SUPPLEMENT NO. 11
FOR

COMPILATION
OF AIR POLLUTANT
EMISSION FACTORS,
THIRD EDITION
(INCLUDING SUPPLEMENTS 1-7)

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

October 1980

Publication No. AP-42

INSTRUCTIONS FOR INSERTING SUPPLEMENT 11

INTO AP-42

Pages iii through v replace same. New Contents.

Pages vii and viii replace same. New Publications In Series.

Page 2.0-1 replaces p. 2-1. Editorial Changes.

Pages 2.1-1 through 2.1-5 replace same. Editorial Changes.

Pages 5.8-3 and 5.8-4 replace same. Editorial Changes.

Pages 5.9-1 through 5.9-6 replace pp. 5.9-1 through 5.9-4. Major Revision.

Add pages 5.23-1 through 5.23-4. New Section.

Add pages 5.24-1 through 5.24-5. New Section.

Pages 6.5-1 and 6.5-2 replace same. Editorial Changes.

Pages 6.10.1-1 through 6.10.1-4,   )
Pages 6.10.2-1 through 6.10.2-5 and)
Pages 6.10.3-1 through 6.10.3-4   ) all replace pp. 6.10-1 through
                                       6.10-4. New Subsections.

Pages 7.2-1 through 7.2-4 replace pp. 7.2-1 through 7.2-3. Major Revision.

Add pages 7.3-9 and 7.3-10. Lead Emission Factors.

Pages 7.5-1 through 7.5-12 replace pp. 7.5-1 through 7.5-6. Major Revision.

Pages 7.11-1 through 7.11-9 replace pp. 7.11-1 through 7.11-4. Major Revision.

Pages 7.15-1 and 7.15-2 replace same. Minor Correction.

Pages 9.1-9 through 9.1-15 replace pp. 9.1-9 through 9.1-13. Major Revision.

Pages E-3 and E-4 replace same. Minor Correction.

Pages a-1 and a-2 replace same. New Technical Report Data Sheet.

CONTENTS

PUBLICATIONS IN SERIES

PUBLICATIONS IN SERIES (CONT'D)

2. SOLID WASTE DISPOSAL

As defined in the Solid Waste Disposal Act of 1965, the term "solid waste" means garbage, refuse, and other discarded solid materials, including solid-waste materials resulting from industrial, commercial, and agricultural operations, and from community activities. It includes both combustibles and noncombustibles.

Solid wastes may be classified into four general categories: urban, industrial, mineral, and agricultural. Although urban wastes represent only a relatively small part of the total solid wastes produced, this category has a large potential for air pollution since in heavily populated areas solid waste is often burned to reduce the bulk of material requiring final disposal [1] The following discussion will be limited to the urban and industrial waste categories.

An average of 5.5 pounds (2.5 kilograms) of urban refuse and garbage is collected per capita per day in the United States.[2] This figure does not include uncollected urban and industrial wastes that are disposed of by other means. Together, uncollected urban and industrial wastes contribute at least 4.5 pounds (2.0 kilograms) per capita per day. The total gives a conservative per capita generation rate of 10 pounds (4.5 kilograms) per day of urban and industrial wastes. Approximately 50 percent of all the urban and industrial waste generated in the United States is burned, using a wide variety of combustion methods with both enclosed and open burning[3]. Atmospheric emissions, both gaseous and particulate, result from refuse disposal operations that use combustion to reduce the quantity of refuse. Emissions from these combustion processes cover a wide range because of their dependence upon the refuse burned, the method of combustion or incineration, and other factors. Because of the large number of variables involved, it is not possible, in general, to delineate when a higher or lower emission factor, or an intermediate value should be used. For this reason, an average emission factor has been presented.

References

1. Solid Waste - It Will Not Go Away. League of Women Voters of the United States. Publication Number 675. April 1971.

2. Black, R.J., H.L. Hickman, Jr., A.J. Klee, A.J. Muchick, and R.D. Vaughan. The National Solid Waste Survey: An Interim Report. Public Health Service, Environmental Control Administration. Rockville, Md. 1968.

3. Nationwide Inventory of Air Pollutant Emissions, 1968. U.S. DHEW, PHS, EHS, National Air Pollution Control Administration. Raleigh, N.C. Publication Number AP-73. August 1970.

2.1 REFUSE INCINERATION

2.1.1 Process Description[1-4]

The most common types of incinerators consist of a refractory-lined chamber with a grate upon which refuse is burned. In some newer incinerators water-walled furnaces are used. Combustion products are formed by heating and burning of refuse on the grate. In most cases, since insufficient underfire (undergrate) air is provided to enable complete combustion, additional over-fire air is admitted above the burning waste to promote complete gas-phase combustion. In multiple-chamber incinerators, gases from the primary chamber flow to a small secondary mixing chamber where more air is admitted, and more complete oxidation occurs. As much as 300 percent excess air may be supplied in order to promote oxidation of combustibles. Auxiliary burners are sometimes installed in the mixing chamber to increase the combustion temperature. Many small-size incinerators are single-chamber units in which gases are vented from the primary combustion chamber directly into the exhaust stack. Single-chamber incinerators of this type do not meet modern air pollution codes.

2.1.2 Definitions of Incinerator Categories[1]

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

1. *Municipal incinerators* — Multiple-chamber units often have capacities greater than 50 tons (45.3 MT) per day and are usually equipped with automatic charging mechanisms, temperature controls, and movable grate systems. Municipal incinerators are also usually equipped with some type of particulate control device, such as a spray chamber or electrostatic precipitator.

2. *Industrial/commercial incinerators* — The capacities of these units cover a wide range, generally between 50 and 4,000 pounds (22.7 and 1,800 kilograms) per hour. Of either single- or multiple-chamber design, these units are often manually charged and intermittently operated. Some industrial incinerators are similar to municipal incinerators in size and design. Better designed emission control systems include gas-fired afterburners or scrubbing, or both.

3. *Trench incinerators* — A trench incinerator is designed for the combustion of wastes having relatively high heat content and low ash content. The design of the unit is simple: a U-shaped combustion chamber is formed by the sides and bottom of the pit and air is supplied from nozzles along the top of the pit. The nozzles are directed at an angle below the horizontal to provide a curtain of air across the top of the pit and to provide air for combustion in the pit. The trench incinerator is not as efficient for burning wastes as the municipal multiple-chamber unit, except where careful precautions are taken to use it for disposal of low-ash, high-heat-content refuse, and where special attention is paid to proper operation. Low construction and operating costs have resulted in the use of this incinerator to dispose of materials other than those for which it was originally designed. Emission factors for trench incinerators used to burn three such materials[7] are included in Table 2.1-1.

4. *Domestic incinerators* — This category includes incinerators marketed for residential use. Fairly simple in design, they may have single or multiple chambers and usually are equipped with an auxiliary burner to aid combustion.

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

Table 2.1-1. EMISSION FACTORS FOR REFUSE INCINERATORS WITHOUT CONTROLS[a]
EMISSION FACTOR RATING: A

Incinerator type	Particulates		Sulfur oxides[b]		Carbon monoxide		Organics[c]		Nitrogen oxides[d]	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Municipal[e]										
Multiple chamber, uncontrolled	30	15	2.5	1.25	35	17.5	1.5	0.75	3	1.5
With settling chamber and water spray system[f]	14	7	2.5	1.25	35	17.5	1.5	0.75	3	1.5
Industrial/commercial										
Multiple chamber[g]	7	3.5	2.5[h]	1.25	10	5	3	1.5	3	1.5
Single chamber[i]	15	7.5	2.5[h]	1.25	20	10	15	7.5	2	1
Trench[j]										
Wood	13	6.5	0.1[k]	0.05	NA[l]	NA	NA	NA	4	2
Rubber tires	138	69	NA	NA	NA	NA	NA	NA	NA	NA
Municipal refuse	37	18.5	2.5[h]	1.25	NA	NA	NA	NA	NA	NA
Controlled air[m]	1.4	0.7	1.5	0.75	Neg	Neg	Neg	Neg	10	5
Flue-fed single chamber[n]	30	15	0.5	0.25	20	10	15	7.5	3	1.5
Flue-fed (modified)[o,p]	6	3	0.5	0.25	10	5	3	1.5	10	5
Domestic single chamber										
Without primary burner[q]	35	17.5	0.5	0.25	300	150	100	50	1	0.5
With primary burner[r]	7	3.5	0.5	0.25	Neg	Neg	2	1	2	1
Pathological[s]	8	4	Neg	Neg	Neg	Neg	Neg	Neg	3	1.5

[a] Average factors given based on EPA procedures for incinerator stack testing.

[b] Expressed as sulfur dioxide.

[c] Expressed as methane.

[d] Expressed as nitrogen dioxide.

[e] References 5 and 8 through 14.

[f] Most municipal incinerators are equipped with at least this much control; see Table 2.1-2 for appropriate efficiencies for other controls.

[g] References 3, 5, 10, 13, and 15.

[h] Based on municipal incinerator data.

[i] References 3, 5, 10, and 15.

[j] Reference 7.

[k] Based on data for wood combustion in conical burners.

[l] Not available.

[m] Reference 9.

[n] References 3, 10, 11, 13, 15, and 16.

[o] With afterburners and draft controls.

[p] References 3, 11, and 15.

[q] References 5 and 10.

[r] Reference 5.

[s] References 3 and 9.

6. *Pathological incinerators* — These are incinerators used to dispose of animal remains and other organic material of high moisture content. Generally, these units are in a size range of 50 to 100 pounds (22.7 to 45.4 kilograms) per hour. Wastes are burned on the hearth in the combustion chamber. The units are equipped with combustion controls and afterburners to ensure good combustion and minimal emissions.

7. *Controlled air incinerators* — These units operate on a controlled combustion principle in which the waste is burned in the absence of sufficient oxygen for complete combustion in the main chamber. This process generates a highly combustible gas mixture that is then burned with excess air in a secondary chamber, resulting in efficient combustion. These units are usually equipped with automatic charging mechanisms and are characterized by the high effluent temperatures reached at the exit of the incinerators.

