA Contract No. 68-02-2526, Mitre Corporation, McLean, VA, June 1978.

5. Final Guideline Document: Control of Sulfuric Acid Mist Emissions from Existing Sulfuric Acid Production Units, EPA 450/2-77-019, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1977.

5.18 SULFUR RECOVERY

5.18.1 Process Description [1,2]

Most of the elemental sulfur produced from hydrogen sulfide (H_2S) is made by the modified Claus process. A simplified flow diagram of this process is shown in Figure 5.18-1. The process consists of the multistage catalytic oxidation of hydrogen sulfide according to the following overall Reaction:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \quad (1)$$

In the first step, one third of the H_2S is reacted with air in a furnace and combusted to SO_2 according to Reaction (2):

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \quad (2)$$

The heat of the reaction is recovered in a waste heat boiler or sulfur condenser.

For gas streams with low concentrations of H_2S (20 - 60%), approximately one third of the gas stream is fed to the furnace and the H_2S is nearly completely combusted to SO_2, while the remainder of the gas is bypassed around the furnace. This is the "split stream" configuration. For gas streams with higher H_2S concentrations, the entire gas stream is fed to the furnace with just enough air to combust one third of the H_2S to SO_2. This is the "partial combustion" configuration. In this configuration, as much as 50 to 60 percent conversion of the hydrogen sulfide to elemental sulfur takes place in the initial reaction chamber by Reaction (1). In extremely low concentrations of H_2S (<25 - 30%), a Claus process variation known as "sulfur recycle" may be used, where product sulfur is recycled to the furnace and burned, raising the effective sulfur level where flame stability may be maintained in the furnaces.

After the reaction furnace, the gases are cooled to remove elemental sulfur and then reheated. The remaining H_2S in the gas stream is then reacted with the SO_2 over a bauxite catalyst at 500 - 600°F (260 - 316°C) to produce elemental sulfur according to Reaction 3:

$$2H_2S + SO_2 \rightleftarrows 3S + 2H_2O \quad (3)$$

Because this is a reversible reaction, equilibrium requirements limit the conversion. Lower temperatures favor elemental sulfur formation, but at too low a temperature, elemental sulfur fouls the catalyst. Because the reaction is exothermic, the conversion attainable in one stage is limited. Therefore, two or more stages are used in series, with interstage cooling to remove the heat of reaction and to condense the sulfur.

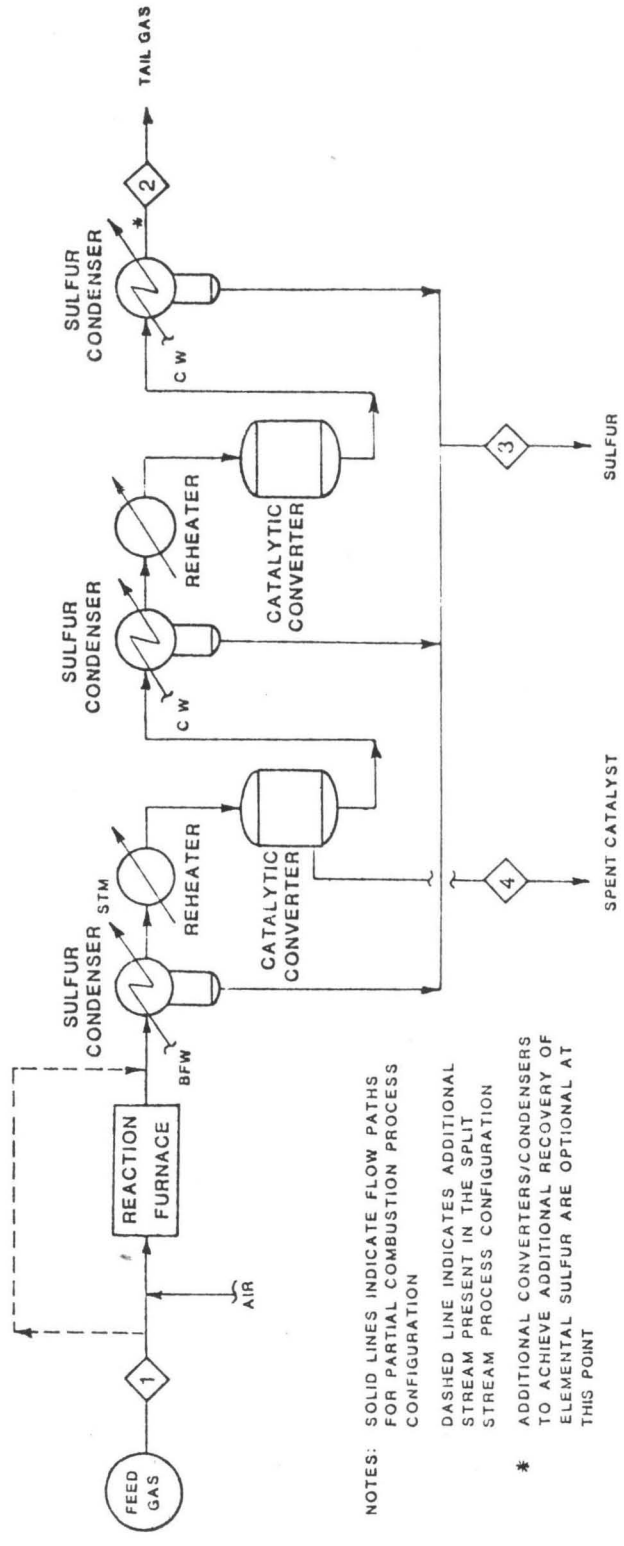

Figure 5.18-1. Typical flow diagram - Claus Process sulfur recovery.

Carbonyl sulfide (COS) and carbon disulfide (CS_2) are formed in the reaction furnace in the presence of carbon dioxide and hydrocarbons:

$$CO_2 + H_2S \rightleftarrows H_2O + COS \quad (4)$$

$$COS + H_2S \rightleftarrows H_2O + CS_2 \quad (5)$$

$$CH_4 + 4S \rightleftarrows CS_2 + 2H_2S \quad (6)$$

About 0.25 to 2.5 percent of the sulfur fed may be lost in this way. Additional sulfur may be lost as vapor, mist or droplets.

5.18.2 Emissions and Controls

Tail gas from a Claus sulfur recovery unit contains a variety of pollutants, including sulfur dioxide, hydrogen sulfide, other reduced sulfur compounds (such as COS and CS_2), carbon monoxide, and volatile organic compounds. If no other controls are used, the tail gas is incinerated, so that the emissions consist mostly of sulfur dioxide. Smaller amounts of carbon monoxide are also emitted.

The emissions of SO_2 (along with H_2S and sulfur vapor) depend directly on the sulfur recovery efficiency of the Claus plant. This efficiency is dependent upon many factors, including the following:

- Number of catalytic conversion stages
- Inlet feed stream composition
- Operating temperatures and catalyst maintenance
- Maintenance of the proper stoichiometric ratio of H_2S/SO_2
- Operating capacity factor

Recovery efficiency increases with the number of catalytic stages used. For example, for a Claus plant fed with 90 percent H_2S, sulfur recovery is approximately 85 percent for one catalytic stage and 95 percent for two or three stages.

Recovery efficiency also depends on the inlet feed stream composition. Sulfur recovery increases with increasing H_2S concentration in the feed stream. For example, a plant having two or three catalytic stages would have a sulfur recovery efficiency of approximately 90 percent when treating a 15 mole percent H_2S feed stream, 93 percent for a 50 mole percent H_2S stream, and 95 percent for a 90 mole percent H_2S stream. Various contaminants in the feed gas reduce Claus sulfur recovery efficiency. Organic compounds in the feed require extra air for combustion, and added water and inert gas from burning these organics decrease sulfur concentrations and thus lower sulfur recovery. Higher molecular weight organics also reduce efficiencies because of soot formation on the catalyst. High concentrations of CO_2 in the feed gas reduce catalyst life.

Since the Claus reactions are exothermic, sulfur recovery is enhanced by removing heat and operating the reactors at as low a temperature as practicable without condensing sulfur on the catalyst. Recovery efficiency also depends on catalyst performance. One to 2 percent loss in recovery efficiency over the period of catalyst life has been reported. Maintenance of the 2:1 stoichiometric ratio of H_2S and SO_2 is essential for efficient sulfur recovery. Deviation above or below this ratio results in a loss of efficiency. Operation of a Claus plant below capacity may also impair Claus efficiency somewhat.

Removal of sulfur compounds from Claus plant tail gas is possible by three general schemes:

1) Extension of the Claus reaction to increase overall sulfur recovery,

2) Conversion of sulfur gases to SO_2, followed by SO_2 removal technology,

3) Conversion of sulfur gases to H_2S, followed by H_2S removal technology.

Processes in the first scheme remove additional sulfur compounds by carrying out the Claus reaction at lower temperatures to shift equilibrium of the Claus reactions toward formation of additional sulfur. The IFP-1, BSR/Selectox, Sulfreen, and Amoco CBA processes use this technique to reduce the concentration of tail gas sulfur compounds to 1500 - 2500 ppm, thus increasing the sulfur recovery of the Claus plant to 99 percent.

In the second class of processes, the tail gas is incinerated to convert all sulfur compounds to SO_2. The SO_2 is then recovered by one of several processes, such as the Wellman-Lord. In the Wellman-Lord and certain other processes, the SO_2 absorbed from the tail gas is recycled to the Claus plant to recover additional sulfur. Processes in this class can reduce the concentration of sulfur compounds in the tail gas to 200 - 300 ppm or less, for an overall sulfur recovery efficiency (including the Claus plant) of 99.9+ percent.

The third method for removal of sulfur compounds from Claus tail gas involves converting the sulfur compounds to H_2S by mixing the tail gas with a reducing gas and passing it over a reducing catalyst. The H_2S is then removed, by the Stretford process (in the Beavon and Clean Air processes) or by an amine absorption system (SCOT process). The Beavon and Clean Air processes recover the H_2S as elemental sulfur, and the SCOT process produces a concentrated H_2S stream which is recycled to the Claus process. These processes reduce the concentration of sulfur compounds in the tail gas to 200 - 300 ppm or less and increase the overall recovery efficiency of the Claus plant to 99.9+ percent.

A New Source Performance Standard for Claus sulfur recovery plants in petroleum refineries was promulgated in March 1978. This standard limits emissions to 0.025 percent by volume (250 ppm) of SO_2 on a dry basis and at zero percent oxygen, or 0.001 percent by volume of H_2S and 0.03 percent by volume of H_2S, COS, and CS_2 on a dry basis and at zero percent oxygen.

Table 5.18-1. EMISSION FACTORS FOR MODIFIED CLAUS SULFUR RECOVERY PLANTS

EMISSION FACTOR RATING: D

Number of Catalytic Stages	Typical Recovery of Sulfur, %[a]	SO_2 Emissions[b] lb/ton	SO_2 Emissions[b] kg/MT
Two, uncontrolled	92 to 95	348 to 211	174 to 105
Three, uncontrolled	95 to 97.5	211 to 167	106 to 84
Four, uncontrolled	96 to 99	167 to 124	84 to 62
Controlled[c]	99 to 99.9	40 to 4	20 to 2

[a] Efficiencies are for feed gas streams with high H_2S concentrations. Gases with lower H_2S concentrations would have lower efficiencies. For example, a 2 or 3 stage plant could have a recovery efficiency of 95% for a 90% H_2S stream, 93% for 50% H_2S, and 90% for 15% H_2S.

[b] Based on net weight of pure sulfur produced. The range in emission fractors corresponds to the range in percentage recovery of sulfur. SO_2 emissions calculated from percentage sulfur recovery by following equation:

$$SO_2 \text{ emissions (kg/MT)} = \frac{(100 - \% \text{ recovery})}{\% \text{ recovery}} \times 2000$$

[c] Lower percent recovery is for control by extended Claus, and higher percent is for conversion to and removal of H_2S or SO_2.

References for Section 5.18

1. E. C. Cavanaugh, et al., Environmental Assessment Data Base for Low/Medium Btu Gasification Technology, Volume II, EPA Contract No. 68-02-2147, Radian Corporation, Austin, TX, September 1977.

2. Standards Support and Environmental Impact Statement, Volume 1: Proposed Standards of Performance for Petroleum Refinery Sulfur Recovery Plants. EPA-450/2-76-016a, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 1976.

3. B. Goar and T. Arrington, "Guidelines for Handling Sour Gas", Oil and Gas Journal, 76(26): 160-164, June 26, 1978.

5.19 SYNTHETIC FIBERS

5.19.1 Process Description[1]

Synthetic fibers are classified into two major categories, semi-synthetic and "true" synthetic. Semi-synthetics, such as 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 addition and other polymerization reactions that form long chain molecules.

True synthetic fibers begin with the preparation of extremely long, chain-like molecules. The polymer is spun in one of four ways:[2] (1) melt spinning, in which molten polymer is pumped through spinneret jets, the polymer solidifying as it strikes the cool air; (2) dry spinning, in which the polymer is dissolved in a suitable organic solvent, and the resulting solution is forced through spinnerets; (3) wet spinning, in which the solution is coagulated in a chemical as it emerges from the spinneret; and (4) core spinning, the newest method, in which a continuous filament yarn together with short-length "hard" fibers is introduced onto a spinning frame in such a way as to form a composite yarn.

5.19.2 Emissions and Controls[1]

In the manufacture of viscose rayon, carbon disulfide and hydrogen sulfide are the major gaseous emissions. Air pollution controls are not normally used to reduce these emissions, but adsorption in activated carbon at an efficiency of 80 to 95 percent, with subsequent recovery of the CS_2 can be accomplished.[3] Emissions of gaseous hydrocarbons may also occur from the drying of the finished fiber. Table 5.19-1 presents emission factors for semi-synthetic and true synthetic fibers.

Table 5.19-1. EMISSION FACTORS FOR SYNTHETIC FIBERS MANUFACTURING
EMISSION FACTOR RATING: E

Type of fiber	Hydrocarbons		Carbon disulfide		Hydrogen sulfide		Oil vapor or mist	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Semi-synthetic								
Viscose rayon[a,b]	–	–	55	27.5	6	3	–	–
True synthetic[c]								
Nylon	7	3.5	–	–	–	–	15	7.5
Dacron	–	–	–	–	–	–	7	3.5

[a]Reference 4.
[b]May be reduced by 80 to 95 percent adsorption in activated charcoal.[3]
[c]Reference 5.

*Mention of company or product names does not constitute endorsement by the Environmental Protection Agency.

References for Section 5.19

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Fibers, Man-Made. In: Kirk-Othmer Encyclopedia of Chemical Technology. New York, John Wiley and Sons, Inc. 1969.

3. Fluidized Recovery System Nabs Carbon Disulfide. Chem. Eng. *70*(8):92-94, April 15, 1963.

4. Private communication between Resources Research, Incorporated, and Rayon Manufacturing Plant. December 1969.

5. Private communication between Resources Research, Incorporated, and E.I. Dupont de Nemours and Company. January 13, 1970.

5.20 SYNTHETIC RUBBER

5.20.1 Process Description[1]

Copolymers of butadiene and styrene, commonly known as SBR, account for more than 70 percent of all synthetic rubber produced in the United States. In a typical SBR manufacturing process, the monomers of butadiene and styrene are mixed with additives such as soaps and mercaptans. The mixture is polymerized to a conversion point of approximately 60 percent. After being mixed with various ingredients such as oil and carbon black, the latex product is coagulated and precipitated from the latex emulsion. The rubber particles are then dried and baled.

5.20.2 Emissions and Controls[1]

Emissions from the 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, which represent a product loss. Potential gaseous emissions are largely controlled by recycling the gas stream back to the process. Emission factors from synthetic rubber plants are summarized in Table 5.20-1.

Table 5.20-1. EMISSION FACTORS FOR SYNTHETIC RUBBER PLANTS: BUTADIENE-ACRYLONITRILE AND BUTADIENE-STYRENE EMISSION FACTOR RATING: E

Compound	Emissions[a,b]	
	lb/ton	kg/MT
Alkenes		
Butadiene	40	20
Methyl propene	15	7.5
Butyne	3	1.5
Pentadiene	1	0.5
Alkanes		
Dimethylheptane	1	0.5
Pentane	2	1
Ethanenitrile	1	0.5
Carbonyls		
Acrylonitrile	17	8.5
Acrolein	3	1.5

[a]The butadiene emission is not continuous and is greatest right after a batch of partially polymerized latex enters the blow-down tank.
[b]References 2 and 3.

References for Section 5.20

1. Air Pollutant Emission Factors. Final Report. Resources Research Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. The Louisville Air Pollution Study. U.S. DHEW, PHS, Division of Air Pollution. Cincinnati, Ohio. 1961. p. 26-27 and 124.

3. Unpublished data from synthetic rubber plant. U.S. DHEW, PHS, EHS, National Air Pollution Control Administration, Division of Air Quality and Emissions Data. Durham, N.C. 1969.

5.21 TEREPHTHALIC ACID

5.21.1 Process Description[1,2]

The main use of terephthalic acid is to produce dimethylterephthalate, which is used for polyester fibers (like Dacron) and films. Terephthalic acid can be produced in various ways, one of which is the oxidation of *p*-xylene by nitric acid. In this process an oxygen-containing gas (usually air), *p*-xylene, and HNO_3 are all passed into a reactor where oxidation by the nitric acid takes place in two steps. The first step yields primarily N_2O; the second step yields mostly NO in the offgas. The terephthalic acid precipitated from the reactor effluent is recovered by conventional crystallization, separation, and drying operations.

5.21.2 Emissions

The NO in the offgas from the reactor is the major air contaminant from the manufacture of terephthalic acid. The amount of nitrogen oxides emitted is roughly estimated in Table 5.21-1.

Table 5.21-1. NITROGEN OXIDES EMISSION FACTORS FOR TEREPHTHALIC ACID PLANTS[a] EMISSION FACTOR RATING: D

Type of operation	Nitrogen oxides (NO)	
	lb/ton	kg/MT
Reactor	13	6.5

[a]Reference 2.

References for Section 5.21

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C. under Contract Number CPA-22-69-119. April 1970.

2. Terephthalic Acid. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 9. New York, John Wiley and Sons, Inc. 1964.

5.22 LEAD ALKYL

by Jake Summers, EPA, and Pacific Environmental Services

5.22.1 Process Description[1]

Two alkyl lead compounds, tetraethyl lead (TEL) and tetramethyl lead (TML), are used as antiknock gasoline additives. Over 75 percent of the 1973 additive production was TEL, more than 90 percent of which was made by alkylation of sodium/lead alloy.

Lead alkyl is produced in autoclaves by the reaction of sodium/lead alloy with an excess of either ethyl (for TEL) or methyl (for TML) chloride in the presence of acetone catalyst. The reaction mass is distilled to separate the product, which is then purified, filtered and mixed with chloride/bromide additives. Residue is sluiced to a sludge pit, from which the bottoms are sent to an indirect steam dryer, and the dried sludge is fed to a reverberatory furnace to recover lead.

Gasoline additives are also manufactured by the electrolytic process, in which a solution of ethyl (or methyl) magnesium chloride and ethyl (or methyl) chloride is electrolyzed, with lead metal as the anode.

5.22.2 Emissions and Controls[1]

Lead emissions from the sodium/lead alloy process consist of particulate lead oxide from the recovery furnace (and, to a lesser extent, from the melting furnace and alloy reactor), alkyl lead vapor from process vents, and fugitive emissions from the sludge pit.

Emissions from the lead recovery furnace are controlled by fabric filters or wet scrubbers. Vapor streams rich in lead alkyl can either be incinerated and passed through a fabric filter or be scrubbed with water prior to incinerating.

Emissions from electrolytic process vents are controlled by using an elevated flare and a liquid incinerator, while a scrubber with toluene as the scrubbing medium controls emissions from the blending and tank car loading/unloading systems.

Table 5.22-1. LEAD ALKYL MANUFACTURE LEAD EMISSION FACTORS[a]
EMISSION FACTOR RATING: B

Process	Lead emission factor		References
	kg/10^3 kg produced	lb/ton produced	
Electrolytic process	0.5	1.0	1,2,3
Sodium/lead alloy process			
Recovery furnace	28	55	1,2,4
Process vents, TEL	2	4	1
Process vents, TML	75	150	1
Sludge pits	0.6	1.2	1

[a]No other pollutant factors available

Table 5.22-2. LEAD ALKYL MANUFACTURE CONTROL EFFICIENCIES[a]

Process	Control	Percent reduction
Sodium/lead alloy process	Fabric filter	99+
	Low energy wet scrubber	80-85
	High energy wet scrubber	95-99

[a]Reference 1

References for Section 5.22

1. *Background Information in Support of the Development of Performance Standards for the Lead Additive Industry*, EPA Contract No. 68-02-2085, PEDCo-Environmental Specialists, Inc., Cincinnati, OH, January 1976.

2. *Control Techniques for Lead Air Emissions*, EPA-450/2-77-012, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1977.

3. W.E. Davis, *Emissions Study of Industrial Sources of Lead Air Pollutants, 1970*, EPA Contract No. 68-02-0271, W.E. Davis and Associates, Leawood, KS, April 1973.

4. R.P. Betz, *et al.*, *Economics of Lead Removal in Selected Industries*, EPA Contract No. 68-02-0611, Battelle Columbus Laboratories, Columbus, OH, August 1973.

5.23 PHARMACEUTICALS PRODUCTION

5.23.1 Process Description

Thousands of individual products are categorized as pharmaceuticals. These products usually are produced in modest quantities in relatively small plants using batch processes. A typical pharmaceutical plant will use the same equipment to make several different products at different times. Rarely is equipment dedicated to the manufacture of a single product.

Organic chemicals are used as raw materials and as solvents, and some chemicals such as ethanol, acetone, isopropanol and acetic anhydride are used in both ways. Solvents are almost always recovered and used many times.

In a typical batch process, solid reactants and solvent are charged to a reactor where they are held (and usually heated) until the desired product is formed. The solvent is distilled off, and the crude residue may be treated several times with additional solvents to purify it. The purified material is separated from the remaining solvent by centrifuge and finally is dried to remove the last traces of solvent. As a rule, solvent recovery is practiced for each step in the process where it is convenient and cost effective to do so. Some operations involve very small solvent losses, and the vapors are vented to the atmosphere through a fume hood. Generally, all operations are carried out inside buildings, so some vapors may be exhausted through the building ventilation system.

Certain pharmaceuticals - especially antibiotics - are produced by fermentation processes. In these instances, the reactor contains an aqueous nutrient mixture with living organisms such as fungi or bacteria. The crude antibiotic is recovered by solvent extraction and is purified by essentially the same methods described above for chemically synthesized pharmaceuticals. Similarly, other pharmaceuticals are produced by extraction from natural plant or animal sources. The production of insulin from hog or beef pancreas is an example. The processes are not greatly different from those used to isolate antibiotics from fermentation broths.

5.23.2 Emissions and Controls

Emissions consist almost entirely of organic solvents that escape from dryers, reactors, distillation systems, storage tanks and other operations. These emissions are exclusively nonmethane organic compounds. Emissions of other pollutants are negligible (except for particulates in unusual circumstances) and are not treated here. It is not practical to attempt to evaluate emissions from individual steps in the production process or to associate emissions with individual pieces of equipment, because of the great variety of batch operations that may be carried out

at a single production plant. It is more reasonable to obtain data on total solvent purchases by a plant and to assume that these represent replacements for solvents lost by evaporation. Estimates can be refined by subtracting the materials that do not enter the air because of being incinerated or incorporated into the pharmaceutical product by chemical reaction.

If plant-specific information is not available, industrywide data may be used instead. Table 5.23-1 lists annual purchases of solvents by U.S. pharmaceutical manufacturers and shows the ultimate disposition of each solvent. Disposal methods vary so widely with the type of solvent that it is not possible to recommend average factors for air emissions from generalized solvents. Specific information for individual solvents must be used. Emissions can be estimated by obtaining plant-specific data on purchases of individual solvents and computing the quantity of each solvent that evaporates into the air, either from information in Table 5.23-1 or from information obtained for the specific plant under consideration. If solvent volumes are given, rather than weights, liquid densities in Table 5.23-1 can be used to compute weights.

Table 5.23-1 gives for each plant the percentage of each solvent that is evaporated into the air and the percentage that is flushed into the sewer. Ultimately, much of the volatile material from the sewer will evaporate and will reach the air somewhere other than the pharmaceutical plant. Thus, for certain applications it may be appropriate to include both the air emissions and the sewer disposal, in an emissions inventory that covers a broad geographic area.

Since solvents are expensive and must be recovered and reused for economic reasons, solvent emissions are controlled as part of the normal operating procedures in a pharmaceutical industry. In addition, most manufacturing is carried out inside buildings, where solvent losses must be minimized to protect the health of the workers. Water or brine cooled condensers are the most common control devices, with carbon adsorbers in occasional use. With each of these methods, solvent can be recovered. Where the main objective is not solvent reuse but is the control of an odorous or toxic vapor, scrubbers or incinerators are used. These control systems are usually designed to remove a specific chemical vapor and will be used only when a batch of the corresponding drug is being produced. Usually, solvents are not recovered from scrubbers and reused, and of course, no solvent recovery is possible from an incinerator.

It is difficult to make a quantitative estimate of the efficiency of each control method, because it depends on the process being controlled, and pharmaceutical manufacture involves hundreds of different processes. Incinerators, carbon adsorbers and scrubbers have been reported to remove greater than 90 percent of the organics in the control equipment inlet stream. Condensers are limited, in that they can only reduce the concentration in the gas stream to saturation at the

condenser temperature, but not below that level. Lowering the temperature will, of course, lower the concentration at saturation, but it is not possible to operate at a temperature below the freezing point of one of the components of the gas stream.

TABLE 5.23-1. SOLVENT PURCHASES AND ULTIMATE DISPOSITION BY PHARMACEUTICAL MANUFACTURERS[a]

Solvent	Annual Purchase (metric tons)	Ultimate Disposition (percent)					Liquid Density lb/gal @ 68°F
		Air Emissions	Sewer	Incineration	Solid Waste or Contract Haul	Product	
Acetic Acid	930	1	82	-	-	17	8.7
Acetic Anhydride	1,265	1	57	-	-	42	9.0
Acetone	12,040	14	22	38	7	19	6.6
Acetonitrile	35	83	17	-	-	-	6.6
Amyl Acetate	285	42	58	-	-	-	7.3
Amyl Alcohol	1,430	99	-	-	-	1	6.8
Benzene	1,010	29	37	16	8	10	7.3
Blendan (AMOCO)	530	-	-	-	-	100	NA
Butanol	320	24	8	1	36	31	6.8
Carbon Tetrachloride	1,850	11	7	82	-	-	13.3
Chloroform	500	57	5	-	38	-	12.5
Cyclohexylamine	3,930	-	-	-	-	100	7.2
o-Dichlorobenzene	60	2	98	-	-	-	10.9
Diethylamine	50	94	6	-	-	-	5.9
Diethyl Carbonate	30	4	71	-	-	25	8.1
Dimethyl Acetamide	95	7	-	-	93	-	7.9
Dimethyl Formamide	1,630	71	3	20	6	-	7.9
Dimethylsulfoxide	750	1	28	71	-	-	11.1
1,4-Dioxane	43	5	-	-	95	-	8.6
Ethanol	13,230	10	6	7	1	76	6.6
Ethyl Acetate	2,380	30	47	20	3	-	7.5
Ethyl Bromide	45	-	100	-	-	-	12.1
Ethylene Glycol	60	-	100	-	-	-	9.3
Ethyl Ether	280	85	4	-	11	-	6.0
Formaldehyde	30	19	77	-	-	4	b
Formamide	440	-	67	-	26	7	9.5
Freons	7,150	0.1	-	-	-	99.9	c
Hexane	530	17	-	15	68	-	5.5
Isobutyraldehyde	85	50	50	-	-	-	6.6
Isopropanol	3,850	14	17	17	7	45	6.6
Isopropyl Acetate	480	28	11	61	-	-	7.3
Isopropyl Ether	25	50	50	-	-	-	6.0
Methanol	7,960	31	45	14	6	4	6.6
Methyl Cellosolve	195	47	53	-	-	-	8.7
Methylene Chloride	10,000	53	5	20	22	-	11.1
Methyl Ethyl Ketone	260	65	12	23	-	-	6.7
Methyl Formate	415	-	74	-	12	14	8.2
Methyl Isobutyl Ketone	260	80	-	-	-	20	6.7
Polyethylene Glycol 600	3	-	-	-	-	100	9.5
Pyridine	3	-	100	-	-	-	8.2
Skelly Solvent B (hexanes)	1,410	29	2	69	-	-	5.6
Tetrahydrofuran	4	-	-	100	-	-	7.4
Toluene	6,010	31	14	26	29	-	7.2
Trichloroethane	135	100	-	-	-	-	11.3
Xylene	3,090	6	19	70	5	-	7.2

[a] These data were reported by 26 member companies of the Pharmaceutical Manufacturers Association, accounting for 53 percent of pharmaceutical sales in 1975.

[b] Sold as aqueous solutions containing 37% to 50% formaldehyde by weight.

[c] Some Freons are gases, and others are liquids weighing 12 - 14 lb/gal.

Reference for Section 5.23

1. Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products, EPA-450/2-78-029, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1978.

5.24 MALEIC ANHYDRIDE

5.24.1 General[1]

The predominant end use of maleic anhydride (MA) is in the production of unsaturated polyester resins for a variety of uses. These laminating resins, which have high structural strength and good dielectric properties, are used in automobile bodies, building panels, molded boats, chemical storage tanks, lightweight pipe, machinery housings, furniture, radar domes, luggage, and bathtubs. Other end products are fumaric acid, agricultural chemicals, alkyd resins, lubricants, copolymers, plastics, succinic acid, surface active agents, and other products. In the United States, the primary raw material used in the production of MA is benzene, with one plant using only n-butane and a second plant using n-butane for 20 percent of its feedstock needs. The MA industry is exhibiting trends to convert the old benzene plants and to build new plants that use n-butane. MA also is a byproduct of the production of phthalic anhydride. It is a solid at room temperature but is a liquid or gas during production. It is a strong irritant to skin, eyes and mucous membranes of the upper respiratory system.

The model MA plant, as described in this section, has a benzene to MA conversion rate of 94.5 percent, has a capacity of 20,600 tons (22,700 MT) of MA produced per year, and runs 8000 hours per year.

Because of a lack of data, this discussion covers only the benzene oxidation process, and not the n-butane process.

5.24.2 Process Description[2]

The following chemical reaction illustrates how MA is produced by the benzene oxidation process.

$$2\ C_6H_6 + 9\ O_2 \xrightarrow[MoO_3]{V_2O_5} 2\ C_4H_2O_3 + H_2O + 4\ CO_2$$

Benzene	Oxygen	$\xrightarrow{\text{Catalyst}}$	Maleic anhydride	Water	Carbon dioxide

Vaporized benzene and air are mixed and heated before entering the tubular reactor. Inside the reactor, the benzene/air mixture is reacted in the presence of a catalyst which contains approximately 70 percent vanadium pentoxide (V_2O_5), with usually 25 to 30 percent molybdenum trioxide (MoO_3), forming a vapor of MA, water and carbon dioxide. The vapor, which may also contain oxygen, nitrogen, carbon monoxide, benzene, maleic acid, formaldehyde, formic acid and other compounds from side reactions, leaves the reactor and is cooled and partially condensed so that about 40 percent of the MA is recovered in a crude liquid state. The effluent is then passed through a separator which directs the liquid to storage and the remaining vapor to the product recovery absorber.

The absorber contacts the vapor with water, producing a liquid of about 40 percent maleic acid. The 40 percent mixture is converted to MA, usually by azeotropic distillation with xylene. Some processes may use a double effect vacuum evaporator at this point. The effluent then flows to the xylene stripping column where the xylene is extracted. This MA is then combined in storage with that from the separator. The molten product is aged to allow color forming impurities to polymerize. These are then removed in a fractionation column, leaving the finished product. The flow diagram shown in Figure 5.24-1 represents a typical process.

MA product is usually stored in liquid form, although it is sometimes flaked and pelletized into briquets and/or bagged.

Table 5.24-1. EMISSION FACTORS FOR MALEIC ANHYDRIDE PRODUCTION[a]

EMISSION FACTOR RATING: C

Type of source	Benzene		VOC[b]	
	lb/ton	kg/MT	lb/ton	kg/MT
Product recovery absorber and refining vacuum system combined vent				
Uncontrolled	134.0	67.0	172.20	86.10
With carbon adsorption[c]	0.68	0.34	0.68	0.34
With incineration	0.68	0.34	0.86	0.43
Storage and handling emissions	d	d	d	d
Fugitive emissions	e	e	e	e
Secondary emissions[f]	-	-	-	-

[a] No data are available for catalytic incineration or for plants converted to n-butane.

[b] For recovery absorber and refining vacuum, VOC can be MA and xylene; for storage and handling, MA, xylene and dust from briqueting operations; for secondary emissions, residual organics from spent catalyst, excess water from dehydration column, vacuum system water, and fractionation column residues. VOC also includes benzene.

[c] Before the exhaust gas stream goes into the carbon adsorber, it is scrubbed with caustic to remove organic acids and water soluble organics. Benzene is the only likely VOC remaining.

[d] See Section 4.3.

[e] See Section 9.1.3.

[f] Secondary emission sources are excess water from dehydration column, vacuum system water, and organics from fractionation column. No data are available on the quantity of these emissions.

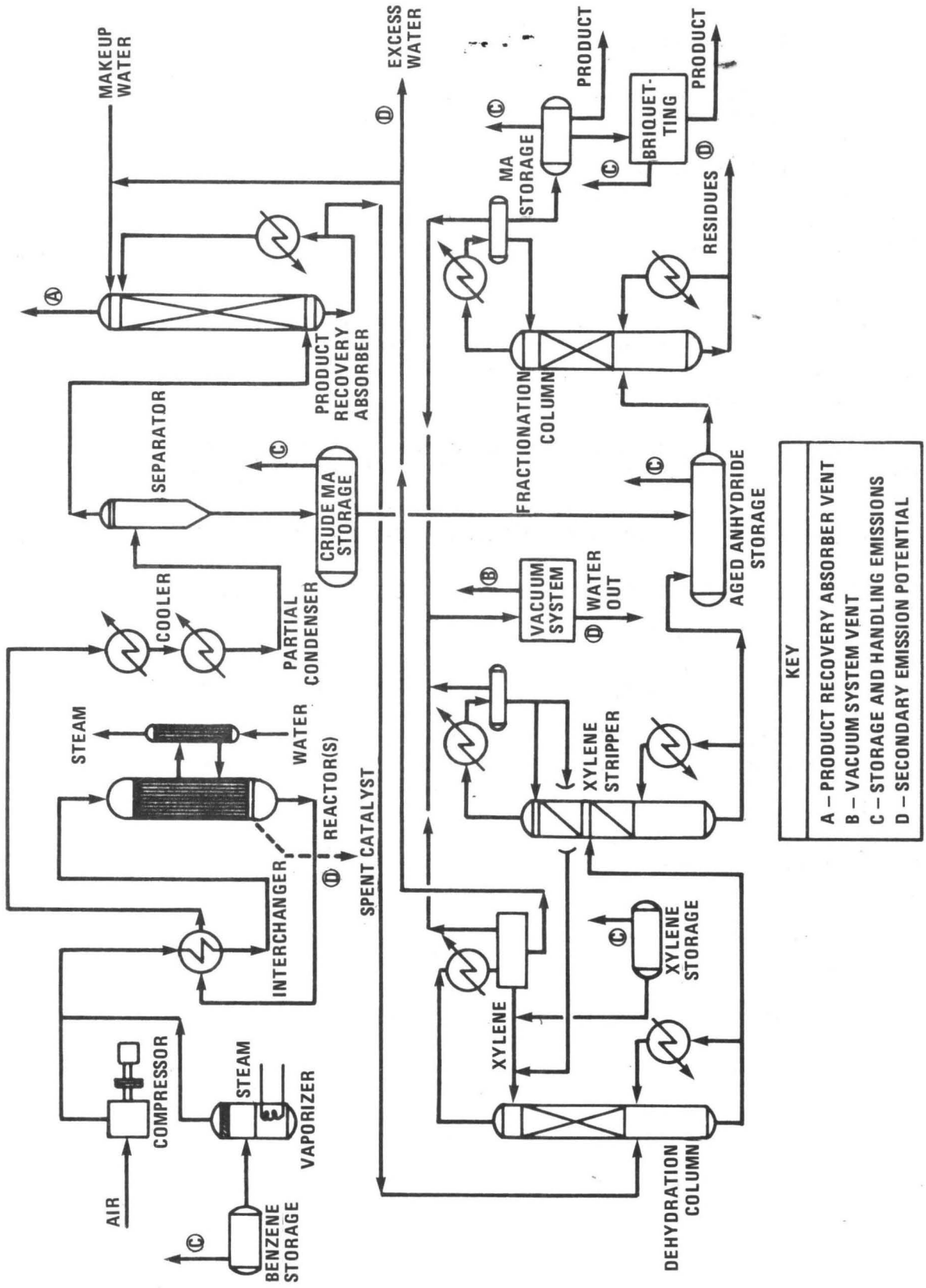

Figure 5.24-1. Process flow diagram for uncontrolled model plant.

5.24.2 Emissions and Controls[2]

The predominant pollutant in MA production, benzene, is emitted as a gas. Essentially all emissions will be from the main process vent of the product recovery absorber. This is the largest vent. Emissions here will include any unreacted benzene, which can constitute 3 to 10 percent of the total benzene feed. The only other exit for process emissions is the refining vacuum system vent. These emissions amount to 0.62 lb/hr (0.28 kg/hr) of MA and xylene.

Emissions also result from the storage and handling of benzene, xylene and MA. The reader is referred to Section 4.3 for an explanation on how to calculate these emissions. MA emissions in the form of dust can result from the briqueting operation, but no data are available on the quantity of such emissions.

Fugitive emissions can contain benzene, xylene, MA and maleic acid. The reader is referred to Section 9.1.3 for fugitive emissions.

Table 5.24-2. UNCONTROLLED EMISSIONS FROM PRODUCT RECOVERY ABSORBER[a]

Component	Wt.%	lb/ton	kg/MT
Nitrogen	73.37	42,812.0	21,406.0
Oxygen	16.67	9,726.0	4,863.0
Water	4.00	2,334.0	1,167.0
Carbon Dioxide	3.33	1,944.0	972.0
Carbon Monoxide	2.33	1,360.0	680.0
Benzene	0.33	134.0	67.0
Formaldehyde	0.05	28.8	14.4
Maleic Acid	0.01	5.6	2.8
Formic Acid	0.01	5.6	2.8
Total		58,350.0	29,175.0

[a]Reference 2.

Potential sources of secondary emissions are spent reactor catalyst, excess water from the dehydration column, vacuum system water, and fractionation column residues. The small amount of residual organics in the spent catalyst after washing have low vapor pressure and produce a small percentage of total emissions. Xylene is the principal organic contamination in the excess water from the dehydration column and the vacuum system water. The residues from the fractionation column are relatively heavey organics, with a molecular weight greater than 116, and they produce a small percentage of total emissions.

Benzene oxidation process emissions can be controlled at the main vent by means of carbon adsorption, thermal incineration or catalytic

incineration. Benzene emissions can be stopped by conversion to the n-butane process. Catalytic incineration and conversion from the benzene process to the n-butane process are not discussed for lack of data. The vent from the refining vacuum system is combined with that of the main process, as a control for refining vacuum system emissions. A carbon adsorption system or an incineration system can be designed and operated at a 99.5 percent removal efficiency for benzene and volatile organic compounds with the operating parameters given in Appendix D of Reference 2.

Fugitive emissions from pumps and valves may be controlled by an appropriate leak detection system and maintenance program. No control devices are presently being used for secondary emissions.

References for Section 5.24

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2. J. F. Lawson, Emission Control Options for the Synthetic Organic Chemicals Manufacturing Industry: Maleic Anhydride Product Report, EPA Contract No. 68-02-2577, Hydroscience, Inc., Knoxville, TN, March 1978.

6. FOOD AND AGRICULTURAL INDUSTRY

Before food and agricultural products are used by the consumer they undergo a number of processing steps, such as refinement, preservation, and product improvement, as well as storage and handling, packaging, and shipping. This section deals with the processing of food and agricultural products and the intermediate steps that present air pollution problems. Emission factors are presented for industries where data were available. The primary pollutant emitted from these processes is particulate matter.

6.1 ALFALFA DEHYDRATING

by Tom Lahre

6.1.1 General [1-3]

Dehydrated alfalfa is a meal product resulting from the rapid drying of alfalfa by artifical means at temperatures above 212°F (100°C). Alfalfa meal is used in chicken rations, cattle feed, hog rations, sheep feed, turkey mash, and other formula feeds. It is important for its protein content, growth and reproductive factors, pigmenting xanthophylls, and vitamin contributions.

A schematic of a generalized alfalfa dehydrator plant is given in Figure 6.1-1. Standing alfalfa is mowed and chopped in the field and transported by truck to a dehydrating plant, which is usually located within 10 miles of the field. The truck dumps the chopped alfalfa (wet chops) onto a self-feeder, which carries it into a direct-fired, rotary drum. Within the drum, the wet chops are dried from an initial moisture content of about 60 to 80 percent (by weight) to about 8 to 16 percent. Typical combustion gas temperatures within the oil- or gas-fired drums range from 1800 to 2000°F (980 to 1092°C) at the inlet to 250 to 300°F (120 to 150°C) at the outlet.

From the drying drum, the dry chops are pneumatically conveyed into a primary cyclone that separates them from the high-moisture, high-temperature exhaust stream. From the primary cyclone, the chops are fed into a hammermill, which grinds the dry chops into a meal. The meal is pneumatically conveyed from the hammermill into a meal collector cyclone in which the meal is separated from the airstream and discharged into a holding bin. Meal is then fed into a pellet mill where it is steam conditioned and extruded into pellets.

From the pellet mill, the pellets are either pneumatically or mechanically conveyed to a cooler, through which air is drawn to cool the pellets and, in some cases, remove fines. Fines removal is more commonly effected in shaker screens following or ahead of the cooler, with the fines being conveyed back into the meal collector cyclone, meal bin, or pellet mill. Cyclone separators may be employed to separate entrained fines in the cooler exhaust and to collect pellets when the pellets are pneumatically conveyed from the pellet mill to the cooler.

Following cooling and screening, the pellets are transferred to bulk storage. Dehydrated alfalfa is most often stored and shipped in pellet form; however, in some instances, the pellets may be ground in a hammermill and shipped in meal form. When the finished pellets or ground pellets are pneumatically transferred to storage or loadout, additional cyclones may be employed for product airstream separation at these locations.

6.1.2 Emissions and Controls [1-3]

Particulate matter is the primary pollutant of concern from alfalfa dehydrating plants although some odors arise from the organic volatiles driven off during drying. Although the major source is the primary cooling cyclone, lesser sources include the downstream cyclone separators and the bagging and loading operations.

Emission factors for the various cyclone separators utilized in alfalfa dehydrating plants are given in Table 6.1-1. Note that, although these sources are common to many plants, there will be considerable variation from the generalized flow diagram in Figure 6.1-1 depending on the desired nature of the product, the physical layout of the plant, and the modifications made for air pollution control. Common variations include ducting the exhaust gas stream from one or more of the downstream cyclones back through the primary cyclone and ducting a portion of the primary cyclone exhaust back into the furnace. Another modification involves ducting a part of the meal collector cyclone exhaust back into the hammermill, with the remainder ducted to the primary cyclone or discharged directly to the atmosphere. Also, additional cyclones may be employed if the pellets are pneumatically rather than mechanically conveyed from the pellet mill to the cooler or if the finished pellets or ground pellets are pneumatically conveyed to storage or loadout.

Table 6.1-1. PARTICULATE EMISSION FACTORS FOR ALFALFA DEHYDRATING PLANTS
EMISSION FACTOR RATING: PRIMARY CYCLONES: A
ALL OTHER SOURCES: C

Sources[a]	Emissions	
	lb/ton of product[b]	kg/MT of product[b]
Primary cyclone	10 [c]	5 [c]
Meal collector cyclone[d]	2.6	1.3
Pellet collector cyclone[e]	Not available	Not available
Pellet cooler cyclone[f]	3	1.5
Pellet regrind cyclone[g]	8	4
Storage bin cyclone[h]	Neg.	Neg.

[a]The cyclones used for product/airstream separation are the air pollution sources in alfalfa dehydrating plants. All factors are based on References 1 and 2.

[b]Product consists of meal or pellets. These factors can be applied to the quantity of incoming wet chops by dividing by a factor of four.

[c]This average factor may be used even when other cyclone exhaust streams are ducted back into the primary cyclone. Emissions from primary cyclones may range from 3 to 35 lb/ton (1.5 to 17.5 kg/MT) of product and are more a function of the operating procedures and process modifications made for air pollution control than whether other cyclone exhausts are ducted back through the primary cyclone. Use 3 to 15 lb/ton (1.5 to 7.5 kg/MT) for plants employing good operating procedures and process modifications for air pollution control. Use higher values for older, unmodified, or less well run plants.

[d]This cyclone is also called the air meal separator or hammermill cyclone. When the meal collector exhaust is ducted back to the primary cyclone and/or the hammermill, this cyclone is no longer a source.

[e]This cyclone will only be present if the pellets are pneumatically transferred from the pellet mill to the pellet cooler.

[f]This cyclone is also called the pellet meal air separator or pellet mill cyclone. When the pellet cooler cyclone exhaust is ducted back into the primary cyclone, it is no longer a source.

[g]This cyclone is also called the pellet regrind air separator. Regrind operations are more commonly found at terminal storage facilities than at dehydrating plants.

[h]Small cyclone collectors may be used to collect the finished pellets when they are pneumatically transferred to storage.

Air pollution control (and product recovery) is accomplished in alfalfa dehydrating plants in a variety of ways. A simple, yet effective technique is the proper maintenance and operation of the alfalfa dehydrating equipment. Particulate emissions can be reduced significantly if the feeder discharge rates are uniform, if the dryer furnace is operated properly, if proper airflows are employed in the cyclone collectors, and if the hammermill is well maintained and not overloaded. It is especially important in this regard not to overdry and possibly burn the chops as this results in the generation of smoke and increased fines in the grinding and pelletizing operations.

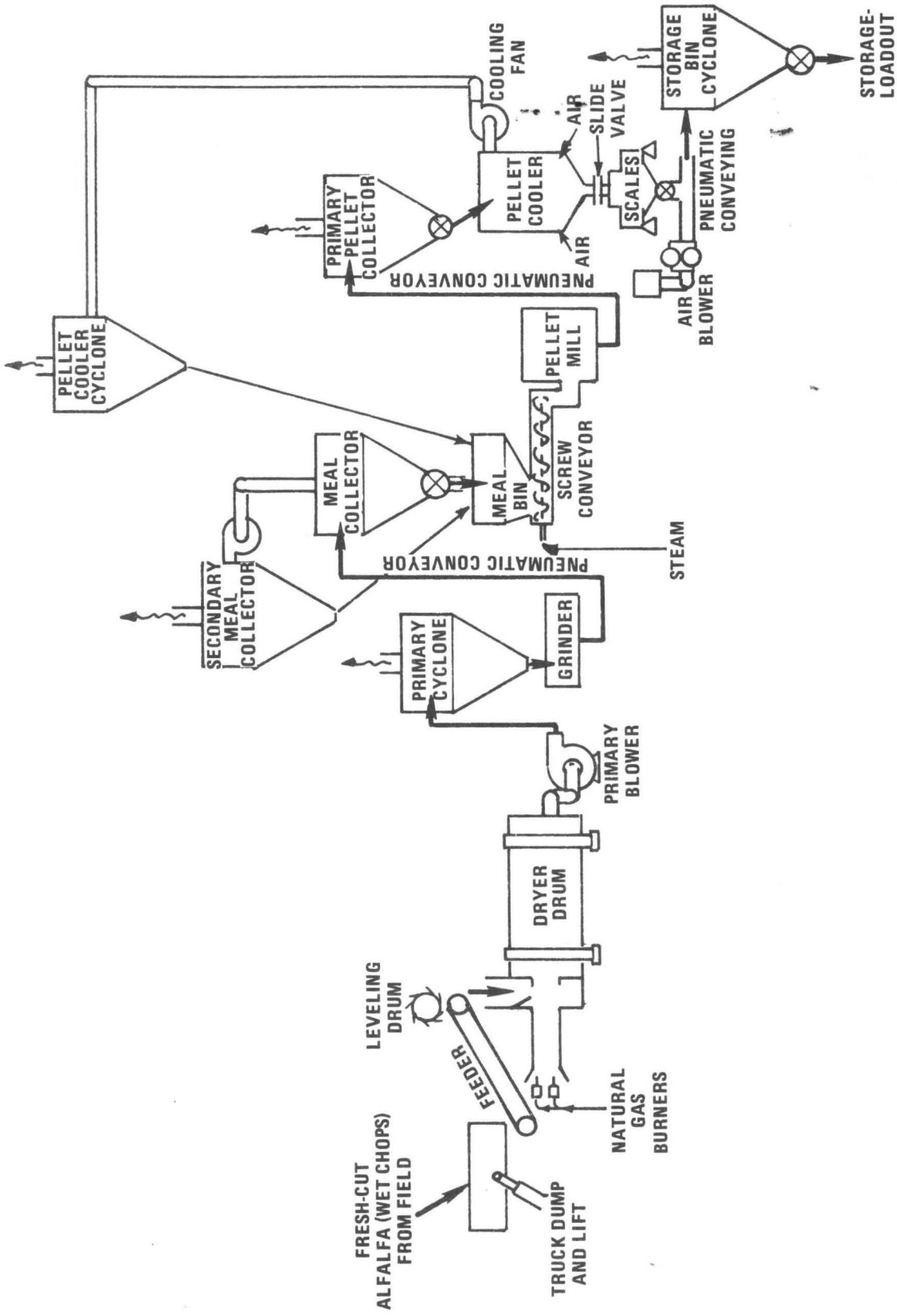

Figure 6.1-1. Generalized flow diagram for alfalfa dehydration plant.