2.1.3 Emissions and Controls[1]

Operating conditions, refuse composition, and basic incinerator design have a pronounced effect on emissions. The manner in which air is supplied to the combustion chamber or chambers has, among all the parameters, the greatest effect on the quantity of particulate emissions. Air may be introduced from beneath the chamber, from the side, or from the top of the combustion area. As underfire air is increased, and increase in fly-ash emissions occurs. Erratic refuse charging causes a disruption of the combustion bed and a subsequent release of large quantities of particulates. Large quantities of uncombusted particulate matter and carbon monoxide are also emitted for an extended period after charging of batch-fed units because of interruptions in the combustion process. In continuously fed units, furnace particulate emissions are strongly dependent upon grate type. The use of rotary kiln and reciprocating grates results in higher particulate emissions than the use of rocking or traveling grates.[14] Emissions of oxides of sulfur are dependent on the sulfur content of the refuse. Carbon monoxide and unburned hydrocarbon emissions may be significant and are caused by poor combustion resulting from improper incinerator design or operating conditions. Nitrogen oxide emissions increase with an increase in the temperature of the combustion zone, an increase in the residence time in the combustion zone before quenching, and an increase in the excess air rates to the point where dilution cooling overcomes the effect of increased oxygen concentration.[14]

Hydrochloric acid emissions were found to approximate 1.0 lb/ton of feed in early work[14] and 1.8 lb/ton in more recent work.[23] The level can be sharply increased in areas where large quantities of plastics are consumed. Methane levels found in recent work[22] range from 0.04 to 0.4 lb/ton of feed.

Table 2.1-2 lists the relative collection efficiencies of particulate control equipment used for municipal incinerators. This control equipment has little effect on gaseous emissions. Table 2.1-1 summarizes the uncontrolled emission factors for the various types of incinerators previously discussed.

Table 2.1-2. COLLECTION EFFICIENCIES FOR VARIOUS TYPES OF MUNICIPAL INCINERATION PARTICULATE CONTROL SYSTEMS[a]

Type of system	Efficiency, %
Settling chamber	0 to 30
Settling chamber and water spray	30 to 60
Wetted baffles	60
Mechanical collector	30 to 80
Scrubber	80 to 95
Electrostatic precipitator	90 to 96
Fabric filter	97 to 99

[a]References 3, 5, 6, and 17 through 21.

References for Section 2.1

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

2. Control Techniques for Carbon Monoxide Emissions from Stationary Sources. U.S. DHEW, PHS, EHS, National Air Pollution Control Administration. Washington, D.C. Publication Number AP-65. March 1970.

3. Danielson, J.A. (ed.). Air Pollution Engineering Manual. U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio, Publication Number 999-AP-40. 1967. p. 413-503.

4. De Marco, J. et al. Incinerator Guidelines 1969. U.S. DHEW, Public Health Service. Cincinnati, Ohio. SW-13TS. 1969. p. 176.

5. Kanter, C. V., R. G. Lunche, and A. P. Fururich. Techniques for Testing Air Contaminants from Combustion Sources. J. Air Pol. Control Assoc. 6(4): 191-199. February 1957.

6. Jens, W. and F.R. Rehm. Municipal Incineration and Air Pollution Control. 1966 National Incinerator Conference, American Society of Mechnical Engineers. New York, May 1966.

7. Burkle, J.O., J.A. Dorsey, and B. T. Riley. The Effects of Operating Variables and Refuse Types on Emissions from a Pilot-Scale Trench Incinerator. Proceedings of the 1968 Incinerator Conference. American Society of Mechanical Engineers. New York. May 1968. p. 34-41.

8. Fernandes, J. H. Incinerator Air Pollution Control. Proceedings of 1968 National Incinerator Conference, American Society of Mechanical Engineers. New York. May 1968. p. 111.

9. Unpublished data on incinerator testing. U.S. DHEW, PHS, EHS, National Air Pollution Control Administration. Durham, N. C. 1970.

10. Stear, J. L. Municipal Incineration: A Review of Literature. Environmental Protection Agency, Office of Air Programs. Research Triangle Park, N.C. OAP Publication Number AP-79. June 1971.

11. Kaiser, E.R. et al. Modifications to Reduce Emissions from a Flue-fed Incinerator. New York University. College of Engineering. Report Number 552.2. June 1959. p. 40 and 49.

12. Unpublished data on incinerator emissions. U.S. DHEW, PHS, Bureau of Solid Waste Management. Cincinnati, Ohio. 1969.

13. Kaiser, E. R. Refuse Reduction Processes in Proceedings of Surgeon General's Conference on Solid Waste Management. Public Health Service. Washington, D.C. PHS Report Number 1729. July 10-20, 1967.

14. Nissen, Walter R. Systems Study of Air Pollution from Municipal Incineration. Arthur D. Little, Inc. Cambridge, Mass. Prepared for National Air Pollution Control Administration, Durham, N.C., under the Contract Number CPA-22-69-23. March 1970.

15. Unpublished source test data on incinerators. Resources Research, Incorporated. Reston, Virginia. 1966-1969.

16. Communication between Resources Research, Incorporated, Reston, Virginia, and Maryland State Department of Health, Division of Air Quality Control, Baltimore, Md. 1969.

17. Rehm, F. R. Incinerator Testing and Test Results. J. Air Pol. Control Assoc. 6:199-204. February 1957.

18. Stenburg, R. L. et al. Field Evaluation of Combustion Air Effects on Atmospheric Emissions from Municipal Incinerations. J. Air Pol. Control Assoc. 12:83-89. February 1962.

19. Smauder, E. E. Problems of Municipal Incineration. (Presented at First Meeting of Air Pollution Control Association, West Coast Section, Los Angeles, California. March 1957.)

20. Gerstle, R. W. Unpublished data: revision of emission factors based on recent stack tests. U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. 1967.

21. A Field Study of Performance of Three Municipal Incinerators. University of California, Berkeley, Technical Bulletin. 6:41, November 1957.

22. Driscol, J. et al. Evaluation of Monitoring Methods and Instrumation for Hydrocarbons and Carbon Monoxide in Stationary Source Emissions. Publication No. EPA-R2-72-106. November 1977.

23. Jahnke, J. A., J. L. Chaney, R. Rollins, and C. R. Fortune. A Reasearch Study of Gaseous Emissions from a Municipal Incinerator. J. Air Pollut. Contr. Assoc. 27:747-753, August 1977.
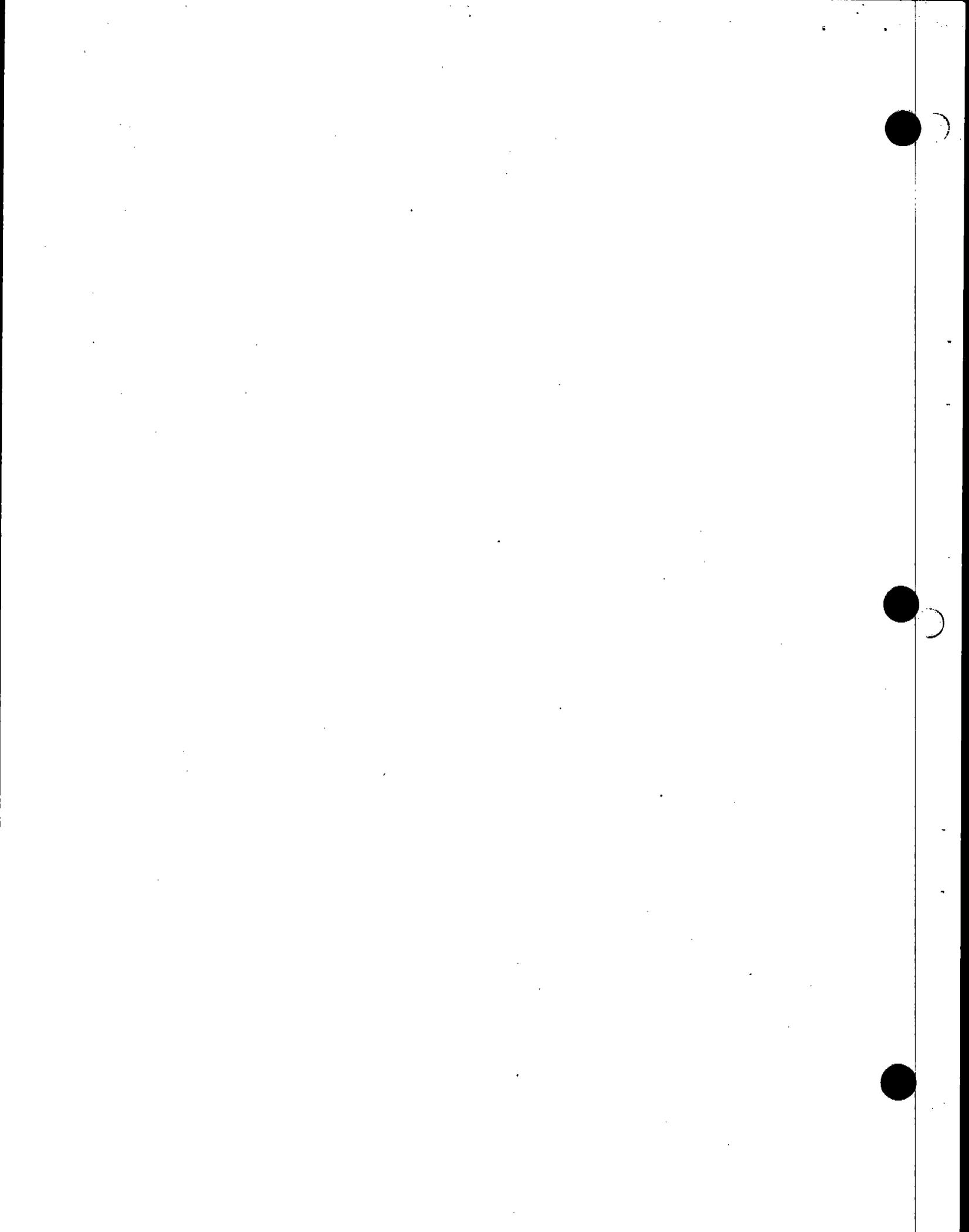
Table 5.8-1. EMISSION FACTORS FOR HYDROFLUORIC ACID MANUFACTURE

Type of Operation and Control	Control efficiency (%)	Gases lb/ton acid	Gases kg/MT acid	Particulates (Spar) lb/ton Fluorospar	Particulates (Spar) kg/MT Fluorospar	Emission Factor Rating
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)	12.5 (HF)			
		30.0 (SiF_4)	15.0 (SiF_4)			D
		45.0 (SO_2)	22.5 (SO_2)			
Caustic scrubber	99	0.2 (HF)	0.1 (HF)			
		0.3 (SiF_4)	0.2 (SiF_4)			
		0.5 (SO_2)	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:

$$4NH_3 \quad + \quad 5O_2 \quad \rightarrow \quad 4NO \quad + \quad 6H_2O \tag{1}$$

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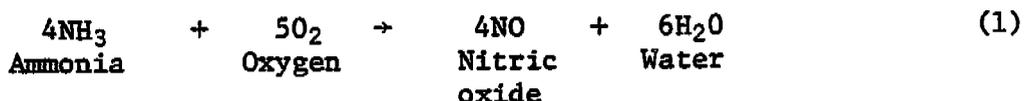
After the process stream is cooled to 100°F (38°C) or less by passage through a cooler/condenser, the nitric oxide reacts with residual oxygen to form nitrogen dioxide:

$$2NO \quad + \quad O_2 \quad \rightarrow \quad 2NO_2 \quad \leftrightarrows \quad N_2O_4 \tag{2}$$

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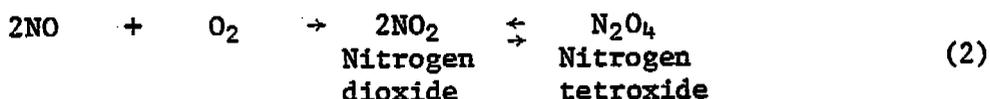
Finally, the gases are introduced into a bubble cap plate absorption column for contact with a countercurrent stream of water. The exothermic reation that occurs is:

$$3NO_2 \quad + \quad H_2O \quad \rightarrow \quad 2HNO_3 \quad + \quad NO \tag{3}$$
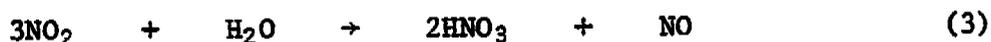
The production of nitric oxide in Reaction 3 necessitates the intro-duction of a secondary air stream into the column to oxidize it into nitrogen dioxide, thereby perpetuating the absorption operation.

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 ascend-ing vapors. Concentrated nitric acid leaves the top of the column as 98
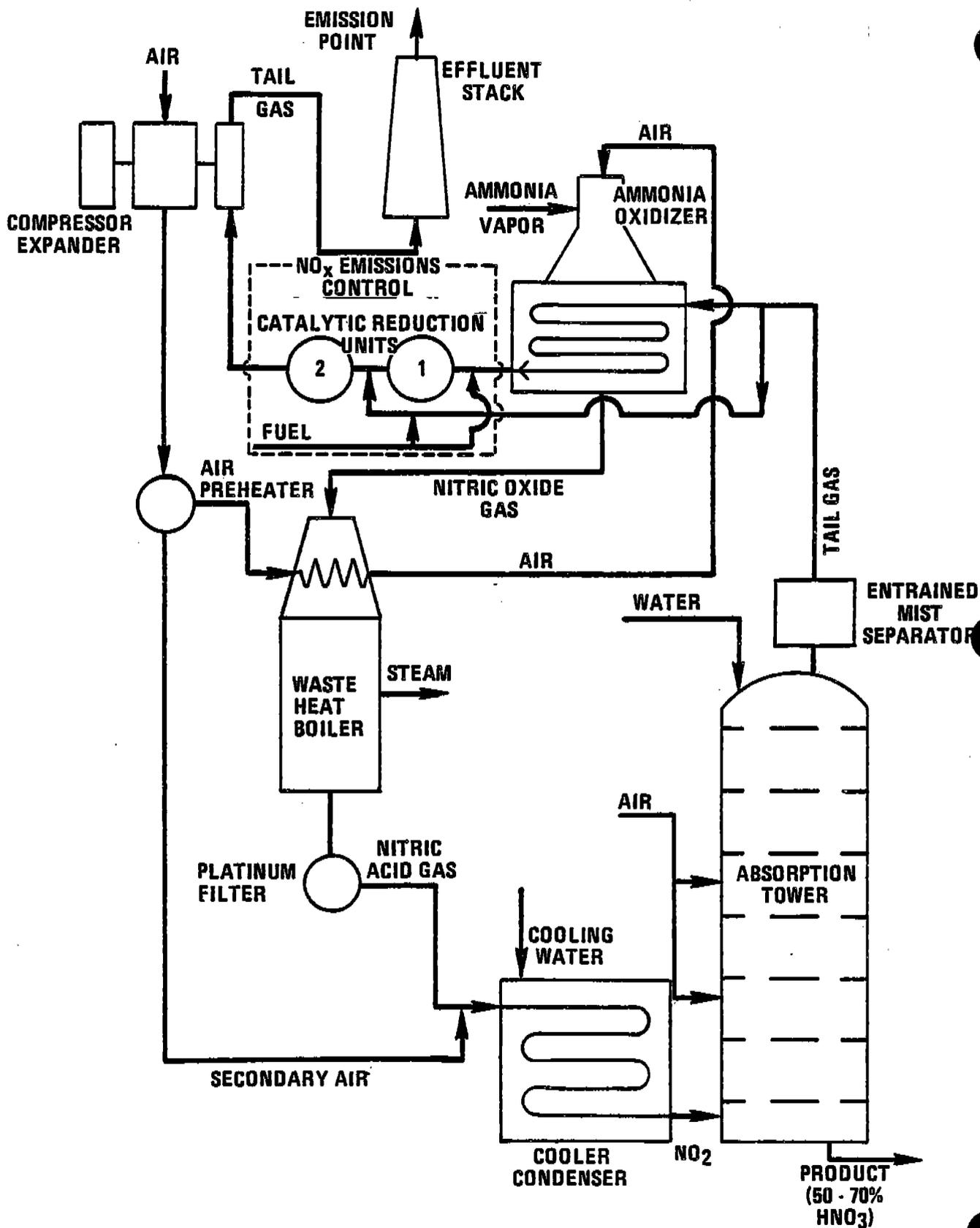
Figure 5.9-1. Flow diagram of typical nitric acid plant using pressure process (high strength acid unit not shown).

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	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.

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.

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.

5.23 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. <u>Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products</u>, 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.

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

Benzene	Oxygen	$\xrightarrow{\text{Catalyst}}$	Maleic anhydride	Water	Carbon dioxide
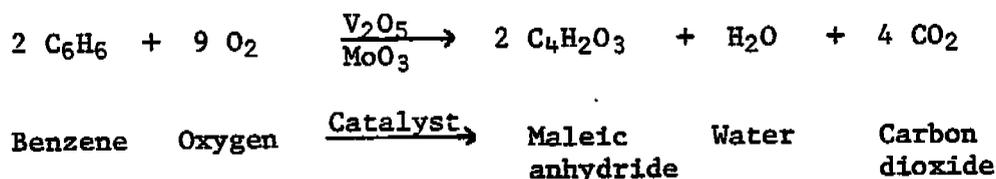
Vaporized benzene and air are mixed and heated before entering the tubular reactor. Inside the reactor, the benzene/air mixture is reacted in the presence of a catalyst which contains approximately 70 percent vanadium pentoxide (V_2O_5), with usually 25 to 30 percent molybdenum trioxide (MoO_3), forming 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.
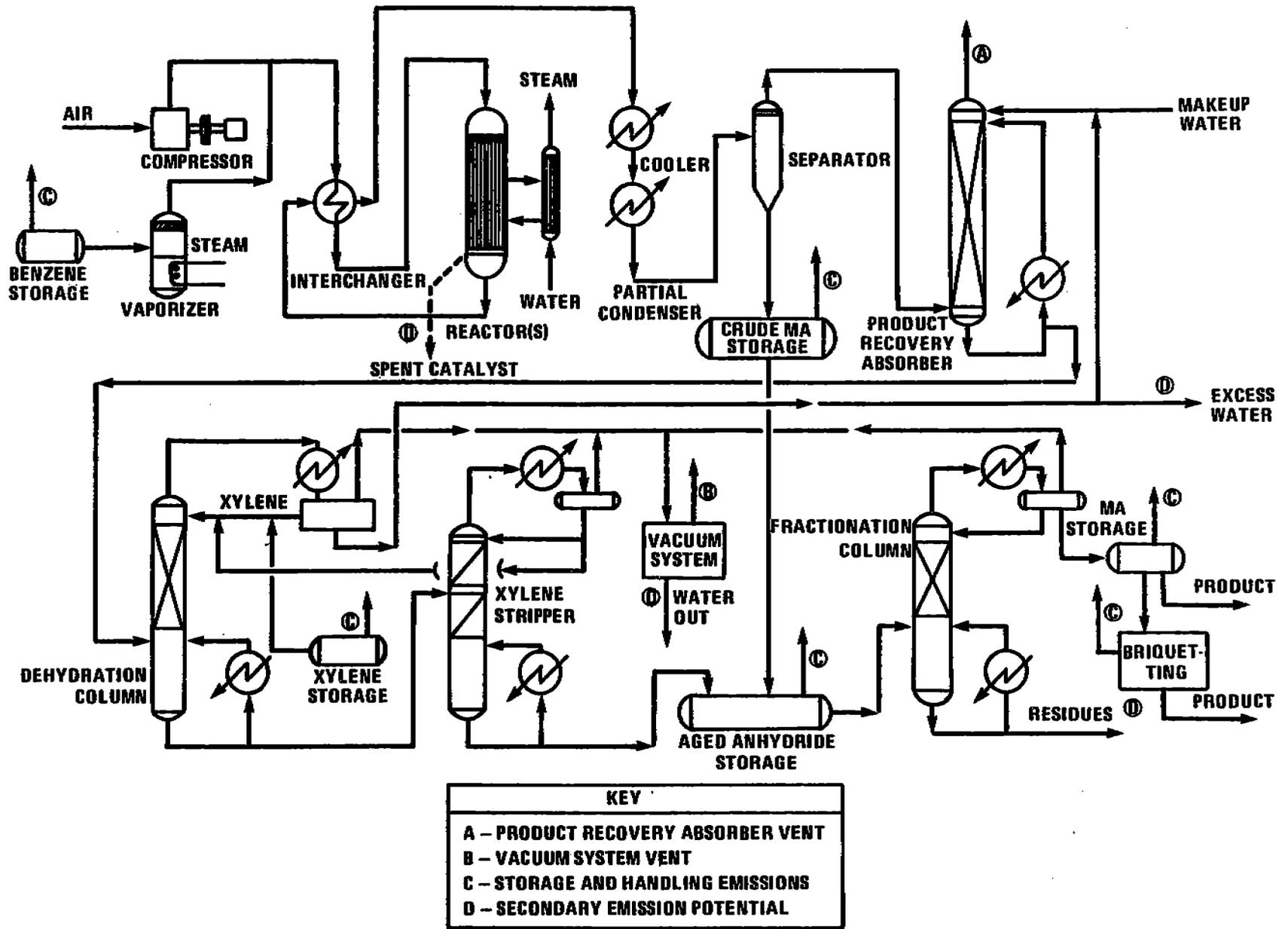
Figure 5.24-1. Process flow diagram for uncontrolled model plant.