Equipment modification provides another means of particulate control. Existing cyclones can be replaced with more efficient cyclones and concomitant air flow systems. In addition, the furnace and burners can be modified or replaced to minimize flame impingement on the incoming green chops. In plants where the hammermill is a production bottleneck, a tendency exists to overdry the chops to increase throughput, which results in increased emissions. Adequate hammermill capacity can reduce this practice.

Secondary control devices can be employed on the cyclone collector exhaust streams. Generally, this practice has been limited to the installation of secondary cyclones or fabric filters on the meal collector, pellet collector, or pellet cooler cyclones. Some measure of secondary control can also be effected on these cyclones by ducting their exhaust streams back into the primary cyclone. Primary cyclones are not controlled by fabric filters because of the high moisture content in the resulting exhaust stream. Medium energy wet scrubbers are effective in reducing particulate emissions from the primary cyclones, but have only been installed at a few plants.

Some plants employ cyclone effluent recycle systems for particulate control. One system skims off the particulate-laden portion of the primary cyclone exhaust and returns it to the furnace for incineration. Another system recycles a large portion of the meal collector cyclone exhaust back to the hammermill. Both systems can be effective in controlling particulates but may result in operating problems, such as condensation in the recycle lines and plugging or overheating of the hammermill.

References for Section 6.1

1. Source information supplied by Ken Smith of the American Dehydrators Association, Mission, Kan. December 1975.

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3. Smith, K.D. Particulate Emissions from Alfalfa Dehydrating Plants - Control Costs and Effectiveness. Final Report. American Dehydrators Association. Mission, Kan. Prepared for Environmental Protection Agency, Research Triangle Park, N.C. Grant No. R801446. Publication No. 650/2-74-007. January 1974.

6.2 COFFEE ROASTING

6.2.1 Process Description[1,2]

Coffee, which is imported in the form of green beans, must be cleaned, blended, roasted, and packaged before being sold. In a typical coffee roasting operation, the green coffee beans are freed of dust and chaff by dropping the beans into a current of air. The cleaned beans are then sent to a batch or continuous roaster. During the roasting, moisture is driven off, the beans swell, and chemical changes take place that give the roasted beans their typical color and aroma. When the beans have reached a certain color, they are quenched, cooled, and stoned.

6.2.2 Emissions[1,2]

Dust, chaff, coffee bean oils (as mists), smoke, and odors are the principal air contaminants emitted from coffee processing. The major source of particulate emissions and practically the only source of aldehydes, nitrogen oxides, and organic acids is the roasting process. In a direct-fired roaster, gases are vented without recirculation through the flame. In the indirect-fired roaster, however, a portion of the roaster gases are recirculated and particulate emissions are reduced. Emissions of both smoke and odors from the roasters can be almost completely removed by a properly designed afterburner.[1,2]

Particulate emissions also occur from the stoner and cooler. In the stoner, contaminating materials heavier than the roasted beans are separated from the beans by an air stream. In the cooler, quenching the hot roasted beans with water causes emissions of large quantities of steam and some particulate matter.[3] Table 6.2-1 summarizes emissions from the various operations involved in coffee processing.

Table 6.2-1. EMISSION FACTORS FOR ROASTING PROCESSES WITHOUT CONTROLS
EMISSION FACTOR RATING: B

Type of process	Pollutant							
	Particulates[a]		NO_x[b]		Aldehydes[b]		Organic acids[b]	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Roaster								
Direct-fired	7.6	3.8	0.1	0.05	0.2	0.1	0.9	0.45
Indirect-fired	4.2	2.1	0.1	0.05	0.2	0.1	0.9	0.45
Stoner and cooler[c]	1.4	0.7	–	–	–	–	–	–
Instant coffee spray dryer	1.4[d]	0.7[d]	–	–	–	–	–	–

[a]Reference 3.
[b]Reference 1.
[c]If cyclone is used, emissions can be reduced by 70 percent.
[d]Cyclone plus wet scrubber always used, representing a controlled factor.

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2. Duprey, R.L. Compilation of Air Pollutant Emission Factors. U.S. DHEW, PHS, National Center for Air Pollution Control. Durham, N.C. PHS Publication Number 999-AP-42. 1968. p. 19-20.

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6.3 COTTON GINNING

6.3.1 General[1]

The primary function of a cotton gin is to separate seed from the lint of raw seed cotton. Approximately one 500-pound bale of cotton can be produced from 1 ton of seed cotton. During ginning, lint dust, fine leaves, and other trash are emitted into the air. The degree of pollution depends on the seed cotton trash content, which depends on the method used to harvest the cotton. Handpicked cotton has a lower trash content than machine-stripped cotton.

6.3.2 Process Description[2]

Figure 6.3-1 is a flow diagram of the typical cotton ginning process. Each of the five ginning steps and associated equipment is described in the following sections.

6.3.2.1 Unloading System — Trucks and trailers transport seed cotton from the field to the gin. Pneumatic systems convey the seed cotton from the vehicles or storage houses to a separator and feed control unit. (Some gins utilize a stone and green boll trap for preliminary trash removal.) The screen assembly in the separator collects the seed cotton and allows it to fall into the feed control unit. The conveying air flows from the separator to a cyclone system where it is cleaned and discharged to the atmosphere.

6.3.2.2 Seed Cotton Cleaning System — Seed cotton is subjected to three basic conditioning processes — drying, cleaning, and extracting — before it enters the gin stand for separation of lint from seed. To ensure adequate conditioning, cotton gins typically use two conditioning systems in series (see Figure 6.3-1).

Cotton dryers are designed to reduce the moisture content of the seed cotton to an optimum level of 6.5 to 8.0 percent. A push-pull high-pressure fan system conveys seed cotton through the tower dryer to the cleaner, which loosens the cotton and removes fine particles of foreign matter such as leaf trash, sand, and dirt. Large pieces of foreign matter (e.g., sticks, stems, and burrs) are removed from the seed cotton by a different process, referred to as "extracting." Several types of extractors are used at cotton gins: burr machines, stick machines, stick and burr machines, stick and green leaf extractors, and extractor-feeders. The burr machine removes burrs and pneumatically conveys them to the trash storage area. The seed cotton then enters a stick (or a stick and green leaf) machine, which removes sticks, leaves, and stems. Afterwards, the seed cotton is pneumatically conveyed to the next processing step.

6.3.2.3 Overflow System — From the final conditioning unit, the seed cotton enters a screw conveyor distributor, which apportions the seed cotton to the extractor-feeders at a controlled rate. When the flow of seed cotton exceeds the limit of the extractor-feeders, the excess seed cotton flows into the overflow hopper. A pneumatic system transfers seed cotton from the overflow hopper back to the extractor-feeder as required.

6.3.2.4 Lint Cotton Handling System — Cotton enters the gin stand through a "huller front," which performs some cleaning. A saw grasps the locks of cotton and draws them through a widely spaced set of "huller ribs," which strip off hulls and sticks. The cotton locks are then drawn into the roll box, where seeds are separated from the fibers. As the seeds are removed, they slide down the face of the ginning ribs and fall to the bottom of the gin stand for subsequent removal to storage. Cotton lint is removed from the saw by a brush or a blast of air and conveyed pneumatically to the lint cleaning system for final cleaning and combing. The lint cotton is separated from the conveying air stream by a separator that forms the lint into a batt. This batt is fed into the first set of lint cleaners, where saws comb the lint cotton and remove leaf particles, grass, and motes.

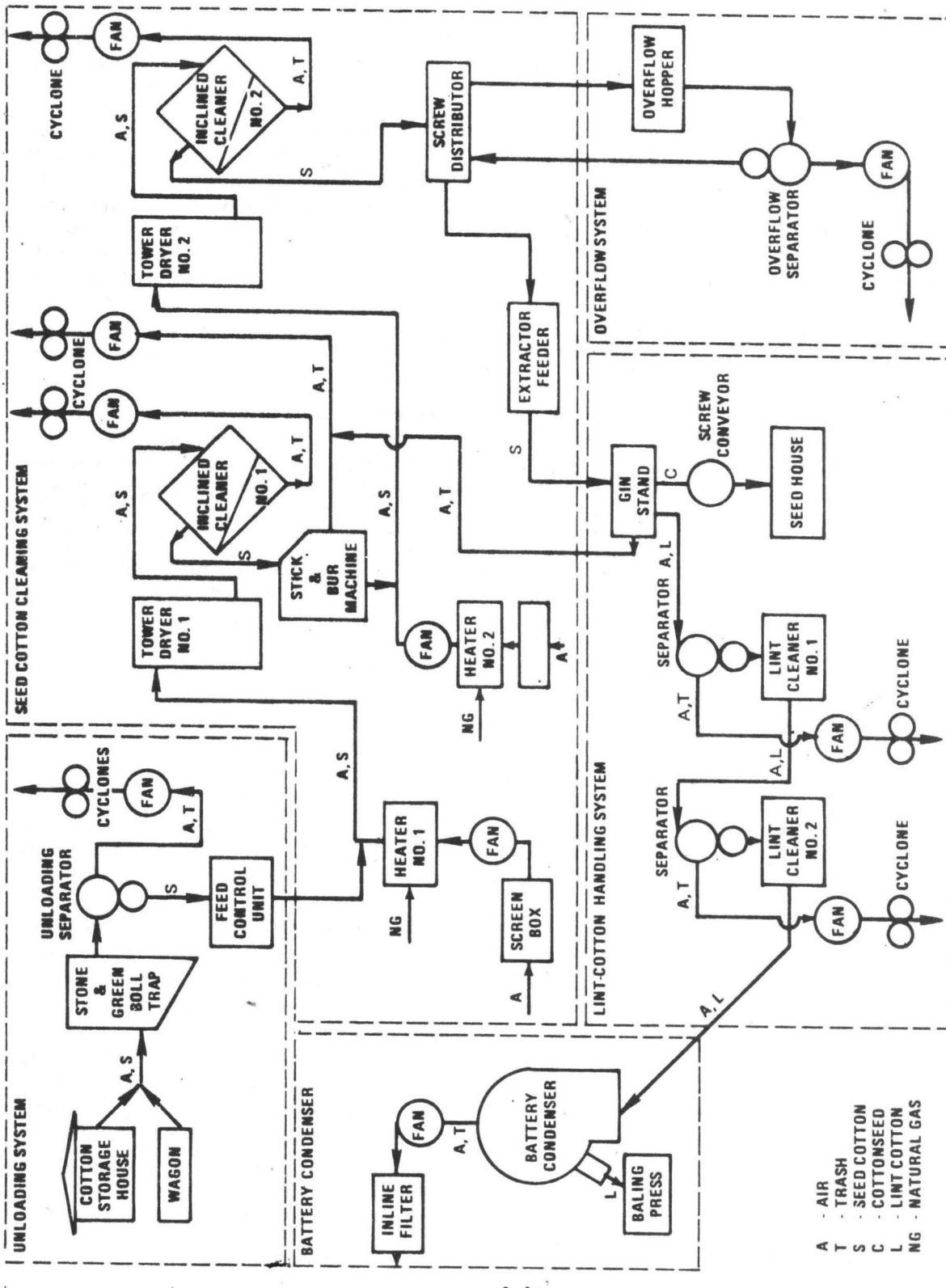

Figure 6.3-1. Flow diagram of cotton ginning process.[2]

6.3.2.5 Battery Condenser and Baling System — Lint cotton is pneumatically transported from the lint cleaning system to a battery condenser, which consists of drums equipped with screens that separate the lint cotton from the conveying air. The conveying air is then discharged through an in-line filter or cyclones before being exhausted to the atmosphere. The batt of lint cotton is then fed into the baling press, which packs it into uniform bales of cotton.

6.3.3 Emissions and Controls

The major sources of particulates from cotton ginning can be arranged into 10 emission source categories based on specific ginning operations (Figure 6.3-2). Three primary methods of particulate control are in use: (1) high efficiency cyclones on the high-pressure fan discharges with collection efficiencies greater than 99 percent,[2] (2) in-line filters on low-pressure fan exhaust vents with efficiencies of approximately 80 percent, and (3) fine screen coverings on condenser drums in the low-pressure systems with efficiencies of approximately 50 percent.[3,4] The unifilter is a new concept for collecting all wastes from cotton gins. It is designed to replace all cyclones, in-line filters, and covered condenser drums, and has a collection efficiency of up to 99 percent.[5]

Table 6.3-1 presents emission factors from uncontrolled cotton ginning operations.[1]

Table 6.3-2 presents emission factors for a typical cotton gin equipped with available control devices; the data base involved cotton gins with a variety of different control devices, including cyclones, in-line filters, screen coverings, and unifilters.[2,6-9] The total emission factor can be expected to vary by roughly a factor of two, depending on the type of seed cotton, the trash content of the seed cotton, the maintenance of control devices, and the plant operation procedures.

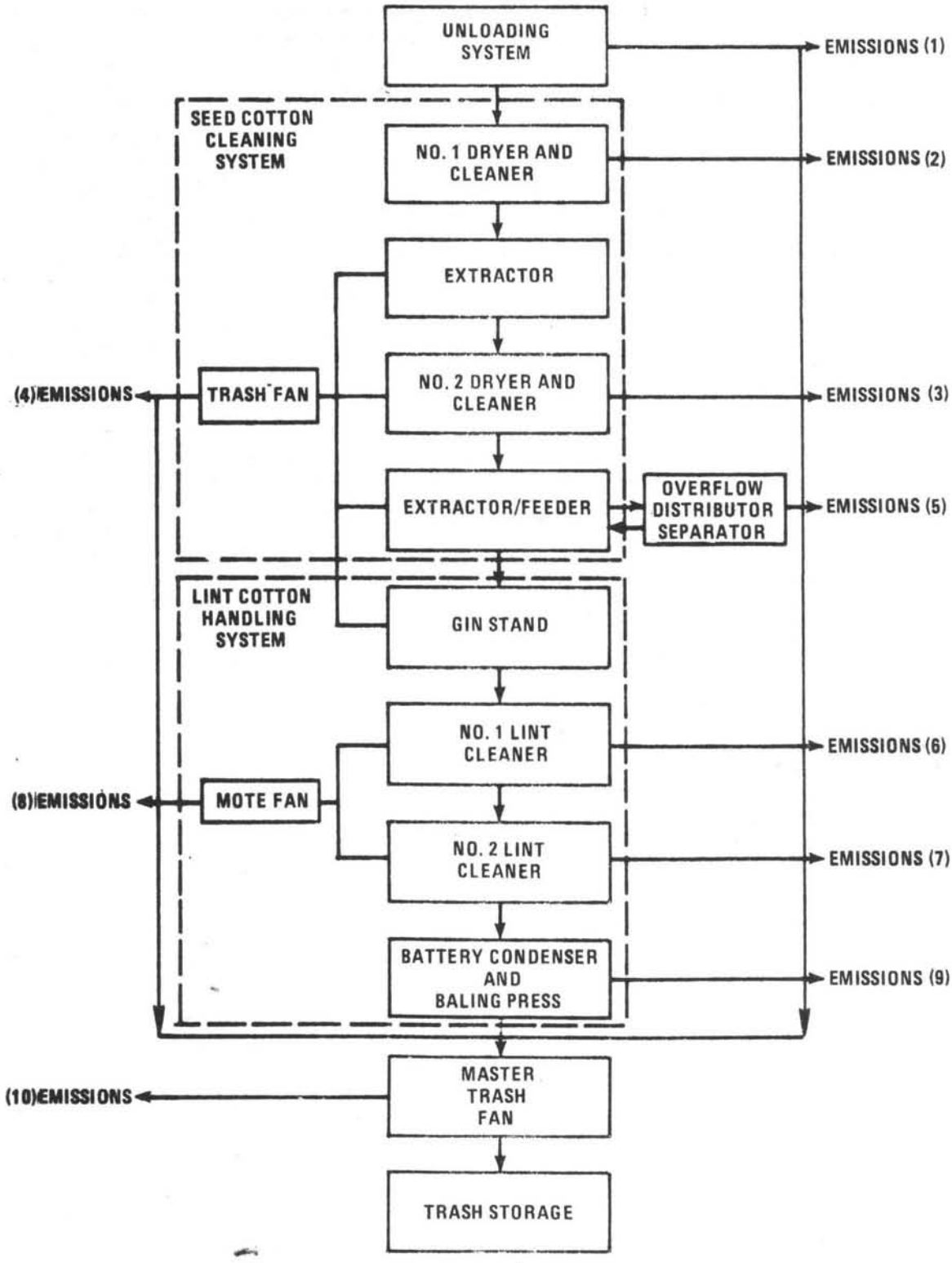

Figure 6.3-2. Emissions from a typical ginning operation.

Table 6.3-1. EMISSION FACTORS FOR COTTON GINNING OPERATIONS WITHOUT CONTROL[a,b]

EMISSION FACTOR RATING: C

Process	Estimated total particulate		Particulates >100 μm settled out, %[c]	Estimated emission factor (released to atmosphere)	
	lb/bale	kg/bale		lb/bale	kg/bale
Unloading fan	5	2.27	0	5.0	2.27
Seed cotton cleaning system					
Cleaners and dryers[d]	1	0.45	70	0.3	0.14
Stick and burr machine	3	1.36	95	0.2	0.09
Miscellaneous[e]	3	1.36	50	1.5	0.68
Total	12	5.44	---	7.0	3.2

[a]Reference 1.
[b]One bale weighs 500 pounds (226 kilograms).
[c]Percentage of the particles that settle out in the plant.
[d]Corresponds to items 1 and 2 in Table 6.3-2.
[e]Corresponds to items 4 through 9 in Table 6.3-2.

Table 6.3-2. PARTICULATE EMISSION FACTORS FOR COTTON GINS WITH CONTROLS[a]
EMISSION FACTOR RATING: C

Emission source[b]	Emission factor	
	lb/bale[c]	g/kg
1. Unloading fan	0.32	0.64
2. No. 1 dryer and cleaner	0.18	0.36
3. No. 2 dryer and cleaner	0.10	0.20
4. Trash fan	0.04	0.08
5. Overflow fan	0.08	0.16
6. No. 1 lint cleaner condenser	0.81	1.62
7. No. 2 lint cleaner condenser	0.15	0.30
8. Mote fan	0.20	0.40
9. Battery condenser	0.19	0.38
10. Master trash fan	0.17	0.34
Total	2.24	4.48

[a]References 2,6-9.
[b]Numbers correspond to those in Figure 6.3-2.
[c]A bale of cotton weighs 500 pounds (227 Kilograms).

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7. Kirk, I.W., T.E. Wright, and K.H. Read. Particulate Emissions from Commercial Cotton Ginning Operations. Southwestern Cotton Ginning Research Laboraory, Mesilla Park, New Mexico. Presented at ASAE 1976 Winter Meeting, Chicago, Illinois. December 1976.

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6.3 COTTON GINNING

6.3.1 General[1]

The primary function of a cotton gin is to take raw seed cotton and separate the seed and the lint. A large amount of trash is found in the seed cotton, and it must also be removed. The problem of collecting and disposing of gin trash is two-fold. The first problem consists of collecting the coarse, heavier trash such as burrs, sticks, stems, leaves, sand, and dirt. The second problem consists of collecting the finer dust, small leaf particles, and fly lint that are discharged from the lint after the fibers are removed from the seed. From 1 ton (0.907 MT) of seed cotton, approximately one 500-pound (226-kilogram) bale of cotton can be made.

6.3.2 Emissions and Controls

The major sources of particulates from cotton ginning include the unloading fan, the cleaner, and the stick and burr machine. From the cleaner and stick and burr machine, a large percentage of the particles settle out in the plant, and an attempt has been made in Table 6.3-1 to present emission factors that take this into consideration. Where cyclone collectors are used, emissions have been reported to be about 90 percent less.[1]

Table 6.3-1. EMISSION FACTORS FOR COTTON GINNING OPERATIONS WITHOUT CONTROLS[a,b]
EMISSION FACTOR RATING: C

Process	Estimated total particulates		Particles > 100 μm settled out, %	Estimated emission factor (released to atmosphere)	
	lb/bale	kg/bale		lb/bale	kg/bale
Unloading fan	5	2.27	0	5.0	2.27
Cleaner	1	0.45	70	0.30	0.14
Stick and burr machine	3	1.36	95	0.20	0.09
Miscellaneous	3	1.36	50	1.5	0.68
Total	12	5.44	–	7.0	3.2

[a]References 1 and 2.
[b]One bale weighs 500 pounds (226 kilograms).

References for Section 6.3

1. Air-Borne Particulate Emissions from Cotton Ginning Operations. U.S. DHEW, PHS, Taft Sanitary Engineering Center. Cincinnati, Ohio. 1960.

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6.4 FEED AND GRAIN MILLS AND ELEVATORS

6.4.1 General[1-3]

Grain elevators are buildings in which grains are gathered, stored, and discharged for use, further processing, or shipping. They are classified as "country," "terminal," and "export" elevators, according to their purpose and location. At country elevators, grains are unloaded, weighed, and placed in storage as they are received from farmers residing within about a 20-mile radius of the elevator. In addition, country elevators sometimes dry or clean grain before it is shipped to terminal elevators or processors.

Terminal elevators receive most of their grain from country elevators and ship to processors, other terminals, and exporters. The primary functions of terminal elevators are to store large quantities of grain without deterioration and to dry, clean, sort, and blend different grades of grain to meet buyer specifications.

Export elevators are similar to terminal elevators except that they mainly load grain on ships for export.

Processing of grain in mills and feed plants ranges from very simple mixing steps to complex industrial processes. Included are such diverse processes as: (1) simple mixing operations in feed mills, (2) grain milling in flour mills, (3) solvent extracting in soybean processing plants, and (4) a complex series of processing steps in a corn wet-milling plant.

6.4.2 Emissions and Controls

Grain handling, milling, and processing include a variety of operations from the initial receipt of the grain at either a country or terminal elevator to the delivery of a finished product. Flour, livestock feed, soybean oil, and corn syrup are among the products produced from plants in the grain and feed industry. Emissions from the feed and grain industry can be separated into two general areas, those occurring at grain elevators and those occurring at grain processing operations.

6.4.2.1 Grain Elevators - Grain elevator emissions can occur from many different operations in the elevator including unloading (receiving), loading (shipping), drying, cleaning, headhouse (legs), tunnel belt, gallery belt, and belt trippers. Emission factors for these operations at terminal, country, and export elevators are presented in Table 6.4-1. All of these emission factors are approximate average values intended to reflect a variety of grain types. Actual emission factors for a specific source may be considerably different, depending on the type of grain, i.e., corn, soybeans, wheat, and other factors such as grain quality.

The emission factors shown in Table 6.4-1 represent the amount of dust generated per ton of grain processed through each of the designated operations (i.e., uncontrolled emission factors). Amounts of grain processed through each of these operations in a given elevator are dependent on such factors as the amount of grain turned (interbin transfer), amount dryed, and amount cleaned, etc. Because the amount of grain passing through each operation is often difficult to determine, it may be more useful to express the emission factors in terms of the amount of grain shipped or received, assuming these amounts are about the same over the long term. Emission factors from Table 6.4-1 have been modified accordingly and are shown in Table 6.4-2 along with the appropriate multiplier that was used as representative of typical ratios of throughput at each operation to the amount of grain shipped or received. This ratio is an approximate value based on average values for turning, cleaning, and drying in each

type of elevator. However, because operating practices in individual elevators are different, these ratios, like the basic emission factors themselves, are more valid when applied to a group of elevators rather than individual elevators.

Table 6.4-1. PARTICULATE EMISSION FACTORS FOR UNCONTROLLED GRAIN ELEVATORS EMISSION FACTOR RATING: B

Type of source	Emission factor[a]	
	lb/ton	kg/MT
Terminal elevators		
Unloaded (receiving)	1.0	0.5
Loading (shipping)	0.3	0.2
Removal from bins (tunnel belt)	1.4	1.7
Drying[b]	1.1	0.6
Cleaning[c]	3.0	1.5
Headhouse (legs)	1.5	0.8
Tripper (gallery belt)	1.0	0.5
Country elevators		
Unloading (receiving)	0.6	0.3
Loading (shipping)	0.3	0.2
Removal from bins	1.0	0.5
Drying[b]	0.7	0.4
Cleaning[c]	3.0	1.5
Headhouse (legs)	1.5	0.8
Export elevators		
Unloading (receiving)	1.0	0.5
Loading (shipping)	1.0	0.5
Removal from bins (tunnel belt)	1.4	0.7
Drying[b]	1.1	0.5
Cleaning[c]	3.0	1.5
Headhouse (legs)	1.5	0.8
Tripper (gallery belts)	1.0	0.5

[a]Emission factors are in terms of pounds of dust emitted per ton of grain processed by each operation. Most of the factors for terminal and export elevators are based on Reference 1. Emission factors for drying are based on References 2 and 3. The emission factors for country elevators are based on Reference 1 and specific country elevator test data in References 4 through 9.

[b]Emission factors for drying are based on 1.8 lb/ton for rack dryers and 0.3 lb/ton for column dryers prorated on the basis of distribution of these two types of dryers in each elevator category, as discussed in Reference 3.

[c]Emission factor of 3.0 for cleaning is an average value which may range from <0.5 for wheat up to 6.0 for corn.

The factors in Tables 6.4-1 or 6.4-2 should not be added together in an attempt to obtain a single emission factor value for grain elevators because in most elevators some of the operations are equipped with control devices and some are not. Therefore, any estimation of emissions must be directed to each operation and its associated control device, rather than the elevator as a whole, unless the purpose was to estimate total potential (i.e., uncontrolled) emissions. An example of the use of emission factors in making an emission inventory is contained in Reference 3.

Table 6.4-2. PARTICULATE EMISSION FACTORS FOR GRAIN ELEVATORS BASED ON AMOUNT OF GRAIN RECEIVED OR SHIPPED[a]

Type of source	Emission factor, lb/ton processed	×	Typical ratio of tons processed to tons received or shipped[d]	=	Emission factor, lb/ton received or shipped
Terminal elevators					
Unloading (receiving)	1.0		1.0		1.0
Loading (shipping)	0.3		1.0		0.3
Removal from bins (tunnel belt)	1.4		2.0		2.8
Drying[b]	1.1		0.1		0.1
Cleaning[c]	3.0		0.2		0.6
Headhouse (legs)	1.5		3.0		4.5
Tripper (gallery belt)	1.0		1.7		1.7
Country elevators					
Unloading (receiving)	0.6		1.0		0.6
Loading (shipping)	0.3		1.0		0.3
Removal from bins	1.0		2.1		2.1
Drying[b]	0.7		0.3		0.2
Cleaning[c]	3.0		0.1		0.3
Headhouse (legs)	1.5		3.1		4.7
Export elevators					
Unloading (receiving)	1.0		1.0		1.0
Loading (shipping)	1.0		1.0		1.0
Removal from bins (tunnel belt)	1.4		1.2		1.7
Drying[b]	1.1		0.01		0.01
Cleaning[c]	3.0		0.2		0.6
Headhouse (legs)	1.5		2.2		3.3
Tripper (gallery belt)	1.0		1.1		1.1

[a]Assume that over the long term the amount received is approximately equal to amount shipped.

[b]See Note[b] in Table 6.4-1.

[c]See Note[c] in Table 6.4-1.

[d]Ratios shown are average values taken from a survey of many elevators across the U.S.[3] These ratios can be considerably different for any individual elevator or group of elevators in the same locale.

Some of the operations listed in the table, such as the tunnel belt and belt tripper, are internal or in-house dust sources which, if uncontrolled, might show lower than expected atmospheric emissions because of internal settling of dust. The reduction in emissions via internal settling is not known, although it is possible that all of this dust is eventually emitted to the atmosphere due to subsequent external operations, internal ventilation, or other means.

Many elevators utilize control devices on at least some operations. In the past, cyclones have commonly been applied to legs in the headhouse and tunnel belt hooding systems. More recently, fabric filters have been utilized at many elevators on almost all types of operations. Unfortunately, some sources in grain elevators present control problems. Control of loadout operations is difficult because of the problem of containment of the emissions. Probably the most difficult operation to control, because of the large flow rate and high moisture content of the exhaust gases, is the dryers. Screenhouses or continuously vacuumed screen systems are available for reducing dryer emissions and have been applied at several facilities. Detailed descriptions of dust control systems for grain elevator operations are contained in Reference 2.

6.4.2.2 Grain Processing Operations - Grain processing operations include many of the operations performed in a grain elevator in addition to milling and processing of the grain. Emission factors for different grain milling and processing operations are presented in Table 6.4-3. Brief discussions of these different operations and the methods used for arriving at the emission factor values shown in Table 6.4-3 are presented below.

Table 6.4-3. PARTICULATE EMISSION FACTORS FOR GRAIN PROCESSING OPERATIONS[1,2,3]
EMISSION FACTOR RATING: D

Type of source	Emission factor[a,b] (uncontrolled except where indicated)	
	lb/ton	kg/MT
Feed mills		
Receiving	1.30	0.65
Shipping	0.50	0.25
Handling	3.00	1.50
Grinding	0.10[c]	0.05[c]
Pellet coolers	0.10[c]	0.05[c]
Wheat mills		
Receiving	1.00	0.50
Precleaning and handling	5.00	2.50
Cleaning house	-	-
Millhouse	70.00	35.00
Durum mills		
Receiving	1.00	0.50
Precleaning and handling	5.00	2.50
Cleaning house	-	-
Millhouse	-	-
Rye milling		
Receiving	1.00	0.50
Precleaning and handling	5.00	2.50
Cleaning house	-	-
Millhouse	70.00	35.00
Dry corn milling		
Receiving	1.00	0.50
Drying	0.50	0.25
Precleaning and handling	5.00	2.50
Cleaning house	6.00	3.00
Degerming and milling	-	-
Oat milling		
Total	2.50[d]	1.25[d]
Rice milling		
Receiving	0.64	0.32
Handling and precleaning	5.00	2.50
Drying	-	-
Cleaning and millhouse	-	-
Soybean mills		
Receiving	1.60	0.80
Handling	5.00	2.50
Cleaning	-	-
Drying	7.20	3.60
Cracking and dehulling	3.30	1.65
Hull grinding	2.00	1.00

Table 6.4-3 (continued). PARTICULATE EMISSION FACTORS FOR GRAIN PROCESSING OPERATIONS[1,2,3]
EMISSION FACTOR RATING: D

Type of source	Emission factor[a,b] (uncontrolled except where indicated)	
	lb/ton	kg/MT
Bean conditioning	0.10	0.05
Flaking	0.57	0.29
Meal dryer	1.50	0.75
Meal cooler	1.80	0.90
Bulk loading	0.27	0.14
Corn wet milling		
Receiving	1.00	0.50
Handling	5.00	2.50
Cleaning	6.00	3.00
Dryers	-	-
Bulk loading	-	-

[a]Emission factors are expressed in terms of pounds of dust emitted per ton of grain entering the plant (i.e., received), which is not necessarily the same as the amount of material processed by each operation.

[b]Blanks indicate insufficient information.

[c]Controlled emission factor (controlled with cyclones).

[d]Controlled emission factor.(This represents several sources in one plant; some controlled with cyclones and others controlled with fabric filters.)

Emission factor data for feed mill operations are sparse. This is partly due to the fact that many ingredients, whole grain and other dusty materials (bran, dehydrated alfalfa, etc.), are received by both truck and rail and several unloading methods are employed. However, because some feed mill operations (handling, shipping, and receiving) are similar to operations in a grain elevator, an emission factor for each of these different operations was estimated on that basis. The remaining operations are based on information in Reference 2.

Three emission areas for wheat mill processing operations are grain receiving and handling, cleaning house, and milling operations. Data from Reference 1 are used to estimate emissions factors for grain receiving and handling. Data for the cleaning house are insufficient to estimate an emission factor, and information contained in Reference 2 is used to estimate the emission factor for milling operations. The large emission factor for the milling operation is somewhat misleading because almost all of the sources involved are equipped with control devices to prevent product losses; fabric filters are widely used for this purpose.

Operations for durum mills and rye milling are similar to those of wheat milling. Therefore, most of these emission factors are assumed equal to those for wheat mill operations.

The grain unloading, handling, and cleaning operations for dry corn milling are similar to those in other grain mills, but the subsequent operations are somewhat different. Also, some drying of corn received at the mill may be necessary prior to storage. An estimate of the emission factor for drying is obtained from Reference 2. Insufficient information is available to estimate emission factors for degerming and milling.

Information necessary to estimate emissions from oat milling is unavailable, and no emission factor for another grain is considered applicable because oats are reported to be dustier than many other grains. The only emission factor data available are for controlled emissions.[2] An overall controlled emission factor of 2.5 lb/ton is calculated from these data.

Emission factors for rice milling are based on those for similar operations in other grain handling facilities. Insufficient information is available to estimate emission factors for drying, cleaning, and mill house operations.

Information contained in Reference 2 is used to estimate emission factors for soybean mills.

Emissions information on corn wet-milling is unavailable in most cases due to the wide variety of products and the diversity of operations. Receiving, handling, and cleaning operations emission factors are assumed to be similar to those for dry corn milling.

Many of the operations performed in grain milling and processing plants are the same as those in grain elevators, so the control methods are similar. As in the case of grain elevators, these plants often use cyclones or fabric filters to control emissions from the grain handling operations (e.g., unloading, legs, cleaners, etc.). These same devices are also often used to control emissions from other processing operations; a good example of this is the extensive use of fabric filters in flour mills. However, there are also certain operations within some milling operations that are not amenable to use of these devices. Therefore, wet scrubbers have found some application, particularly where the effluent gas stream has a high moisture content. Certain other operations have been found to be especially difficult to control, such as rotary dryers in wet corn mills. Descriptions of the emission control systems that have been applied to operations within the grain milling and processing industries are contained in Reference 2.

This section was prepared for EPA by Midwest Research Institute.[10]

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1. Gorman, P.G. Potential Dust Emission from a Grain Elevator in Kansas City, Missouri. Prepared by Midwest Research Institute for Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-0228, Task Order No. 24. May 1974.

2. Shannon, L.J. et al. Emission Control in the Grain and Feed Industry , Volume I - Engineering and Cost Study. Final Report. Prepared for Environmental Protection Agency by Midwest Research Institute. Document No. EPA-450/3-73-003a. Research Triangle Park, N.C. December 1973.

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6.5 FERMENTATION

Process Description[1]

For the purpose of this report only the fermentation industries associated with food will be considered. This includes the production of beer, whiskey, and wine.

The manufacturing process for each of these is similar. The four main brewing production stages and their respective sub-stages are: (1) brewhouse operations, which include (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 to 10 days, (d) removal of settled yeast, and (e) filtration and carbonation; (3) aging, which lasts from 1 to 2 months under refrigeration; and (4) packaging, which includes (a) bottling-pasteurization, and (b) racking draft beer.

The major differences between beer production and whiskey production are the purification and distillation necessary to obtain distilled liquors and the longer period of aging. The primary difference between wine making and beer making is that grapes are used as the initial raw material in wine rather than grains.

Table 6.5-1. EMISSION FACTORS FOR FERMENTATION PROCESSES
EMISSION FACTOR RATING: E

Type of product	Particulates		Hydrocarbons	
	lb/ton	kg/MT	lb/ton	kg/MT
Beer				
Grain handling[a]	See Subsection 6.5.1			
Drying spent grains, etc.[a]				
Whiskey				
Grain handling[a]	3	1.5	–	–
Drying spent grains, etc.[a]	5	2.5	NA	NA
Aging	–	–	10[c]	0.024[d]
Wine	See Subsection 6.5.2			

[a]Based on section on grain processing.
[b]No emission factor available, but emissions do occur.
[c]Pounds per year per barrel of whiskey stored.[2]
[d]Kilograms per year per liter of whiskey stored.
[e]No significant emissions.

References for Section 6.5

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Shreve, R.N. Chemical Process Industries, 3rd Ed. New York, McGraw-Hill Book Company. 1967. p. 591-608.

6.5.1. BEER MAKING

6.5.1.1 General[1-3]

Beer is a beverage of low alcoholic content (2 - 7 percent) made by the fermentation of malted starchy cereal grains. Barley is the principal grain used. The production of beer is carried out in four major stages, brewhouse operations, fermentation, aging and packaging. These processes are shown in Figure 6.5.1-1.

Brewhouse operations include malting of the barley, addition of adjuncts to the barley mash, conversion of the starch in the barley and adjuncts to maltose sugar, separation of wort from the grain, and hopping and boiling of the wort.

In malting, barley is continuously moistened to cause it to germinate. With germination, enzymes are formed which break down starches and proteins to less complex water soluble compounds. The malted barley is dried to arrest the enzyme formation and is ground in a malt or roll mill. Adjuncts, consisting of other grains (ground and unmalted), sugars and syrups, are added to the ground malted barley and, with a suitable amount of water, are charged to the mash tun (tank-like vessel). Conversion of the complex carbohydrates (starch and sugars) and proteins to simpler water soluble fermentable compounds by means of enzyme action takes place in the mash tun, a process called mashing. The mash is sent to a filter press or straining tub (lauter tun) where the wort (unfermented beer) is separated from the spent grain solids. Hops are added to the wort in a brew kettle, where the wort is boiled one and a half to three hours to extract essential substances from the hops, to concentrate the wort, and to destroy the malt enzymes. The wort is strained to remove hops, and sludge is removed by a filter or centrifuge.

Wort is cooled to 10°C (50°F) or lower. During cooling, it absorbs air necessary to start fermentation. The yeast is added and mixed with the wort in line to the fermentation starter tanks. Fermentation, the conversion of the simple sugars in the wort to ethanol and carbon dioxide, is completed in a closed fermenter. The carbon dioxide gas released by the fermentation is collected and later used for carbonating the beer. Cooling to maintain proper fermentation temperature is required because the reaction is exothermic.

After fermentation is complete, beer is stored to age for several weeks at 0°C (32°F) in large closed tanks. It is recarbonated, pumped through a pulp filter, pasteurized at 60°C (140°F) to make it biologically stable, and packaged in bottles and cans. Beer put in kegs for draft sale is not pasteurized.

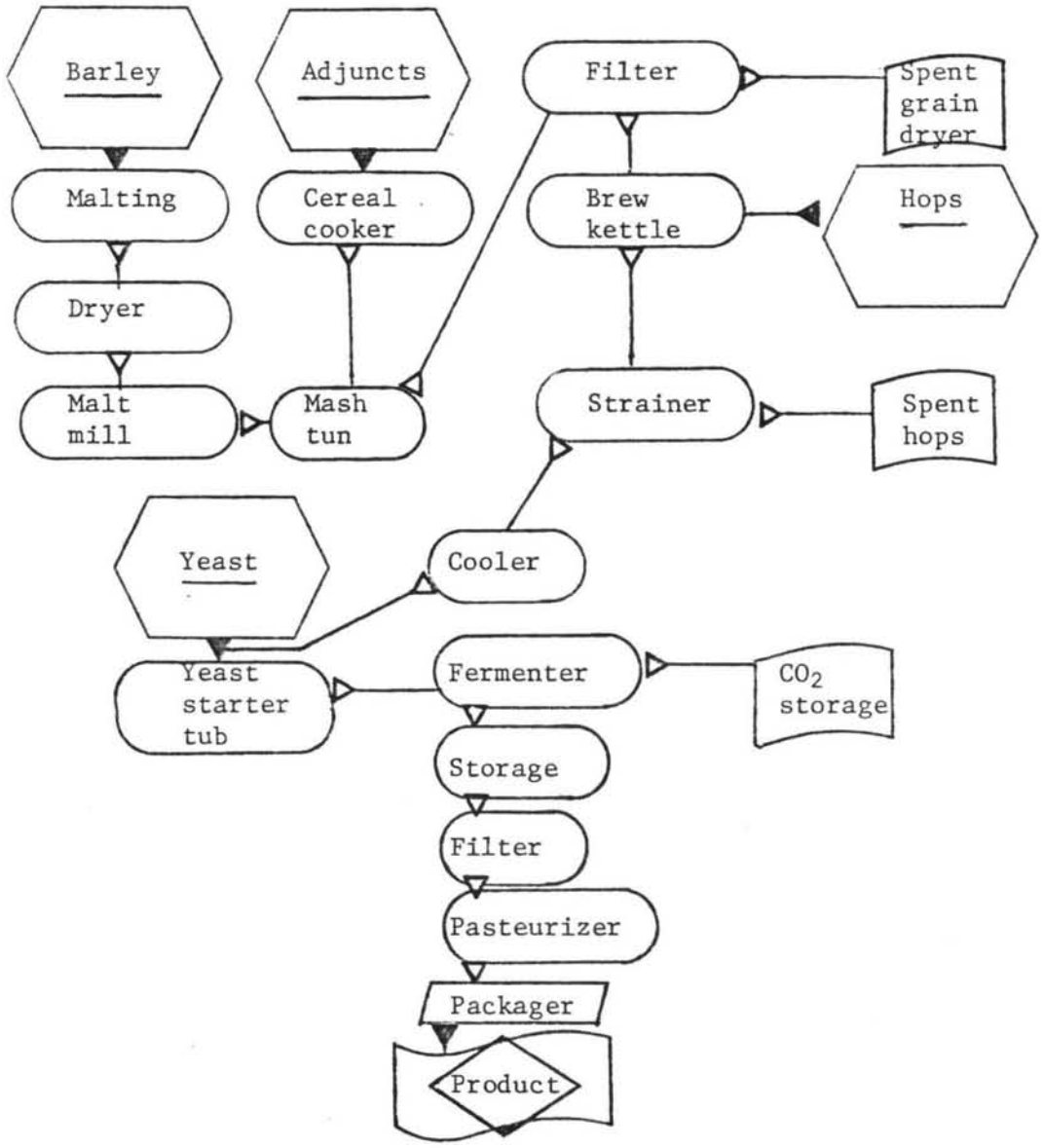

Figure 6.5.1-1. Flow diagram of a beer making process.

6.5.1.2 Emissions and Controls[2-7]

The major emissions from beer making and their sources are particulates and volatile organics, mainly ethanol, from spent grain drying, and particulates from grain handling. Volatile organics (VOC) from fermentation are negligible, and they are fugitive because the fermenters are closed to provide for collecting carbon dioxide. Other brewery processes are minor sources of volatile organics, ethanol and related compounds, such as boiling

wort in the brew kettle and malt drying. An estimate of these emissions is not available.

Fugitive particulate emissions from grain handling and milling at breweries are reduced by operating in well ventilated, low pressure conditions. At grain handling and milling operations, fabric filters are most often used for dust collection. Organics and organic particulate matter from spent grain drying can be controlled by mixing the dryer exhaust with the combustion air of a boiler. A centrifugal fan wet scrubber is the most commonly used control.

TABLE 6.5.1-1. EMISSION FACTORS FOR BEER BREWING[a]

EMISSION FACTOR RATING: D

Source	Particulate	Volatile Organic Compounds
Grain handling	1.5 (3)[b]	
Brew kettle		NA[c]
Spent grain drying	2.5 (5)[b]	1.31 (2.63)[d]
Cooling units		NA[c]
Fermentation		Neg[e]

[a]Expressed in terms of kg/10^6g (lb/ton) of grain handled. Blanks indicate no emissions.
[b]Reference 6.
[c]Factors not available, but negligible amounts of ethanol emissions are suspected.
[d]Reference 4. Mostly ethanol.
[e]Negligible amounts of ethanol, ethyl acetate, isopropyl alcohol, n-propyl alcohol, isoamyl alcohol, and isoamyl acetate emissions are suspected.

References for Section 6.5.1

1. H.E. Høyrup, "Beer and Brewing", Kirk-Othmer Encyclopedia of Chemical Technology, Volume 3, John Wiley and Sons, Inc., New York, 1964, pp. 297-338.

2. R. Norris Shreve, Chemical Process Industries, 3rd Ed., McGraw-Hill Book Company, New York, 1967, pp. 603-605.

3. E.C. Cavanaugh, et al., Hydrocarbon Pollutants from Stationary Sources, EPA-600/7-77-110, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1977.

4. H.W. Bucon, et al., Volatile Organic Compound (VOC) Species Data Manual, Second Edition, EPA-450/4-80-015, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1978.

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7. Peter N. Formica, Controlled and Uncontrolled Emission Rates and Applicable Limitations for Eighty Processes, EPA-340/1-78-004, U.S. Environmental Protection Agency, Research Triangle Park, NC, April 1978.

6.5.2 WINE MAKING

6.5.2.1 General[1-4]

Wine is made by the fermentation of the juice of certain fruits, chiefly grapes. The grapes are harvested when the sugar content is right for the desired product, generally around 20 percent sugar by weight. The industry term for grape sugar content is Degrees Brix, with 1 °Brix equal to 1 gram of sugar per 100 grams of juice.

The harvested grapes are stemmed and crushed, and the juice is extracted. Sulfurous acid, potassium metabisulfite or liquefied SO_2 is used to produce 50 to 200 mg of SO_2, which is added to inhibit the growth of undesirable bacteria and yeasts. For the making of a white wine, the skins and solids are removed from the juice before fermentation. For a red wine, the skins and solids, which color the wine, are left in the juice through the fermentation stage. The pulpy mixture of juice, skins and solids is called a "must".

White wine is generally fermented at about 52°F (11°C), and red wine at about 80°F (27°C). Fermentation takes a week to ten days for white wine and about two weeks for red. Fermentation is conducted in tanks ranging in size from several thousand gallons to larger than 500,000 gallons.

The sugar of the fruit juice is converted into ethanol by the reaction:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

(sugar) (ethanol)

This process takes place in the presence of a specially cultivated yeast. Theoretically, the yield of ethanol should be 51.1 percent by weight of the initial sugar. The actual yield is found to be around 47 percent. The remaining sugar is lost as alcohol or byproducts of complex chemical mechanisms, or it remains in the wine as the result of incomplete fermentation.

When fermentation is complete, the wine goes through a finishing process for clarification. Common clarification procedures are filtration, fining refrigeration, pasteurization and aging. The wine is then bottled, corked or capped, labeled and cased. The finer red and white table wines are aged in the bottle.

6.5.2.2 Emissions and Controls[1,2]

Large amounts of CO_2 gas are liberated by the fermentation process. The gas is passed into the atmosphere through a vent in the top of the tank. Ethanol losses occur chiefly as a result of entrainment in the

CO_2. Factors which affect the amount of ethanol lost during fermentation are temperature of fermentation, initial sugar content, and whether a juice or a must is being fermented (i.e., a white or red wine being made).

Emission factors for wine making are given in Table 6.5.2-1. These emission factors are for juice fermentation (white wine) with an initial sugar content of 20 °Brix. Emission factors are given for two temperatures commonly used for fermentation.

Table 6.5.2-1. ETHANOL EMISSION FACTORS FOR UNCONTROLLED WINE FERMENTATION

EMISSION FACTOR RATING: B

Fermentation temperature	Ethanol Emissions[a,b] $lb/10^3$ gal fermented	g/kl fermented
52°F (11.1°C)[c]	1.06	127.03
80°F (26.7°C)[c,d]	4.79	574.04
Other conditions	e	e

[a] Due primarily to entrainment in CO_2, not evaporation. H_2S, mercaptans and other componments may be emitted in limited quantities, but no test or other information is available.

[b] C_2H_5OH lost in production.

[c] References 1 and 2. For white wine with initial 20° Brix.

[d] For red wine, add correction term for must fermentation (2.4 $lb/10^3$ gal or 287.62 g/kl).

[e] See Equation 1.

Emission factors for wines produced under other conditions can be approximated with the following equation:

$$EF = [0.136T - 5.91] + [(B - 20.4)(T - 15.21)(0.00685)] + [C] \quad (1)$$

where: EF = emission factor, pounds of ethanol lost per thousand gallons of wine made

T = fermentation temperature, °F

B = initial sugar content, °Brix

C = correction term, 0 (zero) for white wine or 2.4 $lb/10^3$ gal for red wine

Although no testing has been done on emissions from wine fermentation without grapes, it is expected that ethanol is also emitted from these operations.

There is potential alcohol loss at various working and storage stages in the production process. Also, fugitive alcohol emissions could occur from disposal of fermentation solids. Ethanol is considered to be a reactive precursor of photochemical oxidants (ozone). Emissions would be highest during the middle of the fermentation season and would taper off towards the end. Since wine facilities are concentrated in certain areas, these areas would be more affected.

Currently, the wine industry uses no means to control the ethanol lost during fermentation.

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1. Source Test Report and Evaluation on Emissions from a Fermentation Tank at E. & J. Gallo Winery, C-8-050, California Air Resources Board, Sacramento, CA, October 31, 1978.

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6.6 FISH PROCESSING

revised by Susan Sercer

6.6.1 Process Description

Fish processing includes the canning of fish and the manufacturing of by-products such as fish oil and fish meal. The manufacturing of fish oil and fish meal are known as reduction processes. A generalized fish processing operation is presented in Figure 6.6-1 .

Two types of canning operations are used. One is the "wet fish" method in which trimmed and eviscerated fish are cooked directly in open cans. The other operation is the "pre-cooked" process in which eviscerated fish are cooked whole and portions are hand selected and packed into cans. The pre-cooked process is used primarily for larger fish such as tuna.

By-product manufacture of rejected whole fish and scrap requires several steps. First, the fish scrap mixture from the canning line is charged to a live steam cooker. After the material leaves the cooker, it is pressed to remove water and oil. The resulting press cake is broken up and dried in a rotary drier.

Two types of driers are used to dry the press cake: direct-fired and steam-tube driers. Direct-fired driers contain a stationary firebox ahead of the rotating section. The hot products of combustion from the firebox are mixed with air and wet meal inside the rotating section of the drier. Exhaust gases are generally vented to a cyclone separator to recover much of the entrained fish meal product. Steam-tube driers contain a cylindrical bank of rotating tubes through which hot, pressurized steam is passed. Heat is indirectly transferred to the meal and the air from the hot tubes. As with direct-fired driers, the exhaust gases are vented to a cyclone for product recovery.

6.6.2 Emissions and Controls

Although smoke and dust can be a problem, odors are the most objectionable emissions from fish processing plants. By-product manufacture results in more of these odorous contaminants than cannery operations because of the greater state of decomposition of the materials processed. In general, highly decayed feedstocks produce greater concentrations of odors than do fresh feedstocks.