KEY

A — PRODUCT RECOVERY ABSORBER VENT
B — VACUUM SYSTEM VENT
C — STORAGE AND HANDLING EMISSIONS
D — SECONDARY EMISSION POTENTIAL

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 heavy 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

1.   B. Dmuchovsky and J. E. Franz, "Maleic Anhydride", _Kirk-Othmer Encyclopedia of Chemical Technology_, Volume 12, John Wiley and Sons, Inc., New York, NY, 1967, pp. 819-837.

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.
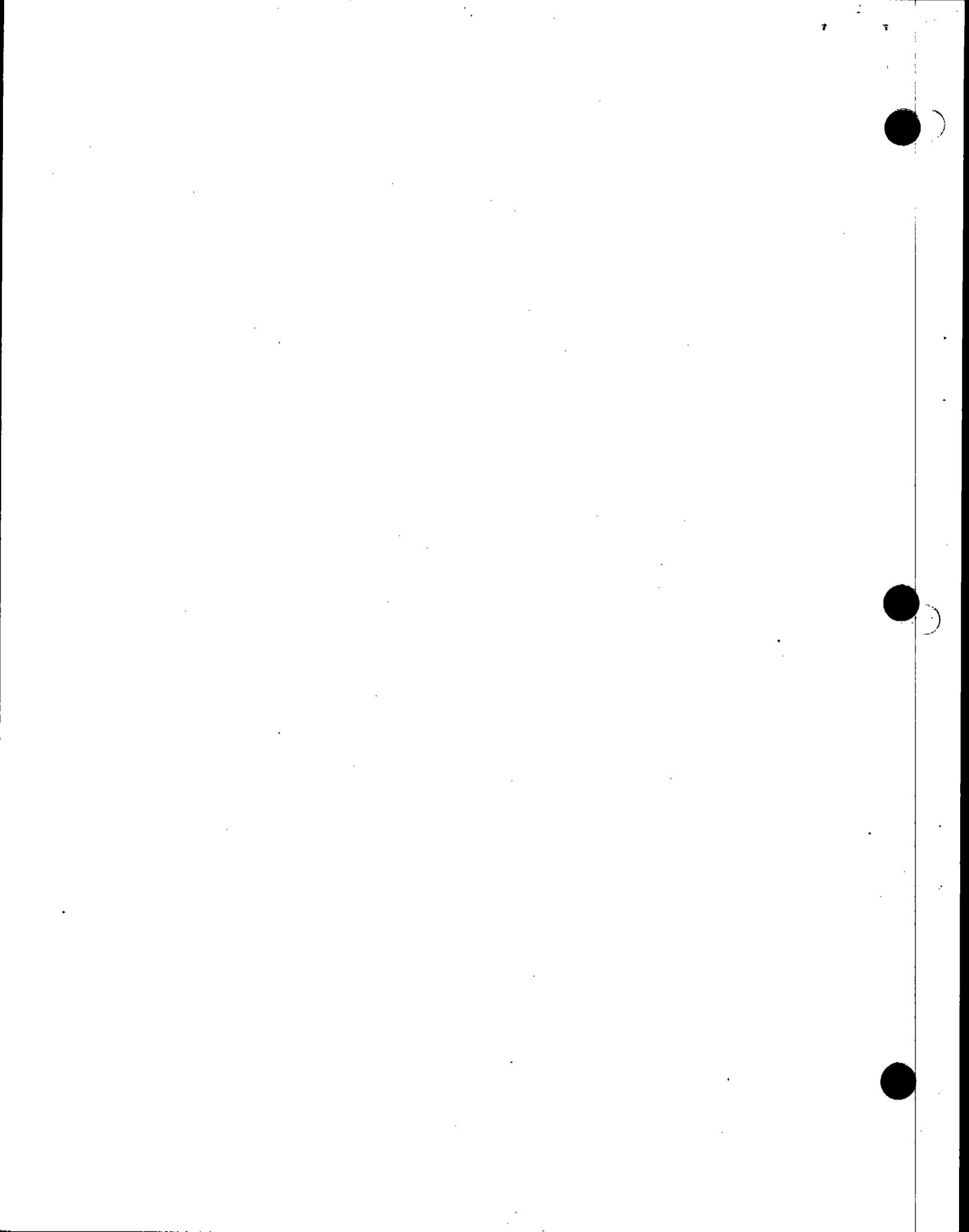
6.5 FERMENTATION

6.5.1 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.

As the following Subsection 6.5.2, Wine Making, implies, the FERMENTATION Section is being expanded as new information is obtained.

Except for the Wine Making information, Table 6.5-1 remains valid until further notice.

2/80

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]	3	1.5	—	—
Drying spent grains, etc.[a]	5	2.5	NA[b]	NA
Whiskey				
Grain handling[a]	3	1.5	—	—
Drying spent grains, etc.[a]	5	2.5	NA	NA
Aging	—	—	10[c]	0.024[d]
Wine				

[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.

6.10 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 fertil-
izer 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 oper-
ations 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.
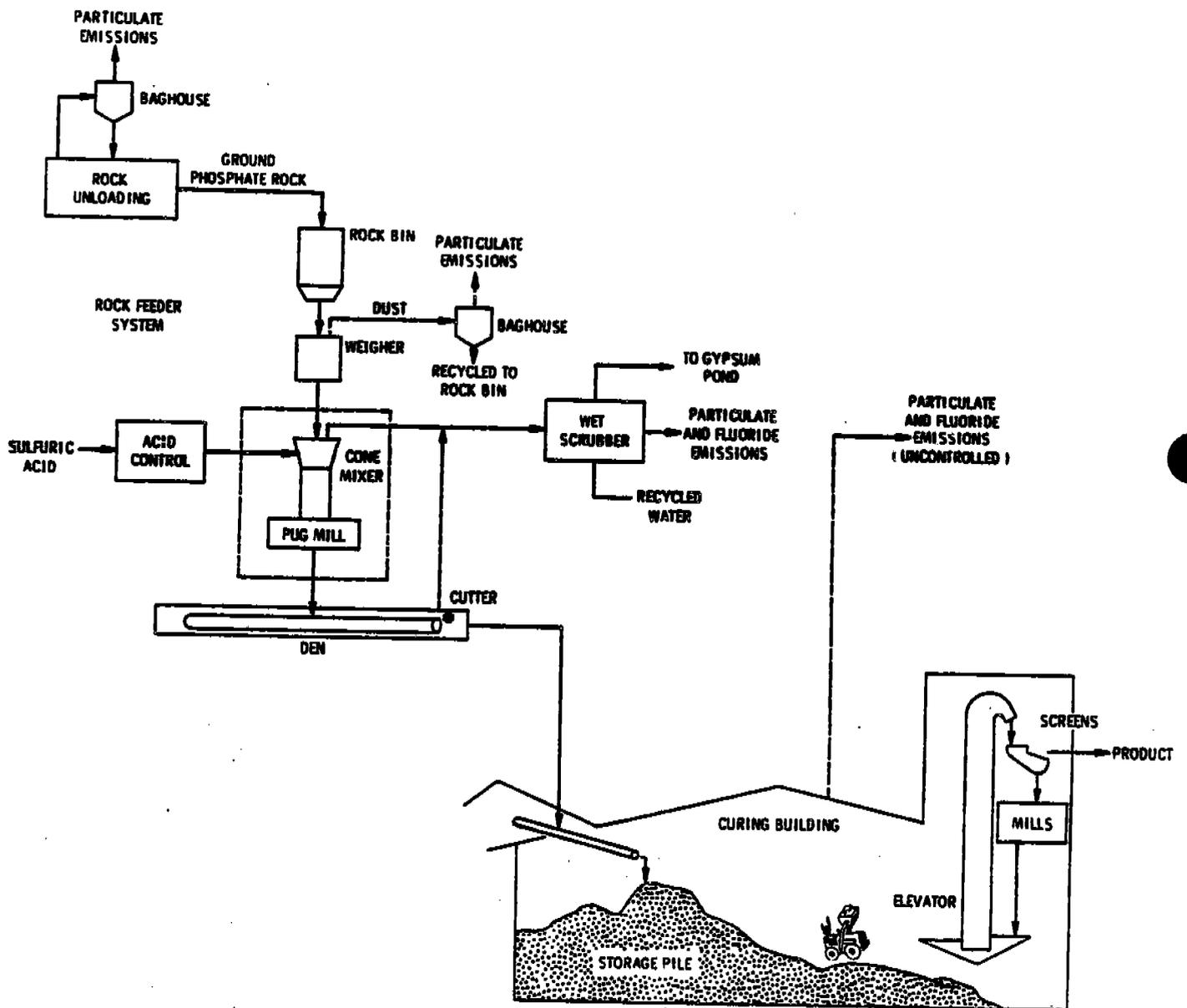
Figure 6.10.1-1. Normal superphosphate process flow diagram.

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 super-phosphate. 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 trans-ports the material along the trough. The basic rotary drum granulator consists of an open ended slightly inclined rotary cylinder, with retain-ing 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 recircu-lated to the screen, and undersize particles are recycled to the granu-lator. 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.
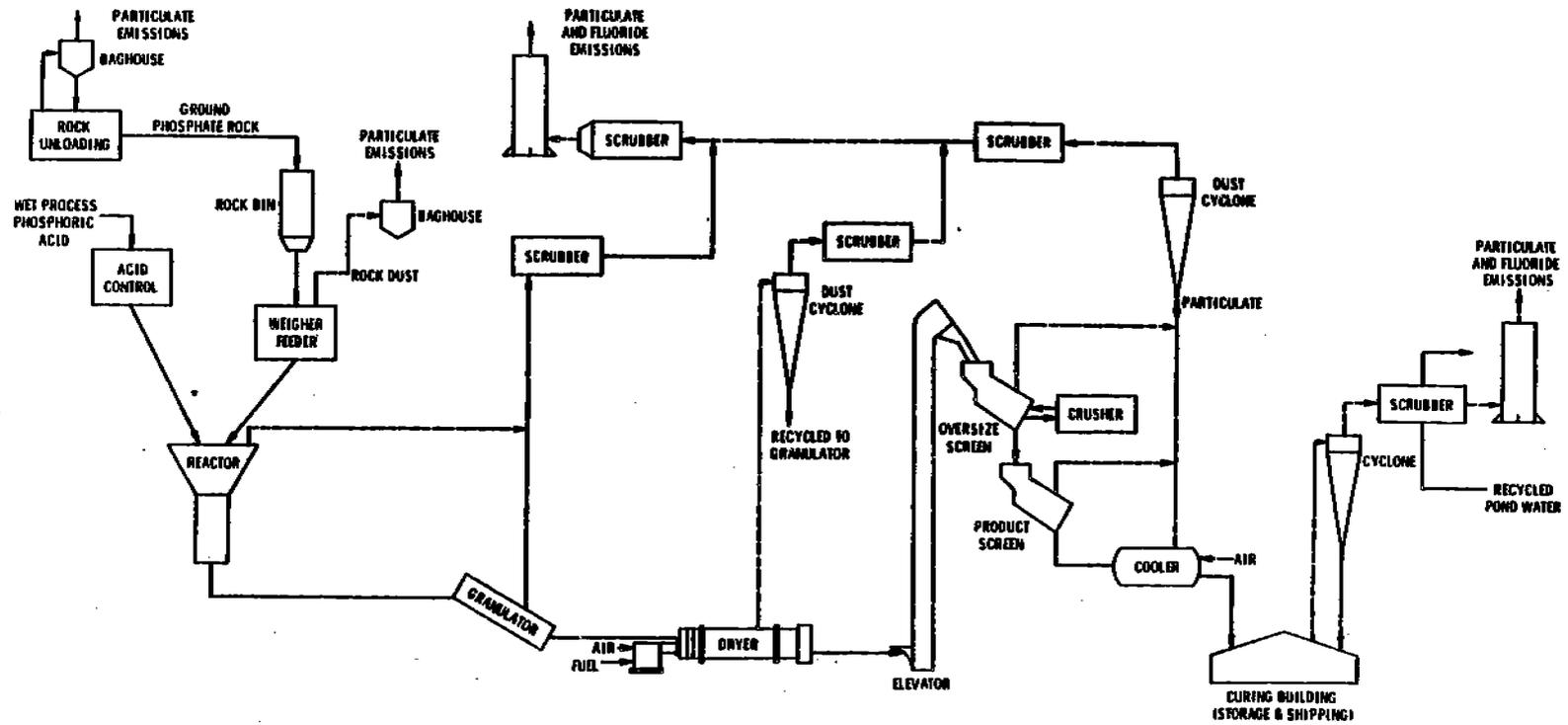
Figure 6.10.2-1. Dorr-Oliver process flow diagram for granular triple superphosphate production.

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	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.
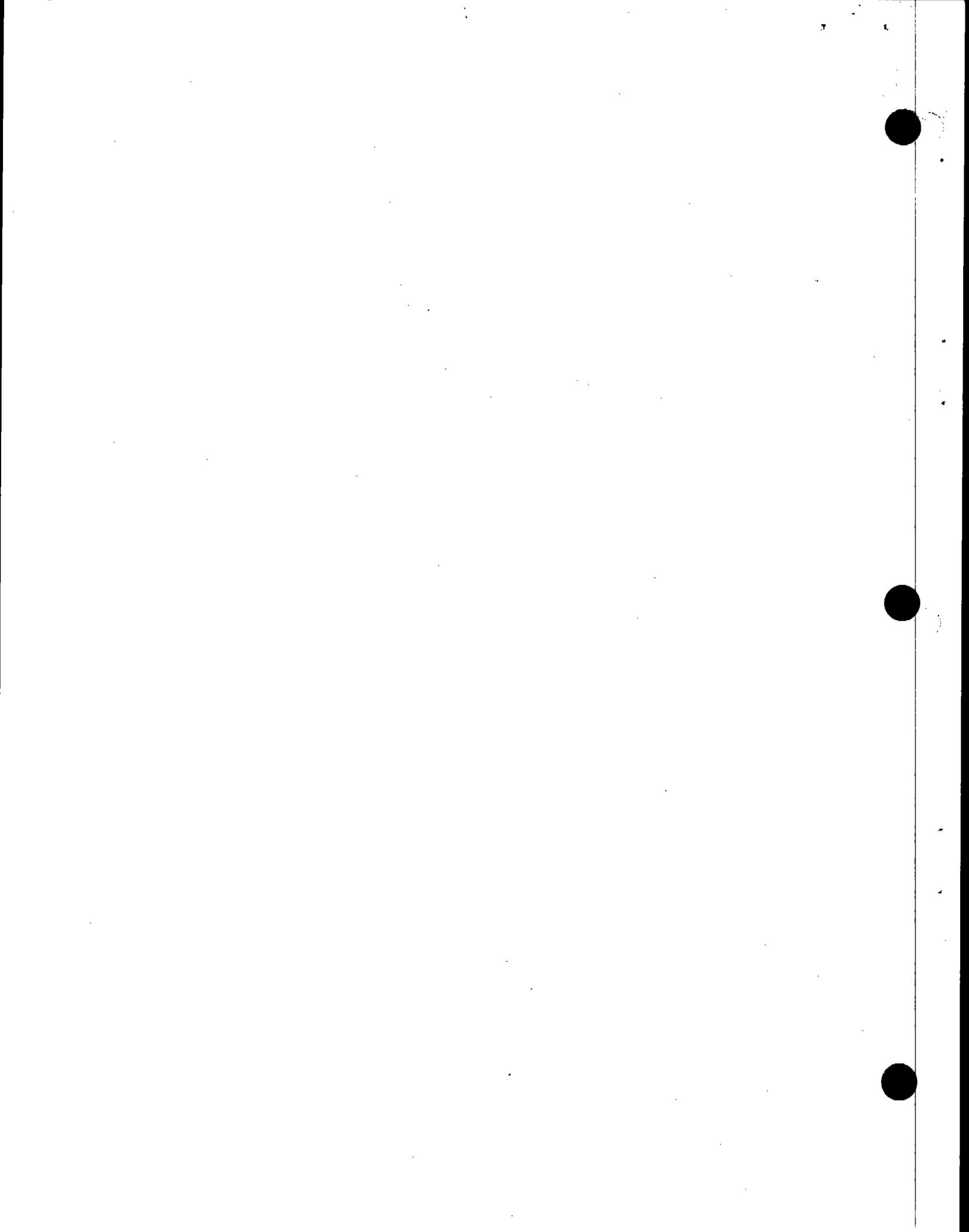
6.10.3 AMMONIUM PHOSPHATES

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.

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

Larry car

Pusher ram

Coke oven

Regenerator

Quench car

Flue
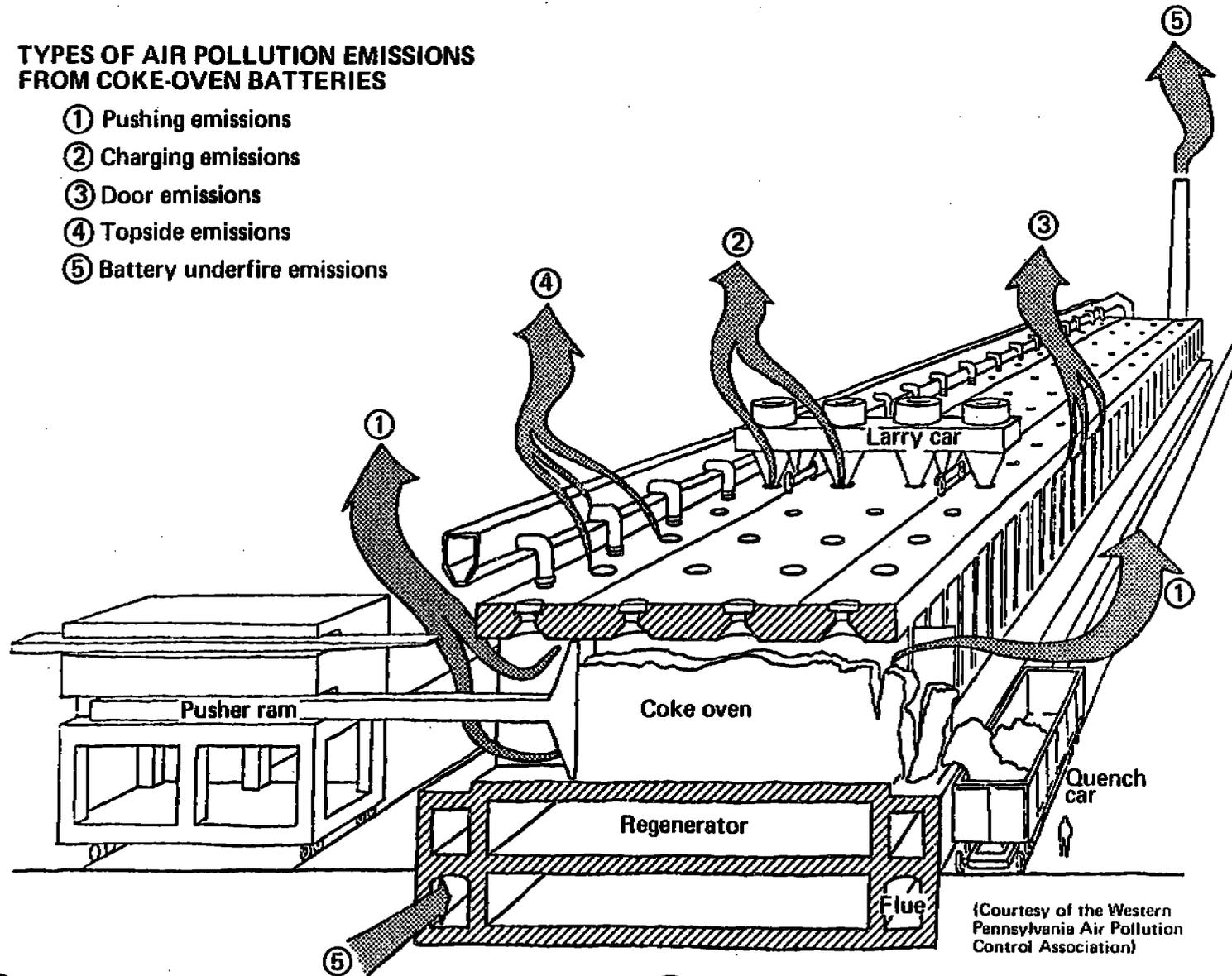
(Courtesy of the Western Pennsylvania Air Pollution Control Association)