The largest odor sources are the fish meal driers. Usually, direct-fired driers emit more odors than steam-tube driers. Direct-fired driers will also emit smoke, particularly if the driers are operated under high temperature conditions. Cyclones are frequently employed on drier exhaust gases for product recovery and particulate emission control.

Odorous gases from reduction cookers consist primarily of hydrogen sulfide [H_2S] and trimethylamine [$(CH_3)_3N$]. Odors from reduction cookers are emitted in volumes appreciably less than from fish meal driers. There are virtually no particulate emissions from reduction cookers.

Some odors are also produced by the canning processes. Generally, the pre-cooked process emits less odorous gases than the wet-fish process. This is because in the pre-cooked process, the odorous exhaust gases are trapped in the cookers, whereas in the wet-fish process, the steam and odorous offgases are commonly vented directly to the atmosphere.

Fish cannery and fish reduction odors can be controlled with afterburners, chlorinator-scrubbers, and condensers. Afterburners are most effective, providing virtually 100 percent odor control; however they are costly from a fuel-use standpoint. Chlorinator-scrubbers have been found to be 95 to 99 percent effective in controlling odors from cookers and driers. Condensers are the least effective control device. Generally, centrifugal collectors are satisfactory for controlling excessive dust emissions from driers.

Emission factors for fish processing are presented in Table 6.6-1.

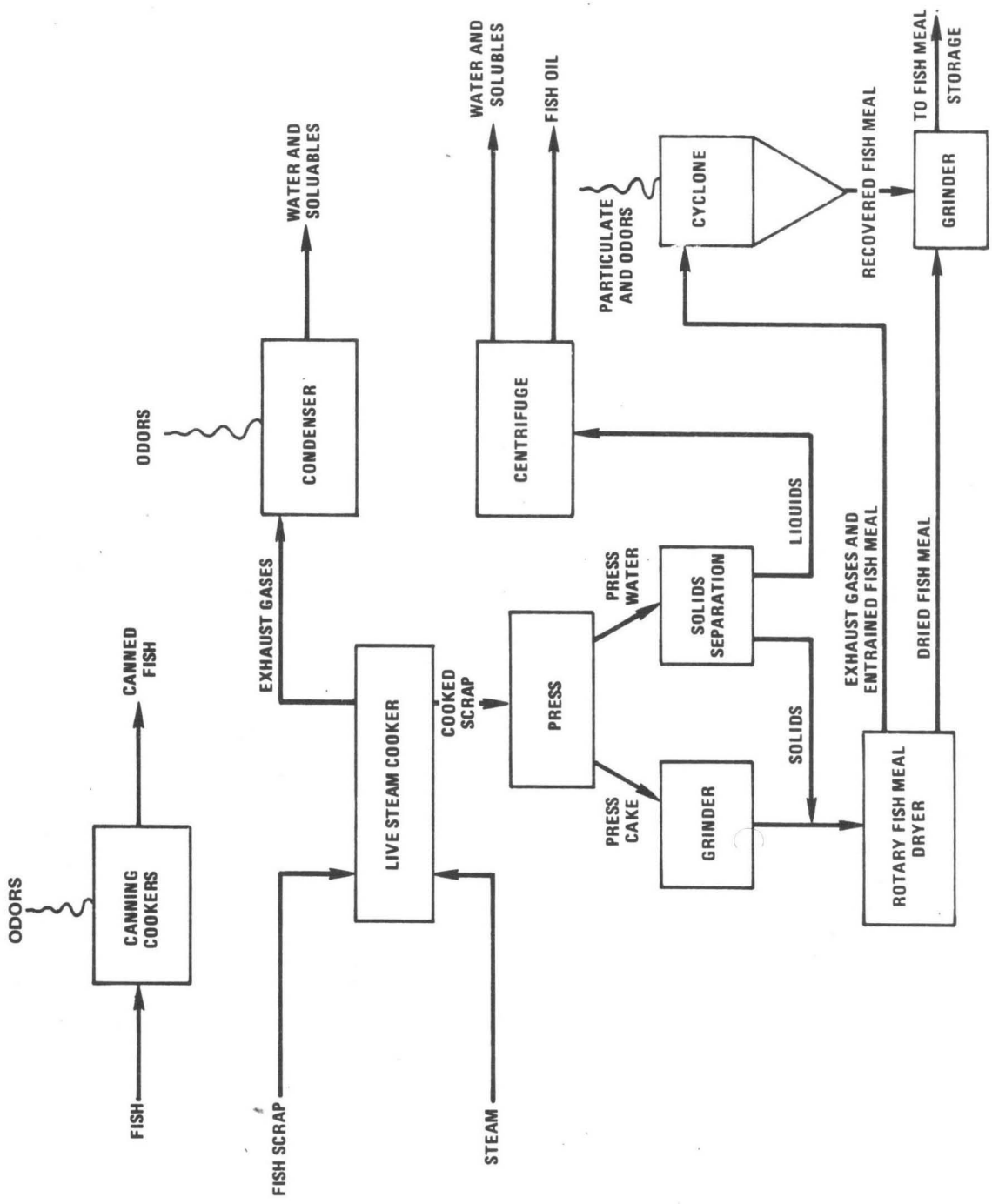

Figure 6.6-1. A generalized fish processing flow diagram.

Table 6.6-1. EMISSION FACTORS FOR FISH PROCESSING PLANTS
EMISSION FACTOR RATING: C

Emission source	Particulates		Trimethylamine $(CH_3)_3N$		Hydrogen sulfide (H_2S)	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Cookers, canning	Neg.[a]	Neg.[a]	NA[b]	NA[b]	NA[b]	NA[b]
Cookers, fish scrap						
Fresh fish	Neg.[a]	Neg.[a]	0.3[c]	0.15[c]	0.01[c]	0.005[c]
Stale fish	Neg.[a]	Neg.[a]	3.5[c]	1.75[c]	0.2[c]	0.10[c]
Dryers	0.1[d]	0.05[d]	NA[d]	NA[d]	NA[d]	NA[d]

[a]Reference 1.

[b]Although it is known that odors are emitted from canning cookers, quantitative estimates are not available.

[c]Reference 2.

[d]Limited data suggest that there is not much difference in particulate emissions between steam tube and direct-fired dryers. Based on reference 1.

References for Section 6.6

1. Walsh, R.T., K.D. Luedtke, and L.K. Smith. Fish Canneries and Fish Reduction Plants. In: Air Pollution Engineering Manual. Danielson, J.A. (ed.). U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. Publication Number 999-AP-40. 1967. p. 760-770.

2. Summer, W. Methods of Air Deodorization. New York, Elsevier Publishing Company. 1963. p. 284-286.

6.7 MEAT SMOKEHOUSES

6.7.1 Process Description[1]

Smoking is a diffusion process in which food products are exposed to an atmosphere of hardwood smoke, causing various organic compounds to be absorbed by the food. Smoke is produced commerically in the United States by three major methods: (1) by burning dampened sawdust (20 to 40 percent moisture), (2) by burning dry sawdust (5 to 9 percent moisture) continuously, and (3) by friction. Burning dampened sawdust and kiln-dried sawdust are the most widely used methods. Most large, modern, production meat smokehouses are the recirculating type, in which smoke is circulated at reasonably high temperatures throughout the smokehouse.

6.7.2 Emissions and Controls[1]

Emissions from smokehouses are generated from the burning hardwood rather than from the cooked product itself. Based on approximately 110 pounds of meat smoked per pound of wood burned (110 kilograms of meat per kilogram of wood burned), emission factors have been derived for meat smoking and are presented in Table 6.7-1.

Emissions from meat smoking are dependent on several factors, including the type of wood, the type of smoke generator, the moisture content of the wood, the air supply, and the amount of smoke recirculated. Both low-voltage electrostatic precipitators and direct-fired afterburners may be used to reduce particulate and organic emissions. These controlled emission factors have also been shown in Table 6.7-1.

Table 6.7-1. EMISSION FACTORS FOR MEAT SMOKING[a,b]
EMISSION FACTOR RATING: D

Pollutant	Uncontrolled		Controlled[c]	
	lb/ton of meat	kg/MT of meat	lb/ton of meat	kg/MT of meat
Particulates	0.3	0.15	0.1	0.05
Carbon monoxide	0.6	0.3	Neg[d]	Neg
Hydrocarbons (CH_4)	0.07	0.035	Neg	Neg
Aldehydes (HCHO)	0.08	0.04	0.05	0.025
Organic acids (acetic)	0.2	0.10	0.1	0.05

[a]Based on 110 pounds of meat smoked per pound of wood burned (110 kg meat/kg wood burned).
[b]References 2, 3, and section on charcoal production.
[c]Controls consist of either a wet collector and low-voltage precipitator in series or a direct-fired afterburner.
[d]With afterburner.

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References for Section 6.7

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Carter, E. Private communication between Maryland State Department of Health and Resources Research, Incorporated. November 21, 1969.

3. Polglase, W.L., H.F. Dey, and R.T. Walsh. Smokehouses. In: Air Pollution Engineering Manual. Danielson, J. A. (ed.). U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. Publication Number 999-AP-40. 1967. p. 750-755.

6.8 AMMONIUM NITRATE FERTILIZERS

6.8.1 General [1,3]

Ammonium nitrate fertilizers are produced by reacting nitric acid and ammonia to form the ammonium nitrate solutions or solids. Essentially four steps are involved in producing solid ammonium nitrate: neutralization, evaporation/concentration, solidification, and final particle characterization and finishing (Figure 6.8-1).

Anhydrous ammonia and 55 percent nitric acid are combined in a neutralizer to produce a 61 percent ammonium nitrate solution, with the heat of reaction concentrating that solution to approximately 83 percent ammonium nitrate before it leaves the neutralizer. The solution is then further concentrated in the evaporator/concentrator before the solid formation step. If a liquid ammonium nitrate product is desired, it is obtained at this point in the process.

Solidification can be achieved by means of prilling, granulation, crystallization, or graining. Prilling, the most common method used, accounts for over 90 percent of the solid product formed. High-density or low-density prills can be produced, depending on the feed solution concentration. High-density prills are preferred in fertilizers because of their excellent blending and spreading characteristics and their long storage life. Low-density prills, while used for fertilizer, are primarily good for blasting agents because of their high porosity. Solid fertilizer production by granulation uses ordinary granulator processes instead of a prilling tower in order to achieve the desired solid product.

An adjusting tank is used in conjunction with the neutralizer to store the 83 percent ammonium nitrate solution from the neutralizer, receive the overflow from a head tank at the top of the prilling tower, and supply the evaporator/concentrator on a demand basis. A lump-dissolving tank is used to recycle substandard material (undersize or oversize). The oversize and/or fine materials enter the tank, dissolve, and are sent to the neutralizer as a weak (~60 percent) recycle liquor.

Final particle characterization and finishing may include sizing, cooling, drying, coating, and preparation for shipment. The actual operations used at a particular plant depend on the product manufactured and the solidification process employed.

6.8.2 Emissions[3]

Emissions from the manufacture of ammonium nitrate consist of particulates and of either ammonia or nitric acid from the neutralizer, depending upon which reactant is added in excess to the process. Normally, ammonia is added in excess because it reduces the particulate loading and opacity of the exhaust stream.

Table 6.8-1 presents emission factors for the different emission points in the prilling process. Except for the dryer and cooler, uncontrolled emission factors are given because most plants operate without controls on the neutralizer, evaporator/concentrator, and prill tower. Coolers and dryers are normally equipped with high-efficiency scrubbers to recover valuable products and recycle them in the process.

In addition to the emissions indicated in Table 6.8-1, particulate matter may escape from coating/bulk loading operations. Emissions from coating operations are estimated to be <6 g/kg under the assumption that a maximum of 10 percent of the coating material used is lost to the atmosphere. Particulates from bulk loading operations are estimated to have an emission factor of <0.01 g/kg of material loaded.

Solid fertilizer produced by granulation or graining amounts to less than 9 percent of the solid fertilizer produced and emissions are only fugitive losses.[3] Table 6.8-2 presents emissions from the granulation process.

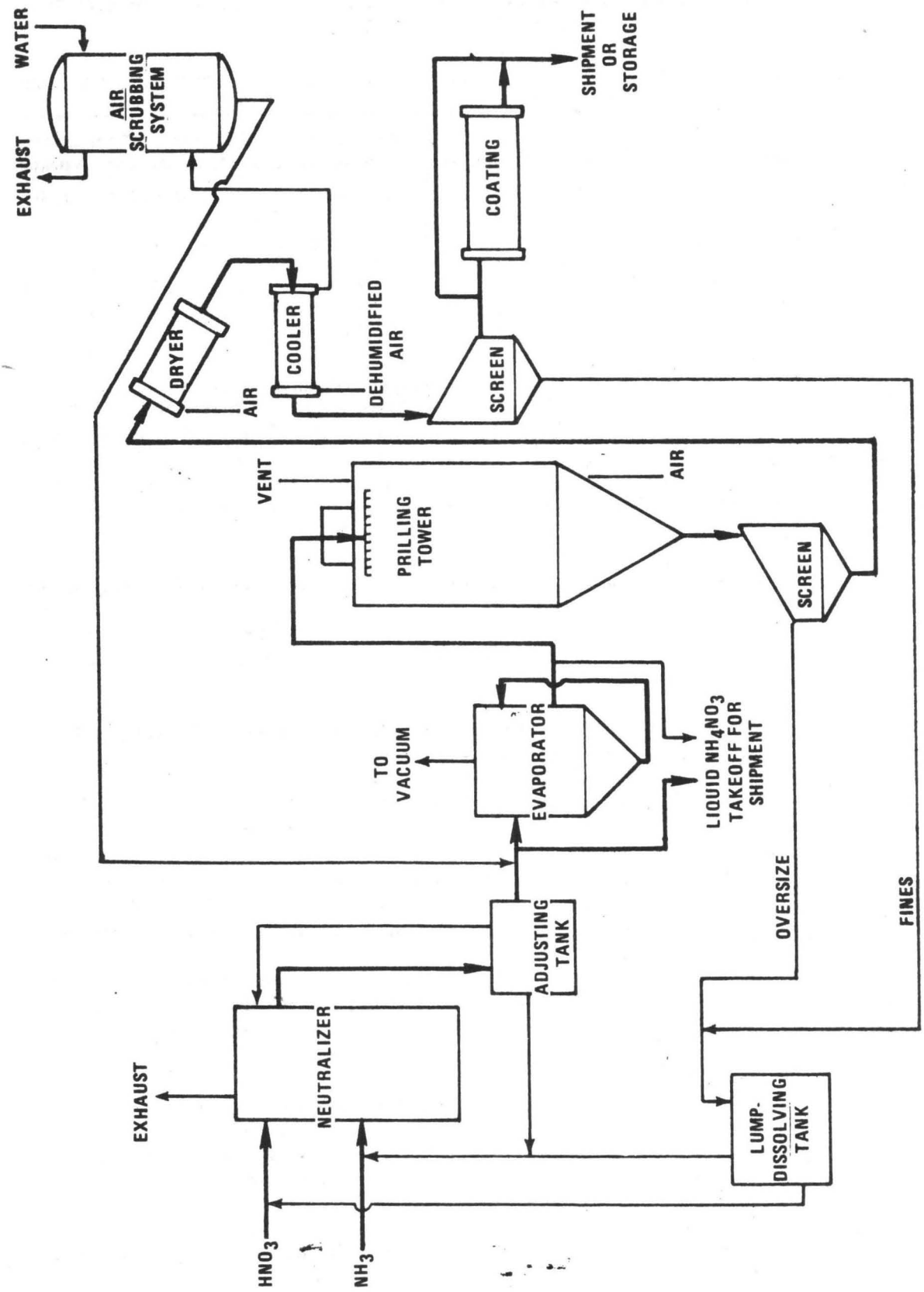


Figure 6.8-1. Prilling process flow diagram.

Table 6.8-1. EMISSION FACTORS FOR AMMONIUM NITRATE FERTILIZER MANUFACTURING [a]
EMISSION FACTOR RATING: A

	High-density prilling						Low-density prilling					
	Particulate		Ammonia		Nitric acid		Particulate		Ammonia		Nitric acid	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/Mt	lb/ton	kg/Mt	lb/ton	kg/Mt
Neutralizer[b]	3.3[c]	1.6[c]	0.86[d]	0.43[d]	≤0.52	≤0.26	0.08[c]	0.04[c]	0.86[d]	0.43[d]	≤0.52	≤0.26
Evaporator/ concentrator	0.94[c]	0.47[c]					0.18[c]	0.09[c]				
Prilling tower	2.7[c]	1.4[c]					1.00[c]	0.50[c]				
Dryer and cooler[e,f]	0.10	0.05					0.08	0.04				
Coating[g,h]	≤ 4.0	≤2.0					≤6.0	≤3.0				
Bulk loading[g]	≤0.02	≤0.01					≤0.02	≤0.01				

[a] Emission factor expressed as lb (kg) per ton [metric ton (MT)] of ammonium nitrate fertilizer produced.
[b] Ammonia or nitric acid released during production is assumed to come from the neutralizer. Available data are insufficient to provide further breakdown of the emissions.
[c] Data are for uncontrolled operations.
[d] Emission ranges of 0.052 to 6.3 lb/ton (0.26 to 3.1 kg/MT) result from variations in plant operation.
[e] Data are for controlled operations using a wet scrubber with an efficiency of 95 percent.
[f] Dryer is not used in high-density prilling.
[g] Fugitive particulate emissions escape from coating and bulk loading operations.
[h] Coating increases the particle emission level of low-density prills. Coatings are not normally applied to high density prills (~3 percent are coated).

Table 6.8-2. EMISSION FACTORS FOR GRANULAR NITRATE FERTILIZER MANUFACTURING WITHOUT CONTROLS[a,b]

EMISSION FACTOR RATING: B

	Particulate		Nitrogen oxides (NO_x)		Ammonia	
Emission point[c]	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Neutralizer [d,e]	-	-	-	-	2	1
Grandulator [f]	0.4	0.2	0.9	0.45	0.5	0.25
Dryers & coolers [f,g]	7	3.5	3	1.5	1.3	0.65

[a] Emission factor expressed as lb (kg) per ton [metric ton (MT)] of fertilizer produced.
[b] Solid formulation by granulation accounts for less than 9 percent of fertilizer production (Reference 3).
[c] Reference 1.
[d] Reference 2.
[e] Controlled factor based on 95 percent recovery in recycle scrubber.
[f] Use of wet cyclones can reduce emissions by 70 percent.
[g] Use of wet-screen scrubber following cyclone can reduce emissions by 95 percent.

6.8.3 Controls[3]

Several systems have been developed for the control of emissions from the prilling tower and the neutralizer. A system using a modified neutralizer may have a 10- to 20-fold reduction in emissions. Wet scrubbing systems for prill towers have been shown to achieve a 90 percent reduction (by weight) in prill tower emissions. Another system, using a special cone in the prill tower and a mist eliminator, has achieved 98.6 percent removal efficiencies on combined exhausts from the prill tower, neutralizer, and evaporator/concentrator.

High-efficiency wet scrubbers are used on cooler and dryer exhausts to recover entrained particulates. The weak ammonium nitrate scrubbing liquor is recycled to the lump-dissolving tank and ultimately back to the system. Removal efficiencies of 95 to 97 percent are standard for these scrubbers due to the large (10 to 1000 μm) size of the particulate. Controlled emission factors are given for dryers and coolers in Table 6.8-1 since the use of controls is standard industry practice.

References for Section 6.8

1. Unpublished source sampling data. Resources Research, Incorporated. Reston, Va.

2. Private communication with personnel from Gulf Design Corporation. Lakeland, Fl.

3. Search, W.J. and R.B. Reznik. Source Assessment: Ammonium Nitrate Production. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/2-77-107i. September 1977.

6.9 ORCHARD HEATERS

by Dennis H. Ackerson

6.9.1 General[1-6]

Orchard heaters are commonly used in various areas of the United States to prevent frost damage to fruit and fruit trees. The five common types of orchard heaters–pipeline, lazy flame, return stack, cone, and solid fuel–are shown in Figure 6.9-1. The pipeline heater system is operated from a central control and fuel is distributed by a piping system from a centrally located tank. Lazy flame, return stack, and cone heaters contain integral fuel reservoirs, but can be converted to a pipeline system. Solid fuel heaters usually consist only of solid briquettes, which are placed on the ground and ignited.

The ambient temperature at which orchard heaters are required is determined primarily by the type of fruit and stage of maturity, by the daytime temperatures, and by the moisture content of the soil and air.

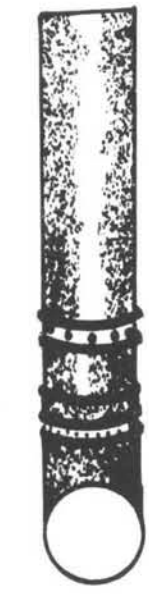
During a heavy thermal inversion, both convective and radiant heating methods are useful in preventing frost damage; there is little difference in the effectiveness of the various heaters. The temperature response for a given fuel rate is about the same for each type of heater as long as the heater is clean and does not leak. When there is little or no thermal inversion, radiant heat provided by pipeline, return stack, or cone heaters is the most effective method for preventing damage.

Proper location of the heaters is essential to the uniformity of the radiant heat distributed among the trees. Heaters are usually located in the center space between four trees and are staggered from one row to the next. Extra heaters are used on the borders of the orchard.

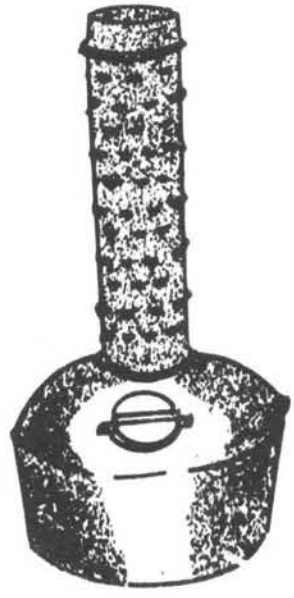
6.9.2 Emissions[1,6]

Emissions from orchard heaters are dependent on the fuel usage rate and the type of heater. Pipeline heaters have the lowest particulate emission rates of all orchard heaters. Hydrocarbon emissions are negligible in the pipeline heaters and in lazy flame, return stack, and cone heaters that have been converted to a pipeline system. Nearly all of the hydrocarbon losses are evaporative losses from fuel contained in the heater reservoir. Because of the low burning temperatures used, nitrogen oxide emissions are negligible.

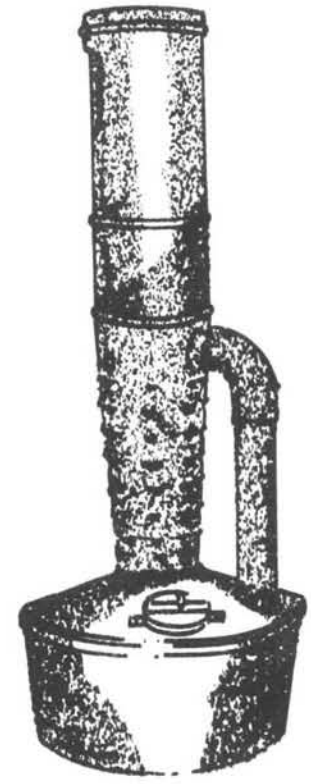
Emission factors for the different types of orchard heaters are presented in Table 6.9-1 and Figure 6.9-2.



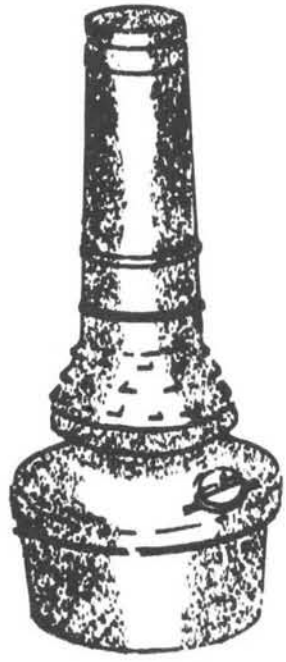
PIPELINE HEATER



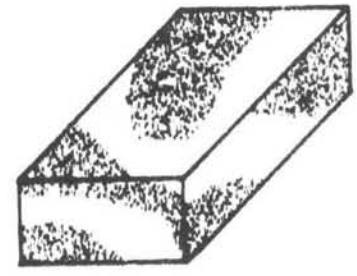
LAZY FLAME



RETURN STACK



CONE STACK



SOLID FUEL

Figure 6.9-1. Types of orchard heaters.[6]

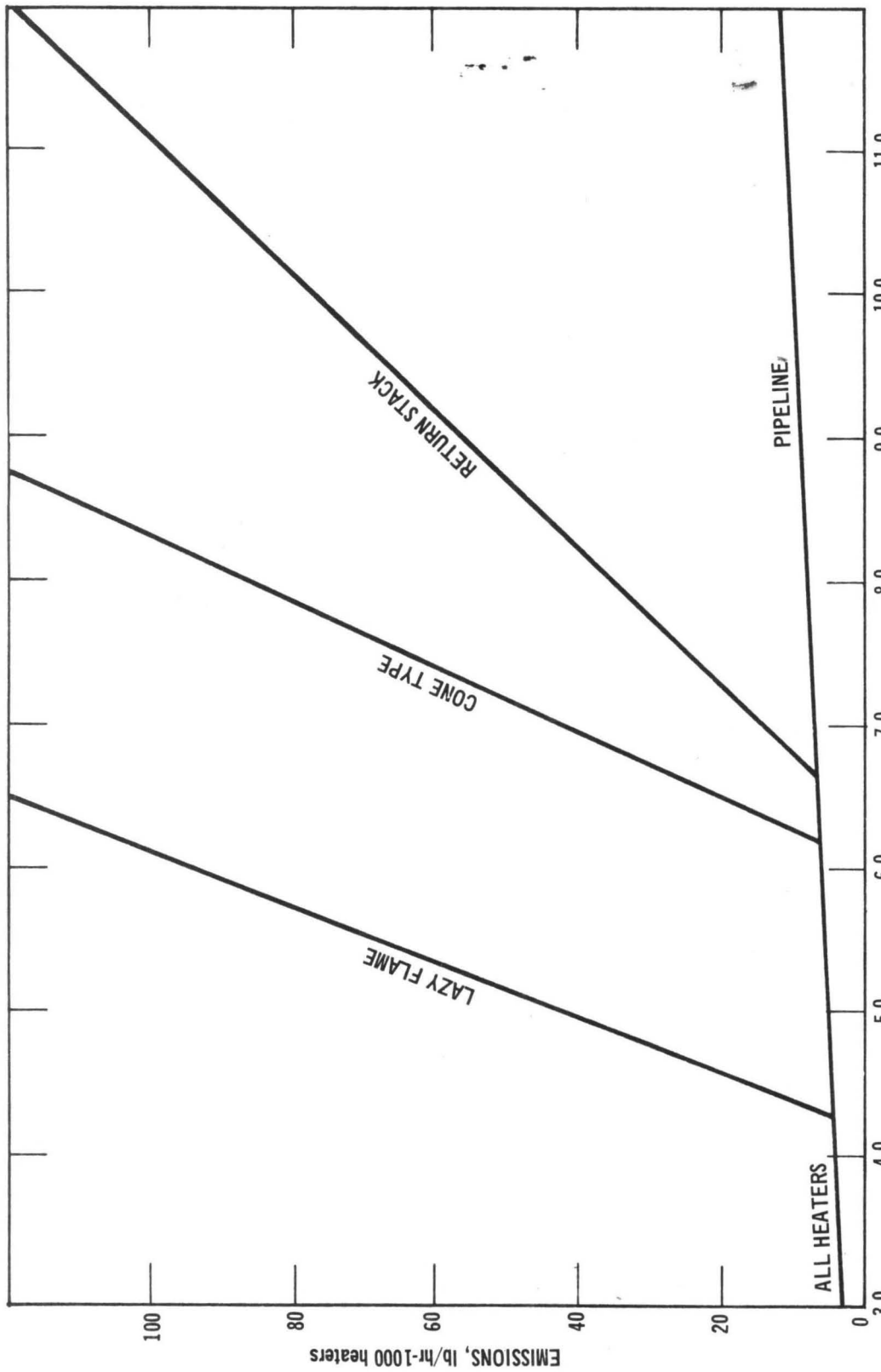


Figure 6.9-2. Particulate emissions from orchard heaters.[3,6]

Table 6.9-1. EMISSION FACTORS FOR ORCHARD HEATERS[a]
EMISSION FACTOR RATING: C

Pollutant	Type of heater				
	Pipeline	Lazy flame	Return stack	Cone	Solid fuel
Particulate					
lb/htr-hr	b	b	b	b	0.05
kg/htr-hr	b	b	b	b	0.023
Sulfur oxides[c]					
lb/htr-hr	0.13S[d]	0.11S	0.14S	0.14S	NA[e]
kg/htr-hr	0.06S	0.05S	0.06S	0.06S	NA
Carbon monoxide					
lb/htr-hr	6.2	NA	NA	NA	NA
kg/htr-hr	2.8	NA	NA	NA	NA
Hydrocarbons[f]					
lb/htr-yr	Neg[g]	16.0	16.0	16.0	Neg
kg/htr-yr	Neg	7.3	7.3	7.3	Neg
Nitrogen oxides[h]					
lb/htr-hr	Neg	Neg	Neg	Neg	Neg
kg/htr-hr	Neg	Neg	Neg	Neg	Neg

[a] References 1,3,4, and 6.

[b] Particulate emissions for pipeline, lazy flame, return stack, and cone heaters are shown in Figure 6.9-2.

[c] Based on emission factors for fuel oil combustion in Section 1.3.

[d] S = sulfur content.

[e] Not available.

[f] Reference 1. Evaporative losses only. Hydrocarbon emissions from combustion are considered negligible. Evaporative hydrocarbon losses for units that are part of a pipeline system are negligible.

[g] Negligible.

[h] Little nitrogen oxide is formed because of the relatively low combustion temperatures.

References for Section 6.9

1. Air Pollution in Ventura County. County of Ventura Health Department, Santa Paula, CA, June 1966.

2. Frost Protection in Citrus. Agricultural Extension Service, University of California, Ventura, CA, November 1967.

3. Personal communication with Mr. Wesley Snowden. Valentine, Fisher, and Tomlinson, Consulting Engineers, Seattle, WA, May 1971.

4. Communication with the Smith Energy Company, Los Angeles, CA, January 1968.

5. Communication with Agricultural Extension Service, University of California, Ventura, CA, October 1969.

6. Personal communication with Mr. Ted Wakai. Air Pollution Control District, County of Ventura, Ojai, CA, May 1972.

6.10 PHOSPHATE FERTILIZERS

6.10.1 NORMAL SUPERPHOSPHATES[1]

6.10.1.1 General

The term "normal superphosphate" is used to designate a fertilizer material containing 15 - 21 percent P_2O_5. It is prepared by reacting ground phosphate rock with 65 - 75 percent sulfuric acid. Rock and acid are mixed in a reaction vessel, held in an enclosed area (den) while the reaction mixture solidifies, and transferred to a storage pile for curing. Following curing, the product is most often ground and bagged for sale as run-of-the-pile product. It can also be granulated, for sale as granulated superphosphate or granular mixed fertilizer. However, this accounts for less than 5 percent of total production. To produce a granular normal superphosphate material, run-of-the-pile material is first fed to a pulverizer to be crushed, ground, and screened. Screened material is sent to a rotary drum granulator and then through a rotary dryer. The material goes through a rotary cooler and on to storage bins for sale as bagged or bulk product. Superphosphate fertilizers are produced at 79 plants in the United States. A generalized flow diagram of the process for the production of normal superphosphate is shown in Figure 6.10.1-1.

6.10.1.2 Emissions and Controls

Sources of emissions at a normal superphosphate plant include rock unloading and feeding, mixer (reactor), den, curing building, and fertilizer handling operations. Rock unloading, handling and feeding generate particulate emissions of phosphate rock dust. The mixer, den and curing building emit gaseous fluorides (HF and SiF_4) and particulates composed of fluoride and phosphate material. Fertilizer handling operations release fertilizer dust.

At a typical normal superphosphate plant, the rock unloading, handling and feeding operations are controlled by a baghouse. The mixer and den are controlled by a wet scrubber. The curing building and fertilizer handling operations normally are not controlled.

Emission factors for the production of normal superphosphate are presented in Table 6.10.1-1. These emission factors are averages based on recent source test data from controlled phosphate fertilizer plants in Florida.

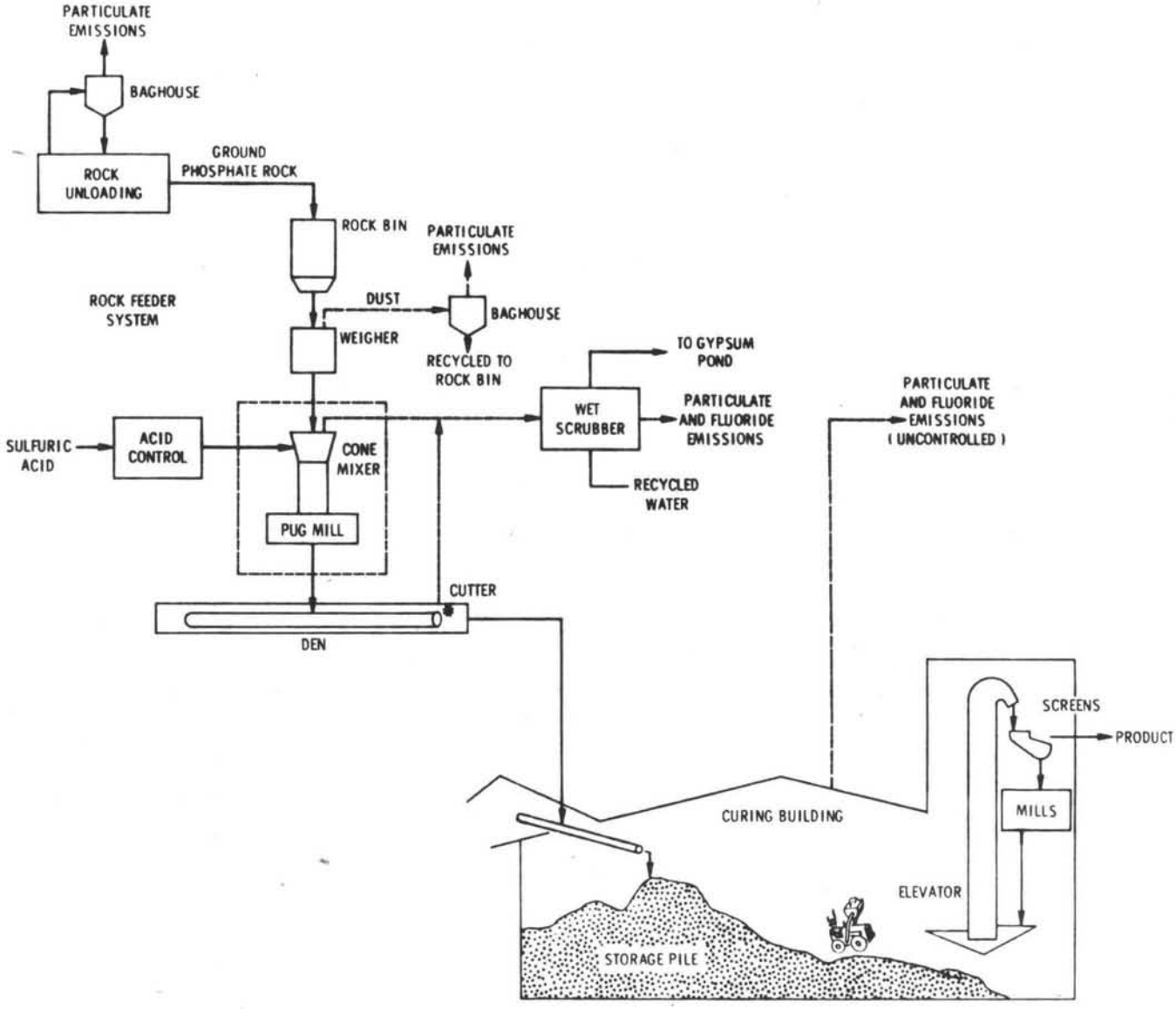


Figure 6.10.1-1. Normal superphosphate process flow diagram.

TABLE 6.10.1-1. EMISSION FACTORS FOR THE PRODUCTION OF NORMAL SUPERPHOSPHATE[a]

EMISSION FACTOR RATING: A

Emission point	Pollutant	Emission factor	
		lb/ton P_2O_5	kg/MT P_2O_5
Rock unloading[b]	Particulate	0.56	0.28
Rock feeding[b]	Particulate	0.11	0.06
Mixer and den[c]	Particulate	0.52	0.26
	Fluoride	0.20	0.10
Curing building[d]	Particulate	7.20	3.60
	Fluoride	3.80	1.90

[a]Reference 1, pp. 74-77, 169.
[b]Factors are for emissions from baghouse with an estimated collection efficiency of 99%.
[c]Factors are for emissions from wet scrubbers with a reported 97% control efficiency.
[d]Uncontrolled.

Particulate emissions from ground rock unloading, storage and transfer systems are controlled by baghouse collectors. These cloth filters have reported efficiencies of over 99 percent. Collected solids are recycled to the process.

Silicon tetrafluoride and hydrogen fluoride emissions, and particulate from the mixer, den and curing building are controlled by scrubbing the offgases with recycled water. Gaseous silicon tetrafluoride in the presence of moisture reacts to form gelatinous silica which has the tendency to plug scrubber packings. The use of conventional packed countercurrent scrubbers and other contacting devices with small gas passages for emissions control is therefore limited. Scrubber types that can be used are cyclonic, venturi, impingement, jet ejector and spray crossflow packed. Spray towers also find use as precontactors for fluorine removal at relatively high concentration levels (greater than 3,000 ppm, or 4.67 g/m^3).

Air pollution control techniques vary with particular plant designs. The effectiveness of abatement systems in removal of fluoride and particulate also varies from plant to plant, depending on a number of factors. The effectiveness of fluorine abatement is determined by (1) inlet fluorine concentration, (2) outlet or saturated gas temperature, (3) composition and temprature of the scrubbing liquid, (4) scrubber type and transfer units, and (5) effectiveness of entrainment separation. Control efficiency is enhanced by increasing the number of scrubbing

stages in series and by using a fresh water scrub in the final stage. Reported efficiencies for fluoride control range from less than 90 percent to over 99 percent, depending on inlet fluoride concentrations and the system employed. An efficiency of 98 percent for particulate control is achievable.

Reference for Section 6.10.1

1. J. M. Nyers, et al., Source Assessment: Phosphate Fertilizer Industry, EPA-600/2-79-019c, U. S. Environmental Protection Agency, Research Triangle Park, NC, May 1979.

6.10.2 TRIPLE SUPERPHOSPHATES

6.10.2.1 General[1]

Triple superphosphate is a fertilizer material of P_2O_5 content over 40 percent, made by reacting phosphate rock and phosphoric acid. The two principal types of triple superphosphate are run-of-the-pile (40 percent of total production) and granular (60 percent of total production). Run-of-the-pile material is essentially a pulverized mass of variable particle size produced in a manner similar to normal superphosphate. Thus, phosphoric acid (50 percent P_2O_5) is reacted in a cone mixer with ground phosphate rock. The resultant slurry begins to solidify on a slow moving conveyer (den) en route to the curing area. At the point of discharge from the den, the material passes through a rotary mechanical cutter that breaks up the solid mass. Coarse run-of-the-pile product is sent to a storage pile and cured for a period of 3 to 5 weeks. The final product is then mined from the "pile" in the curing shed, and then crushed, screened, and shipped in bulk. Granular triple superphosphate yields larger, more uniform particles with improved storage and handling properties. Most of this material is made with the Dorr-Oliver slurry granulation process, illustrated in Figure 6.10.2-1. In this process, ground phosphate rock is mixed with phosphoric acid in a reactor or mixing tank. The phosphoric acid used in this process is appreciably lower in concentration (40 percent P_2O_5) than that used to manufacture run-of-the-pile product, because the lower strength acid maintains the slurry in a fluid state during a mixing period of 1 to 2 hours. A thin slurry is continuously removed and distributed onto dried, recycled fines, where it coats the granule surfaces and builds up its size.

Pugmills and rotating drum granulators are used in the granulation process. A pugmill is composed of a u-shaped trough carrying twin contrarotating shafts, upon which are mounted strong blades or paddles. Their action agitates, shears and kneads the solid/liquid mix and transports the material along the trough. The basic rotary drum granulator consists of an open ended slightly inclined rotary cylinder, with retaining rings at each end and a scraper or cutter mounted inside the drum shell. A rolling bed of dry material is maintained in the unit while the slurry is introduced through distributor pipes set lengthwise in the drum under the bed. Slurry-wetted granules then discharge onto a rotary dryer, where excess water is evaporated and the chemical reaction is accelerated to completion by the dryer heat. Dried granules are then sized on vibrating screens. Oversize particles are crushed and recirculated to the screen, and undersize particles are recycled to the granulator. Product size granules are cooled in a countercurrent rotary drum, then sent to a storage pile for curing. After a curing period of 3 to 5 days, granules are removed from storage, screened, bagged and shipped.

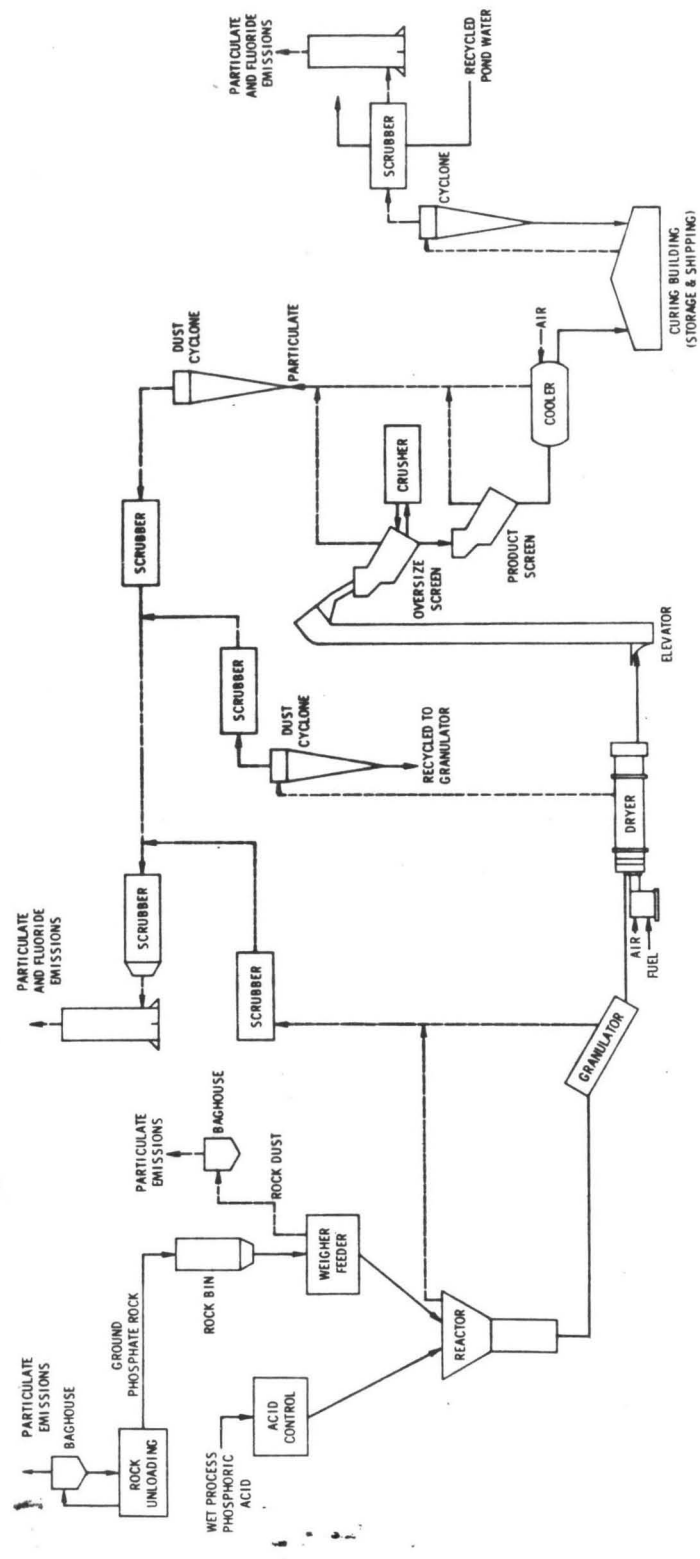


Figure 6.10.2-1. Dorr-Oliver process flow diagram for granular triple superphosphate production.

6.10.2.2 Emissions and Controls[1]

Emissions of fluorine compounds and dust particles occur during the production of granular triple superphosphate. Silicon tetrafluoride and hydrogen fluoride are released by the acidulation reaction and they evolve from the reactors, den, granulator, dryer and cooler. Evolution of fluorides continues at a lower rate in the curing building, as the reaction preceeds. Sources of particulate emissions include the reactor, granulator, dryer, cooler, screens, mills, and transfer conveyors. Additional emissions of particulate result from the unloading, storage and transfer of ground phosphate rock.

At a typical plant, emissions from the reactor, den and granulator are controlled by scrubbing the effluent gas with recycled gypsum pond water. Emissions from the dryer, cooler, screens, mills, product transfer systems, and storage building are sent to a cyclone separator for removal of a portion of the dust before going to wet scrubbers. Baghouses are used to control the fine rock particles generated by the preliminary ground rock handling activities.

Emission factors for the production of run-of-the-pile and granular triple superphosphate are given in Table 6.10.2-1. These emission factors are averages based on recent source test data from controlled phosphate fertilizer plants in Florida.

Particulate emissions from ground rock unloading, storage and transfer systems are controlled by baghouse collectors. These cloth filters have reported efficiencies of over 99 percent. Collected solids are recycled to the process. Emissions of silicon tetrafluoride, hydrogen fluoride, and particulate from the production area and curing building are controlled by scrubbing the offgases with recycled water. Exhausts from the dryer, cooler, screens, mills, and curing building are sent first to a cyclone separator and then to a wet scrubber.

Gaseous silicon tetrafluoride in the presence of moisture reacts to form gelatinous silica, which has the tendency to plug scrubber packings. The use of conventional packed countercurrent scrubbers and other contacting devices with small gas passages for emissions control is therefore limited. Scrubber types that can be used are (1) spray tower, (2) cyclonic, (3) venturi, (4) impingement, (5) jet ejector, and (6) spray-crossflow packed.

Spray towers are used as precontactors for fluorine removal at relatively high concentration levels (greater than 3,000 ppm, or 4.67 g/m^3).

Air pollution control techniques vary with particular plant designs. The effectiveness of abatement systems for the removal of fluoride and particulate also varies from plant to plant, depending on a number of factors. The effectiveness of fluorine abatement is determined by (1)

TABLE 6.10.2-1. CONTROLLED EMISSION FACTORS FOR THE PRODUCTION OF TRIPLE SUPERPHOSPHATES[a]

EMISSION FACTOR RATING: A

Process	Emission point	Pollutant	Controlled emission factor lb/ton P_2O_5	Controlled emission factor kg/MT P_2O_5
Run-of-the-pile triple superphosphate	Rock unloading[b]	Particulate	0.14	0.07
	Rock feeding[b]	Particulate	0.03	0.01
	Cone mixer, den and curing building[c]	Particulate	0.03	0.02
		Fluoride	0.20	0.10
Granular triple superphosphate	Rock unloading[b]	Particulate	0.18	0.09
	Rock feeding[b]	Particulate	0.03	0.02
	Reactor, granulator, dryer, cooler and screens[c]	Particulate	0.10	0.05
		Fluoride	0.24	0.12
	Curing building[c]	Particulate	0.20	0.10
		Fluoride	0.04	0.02

[a]Reference 1, pp. 77-80, 168, 170-171.
[b]Factors are for emissions from baghouses with an estimated collection efficiency of 99%.
[c]Factors are for emissions from wet scrubbers with an estimated 97% control efficiency.

inlet fluorine concentration, (2) outlet or saturated gas temperature, (3) composition and temperature of the scrubbing liquid, (4) scrubber type and transfer units, and (5) effectiveness of entrainment separation. Control efficiency is enhanced by increasing the number of scrubbing stages in series and by using a fresh water scrub in the final stage. Reported efficiencies for fluoride control range from less than 90 percent to over 99 percent, depending on inlet fluoride concentrations and the system employed. An efficiency of 98 percent for particulate control is achievable.

Reference for Section 6.10.2

1. J. M. Nyers, et al., Source Assessment: Phosphate Fertilizer Industry, EPA-600/2-79-019c, U. S. Environmental Protection Agency, Research Triangle Park, NC, May 1979.

6.10.3 AMMONIUM PHOSPHATES

6.10.3.1 General[1]

Ammonium phosphates are produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphate fertilizers are produced in the United States. Ammoniated superphosphates are also produced, by adding normal superphosphate or triple superphosphate to the mixture. This discussion covers only the granulation of phosphoric acid with anhydrous ammonia to produce granular fertilizers. The production of liquid ammonium phosphates and ammoniated superphosphates in fertilizer mixing plants is considered a separate process. Two basic mixer designs are used by ammoniation-granulation plants, the pugmill ammoniator and the rotary drum ammoniator. Approximately 95 percent of ammoniation-granulation plants in the United States use a rotary drum mixer developed and patented by the Tennessee Valley Authority (TVA). In the TVA process, phosphoric acid is mixed in an acid surge tank with 93 percent sulfuric acid (used for product analysis control) and with recycle and acid from wet scrubbers (see Figure 6.10.3-1). Mixed acids are then partially neutralized with liquid or gaseous anhydrous ammonia in a brick lined acid reactor. All phosphoric acid and approximately 70 percent of ammonia are introduced into this vessel.

A slurry of $NH_4H_2PO_4$ and 22 percent water is produced and sent through steam-traced lines to the ammoniator-granulator. Ammonia rich offgases from the reactor are wet scrubbed before exhausting to the atmosphere. Primary scrubbers use raw material-mixed acids as scrubbing liquor, and secondary scrubbers use gypsum pond water.