Table 7.2-1. EMISSION FACTORS FOR COKE MANUFACTURE[a]
EMISSION FACTOR RATING: D (except particulates)

Type of Operation	Particulates[b] lb/ton	kg/MT	Emission Factor Rating	Sulfur Dioxide[c] lb/ton	kg/MT	Carbon Monoxide[c] lb/ton	kg/MT	Volatile Organics[c,d] lb/ton	kg/MT	Nitrogen Oxides (NO_x)[c] lb/ton	kg/MT	Ammonia[c] lb/ton	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

1. Particulate Emission Factors Applicable to the Iron and Steel Industry, EPA-450/4-79-028, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1979.

2. Air Pollution by Coking Plants, United Nations Report: Economic Commission for Europe, ST/ECE/Coal/26, 1968.

3. R. W. Fullerton, "Impingement Baffles To Reduce Emissions from Coke Quenching", Journal of the Air Pollution Control Association, 17:807-809, December 1967.

4. J. Varga and H. W. Lownie, Jr., Final Technological Report on: A Systems Analysis Study of the Integrated Iron and Steel Industry, HEW Contract No. PH 22-68-65, Battelle Memorial Institute, Columbus, OH, May 1969.

7.3 PRIMARY COPPER SMELTING

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, <u>Copper Smelters: Emission Test Report –
    Lead Emissions</u>, EMB Report 79 CUS-14, U. S. Environmental Protection
    Agency, Research Triangle Park, NC, September 1979.

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 furnace. 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,
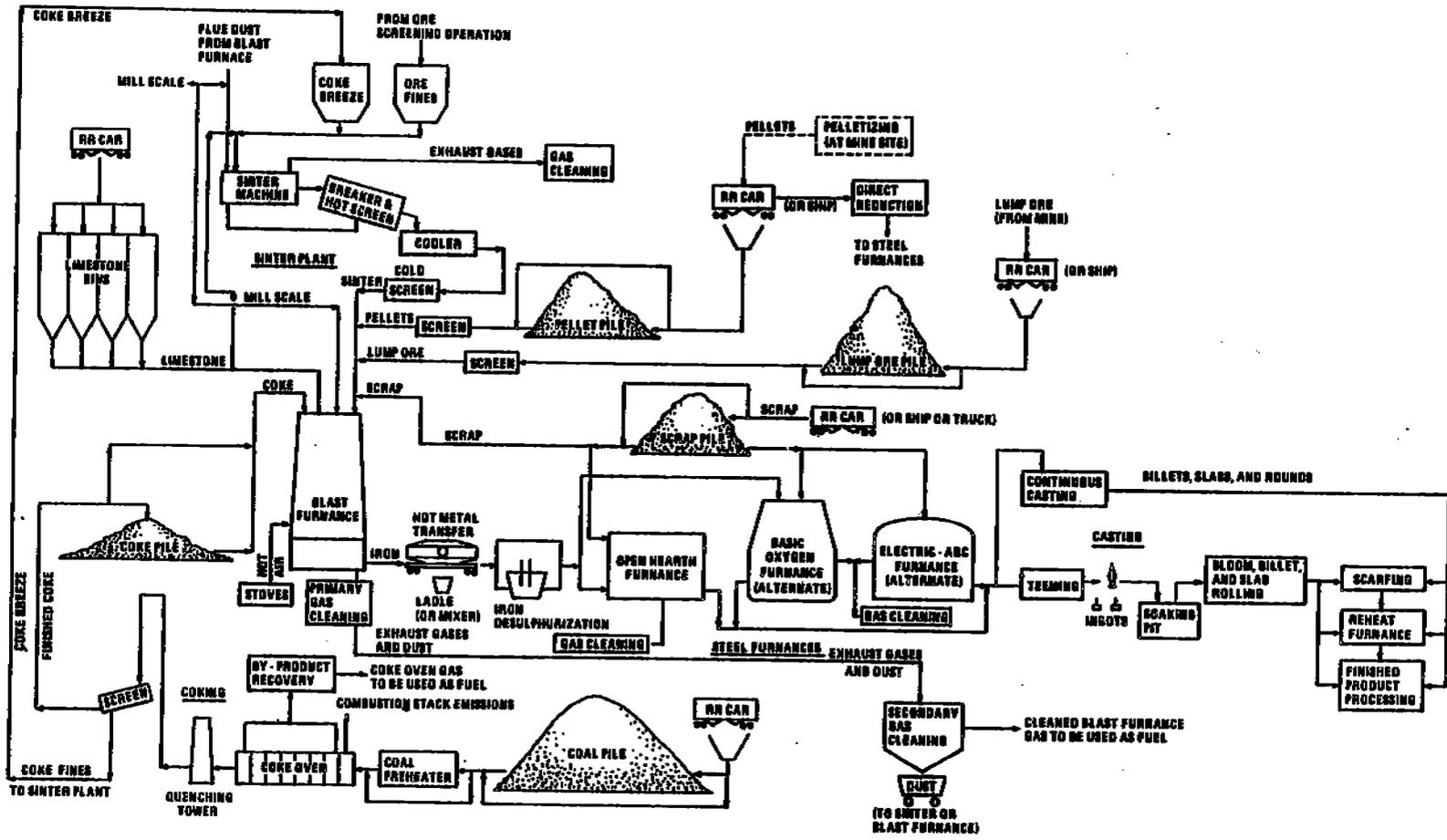
Figure 7.5-1. General flow diagram for the iron and steel industry.

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.

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 non-metal 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

PRETREATMENT   SMELTING   REFINING/CASTING

COLLECTED PARTICULATE MATTER

FUEL

BATTERIES → BATTERY BREAKING

ZINC LEACHING

REVERBERATORY SMELTING

FLUX   FUEL

SEMISOFT LEAD

KETTLE (SOFTENING) REFINING

SOFT LEAD INGOTS

DROSSES, RESIDUES, OVERSIZE SCRAP → CRUSHING

SLAG RESIDUE

FLUX   ALLOYING AGENT   FUEL

HARD LEAD

FUEL

RESIDUES, DIE SCRAP, LEAD-SHEATHED CABLE AND WIRE → ROTARY/TUBE SWEATING

PRETREATED SCRAP

KETTLE (ALLOYING) REFINING

BLAST (CUPOLA) FURNACE SMELTING

FUEL

LIMESTONE   COKE

FUEL   AIR

KETTLE OXIDATION

ALLOYS

FUEL

HIGH LEAD SCRAP → REVERBERATORY SWEATING

FUEL   AIR

REVERBERATORY OXIDATION

BATTERY LEAD OXIDE (Pb AND PbO)

OXIDES, FLUE DUSTS, MIXED SCRAP →

RED LEAD OXIDE (Pb_3O_4)

PURE SCRAP →

YELLOW LEAD OXIDE (PbO)

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		Lead		Sulfur Dioxide		Emission Factor Rating
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	
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.
Reference 1.

[c] 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.

[d] Numbers in parentheses represent ranges of values obtained.

[e] References 8 - 11.

[f] References 11 - 13.

[g] Reference 11.

[h] References 1 and 2.

[i] 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.

References for Section 7.11

1. William M. Coltharp, et al., Multimedia Environmental Assessment of the Secondary Nonferrous Metal Industry (Draft), 2 Volumes, EPA Contract No. 68-02-1319, Radian Corporation, Austin, TX, June 1976.

2. H. Nack, et al., Development of an Approach to Identification of Emerging Technology and Demonstration Opportunities, EPA-650/2-74-048, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1974.

3. J. M. Zoller, et al., A Method of Characterization and Quantification of Fugitive Lead Emissions from Secondary Lead Smelters, Ferroalloy Plants and Gray Iron Foundries (Revised), EPA-450/3-78-003 (Revised), U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1978.

4. John A. Danielson, editor, Air Pollution Engineering Manual, Second Edition, AP-40, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1973, pp. 299-304. Out of Print.

5. Control Techniques for Lead Air Emissions, EPA-450/2-77-012, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1978.

6. Background Information for Proposed New Source Performance Standards, Volume I: Secondary Lead Smelters and Refineries, APTD-1352, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1973.

7. J. W. Watson and K. J. Brooks, <u>A Review of Standards of Performance</u> <u>for New Stationary Sources - Secondary Lead Smelters (Draft)</u>, EPA Contract No. 68-02-2526, The Mitre Corporation, McLean, VA, June 1978.

8. John E. Williamson, <u>et al.</u>, <u>A Study of Five Source Tests on Emissions</u> <u>from Secondary Lead Smelters</u>, EPA Order No. 2PO-68-02-3326, County of Los Angeles Air Pollution Control District, Los Angeles, CA, February 1972.

9. Emission Test No. 72-CI-8, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1972.

10. Emission Test No. 72-CI-7, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1972.

11. A. E. Vandergrift, <u>et al.</u>, <u>Particulate Pollutant Systems Study,</u> <u>Volume I: Mass Emissions</u>, APTD-0743, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1971.

12. Emission Test No. 71-CI-33, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1972.

13. Emission Test No. 71-CI-34, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1972.

14. <u>Technical Guidance for Control of Industrial Process Fugitive</u> <u>Particulate Emissions</u>, EPA-450/3-77-010, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1977.

15. <u>Silver Valley/Bunker Hill Smelter Environmental Investigation</u> <u>(Interim Report)</u>, EPA Contract No. 68-02-1343, PEDCo-Environmental Specialists, Inc., Cincinnati, OH, February 1975.

16. E. I. Hartt, <u>An Evaluation of Continuous Particulate Monitors at a</u> <u>Secondary Lead Smelter</u>, M.S. Report No. O.R.-16, Environmental Protection Service, Environment Canada.

17. J. E. Howes, <u>et al.</u>, <u>Evaluation of Stationary Source Particulate</u> <u>Measurement Methods, Volume V: Secondary Lead Smelters</u>, EPA Contract No. 68-02-0609, Battelle Columbus Laboratories, Columbus, OH, January 1979.
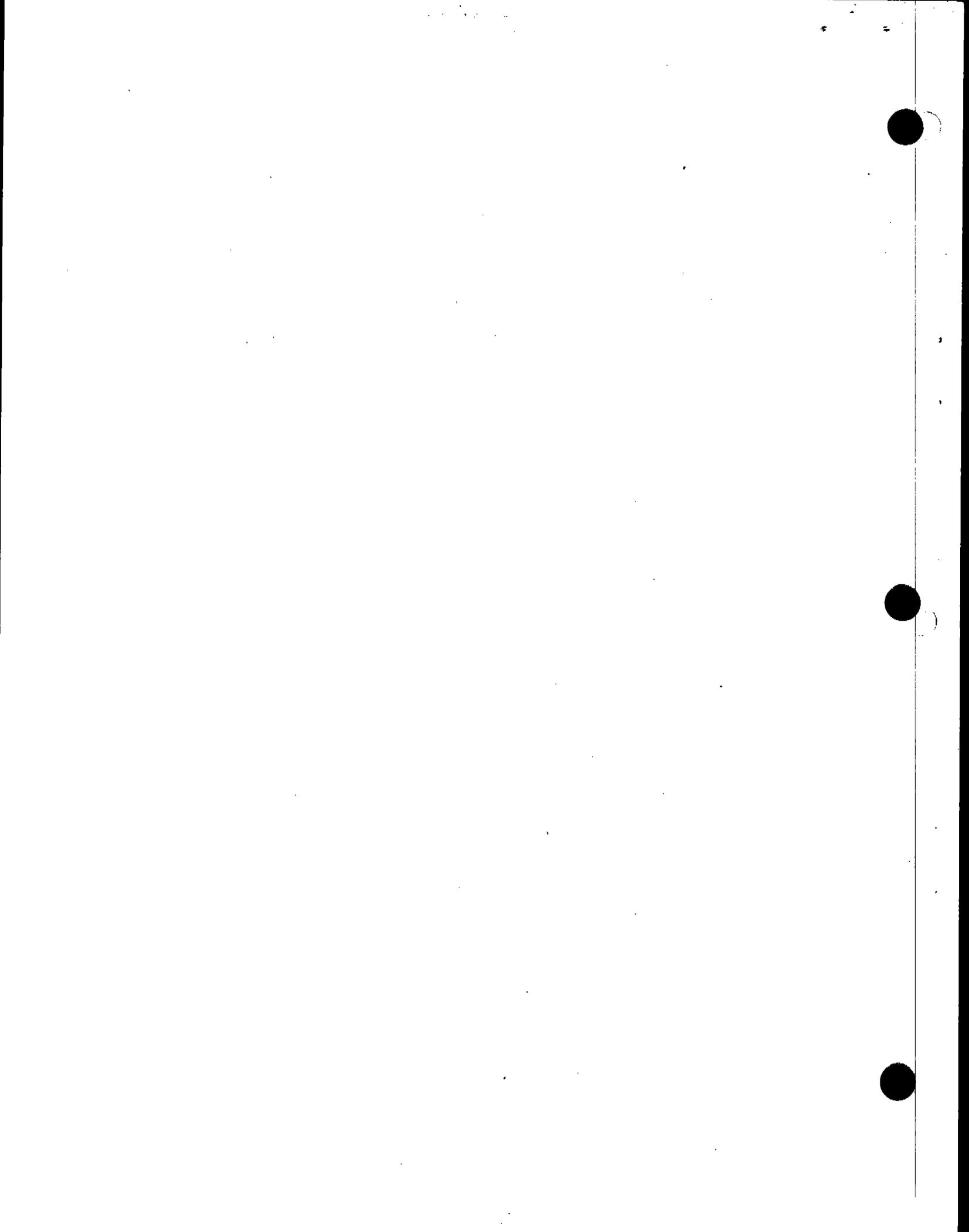
7.15 STORAGE BATTERY PRODUCTION

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/10³ batteries)	(lb/10³ batteries)	(kg/10³ batteries)	(lb/10³ 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

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

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

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

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

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

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

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

Emission Source	Process Stream Type[b]	Emission Factor Units	Emission Factors Uncontrolled Emissions[c]		Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Pipeline valves[d]	II	lb/hr-source kg/day-source	0.059 0.64	(0.030 – 0.110) (0.32 – 1.19)	NA	Monitoring and maintenance programs	A
	III	" "	0.024 0.26	(0.017 – 0.036) (0.18 – 0.39)	NA		A
	IV	" "	0.0005 0.005	(0.0002– 0.0015) (0.002 – 0.016)	NA		A
	V	" "	0.018 0.20	(0.007 – 0.045) (0.08 – 0.49)	NA		A
Open ended valves[d,e]	I	" "	0.005 0.05	(0.0016– 0.016) (0.017 – 0.17)	NA	Installation of cap or plug on open end of valve/line	A
Flanges[d]	I	"	0.00056 0.0061	(0.0002– 0.0025) (0.002 – 0.027)	NA	Monitoring and maintenance programs	A
Pump seals[d]	III	" "	0.25 2.7	(0.16 – 0.37) (1.7 – 4.0)	NA	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlled degassing vents	A
	IV	" "	0.046 0.50	(0.019 – 0.11) (0.21 – 1.2)	NA		A
Compressor seals[d]	II	" "	1.4 15	(0.66 – 2.9) (7.1 – 31)	NA	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlled degassing vents	A
	V	" "	0.11 1.2	(0.05 – 0.23) (0.5 – 2.5)	NA		A
Process drains[d]	I	" "	0.070 0.76	(0.023 – 0.20) (0.25 – 2.2)	NA	Traps and covers	A
Pressure vessel relief valves[d,f] (gas service)	II	" "	0.36 3.9	(0.10 – 1.3) (1.1 – 14)	Negligible	Rupture disks upstream of relief valves and/or venting to a flare	A
Cooling towers	–	lb/10^6 gal cooling water	6		0.70	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D
		kg/10^6 liters cooling water	0.7		0.083		
		lb/10^3 bbl refinery feed[g]	10		1.2		
		kg/10^3 liters refinery feed	0.03		0.004		
Oil/water separators	–	lb/10^3 gal wastewater	5		0.2	Covered separators and/or vapor recovery systems	D
		kg/10^3 liter waste water	0.6		0.024		
		lb/10^3 bbl refinery feed	200		10		
		kg/10^3 liters refinery feed	0.6		0.03		
Storage		See Section 4.3					
Loading		See Section 4.4					

[a] Data from References 2, 4, 12 and 13 except as noted. Overall, less than 1% by weight of the total VOC emissions are ethane.
NA = Not Available.
[b] The volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification numerals and group names and descriptions are:

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

[c] Numbers in parentheses are the upper and lower bounds of the 95% confidence interval for the emission factor.
[d] Data from Reference 17.
[e] The downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.
[f] Emission factor for relief valves in gas service is for leakage, not for emissions caused by vessel pressure relief.
[g] Refinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

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

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

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

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

9.1.3 Fugitive Emissions and Controls

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

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

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

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

9.1.3.2 Storage - All refineries have a feedstock and product storage area, termed a "tank farm", which provides surge storage capacity to assure smooth, uninterrupted refinery operations. Individual storage tank capacities range from less than 1000 barrels to more than 500,000 barrels (160 - 79,500 m^3). Storage tank designs, emissions and emission control technologies are discussed in detail in Section 4.3.

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

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

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

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

TABLE 9.1-3. FUGITIVE VOC EMISSIONS FROM AN OIL REFINERY[17]

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

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

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

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

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

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

References for Section 9.1

1. C. E. Burklin, et al., Revision of Emission Factors for Petroleum Refining, EPA-450/3-77-030, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1977.

2. Atmospheric Emissions from Petroleum Refineries: A Guide for Measurement and Control, PHS No. 763, Public Health Service, U.S. Department of Health, Education and Welfare, Washington, DC, 1960.

3. Background Information for Proposed New Source Standards: Asphalt Concrete Plants, Petroleum Refineries, Storage Vessels, Secondary Lead Smelters and Refineries, Brass or Bronze Ingot Production Plants, Iron and Steel Plants, Sewage Treatment Plants, APTD-1352a, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1973.

4. John A. Danielson (ed.), Air Pollution Engineering Manual (2nd Ed.), AP-40, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1973. Out of Print.

5. Ben G. Jones, "Refinery Improves Particulate Control", Oil and Gas Journal, 69(26):60-62, June 28, 1971.

6. "Impurities in Petroleum", Petreco Manual, Petrolite Corp., Long Beach, CA, 1958.

7. Control Techniques for Sulfur Oxide in Air Pollutants, AP-52, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1969.

8. H. N. Olson and K. E. Hutchinson, "How Feasible Are Giant, One-train Refineries?", Oil and Gas Journal, 70(1):39-43, January 3, 1972.

9. C. M. Urban and K. J. Springer, Study of Exhaust Emissions from Natural Gas Pipeline Compressor Engines, American Gas Association, Arlington, VA, February 1975.

10. H. E. Dietzmann and K. J. Springer, Exhaust Emissions from Piston and Gas Turbine Engines Used in Natural Gas Transmission, American Gas Association, Arlington, VA, January 1974.