The basic rotary drum ammoniator-granulator consists of a slightly inclined open end rotary cylinder with retaining rings at each end, and a scraper or cutter mounted inside the drum shell. A rolling bed of recycled solids is maintained in the units. Slurry from the reactor is distributed on the bed, and the remaining ammonia (approximately 30 percent) is sparged underneath. Granulation, by agglomeration and by coating particules with slurry, takes place in the rotating drum and is completed in the dryer. Ammonia rich offgases pass through a wet scrubber before exhausting to the atmosphere.

Moist ammonium phosphate granules are transferred to a rotary cocurrent dryer and then to a cooler. Before exhausting to the atmosphere, these offgases pass through cyclones and wet scrubbers. Cooled granules pass to a double deck screen, in which oversize and undersize particles are separated from product particles.

6.10.3.2 Emissions and Controls

Air emissions from production of ammonium phosphate fertilizers by ammoniation granulation of phosphoric acid and ammonia result from five process operations. The reactor and ammoniator granulator produce

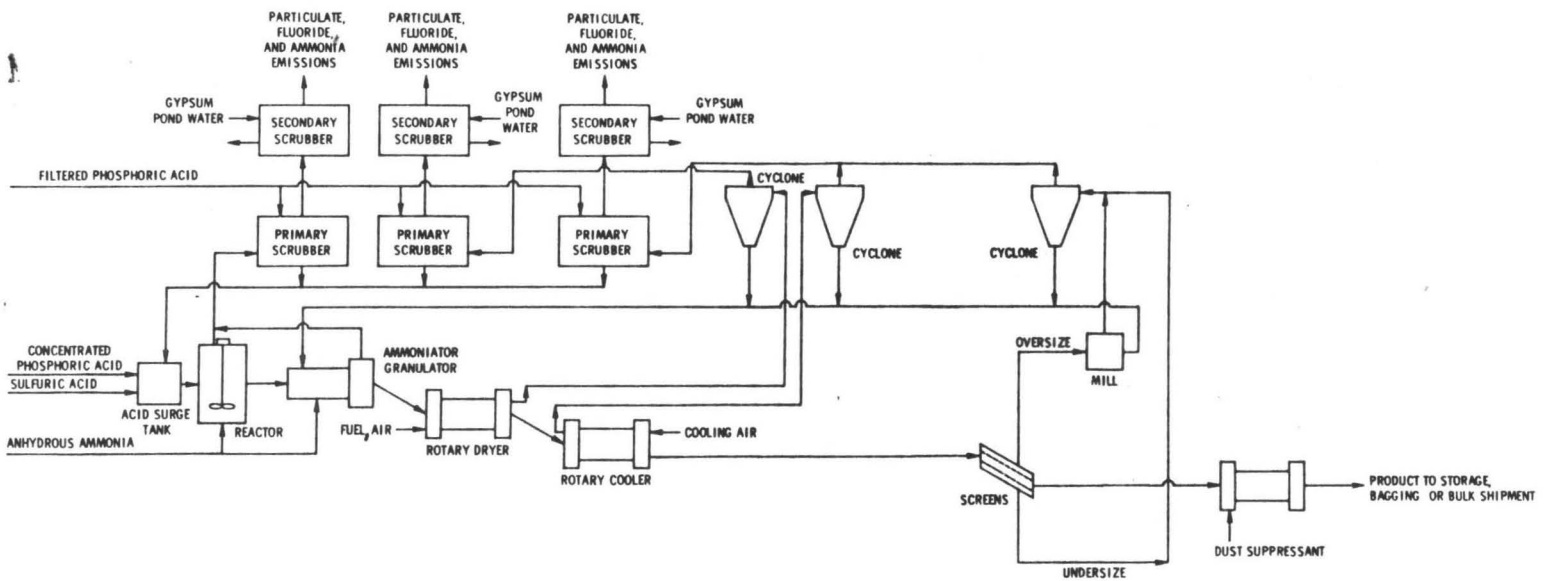


Figure 6.2.3-1. Ammonium phosphate process flow diagram.

emissions of gaseous ammonia, gaseous fluorides (HF and SiF_4) and particulate ammonium phosphates. These two exhaust streams generally are combined and passed through primary and secondary scrubbers.

Exhaust gases from the dryer and cooler also contain ammonia, fluorides and particulates, and these streams commonly are combined and passed through cyclones and primary and secondary scrubbers. Particulate emissions and low levels of ammonia and fluorides from product sizing and material transfer operations are controlled the same way.

Emission factors for ammonium phosphate production are summarized in Table 6.10.3-1. These emission factors are averages based on recent source test data from controlled phosphate fertilizer plants in Florida.

Exhaust streams from the reactor and ammoniator-granulator pass through a primary scrubber, in which phosphoric acid recovers ammonia and particulate. Exhaust gases from the dryer, cooler and screen go first to cyclones for particulate recovery, and from there to primary scrubbers. Materials collected in the cyclone and primary scrubbers are returned to the process. The exhaust is sent to secondary scrubbers, where recycled gypsum pond water is used as a scrubbing liquid to control fluoride emissions. The scrubber effluent is returned to the gypsum pond.

Primary scrubbing equipment commonly includes venturi and cyclonic spray towers, while cyclonic spray towers, impingement scrubbers, and spray-crossflow packed bed scrubbers are used as secondary controls. Primary scrubbers generally use phosphoric acid of 20 to 30 percent as scrubbing liquor, principally to recover ammonia. Secondary scrubbers generally use gypsum and pond water, for fluoride control.

Throughout the industry, however, there are many combinations and variations. Some plants use reactor-feed concentration phosphoric acid (40 percent P_2O_5) in both primary and secondary scrubbers, and some use phosphoric acid near the dilute end of the 20 to 30 percent P_2O_5 range in only a single scrubber. Existing plants are equipped with ammonia recovery scrubbers on the reactor, ammoniator-granulator and dryer, and particulate controls on the dryer and cooler. Additional scrubbers for fluoride removal are common but not typical. Only 15 to 20 percent of installations contacted in an EPA survey were equipped with spray-crossflow packed bed scrubbers or their equivalent for fluoride removal.

Emission control efficiencies for ammonium phosphate plant control equipment have been reported as 94 - 99 percent for ammonium, 75 - 99.8 percent for particulates, and 74 - 94 percent for fluorides.

TABLE 6.10.3-1. AVERAGE CONTROLLED EMISSION FACTORS FOR THE PRODUCTION OF AMMONIUM PHOSPHATES[a]

EMISSION FACTOR RATING: A

Emission Point	Controlled Emission Factors lb/ton P_2O_5	kg/MT P_2O_5
Reactor/ammoniator-granulator		
Fluoride (as F)	0.05	0.02
Particulates	1.52	0.76
Ammonia	b	b
Dryer/cooler		
Fluoride (as F)	0.03	0.02
Particulates	1.50	0.75
Ammonia	b	b
Product sizing and material transfer		
Fluoride (as F)[c]	0.01	0.01
Particulates[c]	0.06	0.03
Ammonia	b	b
Total plant emissions		
Fluoride (as F)[d]	0.08	0.04
Particulates[e]	0.30	0.15
Ammonia	0.14	0.07

[a] Reference 1, pp. 80-83, 173.
[b] No information available. Although ammonia is emitted from these unit operations, it is reported as a total plant emission.
[c] Represents only one sample.
[d] EPA has promulgated a fluoride emission guideline of 0.03 g/kg P_2O_5 input.
[e] Based on limited data from only 2 plants.

Reference for Section 6.10.3

1. J. M. Nyers, et al., Source Assessment: Phosphate Fertilizer Industry, EPA-600/2-79-019c, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1979.

6.11 STARCH MANUFACTURING

6.11.1 Process Description[1]

The basic raw material in the manufacture of starch is dent corn, which contains starch. The starch in the corn is separated from the other components by "wet milling."

The shelled grain is prepared for milling in cleaners that remove both the light chaff and any heavier foreign material. The cleaned corn is then softened by soaking (steeping) it in warm water acidified with sulfur dioxide. The softened corn goes through attrition mills that tear the kernels apart, freeing the germ and loosening the hull. The remaining mixture of starch, gluten, and hulls is finely ground, and the coarser fiber particles are removed by screening. The mixture of starch and gluten is then separated by centrifuges, after which the starch is filtered and washed. At this point it is dried and packaged for market.

6.11.2 Emissions

The manufacture of starch from corn can result in significant dust emissions. The various cleaning, grinding, and screening operations are the major sources of dust emissions. Table 6.11-1 presents emission factors for starch manufacturing.

Table 6.11-1. EMISSION FACTORS FOR STARCH MANUFACTURING[a] EMISSION FACTOR RATING: D

Type of operation	Particulates	
	lb/ton	kg/MT
Uncontrolled	8	4
Controlled[b]	0.02	0.01

[a]Reference 2.
[b]Based on centrifugal gas scrubber.

References for Section 6.11

1. Starch Manufacturing. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. IX. New York, John Wiley and Sons, Inc. 1964.

2. Storch, H. L. Product Losses Cut with a Centrifugal Gas Scrubber. Chem. Eng. Progr. *62*:51-54. April 1966.

6.12 SUGAR CANE PROCESSING

revised by Tom Lahre

6.12.1 General [1-3]

Sugar cane is burned in the field prior to harvesting to remove unwanted foliage as well as to control rodents and insects. Harvesting is done by hand or, where possible, by mechanical means.

After harvesting, the cane goes through a series of processing steps for conversion to the final sugar product. It is first washed to remove dirt and trash; then crushed and shredded to reduce the size of the stalks. The juice is next extracted by one of two methods, milling or diffusion. In milling, the cane is pressed between heavy rollers to squeeze out the juice; in diffusion, the sugar is leached out by water and thin juices. The raw sugar then goes through a series of operations including clarification, evaporation, and crystallization in order to produce the final product. The fibrous residue remaining after sugar extraction is called bagasse.

All mills fire some or all of their bagasse in boilers to provide power necessary in their milling operation. Some, having more bagasse than can be utilized internally, sell the remainder for use in the manufacture of various chemicals such as furfural.

6.12.2 Emissions [2,3]

The largest sources of emissions from sugar cane processing are the openfield burning in the harvesting of the crop and the burning of bagasse as fuel. In the various processes of crushing, evaporation, and crystallization, relatively small quantities of particulates are emitted. Emission factors for sugar cane field burning are shown in Table 2.4-2. Emission factors for bagasse firing in boilers will be included in Chapter 1 in a future supplement.

References for Section 6.12

1. Sugar Cane. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. IX. New York, John Wiley and Sons, Inc. 1964.

2. Darley, E. F. Air Pollution Emissions from Burning Sugar Cane and Pineapple from Hawaii. In: Air Pollution from Forest and Agricultural Burning. Statewide Air Pollution Research Center, University of California, Riverside, Calif. Prepared for Environmental Protection Agency, Research Triangle Park, N.C. under Grant No. R800711. August 1974.

3. Background Information for Establishment of National Standards of Performance for New Sources. Raw Cane Sugar Industry. Environmental Engineering, Inc. Gainesville, Fla. Prepared for Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. CPA 70-142, Task Order 9c. July 15, 1971.

References for Section 6.12

1. Sugar Cane. In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. IX. New York, John Wiley and Sons, Inc. 1964.

2. Cooper, J. Unpublished data on emissions from the sugar cane industry. Air Pollution Control Agency, Palm Beach County, Florida. July 1969.

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6.13 BREAD BAKING

Tom Lahre

6.13.1 General[1,2]

Bakery products generally can be divided into two groups—products leavened by yeast and products chemically leavened by baking powder. Other than yeast bread, which comprises the largest fraction of all yeast leavened baking production, leavened products include sweet rolls, crackers, pretzels, etc. Examples of chemically leavened baking products are cakes, cookies, cake doughnuts, corn bread and baking powder biscuits.

Bread is generally produced by either the straight-dough process or the sponge-dough process. In the straight-dough process, the ingredients are mixed, allowed to ferment, and then baked. In the sponge-dough process, only part of the ingredients are initially mixed and allowed to ferment, with the remainder added to the mix and fermented just prior to baking. The sponge-dough process is more often used by commercial bakeries.

In a commercial bakery, bread dough is fermented from two to four hours prior to baking at about 450°F (232°C). The temperature inside the bread does not exceed 212°F (100°C). The ovens used are predominately direct fired by natural gas. In such ovens, any vapors driven off the bread and any combustion product gases are removed through the same exhaust vent.

6.13.2 Emissions[1,2]

In the leavening process, yeast metabolizes the sugars and starches in the bread dough. During this fermentation stage, various chemical reactions take place, with the end products being primarily carbon dioxide (CO_2) and ethanol (C_2H_5OH). The carbon dioxide is necessary to leaven the dough, thereby increasing its volume. The byproduct ethanol, however, evaporates and leaves the dough. The rate of ethanol production depends on dough temperature, quantity of sweetner and type of yeast.

Laboratory experiments[1] and theoretical estimates[2] suggest that ethanol emissions from the sponge-dough process may range from 5 to 8 pounds per 1000 pounds of bread produced, whereas ethanol emissions from the straight-dough process are only 0.5 pounds per 1000 pounds produced. These factors include ethanol evaporation from all phases of bread production, although most of the emissions occur during baking. Negligible quantities of ethanol remain in the bread following baking. Several other non-methane volatile organic compounds are also emitted from bread production, but in much smaller amounts. The reader should consult References 1 and 2 for details on how these emission factors are derived.

No controls or process modifications are employed to reduce ethanol emissions from bakeries. Some fraction of the ethanol emitted during baking could potentially be destroyed in the direct fired gas ovens, but since the ethanol does not come into contact with the flame zone, this fraction is thought to be insignificant.

References for Section 6.13

1. R.M. Keller, *Nonmethane Organic Emissions from Bread Producing Operations*, EPA-450/4-79-001, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1978.

2. D.C. Henderson, "Commercial Bakeries as a Major Source of Reactive Volatile Organic Gases", *Emission Inventory/Factor Workshop: Volume I*, EPA-450/3-78-042a, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1978.

6.14 UREA

Frank Noonan

6.14.1 General[1]

Urea ($CO[NH_2]_2$) is produced by reacting ammonia and carbon dioxide to form ammonium carbamate ($NH_2CO_2NH_4$), which is then dehydrated to form urea. There are over fifteen production methods which can carry out these reactions. While the basics of the processes are the same, variations occur in vessel design, operating conditions, and type and quantity of recycle of unreacted material. The aqueous solution produced by these processes contains approximately 70 percent urea, and the solution may be sold as is or in solid form.

In the solidification procedure, urea solution is first concentrated in crystallizer or evaporator and then solidified. If in a crystallizer, the crystals are melted and then formed into a solid. If an evaporator is used, it produces a concentrate which is then solidified. In either case, solid urea is formed by prilling or granulation. Additional granular strength and packing resistance are obtained by two methods. In the first, used by about 50 percent of the plants and involving about 9 percent of all solid urea produced, formaldehyde or a phosphate based additive is injected into the fluid material before solid formation. In the second, the sized solid particles are coated with a clay substance. The finished product is usually stored in bulk, shipped in railroad hoppers or trucks, or bagged in 20.4 kg or 36.3 kg sacks. In addition, some urea solution may be transported by pipeline, and some solid by river barge.

Figure 6.14-1 is a flow diagram of the solid urea production process.

6.14.2 Emissions[1]

Emissions from urea manufacture consist of ammonia and particles of solid urea. In solution production, they issue from the bulk loading of the product, and in solid production, they come from the evaporator, prilling tower, granulator, product finishing, bagging and loading, and bulk loading points. The prilling tower and granulator are both emission points, but are alternate, not sequential, steps in the process.

6.14.3 Controls[1]

Applied control technology for the urea industry varies from plant to plant. In the concentration section, emissions are controlled by condensing the evaporator overheads and sewering or selling the product, or by passing the stream through a scrubber. In the solid formation section, control technology depends on the formation process used. In granulation processes, scrubbers are used to control emissions and to recover entrained product. In prilling processes, about 50 percent of the industry uses some form of packed scrubber for control. The others exhaust emissions to the atmosphere. Further technology has not been widely proven. At least six companies are currently trying to develop or to test technology which will reduce prilling tower emissions effectively.

Table 6.14-1. EMISSION FACTORS FOR UREA PRODUCTION[a,b]
EMISSION FACTOR RATING: A

Emitting operation	Emission factor					
	Ammonia			Particulate		
	lb/ton		kg/MT	lb/ton		kg/MT
Solution concentration (controlled)	3.46	(±64%)	1.73	0.214	(±28%)	0.107
Prilling (uncontrolled)	0.80	(±84%)	0.40	3.20	(±17%)	1.60
Granulation	0.50	(±48%)	0.25	0.168 to 0.40	(±29%) (±25%)	0.084 to 0.20
Solid product finishing	–		–	<4.00		<2.00
Solution product bulk loading	0.24		0.12	–		–
Solid product bagging and bulk loading	–		–	<0.30		<0.15

[a]Dashes indicate no emissions from operation.
[b]Percentages represent 95% confidence interval.

Reference for Section 6.14

1. W. J. Search and R. B. Resnik, *Source Assessment: Urea Manufacture*, EPA-600/2-77-107l, U.S. Environmental Protection Agency, Research Triangle Park, NC, November 1977.

6.15 BEEF CATTLE FEEDLOTS

Tom Lahre

6.15.1 General[1]

A beef cattle feedlot is an area in which beef animals are confined for fattening prior to marketing. This fattening, or finish feeding, typically lasts four to five months, during which time the cattle are fed a high energy ration of feed grains and/or forage.

Cattle feedlots range in capacity from several head up to 100,000 cattle. Of the 146,000 beef cattle feedlots in the U.S. in 1973, 2,040 feedlots had a capacity of more than 1,000 head, marketing 65 percent of all finish fed beef cattle. Animal density in feedlots is generally in the range of 12,500 to 125,000 head/km^2.

During its stay in a feedlot, a beef animal will produce over 450 kg of manure (dry weight). Wet manure production is typically about 27 kg per day per head, usually deposited on less than 20 m^2 of surface. Because of the prodigious quantity of manure produced in a feedlot, periodic removal is necessary to prevent unacceptable accumulations. Most cattle manure is applied to nearby land as fertilizer for feed grain production, while some is lagooned, dumped on wastelands, or disposed of through incineration, liming, or pitting. Manure removal frequencies are dictated in part by climatic conditions, animal comfort, labor scheduling, and air and water pollution control potentials. Typically, manure removal is conducted from one to three times per year. When disposal is not immediately possible after removal, the manure may be stockpiled on a nearby open site.

The leading states in the industry are Texas, Nebraska, Iowa, Kansas, Colorado, California, and Illinois. These states contribute 75 percent of all feed cattle marketed and contain 72 percent of the feedlots greater than 1000 head capacity. Feedlots are generally located in low population density regions with access to major transportation routes.

6.15.2 Emissions and Controls[1]

Air pollution from feedlots originates from several points in a feedlot operation, including the holding pens, runoff holding ponds, and alleyways among pens. Major pollutants of concern include fugitive particulate, ammonia and various malodorous gases.

Fugitive particulate is generated several ways. Cattle movement within the holding pens is a primary source. Dust is also generated by wind acting on the dried surfaces and by vehicular traffic on alleyways among the pens. Fugitive particulate emissions from feedlots are composed largely of soil dust and dried manure. The potential for dust generation is greatly increased during prolonged dry periods (e.g., from late spring to midsummer in the Southwest), and when a loose, dry pad of soil and manure is allowed to build up in the pens.

Ammonia is the predominant gaseous pollutant emitted from feedlots. Ammonia is a result of anaerobic decomposition of feedlot surfaces as well as volatilization from urine. Ammonia emissions are generally increased when conditions favor anaerobic decay. For example, although 25 to 40 percent moisture levels are necessary on feedlot surfaces for aerobic decomposition (which is odorless), too much rain or watering, resulting in puddling and wet spots, can trigger increased ammonia production. Ammonia formation may also occur when anaerobic conditions exist in the manure stockpiles and runoff holding ponds. In general, higher ammonia emissions are associated with higher temperatures and humidity, overly wet conditions, and feedlot disturbances such as mounding or manure removal.

A number of extremely odorous compounds (amines, sulfides, mercaptans) may also result from anaerobic decomposition of solid manure beneath the feedlot surface as well as in the runoff holding ponds.

Generally, the same conditions that favor ammonia production will enhance the evolution of these other gases, as well.

No air pollutant control devices are applied to feedlots because of the fugitive nature of the emissions. The most effective controls involve various housekeeping measures designed to eliminate conditions that favor the generation of dust and odors. For example, measures that help to maintain sufficient moisture levels in the feedlot surface areas and manure stockpiles will reduce the generation of dust. One of the most effective dust control techniques is periodic application of water to the dry feedlot surface, by either permanent sprinkling systems or mobile tank trucks. However, care must be taken to avoid overwatering, which can cause wet spots conducive to anaerobic decay and subsequent malodors. Increasing the cattle density in the pens may also help maintain high enough moisture levels to limit particulate generation. In addition, some dust control is effected by minimizing the accumulation of dry and pulverized manure on the surfaces of the feedlots. A maximum depth of 2 to 8 cm of loose, dry manure is recommended for increasing the effectiveness of dust control procedures.

Odor and ammonia control are best effected by housekeeping measures that enhance aerobic rather than anaerobic decomposition of the cattle wastes. For example, besides reducing dust emissions, sprinkling provides moisture for aerobic biodegradation of the manure. Good drainage must be provided, however, and overwatering must be avoided. Deep accumulations of manure of slurry consistency can optimize anaerobic conditions. Hence, feedlot surfaces should be periodically scraped to remove such accumulations. Scraping should be done carefully, so that only the surface layer is disturbed. Manure stockpiles should not be allowed to get too large, too wet, or encrusted, and they should be disposed of within four or five days. If the stockpiles are composted, the manure should be piled in long narrow windrows to allow access for turning the piles to promote aerobic conditions and to enable rapid control of spontaneous combustion fires. Anaerobic conditions can be reduced in runoff holding ponds by removing solids from the runoff, by adding more water to the ponds to dilute the nutrient content, and by aeration of the surface. Runoff water also may be treated chemically to suppress the release of malodorous gases.

Emission factors for feedlot operations are shown in Table 6.15-1. These factors should be considered at best to be crude estimates of potential emissions from feedlots where no measures are employed to control dust or odors. The limitations of these factors are more fully discussed in the footnote to Table 6.15-1. The reader should consult Reference 1 for a detailed discussion of the emissions and control information available on beef cattle feedlots.

Table 6.15-1. EMISSION FACTORS FOR BEEF CATTLE FEEDLOTS[a]
EMISSION FACTOR RATING: E

Pollutant	Feedlot capacity basis lb (kg) per day per 1000 head capacity	Feedlot throughput basis ton (metric ton) per 1000 head throughput
Particulate[b]	280 (130)	27 (25)
Ammonia[c]	11 (5)	1.1 (1)
Amines[c]	0.4 (0.2)	0.044 (0.04)
Total sulfur compounds[c]	1.7 (0.8)	0.15 (0.14)

[a]These factors represent general feedlot operations with no housekeeping measures for air pollution control. Because of the limited data available on emissions and the nature of the techniques utilized to develop emission factors, Table 6.15-1 should only be used to develop order-of-magnitude estimates of feedlot emissions. All factors are based on information compiled in Reference 1.

[b]These factors represent emissions during a dry season at a feedlot where watering as a dust control measure would not be a common practice. No data are available to estimate emission factors for feedlots during periods of abundant precipitation or where watering and other housekeeping measures are employed for dust control.

[c]These factors represent emission factors for feedlots that have not been chemically treated and where no special housekeeping measures are employed for odor control.

Reference for Section 6.15

1. J.A. Peters and T.R. Blackwood, *Source Assessment: Beef Cattle Feedlots*, EPA-600/2-77-107, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1977.

6.16 DEFOLIATION AND HARVESTING OF COTTON

Rob McConnell

6.16.1 General

Wherever it is grown in the U.S., cotton is defoliated or disiccated prior to harvest. Defoliants are used on the taller varieties of cotton which are machine picked for lint and seed cotton, while desiccants usually are used on short, stormproof cotton varieties of lower yield that are harvested by mechanical stripper equipment. More than 99 percent of the national cotton area is harvested mechanically. The two principal harvest methods are machine picking, with 70 percent of the harvest from 61 percent of the area, and machine stripping, with 29 percent of the harvest from 39 percent of the area. Picking is practiced throughout the cotton regions of the U.S., while stripping is limited chiefly to the dry plains of Texas and Oklahoma.

Defoliation may be defined as the process by which leaves are abscised from the plant. The process may be initiated by drought stress, low temperatures or disease, or it may be chemically induced by topically applied defoliant agents or by overfertilization. The process helps lodged plants to return to an erect position, removes the leaves which can clog the spindles of the picking machine and strain the fiber, accelerates the opening of mature bolls, and reduces boll rots. Desiccation by chemicals is the drying or rapid killing of the leaf blades and petioles, with the leaves remaining in a withered state on the plant. Harvest-aid chemicals are applied to cotton as water-based spray, either by aircraft or by a ground machine.

Mechanical cotton pickers, as the name implies, pick locks of seed cotton from open cotton bolls and leave the empty burs and unopened bolls on the plant. Requiring only one operator, typical modern pickers are self propelled and can simultaneously harvest two rows of cotton at a speed of 1.1 to 1.6 meters per second (2.5 - 3.6 mph). When the picker basket gets filled with seed cotton, the machine is driven to a cotton trailer at the edge of the field. As the basket is hydraulically raised and tilted, the top swings open, allowing the cotton to fall into the trailer. When the trailer is full, it is pulled from the field, usually by pick-up truck, and taken to a cotton gin.

Mechanical cotton strippers remove open and unopened bolls, along with burs, leaves and stems from cotton plants, leaving only bare branches. Tractor-mounted, tractor-pulled or self propelled, strippers require only one operator. They harvest from one to four rows of cotton at speeds of 1.8 to 2.7 m/s (4.0 - 6.0 mph). After the cotton is stripped, it enters a conveying system that carries it from the stripping unit to an elevator. Most conveyers utilize either augers or a series of rotating spike-toothed cylinders to move the cotton, accomplishing some cleaning by moving the cotton over perforated, slotted or wire mesh screen. Dry plant material (burs, stems and leaves) is crushed and dropped through openings to the ground. Blown air is sometimes used to assist cleaning.

6.16.2 Emissions and Controls

Emission factors for the drifting of major chemicals applied to cotton are compiled from literature and reported in Reference 1. In addition, drift losses from arsenic acid spraying were developed by field testing. Two off-target collection stations, with six air samplers each, were located downwind from the ground spraying operations. The measured concentration was applied to an infinite line source atmosphere diffusion model (in reverse) to calculate the drift emission rate. This was in turn used for the final emission factor calculation. The emissions occur from July to October, preceding by two weeks the period of harvest in each cotton producing region. The drift emission factor for arsenic acid is eight times lower than previously estimated, since Reference 1 used a ground rig rather than an airplane, and because of the low volatility of arsenic acid. Various methods of controlling drop size, proper timing of application, and modification of equipment are practices which can reduce drift hazards. Fluid additives have been used that increase the viscosity of the spray formulation, and thus decrease the number of fine droplets ($<100\ \mu m$).

Spray nozzle design and orientation also control the droplet size spectrum. Drift emission factors for the defoliation of desiccation of cotton are listed in Table 6.16-1.

Table 6.16-1. EMISSION FACTORS FOR DEFOLIATION OR DESICCATION OF COTTON[a]

EMISSION FACTOR RATING: C

Pollutant	Emission factor[b]	
	lb/ton	g/kg
Sodium chlorate	20.0	10.0
DEF	20.0	10.0
Arsenic acid	12.2	6.1
Paraquat	20.0	10.0

[a]Reference 1
[b]Factor is in terms of quantity of drift per quantity applied.

Three unit operations are involved in mechanical harvesting of cotton: harvesting, trailer loading (basket dumping) and transport of trailers in the field. Emissions from these operations are in the form of solid particulates. Particulate emissions (<7 μm mean aerodynamic diameter) from these operations were developed in Reference 2. The particulates are composed mainly of raw cotton dust and solid dust, which contains free silica. Minor emissions include small quantities of pesticide, defoliant and desiccant residues that are present in the emitted particulates. Dust concentrations from harvesting were measured by following each harvesting machine through the field at a constant distance directly downwind from the machine, while staying in the visible plume centerline. The procedure for trailer loading was the same, but since the trailer is stationary while being loaded, it was necessary only to stand a fixed distance directly downwind from the trailer while the plume or puff passed over. Readings were taken upwind of all field activity to get background concentrations. Particulate emission factors for the principal types of cotton harvesting operations in the U.S. are shown in Table 6.16-2. The factors are based on average machine speed of 1.34 m/s (3.0 mph) for pickers and 2.25 m/s (5.03 mph) for strippers, on a basket capacity of 109 kg (240 lb), on a trailer capacity of 6 baskets, on a lint cotton yield of 63.0 metric tons/km^2 (1.17 bale/acre) for pickers and 41.2 metric tons/km^2 (.77 bale/acre) for strippers, and on a transport speed of 4.47 m/s (10.0 mph). Analysis of particulate samples showed average free silica content of 7.9 percent for mechanical cotton picking and 2.3 percent for mechanical cotton stripping. Estimated maximum percentages for pesticides, defoliants and desiccants from harvesting are also noted in Table 6.16-2. No current cotton harvesting equipment or practices provide for control of emissions. In fact, equipment design and operating practices tend to maximize emissions. Preharvest treatment (defoliation and desiccation) and harvest practices are timed to minimize moisture and trash content, so they also tend to maximize emissions. Soil dust emissions from field transport can be reduced by lowering vehicle speed.

Table 6.16-2. PARTICULATE EMISSION FACTORS FOR COTTON HARVESTING OPERATIONS[a]

EMISSION FACTOR RATING: C

Type of harvester	Harvesting		Trailer loading		Transport		Total	
	kg/km²	lb/mi²	kg/km²	lb/mi²	kg/km²	lb/mi²	kg/km²	lb/mi²
Picker[c]								
Two-row, with basket	.46	2.6	.070	.40	.43	2.5	.96	5.4
Stripper[d]								
Two-row, pulled trailer	7.4	42	–[b]	–	.28	1.6	7.7	44
Two-row, with basket	2.3	13	.092	.52	.28	1.6	2.7	15
Four-row, with basket	2.3	13	.092	.52	.28	1.6	2.7	15
Weighted average[e]	4.3	24	.056	.32	.28	1.6	4.6	26

[a]Emission factors are from Reference 2 for particulate of <7 μm mean aerodynamic diameter.

[b]Not applicable

[c]Free silica content is 7.9%; maximum content of pesticides and defoliants is 0.02%.

[d]Free silica content is 2.3%; maximum content of pesticides and desiccants is 0.2%.

[e]The weighted average stripping factors are based on estimates that 2% of all strippers are four-row models with baskets, and of the remainder, 40% are two-row models pulling trailers and 60% are two-row models with mounted baskets.

References for Section 6.16

1. J. A. Peters and T. R. Blackwood, *Source Assessment: Defoliation of Cotton–State of the Art*, EPA-600/2-77-107g, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1977.

2. J. W. Snyder and T. R. Blackwood, *Source Assessment: Mechanical Harvesting of Cotton–State of the Art*, EPA-600/2-77-107d, U. S. Environmental Protection Agency, Research Triangle Park, NC, July 1977.

6.17 HARVESTING OF GRAIN

6.17.1 General[1]

Harvesting of grain refers to the activities performed to obtain the cereal kernels of the plant for grain or the entire plant for forage and/or silage uses. These activities are accomplished by machines that cut, thresh, screen, clean, bind, pick, and shell the crops in the field. Harvesting also includes loading harvested crops into trucks and transporting crops on the grain field.

Crops harvested for their cereal kernels are cut as close as possible to the inflorescence (the flowering portion containing the kernels). This portion is threshed, screened and cleaned to separate the kernels. The grain is stored in the harvest machine while the remainder of the plant is discharged back onto the field.

Combines perform all of the above activities in one operation. Binder machines only cut the grain plants and tie them into bundles or leave them in a row in the field (called a windrow). The bundles are allowed to dry for threshing later by a combine with a pickup attachment.

Corn harvesting requires the only exception to the above procedures. Corn is harvested by mechanical pickers, picker/shellers, and combines with corn head attachments. These machines cut and husk the ears from the standing stalk. The sheller unit also removes the kernels from the ear. After husking, a binder is sometimes used to bundle entire plants into piles (called shocks) to dry.

For forage and/or silage, mowers, crushers, windrowers, field choppers, binders, and similar cutting machines are used to harvest grasses, stalks and cereal kernels. These machines cut the plants as close to the ground as possible and leave them in a windrow. The plants are later picked up and tied by a baler.

Harvested crops are loaded onto trucks in the field. Grain kernels are loaded through a spout from the combine, and forage and silage bales are manually or mechanically placed in the trucks. The harvested crop is then transported from the field to a storage facility.

6.17.2 Emissions and Controls[1]

Emissions are generated by three grain harvesting operations, (1) crop handling by the harvest machine, (2) loading of the harvested crop into trucks, and (3) transport by trucks on the field. Particulate matter, composed of soil dust and plant tissue fragments (chaff) may be entrained by wind. Particulate emissions from these operations (<7μm mean aerodynamic diameter) are developed in Reference 1. For this study, collection stations with air samplers were located downwind (leeward) from the harvesting operations, and dust concentrations were

measured at the visible plume centerline and at a constant distance behind the combines. For product loading, since the trailer is stationary while being loaded, it was necessary only to take measurements a fixed distance downwind from the trailer while the plume or puff passed over. The concentration measured for harvesting and loading was applied to a point source atmospheric diffusion model to calculate the source emission rate. For field transport, the air samplers were again placed a fixed distance downwind from the path of the truck, but this time the concentration measured was applied to a line source diffusion model. Readings taken upwind of all field activity gave background concentrations. Particulate emission factors for wheat and sorghum harvesting operations are shown in Table 6.17-1.

There are no control techniques specifically implemented for the reduction of air pollution emissions from grain harvesting. However, several practices and occurences do affect emission rates and concentration. The use of terraces, contouring, and stripcropping to inhibit soil erosion will suppress the entrainment of harvested crop fragments in the wind. Shelterbelts, positioned perpendicular to the prevailing wind, will lower emissions by reducing the wind velocity across the field. By minimizing tillage and avoiding residue burning, the soil will remain consolidated and less prone to disturbance from transport activities.

Table 6.17-1. EMISSION RATES/FACTORS FROM THE HARVESTING GRAIN[a]

EMISSION FACTOR RATING: D

	Emission rate[b]				Emission factor[c]			
	Wheat		Sorghum		Wheat		Sorghum	
Operation	lb/hr	mg/sec	lb/hr	mg/sec	lb/mi^2	g/km^2	lb/mi^2	g/km^2
Harvest machine	0.027	3.4	0.18	23.0	0.96	170.0	6.5	1100.0
Truck loading	0.014	1.8	0.014	1.8	0.07	12.0	0.13	22.0
Field transport	0.37	47.0	0.37	47.0	0.65	110.0	1.2	200.0

[a] Reference 1.

[b] Assumptions from Reference 1 are an average combine speed of 3.36 meters per second, combine swath width of 6.07 meters, and a field transport speed of 4.48 meters per second.

[c] In addition to Note b, assumptions are a truck loading time of six minutes, a truck capacity of .052 km^2 for wheat and .029 km^2 for sorghum, and a filed truck travel time of 125 seconds per load.

Reference for Section 1.14

1. R. A. Wachten and T. R. Blackwood, Source Assessment: Harvesting of Grain, State of the Art, EPA-600/2-79-107f, U. S. Environmental Protection Agency, Research Triangle Park, NC, July 1977.

6.18 AMMONIUM SULFATE MANUFACTURE

6.18.1 General[1]

Ammonium sulfate, $[NH_4]_2SO_4$, is commonly used as a fertilizer. About 90 percent of ammonium sulfate is produced by three types of facilities, caprolactam byproduct, synthetic, and coke oven byproduct plants. The remainder is produced as a byproduct of nickel manufacture from ore concentrates, methyl methacrylate manufacture, and ammonia scrubbing of tail gas at sulfuric acid plants.

During the manufacture of caprolactam, $[CH_2]_5COHN$, ammonium sulfate is produced from the oximation process stream and the rearrangement reaction stream. Synthetic ammonium sulfate is produced by the direct combination of ammonia and sulfuric acid in a reactor. Coke oven byproduct ammonium sulfate is produced by reacting ammonia recovered from coke oven offgas with sulfuric acid. Figure 6.18-1 is a process flow diagram for each of the three primary commercial processes.

After formation of the ammonium sulfate solution, operations of each process are similar. Ammonium sulfate crystals are formed by continuously circulating an ammonium sulfate liquor through an evaporator to thicken the solution. Ammonium sulfate crystals are separated from the liquor in the centrifuge. The saturated liquor is returned to the dilute ammonium sulfate brine of the evaporator. The crystals, with about 1 to 2.5 percent moisture by weight after the centrifuge, are fed to either a fluidized bed or rotary drum dryer. Fluidized bed dryers are continuously steam heated, and rotary dryers are either directly fired with oil or natural gas, or they use steam heated air. At coke oven byproduct plants, rotary drum dryers may be used in place of a centrifuge and dryer. On the filter of these dryers, a crystal layer is deposited which is removed from the drum by a scraper or a knife.

The volume of ammonium sulfate in the dryer exhaust gas varies according to production process and dryer type. A gas flow rate of 620 scm/Mg of product (20,000 scf/ton) is considered representative of a direct fired rotary drum dryer. A gas flow of 2,500 scm/Mg of product (80,000 scf/ton) is considered representative of a steam heated fluidized bed dryer. Dryer exhaust gases are passed through a particulate collection device, usually a wet scrubber, for product recovery and for pollution control.

The ammonium sulfate crystals are conveyed from the dryer to an enclosure where they are screened to product specifications, generally to coarse and fine products. The screening is enclosed to control dust in the building.

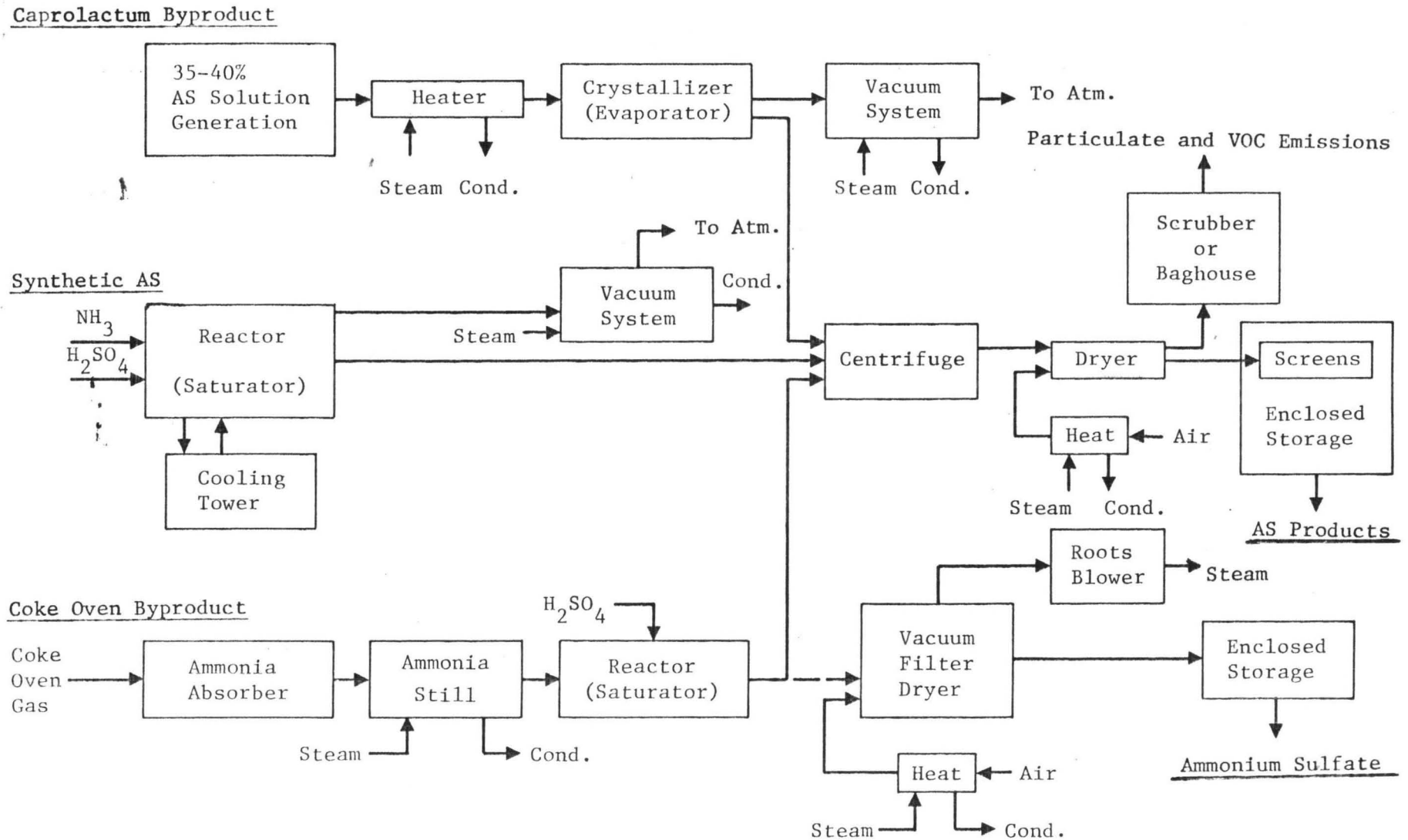

Figure 6.18-1. Diagram of Ammonium Sulfate (AS) processes.

6.18.2 Emissions and Controls

Ammonium sulfate particulate is the principal pollutant emitted to the atmosphere from the manufacturing plants, nearly all of it being contained in the gaseous exhaust of the dryers. Other plant processes, such as evaporation, screening, and materials handling, are not significant sources of emissions.

The particulate emission rate of a dryer depends on the gas velocity and the particle size distribution. Since gas velocity varies according to the dryer type, emission rates also vary. Generally, the gas velocity of fluidized bed dryers is higher than for most rotary drum dryers, and particulate emission rates are also higher. The smaller the particle, the easier it is removed by the gas stream of either type of dryer.

At caprolactam byproduct plants, volatile organic compounds (VOC) are emitted from the dryers. Emissions of caprolactam vapor are at least two orders of magnitude lower than the particulate emissions.

Wet scrubbers, such as venturi and centrifuge, are most suitable for reducing particulate emissions from the dryers. Wet scrubbers use process streams as the scrubbing liquid. This allows the collected particulate to be recycled easily to the production system.

Table 6.18-1 shows the uncontrolled and controlled emission factors for the various dryer types. The VOC emissions shown in Table 6.18-1 apply only to caprolactam byproduct plants which may use either a fluidized bed or rotary drum dryer.

TABLE 6.18-1. EMISSION FACTORS FOR AMMONIUM SULFATE MANUFACTURE[a]

EMISSION FACTOR RATING: B

Dryer Type & Controls	Particulates		Volatile Organic Compounds[b]	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Rotary dryers				
Uncontrolled	23	46	0.74	1.48
Wet scrubber	0.12	0.24	0.11	0.22
Fluidized bed dryers				
Uncontrolled	109	218	0.74	1.48
Wet scrubber	0.14	0.28	0.11	0.22

[a]Expressed as emissions by weight per unit of ammonium sulfate production by weight.

[b]VOC emissions occur only at caprolactam plants using either type of dryer. The emissions are caprolactam vapor.

Reference for Section 6.18

1. Ammonium Sulfate Manufacture - Background Information for Proposed Emission Standards, EPA-450/3-79-034a, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1979.

7.1 PRIMARY ALUMINUM PRODUCTION

7.1.1 Process Description[1,2]

The base ore for primary aluminum production is bauxite, a hydrated oxide of aluminum consisting of 30 to 70 percent alumina (Al_2O_3) and lesser amounts of iron, silicon and titanium. The bauxite ore is first purified to alumina by the Bayer process, and this is then reduced to elemental aluminum. The production of alumina and the reduction of alumina to aluminum are seldom accomplished at the same location. A schematic diagram of the primary production of aluminum is shown at Figure 7.1-1.

In the Bayer process, the ore is dried, ground in ball mills and mixed with sodium hydroxide to yield aluminum hydroxide. Iron oxide, silica and other impurities are removed by settling, dilution and filtration. Aluminum hydroxide is precipitated from the solution by cooling and is then calcined to produce pure alumina, as in the reaction:

$$\underset{\text{Aluminum hydroxide}}{2\,Al(OH)_3} \xrightarrow{\text{heat}} \underset{\text{Water}}{3\,H_2O} + \underset{\text{Alumina}}{Al_2O_3} \qquad (1)$$

Aluminum metal is manufactured by the Hall-Heroult process, which involves the electrolytic reduction of alumina dissolved in a molten salt bath of cryolite (Na_3AlF_6) and various salt additives:

$$\underset{\text{Alumina}}{2Al_2O_3} \xrightarrow{\text{Electrolysis}} \underset{\text{Aluminum}}{4Al} + \underset{\text{Oxygen}}{3O_2} \qquad (2)$$

The electrolysis occurs in shallow rectangular cells, or "pots", which are steel shells lined with carbon. Carbon blocks extending into the pot serve as the anodes, and the carbon lining the steel shell acts as the cathode. Cryolite functions as both the electrolyte and the solvent for the alumina. Electrical resistance to the current passing between the electrodes generates heat that maintains cell operating temperatures between 950° and 1000°C (1730° and 1830°F). Aluminum is deposited at the cathode, where it remains as molten metal below the surface of the cryolite bath. The carbon anodes are continuously depleted by the reaction of oxygen (formed during the reaction) and anode carbon, to produce carbon monoxide and carbon dioxide. The carbon consumption and other raw material and energy requirements for aluminum production are summarized in Table 7.1-1. The aluminum product is periodically tapped beneath the cryolite cover and is fluxed to remove trace impurities.

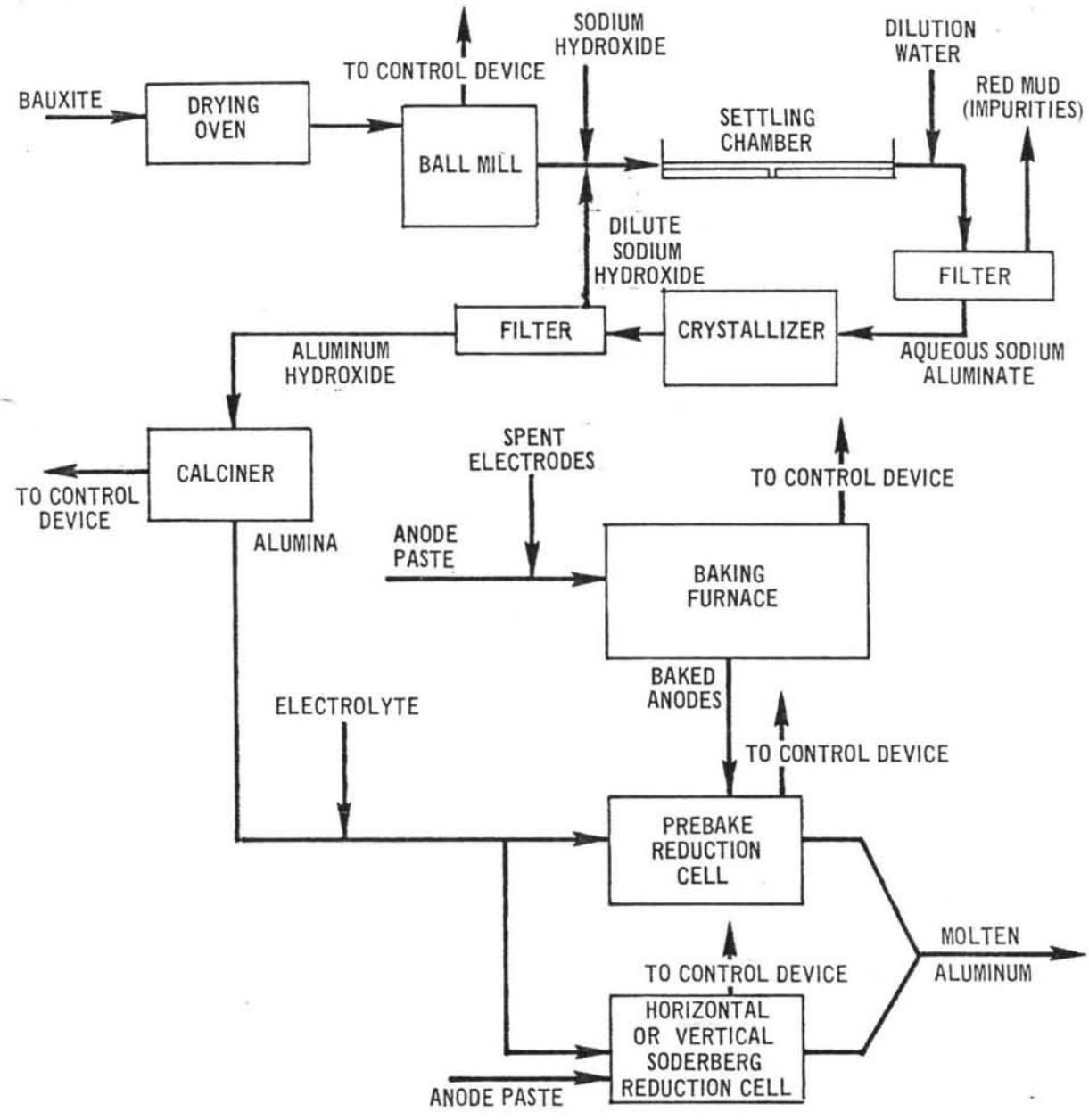

Figure 7.1-1. Schematic diagram of primary aluminum production process.

Figure 7.1-1

TABLE 7.1-1. RAW MATERIAL AND ENERGY REQUIREMENTS FOR ALUMINUM PRODUCTION

Parameter	Typical value
Cell operating temperature	~950°C (~1740°F)
Current through pot line	60,000 - 125,000 amperes
Voltage drop per cell	4.3 - 5.2
Current efficiency	85 - 90%
Energy required	13.2 - 18.7 kwh/kg aluminum (6.0 - 8.5 kwh/lb aluminum)
Weight alumina consumed	1.89 - 1.92 kg (lb) AL_2O_3/kg (lb) aluminum
Weight electrolyte fluoride consumed	0.03 - 0.10 kg (lb) fluoride/kg (lb) aluminum
Weight carbon electrode consumed	0.45 - 0.55 kg (lb) electrode/kg (lb) aluminum

Aluminum reduction cells are distinguished by the anode configuration used in the pots. Three types of pots are currently used, prebaked (PB), horizontal stud Soderberg (HSS), and vertical stud Soderberg (VSS). Most of the aluminum produced in the U. S. is processed in PB cells. These cells use anodes that are press formed from a carbon paste and baked in a direct fired ring furnace or indirect fired tunnel kiln. Volatile organic vapors from the coke and pitch paste comprising the anodes are emitted, and most are destroyed in the baking furnace. The baked anodes, typically 14 to 24 per cell, are attached to metal rods and serve as replaceable anodes.

In reduction, the carbon anodes are lowered into the cell and consumed at a rate of about 2.5 cm (1 in.) per day. Prebaked cells are preferred over Soderberg cells for their lower power requirements, reduced generation of volatile pitch vapors from the carbon anodes, and provision for better cell hooding to capture emissions.

The second most commonly used reduction cell is the horizontal stud Soderberg. This type of cell uses a "continuous" carbon anode. A green anode paste of pitch and coke is periodically added at the top of the superstructure and is baked by the heat of the cell to a solid mass as the material moves down the casing. The cell casing consists of aluminum sheeting and perforated steel channels, through which electrode connections or studs are inserted horizontally into the anode paste. During reduction, as the baking anode is lowered, the lower row of studs and the bottom channel are removed and the flexible electrical connectors are moved to a

higher row. Heavy organics from the anode paste are added to the cell emissions. The heavy tars can cause plugging of ducts, fans and emission control equipment.

The vertical stud Soderberg cell is similar to the HSS cell, except that the studs are mounted vertically in the anode paste. Gases from the VSS cells can be ducted to gas burners and the tars and oils combusted. The construction of the VSS cell prevents the installation of an integral gas collection device, and hooding is restricted to a canopy or skirt at the base of the cell where the hot anode enters the cell bath.

7.1.2 Emissions and Controls[1-3,9]

Controlled and uncontrolled emission factors for sulfur oxides, fluorides and total particulates are presented in Table 7.1-2. Fugitive particulate and fluoride emission factors for reduction cells are also presented in this table.

Emissions from aluminum reduction processes consist primarily of gaseous hydrogen fluoride and particulate fluorides, alumina, carbon monoxide, hydrocarbons or organics, and sulfur dioxide from the reduction cells and the anode baking furnaces. Large amounts of particulates are also generated during the calcining of aluminum hydroxide, but the economic value of this dust is such that extensive controls have been employed to reduce emissions to relatively small quantities. Small amounts of particulates are emitted from the bauxite grinding and materials handling processes.

The source of fluoride emissions from reduction cells is the fluoride electrolyte, which contains cryolite, aluminum fluoride (AlF_3), and fluorspar (CaF_2). For normal operation, the weight, or "bath", ratio of sodium fluoride (NaF) to AlF_3 is maintained between 1.36 and 1.43 by the addition of Na_2CO_3, NaF and AlF_3. Experience has shown that increasing this ratio has the effect of decreasing total fluoride effluents. Cell fluoride emissions are also decreased by lowering the operating temperature and increasing the alumina content in the bath. Specifically, the ratio of gaseous (mainly hydrogen fluoride and silicon tetrafluoride) to particulate fluorides varies from 1.2 to 1.7 with PB and HSS cells, but attains a value of approximately 3.0 with VSS cells.

Particulate emissions from reduction cells consist of alumina and carbon from anode dusting, cryolite, aluminum fluoride, calcium fluoride, chiolite ($Na_5Al_3F_{14}$) and ferric oxide. Representative size distributions for particulate emissions from PB cells and HSS cells are presented in Table 7.1-3. Particulates less than 1 micron in diameter represent the largest fraction (35 - 44 percent) of uncontrolled emissions. Uncontrolled particulate emissions from one HSS cell had a mass mean particle diameter of 5.5 microns. Thirty percent by mass of the particles were submicron, and 16 percent were less than 0.2μ in diameter.[7]

TABLE 7.1-2. EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a]

EMISSION FACTOR RATING: A

Operation	Total Particulate[b] kg/Mg	Total Particulate[b] lb/ton	Gaseous Fluoride (HF) kg/Mg	Gaseous Fluoride (HF) lb/ton	Particulate Fluoride (F) kg/Mg	Particulate Fluoride (F) lb/ton	Sulfur Oxides kg/Mg	Sulfur Oxides lb/ton	References
Bauxite grinding									
Uncontrolled	3.0	6.0	Neg	Neg	NA	NA	NA	NA	1,3
Spray tower	0.9	1.8	Neg	Neg	NA	NA	NA	NA	1,3
Floating bed scrubber	0.85	1.7	Neg	Neg	NA	NA	NA	NA	1,3
Quench tower and spray screen	0.5	1.0	Neg	Neg	NA	NA	NA	NA	1,3
Electrostatic precipitator (ESP)	0.06	0.12	Neg	Neg	NA	NA	NA	NA	1,3
Aluminum hydroxide calcining									
Uncontrolled	100.0	200.0	Neg	Neg	NA	NA	NA	NA	1,3
Spray tower	30.0	60.0	Neg	Neg	NA	NA	NA	NA	1,3
Floating bed scrubber	28.0	56.0	Neg	Neg	NA	NA	NA	NA	1,3
Quench tower	17.0	34.0	Neg	Neg	NA	NA	NA	NA	1,3
ESP	2.0	4.0	Neg	Neg	NA	NA	NA	NA	1,3
Anode baking furnace									
Uncontrolled	1.5	3.0	0.45	0.9	0.05	0.1	0.7-2	1.4-4	2,9
Fugitive	NA	NA	NA	NA	NA	NA	NA	NA	
Spray tower	0.375	0.75	0.02	0.04	0.015	0.03	NA	NA	9
ESP	0.375	0.75	0.02	0.04	0.015	0.03	NA	NA	2
Dry alumina scrubber	0.03	0.06	0.0045	0.009	0.001	0.002	NA	NA	2,9
Prebake cell									
Uncontrolled	47.0	94.0	12.0	24.0	10.0	20.0	30.0[c]	60.0[c]	1,2,9
Fugitive	2.5	5.0	0.6	1.2	0.5	1.0	NA	NA	2,9
Emissions to collector	44.5	89.0	11.4	22.8	9.5	19.0	NA	NA	2
Multiple cyclones	9.8	19.6	11.4	22.8	2.1	4.2	NA	NA	2
Dry alumina scrubber	0.9	1.8	0.1	0.2	0.2	0.4	NA	NA	2,9
Dry ESP + spray tower	2.25	4.5	0.7	1.4	1.7	3.4	NA	NA	2,9
Spray tower	8.9	17.8	0.7	1.4	1.9	3.8	NA	NA	2
Floating bed scrubber	8.9	17.8	0.25	0.5	1.9	3.8	NA	NA	2
Coated bag filter dry scrubber	0.9	1.8	1.7	3.4	0.2	0.4	NA	NA	2
Cross flow packed bed	13.15	26.3	3.35	6.7	2.8	5.6	NA	NA	9
Dry + secondary scrubber	0.35	0.7	0.2	0.4	0.15	0.3	NA	NA	9

TABLE 7.1-2 (cont.) EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a]

EMISSION FACTOR RATING: A

Operation	Total Particulate[b] kg/Mg	Total Particulate[b] lb/ton	Gaseous Fluoride (HF) kg/Mg	Gaseous Fluoride (HF) lb/ton	Particulate Fluoride (F) kg/Mg	Particulate Fluoride (F) lb/ton	Sulfur Oxides kg/Mg	Sulfur Oxides lb/ton	References
Vertical Soderberg stud cell									
Uncontrolled	39.0	78.0	16.5	33.0	5.5	11.0	NA	NA	2,9
Fugitive	6.0	12.0	2.45	4.9	0.85	1.7	NA	NA	9
Emissions to collector	33.0	66.0	14.05	28.1	4.65	9.3	NA	NA	9
Spray tower	8.25	16.5	0.15	0.3	1.15	2.3	NA	NA	2
Venturi scrubber	1.3	2.6	0.15	0.3	0.2	0.4	NA	NA	2
Multiple cyclones	16.5	33.0	14.05	28.1	2.35	4.7	NA	NA	2
Dry alumina scrubber	0.65	1.3	0.15	0.3	0.1	0.2	NA	NA	2
Scrubber + wet ESP + spray screen + scrubber	3.85	7.7	0.75	1.5	0.65	1.3	NA	NA	2,9
Horizontal Soderberg stud cell									
Uncontrolled	49.0	98.0	11.0	22.0	6.0	12.0	NA	NA	2,9
Fugitive	5.0	10.0	1.1	2.2	0.6	1.2	NA	NA	2,9
Emissions to collector	44.0	88.0	9.9	19.8	5.4	10.8	NA	NA	2,9
Spray tower	11.0	22.0	3.75	7.5	1.35	2.7	NA	NA	2,9
Floating bed scrubber	9.7	19.4	0.2	0.4	1.2	2.4	NA	NA	2
Scrubber + wet ESP	0.9	1.8	0.1	0.2	0.1	0.2	NA	NA	2,9
Wet ESP	0.9	1.8	0.5	1.0	0.1	0.2	NA	NA	9
Dry alumina scrubber	0.9	1.8	0.2	0.4	0.1	0.2	NA	NA	9

[a] For bauxite grinding, expressed as kg/Mg (lb/ton) of bauxite processed. For calcining of aluminum hydroxide, expressed as kg/Mg (lb/ton) of alumina produced. All other factors per Mg (ton) of molten aluminum product. Emission factors for sulfur oxides have C ratings. NA = Information not available.

[b] Includes particulate fluorides.

[c] Reference 2. Estimates for SO_x based on 3% sulfur in coke.

Emissions from reduction cells also include hydrocarbons or organics, carbon monoxide and sulfur oxides. Small amounts of hydrocarbons are released by PB pots, and larger amounts are emitted from HSS and VSS pots. In vertical cells, these organics are incinerated in integral gas burners. Sulfur oxides originate from sulfur in the anode coke and pitch. The concentrations of sulfur oxides in VSS cell emissions range from 200 to 300 ppm. Emissions from PB plants usually have SO_2 concentrations ranging from 20 to 30 ppm.

TABLE 7.1-3. REPRESENTATIVE PARTICLE SIZE DISTRIBUTIONS OF UNCONTROLLED EMISSIONS FROM PREBAKED AND HORIZONTAL STUD SODERBERG CELLS[a]

Size range (μ)	Particles (wt %)	
	PB	HSS
<1	35	44
1 to 5	25	26
5 to 10	8	8
10 to 20	5	6
20 to 44	5	4
>44	22	12

[a]Reference 1.

Emissions from anode bake ovens include the products of fuel combustion, high boiling organics from the cracking, distillation and oxidation of paste binder pitch, sulfur dioxide from the carbon paste, fluorides from recycled anode butts, and other particulate matter. The concentrations of uncontrolled emissions of SO_2 from anode baking furnaces range from 5 to 47 ppm (based on 3 percent sulfur in coke).[8]

Casting emissions are mainly fumes of aluminum chloride, which may hydrolyze to HCl and Al_2O_3.

A variety of control devices has been used to abate emissions from reduction cells and anode baking furnaces. To control gaseous and particulate fluorides and particulate emissions, one or more types of wet scrubbers (spray tower and chambers, quench towers, floating beds, packed beds, venturis, and self induced sprays) have been applied to all three types of reduction cells and to anode baking furnaces. Also, particulate control methods such as electrostatic precipitators (wet and dry), multiple cyclones and dry alumina scrubbers (fluid bed, injected, and coated filter types) have been employed with baking furnaces and on all three cell types. Also, the alumina adsorption systems are being used on all three cell types for controlling both gaseous and particulate fluorides by passing the pot offgases through the entering alumina

feed, on which the fluorides are absorbed. This technique has an overall control efficiency of 98 to 99 percent. Baghouses are then used to collect residual fluorides entrained in the alumina and to recycle them to the reduction cells. Wet electrostatic precipitators approach adsorption in particulate removal efficiency but must be coupled to a wet scrubber or coated baghouse to catch hydrogen fluoride.

Scrubber systems also remove a portion of the SO_2 emissions. These emissions could be reduced by wet scrubbing or by reducing the quantity of sulfur in the anode coke and pitch, i.e., calcinating the coke.

In the aluminum hydroxide calcining, bauxite grinding and materials handling operations, various dry dust collection devices such as centrifugal collectors, multiple cyclones, or electrostatic precipitators and/or wet scrubbers have been used.

Potential sources of fugitive particulate emissions in the primary aluminum industry are bauxite grinding, materials handling, anode baking and the three types of reduction cells (see Table 7.1-2). These fugitives probably have particle size distribution similar to those presented in Table 7.1-3.

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7.2 COKE MANUFACTURING

7.2.1 Process Description

Coking is the process of destructive distillation, or the heating of coal in an atmosphere of low oxygen content. During this process, organic compounds in the coal break down to yield gases and a relatively involatile residue. The primary method for the manufacture of coke is the byproduct method, which accounts for more than 98 percent of U.S. coke production.

The byproduct method is oriented to the recovery of gases produced during the coking cycle. Narrow rectangular slot-type coking ovens are constructed of silica brick, and a battery is commonly made up of a series of 40 to 70 of these ovens interspaced with heating flues. A larry car runs along the top of the coke battery, charging the ovens with coal through ports. After each charging, the ports are sealed, and heat is supplied to the ovens by combustion of gases passing through the flues between the ovens. The fuels used in the combustion process are natural gas, coke oven gas or blast furnace gas. In the ovens, coke is formed first near the brick walls and then toward the center, where temperatures are 2000° - 2100°F (1100° - 1150°C). After a period of 16 - 20 hours, the coking process is complete. Coke is pushed by a ram from the oven into a quenching car. The quenching car of hot coke is moved by rail to the quench tower, where several thousand gallons of water are used to cool the coke. The coke is allowed to dry and is separated into various sizes for future use. See Figure 7.5-1 of this document for a flow diagram of an integrated iron and steel plant which contains the coking operations.

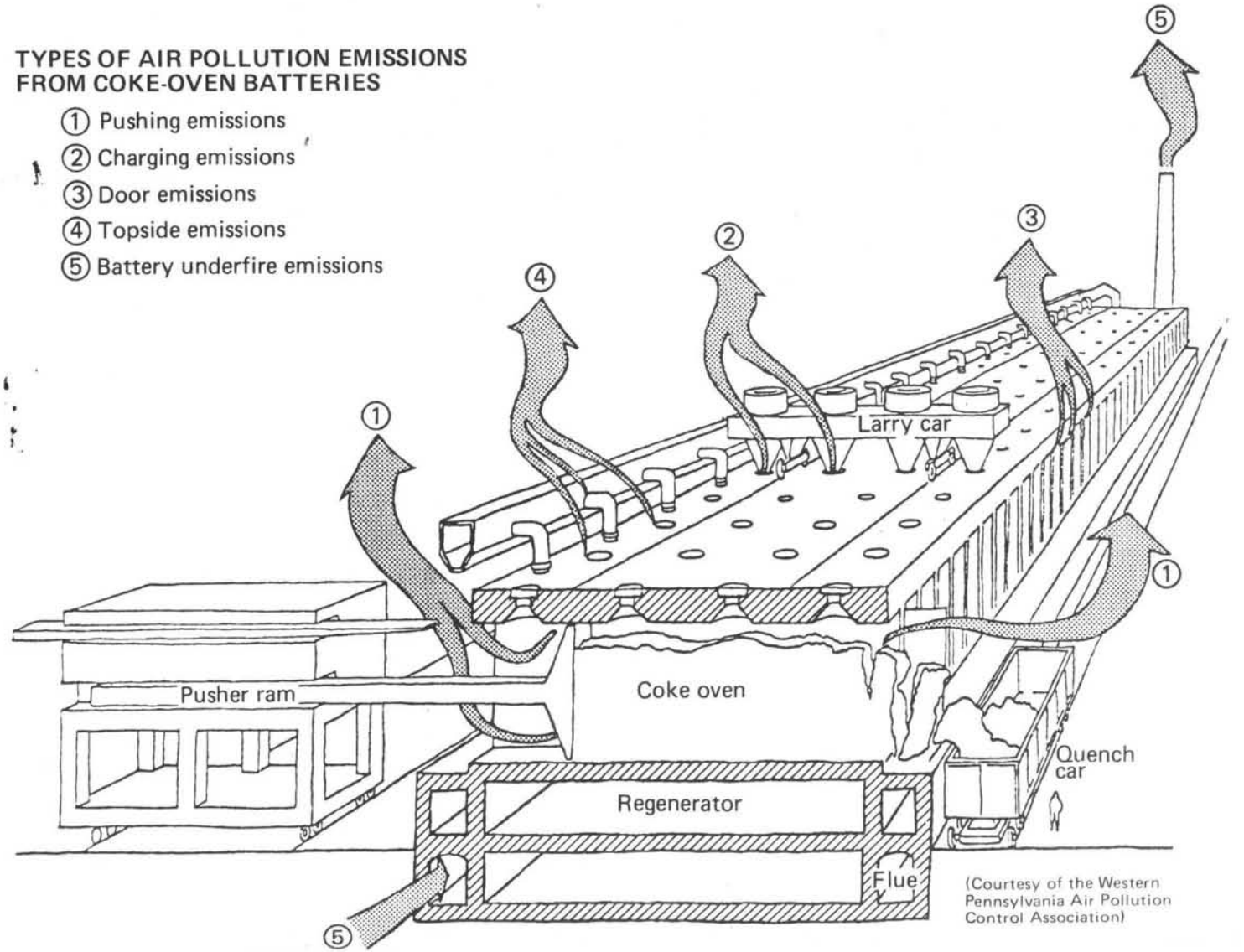
7.2.2 Emissions[1]

Particulates, volatile organic compounds, carbon monoxide and other emissions originate from the following byproduct coking operations: (1) coal preheating (if used), (2) charging of coal into the incandescent ovens, (3) oven leakage during the coking period, (4) pushing the coke out of the ovens, (5) quenching the hot coke and (6) combustion stacks. Gaseous emissions from the byproduct ovens during the coking process 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, xylene) and pyridine. These unit operations are potential sources of volatile organic compounds.

Oven charging operations and leakage around poorly sealed coke oven doors and lids are major sources of emissions from byproduct ovens. Emissions also occur when finished coke is pushed into the quench cars and during the quenching operation. The combustion process is also a source of pollutant emissions. As the combusting gases pass through the coke oven heating flues, emissions from the ovens may leak into the stream. Also, if the coke oven gas is not desulfurized, the combustion process will emit sulfur dioxide. Figure 7.2-1 is a depiction of a coke oven battery showing the major air pollution sources.

TYPES OF AIR POLLUTION EMISSIONS FROM COKE-OVEN BATTERIES

① Pushing emissions
② Charging emissions
③ Door emissions
④ Topside emissions
⑤ Battery underfire emissions



(Courtesy of the Western Pennsylvania Air Pollution Control Association)

Table 7.2-1. EMISSION FACTORS FOR COKE MANUFACTURE[a]
EMISSION FACTOR RATING: D (except particulates)

Type of Operation	Particulates[b] lb/ton	Particulates[b] kg/MT	Emission Factor Rating	Sulfur Dioxide[c] lb/ton	Sulfur Dioxide[c] kg/MT	Carbon Monoxide[c] lb/ton	Carbon Monoxide[c] kg/MT	Volatile Organics[c,d] lb/ton	Volatile Organics[c,d] kg/MT	Nitrogen Oxides (NO_2)[c] lb/ton	Nitrogen Oxides (NO_2)[c] kg/MT	Ammonia[c] lb/ton	Ammonia[c] kg/MT
Coal Preheaters													
Uncontrolled	7.0	3.5	C	-	-	-	-	-	-	-	-	-	-
Controlled by scrubber	0.65	0.325	C	-	-	-	-	-	-	-	-	-	-
Coal Charging													
Uncontrolled	0.85	0.425	C	0.02	0.01	0.6	0.3	2.5	1.25	0.03	0.015	0.02	0.01
Controlled larry car vented to scrubber	0.02	0.01	C	-	-	-	-	-	-	-	-	-	-
Sequential charging	0.016	0.008	C	-	-	-	-	-	-	-	-	-	-
Door Leaks (Uncontrolled)	0.51	0.255	B	-	-	0.6	0.3	1.5	0.75	0.01	0.005	0.06	0.03
Coke Pushing													
Suspended particulates													
Uncontrolled (measured in duct venting coke side shed)	0.47	0.235	A	-	-	-	-	-	-	-	-	-	-
Controlled (water sprays)	0.39	0.195	A	-	-	-	-	-	-	-	-	-	-
Total particulates (suspended plus dust fall)													
Uncontrolled	2.0	1.0	B	-	-	0.07	0.035	0.2	0.1	-	-	0.1	0.05
Controlled (water sprays)	1.2	0.6	B	-	-	-	-	-	-	-	-	-	-
Controlled (enclosed coke car and guide, vented to scrubber)	0.024	0.012	C	-	-	-	-	-	-	-	-	-	-
Quenching (Controlled by Baffles)	1.0	0.5	A	-	-	-	-	-	-	-	-	-	-
Combustion Stacks (Uncontrolled)	0.58	0.29	B	4.0[e]	2.0	-	-	-	-	-	-	-	-

[a] Emission factors expressed as units per weight of coal charged. Dash indicates no available data.
[b] Reference 1.
[c] References 2 and 3.
[d] Expressed as methane.
[e] Reference 4. The sulfur dioxide factor is based on the following representative conditions: (1) sulfur content of coal charged to oven is 0.8 weight %; (2) about 33 weight % of total sulfur in the coal charged to oven is transferred to the coke oven gas; (3) about 40% of coke oven gas is burned during the underfiring operation, and the remainder is used in other parts of the steel operation, where the rest of the sulfur dioxide is discharged - about 6 lb/ton (3 kg/MT) of coal charged; and (4) gas used in underfiring has not been desulfurized.

Associated with the byproduct coke oven process are open source fugitive dust operations. These include material handling operations of unloading, storing, grinding and sizing of coal, and the screening, crushing, storing and loading of coke. Fugitive emissions also come from vehicles traveling on paved and unpaved surfaces. These emissions and the parameters that influence them are discussed in more detail in Section 7.5 and Chapter 11 of this document. The emission factors for coking operations are summarized in Table 7.2-1. Extensive information on the data used to develop the particulate emission factors is found in Reference 1.

References for Section 7.2

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7.3 PRIMARY COPPER SMELTING

7.3.1 Process Description[1,3,7]

Pyrometallurgical smelting methods are utilized extensively in the United States to produce copper from sulfide ores. These ores usually contain less than 1 percent copper and therefore must be concentrated before being transported to the smelter. Concentration to 15 to 35 percent copper is accomplished by crushing, grinding, and flotation at the mine site. Sulfur content of the concentrate is generally 25 to 35 percent. Most of the remaining concentrate is iron (25 percent) and water (10 percent). Some concentrates also contain significant quantities of arsenic, cadmium, lead, boron, antimony, and other heavy metals.

The most common configuration of operations for pyrometallurgical smelters in the United States includes roasting, reverberatory or electric furnace smelting, and converting to produce blister copper (99+ percent pure copper) from concentrate. The remaining impurities are usually removed by fire refining and electrolytic refining. Figure 7.3-1 is a generalized flowsheet for this combination of operations. About half of the smelters in the United States do not use the roasting step and instead feed wet or "green" charge directly to the smelting furnace.

In roasting, concentrate is heated in air, eliminating 20 to 50 percent of the sulfur as sulfur dioxide (SO_2). Relatively volatile impurities such as antimony, arsenic, and bismuth are also driven off, and some of the iron is converted to oxides, which combine with slag in ensuing processes. Concentrate is mixed with a siliceous flux (often a low-grade ore) to produce the roaster charge material. The roasted product, called calcine, serves as a dried and preheated charge for the smelting furnace. Either multiple-hearth or fluidized-bed roaster furnaces are used for roasting copper concentrate. Because there is less air dilution, higher SO_2 concentrations are present in fluidized-bed roaster gases than in multiple-hearth roaster gases.

The second step is smelting. In this process, hot calcines from the roaster or raw unroasted concentrate are fused with limestone and siliceous flux in reverberatory or electric-arc furnaces to produce copper matte. Copper matte is primarily miscible liquid sulfides and some heavy metals. In reverberatory furnace operation, heat is supplied by combustion of oil, gas, or pulverized coal, and is reflected from the roof of the furnace onto the charge. As the charge is melted, copper, iron, and sulfur form cuprous sulfide (Cu_2S) and ferrous sulfide (FeS). Other minerals combine with fluxes, forming slag. Slag floats on top of the molten bath and is removed continuously. Copper matte remains in the furnace until poured. Normal smelting furnace operations produce a matte that contains 40 to 45 percent copper.

For smelting in electric-arc furnaces, heat is generated by an electric current passing through carbon electrodes that are lowered into the slag layer of the molten bath. Electric furnaces do not produce fuel combustion gases; therefore, gas flow rates are lower and SO_2 concentrations are higher in electric furnace effluent streams than in reverberatory furnace gases.

The final step in the production of blister copper is converting. Converting is normally performed in Peirce-Smith converters, which consist of a cylindrical steel shell mounted on trunnions at either end and rotated about its major axis. An opening in one side of the converter functions as a mouth through which molten matte, siliceous flux, and scrap copper are charged to the converter and gaseous products are vented. Air or oxygen-enriched air is blown through the metal; FeS is oxidized and combined with the flux to form a slag, which floats on the surface. Relatively pure Cu_2S (called "white metal") is collected in the bottom of the converter. After removal of slag, a renewed air blast oxidizes the sulfide sulfur to SO_2 leaving blister copper in the converter.

Hoboken converters have recently been installed at one U.S. smelter to replace the standard Peirce-Smith converters. The metallurgical operations of the Hoboken unit are the same as those of the Peirce-Smith unit; however, to prevent dilution air from entering the exhaust gas stream, the Hoboken converter is fitted with a stationary side flue instead of a movable hood.

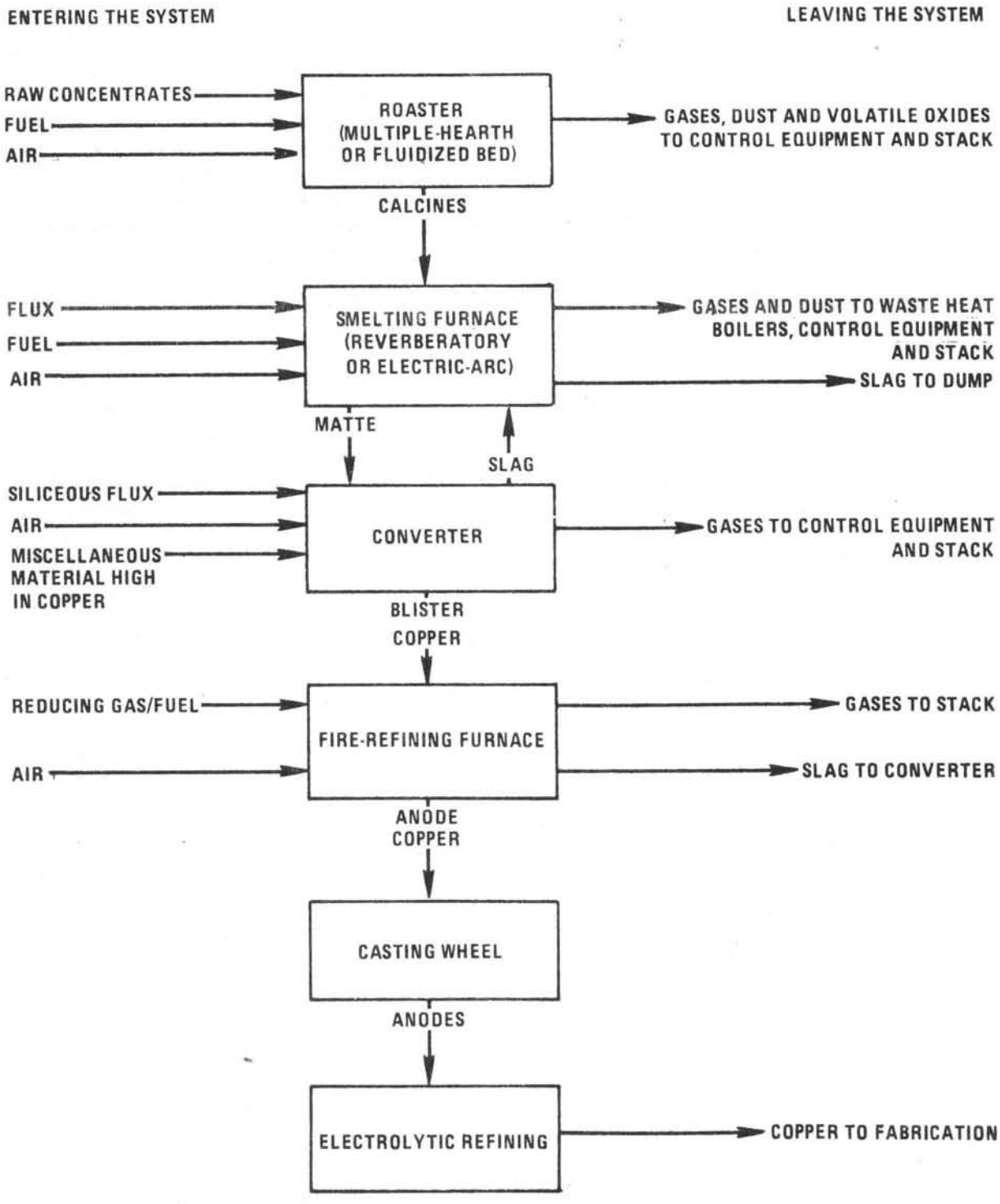

Figure 7.3-1. Typical primary copper smelter flowsheet.

In a newer process, roasting and smelting are combined in one operation to produce a high-grade copper matte from concentrates and fluxes using a flash furnace. Fuel is supplied to sustain combustion reactions, but most of the heat necessary for smelting is generated autogenously by the oxidation of the sulfides in the concentrate. The flash smelting operation has also been applied to the oxidation of matte to blister copper in the continuous smelting process. Continuous smelting systems that have been operated at foreign smelters include the Noranda, WORCRA, Mitsubishi, and TBRC (top-blown rotary converter) processes.

Blister copper usually contains from 98.5 to 99.5 percent pure copper. Impurities may include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, and zinc. To further purify the blister copper, fire refining and electrolytic refining are used. In fire refining, air is blown through the metal to oxidize remaining impurities; these are removed as a slag, and the remaining metal bath is subjected to a reducing atmosphere to reconvert cuprous oxide to copper. The fire-refined copper is cast into anodes and further refined electrolytically.

Electrolytic refining involves separation of copper from impurities by electrolysis in a solution containing copper sulfate and sulfuric acid. Metallic impurities precipitate from the solution and form a sludge that is removed and treated for recovery of precious metals. The copper produced is 99.95 to 99.97 percent pure.

Hydrometallurgical processes are usually applied to recovery of copper from oxide ores, but their application in U.S. plants is limited.

7.3.2 Emissions and Controls

Particulates and sulfur dioxide are the principal air contaminants emitted at primary smelters. In some cases, these emissions are generated directly as a result of the processes involved, as in the liberation of SO_2 from the ore or the volatilization of trace elements to oxide fumes. Significant quantities of fugitive emissions are generated during material handling operations and charging and tapping of furnaces.

Mutiple-hearth and fluidized-bed roasters are sources of both particulates and sulfur oxides. Particulates consist of oxides of the metals that are found in the concentrate. Copper and iron oxides are the primary constituents, but other oxides such as those of arsenic, antimony, cadmium, lead, mercury, and zinc may also be present with metallic sulfates and sulfuric acid. Combustion products from fuel burning also contribute to the particulate emissions from multiple-hearth roasters. Control of particulates from roaster gases is standard practice because of the value of the recovered copper in the dust and because of the presence of toxic particulates such as arsenic. Cyclones and scrubbers may be used for coarse particulate removal and are usually followed by electrostatic precipitators (ESPs) or fabric filters for collection of fines.

Smelting furnaces also emit significant quantities of oxidized metal particulates and SO_2. Particulate collection systems for smelting furnaces are similar to those used for roasters. Reverberatory furnace offgases are usually routed through low-velocity balloon flues and waste heat boilers to recover large particles and heat, then routed through electrostatic precipitators. Overall collection efficiencies of 95 to 99 percent for ESP systems are normal for these applications. Efficiencies as high as 99.7 percent have been reported.

Converter flue gases also contain particulates and SO_2. In the standard Peirce-Smith converter, flue gases are captured during the blowing phase by movable hooding covering the converter mouth opening. To prevent the hood freezing to the converter due to splashing of molten metal, there is a gap between the hood and the vessel. Sophisticated draft control devices that maintain a negative pressure at the gap to draw air in for cooling and to prevent fugitive emissions have been developed. During charging and pouring operations, significant fugitive emissions may occur when the hooding is removed to allow crane access.

Remaining smelter processes handle material that contains very little sulfur; hence SO_2 emissions from these processes are relatively insignificant. Particulate emissions from fire-refining operations, however, may still be of concern. Electrolytic refining does not produce emissions unless the associated sulfuric acid tanks are open to the atmosphere. Crushing and grinding systems used in ore, flux, and slag processing also contribute to fugitive dust problems.

Control of SO_2 emissions from smelter sources is most commonly performed in a single- or double-contact sulfuric acid manufacturing plant. Use of a sulfuric acid plant on copper smelter effluent gas streams requires that gas be free from particulate matter and that a certain minimum SO_2 concentration be maintained. Table 7.3-1 shows typical average SO_2 concentrations for the various smelter unit offgases. These offgas streams may be treated individually, or weak and strong concentration streams may be blended. Typically, single-contact acid plants achieve 96.5 to 97 percent conversion of SO_2 to acid with approximately 2000 ppm SO_2 remaining in the acid plant effluent gas. Double-contact acid plants collect 98 percent of the SO_2 and emit about 500 ppm SO_2. Absorption of the SO_2 in dimethylaniline (DMA) solution has also been used in U.S. smelters for production of liquid SO_2.

Table 7.3-1. AVERAGE SULFUR DIOXIDE CONCENTRATIONS IN OFFGASES FROM PRIMARY COPPER SMELTING SOURCES

Unit	Sulfur dioxide concentration, percent
Multiple-hearth roaster	1.5-3
Fluidized-bed roaster	10-12
Reverberatory furnace	0.5-1.5
Electric-arc furnace	4-8
Flash-smelting furnace	10-20
Continuous smelting furnace	5-15
Peirce-Smith converter	4-7
Hoboken converter	8
Single-contact H_2SO_4 plant	0.2
Double-contact H_2SO_4 plant	0.05

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

No control practices for nitrogen oxides, carbon monoxide, or hydrocarbon emissions, which are found in the offgas streams from units requiring fuel combustion are currently utilized in U.S. smelters. Multiple-hearth roasters, reverberatory furnaces, converters, and refining furnaces are sources of these contaminants. Data are available for assigning emission factors for NO_x emissions from reverberatory furnaces and converters in only one smelter configuration (Table 7.3-2). Data for assigning emission factors for CO and hydrocarbons are unavailable.

Actual emissions from a particular smelter unit depend upon the configuration of equipment in the smelting plant and the operating parameters employed. Table 7.3-2 summarizes the emission factors for the major units for various smelter configurations. Other potential emission sources, which have not been quantified, include ore crushing and preparation, flux crushing, ore storage, concentrate drying, slag dumping, fire refining, and copper casting.

Table 7.3-2. EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a,b]
EMISSION FACTOR RATING: B

Smelter configuration	Unit	Control[c]	Particulates[d]		SO_2[d]		SO (as H_2SO_4)[d]		NO_x (as NO_2)[d]	
			lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Reverberatory furnace followed by converters	Reverb.	None	36	18	390	195	0.81	0.41	0.09	0.045
		ESP	22	11						
	Converter	None	42	21	860	430			0.05	0.025
		ESP	2.5	1.3						
		ESP + SCAP	0.28	0.14	27	14	0.06	0.03		
Multiple-hearth roaster followed by reverberatory furnace and converters	Roaster	None	45	22.5	410	205				
		Baghouse	0.2	0.1						
	Roaster and reverb.[e]	None			450	230	1.5	0.75		
		ESP	4.8	2.4						
		Spray Chamber + ESP	1.4	0.7						
	Converter	None	42	21	540	270				
		ESP	2.9	1.5						
		ESP + SCAP	0.38	0.19	61	31	0.14	0.07		
		ESP + DCAP	0.38	0.19	0.62	0.31				
Fluidized-bed roaster followed by reverberatory furnace and converters	Roaster	None	55	28	540	270				
		Baghouse + SCAP	0.1	0.05	2	1				
	Reverb.	ESP	2.4	1.2	66	33	0.22	0.11		
	Converter	ESP + SCAP	1.1	0.55						
Fluidized-bed roaster followed by electric furnace and converters	Roaster	None	55	28	540	270				
		Baghouse + SCAP	0.1	0.05	2	1				
	Furnace	None			131	66				
	Converter	None			444	222				
Total uncontrolled smelter		None	135	66.5	1,254	627				

[a]Emission factors are expressed as units per unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal.

[b]Other potential emission sources include (1) ore storage, crushing, and handling, (2) flux crushing and handling, (3) concentrate drying and handling, (4) slag dumping, (5) fire refining, and (6) copper casting, but emission rates have not been quantified.

[c]ESP = electrostatic precipitator
SCAP = single-contact acid plant
DCAP = double-contact acid plant

[d]References 2, 4, 5, 6, 7, and 8. Additional information was furnished by the following agencies.
Arizona Department of Health Services, Phoenix, Arizona
Montana State Department of Health and Environmental Sciences, Helena, Montana
Puget Sound Air Pollution Control District, Seattle, Washington
New Mexico Environmental Improvement Agency, Santa Fe, New Mexico

[e]Roaster and reverberatory furnace emissions are combined and therefore a single set of emission factors is provided.

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7.3 PRIMARY COPPER SMELTING

Charles Masser

7.3.3 Fugitive Emission Factors

Potential sources of fugitive particulate emissions in the copper industry are roasting, smelting, converting and fire refining. Table 7.3-3 shows the potential uncontrolled fugitive emission factors from these sources.

Fifteen percent of the particulate emissions from roasting are less than 10 μm, and 50 percent of those from reverberatory furnaces are less than 37 μm.[10,11] The mean particulate diameter of converter emissions is 44 μm. Sixteen percent of pouring and casting emissions are less than 10 μm, and 46 percent are less than 74 μm.[11]

Table 7.3-3. POTENTIAL FUGITIVE EMISSION FACTORS FOR UNCONTROLLED PRIMARY COPPER SMELTERS

EMISSION FACTOR RATING: E

Type of operation	Particulates[a]	
	lb/ton	kg/MT
Roasting[b]	23.00	11.50
Reverberatory smelting furnace[c]	8.50	4.25
Converter[b,d]	10.50	5.25
Fire refining furnace (anode furnace and casting)[d,e]	1.90	0.95

[a]Factors expressed as units per units of end product.

[b]Based on material balance, using same percentage estimated for SO_2 from Reference 12.

[c]Reference 13.

[d]Reference 14.

[e]Reference 15.

Additional References for Section 7.3

10. *Control Techniques for Lead Air Emissions*, EPA-450/2-77-012, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1978.

11. L.J. Shannon and P.G. Gorman, *Particulate Pollutant System Study, Vol. III: Emission Characteristics*, EPA Contract No. 22-69-104, Midwest Research Institute, Kansas City, MO, 1971.

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7.3.4 Lead Emission Factors

Lead particulate emissions occur during roasting, smelting, converting and refining operations. In converting, some control is effected by moveable hoods placed over the converter mouth. Emissions from this phase, high in particulate and sulfur dioxide, are ducted to electrostatic precipitators or cyclones for particle removal and then to single or double contact sulfuric acid plants.

Significant fugitive emissions occur during materials handling and furnace charging and tapping. Fugitive gases and dust from roasting and smelting (calcine transfer) are usually controlled by cyclones, precipitators, or in newer plants, baghouses.

Some operations are intermittant, like calcine transfer to furnaces and copper matte and slag tapping from furnaces.

No emission data are available for refining operations and controlled smelting, and only one data point for roasting controlled by a precipitator.

Table 7.3-4 shows potential lead emission factors from these sources.

Table 7.3-4. LEAD EMISSION FACTORS FOR PRIMARY COPPER SMELTERS

EMISSION FACTOR RATING: B

Operation	Emission Factor[a] lb/ton	kg/MT
Roasting		
Uncontrolled	0.0536 (0.0087 - 0.0994)	0.0268 (0.0043 - 0.0497)
Controlled[b]	0.1386	0.0693
Smelting	0.0579 (0.0016 - 0.2368)	0.0289 (0.0008 - 0.1184)
Converting		
Uncontrolled	0.1233 (0.0135 - 0.2065)	0.0617 (0.0068 - 0.1033)
Controlled	0.0785 (0.0067 - 0.1377)	0.0393 (0.0034 - 0.0689)
Refining	NA	NA

[a]Reference 16. Ranges in parentheses. NA: no data available.
[b]Only datum available.

Additional Reference for Section 7.3

16. D. Ringwald and T. Rooney, Copper Smelters: Emission Test Report - Lead Emissions, EMB Report 79 CUS-14, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 1979.

7.4 FERROALLOY PRODUCTION

7.4.1 Process Description[1,2]

Ferroalloy is the generic term for alloys consisting of iron and one or more other metals. Ferroalloys are used in steel production as alloying elements and deoxidants. There are three basic types of ferroalloys: (1) silicon-based alloys, including ferrosilicon and calciumsilicon; (2) manganese-based alloys, including ferromanganese and silicomanganese; and (3) chromium-based alloys, including ferrochromium and ferrosilicochrome.

The four major procedures used to produce ferroalloy and high-purity metallic additives for steelmaking are: (1) blast furnace, (2) electrolytic deposition, (3) alumina silico-thermic process, and (4) electric smelting furnace. Because over 75 percent of the ferroalloys are produced in electric smelting furnaces, this section deals only with that type of furnace.

The oldest, simplest, and most widely used electric furnaces are the submerged-arc open type, although semi-covered furnaces are also used. The alloys are made in the electric furnaces by reduction of suitable oxides. For example, in making ferrochromium the charge may consist of chrome ore, limestone, quartz (silica), coal and wood chips, along with scrap iron.

7.4.2 Emissions[3]

The production of ferroalloys has many dust- or fume-producing steps. The dust resulting from raw material handling, mix delivery, and crushing and sizing of the solidified product can be handled by conventional techniques and is ordinarily not a pollution problem. By far the major pollution problem arises from the ferroalloy furnaces themselves. The conventional submerged-arc furnace utilizes carbon reduction of metallic oxides and continuously produces large quantities of carbon monoxide. This escaping gas carries large quantities of particulates of submicron size, making control difficult.

In an open furnace, essentially all of the carbon monoxide burns with induced air at the top of the charge, and CO emissions are small. Particulate emissions from the open furnace, however, can be quite large. In the semi-closed furnace, most or all of the CO is withdrawn from the furnace and burns with dilution air introduced into the system. The unburned CO goes through particulate control devices and can be used as boiler fuel or can be flared directly. Particulate emission factors for electric smelting furnaces are presented in Table 7.4-1. No carbon monoxide emission data have been reported in the literature.

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Table 7.4-1. EMISSION FACTORS FOR FERROALLOY PRODUCTION IN ELECTRIC SMELTING FURNACES[a] EMISSION FACTOR RATING: C

Type of furance and product	Particulates	
	lb/ton	kg/MT
Open furnace		
50% FeSi[b]	200	100
75% FeSi[c]	315	157.5
90% FeSi[b]	565	282.5
Silicon metal[d]	625	312.5
Silicomanganese[e]	195	97.5
Semi-covered furnace		
Ferromanganese[e]	45	22.5

[a]Emission factors expressed as units per unit weight of specified product produced.
[b]Reference 4.
[c]References 5 and 6.
[d]References 4 and 7.
[e]Reference 6.

References for Section 7.4

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc., Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.

2. Ferroalloys: Steel's All-purpose Additives. The Magazine of Metals Producing. February 1967.

3. Person, R. A. Control of Emissions from Ferroalloy Furnace Processing. Niagara Falls, New York. 1969.

4. Unpublished stack test results. Resources Research, Incorporated. Reston, Virginia.

5. Ferrari, R. Experiences in Developing an Effective Pollution Control System for a Submerged-Arc Ferroalloy Furnace Operation. J. Metals. p. 95-104, April 1968.

6. Fredriksen and Nestaas. Pollution Problems by Electric Furnace Ferroalloy Production. United Nations Economic Commission for Europe. September 1968.

7. Gerstle, R. W. and J. L. McGinnity. Plant Visit Memorandum. U. S. DHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio. June 1967.

7.5 IRON AND STEEL PRODUCTION

7.5.1 Process Description and Emissions[1,2]

Iron and steel manufacturing may be grouped into eight generic process operations: (1) coke production, (2) sinter production, (3) iron production, (4) steel production, (5) semi-finished product preparation, (6) finished product preparation, (7) heat and electricity supply and (8) handling and transport of raw, intermediate and waste materials. Figure 7.5-1, a general flow diagram of the iron and steel industry, interrelates these categories. The first category, coke production, is discussed in detail in Section 7.2 of this publication, and additional information on the handling and transport of materials is found in Chapter 11.

Sinter Production - The sintering process converts fine sized raw materials such as fine iron ore, coke breeze, fluxstone, mill scale, and flue dust into an agglomerated product of suitable size for charging into the blast furnance. The materials are mixed with water to provide cohesiveness in a mixing mill, then placed on a continuous moving grate called the sinter strand. A burner hood above the front third of the sinter strand ignites the coke in the mixture. Once ignited, combustion is self supporting and provides sufficient heat, 2400 - 2700°F (1300 - 1480°C), to cause surface melting and agglomeration of the mix. On the underside of the sinter machine lie windboxes that draw the combusted air down through the material bed into a common duct which leads to a particulate control device. The fused sinter is discharged at the end of the sinter machine, where it is crushed and screened. The undersize portion is recycled to the mixing mill. The remaining sinter is cooled in the open air by water spray or by mechanical fan to draw off the heat from the sinter. The cooled sinter is screened for a final time, with the fines being recycled and the rest being sent to charge the blast furnaces.

Emissions occur at several points in the sintering process. Points of particulate generation are (1) the windbox, (2) the discharge (sinter crusher and hot screen), (3) the cooler and (4) the cold screen. In addition to these sources, there are the inplant transfer stations, which generate emissions which can be controlled by localized enclosures. All the above sources except the cooler are normally vented to one or two control systems.

Iron Production - Iron is produced in blast furnaces, which are large refractory-lined chambers into which iron as natural ore, or agglomerated products such as pellets or sinter, coke, and limestone, are charged and allowed to react with large amounts of hot air to produce molten iron. Slag and blast furnace gases are byproducts of this operation. The average charge to produce one unit weight of iron requires 1.7 unit weights of iron bearing charge, 0.55 unit weights of coke, 0.2 unit weights of limestone, and 1.9 unit weights of air. Average blast furnace byproducts consist of 0.3 unit weights of slag,

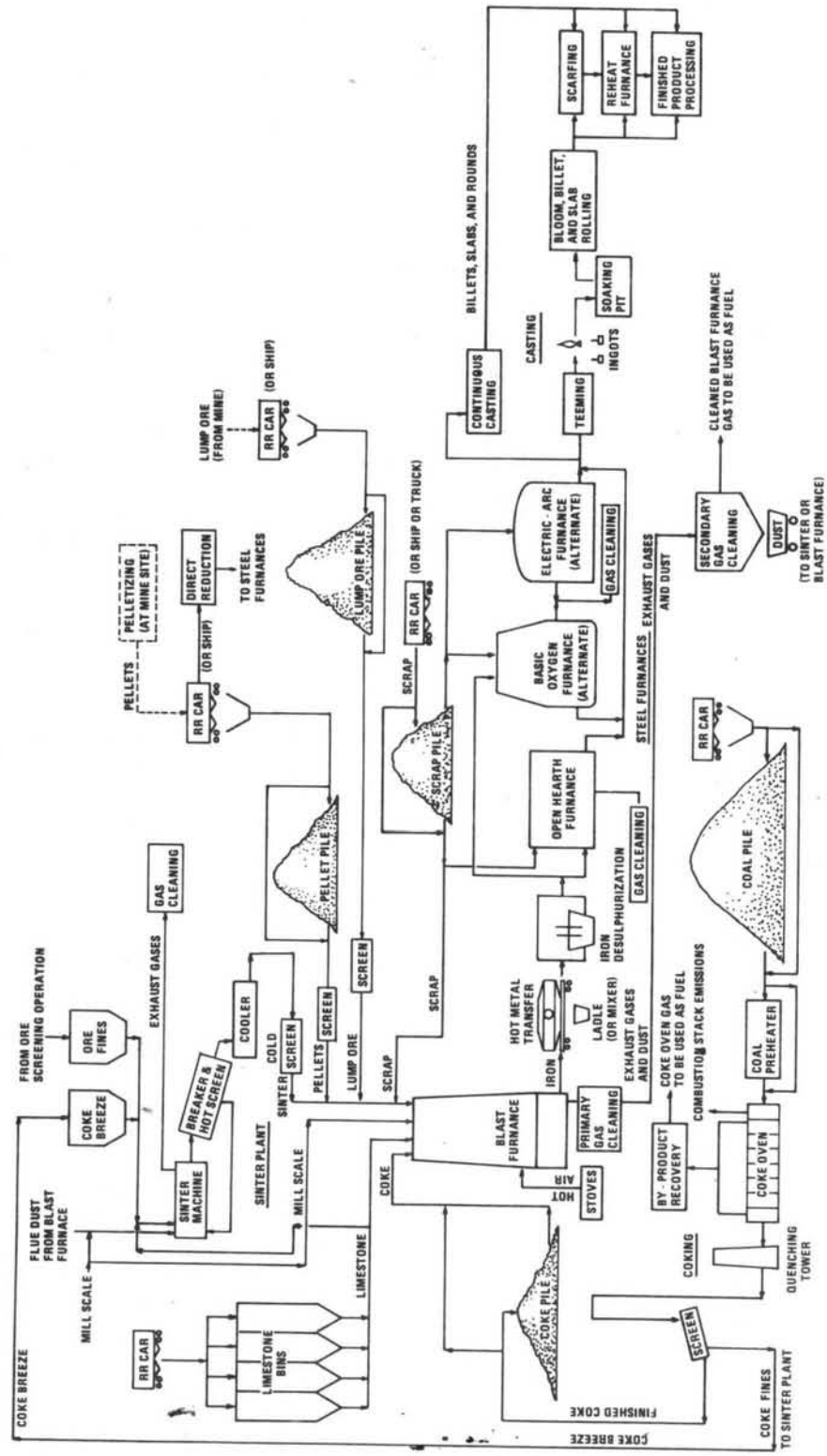

Figure 7.5-1. General flow diagram for the iron and steel industry.

0.05 unit weights of flue dust, and 3.0 unit weights of gas per unit of iron produced. The flue dust and other iron ore fines from the process are converted into useful blast furnace charge by the sintering operation.

Because of its high carbon monoxide content, this blast furnace gas has a low heating value, about 75 - 90 BTU/ft^3 (2790 - 3350 J/1^3) and is used as a fuel within the steel plant. Before it can be efficiently oxidized, however, the gas must be cleaned of particulate. Initially, the gases pass through a settling chamber or dry cyclone to remove about 60 percent of the particulate. Next, the gases undergo a one or two stage cleaning operation. The primary cleaner is normally a wet scrubber, which removes about 90 percent of the remaining particulate. The secondary cleaner is a high energy wet scrubber (usually a venturi) or an electrostatic precipitator, either of which can remove up to 90 percent of the particulate that has passed through the primary cleaner. Applied together, these control devices provide a clean fuel of less than 0.02 gr/ft^3 (0.05 g/m^3) for use within the steel plant.

Emissions occur during the production of iron when there is a blast furnace "slip" and during hot metal transfer operations in the cast house. All of the gas generated in the blast furnace is normally cleaned and used for fuel. Conditions such as "slips", however, can cause instantaneous emissions of carbon monoxide and particulates. Slips occur when a stratum of the material charged to a blast furnace does not settle with the material below it, thus leaving a gas filled space between the two portions of the charge. When this unsettled stratum of charge collapses, the displaced gas may cause the top gas pressure to increase above the safety limit, thus opening a counter-weighted bleeder valve to the atmosphere. Improvements in techniques for handling blast furnace burden have greatly reduced these occurrences.

Steel Making Process - Basic Oxygen Furnace - The basic oxygen process is employed to produce steel, from a furnace charge typically composed of 70 percent molten blast furnace metal and 30 percent scrap metal, by use of a stream of commercially pure oxygen to oxidize the impurities, principally carbon and silicon. Most of the basic oxygen furnaces (BOF) in the United States have oxygen blown through a lance in the top of the furnace. However, the Quiet-Basic Oxygen Process (Q-BOP), which is growing in use, has oxygen blown through tuyeres in the bottom of the furnace. Cycle times for the basic oxygen process range from 25 to 45 minutes.

The large quantities of carbon monoxide (CO) produced by the reactions in the BOF can be combusted at the mouth of the furnace and then vented to gas cleaning devices, as with open hoods, or the combustion can be suppressed at the furnace mouth, as with closed hoods. The term "closed hood" is actually a misnomer, since the opening at the furnace mouth is large enough to allow approximately 10 percent of theoretical air to enter. Nearly all the Q-BOPs in the United States have closed hoods, and most of the new top blown furnaces are being designed with closed hoods. Most furnaces installed before 1975 are of the open hood design.

TABLE 7.5-1. SILT CONTENT VALUES APPLICABLE TO THE IRON AND STEEL INDUSTRY[3,4]

Source	Number of tests	Range of silt content (%)	Average silt (%)
Unpaved roads	12	4 - 13	7.3
Paved roads	9	1.1 - 13	5.9
Material handling activities and storage pile wind erosion			
Coal	7	2 - 7.7	5.0
Iron ore pellets	10	1.4 - 13	4.9
Lump iron ore	9	2.8 - 19	9.5
Coke breeze	1	-	5.4
Slag	3	3 - 7.3	5.3
Blended ore	1	-	15.0
Sinter	1	-	0.7
Limestone	1	-	0.4
Flue dust	2	14 - 23	18.0

TABLE 7.5-2. SURFACE MOISTURE CONTENT VALUES APPLICABLE TO THE IRON AND STEEL INDUSTRY[3,4]

Source	Number of tests	Range of surface moisture content (%)	Average surface moisture content (%)
Material handling activities and storage pile wind erosion			
Coal	6	2.8 - 11	4.8
Iron ore pellets	8	0.64 - 3.5	2.1
Lump iron ore	6	1.6 - 8.1	5.4
Coke breeze	1	-	6.4
Slag	3	0.25 - 2.2	0.9
Blended ore	1	-	6.6
Flue dust	1	-	12.4

There are several sources of emissions in the basic oxygen furnace steel making process. The emission sources are (1) the furnace mouth during refining - collected by local full (open) or suppressed (closed) combustion hoods, (2) hot metal transfer to charging ladle, (3) charging scrap and hot metal, (4) dumping slag and (5) tapping steel.

TABLE 7.5-3. SURFACE LOADING ON TRAVELED LANES OF PAVED ROADS IN IRON AND STEEL PLANTS[3,4]

Number of tests	Range of surface loading (lb/mile)	Average surface loading (lb/mile)
9	65 - 17,000	2,700

Steel Making Process - Electric Arc Furnaces - Electric arc furnaces (EAF) are used to produce carbon and alloy steels. The charge to an EAF is nearly always 100 percent scrap. Direct arc electrodes extending through the roof of the furnace melt the scrap. An oxygen lance may or may not be used to speed the melting and refining process. Cycles range from 1 1/2 to 5 hours for carbon steel and from 5 to 10 hours for alloy steel.

There are several sources of emissions in the electric arc furnace steel making process. They are (1) emissions from the melting and refining often vented through a hole in the furnace roof, (2) charging scrap, (3) dumping slag and (4) tapping steel. In interpreting and using emission factors for EAFs, it is important to know what configuration one is dealing with. For example, if an EAF has a building evacuation system, the emission factor before the control device would represent all melting, refining, charging, tapping and slagging emissions which ascended to the building roof. Reference 2 has additional details on various configurations used to control electric arc furnaces.

Steel Making Process - Open Hearth Furnaces - In the open hearth furnace (OHF), a mixture of scrap iron and steel and hot metal (molten iron) is melted in a shallow rectangular basin or "hearth". Burners producing a flame above the charge provide the heat necessary for melting. The mixture of scrap and hot metal can vary from 100 percent scrap to 100 percent hot metal, but a half and half mixture is a reasonable industry-wide average. The process may or may not be oxygen lanced, affecting the process cycle times, which are approximately 8 hours and 10 hours respectively.

There are several sources of emissions in the open hearth furnace steel making process. The activities generating emissions are (1) transferring hot metal, (2) melting and refining the heat, (3) charging of scrap and/or hot metal, (4) dumping slag and (5) tapping steel.

Semifinished Product Preparation - After the steel has been tapped, the molten metal is teemed into ingots which are later heated to form other shapes, such as blooms, billets or slabs. The molten metal may also

TABLE 7.5-4. PARTICULATE EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]

Source	Units	Emission Factors		Emission Factor Rating
Blast Furnances				
Slips	lb(kg)/slip	87.0	(39.5)	D
Uncontrolled cast house emissions	lb/T (kg/MT) hot metal			
Monitor		0.6	(0.3)	B
Tap hole and trough (not runners)		0.3	(0.15)	B
Sintering				
Windbox emissions	lb/T (kg/MT) finished sinter			
Uncontrolled				
Leaving grate		11.1	(5.56)	B
After coarse particulate removal		8.7	(4.35)	A
Controlled by dry ESP		1.6	(0.8)	B
Controlled by wet ESP		0.17	(0.085)	B
Controlled by scrubber		0.47	(0.235)	B
Controlled by cyclone		1.0	(0.5)	B
Sinter discharge (breaker and hot screens)	lb/T (kg/MT) finished sinter			
Uncontrolled		6.8	(3.4)	B
Controlled by baghouse		0.1	(0.05)	B
Controlled by orifice scrubber		0.59	(0.295)	A
Windbox and discharge	lb/T (kg/MT) finished sinter			
Controlled by baghouse		0.3	(0.15)	A

Table 7.5-4 (cont.). PARTICULATE EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]

Source	Units	Emission Factors		Emission Factor Rating
Basic Oxygen Furnaces				
Top blown furnace melting and refining	lb/T (kg/MT) steel			
Uncontrolled		28.5	(14.25)	B
Controlled by open hood vented to:				
ESP		0.13	(0.065)	A
Scrubber		0.09	(0.045)	B
Controlled by closed hood vented to:				
Scrubber		0.0068	(0.0034)	A
Q-BOP melting and refining	lb/T (kg/MT) steel			
Controlled by scrubber		0.056	(0.028)	A
Charging	lb/T (kg/MT) hot metal			
At source		0.6	(0.3)	A
At building monitor		0.142	(0.071)	B
Tapping	lb/T (kg/MT) steel			
At source		0.92	(0.46)	A
At building monitor		0.29	(0.145)	B
Hot metal transfer	lb/T (kg/MT) hot metal			
At source		0.19	(0.095)	A
At building monitor		0.056	(0.028)	B
BOF monitor (all sources)	lb/T (kg/MT) steel	0.5	(0.25)	B
Electric Arc Furnaces				
Melting and refining	lb/T (kg/MT) steel			
Uncontrolled				
Carbon steel		38.0	(19.0)	C

Table 7.5-4 (cont.). PARTICULATE EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]

Source	Units	Emission Factors		Emission Factor Rating
Charging, tapping and slagging	lb/T (kg/MT) steel			
Uncontrolled emissions escaping monitor		1.4	(0.7)	C
Melting, refining, charging, tapping and slagging	lb/T (kg/MT) steel			
Uncontrolled				
Alloy steel		11.3	(5.65)	A
Carbon steel		50.0	(25.0)	C
Controlled by:				
Configuration 1 (building evacuation to baghouse for alloy steel)		0.3	(0.15)	A
Configuration 2 (DSE plus charging hood vented to common baghouse for carbon steel)		0.043	(0.0215)	C
Open Hearth Furnaces				
Melting and refining	lb/T (kg/MT) steel			
Uncontrolled		21.1	(10.55)	A
Controlled by ESP		0.28	(0.14)	A
Roof monitor emissions		0.168	(0.084)	C
Teeming				
Leaded steel	lb/T (kg/MT) steel			
Uncontrolled (as measured at the source)		0.81	(0.405)	A
Controlled by side-draft hood vented to baghouse		0.0038	(0.0019)	A

Table 7.5-4 (cont.). PARTICULATE EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]

Source	Units	Emission Factors		Emission Factor Rating
Unleaded steel				
Uncontrolled (as measured at the source)		0.07	(0.035)	A
Controlled by side-draft hood vented to baghouse		0.0016	(0.0008)	A
Machine Scarfing				
Uncontrolled	lb/T (kg/MT) metal through scarfer	0.1	(0.05)	B
Controlled by ESP		0.023	(0.0115)	A
Miscellaneous Combustion Sources[b]				
Boilers, soaking pits and slab reheat furnaces	lb/10^6 Btu (kg/10^9J)			
Blast furnace gas		0.035	(0.015)	D
Coke oven gas		0.012	(0.0052)	D

[a] Reference 2. ESP: Electrostatic precipitator. DSE: Direct shell evacuation.
[b] For fuels such as coal, fuel oil and natural gas, use the emission factors presented in Chapter 1 of this document. The rating for these fuels in boilers is A, and in soaking pits and slab reheat furnaces is D.

bypass this entire process and go through a continuous casting operation. The product next goes through a process of surface preparation of semi-finished steel (scarfing). A scarfing machine removes surface defects from the steel billets, blooms and slabs before shaping or rolling by applying jets of oxygen to the surface of the steel, which is at orange heat, thus removing a thin upper layer of the metal by rapid oxidation. Scarfing can normally be performed by machine on hot semifinished steel or by hand on cold or slightly preheated semifinished steel. Emissions occur during teeming as the molten metal is poured. Emissions also occur when the semifinished steel products are manually or machine scarfed to remove surface defects.

Miscellaneous Combustion Sources - Iron and steel plants require energy in the form of heat or electricity for every plant operation. Some energy intensive operations that produce emissions on plant property are boilers, soaking pits and slab furnaces, burning such fuels as coal, No. 2 fuel oil, natural gas, coke oven gas or blast furnace gas. In soaking pits, ingots are heated such that the temperature distribution over the cross section of the ingots is acceptable and the surface temperature is uniform for further rolling into semifinished products (blooms, billets and slabs). In slab furnaces, a slab is heated before being rolled into finished products (plates, sheets or strips). The emissions from the combustion of natural gas, fuel oil or coal for boilers can be found in Chapter 1 of this document. Emissions from these same fuels used in soaking pits or slab furnaces can be estimated to be the same as those for boilers, but since this is an estimate, the factor rating drops to D.

Emission factor data for blast furnace gas and coke oven gas are not available and therefore must be estimated. There are three facts available for making the estimation. First, the gas exiting the blast furnace passes through primary and secondary cleaners and can be cleaned to less than 0.02 gr/ft^3 (0.05 g/m^3). Second, nearly one third of the coke oven gas is methane. Lastly, there are no blast furnace gas constituents that generate particulate when burned. The combustible constituent of blast furnace gas is CO, which burns clean. Based on facts one and three, the emission factor for the combustion of blast furnace gas is equal to the particulate loading of that fuel, 2.9 pounds per million cubic feet (0.05 g/m^3).

Emissions for combustion of coke oven gas can be estimated in the same fashion. Assume that cleaned coke oven gas has as much particulate as cleaned blast furnace gas. Since one third of the coke oven gas is methane, the main component of natural gas, it is assumed that the combustion of this methane in coke oven gas generates 3.3 $lb/10^6$ ft^3 (0.06 g/m^3) of particulate. Thus, the emission factor for the combustion of coke oven gas is the sum of the particulate loading and that generated by the methane combustion, or 6.2 pounds per million cubic feet (0.1 g/m^3).

Open Dust Sources - In addition to process emission sources, open dust sources contribute to the atmospheric particulate burden. Open dust sources include (1) vehicular traffic on paved and unpaved roads, (2) raw material handling outside of buildings and (3) wind erosion from storage piles and exposed terrain. Vehicular traffic consists of plant personnel and visitor vehicles, plant service vehicles, and trucks handling raw materials, plant deliverables, steel products and waste materials. Raw material is handled by clamshell buckets, bucket/ladder conveyors, rotary railroad dumps, bottom railroad dumps, front end loaders, truck dumps, and conveyor transfer stations, all of which disturb the raw material and expose fines to the wind. Even fine material resting on flat areas or in storage piles is exposed and is subject to wind erosion. It is not unusual to have several million tons of raw materials stored at a plant and to have in the range of 10 to 100 acres of flat exposed area there.

Table 7.5-5. UNCONTROLLED CARBON MONOXIDE EMISSION FACTORS FOR IRON AND STEEL MILLS[a]

EMISSION FACTOR RATING: C

Source	lb/ton	kg/MT
Sintering[b] windbox	44	22
Basic oxygen furnace	138	69
Electric arc furnace	18	9

[a]Reference 5.
[b]Pounds/kilograms per ton/metric ton of finished sinter.

Empirically derived predictive emission factor equations for open dust sources have been developed and are presented in Chapter 11 of this document. The predictive emission factor equations in Chapter 11 can be used for all facilities having open dust sources, not just for iron and steel plants. However, there are several independent parameters in these equations for which data have been obtained from iron and steel plants.[2] These parameters are raw material silt and moisture content, paved and unpaved road material silt content, and total surface dust loading on paved roads. Tables 7.5-1 through 7.5-3 show the results of silt, moisture and loading analysis of collected field samples. The number of samples obtained, the range of values measured and the mean values of the parameters are given for each type of material. Samples listed in Tables 7.5-1 through 7.5-3 were collected at as many as twelve different iron and steel plants, in a wide range of geographic locations.

NOTICE: The above mention of equations in Chapter 11 refers to equations in revisions still impending when this printing went to press. In the interim, please see Reference 2 for the correct equations.

Particulate emission factors for iron and steel plant processes are found in Table 7.5-4. These emission factors are a result of an extensive investigation by EPA and the American Iron and Steel Institute.[2] Emission factors for carbon monoxide are found in Table 7.5-5.[5]

References for Section 7.5

1. H. E. McGannon, ed., The Making, Shaping and Treating of Steel, U. S. Steel Corporation, Pittsburgh, PA, 1971.

2. T. A. Cuscino, Jr., Particulate Emission Factors Applicable to the Iron and Steel Industry, EPA-450/4-79-029, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1979.

3. R. Bohn, et al., Fugitive Emissions from Integrated Iron and Steel Plants, EPA-600/2-78-050, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1978.

4. C. Cowherd, Jr., et al., Iron and Steel Plant Open Source Fugitive Emission Evaluation, EPA-600/2-79-103, U. S. Environmental Protection Agency, Research Triangle Park, NC, May 1979.

5. Control Techniques for Carbon Monoxide Emissions from Stationary Sources, AP-65, U. S. Department of Health, Education and Welfare, Washington, DC, March 1970.

Emissions from open hearths consist of particulates and small amounts of fluorides when fluoride-bearing ore, fluorspar, is used in the charge. The particulates are composed primarily of iron oxides, with a large portion (45 to 50 percent) in the 0 to 5 micrometer size range. The quantity of dust in the off-gas increases considerably when oxygen lancing is used (see Table 7.5-1).

The devices most commonly used to control the iron oxide and fluoride particulates are electrostatic precipitators and high-energy venturi scrubbers, both of which effectively remove about 98 percent of the particulates. The scrubbers also remove nearly 99 percent of the gaseous fluorides and 95 percent of the particulate fluorides.

7.5.1.2.2 Basic Oxygen Furnaces[2,3]–The basic oxygen process, also called the Linz-Donawitz (LD) process, is employed to produce steel from a furnace charge composed of approximately 70 percent molten blast-furnace metal and 30 percent scrap metal by use of a stream of commercially pure oxygen to oxidize the impurities, principally carbon and silicon.

The reaction that converts the molten iron into steel generates a considerable amount of particulate matter, largely in the form of iron oxide, although small amounts of fluorides may be present. Probably as the result of the tremendous agitation of the molten bath by the oxygen lancing, the dust loadings vary from 5 to 8 grains per standard cubic foot (11 to 18 grams/standard cubic meter) and high percentages of the particles are in the 0 to 5 micrometer size range.

In addition, tremendous amounts of carbon monoxide (140 lb/ton of steel and more) are generated by the reaction. Combustion in the hood, direct flaring, or some other means of ignition is used in the stack to reduce the actual carbon monoxide emissions to less than 3 lb/ton (1.5 kg/MT).

The particulate control devices used are venturi scrubbers and electrostatic precipitators, both of which have overall efficiencies of 99 percent. Furthermore, the scrubbers are 99 percent efficient in removing gaseous fluorides (see Table 7.5-1).

7.5.1.2.3 Electric Arc Furnaces[2,3]–Electric furnaces are used primarily to produce special alloy steels or to melt large amounts of scrap for reuse. Heat is furnished by direct-arc electrodes extending through the roof of the furnace. In recent years, oxygen has been used to increase the rate of uniformity of scrap-melt-down and to decrease power consumption.

The particulates, primarily oxides of iron, manganese, aluminum, and silicon, that evolve when steel is being processed in an electric furnace result from the exposure of molten steel to extremely high temperatures. The quantity of these emissions is a function of the cleanliness and composition of the scrap metal charge, the refining procedure used (with or without oxygen lancing), and the refining time. As with open hearths, many of the particulates (40 to 75 percent) are in the 0 to 5 micrometer range. Additionally, moderate amounts of carbon monoxide (15 to 20 lb/ton) are emitted.

Particulate control devices most widely used with electric furnaces are venturi scrubbers, which have a collection efficiency of approximately 98 percent, and bag filters, which have collection efficiencies of 99 percent or higher.

7.5.1.3 Scarfing[3]–Scarfing is a method of surface preparation of semi-finished steel. A scarfing machine removes surface defects from the steel billets and slabs, before they are shaped or rolled, by applying jets of oxygen to the surface of the steel, which is at orange heat, thus removing a thin upper layer of the metal by rapid oxidation.

Emissions from scarfing operations consist of iron oxide fumes. The rate at which particulates are emitted is dependent on the condition of the billets or slabs and the amount of metal removal required (Table 7.5-1). Emission control techniques for the removal of fine particles vary among steel producers, but one of the most commonly used devices is the electrostatic precipitator, which is approximately 94 percent efficient.

Table 7.5-1. EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]
EMISSION FACTOR RATINGS: A (PARTICULATES AND CARBON MONOXIDE)
C (FLUORIDES)

Type of operation	Total particulates		Carbon monoxide		Fluorides[c,d]			
					Gaseous (HF)		Particulates (CaF_2)	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Pig iron production								
Blast furnaces[e]								
Ore charge, uncontrolled	110	55	1750 (1400 to 2100)	875 (700 to 1050)	–	–	–	–
Agglomerates charge, uncontrolled	40	20	–	–	–	–	–	–
Total, uncontrolled	150 (130 to 200)	75 (65 to 100)	1750 (1400 to 2100)	875 (700 to 1050)	–	–	–	–
Settling chamber or dry cyclone	60	30	–	–	–	–	–	–
Plus wet scrubber	15	7.5	–	–	–	–	–	–
Plus venturi or electrostatic precipitator	1.5	0.75	–	–	–	–	–	–
Sintering[f]								
Windbox, uncontrolled[g]	20	10	–	–	–	–	–	–
Dry cyclone	2.0	1.0	–	–	–	–	–	–
Dry cyclone plus electrostatic precipitator	1.0	0.5	–	–	–	–	–	–
Dry cyclone plus wet scrubber	0.04	0.02	–	–	–	–	–	–
Discharge, uncontrolled	22	11	44	22	–	–	–	–
Dry cyclone	2.2	1.1	44	22	–	–	–	–
Dry cyclone plus electrostatic precipitator	0.11	0.055	44	22	–	–	–	–
Steel production								
Open hearth[h]								
No oxygen lance, uncontrolled	8.3 (5.8 to 12.0)	4.15 (2.9 to 6.0)	–	–	0.100	0.05	0.030	0.015
Venturi scrubber	0.17	0.085	–	–	0.011	0.0055	0.0015	0.0008
Electrostatic precipitator	0.17	0.085	–	–	0.100	0.050	0.0006	0.0003
Oxygen lance, uncontrolled	17.4 (9.3 to 22.0)	8.7 (4.65 to 11.0)	–	–	0.100	0.050	0.030	0.015

Table 7.5-1 (continued). EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]
EMISSION FACTOR RATINGS: A (PARTICULATES AND CARBON MONOXIDE)
C (FLUORIDES)

Type of operation	Total particulates		Carbon monoxide		Fluorides[c,d]			
					Gaseous (HF)		Particulates (CaF_2)	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Venturi scrubber	0.17	0.085	–	–	0.011	0.0055	0.0015	0.0008
Electrostatic precipitator	0.35	0.175	–	–	0.100	0.050	0.0006	0.0003
Basic oxygen, uncontrolled[j]	51 (32 to 86)	25.5 (16 to 43)	139 (104 to 237)	69.5 (52.0 to 118.5)	Neg	Neg	0.200	0.100
Venturi scrubber	0.51	0.255	–	–	–	–	0.002	0.001
Electrostatic precipitator	0.51	0.255	–	–	–	–	0.002	0.001
Spray chamber	15.3	7.65	–	–	–	–	0.060	0.030
Electric arc[k]								
No oxygen lance[l], uncontrolled	9.2 (7.0 to 10.6)	4.6 (3.5 to 5.3)	18	9	0.012	0.006	0.238	0.119
Venturi scrubber	0.18	0.09	18	9	0.0018	0.0009	0.011	0.0055
Electrostatic precipitator	0.28 to 0.74	0.14 to 0.37	18	9	0.012	0.006	0.011	0.0055
Baghouse	0.09	0.045	18	9	0.012	0.006	0.0024	0.0012
Oxygen lance[m], uncontrolled	11	5.5	18	9	0.012	0.006	0.238	0.119
Venturi scrubber	0.22	0.11	18	9	0.0018	0.0009	0.011	0.0055
Electrostatic precipitator	0.33 to 0.88	0.165 to 0.44	18	9	0.012	0.006	0.011	0.0055
Baghouse	0.11	0.055	18	9	0.012	0.006	0.0024	0.0012
Scarfing[n], uncontrolled	≤ 1	≤ 0.5	–	–	–	–	–	–
Electrostatic precipitator	≤ 0.06	≤ 0.03	–	–	–	–	–	–
Venturi scrubber	≤ 0.02	≤ 0.01	–	–	–	–	–	–

[a] Emission factors expressed as units per unit weight of metal produced.
[b] Numbers in parentheses after uncontrolled values are ranges. Controlled factors are calculated using average uncontrolled factors and observed equipment efficiencies.
[c] Reference 4.
[d] Value included in "Total Particulates" figure.
[e] References 2, 3, and 5.
[f] These factors should be used to estimate particulate and carbon monoxide emissions from the entire blast furnace operation. The total particulate factors for ore charging and agglomerates charging apply only to those operations.
[g] Reference 3.
[h] Approximately 0.3 pounds of sulfur dioxide per ton (0.15 kg/MT) of sinter is produced at windbox.
[i] References, 2, 3, 5, and 6.
[j] References 2 through 10.
[k] Values are for carbon type electric arc furnaces. For alloy type furnaces, multiply given values by 2.80.
[l] References 2 through 5.
[m] References 3 and 4.
[n] Factors are based on operating experience and engineering judgment.

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7.6 PRIMARY LEAD SMELTING

7.6.1 Process Description [1-3]

Lead is usually found naturally as a sulfide ore containing small amounts of copper, iron, zinc and other trace elements. It is normally concentrated at the mine from an ore of 3 to 8 percent lead to an ore concentrate of 55 to 70 percent lead, containing from 13 to 19 percent, by weight, free and uncombined sulfur. A typical flow sheet for the production of lead metal from ore concentrate is shown in Figure 7.6-1.

Processing involves three major steps:

- Sintering, in which the concentrated lead and sulfur are oxidized to produce lead oxide and sulfur dioxide. (Simultaneously, the charge concentrates, recycled sinter, sand and other inert materials are agglomerated to form a dense, permeable substance called sinter.)

- Reducing the lead oxide contained in the sinter to produce molten lead bullion.

- Refining the lead bullion to eliminate any impurities.

7.6.1.1 Sintering - Sinter is produced by a sinter machine, a continuous steel pallet conveyor belt moved by gears and sprockets. Each pallet consists of perforated or slotted grates, beneath which are windboxes connected to fans that provide a draft through the moving sinter charge. Depending on the direction of this draft, the sinter machine is either of the updraft or downdraft type. Except for the draft direction, however, all machines are similar in design, construction and operation.

The sintering reaction is autogenous, occuring at a temperature of approximately 1800°F (1000°C):

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \qquad (1)$$

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

Of the two kinds of sintering machines used, the updraft design is superior for many reasons. First, the sinter bed thickness is more permeable (and hence can be larger), thereby permitting a higher production rate than that of a downdraft machine of similar dimensions. Secondly, the small amounts of elemental lead that form during sintering will solidify at their point of formation in updraft machines, whereas, in downdraft operation, the metal tends to flow downward and collect on the grates or at the bottom of the sinter charge, thus causing increased pressure drop and attendant reduced blower capacity. In addition, the updraft system exhibits the capability of producing sinter of higher lead content and requires less maintenance than the downdraft machine. Finally, and most important from an air pollution control standpoint, updraft sintering can produce a single strong SO_2 effluent stream from the operation, by use of weak gas recirculation. This, in turn, permits more efficient and economical use of control methods such as sulfuric acid recovery devices.

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

The furnace is charged with a mixture of sinter (80 - 90 percent of charge), metallurgical coke (8 - 14 percent of charge), and other materials, such as limestone, silica, litharge, slag-forming constituents, and various recycled and cleanup materials. In the furnace, the sinter is reduced to lead bullion by reactions (2) through (6).

$$PbO + CO \rightarrow Pb + CO_2 \quad (2)$$

$$C + O_2 \rightarrow CO_2 \quad (3)$$

$$C + CO_2 \rightarrow 2CO \quad (4)$$

$$2PbO + PbS \rightarrow 3Pb + SO_2 \quad (5)$$

$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2 \quad (6)$$

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

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

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

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

- Removal of antimony, tin and arsenic.

- Removal of precious metals by Parke's Process, in which zinc combines with gold and silver to form an insoluble intermetallic at operating temperatures.

- Vacuum removal of zinc.

- Removal of bismuth using the Betterson Process, which is the addition of calcium and magnesium to form an insoluble compound with the bismuth that is skimmed from the kettle.

- Removal of remaining traces of metal impurities by addition of NaOH and $NaNO_3$.

The final refined lead, commonly of 99.990 to 99.999 percent purity, is then cast into 100 pound pigs for shipment.

7.6.2 Emissions and Controls[1,2]

Each of the three major lead smelting process steps generates substantial quantities of particulates and/or sulfur dioxide.

Nearly 85 percent of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. In handling process offgases, either a single weak stream is taken from the machine hood at less than 2 percent SO_2, or two streams are taken, one strong stream (5 - 7 percent SO_2) from the feed end of the machine and one weak stream (<0.5 percent SO_2) from the discharge end. Single stream operation has been

used when there is little or no market for recovered sulfur, so that the uncontrolled weak SO_2 stream is emitted to the atmosphere. When sulfur removal is required, however, dual stream operation is preferred. The strong stream is sent to a sulfuric acid plant, and the weak stream is vented to the atmosphere after removal of particulates.

Table 7.6-1. EMISSION FACTORS FOR PRIMARY LEAD SMELTING PROCESSES WITHOUT CONTROLS[a]

EMISSION FACTOR RATING: B

Process	Particulates		Sulfur dioxide	
	lb/ton	kg/MT	lb/ton	kg/MT
Ore crushing[b]	2.0	1.0	-	-
Sintering (updraft)[c]	213.0	106.5	550.0	275.0
Blast furnace[d]	361.0	180.5	45.0	22.5
Dross reverberatory furnace[b]	20.0	10.0	Neg	Neg
Materials handling[b]	5.0	2.5	-	-

[a] Ore crushing emission factors expressed as lb/ton (kg/MT) of crushed ore. All other emission factors expressed as lb/ton (kg/MT) of lead product.
[b] Reference 2.
[c] References 1, 4, 5 and 6.
[d] References 1, 2 and 7.

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

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

The particulate emissions from sinter machines range from 5 to 20 percent of the concentrated ore feed. When expressed in terms of product weight, a typical emission is estimated to be 213 lb/ton (106.5 kg/MT) of lead produced. This value, along with other particulate and SO_2 factors, appears in Table 7.6-1.

Table 7.6-2. PARTICLE SIZE DISTRIBUTION OF FLUE DUST FROM UPDRAFT SINTERING MACHINES

Size (μm)	Percent by weight
20 - 40	15 - 45
10 - 20	9 - 30
5 - 10	4 - 19
<5	1 - 10

Typical material balances from domestic lead smelters indicate that about 15 percent of the sulfur in the ore concentrate fed to the sinter machine is eliminated in the blast furnace. However, only half of this amount (about 7 percent of the total sulfur in the ore) is emitted as SO_2. The remainder is captured by the slag. The concentration of this SO_2 stream can vary from 500 to 2500 ppm, by volume (1.4 - 7.2 g/m^3), depending on the amount of dilution air injected to oxidize the carbon monoxide and to cool the stream before baghouse particulate removal.

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

Virtually no sulfur dioxide emissions are associated with the various refining operations. However, a small amount of particulate is generated by the dross reverberatory furnace, about 20 lb/ton (10 kg/MT) of lead.

Finally, minor quantities of particulates are generated by ore crushing and materials handling operations. These emission factors are also presented in Table 7.6-1.

Table 7.6-2 is a listing of size distributions of flue dust from updraft sintering machine effluent. Though these are not fugitive emissions, the size distributions may closely resemble those of the fugitive emissions. Particulate fugitive emissions from the blast furnace consist basically of lead oxides, 92 percent of which are less than 4 μm in size. Uncontrolled emissions from a lead dross reverberatory furnace are mostly less than 1 μm, and this may also be the case with the fugitive emissions.

Table 7.6-3. EFFICIENCIES OF REPRESENTATIVE CONTROL DEVICES USED WITH PRIMARY LEAD SMELTING OPERATIONS

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

[a] Reference 2.
[b] Reference 1.
[c] High particulate control efficiency due to action of acid plant gas cleaning system. Based on SO_2 inlet concentrations of 5-7%, typical outlet emission levels are 2000 ppm (5.7 g/m^3) for single contact and 500 ppm (1.4 g/m^3) for dual contact.
[d] Collection efficiency for a two stage uncontrolled Claus type plant. Refer to Section 5.18 for more information.
[e] Based on SO_2 inlet concentrations of 4-6%, typical outlet emission levels range from 500-3000 ppm (1.4-8.6 g/m^3).
[f] Based on SO_2 inlet concentrations of 1.5-2.5%, typical outlet emission level is 1200 ppm (3.4 g/m^3).

Table 7.6-4. POTENTIAL FUGITIVE EMISSION FACTORS FOR PRIMARY LEAD SMELTING PROCESSES WITHOUT CONTROLS[a,b]

EMISSION FACTOR RATING: E

Process	Particulates	
	lb/ton	kg/MT
Ore mixing and pelletizing (crushing)	2.26	1.13
Car charging (conveyor loading and transfer) of sinter	0.50	0.25
Sinter machine leakage[c]	0.68	0.34
Sinter return handling	9.00	4.50
Sinter machine discharge, sinter crushing and screening[c]	1.50	0.75
Sinter transfer to dump area	0.20	0.10
Sinter product dump area	0.01	0.005
Blast furnace (charging, blow condition, tapping)	0.16	0.08
Lead pouring to ladle, transferring, and slag pouring[d]	0.93	0.47
Slag cooling[e]	0.47	0.24
Zinc fuming furnace vents	4.60	2.30
Dross kettle	0.48	0.24
Reverberatory furnace leakage	3.00	1.50
Silver retort building	1.80	0.90
Lead casting	0.87	0.44

[a] All factors are expressed in units per end product lead produced, except sinter operations, which are expressed in units per sinter or sinter handled/transferred/charged.

[b] Reference 8, except where noted.

[c] References 9 and 10. Engineering judgement using steel sinter machine leakage emission factor.

[d] Reference 2.

[e] Reference 2. Engineering judgement, estimated to be half the magnitude of lead pouring and ladling operations.

Emission controls on lead smelter operations are for particulates and sulfur dioxide. The most commonly employed high efficiency particulate control devices are fabric filters and electrostatic precipitators, which often follow centrifugal collectors and tubular coolers (pseudogravity collectors). Three of the 6 lead smelters presently operating in the United States use single absorption sulfuric acid plants for control of sulfur dioxide emissions from sinter machines and, occasionally, from blast furnaces. Single stage plants can attain SO_x levels of 2000 ppm (5.7 g/m^3), and dual stage plants can attain levels of 550 ppm (1.6 g/m^3). Typical efficiencies of dual stage sulfuric acid plants in removing sulfur oxides can exceed 99 percent. Other technically feasible SO_2 control methods are elemental sulfur recovery plants and dimethylaniline (DMA) and ammonia absorption processes. These methods and their representative control efficiencies are listed in Table 7.6-3.

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7.7 ZINC SMELTING

7.7.1 Process Description[1,2]

As stated previously, most domestic zinc comes from zinc and lead ores. Another important source of raw material for zinc metal has been zinc oxide from fuming furnaces. For efficient recovery of zinc, sulfur must be removed from concentrates to a level of less than 2 percent. This is done by fluidized beds or multiple-hearth roasting occasionally followed by sintering. Metallic zinc can be produced from the roasted ore by the horizontal or vertical retort process or by the electrolytic process if a high-purity zinc is needed.

7.7.2 Emissions and Controls[1,2]

Dust, fumes, and sulfur dioxide are emitted from zinc concentrate roasting or sintering operations. Particulates may be removed by electrostatic precipitators or baghouses. Sulfur dioxide may be converted directly into sulfuric acid or vented. Emission factors for zinc smelting are presented in Table 7.7-1.

Table 7.7-1. EMISSION FACTORS FOR PRIMARY ZINC SMELTING WITHOUT CONTROLS[a]
EMISSION FACTOR RATING: B

Type of operation	Particulates		Sulfur oxides	
	lb/ton	kg/MT	lb/ton	kg/MT
Roasting (multiple-hearth)[b]	120	60	1100	550
Sintering[c]	90	45	d	d
Horizontal retorts[e]	8	4	–	–
Vertical retorts[e]	100	50	–	–
Electrolytic process	3	1.5	–	–

[a]Approximately 2 unit weights of concentrated ore are required to produce 1 unit weight of zinc metal. Emission factors expressed as units per unit weight of concentrated ore produced.
[b]References 3 and 4.
[c]References 2 and 3.
[d]Included in SO_2 losses from roasting.
[e]Reference 3.

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7.8 SECONDARY ALUMINUM OPERATIONS

7.8.1 General

Secondary aluminum operations involve the cleaning, melting, refining and pouring of aluminum recovered from scrap. The processes used to convert scrap aluminum to secondary aluminum products such as lightweight metal alloys for industrial castings and ingots are presented in Figure 7.8-1. Production involves two general classes of operation, scrap treatment and smelting/refining.

Scrap treatment involves receiving, sorting and processing scrap to remove contaminants and to prepare the material for smelting. Processes based on mechanical, pyrometallurgical and hydrometallurgical techniques are used, and those employed are selected to suit the type of scrap processed.

The smelting/refining operation generally involves the following steps:

- charging
- melting
- fluxing
- alloying
- mixing
- demagging
- degassing
- skimming
- pouring

All of these steps may be involved in each operation, with process distinctions being in the furnace type used and in emission characteristics. However, as with scrap treatment, not all of these steps are necessarily incorporated into the operations at a particular plant. Some steps may be combined or reordered, depending on furnace design, scrap quality, process inputs and product specifications.

Scrap treatment - Purchased aluminum scrap undergoes inspection upon delivery. Clean scrap requiring no treatment is transported to storage or is charged directly into the smelting furnace. The bulk of the scrap, however, must be manually sorted as it passes along a steel belt conveyor. Free iron, stainless steel, zinc, brass and oversized materials are removed. The sorted scrap then goes to appropriate scrap treating processes or is charged directly to the smelting furnace.

Sorted scrap is conveyed to a ring crusher or hammer mill, where the material is shredded and crushed, with the iron torn away from the aluminum. The crushed material is passed over vibrating screens to remove dirt and fines, and tramp iron is removed by magnetic drums and/or belt separators. Baling equipment compacts bulky aluminum scrap into 1 x 2 meter (3 x 6 foot) bales.

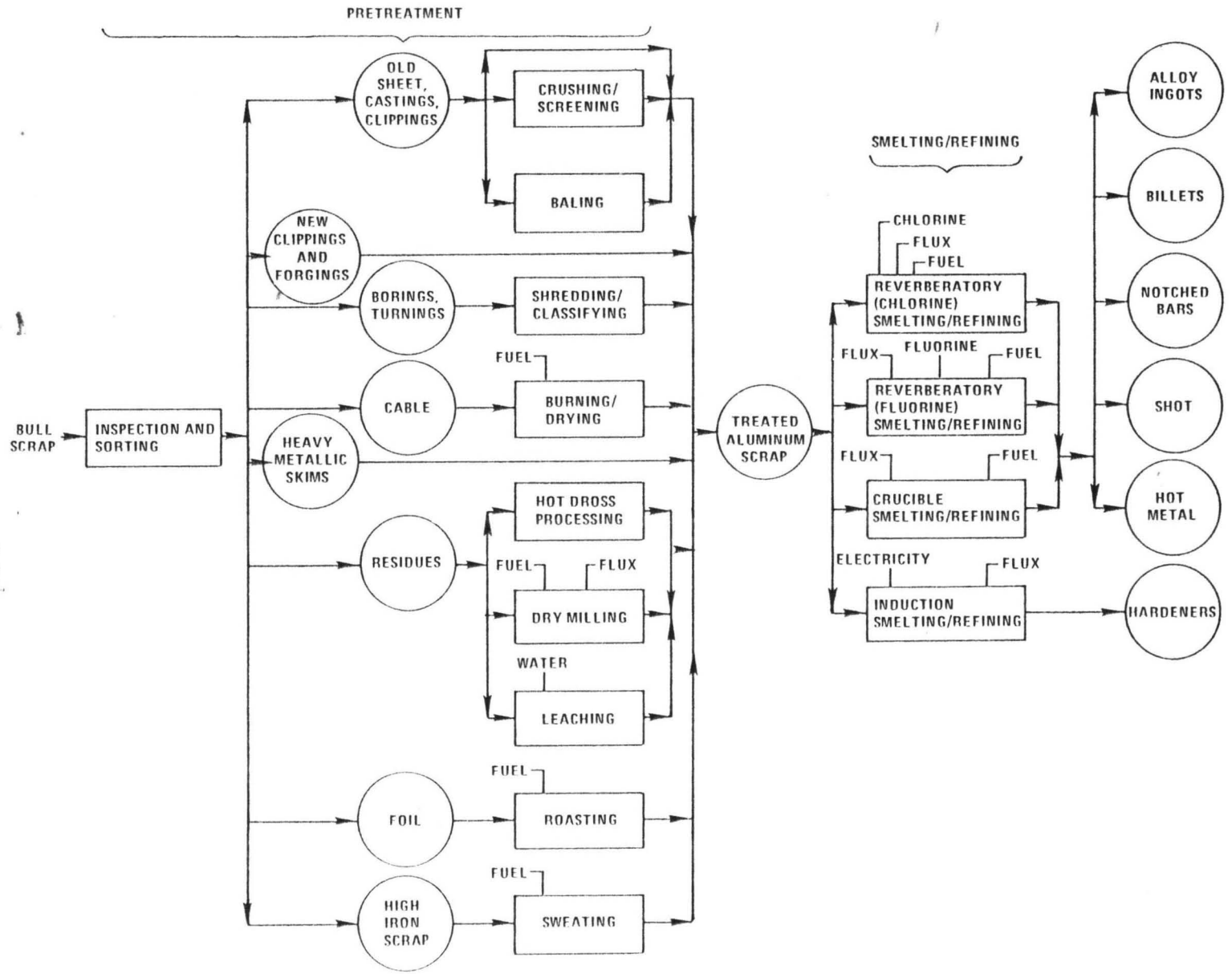


Figure 7.8-1. Process flow diagram for the secondary aluminum processing industry.

Pure aluminum cable with steel reinforcement or insulation is cut by alligator type shears and granulated or further reduced in hammer mills, to separate the iron core and the plastic coating from the aluminum. Magnetic processing accomplishes iron removal, and air classification separates the insulation.

Borings and turnings, in most cases, are treated to remove cutting oils, greases, moisture and free iron. The processing steps involved are (a) crushing in hammer mills or ring crushers, (b) volatilizing the moisture and organics in a gas or oil fired rotary dryer, (c) screening the dried chips to remove aluminum fines, (d) removing iron magnetically and (e) storing the clean dried borings in tote boxes.

Aluminum can be recovered from the hot dross discharged from a refining furnace by batch fluxing with a salt/cryolite mixture in a mechanically rotated, refractory lined barrel furnace. The metal is tapped periodically through a hole in its base. Secondary aluminum recovery from cold dross and other residues from primary aluminum plants is carried out by means of this batch fluxing in a rotary furnace. In the dry milling process, cold aluminum laden dross and other residues are processed by milling, screening and concentrating to obtain a product containing at least 60-70 percent aluminum. Ball, rod or hammer mills can be used to reduce oxides and nonmetallics to fine powders. Separation of dirt and other unrecoverables from the metal is achieved by screening, air classification and/or magnetic separation.

Leaching involves (a) wet milling, (b) screening, (c) drying and (d) magnetic separation to remove fluxing salts and other non-recoverables from drosses, skimmings and slags. First, the raw material is fed into a long rotating drum or an attrition or ball mill where soluble contaminants are leached. The washed material is then screened to remove fines and dissolved salts and is dried and passed through a magnetic separator to remove ferrous materials. The nonmagnetics then are stored or charged directly to the smelting furnace.

In the roasting process, carbonaceous materials associated with aluminum foil are charred and then separated from the metal product.

Sweating is a pyrometallurgical process used to recover aluminum from high iron content scrap. Open flame reverberatory furnaces may be used. Separation is accomplished as aluminum and other low melting constituents melt and trickle down the hearth, through a grate and into air cooled molds or collecting pots. This product is termed "sweated pig". The higher melting materials, including iron, brass and oxidation products formed during the sweating process, are periodically removed from the furnace.

Smelting/refining - In reverberatory (chlorine) operations, reverberatory furnaces are commonly used to convert clean sorted scrap, sweated pigs or some untreated scrap to specification ingots, shot or hot metal. The scrap is first charged to the furnace by some mechanical means, often through charging wells designed to permit introduction of chips and light scrap below the surface of a previously melted charge ("heel"). Batch processing is generally practiced for alloy ingot production, and continuous feeding and pouring are generally used for products having less strict specifications.

Cover fluxes are used to prevent air contact with and consequent oxidation of the melt. Solvent fluxes react with nonmetallics such as burned coating residues and dirt to form insolubles which float to the surface as part of the slag.

Alloying agents are charged through the forewell in amounts determined by product specifications. Injection of nitrogen or other inert gases into the molten metal can be used to aid in raising dissolved gases (typically hydrogen) and intermixed solids to the surface.

Demagging reduces the magnesium content of the molten charge from approximately 0.3 to 0.5 percent (typical scrap value) to about 0.1 percent (typical product line alloy specification). When demagging with chlorine gas, chlorine is injected under pressure through carbon lances to react with magnesium and aluminum as it bubbles to the surface. Other chlorinating agents, or fluxes, are sometimes used, such as anhydrous aluminum chloride or chlorinated organics.

In the skimming step, contaminated semisolid fluxes (dross, slag or skimmings) are ladled from the surface of the melt and removed through the forewell. The melt is then cooled before pouring.

The reverberatory (fluorine) process is similar to the reverberatory (chlorine) smelting/refining process, except that aluminum fluoride (AlF_3) is employed in the demagging step instead of chlorine. The AlF_3 reacts with magnesium to produce molten metal aluminum and solid magnesium fluoride salt which floats to the surface of the molten aluminum and is skimmed off.

The crucible smelting/refining process is used to melt small batches of aluminum scrap, generally limited to 500 kg (1000 lb) or less. The metal treating process steps are essentially the same as those of reverberatory furnaces.

The induction smelting/refining process is designed to produce hardeners by blending pure aluminum and hardening agents in an electric induction furnace. The process steps include charging scrap to the furnace, melting, adding and blending the hardening agent, skimming, pouring and casting into notched bars.

7.8.2 Emissions and Controls[1]

Table 7.8-1 presents emission factors for the principal emission sources in secondary aluminum operations. Although each step in scrap treatment and smelting/refining is a potential source of emissions, emissions from most of the processing operations are either not characterized here or emit only small amounts of pollutants.

Crushing/screening produces small amounts of metallic and nonmetallic dust. Baling operations produce particulate emissions, primarily dirt and alumina dust resulting from aluminum oxidation. Shredding/classifying also emits small amounts of dust. Emissions from these processing steps are normally uncontrolled.

Burning/drying operations emit a wide range of pollutants. Afterburners are used generally to convert unburned hydrocarbons to CO_2 and H_2O. Other gases potentially present, depending on the composition of the organic contaminants, include chlorides, fluorides and sulfur oxides. Oxidized aluminum fines blown out of the dryer by the combustion gases comprise particulate emissions. Wet scrubbers are sometimes used in place of afterburners.

Mechanically generated dust from the rotating barrel dross furnace constitutes the main air emission of hot dross processing. Some fumes are produced from the fluxing reactions. Fugitive emissions are controlled by enclosing the barrel in a hood system and by ducting the stream to a baghouse. Furnace offgas emissions, mainly fluxing salt fume, are controlled by a venturi scrubber.

In dry milling, large amounts of dust are generated from the crushing, milling, screening, air classification and materials transfer steps. Leaching operations may produce particulate emissions during drying. Emissions from roasting are particulates from the charring of carbonaceous materials.

Emissions from sweating furnaces vary with the feed scrap composition. Smoke may result from incomplete combustion of organic contaminants (e.g., rubber, oil and grease, plastics, paint, cardboard, paper) which may be present. Fumes can result from oxidation of magnesium and zinc contaminants and from fluxes in recovered drosses and skims.

Atmospheric emissions from reverberatory (chlorine) smelting/refining represent a significant fraction of the total particulate and gaseous effluents generated in the secondary aluminum industry. Typical furnace effluent gases contain combustion products, chlorine, hydrogen chloride and metal chlorides of zinc, magnesium and aluminum, aluminum oxide and various metals and metal compounds, depending on the quality of scrap charged. Particulate emissions from one secondary aluminum smelter have a size distribution of $D_{50} = 0.4\mu$.[3]

TABLE 7.8-1. PARTICULATE EMISSION FACTORS FOR SECONDARY ALUMINUM OPERATIONS[a]

Operation	Uncontrolled		Baghouse		Electrostatic precipitator		Emission Factor Rating
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	
Sweating furnace[b]	7.25	14.5	1.65	3.3	-	-	C
Smelting							
Crucible furnace[b]	0.95	1.9	-	-	-	-	C
Reverberatory furnace[c]	2.15	4.3	0.65[e]	1.3[e]	0.65	1.3	B
Chlorination station[d]	500	1000	25	50	-	-	B

[a]Reference 2. Emission factors expressed as units per unit weight of metal processed. Factors apply only to Al metal recovery operations.
[b]Based on averages of two source tests.
[c]Based on averages of ten source tests. Standard deviation of uncontrolled emission factor is 17.5 kg/Mg (3.5 lb/ton), that of controlled factor is 0.15 kg/Mg (0.3 lb/ton).
[d]Expressed as kg/Mg (lb/ton) of chlorine used. Based on averages of ten source tests. Standard deviation of uncontrolled emission factor is 215 kg/Mg (430 lb/ton), of controlled factor, 18 kg/Mg (36 lb/ton).
[e]This factor may be lower if a coated baghouse is used.

Emissions from reverberatory (fluorine) smelting/refining are similar to those from reverberatory (chlorine) smelting/refining. The use of AlF_3 rather than chlorine in the demagging step reduces demagging emissions. Fluorides are emitted as gaseous fluorides (hydrogen fluoride, aluminum and magnesium fluoride vapors, and silicon tetrafluoride) or as dusts. Venturi scrubbers are usually used for fluoride emission control.

References for Section 7.8

1. W.M. Coltharp, et al., Multimedia Environmental Assessment of the Secondary Nonferrous Metal Industry, Draft Final Report, 2 vols., EPA Contract No. 68-02-1319, Radian Corporation, Austin, TX, June 1976.

2. W.F. Hammond and S.M. Weiss, Unpublished report on air contaminant emissions from metallurgical operations in Los Angeles County, Los Angeles County Air Pollution Control District, July 1964.

3. R.A. Baker, et al., Evaluation of a Coated Baghouse at a Secondary Aluminum Smelter, EPA Contract No. 68-02-1402, Environmental Science and Engineering, Inc., Gainesville, FL, October 1976.

4. Air Pollution Engineering Manual, 2d Edition, AP-40, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1973. Out of Print.

5. E.J. Petkus, "Precoated Baghouse Control for Secondary Aluminum Smelting", Presented at the 71st Annual Meeting of the Air Pollution Control Association, Houston, TX, June 1978.

7.9 SECONDARY COPPER SMELTING AND ALLOYING

7.9.1 Process Description[1,2]

The secondary copper industry processes scrap metals for the recovery of copper. Products include refined copper or copper alloys in forms such as ingots, wirebar, anodes, and shot. Copper alloys are combinations of copper with other materials, notably, tin, zinc, and lead. Also, for special applications, combinations include such metals as cobalt, manganese, iron, nickel, cadmium, and beryllium and nonmetals such as arsenic and silicon.

The principal processess involved in copper recovery are scrap metal pretreatment and smelting. Pretreatment includes cleaning and concentration to prepare the material for the smelting furnace. Smelting involves heating and treating the scrap to achieve separation and purification of specific metals.

The feed material used in the recovery process can be any metallic scrap containing a useful amount of copper, bronze (copper and tin), or brass (copper and zinc). Traditional forms are punchings, turnings and borings, defective or surplus goods, metallurgical residues such as slags, skimmings, and drosses, and obsolete, worn out, or damaged articles including automobile radiators, pipe, wire, bushings, and bearings.

The type and quality of the feed material determines the processes the smelter will use. Due to the large variety of possible feed materials available, the method of operation varies greatly between plants. Generally, a secondary copper facility deals with less pure raw materials and produces a more refined product, whereas brass and bronze alloy processors take cleaner scrap and do less purification and refining. Figure 7.9-1 is a flowsheet depicting the major processes that can be expected in a secondary copper smelting operation. A brass and bronze alloying operation is shown in Figure 7.9-2.

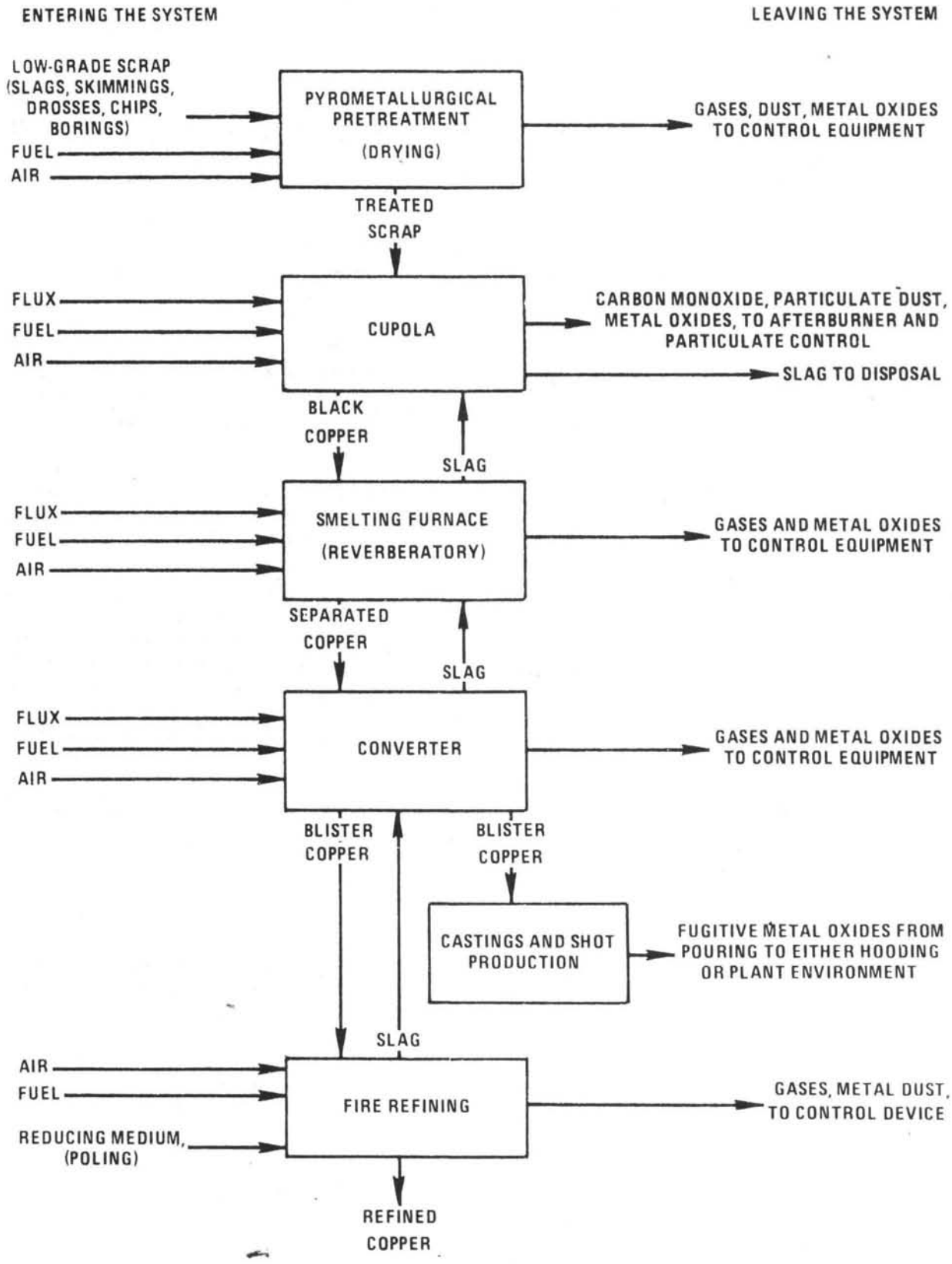
Pretreatment of the feed material can be accomplished using several different procedures, either separately or in combination. Feed scrap is concentrated by manual and mechanical methods such as sorting, stripping, shredding, and magnetic separation. Feed scrap is sometimes briquetted in a hydraulic press. Pyrometallurgical pretreatment may include sweating, burning of insulation (especially from wire scrap), and drying (burning off oil and volatiles) in rotary kilns. Hydrometallurgical methods include flotation and leaching, with chemical recovery.

In smelting, low-grade scrap is melted in a cupola furnace, producing "black copper" (70 to 80 percent Cu) and slag; these are often separated in a reverberatory furnace, from which the melt is transferred to a converter or electric furnace to produce "blister" copper, which is 90 to 99 percent Cu.

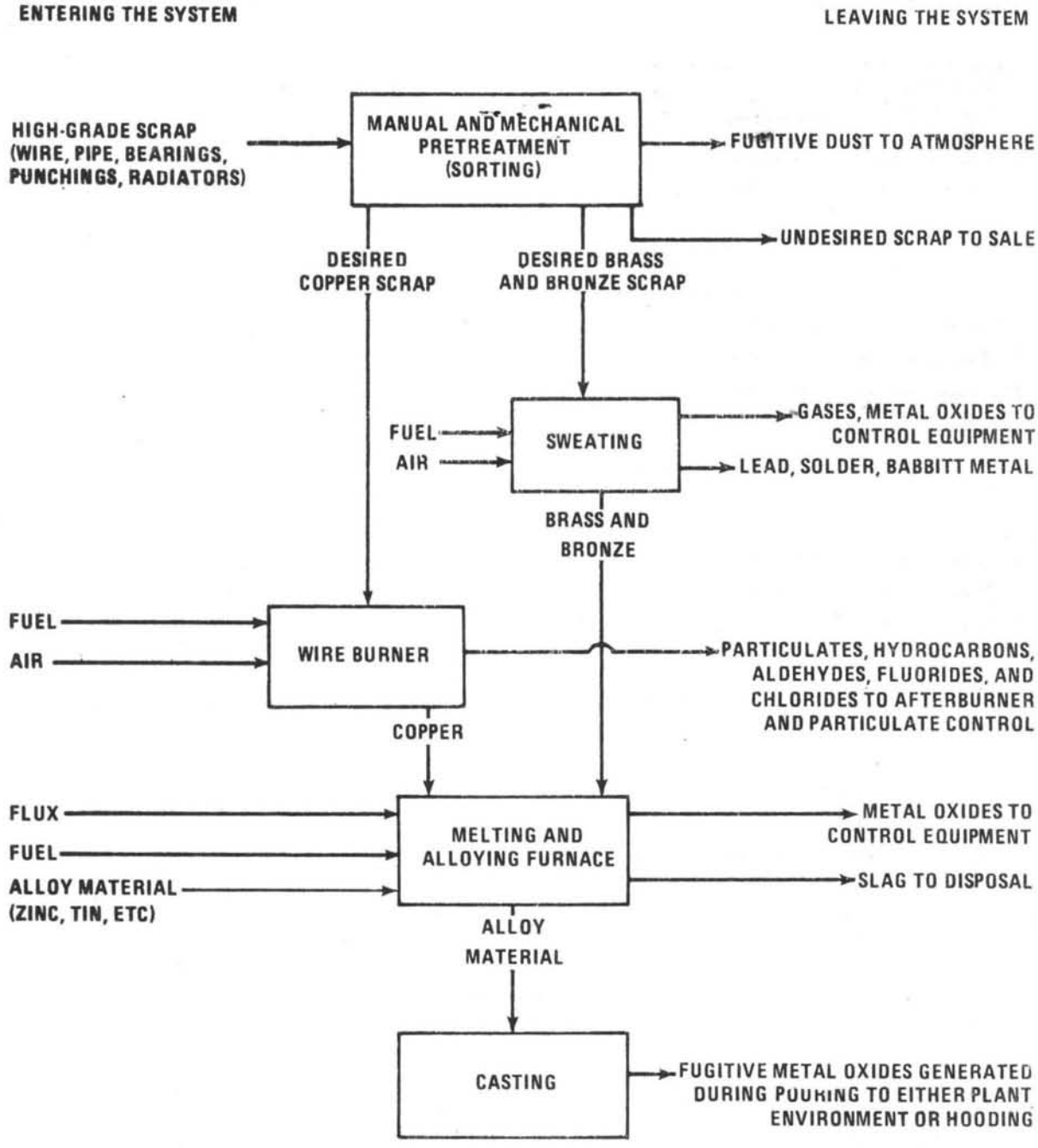
Blister copper may be poured to produce shot or castings, but is often further refined electrolytically or by fire refining. The fire-refining process is essentially the same as that described for the primary copper smelting industry (Section 7.3.1). The sequence of events in fire-refining is (1) charging, (2) melting in an oxidizing atmosphere, (3) skimming the slag, (4) blowing with air or oxygen, (5) adding fluxes, (6) "poling" or otherwise providing a reducing atmosphere, (7) reskimming, and (8) pouring.

To produce bronze or brass rather than copper, an alloying operation is required. Clean, selected bronze and brass scrap is charged to a melting furnace with alloys to bring the resulting mixture to the desired final composition. Fluxes are added to remove impurities and to protect the melt against oxidation by air. Air or oxygen may be blown through the melt to adjust the composition by oxidizing excess zinc.

With zinc-rich feed such as brass, the zinc oxide concentration in the exhaust gas is sometimes high enough to make recovery for its metal value desirable. This process is accomplished by vaporizing the zinc from the melt at high temperature and capturing the oxide downstream in a process baghouse.



7.9-1. Low-grade copper recovery.



7.9-2. High-grade brass and bronze alloying.

The final step is always casting of the suitably alloyed or refined metal into a desired form, i.e, shot, wirebar, anodes, cathodes, ingots, or other cast shapes. The metal from the melt is usually poured into a ladle or a small pot, which serves the functions of a surge hopper and a flow regulator, then into a mold.

7.9.2 Emissions and Controls

The principal pollutants emitted from secondary copper smelting activities are particulate matter in various forms. Removal of insulation from wire by burning causes particulate emissions of metal oxides and unburned insulation. Drying of chips and borings to remove excess oils and cutting fluids can cause discharges of large amounts of dense smoke consisting of soot and unburned hydrocarbons. Particulate emissions from the top of a cupola furnace consist of metal oxide fumes, dirt, and dust from limestone and coke.

The smelting process utilizes large volumes of air to oxidize sulfides, zinc, and other undesirable constituents of the feed. This procedure generates much particulate matter in the exit gas stream. The wide variation among furnace types, charge types, quality, extent of pretreatment, and size of charge is reflected in a broad spectrum of particle sizes and variable grain loadings in the escaping gases. One major factor contributing to differences in emission rates is the amount of zinc present in scrap feed materials; the low-boiling zinc evaporates and combines with air oxygen to give copious fumes of zinc oxide.

Metal oxide fumes from furnaces used in secondary smelters have been controlled by baghouses, electrostatic precipitators, or wet scrubbers. Efficiency of control by baghouses may be better than 99 percent, but cooling systems are needed to prevent the hot exhaust gases from damaging or destroying the bag filters. A two-stage system employing both water jacketing and radiant cooling is common. Electrostatic precipitators are not as well suited to this application, having a low collection efficiency for dense particulates such as oxides of lead and zinc. Wet scrubber installations are also relatively ineffective in the secondary copper industry. Scrubbers are useful mainly for particles larger than 1 micron, (μm) but the metal oxide fumes generated are generally submicron in size.

Particulate emissions associated with drying kilns can be similarly controlled. Drying temperatures up to 150° C (300° F) produce relatively cool exhaust gases, requiring no precooling for control by baghouses.

Wire burning generates much particulate matter, largely unburned combustibles. These emissions can be effectively controlled by direct-flame afterburners, with an efficiency of 90 percent or better if the afterburner combustion temperature is maintained above 1000° C (1800° F). If the insulation contains chlorinated organics such as polyvinyl chloride, hydrogen chloride gas will be generated and will not be controlled by the afterburner.

One source of fugitive emissions in secondary smelter operations is charging of scrap into furnaces containing molten metals. This often occurs when the scrap being processed is not sufficiently compact to allow a full charge to fit into the furnace prior to heating. The introduction of additional material onto the liquid metal surface produces significant amounts of volatile and combustible materials and smoke, which can escape through the charging door. Briquetting the charge offers a possible means of avoiding the necessity of such fractional charges. When fractional charging cannot be eliminated, fugitive emissions are reduced by turning off the furnace burners during charging. This reduces the flow of exhaust gases and enhances the ability of the exhaust control system to handle the emissions.

Metal oxide fumes are generated not only during melting, but also during pouring of the molten metal into the molds. Other dusts may be generated by the charcoal, or other lining, used in association with the mold. Covering the metal surface with ground charcoal is a method used to make "smooth-top" ingots. This process creates a shower or sparks, releasing emissions into the plant environment at the vicinity of the furnace top and the molds being filled.

Emission factor averages and ranges for six different types of furnaces are presented in Table 7.9-1.

Table 7.9-1. PARTICULATE EMISSION FACTORS FOR FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES[a,b]

EMISSION FACTOR RATING: B

Furnace and charge type	Control equipment[c]	Emissions			
		Avg kg/MT	Range kg/MT	Avg lb/ton	Range lb/ton
Cupola					
Scrap copper	0	0.002	-	0.003	-
Insulated copper wire	0	120	-	230	-
	1	5	-	10	-
Scrap copper and brass	0	35	30-40	70	60-80
	1	1.2	1.0-1.4	2.4	2.0-2.8
Reverberatory					
Copper	0	2.6	0.4-15	5.1	0.8-30
	2	0.2	0.1-0.3	0.4	0.3-0.6
Brass and bronze	0	18	0.3-35	36	0.6-70
	2	1.3	0.3-2.5	2.6	0.05-5
Rotary					
Brass and bronze	0	150	50-250	300	100-500
	1	7	3-10	13	6-19
Crucible and pot					
Brass and bronze	0	11	1-20	21	2-40
	1	0.5	0.1-1	1	0.1-2
Electric arc					
Copper	0	2.5	1-4	5	2-8
	2	0.5	0.02-1.0	1	0.04-2
Brass and bronze	0	5.5	2-9	11	4-18
	2	3	-	6	-
Electric induction					
Copper	0	3.5	-	7	-
	2	0.25	-	0.5	-
Brass and bronze	0	10	0.3-20	20	0.5-40
	2	0.35	0.01-0.65	0.7	0.01-1.3

[a] All factors given in terms of raw materials charged to unit.

[b] The information for Table 7.9-1 was based on unpublished data furnished by the following:
Philadelphia Air Management Services, Philadelphia, Pennsylvania.
New Jersey Department of Environmental Protection, Trenton, New Jersey.
New Jersey Department of Environmental Protection, Metro Field Office, Springfield, New Jersey.
New Jersey Department of Environmental Protection, Newark Field Office, Newark, New Jersey.
New York State Department of Environmental Conservation, New York, New York.
The City of New York Department of Air Resources, New York, New York.
Cook County Department of Environmental Control, Maywood, Illinois.
Wayne County Department of Health, Air Pollution Control Division, Detroit, Michigan.
City of Cleveland Department of Public Health and Welfare, Division of Air Pollution Control, Cleveland, Ohio.
State of Ohio Environmental Protection Agency, Columbus, Ohio.
City of Chicago Department of Environmental Control, Chicago, Illinois.
South Coast Air Quality Management District, Los Angeles, California.

[c] Control equipment: 0 signifies none operated
1 indicates electrostatic precipitator
2 indicates baghouse filter system

References for Section 7.9

1. Air Pollution Aspects of Brass and Bronze Smelting and Refining Industry. U.S. Department of Health, Education and Welfare, National Air Pollution Control Administration, Raleigh, N. C. Publication No. AP-58. November 1969.

2. Air Pollution Engineering Manual (2nd Ed.). John A. Danielson, Air Pollution Control District, County of Los Angeles (ed.). U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. AP-40. May 1973.

3. Emission Factors and Emission Source Information for Primary and Secondary Copper Smelters. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-450/3-77-051. December 1977.

7.9 SECONDARY COPPER SMELTING AND ALLOYING *Charles Masser*

7.9.3 Fugitive Emission Factors

Potential sources of fugitive particulate emissions from secondary smelting and alloying operations are sweating, drying, insulation burning, smelting furnaces and casting. Table 7.9-2 shows these sources and their corresponding emission factors.

No data are presently available concerning size characteristics of the fugitive emissions.

Table 7.9-2. POTENTIAL FUGITIVE PARTICULATE EMISSION FACTORS FOR UNCONTROLLED COPPER SMELTING AND ALLOYING

EMISSION FACTOR RATING: E

Types of operation	Particulates[a]	
	lb/ton	kg/MT
Sweating furnace[b]	0.75	0.38
Rotary dryer[b]	13.75	6.88
Insulation burning[c]	13.75	6.88
Electric induction furnace[d]	0.14	0.07
Reverberatory furnace[e]	5.27	2.64
Rotary furnace[d]	4.43	2.22
Crucible furnace[e]	0.49	0.25
Cupola (blast) furnace[e]	3.66	1.83
Casting[b]	0.015	0.008

[a]Factors are expressed as units per volume of scrap processed, except casting, which is expressed as units per volume cast.
[b]Engineering judgement assuming that fugitive emissions are equal to 5% of stack emissions shown in Reference 4.
[c]Engineering judgement assuming that fugitive emissions are equal to 5% of stack emission factor shown in Reference 5.
[d]Engineering judgement assuming that fugitive emissions are equal to 5% of stack emission factor shown in Reference 1.
[e]Engineering judgement, average of two sets of data, assuming that fugitive emissions are equal to 5% of stack emission factors shown in References 1 and 5.

Additional References for Section 7.9

4. *Multimedia Environmental Assessment of the Secondary Nonferrous Metal Industry, Volume II: Industry Profile*, EPA Contract no. 68-02-1319, Radian Corporation, Austin, TX, June 1976.

5. *Particulate Pollutant System Study, Volume III: Handbook of Emission Properties*, EPA Contract No. 22-69-104, Midwest Research Institute, Kansas City, MO, May 1971.

7.10 GRAY IRON FOUNDRIES

7.10.1 General[1]

Gray iron foundries produce gray iron castings by melting, alloying and molding pig iron and scrap iron. The process flow diagram of a typical gray iron foundry is presented in Figure 7.10-1. The four major processing operations of the typical gray iron foundry are raw materials handling, metal melting, mold and core production, and casting and finishing.

Raw Materials Handling - The raw material handling operations include the receiving, unloading, storage and conveying of all raw materials for the foundry. The raw materials used by gray iron foundries are pig iron, iron and steel scrap, foundry returns, metal turnings, alloys, carbon additives, coke, fluxes (limestone, soda ash, fluorspar, calcium carbide), sand, sand additives, and binders. These raw materials are received in ships, railcars, trucks and containers, transferred by truck, loaders and conveyers to both open piles and enclosed storage areas, and then transferred by similar means from storage to the processes.

Metal Melting - Generally the first step in the metal melting operations is scrap preparation. Since scrap is normally purchased in the proper size for furnace feed, scrap preparation primarily consists of scrap degreasing. This is very important for electric induction furnaces, as organics on scrap can cause an explosion. Scrap may be degreased with solvents, by centrifugation or by combustion in an incinerator or heater, or it may be charged without treatment, as is often the case with cupola furnaces. After preparation, the scrap, iron, alloy and flux are weighed and charged to the furnace.

The cupola furnace is the major type of furnace used in the gray iron industry today. It is typically a vertical refractory lined cylindrical steel shell, charged at the top with alternate layers of metal, coke and flux. Larger cupolas are water cooled instead of refractory lined. Air introduced at the bottom of the cupola burns the coke to melt the metal charge. Typical melting capacities range from 0.5 to 14 Mg (1 - 27 tons) per hour, with a few larger units approaching 50 Mg (100 tons) per hour. Cupolas can be tapped either continuously or intermittently from a side tap hole at the bottom of the furnace.

Electric arc furnaces, used to a lesser degree in the gray iron industry, are large refractory lined steel pots fitted with a refractory lined roof through which three graphite electrodes are inserted. The metal charge is heated to melting by electrical arcs produced by the current flowing between the electrodes and the charge. Electric arc furnaces are charged with raw material through the removed lid, by a chute through the lid, or through a door in

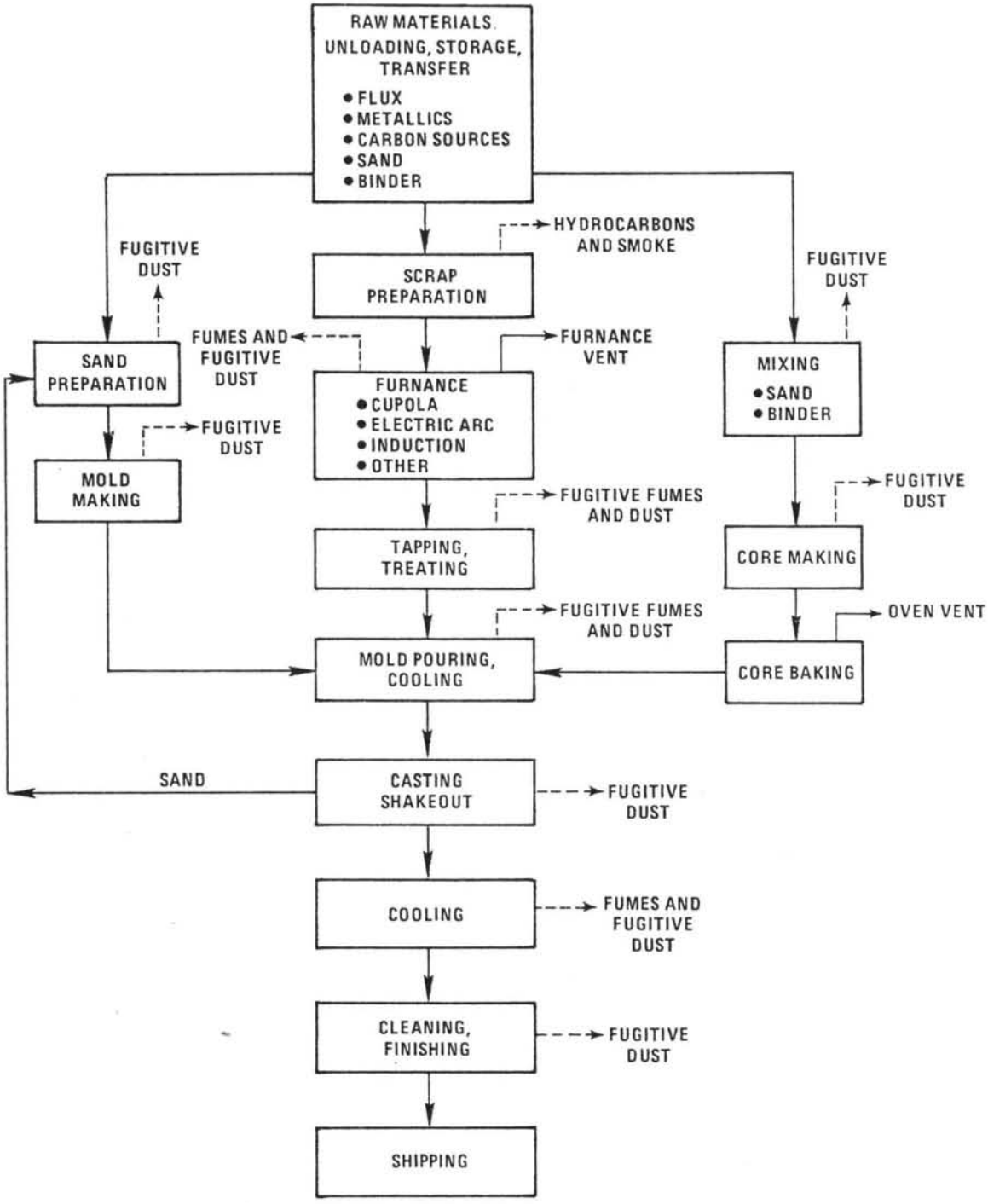


Figure 7.10-1. Typical flow diagram of a grey iron foundry.

the side. The molten metal is tapped by tilting and pouring through a hole in the side. Melting capacities range up to 10 Mg (20 tons) per hour.

A third furnace type used in the gray iron industry is the electric induction furnace. Induction furnaces are vertical refractory lined cylinders surrounded by electrical coils energized with alternating current. The resulting fluctuating magnetic field heats the metal. Induction furnaces are kept closed except when charging, skimming and tapping. The molten metal is tapped by tilting and pouring through a hole in the side. Induction furnaces are also used with other furnaces to hold and superheat the charge after melting and refining in another furnace.

A small percentage of melting in the gray iron industry is also done in air furnaces, reverberatory furnaces, pot furnaces and indirect arc furnaces.

The basic melting process operations are 1) furnace charging, in which the metal, scrap, alloys, carbon and flux are added to the furnace, 2) melting, during which the furnace remains closed, 3) backcharging, which involves the addition of more metal and, possibly, alloys, 4) refining and treating, during which the chemistry is adjusted, 5) slag removing, and 6) tapping molten metal into a ladle or directly into molds.

Mold and Core Production - Cores are molded sand shapes used to make the internal voids in castings, and molds are forms used to shape the exterior of castings. Cores are made by mixing sand with organic binders, molding the sand into a core, and baking the core in an oven. Molds are prepared by using a mixture of wet sand, clay and organic additives to make the mold shapes, and then by drying with hot air. Increasingly, cold setting binders are being used in both core and mold production. Used sand from shakeout operations is recycled to the sand preparation area to be cleaned, screened and reused to make molds.

Casting and Finishing - When the melting process is complete, the molten metal is tapped and poured into a ladle. At this point, the molten metal may be treated by addition of magnesium to produce ductile iron by the addition of soda ash or lime to remove sulfur. At times, graphite may be innoculated to adjust carbon levels. The treated molten metal is then poured into molds and allowed partially to cool. The partially cooled castings are placed on a vibrating grid where the mold and core sand is shaken away from the casting. The sand is returned to the mold manufacturing process, and the castings are allowed to cool further in a cooling tunnel.

In the cleaning and finishing process, burrs, risers and gates are broken off or ground off to match the contours of the castings, after which the castings are shot blasted to remove remaining mold sand and scale.

TABLE 7.10-1. EMISSION FACTORS FOR GRAY IRON FURNACES[a]

EMISSION FACTOR RATING: B

Furnace Type	Particulates kg/Mg	Particulates lb/ton	Carbon Monoxide kg/Mg	Carbon Monoxide lb/ton	Sulfur Dioxide kg/Mg	Sulfur Dioxide lb/ton	Nitrogen Oxides kg/Mg	Nitrogen Oxides lb/ton	VOC kg/Mg	VOC lb/ton	Lead[b] kg/Mg	Lead[b] lb/ton
Cupola[c,d]												
Uncontrolled	8.5 (3-17)[e]	17 (5-34)[e]	145[f]	73[f]	0.6S[g]	1.25S[g]	-	-	-	-	0.05-0.6	0.1-1.1
Wet cap	4	8	-	-	-	-	-	-	-	-	-	-
Impingement scrubber	2.5	5	-	-	-	-	-	-	-	-	-	-
High energy scrubber	0.4	0.8	-	-	0.3S[g]	0.6S[g]	-	-	-	-	-	-
Electrostatic precipitator	0.3	0.6	-	-	-	-	-	-	-	-	-	-
Bag filter	0.1	0.2	-	-	-	-	-	-	-	-	-	-
Electric Arc[h]	5 (3-10)[e]	10 (5-20)[e]	0.5-19	1-37	neg	neg	.02-.3	.04-.6	.03-.15	.06-.3	-	-
Electric Induction[c]	0.75	1.5	neg	neg	neg	neg	-	-	-	-	.005-.05	.009-0.1
Reverberatory[c]	1	2	-	-	-	-	-	-	-	-	.006-.07	.012-0.14

[a] Expressed as weight of pollutant per weight of gray iron produced. Neg = negligible.
[b] References 4 and 9-12.
[c] References 2-5.
[d] Approximately 85% of the total charge is metal. For every unit weight of coke in the charge, 7 units of gray iron are produced.
[e] Values in parentheses represent the range of expected values.
[f] Reference 6.
[g] Reference 1. S represents % sulfur in the coke. This factor assumes 30% of the sulfur is converted to SO_2.
[h] References 1 and 8.

TABLE 7.10-2. EMISSION FACTORS FOR FUGITIVE PARTICULATES FROM GRAY IRON FOUNDRIES[a]

EMISSION FACTOR RATING: D

Process	Emissions kg/Mg	Emissions lb/ton	Emitted to Work Environment kg/Mg	Emitted to Work Environment lb/ton	Emitted to Atmosphere kg/Mg	Emitted to Atmosphere lb/ton
Scrap and Charge Handling, Heating[b]	0.3	0.6	0.25	0.5	0.1	0.2
Magnesium Treatment[b]	2.5	5	2.5	5	0.5	1
Innoculation[c]	1.5 - 2.5	3 - 5	-	-	-	-
Pouring[b]	2.5	5	2.5	5	1	2
Cooling[b]	5	10	4.5	9	0.5	1
Shakeout[b]	16	32	6.5	13	0.5	1
Cleaning, Finishing[b]	8.5	17	0.15	0.3	0.05	0.1
Sand Handling, Preparation, Mulling[b]	20	40	13	26	1.5	3
Core Making, Baking[b]	0.6	1.1	0.6	1.1	0.6	1.1

[a] Expressed as weight of pollutant per weight of metal melted.
[b] Reference 1, p. III-13.
[c] Reference 7, p. 2-83.

7.10.2 Emissions and Controls[1]

Emissions from the raw materials handling operations consist of fugitive particulates generated from the receiving, unloading, storage and conveying of all raw materials for the foundry. These emissions are controlled by enclosing the major emission points and routing the air from the enclosures through fabric filters or wet collectors.

Scrap preparation using heat will emit smoke, organics and carbon monoxide, and preparation using solvent degreasers will emit organics. (See Section 4.6, Solvent Degreasing.) Catalytic incinerators and afterburners can be applied to control about 95 percent of the organics and carbon monoxide.

Emissions from melting furnaces consist of particulates, carbon monoxide, organics, sulfur dioxide, nitrogen oxides and small quantities of chlorides and fluorides. The particulates, chlorides and fluorides are generated by flux, incomplete combustion of coke, carbon additives, and dirt and scale on the scrap charge. Organics on the scrap and the reactivity of the coke effect carbon monoxide emissions. Sulfur dioxide emissions, characteristic of cupola furnaces, are attributable to sulfur in the coke.

The highest concentration of furnace emissions occurs during charging, backcharging, alloying, slag removal, and tapping operations, when the furnace lids and doors are opened. Generally, these emissions have escaped into the furnace building and have been vented through roof vents. Controls for emissions during the melting and refining operations usually concern venting the furnace gases and fumes directly to a collection and control system. Controls for fugitive furnace emissions involve the use of roof hoods or special hoods in the proximity of the furnace doors, and of tapping ladles to capture emissions and to route them to emission control systems.

High energy scrubbers and bag filters with respective efficiencies greater than 95 percent and 98 percent are used to control particulate emissions from cupolas and electric arc furnaces in the U.S. Afterburners achieving 95 percent control are used for reducing organics and carbon monoxide emissions from cupolas. Normally, induction furnaces are uncontrolled.

The major pollutants from mold and core production are particulates from sand reclaiming, sand preparation, sand mixing with binders and additives, and mold and core forming. There are organics, CO and particulate emissions from core baking, and organic emissions from mold drying. Bag filters and high energy scrubbers can be used to control particulates from mold and core production. Afterburners and catalytic incinerators can be used to control organics and carbon monoxide emissions.

TABLE 7.10-3. SIZE DISTRIBUTION FOR PARTICULATE EMISSIONS FROM THREE ELECTRIC ARC FURNACE INSTALLATIONS[a]

Particle Size (μ)	Foundry A	Foundry B	Foundry C
<1	5	8	18
<2	15	54	61
<5	28	80	84
<10	41	89	91
<15	55	93	94
<20	68	96	96
<50	98	99	99

[a]Reference 1, p. III-39.

TABLE 7.10-4. SIZE DISTRIBUTION FOR PARTICULATE EMISSIONS FROM EIGHTEEN CUPOLA FURNACE INSTALLATIONS[a]

Particle Size (μ)	Cumulative % Less Than Indicated Size
<2	14
<5	24
<10	34
<20	44
<50	61
<100	78
<200	93

[a]Reference 1, p. III-33.

In the casting operations, large quantities of particulates can be generated in the treating and innoculation steps before pouring. Emissions from pouring consist of fumes, carbon monoxide, organics, and particulates evolved from the mold and core materials when contacted with molten iron. These emissions continue to evolve as the mold cools. A significant quantity of particulate emissions is also generated during the casting shakeout operation. Particulate emissions from shakeout can be controlled by either high energy scrubbers or bag filters. Emissions from pouring are normally uncontrolled or are ducted into other exhaust streams.

Emissions from finishing operations are of large particulates emitted during the removal of burrs, risers and gates, and during the blasting process. Particulates from finishing operations are usually large in size and are easily controlled by cyclones.

Emission factors for melting furnaces are presented in Table 7.10-1, and emission factors for fugitive particulates are presented in Table 7.10-2. Typical particle size distributions for emissions from electric arc and cupola furnaces are presented in Table 7.10-3 and Table 7.10-4.

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7.11 SECONDARY LEAD PROCESSING

7.11.1 Process Description [1-7]

The secondary lead industry processes a variety of leadbearing scrap and residue to produce lead and lead alloy ingots, battery lead oxide, and lead pigments (Pb_3O_4 and PbO). Processing may involve scrap pretreatment, smelting and refining/casting. Processes typically used in each operation are shown in Figure 7.11-1.

7.11.1.1 Scrap pretreatment is the partial removal of metal and nonmetal contaminants from leadbearing scrap and residue. Processes used for scrap pretreatment include battery breaking, crushing and sweating. Battery breaking is the draining and crushing of batteries followed by manual screening to separate the lead from nonmetallic materials. This separated lead scrap is then mixed with other scraps and smelted in reverberatory or blast furnaces. Oversize pieces of scrap and residues are usually crushed by jaw crushers. Sweating separates lead from high-melting metals in direct gas or oil fired rotary or reverberatory furnaces. Rotary furnaces are typically used to process low lead content scrap and residue, while reverberatory furnaces are used to process high lead content scrap. The partially purified lead is periodically tapped for further processing in smelting furnaces or pot furnaces.

7.11.1.2 Smelting is the production of purified lead by melting and separating lead from metal and nonmetallic contaminants and by reducing oxides to elemental lead. Reverberatory smelting furnaces are used to produce a semisoft lead product that typically contains 3-4 percent antimony. Blast furnaces produce hard or antimonial lead containing about 10 percent antimony.

A reverberatory furnace produces semisoft lead from a charge of lead scrap, metallic battery parts, oxides, drosses and other residues. The furnace consists of a rectangular shell lined with refractory brick and fired directly with oil or gas to a temperature of 2300°F (1250°C). The material to be melted is heated by direct contact with combustion gases. The furnace can process about 50 tons per day (45 MT/day). About 47 percent of the charge is typically recovered as lead product and is periodically tapped into molds or holding pots. Forty-six percent of the charge is removed as slag and subsequently processed in blast furnaces. The remaining 7 percent of the furnace charge escapes as dust or fume.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (typically about 4.5 percent of the charge), scrap iron (about 4.5 percent), limestone (about 3 percent), coke (about 5.5 percent), and oxides, pot furnace refining drosses, and reverberatory slag (comprising the remaining 82.5 percent of the charge). The proportions of rerun slags, limestone and coke vary respectively to as high as 8 percent, 10 percent, and 8 percent of the charge. Processing capacity of the blast furnace ranges from 20 - 80 tons per day (18 - 73 MT/day).

Similar to iron cupolas, the furnaces consist of vertical steel cylinders lined with refractory brick. Combustion air at 0.5 - 0.75 psig is introduced at the bottom of the furnace through tuyeres. Some of the coke combusts to melt the charge, while the remainder reduces lead oxides to elemental lead. The furnace exhausts at temperatures of 1200 - 1350°F (650 - 730°C).

As the lead charge melts, limestone and iron float to the top of the molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate. The product lead constitutes roughly 70 percent of the charge. From the holding pot, the lead is usually cast into large ingots, called pigs or sows.

About 18 percent of the charge is recovered as slag, with about 60 percent of this being a sulfurous slag called matte. Roughly 5 percent of the charge is retained for reuse, and the remaining 7 percent of the charge escapes as dust or fume.

7.11.1.3 Refining/casting is the use of kettle type furnaces in remelting, alloying, refining and oxidizing processes. Materials charged for remelting are usually lead alloy ingots which require no further processing before casting. The furnaces used for alloying, refining and oxidizing are usually gas fired, and operating temperatures range from 700 - 900°F (375 - 485°C).

Alloying furnaces simply melt and mix ingots of lead and alloy material. Antimony, tin, arsenic, copper and nickel are the most common alloying materials.

Refining furnaces remove copper and antimony to produce soft lead, and they remove arsenic, copper and nickel to produce hard lead. Sulfur may be added to the molten lead bath to remove copper. Copper sulfide skimmed off as dross may subsequently be processed in a blast furnace to recover residual lead. Aluminum chloride flux may be used to remove copper, antimony and nickel. The antimony content can be reduced to about 0.02 percent by bubbling air through the molten lead. Residual antimony can be removed by adding sodium nitrate and sodium hydroxide to the bath and skimming off the resulting dross. Dry drossing consists of adding sawdust to the agitated mass of molten metal. The sawdust supplies carbon to help separate globules of lead suspended in the dross and to reduce some of the lead oxide to elemental lead.

Oxidizing furnaces are either kettle or reverberatory furnaces which oxidize lead and entrain the product lead oxides in the combustion air stream. The product is subsequently recovered in baghouses at high efficiency.

7.11.2 Emissions and Controls [1,4,5]

Emission factors for uncontrolled processes and fugitive particulate emissions are in Tables 7.11-1 and 7.11-2, respectively.

Reverberatory and blast furnaces account for about 88 percent of the total lead emissions from the secondary lead industry. Most of the remaining processes are small emission sources with undefined emission characteristics.

Emissions from battery breaking mainly consist of sulfuric acid mist and dusts containing dirt, battery case material and lead compounds. Emissions from crushing are also mainly dusts.

Emissions from sweating operations consist of fume, dust, soot particulates and combustion products, including sulfur dioxide. The sulfur dioxide emissions are from the combustion of sulfur compounds in the scrap and fuel. Dusts range in size from 5 - 20 μm, while unagglomerated lead fumes range in size from 0.07 - 0.4 μm, with an average diameter of 0.3 μm. Particulate loadings in the stack gas from reverberatory sweating range from 1.4 - 4.5 grains per cubic foot (3.2 - 10.3 g/m^3). Baghouses usually control sweating emissions, with removal efficiencies exceeding 99 percent. The emission factors for lead sweating in Table 7.11-1 are based on measurements at similar sweating furnaces in other secondary metals processing industries, and are not based on measurements at lead sweating furnaces.

Reverberatory smelting furnaces emit particulates and oxides of sulfur and nitrogen. Particulates consist of oxides, sulfides and sulfates of lead, antimony, arsenic, copper and tin, as well as unagglomerated lead fume. Particulate loadings range from 7 - 22 grains per cubic foot (16 - 50 g/m^3). Emissions are generally controlled with settling and cooling chambers followed by a baghouse. Control efficiencies generally exceed 99 percent, as shown in Table 7.11-3. Wet scrubbers are sometimes used to reduce sulfur dioxide emissions. However, because of the small particles emitted, scrubbers are not as widely used as baghouses for particulate control.

Two chemical analyses by electron spectroscopy showed the particulates to consist of 38 - 42 percent lead, 20 - 30 percent tin, and about 1 percent zinc.[16] Typically, particulates from reverberatory smelting furnaces comprise about 20 percent lead.

Emissions from blast furnaces occur at charging doors, the slag tap, the lead well, and the furnace stack. The emissions are combustion gases (including carbon monoxide, hydrocarbons, and oxides of sulfur and nitrogen) and particulates. Emissions from the charging doors and the slag tap are hooded and routed to the devices treating the furnace stack emissions. Reverberatory furnace particulates are larger than those emitted from blast furnaces and are thus suitable for control by scrubbers

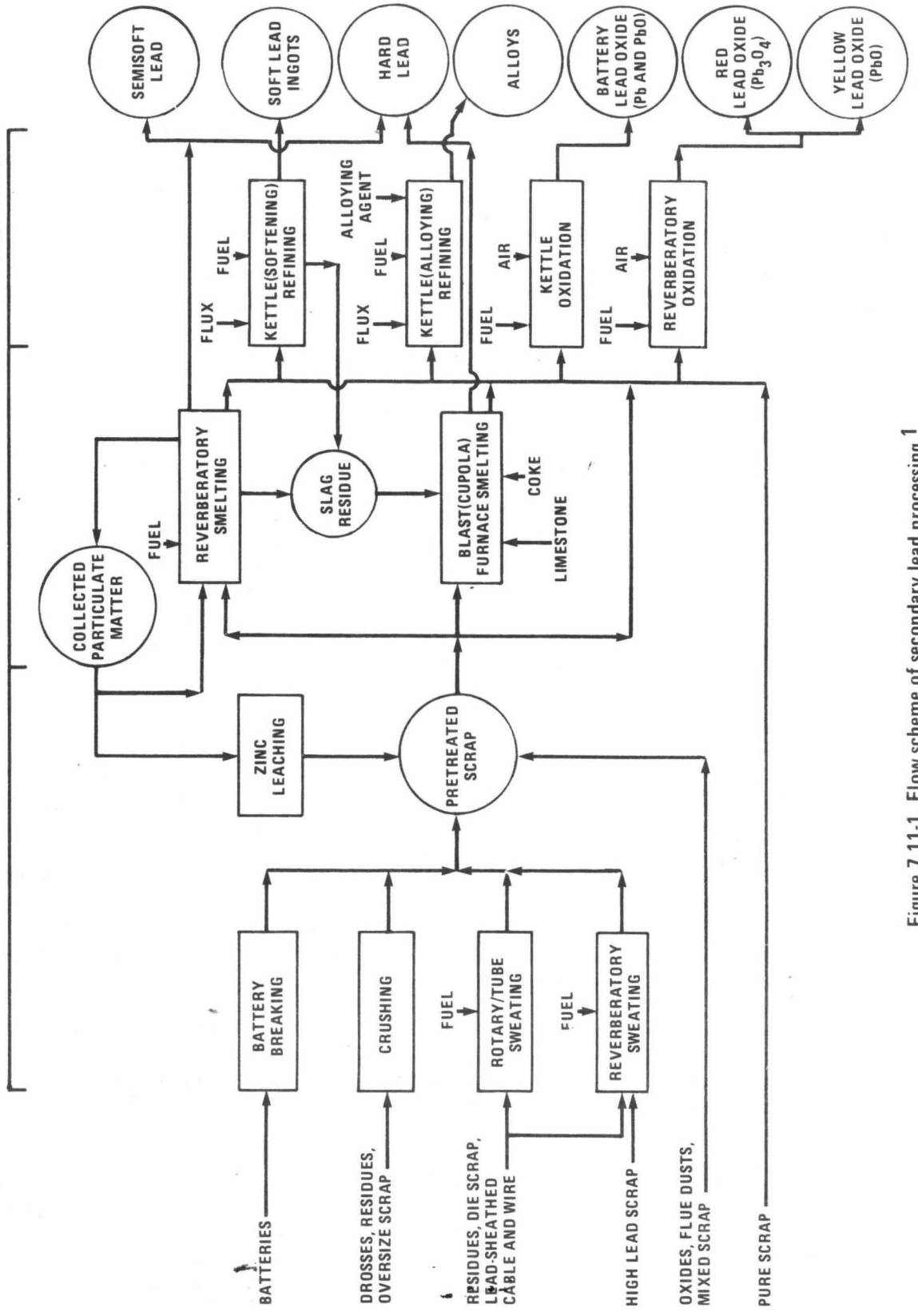

Figure 7.11-1. Flow scheme of secondary lead processing.[1]

Table 7.11-2. FUGITIVE EMISSION FACTORS FOR SECONDARY LEAD PROCESSING

EMISSION FACTOR RATING: E

Source	Particulates[a]		Lead[b]	
	lb/ton	kg/MT	lb/ton	kg/MT
Sweating	1.6 - 3.5	0.8 - 1.8	0.4 - 1.8	0.2 - 0.4
Smelting	2.8 - 15.7	1.4 - 7.9	0.6 - 3.6	0.3 - 1.8
Kettle Refining	0.04	0.02	0.01	0.005
Casting[c]	0.88	0.44	0.2	0.1

[a] Based on an engineering estimate that fugitive emissions equal 5% of the uncontrolled stack emissions. All factors except that for casting are based on the amount of charge to the process. The casting factor is based on the amount of lead cast. Reference 14.

[b] Factors are based on an approximation that particulate emissions contain 23% lead. References 3 and 5.

[c] Factors based on limited tests of a roof monitor over casting operations at a primary smelter.

or fabric filters downstream of coolers. Efficiencies for various control devices are shown in Table 7.11-3. In one application, fabric filters alone captured over 99 percent of the blast furnace particulate emissions.

Table 7.11-3. EFFICIENCIES OF PARTICULATE CONTROL EQUIPMENT ASSOCIATED WITH SECONDARY LEAD SMELTING FURNACES

Control device	Furnace type	Particulate control efficiency, %
Fabric filter[a]	Blast	98.4
	Reverberatory	99.2
Dry cyclone plus fabric filter[a]	Blast	99.0
Wet cyclone plus fabric filter[b]	Reverberatory	99.7
Settling chamber plus dry cyclone plus fabric filter[c]	Reverberatory	99.8
Venturi scrubber plus demister[d]	Blast	99.3

[a] Reference 8.
[b] Reference 9.
[c] Reference 10.
[d] Reference 12.

The size distribution for blast furnace particulates recovered by an efficient fabric filter is reported in Table 7.11-4. Particulates recovered from another blast furnace contained about 80 - 85 percent lead sulfate and lead chloride, 4 percent tin, 1 percent cadmium, 1 percent zinc, 0.5 percent each antimony and arsenic, and less than 1 percent organic matter.[17]

Kettle furnaces for melting, refining and alloying are relatively minor emission sources. The kettles are hooded, with fumes and dusts typically vented to baghouses and recovered with efficiencies exceeding 99 percent. Twenty measurements of the uncontrolled particulates from kettle furnaces showed a mass median aerodynamic particle diameter of 18.9 μm, with particle size ranging from 0.05 - 150 μm. Three chemical analyses by electron spectroscopy showed the composition of particulates to vary from 12 - 17 percent lead, 5 - 17 percent tin, and 0.9 - 5.7 percent zinc.[16]

Emissions from oxidizing furnaces are economically recovered with baghouses. The particulates are mostly lead oxide, but they also contain amounts of lead and other metals. The oxides range in size from 0.2 - 0.5 μm. Controlled emissions have been reported to be as low as 0.2 - 2.8 pounds per ton (0.1 - 1.4 kg/MT).

Table 7.11-1. EMISSION FACTORS FOR SECONDARY LEAD PROCESSING[a]

Source	Particulates lb/ton	Particulates kg/MT	Lead lb/ton	Lead kg/MT	Sulfur Dioxide lb/ton	Sulfur Dioxide kg/MT	Emission Factor Rating
Battery breaking[b]	NA	NA	NA	NA	NA	NA	---
Crushing[b]	NA	NA	NA	NA	NA	NA	---
Sweating[b]	32-70	16-35	7-16[c]	4-8[c]	NA	NA	E
Leaching[b]	Neg	Neg	Neg	Neg	Neg	Neg	---
Smelting[d]							
Reverberatory	147 (56-313)[e]	74 (28-157)[e]	34 (13-72)[c]	17 (6-36)[c]	80 (71-88)[e]	40 (36-44)[e]	B
Blast (cupola)[d]	193 (21-381)[f]	97 (11-191)[f]	44 (5-88)[c]	22 (2-44)[c]	53 (18-110)[f]	27 (9-55)[f]	B
Kettle refining	0.8[g]	0.4[g]	0.2[c]	0.1[c]	NA	NA	B
Oxidation[h]							
Kettle	<40[i]	<20[i]	NA	NA	NA	NA	E
Reverberatory	NA	NA	NA	NA	NA	NA	---

[a] All emission factors are based on the quantity of material charged to the furnace (except particulate kettle oxidation).
[b] NA = data not available. Neg = negligible.
[c] Reference 1.
[d] Emission factor rating of E. Emission factors for lead emissions are based on an approximation that particulate emissions contain 23% lead. References 3 and 5.
[e] Numbers in parentheses represent ranges of values obtained.
[f] References 8 - 11.
[g] References 11 - 13.
[h] Reference 11.
[i] References 1 and 2.
Essentially all of the product lead oxide is entrained in an air stream and subsequently recovered by a baghouse with average collection efficiencies in excess of 99%. The reported value represents emissions of lead oxide that escape a baghouse used to collect the lead oxide product. The emission factor is based on the amount of lead oxide produced and represents an approximate upper limit for emissions.

Table 7.11-4. PARTICLE SIZE DISTRIBUTION OF PARTICULATES RECOVERED FROM A COMBINED BLAST AND REVERBERATORY FURNACE GAS STREAM WITH BAGHOUSE CONTROL[a]

Particle Size Range, μm	Fabric filter catch, wt %
0 to 1	13.3
1 to 2	45.2
2 to 3	19.1
3 to 4	14.0
4 to 16	8.4

[a] Reference 4, Table 86.

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7.12 SECONDARY MAGNESIUM SMELTING

7.12.1 Process Description[1]

Magnesium smelting is carried out in crucible or pot-type furnaces that are charged with magnesium scrap and fired by gas, oil, or electric heating. A flux is used to cover the surface of the molten metal because magnesium will burn in air at the pouring temperature (approximately 1500°F or 815°C). The molten magnesium, usually cast by pouring into molds, is annealed in ovens utilizing an atmosphere devoid of oxygen.

7.12.2 Emissions[1]

Emissions from magnesium smelting include particulate magnesium (MgO) from the melting, nitrogen oxides from the fixation of atmospheric nitrogen by the furnace temperatures, and sulfur dioxide losses from annealing oven atmospheres. Factors affecting emissions include the capacity of the furnace; the type of flux used on the molten material; the amount of lancing used; the amount of contamination of the scrap, including oil and other hydrocarbons; and the type and extent of control equipment used on the process. The emission factors for a pot furnace are shown in Table 7.12-1.

Table 7.12-1. EMISSION FACTORS FOR MAGNESIUM SMELTING EMISSION FACTOR RATING: C

Type of furnace	Particulates[a] lb/ton	Particulates[a] kg/MT
Pot furnace		
Uncontrolled	4	2
Controlled	0.4	0.2

[a]References 2 and 3. Emission factors expressed as units per unit weight of metal processed.

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7.13 STEEL FOUNDRIES

7.13.1 Process Description[1]

Steel foundries produce steel castings by the melting, alloying and molding of pig iron and steel scrap. The process flow diagram of a typical steel foundry is presented in Figure 7.13-1. The major processing operations of the typical steel foundry are raw materials handling, metal melting, mold and core production, and casting and finishing.

Raw Materials Handling - The raw material handling operations include the receiving, unloading, storage and conveying of all raw materials for the foundry. Some of the raw materials used by steel foundries are pig iron, iron and steel scrap, foundry returns, metal turnings, alloys, carbon additives, fluxes (limestone, soda ash, fluorspar, calcium carbide), sand, sand additives, and binders. These raw materials are received in ships, railcars, trucks, and containers, and are transferred by trucks, loaders, and conveyors to both open pile and enclosed storage areas. They are then transferred by similar means from storage to the subsequent processes.

Metal Melting - Generally, the first step in the metal melting operations is scrap preparation. Since scrap is normally purchased in the proper size for furnace feed, preparation primarily consists of scrap degreasing. This is very important for electric induction furnaces, as organics on scrap can be explosive. Scrap may be degreased with solvents, by centrifugation or by incinerator or preheater combustion. After preparation, the scrap, metal, alloy, and flux are weighed and charged to the furnace.

Electric arc furnaces are used almost exclusively in the steel foundry for melting and formulating steel. Electric arc furnaces are large refractory lined steel pots, fitted with a refractory roof through which three graphite electrodes are inserted. The metal charge is melted with resistive heating generated by electrical current flowing among the electrodes and through the charge. Electric arc furnaces are charged with raw materials by removing the lid, through a chute opening in the lid, or through a door in the side. The molten metal is tapped by tilting and pouring through a hole in the side. Melting capacities range up to 10 megagrams (11 tons) per hour.

A second, less common, furnace used in steel foundries is the open hearth furnace, a very large shallow refractory lined vessel which is operated in a batch manner. The open hearth furnace is fired at alternate ends, using the heat from the waste combustion gases to heat the incoming combustion air.

A third furnace used in the steel foundry is the induction furnace. Induction furnaces are vertical refractory lined cylinders

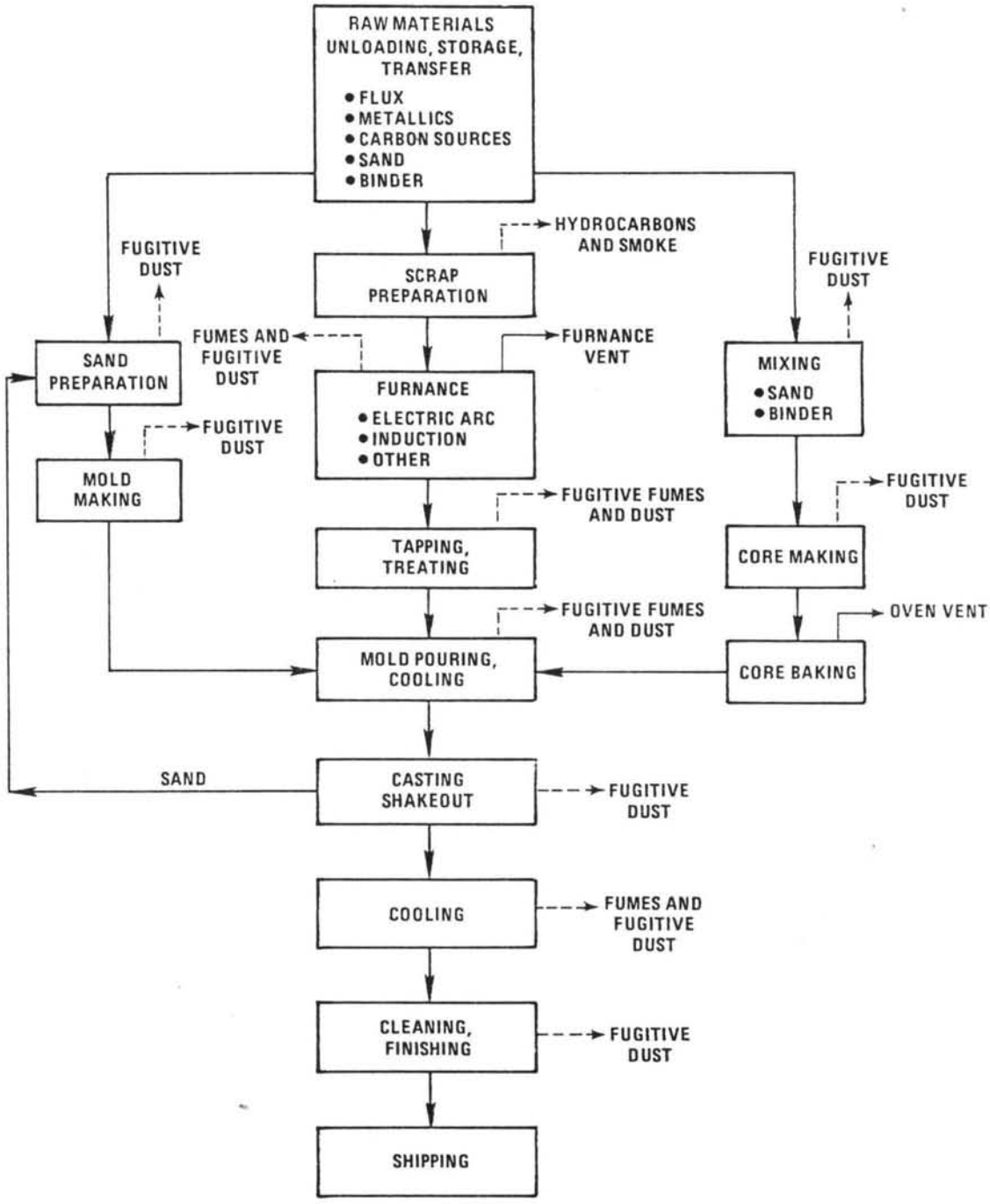

Figure 7.13-1. Typical flow diagram of a steel foundry.

surrounded by electrical coils energized with alternating current. The resulting fluctuating magnetic field heats the metal. Induction furnaces are kept closed except when charging, skimming and tapping. The molten metal is tapped by tilting and pouring through a hole in the side. Induction furnaces are also used with other furnaces, to hold and superheat a charge melted and refined in the other furnaces. A very small fraction of the secondary steel industry also uses crucible and pneumatic converter furnaces.

The basic melting process operations are 1) furnace charging, in which metal, scrap, alloys, carbon, and flux are added to the furnace, 2) melting, during which the furnace remains closed, 3) backcharging, which is the addition of more metal and possibly alloys, 4) refining, during which the carbon content is adjusted, 5) oxygen lancing, which is injecting oxygen into the molten steel to dislodge slag and to adjust the chemistry of the metal, 6) slag removal, and 7) tapping the molten metal into a ladle or directly into molds.

Mold and Core Production - Cores are forms used to make the internal voids in castings, and molds are forms used to shape the casting exterior. Cores are made of sand with organic binders, molded into a core and baked in an oven. Molds are made of wet sand with clay and organic additives, dried with hot air. Increasingly, coal setting binders are being used in both core and mold production. Used sand from castings shakeout operations is recycled to the sand preparation area, where it is cleaned, screened and reused.

Casting and Finishing - When the melting process is complete, the molten metal is tapped and poured into a ladle. At this time, the molten metal may be treated by adding alloys and/or other chemicals. The treated metal is then poured into molds and is allowed partially to cool under carefully controlled conditions. Molten metal may be poured directly from the furnace to the mold.

When partially cooled, the castings are placed on a vibrating grid, and the sand of the mold and core are shaken away from the casting. The sand is recycled to the mold manufacturing process, and the casting is allowed to cool further.

In the cleaning and finishing process, burrs, risers and gates are broken or ground off to match the contour of the casting. Afterward, the castings are usually shot blasted to remove remaining mold sand and scale.

7.13.2 Emissions and Controls[1]

Emissions from the raw materials handling operations are fugitive particulates generated from receiving, unloading, storage and conveying all raw materials for the foundry. These emissions are controlled by enclosing the major emission points and routing the air from the enclosures through fabric filters.

Emissions from scrap preparation consist of hydrocarbons if solvent degreasing is used, and consist of smoke, organics and carbon monoxide if heating is used. Catalytic incinerators and afterburners of approximately 95 percent control efficiency for carbon monoxide and organics can be applied to these sources.

Emissions from melting furnaces are particulates, carbon monoxide, organics, sulfur dioxide, nitrogen oxides, and small quantities of chlorides and fluorides. The particulates, chlorides and fluorides are generated by the flux, the carbon additives, and dirt and scale on the scrap charge. Organics on the scrap and the carbon additives effect CO emissions. The highest concentrations of furnace emissions occur during charging, backcharging, alloying, oxygen lancing, slag removal, and tapping operations, when the furnace lids and doors are opened. Characteristically, these emissions have escaped into the furnace building and have been vented through roof vents. Controls for emissions during the melting and refining operations focus on venting the furnace gases and fumes directly to an emission collection duct and control system. Controls for fugitive furnace emissions involve either the use of building roof hoods or of special hoods near the furnace doors, to collect emissions and route them to emission control systems. Emission control systems commonly used to control particulate emissions from electric arc and induction furnaces are bag filters, cyclones and venturi scrubbers. The capture efficiencies of the collection systems, presented in Table 7.13-1, range from 80 to 100 percent. Usually, induction furnaces are uncontrolled.

The major pollutants from mold and core production are particulates from sand reclaiming, sand preparation, sand mixing with binders and additives, and mold and core forming. There are volatile organics (VOC), CO and particulate emissions from core baking, and VOC emissions from mold drying. Bag filters and high energy scrubbers can be used to control particulates from mold and core production. Afterburners and catalytic incinerators can be used to control VOC and CO emissions.

In the casting operations, large quantities of particulates can be generated in the steps prior to pouring. Emissions from pouring consist of fumes, CO, VOC, and particulates from the mold and core materials when contacted by the molten steel. As the mold cools, emissions continue. A significant quantity of particulate emissions is also generated during the casting shakeout operation. The particulate emissions from the shakeout operations can be controlled by either high efficiency cyclones or bag filters. Emissions from pouring are usually uncontrolled.

Emissions from finishing operations consist of large particulates from the removal of burrs, risers and gates, and during shot blasting. Particulates from finishing operations typically are large and are generally controlled by cyclones.

TABLE 7.13-1. EMISSION FACTORS FOR STEEL FOUNDRIES

EMISSION FACTOR RATING: A

Process	Particulates[a] kg/Mg	Particulates[a] lb/ton	Nitrogen oxides kg/Mg	Nitrogen oxides lb/ton
Melting				
Electric arc[b,c]	6.5 (2 to 20)	13 (4 to 40)	0.1	0.2
Open hearth[d,e]	5.5 (1 to 10)	11 (2 to 20)	0.005	0.01
Open hearth oxygen lanced[f,g]	5 (4 to 5.5)	10 (8 to 11)	-	-
Electric induction[h]	0.05	0.1	-	-

[a] Expressed as units per unit weight of metal processed. If the scrap metal is very dirty or oily, or if increased oxygen lancing is employed, the emission factor should be chosen from the high side of the factor range.
[b] Electrostatic precipitator, 92 - 98% control efficiency; baghouse (fabric filter), 98 - 99% control efficiency; venturi scrubber, 94 - 98% control efficiency.
[c] References 2 - 10.
[d] Electrostatic precipitator, 95 - 98.5% control efficiency; baghouse, 99.9% control efficiency; venturi scrubber, 96 - 99% control efficiency.
[e] References 2, 11 - 13.
[f] Electrostatic precipitator, 95 - 98% control efficiency; baghouse, 99% control efficiency; venturi scrubber, 95 - 98% control efficiency.
[g] References 6 and 14.
[h] Usually not controlled.

Emission factors for melting furnaces in the steel foundry are presented in Table 7.13-1.

Although no emission factors are available for nonfurnace emission sources in steel foundries, they are very similar to those in iron foundries.[1] Nonfurnace emission factors and particle size distributions for iron foundry emission sources are presented in Section 7.10, Gray Iron Foundries.

References for Section 7.13

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2. J.J. Schueneman, et al., Air Pollution Aspects of the Iron and Steel Industry, National Center for Air Pollution Control, Cincinnati, OH, June 1963.

3. Foundry Air Pollution Control Manual, 2nd Ed., Foundry Air Pollution Control Committee, Des Plaines, IL, 1967.

4. R.S. Coulter, "Smoke, Dust, Fumes Closely Controlled in Electric Furnaces", Iron Age, 173:107-110, January 14, 1954.

5. Air Pollution Aspects of the Iron and Steel Industry, p. 109.

6. J.M. Kane and R.V. Sloan, "Fume Control Electric Melting Furnaces", American Foundryman, 18:33-34, November 1950.

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8. C.A. Faist, "Electric Furnace Steel", Proceedings of the American Institute of Mining and Metallurgical Engineers, 11:160-161, 1953.

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12. A.C. Elliot and A.J. Freniere, "Metallurgical Dust Collection in Open Hearth and Sinter Plant", Canadian Mining and Metallurgical Bulletin, 55(606):724-732, October 1962.

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7.14 SECONDARY ZINC PROCESSING

7.14.1 Process Description[1,2]

The secondary zinc industry processes obsolete and scrap materials to recover zinc as slabs, dust and zinc oxide. Processing involves three operations, scrap pretreatment, melting and refining. Processes typically used in each operation are shown in Figure 7.14-1. Molten product zinc may be used in zinc galvanizing.

Scrap Pretreatment - Pretreatment is the partial removal of metal and other contaminants from scrap containing zinc. Sweating separates zinc from high melting metals and contaminants by melting the zinc in kettle, rotary, reverberatory, muffle or electric resistance furnaces. The product zinc then is usually directly used in melting, refining or alloying processes. The high melting residue is periodically raked from the furnace and further processed to recover zinc values. These residues may be processed by crushing/screening to recover impure zinc or by sodium carbonate leaching to produce zinc oxide.

In crushing/screening, zinc bearing residues are pulverized or crushed to break the physical bonds between metallic zinc and contaminants. The impure zinc is then separated in a screening or pneumatic classification step.

In sodium carbonate leaching, the zinc bearing residues are converted to zinc oxide, which can be reduced to zinc metal. They are crushed and washed to leach out zinc from contaminants. The aqueous stream is then treated with sodium carbonate, precipitating zinc as the hydroxide or carbonate. The precipitate is then dried and calcined to convert zinc hydroxide into crude zinc oxide. The ZnO product is usually refined to zinc at primary zinc smelters.

Melting - Zinc is melted at 425-590°C (800-1100°F) in kettle, crucible, reverberatory and electric induction furnaces. Zinc to be melted may be in the form of ingots, reject castings, flashing or scrap. Ingots, rejects and heavy scrap are generally melted first, to provide a molten bath to which light scrap and flashing are added. Before pouring, a flux is added and the batch agitated to separate the dross accumulating during the melting operation. The flux floats the dross and conditions it so it can be skimmed from the surface. After skimming, the melt can be poured into molds or ladles.

Refining/Alloying - Additional processing steps may involve alloying, distillation, distillation and oxidation, or reduction. Alloying produces mainly zinc alloys from pretreated scrap. Often the alloying operation is combined with sweating or melting.

Distillation retorts and furnaces are used to reclaim zinc from alloys or to refine crude zinc. Retort distillation is the

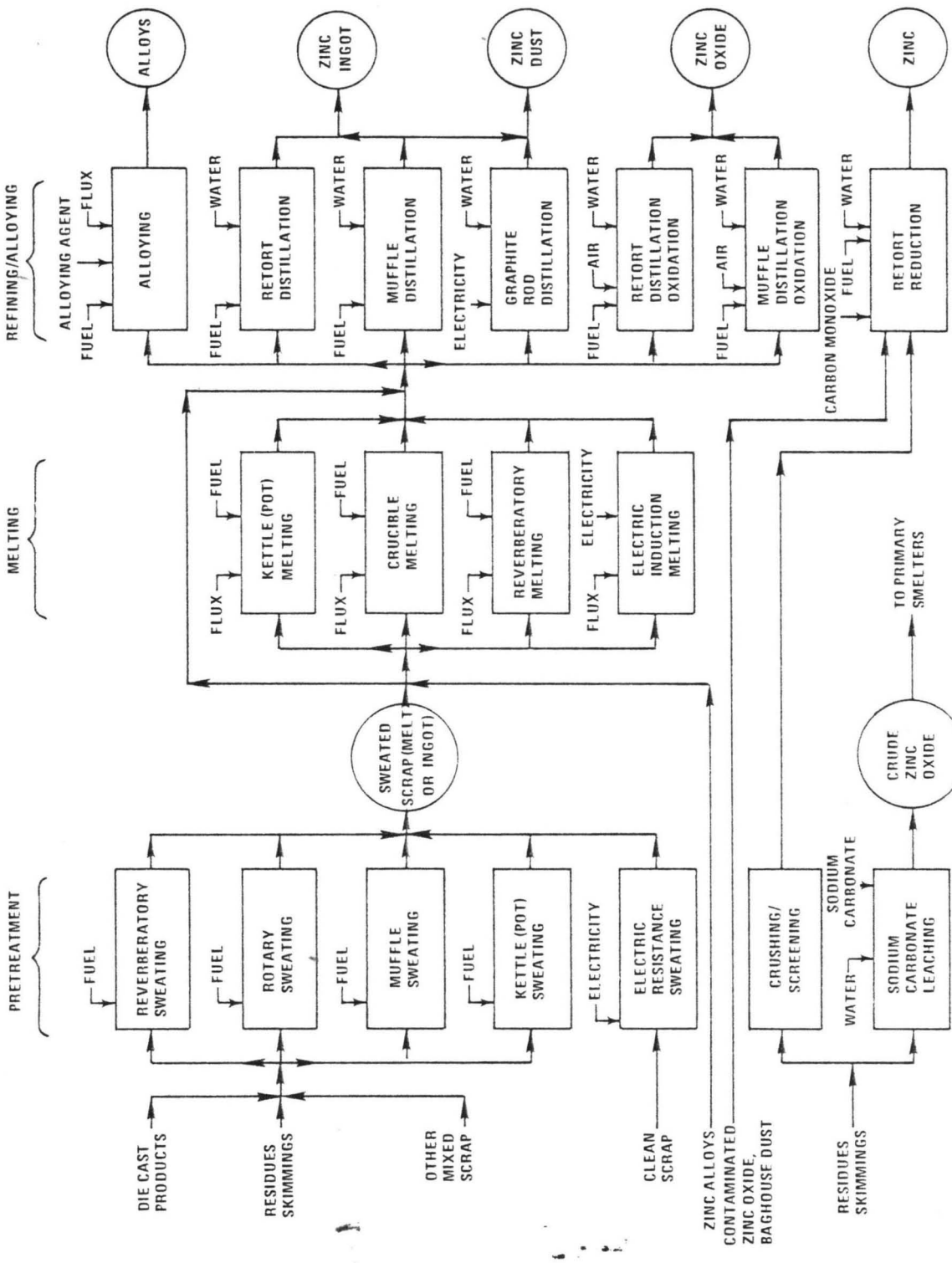

Figure 7.14-1. Process flow diagram of secondary zinc processing.

TABLE 7.14-1. UNCONTROLLED PARTICULATE EMISSION FACTORS FOR SECONDARY ZINC SMELTING[a]

EMISSION FACTOR RATING: C

Operation	Emissions kg/Mg	Emissions lb/ton
Reverberatory sweating[b]		
clean metallic scrap	Negligible	Negligible
general metallic scrap	6.5	13
residual scrap	16	32
Rotary sweating[c]	5.5-12.5	11-25
Muffle sweating[c]	5.4-16	10.8-32
Kettle sweating[b]		
clean metallic scrap	Negligible	Negligible
general metallic scrap	5.5	11
residual scrap	12.5	25
Electric resistance sweating[c]	<5	<10
Crushing/screening[c]	0.5-3.8	1.0-7.5
Sodium carbonate leaching		
crushing/screening[c]	0.5-3.8	1.0-7.5
calcining[d]	44.5	89
Kettle (pot) melting[d]	0.05	0.1
Crucible melting	DNA	DNA
Reverberatory melting	DNA	DNA
Electric induction melting	DNA	DNA
Alloying	DNA	DNA
Retort and muffle distillation		
pouring[c]	0.2-0.4	0.4-0.8
casting[c]	0.1-0.2	0.2-0.4
muffle distillation[d]	22.5	45
Graphite rod distillation[c,e]	Negligible	Negligible
Retort distillation/oxidation[f]	10-20	20-40
Muffle distillation/oxidation[f]	10-20	20-40
Retort reduction	23.5	47
Galvanizing[d]	2.5	5

[a] Expressed as units per unit weight of feed material processed for crushing/screening, skimming/residues processed; for kettle (pot) melting and retort and muffle distillation operations, metal product. Galvanizing factor expressed in units per unit weight of zinc used. DNA: Data not available.

[b] Reference 3.

[c] Reference 4.

[d] References 5-7.

[e] Reference 1.

[f] Reference 4. Factor units per unit weight of ZnO produced. The product zinc oxide dust is totally carried over in the exhaust gas from the furnace and is recovered with 98-99% efficiency.

vaporization at 980-1250°C (1800-2280°F) of elemental zinc with its subsequent condensation as zinc dust or liquid zinc. Rapid cooling of the vapor stream below the zinc melting point produces zinc dust, which can be removed from the condenser and packaged. If slab zinc is the desired product, the vapors are condensed slowly at a higher temperature. The resultant melt is cast into ingots or slabs. Muffle distillation furnaces produce principally zinc ingots, and graphite rod resistance distillation produces zinc dust.

Retort and muffle furnace distillation and oxidation processes produce zinc oxide dust. These processes are similar to distillation through the vaporization step. In contrast, for distillation/oxidation, the condenser is omitted, and the zinc vapor is discharged directly into an air stream leading to a refractory lined combustion chamber. Excess air is added to complete oxidation and to cool the product. The zinc oxide product is usually collected in a baghouse.

In retort reduction, zinc metal is produced by the reaction of carbon monoxide and zinc oxide to yield zinc and carbon dioxide. Carbon monoxide is supplied by the partial oxidation of the coke. The zinc is recovered by condensation.

Zinc Galvanizing - Zinc galvanizing is the coating of clean oxide free iron or steel with a thin layer of zinc by immersion in molten zinc. The galvanizing occurs in a vat or in dip tanks containing molten zinc and cover flux.

7.14.2 Emissions and Controls[1,2]

Factors for uncontrolled point source and fugitive particulate emissions are tabulated in Tables 7.14-1 and 7.14-2 respectively.

Emissions from sweating and melting operations consist principally of particulates, zinc fumes, other volatile metals, flux fumes and smoke generated by the incomplete combustion of grease, rubber and plastics in the zinc bearing feed material. Zinc fumes are negligible at low furnace temperatures, for they have a low vapor pressure even at 480°C (900°F). With elevated temperatures, however, heavy fuming can result. Flux emissions are minimized by the use of a nonfuming flux. Substantial emissions may arise from incomplete combustion of carbonaceous material in the zinc scrap. These contaminants are usually controlled by afterburners. Further emissions are the products of combustion of the furnace fuel. Since the furnace fuel is usually natural gas, these emissions are minor. In reverberatory furnaces, the products of fuel combustion are emitted with the other emissions. Other furnaces emit the fuel combustion products as a separate emission stream.

Particulates from sweating and melting are mainly hydrated $ZnCl_2$ and ZnO, with small amounts of carbonaceous material. Chemical

TABLE 7.14-2. FUGITIVE PARTICULATE UNCONTROLLED EMISSION FACTORS FOR SECONDARY ZINC SMELTING

EMISSION FACTOR RATING: E

Operation	Particulate	
	kg/Mg	lb/ton
Reverberatory sweating[b]	0.63	1.30
Rotary sweating[b]	0.45	0.90
Muffle sweating[b]	0.54	1.07
Kettle (pot) sweating[b]	0.28	0.56
Electric resistance sweating[b]	0.25	0.50
Crushing/screening[c]	2.13	4.25
Sodium carbonate leaching	DNA	DNA
Kettle (pot) melting furnace[b]	0.0025	0.005
Crucible melting furnace[d]	0.0025	0.005
Reverberatory melting furnace[b]	0.0025	0.005
Electric induction melting[b]	0.0025	0.005
Alloying retort distillation	DNA	DNA
Retort and muffle distillation	1.18	2.36
Casting[b]	0.0075	0.015
Graphite rod distillation	DNA	DNA
Retort distillation/oxidation	DNA	DNA
Muffle distillation/oxidation	DNA	DNA
Retort reduction	DNA	DNA

[a] Reference 8. Expressed as units per end product, except factors for crushing/screening and electric resistance furnaces, which are expressed as units per unit of scrap processed. DNA: Data not available.

[b] Estimate based on stack emission factor given in Reference 1, assuming fugitive emissions to be equal to 5% of stack emissions.

[c] Reference 1. Average of reported emission factors.

[d] Engineering judgement, assuming fugitive emissions from crucible melting furnace to be equal to fugitive emissions from kettle (pot) melting furnace.

analyses of particulate emissions from kettle sweat are shown in Table 7.14-3.

TABLE 7.14-3. COMPOSITION OF PARTICULATE EMISSIONS FROM KETTLE SWEAT PROCESSING[a]

Component	Percent
$ZnCl_2$	14.5 - 15.3
ZnO	46.9 - 50.0
NH_4Cl	1.1 - 1.4
Al_2O_3	1.0 - 2.7
Fe_2O_3	0.3 - 0.6
PbO	0.2
H_2O (in $ZnCl_2 \cdot 4H_2O$)	7.7 - 8.1
Oxide of Mg, Sn, Ni, Si, Ca, Na	2.0
Carbonaceous material	10.0
Moisture (deliquescent)	5.2 - 10.2

[a]Reference 3.

These particulates also contain Cu, Cd, Mn and Cr. Another analysis showed the following composition: 4 percent $ZnCl_2$, 77 percent ZnO, 4 percent H_2O, 4 percent metal chlorides and 10 percent carbonaceous matter.[4] These particulates vary widely in size. Particulates from kettle sweating of residual zinc scrap had the following size distributions:

60% 0 - 10μ

17% 11 - 20μ

23% >20μ

Particulates from kettle sweating of metallic scrap had mean particle size distributions ranging from $D_{p50} = 1.1\mu$ to $D_{p50} = 1.6\mu$.[3] Emissions from a reverberatory sweat furnace had an approximate $D_{p50} = 1\mu$.

Baghouses are most commonly used to recover particulate emissions from sweating and melting. In one application on a muffle sweating

furnace, a cyclone and baghouse achieved particulate recovery efficiencies in excess of 99.7 percent.[4] In another application on a reverberatory sweating furnace, a baghouse removed 96.3 percent of the particulates, reducing the dust loading from 0.513 g/Nm^3 to 0.02 g/Nm^3.[2] Baghouses show similar efficiencies in removing particulates from exhaust gases of melting furnaces.

Crushing and screening operations are also sources of dust emissions. These particulates are composed of Zn, Al, Cu, Fe, Pb, Cd, Sn and Cr, and they can be recovered from hooded exhausts by baghouses.

The sodium carbonate leaching process produces particulate emissions of ZnO dust during the calcining operation. This dust can be recovered in baghouses, although $ZnCl_2$ in the dust may cause plugging problems.

Emissions from refining operations are mainly metallic fumes. These fume and dust particles are quite small, with sizes ranging from 0.05 - 1μ.[2] Distillation/oxidation operations emit their entire ZnO product in the exhaust gas. The ZnO has a very small particle size (0.03 to 0.5μ) and is recovered in baghouses with typical collection efficiencies of 98-99 percent.[4]

Some emissions of zinc oxide occur during galvanizing, but these emissions are small because of the bath flux cover and the relatively low temperature maintained in the bath.

Data describing the particle size distribution of fugitive emissions are unavailable. These emissions are probably similar in size to stack emissions.

References for Section 7.14

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7. W.F. Hammond, Data on Nonferrous Metallurgical Operations, Los Angeles County Air Pollution Control District, Los Angeles, CA, November 1966.

8. Assessment of Fugitive Particulate Emission Factors for Industrial Processes, EPA-450/3-78-107, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1978.

7.15 STORAGE BATTERY PRODUCTION

by Jake Summers, EPA and Pacific Environmental Services

7.15.1 Process Description

Lead/acid storage batteries are produced from lead alloy ingots and lead oxide. The latter may or may not be manufactured at the same plant (Section 7.16).

Molten lead is pumped or flows directly from pot furnaces into the molds that form the battery grids. Batches of lead sulfate paste are blended by mixing lead oxide, water, sulfuric acid, an organic expander and other constituents. Pasting machines force the stiff mixture into the interstices of the grids (which are thereafter referred to as plates).

The plates are cured and stacked in an alternating positive and negative block formation, with insulators between them. They are then fastened together either by a burning operation (welding leads to the tabs of each pair of positive and negative plates) or by a "cast on strip" process (in which molten lead is poured around and between the plate tabs). Positive and negative terminals are then welded to each element, which can go to either the wet or dry battery assembly line. Pot furnaces are used for reclaiming defective lead parts.

7.15.2 Emissions and Controls[1]

Grid casting furnaces and machines, paste mixers, plate dryers, reclaim furnaces and parts casting machines can be controlled by low- to medium-energy impingement and entrainment scrubbers. "Three process" (element stacking, lead burning and battery casting) emissions can be controlled by pulse jet fabric filters. Waste material caught in control systems is recycled to recover the lead.

Table 7.15-1. STORAGE BATTERY PRODUCTION EMISSION FACTORS[a]

EMISSION FACTOR RATING: B

Process	Particulate emission factor		Lead emission factor	
	(kg/10^3 batteries)	(lb/10^3 batteries)	(kg/10^3 batteries)	(lb/10^3 batteries)
Grid casting	0.8	1.8	0.4	0.9
Paste mixing	1.0	2.2	0.5	1.1
Lead oxide mill (baghouse outlet)	0.10	0.24	0.05	0.12
Three-process operation[b]	13.2	29.2	6.6	14.6
Lead reclaim furnace	0.70	1.54	0.35	0.77
Small parts casting	0.09	0.19	0.05	0.10
Formation	14.0[c]	32.0[c]	N/A	N/A
Storage battery production (total)	29.9	67.2	8	17.6

[a]References 2-6
[b]Stacking, lead burning and battery assembly
[c]H_2SO_4

Table 7.15-2. STORAGE BATTERY PRODUCTION CONTROL EFFICIENCIES[a]

Process	Control	Percent reduction
Storage battery production (total)	Low- to medium-energy impingement and entrainment scrubbers	85 – 90+
	Pulse jet fabric filter	95 – 99+

[a]Reference 1

References for Section 7.15

1. *Background Information in Support of the Development of Performance Standards for the Lead Additive Industry*, EPA Contract No. 68-02-2085, PEDCo-Environmental Specialists, Inc., Cincinnati, OH, January 1976.

2. *Control Techniques for Lead Air Emissions*, EPA-450/2-77-012, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1977.

3. *Screening Study To Develop Background Information and To Determine the Significance of Emissions from the Lead/Acid Battery Industry*, EPA Contract No. 68-02-0299, Vulcan-Cincinnati, Inc., Cincinnati, OH, December 1972.

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5. *Particulate and Lead Emission Measurements from Lead Oxide Plants*, EPA Contract No. 68-02-0226, Monsanto Research Corp., Dayton, OH, August 1973.

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7.16 LEAD OXIDE AND PIGMENT PRODUCTION

by Jake Summers, EPA, and Pacific Environmental Services

7.16.1 General

Lead oxide is used in the manufacture of lead/acid storage batteries (Section 7.15) and as a pigment in paints. Black oxide, which is used exclusively in storage batteries, contains 60 to 80 percent litharge (PbO) the remainder being finely divided metallic lead.[1] The major lead pigment is red lead (Pb_3O_4), which is used principally in ferrous metal protective paints. Other lead pigments include white lead and lead chromates.

Most lead oxides and many lead pigments are derived from lead monoxide (PbO) in the form of litharge, which is produced by (1) partially oxidizing lead and milling it into a powder, which is then completely oxidized in a reverberatory furnace; (2) oxidizing and stirring pig lead in a reverberatory furnace or rotary kiln; (3) running molten lead into a cupelling furnace; or (4) atomizing molten lead in a flame. The product must be cooled quickly to below 300°C (572°F) to avoid formation of red lead.[2]

Black oxide is usually produced (in the same furnace in which the litharge is made) by either the ball mill or Barton process. Cyclones and fabric filters collect the product. Red lead is produced by oxidizing litharge in a reverberatory furnace. Basic carbonate white lead production is based on the reaction of litharge with acetic acid or acetate ions. White leads other than carbonates are made either by chemical or fuming processes. Chromate pigments are generally manufactured by precipitation or calcination.

7.16.2 Emissions and Controls

Automatic shaker type fabric filters, often preceded by cyclone mechanical collectors or settling chambers, are the almost universal choice for collecting lead oxides and pigments. Where fabric filters are not appropriate, scrubbers are used, resulting in higher emissions. The ball mill and Barton processes of black oxide manufacturing recover the lead product by these two means. Collection of dust and fumes from the production of red lead is likewise an economic necessity, since particulate emissions, although small, are about 90 percent lead. Data on emissions from the production of white lead pigments are not available, but they have been estimated because of health and safety regulations. The emissions from dryer exhaust scrubbers account for over 50 percent of the total lead emitted in lead chromate production.

Table 7.16-1. LEAD OXIDE AND PIGMENT PRODUCTION EMISSION FACTORS[a]

EMISSION FACTOR RATING: B

Process	Particulate		Lead emission factor		References
	lb/ton produced	kg/10^3 kg produced	lb/ton produced	kg/10^3 kg produced	
Lead oxide production:					
Barton pot[b]	0.43-0.85	0.21-0.43	0.44	0.22	4,6,7
Calcining furnace	c	c	14.0	7.0	6
Pigment production:					
Red lead[b]	1.0[d]	0.5[d]	0.9	0.5	4,5
White lead[b]	c	c	0.55	0.28	4,5
Chrome pigments:	c	c	0.13	0.065	4,5

[a]Reference 4, pp. 4-283 and 4-287.

[b]Measured at baghouse outlet. Baghouse is considered process equipment.

[c]Data not available.

[d]Only PbO and oxygen used in red lead production, so particulate emissions assumed to be about 90% lead.

Table 7.16-2. LEAD OXIDE AND PIGMENT PRODUCTION CONTROL EFFICIENCIES

Process	Control	Percent reduction
Lead oxide and pigment production	Mechanical shaker fabric filter (preceded by dry cyclone or settling chamber)	99[a]
	Scrubber	70-95[b]

[a]Reference 3.

[b]Reference 4.

References for Section 7.16

1. E. J. Ritchie, *Lead Oxides*, Independent Battery Manufacturers Association, Inc., Largo, FL, 1974.

2. W. E. Davis, *Emissions Study of Industrial Sources of Lead Air Pollutants, 1970*, EPA Contract No. 68-02-0271, W. E. Davis and Associates, Leawood, KS, April 1973.

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5. R. P. Betz, *et al.*, *Economics of Lead Removal in Selected Industries*, EPA Contract No. 68-02-0299, Battelle Columbus Laboratories, Columbus, OH, December 1972.

6. Emission Test No. 74-PB-0-1, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1973.

7.17 MISCELLANEOUS LEAD PRODUCTS

by Jake Summers, EPA, and Pacific Environmental Services

7.17.1 Type Metal Production

7.17.1.1 General – Lead type, used primarily in the letterpress segment of the printing industry, is cast from a molten lead alloy and remelted after use. Linotype and monotype processes produce a mold, while the stereotype process produces a plate for printing. All type metal is an alloy consisting of 60 to 85 percent recovered lead, with antimony, tin and a small amount of virgin metal.

7.17.1.2 Emissions and Controls – The melting pot is the major source of emissions, containing hydrocarbons as well as lead particulates. Pouring the molten metal into the molds involves surface oxidation of the metal, possibly producing oxidized fumes, while the trimming and finishing operations emit lead particles. It is estimated that 35 percent of the total emitted particulate is lead.[1]

Approximately half of the current lead type operations control lead emissions, by about 80 percent. The other operations are uncontrolled.[2] The most frequently controlled sources are the main melting pots and drossing areas. Linotype equipment does not require controls when operated properly. Devices in current use on monotype and stereotype lines include rotoclones, wet scrubbers, fabric filters, and electrostatic precipitators, all which can be used in various combinations.

7.17.2 Can Soldering

7.17.2.1 Process Description – Side seams of cans are soldered on a machine consisting of a solder-coated roll operating in a bath of molten solder, typically containing 98 percent lead. After soldering, excess is wiped away by a rotating cloth buffer, which creates some dust (Table 7.17-1).[3]

7.17.2.2 Emissions and Controls – Hoods, exhaust ducts and mechanical cyclones (Table 7.17-2) collect the large flakes generated at the wiping station, but some dust escapes in the form of particles 20 microns or smaller, with a lead content of 3 to 38 percent. Maintaining a good flux cover is the most effective means of controlling lead emissions from the solder batch. Low energy wet collectors or fabric filters can also control lead emissions from can soldering.

7.17.3 Cable Covering

7.17.3.1 Process Description – About 90 percent of the lead cable covering produced in the United States is lead cured jacketed cables, and 10 percent is on lead sheathed cables. In preparation of the former type, an unalloyed lead cover applied in the vulcanizing treatment during the manufacture of rubber-insulated cable must be stripped from the cable and remelted.

Lead coverings are applied to insulated cable by hydraulic extrusion of solid lead around the cable. Molten lead is continuously fed into an extruder or screw press, where it solidifies as it progresses. A melting kettle supplies lead to the press.

7.17.3.2 Emissions and Controls – The melting kettle is the only source of atmospheric lead emissions, and it is generally uncontrolled.[4] Average particle size is approximately 5 microns, with a lead content of about 70 to 80 percent.[3,5]

Cable covering processes do not usually include particulate collection devices, although fabric filters, rotoclone wet collectors and dry cyclone collectors can reduce lead emissions (Table 7.17-2). Lowering and controlling the melt temperature, enclosing the melting unit and using fluxes to provide a cover on the melt can also minimize emissions.

Table 7.17-1 EMISSION FACTORS FOR MISCELLANEOUS SOURCES[a]

EMISSION FACTOR RATING: C

Process	Particulate emission factor		Lead emission factor		References
	Metric	English	Metric	English	
Type metal production	0.4 kg/10^3 kg Pb proc[b]	0.7 lb/ton Pb proc[b]	0.13 kg/10^3 kg Pb proc	0.25 lb/ton Pb proc	2,7
Can soldering	0.8 × 10^6 baseboxes prod[c]	0.9 ton/10^6 baseboxes prod[c]	160 kg/10^6 baseboxes prod[f]	0.18 ton/10^6 baseboxes prod	7
Cable covering	0.3 kg/10^3 kg Pb proc[d]	0.6 lb/ton Pb proc[d]	0.25 kg/10^3 kg Pb proc	0.5 lb/ton Pb proc	3,5,7
Metallic lead products					
Ammunition	e	e	≤0.5 kg/10^6 kg Pb proc	1.0 lb/10^3 ton Pb proc	3,7
Bearing metals	e	e	negligible	negligible	3,7
Other sources of lead	e	e	0.8 kg/10^3 kg Pb proc	1.5 lb/ton Pb proc	3,7

[a]Proc = processed; prod = produced.
[b]Calculated on the basis of 35% of the total (Reference 1).
[c]Reference 7, pp. 4-297 and 4-298.
[d]Reference 7, p. 4-301.
[e]Data not available.
[f]Basebox = 20.23 m^2 (217.8 ft^2), standard tin plate sheet area.

Table 7.17-2. CAN SOLDERING AND CABLE COVERING CONTROL EFFICIENCIES

Process	Control	Percent reduction
Can soldering	Mechanical cyclone	75 +
Cable covering	Fabric filter	99.9
	Rotoclone wet collector	75-85
	Dry cyclone collector	45 +

[a]Reference 7

7.17.4 Metallic Lead Products

7.17.4.1 General – Lead is consumed and emitted in the manufacture of ammunition, bearing metals and other lead products. Lead used in the manufacture of ammunition is melted and alloyed before it is cast, sheared, extruded, swaged or mechanically worked. Some lead is also reacted to form lead azide, a detonating agent. Lead is used in bearing manufacture by alloying it with copper, bronze, antimony and tin.

Other lead products include terne metal (a plating alloy), weights and ballasts, caulking lead, plumbing supplies, roofing materials, casting metal foil, collapsible metal tubes and sheet lead. Lead is also used for galvanizing, annealing and plating. It is usually melted and cast prior to mechanical forming operations.

7.17.4.2 Emissions and Controls – Little or no air pollution control equipment is currently used by manufacturers of metallic lead products.[6] Emissions from bearing manufacture are negligible, even without controls.[3]

References for Section 7.17

1. N. J. Kulujian, *Inspection Manual for the Enforcement of New Source Performance Standards: Portland Cement Plants*, EPA Contract No. 68-02-1355, PEDCo-Environmental Specialists, Inc., Cincinnati, OH, January 1975.

2. *Atmospheric Emissions from Lead Typesetting Operation Screening Study*, EPA Contract No. 68-02-2085, PEDCo-Environmental Specialists, Inc., Cincinnati, OH, January 1976.

3. W. E. Davis, *Emissions Study of Industrial Sources of Lead Air Pollutants, 1970*, EPA Contract No. 68-02-0271, W. E. Davis Associates, Leawood, KS, April 1973.

4. R. P. Betz, *et al.*, *Economics of Lead Removal in Selected Industries*, EPA Contract No. 68-02-0611, Battelle Columbus Laboratories, Columbus, OH, August 1973.

5. E. P. Shea, *Emissions from Cable Covering Facility*, EPA Contract No. 68-02-0228, Midwest Research Institute, Kansas City, MO, June 1973.

6. *Mineral Industry Surveys: Lead Industry in May 1976*, Bureau of Mines, U.S. Department of the Interior, Washington, DC, August 1976.

7. *Control Techniques for Lead Air Emissions*, EPA-450/2-77-012, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1977.

7.18 LEADBEARING ORE CRUSHING AND GRINDING

by Jake Summers, EPA, and Pacific Environmental Services

7.18.1 Process Description

Lead and zinc ores are normally deep mined, whereas copper ores are open pit mined. Lead, zinc and copper are usually found together (in varying percentages) in combination with sulfur and/or oxygen.

In underground mines, the ore is disintegrated by percussive drilling machines, run through a primary crusher, and then conveyed to the surface. In open pit mines, ore and gangue are loosened and pulverized by explosives, scooped up by mechanical equipment, and transported to the concentrator.

Standard crushers, screens, and rod and ball mills classify and reduce the ore to powders in the 65 to 325 mesh range. The finely divided particles are separated from the gangue and are concentrated in a liquid medium by gravity and/or selective flotation, then cleaned, thickened and filtered. The concentrate is dried prior to shipment to the smelter.

7.18.2 Emissions and Controls

Lead emissions are basically fugitive, caused by drilling, blasting, loading, conveying, screening, unloading, crushing and grinding. The primary means of control are good mining techniques and equipment maintenance. These practices include enclosing the truck loading operation, wetting or covering truck loads and stored concentrates, paving the road from mine to concentrator, sprinkling the unloading area, and preventing leaks in the crushing and griding enclosures. Cyclones and fabric filters can be used in the milling operations.

Particulate and lead emission factors for lead ore crushing and materials handling operations are given in Table 7.18-1. Lead emissions from the mining and milling of copper ores are negligible.

Table 7.18-1. EMISSION FACTORS FOR ORE CRUSHING AND GRINDING

EMISSION FACTOR RATING: B

Type of ore	Particulate emission factor[a]		Lead emission factor[b]	
	lb/ton processed	kg/10^3 kg processed	lb/ton processed	kg/10^3 kg processed
Pb[c]	6.0	3.0	0.3	0.15
Zn	6.0	3.0	0.012	0.006
Cu	6.4	3.2	0.012	0.006
Pb-Zn	6.0	3.0	0.12	0.06
Cu-Pb	6.4	3.2	0.12	0.06
Cu-Zn	6.4	3.2	0.012	0.006
Cu-Pb-Zn	6.4	3.2	0.12	0.06

[a]Reference 1, pp. 4-39

[b]References 1-5

[c]Refer to Section 7.6

References for Section 7.18

1. *Control Techniques for Lead Air Emissions*, EPA-450/2-77-012, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1977.

2. W. E. Davis, *Emissions Study of Industrial Sources of Lead Air Pollutants, 1970*, EPA Contract No. 68-02-0271, W. E. Davis and Associates, Leawood, KS, April 1973.

3. *Environmental Assessment of the Domestic Primary Copper, Lead, and Zinc Industry*, EPA Contract No. 68-02-1321, PEDCO-Environmental Specialists, Inc., Cincinnati, OH, September 1976.

4. Communication with Mr. J. Patrick Ryan, Bureau of Mines, U. S. Department of the Interior, Washington, DC, September 9, 1976.

5. B. G. Wixson and J. C. Jennett, "The New Lead Belt in the Forested Ozarks of Missouri", *Environmental Science and Technology*, *9(13)*:1128-1133, December 1975.