11. M. G. Klett and J. B. Galeski, Flare Systems Study, EPA-600/2-76-079, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1976.

12. Evaporation Loss in the Petroleum Industry, Causes and Control, API Bulletin 2513, American Petroleum Institute, Washington, DC, 1959.

13. Hydrocarbon Emissions from Refineries, API Publication No. 928, American Petroleum Institute, Washington, DC, 1973.

14. R. A. Brown, et al., Systems Analysis Requirements for Nitrogen Oxide Control of Stationary Sources, EPA-650/2-74-091, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1974.

15. R. P. Hangebrauck, et al., Sources of Polynuclear Hydrocarbons in the Atmosphere, 999-AP-33, Public Health Service, U.S. Department of Health, Education and Welfare, Washington, DC, 1967.

16. W. S. Crumlish, "Review of Thermal Pollution Problems, Standards, and Controls at the State Government Level", Presented at the Cooling Tower Institute Symposium, New Orleans, LA, January 30, 1966.

17. Assessment of Atmospheric Emissions from Petroleum Refining, EPA-600/2-80-075a through -075d, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980.
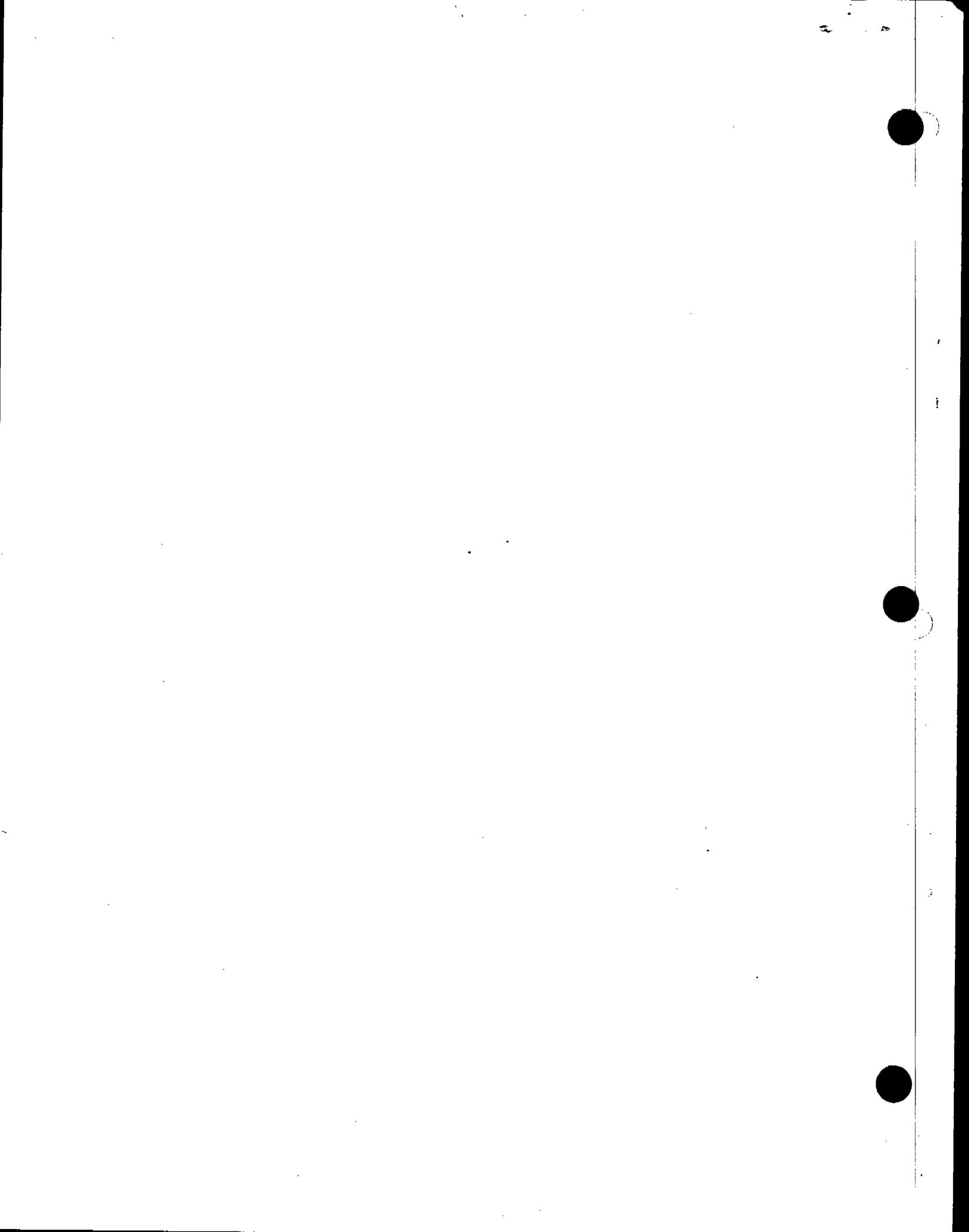
AP-42 Section	Process	Emission factor[a,b]		References
		Metric	English	
	Open hearth			
	Lancing	0.07 kg/MT steel	0.14 lb/ton steel	1
	No lancing	0.035 kg/MT steel	0.07 lb/ton steel	1
	Basic oxygen furnace (BOF)	0.1 kg/MT steel	0.2 lb/ton steel	1,23,25
	Electric arc furnace			
	Lancing	0.11 kg/MT steel	0.22 lb/ton steel	1,28
	No lancing	0.09 kg/MT steel	0.18 lb/ton steel	1
7.6	Primary lead smelting			
	Ore crushing and grinding	0.15 kg/MT ore	0.3 lb/ton ore	29
	Sintering	4.2-170 kg/MT Pb prod	8.4-340 lb/ton Pb prod	1,21,22, 30-33
	Blast furnace	8.7-50 kg/MT Pb prod	17.5-100 lb/ton Pb prod	1,30,32, 33,35,36
	Dross reverberatory furnace	1.3-3.5 kg/MT Pb prod	2.6-7.0 lb/ton Pb prod	1,18,30, 34,36
7.7	Zinc smelting			
	Ore unloading, storage, transfer	0.035-0.1 kg/MT ore	0.07-0.2 lb/ton ore	1
	Sintering	13.5-25 kg/MT ore	27-50 lb/ton ore	1,30,38
	Horizontal retorts	1.2 kg/MT ore	2.4 lb/ton ore	1,30,38
	Vertical retorts	2-2.5 kg/MT ore	4-5 lb/ton ore	1,30,38
7.9	Secondary copper smelting and alloying			
	Reverberatory furnace (high lead alloy 58% Pb)	25 kg/MT prod	50 lb/ton prod	1,26,39-41
	Red and yellow brass (15% Pb)	6.6 kg/MT prod	13.2 lb/ton prod	1,26,39-41
	Other alloys (7% Pb)	2.5 kg/MT prod	5 lb/ton prod	1,26,39-41
7.10	Gray iron foundries			
	Cupola	0.05-0.6 kg/MT prod	0.1-1.1 lb/ton prod	1,3,26, 42,43

AP-42 Section	Process	Emission factor[a,b]		References
		Metric	English	
	Reverberatory furnace	0.006–0.7 kg/MT prod	0.012–0.14 lb/ton prod	1
	Electric induction furnace	0.005–.05 kg/MT prod	0.009–0.1 lb/ton prod	1
7.11	Secondary lead smelting			
	Reverberatory furnace	27 kg/MT Pb prod	53 lb/ton Pb prod	1,38,42–46
	Blast cupola furnace	28 kg/MT Pb prod	56 lb/ton Pb prod	38,42–46
	Refining kettles	0.1 kg/MT Pb prod	0.21 lb/ton Pb prod	46
7.15	Storage battery production (total)	8 kg/10³ batteries	17.7 lb/10³ batteries	1,55–58
	Grid casting	0.4 kg/10³ batteries	0.9 lb/10³ batteries	1,55–58
	Lead oxide mill (baghouse outlet)	0.05 kg/10³ batteries	0.12 lb/10³ batteries	1,55–58
	Three-process operations[c]	6.6 kg/10³ batteries	14.6 lb/10³ batteries	1,55–58
	Lead reclaim furnace	0.35 kg/10³ batteries	0.77 lb/10³ batteries	1,55–58
	Small parts casting	0.05 kg/10³ batteries	0.10 lb/10³ batteries	1,55–58
7.16	Lead oxide and pigment production			
	Barton pot (baghouse outlet)	0.22 kg/MT prod	0.44 lb/ton prod	1,61,62
	Calcining furnace	7 kg/MT prod	14 lb/ton prod	61
	Red lead (baghouse outlet)	0.5 kg/MT prod	0.9 lb/ton prod	1,54
	White lead (baghouse outlet)	0.28 kg/MT prod	0.55 lb/ton prod	1,54
	Chrome pigments	0.065 kg/MT prod	0.13 lb/ton prod	1,54
7.17	Miscellaneous lead products			
	Type metal production	0.13 kg/MT Pb proc	0.25 lb/ton Pb proc	1,63
	Can soldering	160 kg/10⁶ baseboxes[d] prod	0.18 ton/10⁶ baseboxes prod	1
	Cable covering	0.25 kg/MT proc	0.5 lb/ton Pb proc	1,3,64

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. AP-42, Supplement 11	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Supplement No. 11 for <u>Compilation of Air Pollutant Emission Factors, Third Edition</u>, AP-42		5. REPORT DATE <u>October 1980</u>
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Monitoring and Data Analysis Division		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Air, Noise and Radiation Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPORT AND PERIOD COVERED <u>Supplement</u>
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

In this Supplement for <u>Compilation of Air Pollutant Emission Factors</u>, AP-42, revised and updated emissions data are presented for Nitric Acid; Pharmaceuticals Production; Maleic Anhydride; Normal and Triple Superphates and Ammonium Phosphates; Coke Manufacturing; Primary Copper Smelting; Iron and Steel Production; Secondary Lead Processing; and Petroleum Refining.

17.		KEY WORDS AND DOCUMENT ANALYSIS		
a.	DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c.	COSATI Field/Group
Fuel combustion Emissions Emission factors Stationary sources Lead emissions				

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 96
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE