CONTROL TECHNIQUES FOR CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

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PREFACE

Throughout the development of Federal air pollution legislation, the Congress has consistently found that the States and local governments have the primary responsibility for preventing and controlling air pollution at its source. Further, the Congress has consistently declared that it is the responsibility of the Federal government to provide technical and financial assistance to State and local governments so that they can undertake these responsibilities.

These principles were reiterated in the 1967 amendments to the Clean Air Act. A key element of that Act directs the Secretary of Health, Education, and Welfare to collect and make available information on all aspects of air pollution and its control. Under the Act, the issuance of control techniques information is a vital step in a program designed to assist the States in taking responsible technological, social, and political action to protect the public from the adverse effects of air pollution.

Briefly, the Act calls for the Secretary of Health, Education, and Welfare to define the broad atmospheric areas of the Nation in which climate meteorology and topography, all of which influence the capacity of air to dilute and disperse pollution, are generally homogeneous.

Further, the Act requires the Secretary to define those geographical regions in the country where air pollution is a problem—whether interstate or intrastate. These air quality control regions are designated on the basis of meteorological, social, and political factors which suggest that a group of communities should be treated as a unit for setting limitations on concentrations of atmospheric pollutants. Concurrently, the Secretary is required to issue air quality criteria for those pollutants he believes may be harmful to health or welfare, and to publish related information on the techniques which can be employed to control the sources of those pollutants.

Once these steps have been taken for any region, and for any pollutant or combination of pollutants, then the State or States responsible for the designated region are on notice to develop ambient air quality standards applicable to the region for the pollutants involved, and to develop plans of action for meeting the standards.

The Department of Health, Education, and Welfare will review, evaluate, and approve these standards and plans and, once they are approved, the States will be expected to take action to control pollution sources in the manner outlined in their plans.

At the direction of the Secretary, the National Air Pollution Control Administration has established appropriate programs to carry out the several Federal responsibilities specified in the legislation.

Control Techniques for Carbon Monoxide Emissions from Stationary Sources is one of a series of documents to be produced under the program established to carry out the responsibility for developing and distributing control technology information. Previously, on February 11, 1969, control technique information was published for sulfur oxides and particulate matter.

In accordance with the Clean Air Act, a National Air Pollution Control Techniques Advisory Committee was established, having a membership broadly representative of industry, universities, and all levels of government. The committee, whose members are listed following this discussion, provided invaluable advice in identifying the best possible methods for controlling the pollution sources, assisted in determining the costs involved, and gave major assistance in drafting this document.

As further required by the Act, appropriate Federal departments and agencies, also listed on the following pages, were consulted prior to issuance of this document. A Federal consultation committee, comprising members designated by the heads of 17 departments and agencies, reviewed the document, and met with staff personnel of the National Air Pollution Control Administration to discuss its contents.

During 1967, at the initiation of the Secretary of Health, Education, and Welfare, several government-industry task groups were formed to explore mutual problems relating to air pollution control. One of these, a task group on control technology research and development, looked into ways that industry representatives could participate in the review of the control techniques reports. Accordingly, several industrial representatives, listed on the following pages, reviewed this document and provided helpful comments and suggestions. In addition, certain consultants to the National Air Pollution Control Administration also revised and assisted in preparing portions of this document. These also are listed on the following pages.

The Administration is pleased to acknowledge efforts of each of the persons specifically named, as well as those of the many not so listed who contributed to the publication of this volume. In the last analysis, however, the National Air Pollution Control Administration is responsible for its content.

The control of air pollutant emissions is a complex problem because of the variety of sources and source characteristics. Technical factors frequently make necessary the use of different control procedures for different types of sources. Many techniques are still in the development stage, and prudent control strategy may call for the use of interim methods until these techniques are perfected. Thus, we can expect that we will continue to improve, refine, and periodically revise the control techniques information so that it will continue to reflect the most up-to-date knowledge available.

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SUMMARY

Carbon monoxide (CO) is a colorless, odorless, tasteless gas, about 97 percent as heavy as air. It is a major pollutant, by quantity, having a current annual emission rate within the United States of about 100 million tons.

Carbon monoxide is formed when carbonaceous fuels are burned with insufficient oxygen to form carbon dioxide (CO_2). It is also copiously formed from CO_2 at high temperatures under reducing conditions. It is the first product in the oxidation of the carbon in a fuel. Even if there is sufficient oxygen for complete reaction to form CO_2, the latter may still break down to form CO, owing to the dissociation brought about by high temperatures. Dissociation of CO_2 to CO for the temperatures cited are listed in Table 1.

Table 1. DISSOCIATION OF CO_2 TO CO

Temperature, °F	Percentage dissociation
1,340	2×10^{-5}
2,060	1.5×10^{-2}
2,780	5.5×10^{-1}
2,960	1.0
3,140	1.8
3,495	5.0

Some CO can, therefore, form in high-temperature furnaces, even from CO_2 itself. If the equilibrium, $CO_2 \rightleftarrows CO + O$, is "frozen" by rapid cooling, some of the CO does not have time to recombine and persists. Low cooling rates reduce CO emissions. Lean fuel-air mixtures favor low CO concentrations. CO emissions would be increased, however, by recycling cold flue gas to lean mixtures.

SOURCES OF CARBON MONOXIDE

Estimated emissions of CO within the United States during 1968 are given in Table 2.

Table 2. ESTIMATED CO EMISSIONS IN THE UNITED STATES DURING 1968 (10^6 tons)

Source	Emissions
Transportation	63.8
Fuel combustion in stationary sources	1.8
Solid waste burning	7.8
Industrial processes	9.7
Forest and structural fires	5.0
Prescribed agricultural and forest burning	10.7
Coal refuse fires	1.2
Total	100.0

Table 2 does not include estimates of emissions from use of explosives and some relatively small sources such as the electrochemical and electrometallurgical industries.

By far the greatest source of CO emissions is the automobile. Automobile emissions are covered in detail in a companion document, AP-66, *Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources.*

Major emissions include forest fires, structural fires, and burning banks of coal refuse. Industrial sources include foundries, petroleum refineries, and kraft pulp mills. Burning of solid waste produces more CO than all the conventional stationary fuel combustion sources. Tables 3 and 4 are summaries of the methods employed for controlling CO emissions.

Table 3. SUMMARY OF METHODS FOR CONTROLLING CARBON MONOXIDE EMISSIONS FROM STATIONARY COMBUSTION SOURCES

Control method	Remarks
Change of fuel or energy source	
Change to gas from oil and coal	Accepted emission factors for burning of coal, oil, and gas show decreasing CO emissions for these three fuels, in the order given. But CO emissions from boilers and furnaces are so low a fraction of total CO emissions that fuel change is not justified.
Change to nuclear power or hydroelectric generation	Use of nuclear power is expected to grow; hydroelectric generation will grow slowly. Nuclear power involves generation of some CO due to the periodic test operation of standby power-generating units employing conventional fuels.
Replace industrial, commercial, and household thermal requirements with central power	Generation of electric power is increasing. CO emissions are easier to control at a central power plant than at small installations and households. Efficiency is lower for indirect use of fuel through electricity than for direct burning. Reduction in local CO concentrations may result in increased oxides of nitrogen (NO_x) emissions at distant power plants.
Combustion control	
Air supply	A well-adjusted gas-fired boiler may emit less than 1 ppm of CO, but may emit more than 50,000 ppm if insufficient combustion air is supplied. Insufficient air always causes CO formation; too much air may do the same by flame quench.
Residence time	Short residence times tend to cause more CO in exit gases. Proper residence time allows the use of less excess air.
Temperature	High temperature is desirable, but dissociation of CO_2 into CO becomes noticeable at 2,800°F. Rapid cooling and low oxygen concentration tend to hinder recombination of CO_2. Flame temperatures above 3,000°F are conducive to formation of oxides of nitrogen (NO_x).
Mixing	Good mixing is very important for burning of CO; appliance and burner design should facilitate mixing.
Flame contact	Contact of flame with cold surfaces tends to form CO by quenching, i.e., it reduces residence time at effective oxidation temperature.
Change of waste disposal method	
Sanitary landfill	Replaces open-burning and incineration.
Various treatments for coal-waste piles	These are not deliberately burned, but ignite by spontaneous combustion or accident. See AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.*

Table 4. SUMMARY OF METHODS FOR CONTROLLING CARBON MONOXIDE EMISSIONS FROM STATIONARY PROCESS SOURCES

Source	Control method	Remarks
Iron and steel industry		
Blast furnace	CO generated is burned as fuel	Emissions can be produced by faulty equipment and accidents.
Grey iron cupola	Flame afterburner	Not all controlled.
Basic oxygen steel furnace	Burned inside hood and dispersed by stack	Collection for use as fuel not common in United States.
Sintering furnace	None	
Coke oven	Proper design, scheduling, operation, and maintenance	Controls are same as those to control particulates and SO_2. See AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.*
Petroleum industry		
Petroleum catalytic cracking unit	Burned as fuel in CO boiler	CO produced during regeneration of catalyst. Burning as fuel usually requires supplementary fuel for stability.
Petroleum fluid coker	Burned as fuel in CO boiler	Gas produced in coker burning section of coking unit is rich in CO.
Chemical industry	Most commonly burned as waste	Moderate amounts generated in chemical industry as a whole, but this actually occurs only in specified segments of the industry. Emissions are from gas purging, leaks, abnormal operations such as startup, upsets and shutdown, or relief of overpressure.

COSTS OF CONTROLS

Determining the costs involved in control of CO emissions is seldom straightforward, and is often impossible.

Enormous amounts of CO are generated in a blast furnace, but this gas is cleaned and used as fuel. Cleaning entails removing particulate matter; and if costs were to be allocated to air pollution control, it would be logical to allocate them to particulate removal rather than to CO removal. Particulates also constitute the real air pollution problem in the operation of the basic oxygen furnace. The CO generated is usually burned, or it can be collected for use as fuel. If the CO is collected for fuel, the cost of the gasholder and associated piping could be allocated to utilities rather than to CO air pollution control. Total costs are, of course, not necessarily recovered in the heating value of the CO collected.

The chemical industry generates a moderate amount of CO in reforming operations that usually has to be removed by suitable processes in order to make the desired product—hydrogen, or a mixture of hydrogen and nitrogen. If CO is burned in a waste-gas flare, the costs of flare operation could be allocated to CO control unless the flare is used to burn various waste gases from other chemical processes.

The economics of a CO boiler serving a petroleum catalytic cracking unit are separable from those of any equipment required to clean the boiler feed gas. In this case, the boiler handles only clean CO-rich gas, and abates only CO emissions. Costs of such a boiler and its auxiliaries should, however, be based on engineering study and cost quotations from CO boiler suppliers.

Cost estimates for CO control, when applicable, may be made by the general methods described in AP-51, *Control Techniques for Particulate Air Pollutants.*

CONTROL TECHNIQUES FOR CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

1. INTRODUCTION

Pursuant to authority delegated to the Commissioner of the National Air Pollution Control Administration, *Control Techniques For Carbon Monoxide Emissions From Stationary Sources* is issued in accordance with Section 107c of the Clean Air Act, as amended (42 U.S.C. 1857–18571).

This document has been prepared to summarize current information on sources of carbon monoxide (CO) emissions, methods of control, and costs and cost-effectiveness of controls.

Carbon monoxide is a chemical compound of carbon and oxygen. A gas at all temperatures above −218°F, CO has a density 96.5 percent of that of air, is quite stable up to very high temperatures, is odorless, and is toxic. Carbon monoxide is one of the products of incomplete combustion of carbonaceous fuels and is formed whenever carbon-bearing materials burn, if the oxygen furnished is less than that required to form carbon dioxide (CO_2). Carbon monoxide is also readily formed from CO_2 in the presence of hot carbon-bearing materials.

Carbon monoxide in the atmosphere may have adverse effects upon health, and reduction of emissions of this pollutant may be of importance to an effective air pollution abatement program. Carbon monoxide originates from a variety of sources, and the available control techniques vary in type, application, effectiveness, and cost.

The control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. The devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are recommended as the techniques generally applicable to the broad range of CO emission control problems.

Many agricultural, commercial, industrial, and municipal processes and activities that generate CO are described individually in this document. Various techniques that can be applied to control emissions of CO from these sources are reviewed and compared, and equipment costs are included, also.

Although exhaust from automobiles constitutes by far the greatest source of CO in the atmosphere, this emission category is not discussed comprehensively in this document. It is, however, treated extensively in a separate document, AP–66, *Control Techniques For Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions From Mobile Sources.*

While some data are presented on quantities of CO emitted to the atmosphere, the effects of CO on health and welfare are considered in a companion document AP–62, *Air Quality Criteria for Carbon Monoxide.*

2. SOURCES OF CARBON MONOXIDE

Carbon monoxide is one of the products produced by the incomplete combustion of carbonaceous material; it is formed, for instance, when carbonaceous material is burned in a reducing atmosphere, in which the available oxygen is not sufficient to burn the material completely to carbon dioxide. Because such conditions exist in the cylinders of the gasoline internal-combustion engine, and because of the large number of automobiles in use, CO emissions from this source conspicuously exceed those from any combination of other sources.

Table 2–1 is a summary of estimated annual emissions of CO within the United States during 1968. No figures are available for a few operations, such as certain metallurgical operations and the use of explosives. Table 2–1 shows that the sum of the CO emissions was approximately 100 million tons.

Large amounts of CO are produced and handled by industry; but, in most cases, this is used as fuel or raw material, and emissions result only from leaks or abnormal operation. Based on data from Section 4.1, total production of CO by pig-iron blast furnaces, for instance, was estimated to be about 90 million tons in 1968–even more than that generated by the gasoline internal-combustion engine, but only a small fraction of this CO escapes from the blast furnace operations.

Almost 60 percent of the CO emissions summarized in Table 2–1 is due to the motor vehicle; it is also interesting to note the relatively large contribution that still arises from the use of wood as fuel. The small values of CO emissions indicated for burning natural gas must not convey the impression that complete combustion necessarily takes place when gas is burned; actually, copious quantities of CO can be formed if this fuel is burned with too little air.

Most of the emissions given in Table 2–1 were estimated by the National Inventory of Air Pollutant Emission Control Section of the National Air Pollution Control Administration, using emission factors from reference 1 or as developed in this document. Derivation of a few of the emissions is illustrated in some of the sections of this document.

Table 2–1. SUMMARY OF ESTIMATED CARBON MONOXIDE EMISSIONS[2] IN THE UNITED STATES DURING 1968 (tons/year)

Source	Emissions
Mobile fuel combustion	
Motor vehicles	
Gasoline	59,000,000
Diesel	160,000
Aircraft[a]	2,400,000
Railroad	120,000
Vessels	310,000
Non-highway users	1,800,000
Stationary fuel combustion	
Coal	770,000
Fuel oil	50,000
Natural gas	3,000
Wood	1,010,000
Solid waste	
Incineration	800,000
Open burning	3,400,000
Conical burners	3,600,000
Coal-refuse fires	1,200,000
Structural fires	250,000
Forest fires	
Wild fires	4,740,000
Prescribed burning	2,480,000
Agricultural burning	8,250,000

Table 2–1 (continued). SUMMARY OF ESTIMATED CARBON MONOXIDE EMISSIONS[2] IN THE UNITED STATES DURING 1968
(tons/year)

Source	Emissions
Industrial processes	
Blast-furnace sinter plants	2,400,000
Gray-iron cupolas	3,600,000
Basic oxygen furnaces	100,000
Beehive coke ovens	20,000
Kraft recovery furnaces, lime kilns	830,000
Carbon black	350,000
Petroleum catalytic cracking units	2,200,000
Fluid coking burners	160,000
Methanol	4,000
Formaldehyde	34,000
Subtotal	100,041,000
Ammonia	b
Metallurgical electric furnaces	b
Zinc and lead reduction	b
Aluminum reduction	b
Calcium carbide furnaces	b
Silicon carbide furnaces	b
Phosphorus furnaces	b
Explosions (blasting, etc.)	b

[a] This includes emissions during cruising.

[b] Although these sources are thought to be emitters of CO, no data are available and no emission factors have been developed.

2.1 REFERENCES FOR SECTION 2

1. Duprey, R. L. Compilation of Air Pollutant Emission Factors. U.S. DHEW, PHS, CPEHS, National Center for Air Pollution Control. Durham, N. C. PHS Publication 999–AP–42. 1968. 67 p.
2. National Air Pollution Control Administration, Reference Book of Nationwide Emissions. U.S. DHEW, PHS, CPEHS, NAPCA. Durham, N. C.

3. STATIONARY COMBUSTION SOURCES

3.1 SOURCES

Stationary combustion sources include steam-electric generating plants and industrial, commercial, and domestic combustion units. These sources burn large quantities of coal, fuel oil, and natural gas, and lesser amounts of other fuels such as coke oven gas or tar, coke, refinery gas, blast furnace gas, wood, bagasse, or other waste- or byproduct-type fuels. Estimated fossil fuel consumption for various stationary combustion sources is shown in Table 3–1.

The nearly 1,000 steam-electric generating plants in the United States[4] burn coal, residual fuel oil, or natural gas. Projections of United States power generation for various energy sources are shown in Table 3–2.

Table 3–2. ESTIMATED UNITED STATES POWER GENERATION FOR VARIOUS ENERGY SOURCES[4]
(10^9 kw-hr)

Energy source	1968	1980	1990
Coal	683	1,225	1,630
Oil	104	205	220
Gas	305	485	620
Hydroelectric	222	274	316
Nuclear	12	901	3,066
Total	1,326	3,090	5,852

The steam boiler is the most common industrial stationary combustion device. Other types of boilers or heaters used by industry employ hot water, molten salt, organic liquids, and mercury. Fired stills, heaters, ovens, and furnaces are also used. The fuels most commonly used in these devices are: coal, natural gas, or petroleum-derived fuel oils. Industrial sources burning other fuels are often considered to be industrial process sources or incineration sources; there is, however, no fundamental difference be-

Table 3–1. ESTIMATED UNITED STATES FUEL CONSUMPTION FOR SELECTED STATIONARY COMBUSTION SOURCES IN 1966
(10^{12} Btu)

Fuel	Type of use			
	Domestic and commercial	Industrial	Power generation	Total
Coal, including[a] anthracite and lignite[a]	610	2,600	6,400	9,610
Fuel oil[b]	4,440[c]	1,840[d]	910[e]	7,190
Natural gas[f]	5,760	6,960[g]	2,610	15,330
Total	10,810	11,400	9,920	32,130

[a] Based on reference 1 and heating value of 12,000 Btu/lb.

[b] Based on reference 2 and heating values as indicated.

[c] Heating value of 142,000 Btu/gal.

[d] Heating value of 150,000 Btu/gal; includes military fuel.

[e] Heating value of 150,000 Btu/gal.

[f] Based on reference 3 and heating value of 1,000 Btu/ft^3.

[g] Includes refinery and pipeline fuel.

tween these and stationary combustion sources.

There are more than 30 million domestic and commercial space-heating plants in the United States.[5] These plants burn coal, natural gas, or petroleum fuel oil. A few space-heating plants burn liquefied petroleum or natural gas products, and more than 2.5 million homes are heated by electrical energy. Other minor domestic stationary combustion sources include kitchen ranges, clothes driers, and hot water heaters. Commercial heating systems are commonly steam-type systems. Hot water and warm air systems are also used.

3.2 EMISSIONS

3.2.1 Quantity of Emissions

Nationally, the quantity of CO emissions from oil-fired and gas-fired stationary combustion sources is estimated to be negligible in comparison with the 100 million tons emitted from all sources. Emissions from coal-fired sources are estimated at less than 1 percent of total United States CO emissions.

3.2.2 Formation of Carbon Monoxide

Carbon monoxide is formed as an intermediate product of reactions between carbonaceous fuels and oxygen.[6] When less than the theoretical amount of oxygen required for complete combustion is supplied, CO is a final product of the reaction. Under these conditions, CO concentrations may exceed 50,000 ppm.

Formation of the oxides of carbon is a simple process only when pure carbon and pure oxygen are involved. The burning of carbonaceous fuels, in general, is a very complicated process involving formation of CO before CO_2 is formed.[6] If the temperature of combustion is high enough, dissociation of the CO_2 begins:

$$CO_2 \rightleftharpoons CO + O$$

Actually, CO is a very stable substance at high temperature, as indicated by Table 3–3.

Table 3–3. BOND ENERGIES OF SOME SIMPLE CHEMICAL SUBSTANCES[7]

Substance	Bond	Bond energy, Kcal/mol
Carbon monoxide	C–O	256.7
Carbon dioxide	O═C–O	128
Propane	C_3H_7–H	98
Acetylene	HC≡CH	230

In order for a chemical reaction to take place, chemical bonds must be broken and formed. Bond energies are a measure of the difficulty in breaking a chemical bond. Table 3–3 indicates a higher bond energy for CO than for acetylene, which is notorious for its stability at electric arc temperatures; CO is indeed known to be stable at very high temperature. Conversely, propane is easily cracked or decomposed at moderate temperatures, and the bond energy is seen to be low. The bond energy for CO_2 is moderately low, and experience shows that it is not difficult to remove an atom of oxygen from CO_2 by dissociation to form CO. For these reasons then, a second mechanism of CO formation is high-temperature dissociation of CO_2, or hindering of the combination of CO and oxygen by virtue of temperature. Thus, raising the temperature increases the concentration of CO in the thermodynamic sense.

The reaction rates increase with temperature. Increase of oxygen concentration tends to decrease the CO concentration by affording a greater chance for collision of CO and oxygen molecules (actually, hydroxyl radicals) to form CO_2.[6]

3.2.3 Effect of Design on Emissions

For minimum CO emissions, combustion equipment is designed for rapid reaction rates and long reaction time. Rapid reaction rates are promoted by providing for intimate contact between fuel and air, furnishing sufficient air for combustion, increasing combustion temperature by preheating the fuel and air, limiting the amount of excess air, and minimizing heat loss during oxidation of the fuel. After complete oxidation of the fuel, slow cooling of the combustion gases promotes more complete oxidation of CO to CO_2. Some of the conditions favorable to complete fuel combustion tend to promote formation of nitrogen oxides. High flame temperatures are the most effective of these conditions.

For units firing powdered coal, the effect of method of boiler-firing on CO emissions is given in Table 3–4.

Table 3–4. CARBON MONOXIDE EMISSIONS FROM SUSPENSION COAL-FIRED BOILER UNITS[8]
(lb/10^6 Btu)

Type of firing	CO emissions
Vertical	0.017
Corner	0.011
Front wall	0.005
Spreader stoker	0.029
Horizontally opposed	0.044

Emissions from some grate-fired coal-burning units are given in Table 3–5.

Table 3–5. CARBON MONOXIDE EMISSIONS FROM GRATE-FIRED COAL-BURNING UNITS[8]

Type unit	Unit size, 10^6 Btu/hr	CO emissions, lb/10^6 Btu
Chain grate	147	0.51
Spreader stoker	59.2	<0.1
Underfeed stoker	4.4	0.16
Underfeed stoker	3.0	0.14
Underfeed stoker	0.066	1.1
Hand-fired stoker	0.115	3.5

The data in Tables 3–4 and 3–5 indicate that furnace design and firing method can affect the quantity of CO emissions.

3.2.4 Emission Rates

Although emission factors are used for estimating CO emissions from various kinds of stationary combustion sources, the accuracy of the numbers used is insufficient for other than a qualitative comparison among various fuels and equipment. It is not firmly established that there are differences among CO emissions from coal-, gas-, and oil-fired power boilers. Coal-fired stoker or grate-type commercial or industrial combustion equipment probably emits more CO per unit of heat input than equivalent oil- or gas-fired units; it is firmly established that well-adjusted, domestic coal-fired units emit more CO than well-adjusted, equivalent-sized oil- or gas-fired equipment.

When coal-, oil-, or gas-fired stationary combustion equipment is operated with an insufficient air supply, CO emission rates can be several thousand times as great as emissions from well-adjusted units. Under these conditions, oil-fired and coal-fired units emit dense smoke, but gas-fired equipment must be badly out of adjustment to emit smoke.

3.3 CONTROL TECHNIQUES

The following techniques are known for control of carbon monoxide emissions from stationary combustion sources:

1. Good practice.
2. Energy conservation.
3. Energy source substitution.
4. Source relocation.
5. Source shutdown.
6. Gas cleaning.

3.3.1 Good Practice

Good practice is the most practical technique for reduction of CO emissions from stationary combustion sources. Good practice involves proper design, application, installation, operation, and maintenance of the combustion equipment and auxiliary systems.

Guidelines for good practice are published by the fuel industry, equipment manufacturers, engineering associations, and government agencies. Stationary combustion units should be operated within their design limits and according to the recommendations of the manufacturer or other authority on proper operating practices. Combustion units and components should be kept in good repair to continue to meet design specifications. Sensitive CO monitoring systems are helpful in indicating the need for combustion system repair. Other sources of information on good practice are:

1. Air Pollution Control Association.
2. American Boiler Manufacturers Association.
3. American Petroleum Institute.
4. American Society of Heating, Refrigerating, and Air-Conditioning Engineers.
5. American Society of Mechanical Engineers.
6. Edison Electrical Institute.
7. The Institute of Boiler and Radiator Manufacturers.

8. Insurance agencies.
9. Mechanical Contractors Association of America.
10. National Academy of Sciences–National Research Council.
11. National Coal Association.
12. National Fire Protection Association.
13. National Oil Fuel Institute.
14. National Warm Air Heating and Air-Conditioning Association.
15. U.S. Bureau of Mines.
16. State and local air pollution control agencies.

Proper fuel-air ratio adjustment is of major importance for reduction of CO emissions from stationary combustion sources. Flue gases from the best-designed combustion unit may contain substantial concentrations of CO if insufficient air is provided for combustion. Carbon monoxide emissions also increase when excessive air is admitted to cool combustion temperature below the optimum for maximum oxidation of fuel and CO. As a rule of thumb, coal- and oil-fired units may be adjusted for 10 to 12 percent CO_2 on a dry basis, and natural-gas-fired units may be adjusted for 8 to 10 percent CO_2 on a dry basis. Since many units are designed to perform best at values outside these ranges, the combustion equipment manufacturer or other combustion experts should be consulted on proper fuel-air ratio adjustments for individual combustion units.

As an alternative to using CO_2 as a criterion, oil-, gas-, or pulverized-coal-fired units may be adjusted for 0.2 to 3.0 percent oxygen for well-designed combustion units. It should be noted, however, that operation at very high combustion temperatures may yield excessive oxides of nitrogen. Examples of this are well known in the boiler industry.

Carbon monoxide emissions can be minimized by designing for (1) a high combustion temperature; (2) intimate contact among fuel, oxygen, and combustion gases; (3) sufficient reaction time; and (4) low effluent temperature.

Combustion systems should be selected on the basis of application and designed to meet specified load requirements. In addition, the fuel-handling system, draft system, fuel-burning system, flues and stacks, ash-handling system, and combustion controls must be properly selected, integrated, and designed to handle the load and the fuel to be burned.

Selection of the size, number, and type of burners depends upon the type of furnace. For systems involving new furnace installations, the combustion space and heat distribution pattern can be arranged to suit any particular type of burner, whereas on existing combustion systems, the burner must be selected to fit the existing design.

Stationary combustion units are designed to operate within a specific range of load conditions. In systems requiring a wide range of heat releases, it may be desirable to utilize multiple burners, since there is a limitation to the burner-turndown ratio available. If such a unit is operated outside design limits, excessive emissions of CO or excessive oxygen in the flue gas may result. It is, therefore, necessary that the load be accurately estimated before stationary combustion systems are selected and installed.

Firing in excess of the design rate of the combustion system–overloading–is perhaps the greatest cause of excessive CO emissions from a stationary combustion source. Commonly available oil burners and defects of operation that may result in CO pollution are noted in Table 3–6.

Before any fuel can be ignited, it must first become a vapor. Thus, the extent of atomization of oil is extremely important to efficient burner operation and CO emission abatement. For a given quantity of oil, the smaller the oil particle, the greater will be the area exposed to the air, and the more readily the proper air-fuel mixture can be ignited. High-combustion efficiency, rapid ignition, and higher flame temperature are produced when the proper amount of air necessary for complete combustion is supplied. The degree of fineness of atomization is, therefore, of prime importance in the proper functioning of an oil burner. With the complete atomization of oil, complete combustion can be secured with the stoichiometric amount of air. Any air in excess of that required for complete combustion causes fuel waste, because waste-gas

Table 3–6. CLASSIFICATION OF OIL BURNERS ACCORDING TO APPLICATION AND LIST OF POSSIBLE DEFECTS[9]

Burner type	Applications	Oil type usually used	Defects that cause excessive CO emissions
Domestic			
Pressure atomizing	Residential furnaces, water heaters	No. 1 or 2	Increased viscosity of oil, nozzle wear, clogged flue gas passages or chimney, clogged air inlet, oil rate in excess of design
Rotary	Residential furnaces, water heaters	No. 1 or 2	Increased viscosity of oil, clogged nozzle or air supply, oil rate in excess of design
Vaporizing	Residential furnaces, water heaters	No. 1	Fuel variations, clogged flue gas passages or chimney, clogged air supply
Commercial, Industrial			
Pressure atomizing	Steam boilers, process furnaces	No. 4, 5	Oil preheat too low or too high, nozzle wear, nozzle partly clogged, impaired air supply, clogged flue gas passages, poor draft, overloading
Horizontal rotary cup	Steam boilers, process furnaces	No. 4,5,6	Oil preheat too low or too high, burner partly clogged or dirty, impaired air supply, clogged flue gas passages, poor draft, overloading
Steam atomizing	Steam boilers, process furnaces	No. 5, 6	Oil preheat too low or too high, burner partly clogged or dirty, impaired air supply, clogged flue gas passages, poor draft, overloading, insufficient atomizing pressure
Air atomizing	Steam boilers, process furnaces	No. 5	Oil preheat too low or too high, burner partly clogged or dirty, impaired air supply, clogged flue gas passages, poor draft, overloading, insufficient atomizing pressure

volume increases and the additional fuel required to heat it represents a loss.

The flue area or vent opening in a furnace or boiler serves to deliver the products of combustion to the atmosphere. A second function is to maintain the desired furnace pressure. In some furnaces, it is desirable to maintain a positive pressure; in others, a zero or slightly negative pressure is desired.

Efficiency of combustion depends partly on flue area. In order to maintain the desired combustion rate, it is necessary to correctly size the flue or vent opening. Too small a flue opening acts as an impediment to the flow of gases and products of combustion attempting to escape. This restriction produces a back pressure, which hinders the flow of fresh air to the combustion chamber and thereby reduces the quantity of fuel that can be burned efficiently. When this happens, all attempts to increase the rate of burning beyond the limit imposed by the restriction result in the creation of CO. In addition, a drop in furnace temperature results, with possible flame extinguishment.

When flue-area openings are excessively large, the products of combustion leave the furnace too fast under fixed chimney draft, and the furnace pressure decreases. This pressure drop results in an infiltration of excess air, with consequent fuel waste, variation in furnace atmosphere, difficulty in maintaining desired temperature and uniform heat distribution, and possible ignition failure. This, too, may result in an increase in CO emissions when coal or oil is being burned.

Exclusive of the selection of fuel, the most important feature to consider for purposes of

CO abatement in stationary fuel combustion sources is the combustion control system. Major innovations in combustion equipment design have taken place in this area. Combustion control equipment is primarily concerned with two functional aspects, namely, adjustment of the fuel supply under variation of load demand, and correction and control of the fuel-air ratio corresponding to the fuel supply.

Generally, any form of automatic combustion control of the fuel-air ratio offers the potential of increased efficiency, lower CO emissions, and lower operating costs than does a manually operated system. The more complex and larger the installation or the greater the load fluctuation, the more complex and comprehensive are the controls that can be justified. The primary purpose of such controls is to limit fuel consumption, follow load demands without lags, increase safety and reduce ambient air pollution. Variations in load are very rapidly reflected in operating conditions, which may not elicit sufficiently rapid response from an operator in a manually operated system.

Control systems are of the following three general types:

1. The on-off control system is the simplest control system available. This system regulates the fuel and air flow to the boiler burner system by a pressure signal from a steam header or the boiler drum. As the steam pressure varies between set limits, the burners either light off or shut down. This method of control is the least effective for maintaining a well-balanced fuel-air ratio. The CO emission or excess air is, therefore, usually higher from boilers using this control system. This occurs because the boiler is constantly being heated or cooled, an even combustion temperature is not maintained, and complete combustion of the fuel is achieved during only part of the cycle. This type of control is used on small fire-tube boilers, heaters, etc., where simple controls are specified to minimize investment.

2. The position-control system will adjust the fuel-air ratio to the boiler requirements. Like on-off control, position control regulates by steam pressure. As the boiler pressure varies due to supply and demand, the control system adjusts the dampers in the air system as well as the fuel valve. The system can follow a slightly fluctuating load and produce a more acceptable fuel-air ratio over the operating range.

   This type of control system would be most common on package and medium-sized boilers.

3. The most elaborate system for combustion control is the metering system. This system anticipates load, and is found almost exclusively on utility boilers. The system measures steam flow and pressure, fuel flow, and air flow, and compares steam requirements with the feed-water input to determine the correct firing rate. A feedback control system provides rapid response. When operating properly, this system offers the best continuous fuel-air ratio for the desired operating range.

In summary, although the on-off combustion control system is simplest, it offers the least amount of control over the fuel-air ratio of the three general types of combustion systems. The position-control system is more complicated, and it can vary the fuel-air ratio to produce a more efficient firing rate over a range of loads. Of the three systems, the metering system is the most sensitive to load variation, and is able to control the fuel-air ratio over constant, as well as fluctuating, load conditions.

The following example illustrates how the proper application of basic engineering principles to furnace design can facilitate the lowering of overall fuel requirements and substantially lessen the likelihood of ambient air pollution by CO from two major sources, fuel and CO-bearing offgases. The example points up the importance of refractory selection and combustion chamber design.

To maintain ignition stability during transient events accompanying operating-load fluctuations on CO boilers for fluid catalytic cracking units, equilibrium temperatures in the range of 1,800 °F are desirable to assure complete consumption of the CO-bearing offgas. Combustion can be achieved with stable ignition, however, in a temperature range as low as 1,500° to 1,600°F in hot refractory combustors under proper conditions. If the combustion chamber design promotes thorough mixing of auxiliary fuel and gas, and if the chamber is sized to provide adequate residence time, CO combustion can take place at lower temperatures and less auxiliary fuel will be used because of the efficiency of combustion.

To insure gas ignition during the transient flows accompanying load changes and varying rates of coke burn, the combustion chamber construction should assure complete conversion of CO to CO_2 over the widest possible operating temperature range. Unsuited to this purpose are low-heat-capacity furnace settings of typical insulating firebrick and combustion volumes surrounded by cold, heat-absorbing surfaces. In contrast, it is desirable to provide refractory furnace enclosures having maximum heat storage or thermal "fly wheel" effect, to protect from loss of ignition and pulsating detonation. Stable operation is promoted by adequate size of the combustion chamber, which insures sufficient gas residence time, and by high heat capacity setting, which enhances stable operation.

In addition, maximum contact of the hot refractory walls and the fuel gases greatly accelerates the rate of combustion. The more hot refractory that is available, the less will be the dependence on auxiliary burners for ignition. In the ideal design, ignition is sustained by stored radiant heat energy in the refractory setting, rather than by direct mixing with hot gases generated by the auxiliary burners. When sufficient hot refractory is provided, the CO continues to burn stably, even if the auxiliary burners are out of service.

From the above, it follows that the presence of any heat sink, particularly a relatively cold surface, in contact with the combustion chamber, greatly increases the difficulty of obtaining good CO combustion and, thus, increases CO emissions.

In order to ignite the CO, the temperature of the air-CO mixture must be raised to at least 1,200° F. After this substantial additional heat energy is brought into the system, the CO ignites and contributes to a further increase in temperature.

If, however, the combustion chamber and burner ports are of sufficient number and arrangement that the CO is fed gradually and at an increasing rate into a stream of much hotter combustion gases, without any major chilling effect, then a much more reliable and complete conversion of CO to CO_2 can be achieved with a minimum auxiliary fuel requirement. Many small burners, coordinated with well-distributed CO ports, enhance combustion conditions.

3.3.2 Energy Source Substitution

CO emissions can be reduced by substitutions among fossil fuels. Table 3–7 gives emission factors for the small heat-release rate of 10 million Btu per hour. The table data were estimated from data in reference 10.

Table 3–7. ESTIMATED CARBON MONOXIDE EMISSION RATES FROM FOSSIL FUELS AT DUTY OF 10^7 Btu/hr (lb/hr)

Fuel	CO
Coal	20
Oil	0.134
Natural gas	0.0038

The relative emission rate from coal combustion decreases with increasing size of combustion unit. Substitution of gas- or oil-fired units for coal-burning grate- or stoker-type units can reduce CO emissions.

Hydroelectric power is too limited in growth potential in the United States to be considered as a substitute for fossil-fuel energy. Nuclear power generation would not entirely eliminate CO emissions, because of the need for standby fossil-fuel power-generating facilities at these stations.

The subject of fuel substitution is probably academic for large, well-operated units like power plants, because of their low CO emission rates; however, conversion from coal to oil or gas can reduce emissions from homes and other numerous small users concentrated in very limited areas.

3.4 REFERENCES FOR SECTION 3

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4. INDUSTRIAL PROCESS SOURCES

4.1 IRON AND STEEL INDUSTRY

Carbon monoxide is generated during several stages in the production of iron and steel, beginning with the sinter plant for beneficiating iron ore; the blast furnace for producing hot metal; and the basic oxygen, open-hearth, and electric furnaces for producing steel. Emissions from sinter plants are significant. Blast furnaces generate large amounts of CO, but emissions are insignificant since the gases are cleaned and used as fuel. Some recent basic oxygen furnace designs also have provisions to cool and clean the offgas, which could then be used as fuel. In the open-hearth furnace, excess air supplied to the end-fired burners completely consumes the CO released from the metal bath. The small amount of CO released from electric furnaces burns at the electrode ports. Coke ovens generate a significant amount of CO, but most of it is collected with the coke oven-gas and used as fuel. Cupola furnaces also produce a significant amount of CO, and only a few are being controlled. The heating furnaces and boilers used in the steel mills are subject to the same problems as other boiler operations.

4.1.1 Iron Ore Beneficiation (Sinter Plants)

Iron ore is beneficiated by grinding, concentrating it magnetically, and sintering of the concentrate in the form of coke or pellets suitable for use as a burden for blast furnaces. The total sinter plant capacity in the United States in 1960 was 65 million tons of sinter

Table 4–1. GASEOUS EMISSIONS FROM SINTERING OPERATIONS[2]

Experiment No.	Fuel		Water, %	Atmosphere	Specific volume,[a] ft^3/ton	Mean temperature of lower bed, °C	Gas, %		Composition	
	Nature	%					CO_2	CO	O_2, %	$\frac{CO}{CO + CO_2}$
A-1	Coke–1/8 in.	4	3.5	Air	31,500	1,440	4.7	1.1	15.2	0.19
A-2	Coke–1/8 in.	4	3.5	Air	32,100	1,440	4.6	1.1	15.0	0.19
B	Charcoal–1/8 in.	3.5	3.5	Air	31,400	1,090	4.7	2.5	13.9	0.35
C-1	Coke–100 mesh	4	3.5	Air	32,000	1,380	6.6	1.7	12.8	0.21
C-2	Coke–100 mesh	4	3.5	Air	31,600	1,370	6.8	1.8	12.6	0.21
D	Charcoal–1/8 in.	3.5	3.5	O_2 9% N_2 91%	34,400	1,290	3.9	1.9	4.2	0.33
E	Graphitized electrode–1/8 in.	3.5	3.5	Air	35,800	1,520	4.8	0.5	15.0	0.095
F	Flue dust (16.3%C)	21.5	3.5	Air	37,800	1,250	2.5	1.05	17.5	0.30

[a] Specific volume per ton of raw sinter mix or approximately 0.75 ton finished sinter.

coke and 15 million tons of pellets. Capacity in 1970 is expected to be 75 million tons of sinter and 40 million tons of pellets.[1]

Carbon monoxide emissions from sintering operations can be estimated from Table 4–1. A typical value is taken as 450 cubic feet per ton of raw sinter mix or 600 cubic feet per ton of finished sinter. This is about 33 pounds of CO per ton of raw sinter mix or 44 pounds of CO per ton of finished sinter. Carbon monoxide emissions from firing pellets can be expected to be approximately the same.

From the previously cited capacity projections, 1968 production of sinter is estimated as 73 million tons and pellet production as 35 million tons. Carbon monoxide emissions from 1968 production are calculated to be 1.62 million tons per year for sinter and 780,000 tons per year for pellets.

4.1.2 Blast Furnaces

A blast furnace is a large cylindrical structure, approximately 100 feet high, made of steel, and lined with refractory brick. Iron ore, coke, and limestone are charged at the top, and heated air is blown in at the bottom. The coke is preheated by the hot gases ascending from the hearth so that, when it reaches the lower portion of the furnace and comes in contact with the air of the hot blast, it will burn with great intensity. At the high temperatures that exist at this location (above 3,000°F), CO_2 is not stable because of the large quantity of carbon present as coke. For this reason, if any CO_2 forms, it reacts immediately with C to form CO.

Consequently, the combustion of coke in the blast furnace can be expressed by the following chemical equation:

$$C + 1/2\, O_2 \rightarrow CO$$

In modern blast-furnace operations, between 600 and 900 pounds of carbon react in this manner for every ton of hot metal produced.[3] This forms between 1,400 and 2,100 pounds of CO. Carbon monoxide reduces the iron oxides to metallic iron. Chemical equilibrium prevents all the CO from being used. Gases leaving the furnace contain about 25 to 30 percent CO.[4]

The CO content of the blast-furnace gas gives the gas a heating value of about 100 Btu per cubic foot. Furnace gas can thus be used as fuel, but first, must be cleaned, since it contains 7 to 30 grains of dust per standard cubic foot. The usual cleaning system is composed of a dust catcher (settling chamber), a primary cleaner, and a secondary cleaner. The primary cleaner usually consists of some type of medium-efficiency scrubber. The secondary cleaner may consist of a high-pressure-drop venturi scrubber, a rotary disintegrator, or an electrostatic precipitator. The venturi scrubber is more likely to be used with a blast furnace that can operate at relatively high top-pressure.

Blast-furnace gas is used to preheat the blast air, before its injection into the furnace through the tuyeres, to intensify and speed up the burning of the coke required for the smelting operation. The air blast is heated in "stoves," which are cylindrical steel vessels, lined with a refractory. They have an upward passage for combustion and downward passage filled with checkerwork to absorb the heat. There are usually three stoves per furnace, and they are alternately "on gas" and "on blast." Modern stoves for large furnaces are 26 to 28 feet in diameter and about 120 feet high.[3]

Only a part of the blast-furnace gas is required for heating the stoves. The remainder is used for steam generation, heating of soaking pits, underfiring of coke ovens, and other miscellaneous heating uses.

4.1.2.1 *Emissions*

As stated above, all the CO generated in the blast furnace is normally used for fuel; abnormal conditions, however, can cause emissions of dust and CO. "Slips" are the principal cause of such emissions. A slip is caused by an initial wedging or bridging of the stock in the furnace. When this occurs, the material underneath continues to move downward, and a void is created. The void tends to increase in size until the "bridge" collapses. Accompanying the sudden downward movement of the stock above the bridge is a rush of gas to the top of the furnace.[3] This occurrence causes abnormally high pressures—much greater than can be handled through the gas-cleaning equipment.[4] When this happens, bleeders or safety valves open to release the pressure, and a cloud of dust and CO is emitted into the atmosphere.

4.1.2.2 *Control Techniques*

Blast furnace operators are constantly striving to reduce the incidence of slips and, thereby, increase efficiency and production and reduce air pollutant emissions. Furthermore, with increased understanding of the cause of slips, further steps are being taken to utilize practices and procedures to eliminate them. The use of sinter, with a reduction in the amount of fines fed to blast furnaces, has resulted in smoother operations.

The improvements made in blast-furnace feed materials and in instrumentation have reduced the number of malfunctions known as "slips" occurring in blast furnaces almost to the vanishing point. In addition, a change in the piping system and in the permissible top pressure has made it possible to contain the emissions from most slips that actually do occur. As a result, it is very rare today for a slip of such magnitude to occur as to spring the escape valves high on the furnace and allow the heavily dust-laden gases to escape to the outside.[5]

4.1.3 Basic Oxygen Furnaces

The basic oxygen process is employed to produce steel from hot blast-furnace metal and some added scrap metal, by use of a stream of commercially pure oxygen to oxidize the impurities, principally carbon and silicon.

The basic oxygen furnace is an unheated, pear-shaped vessel, mounted on trunnions. It is in the upright position during the blowing cycle. The charge, which occupies only a small portion of the total volume of the vessel, is refined by a high-velocity oxygen jet from a water-cooled lance that is lowered vertically through the vessel mouth to within a predetermined distance above the surface of the bath. The distance between lance and surface varies during the blow from 7 to 2.5 feet in various plants.[6]

Dark brown smoke evolves, at the start of the blow, from oxidation of the iron. It persists until the silicon, manganese, and phosphorus begin to oxidize; then these oxides enter the slag. Next, carbon is oxidized and evolved, chiefly as CO. An excess of air is usually mixed with the gases to burn the CO as the offgasses are collected. This eliminates the possibility of an explosion from ignition within the exhaust system. Many furnaces are equipped with waste-heat boilers for thermal recovery from burning of the CO.[7]

4.1.3.1 *Emissions*

The charge to a basic oxygen furnace usually consists of hot metal and scrap in the ratio of 70 to 30, plus burnt lime. Based on this charge, the offgas will produce about 124 to 152 pounds of CO per ton of steel. After aspirated air is added to the offgas, the weight of dry gas will increase to about 1,800 to 2,000 pounds per ton of steel and will contain from 0 to about 2.6 pounds of CO after combustion.

During the normal operation of an iron and steel plant, only small amounts of CO would reach the atmosphere from this source.[7]

4.1.3.2 *Control Techniques*

The high-velocity oxygen stream impinging on the surface of the molten iron in a basic oxygen furnace generates extreme heat, and causes the formation of large amounts of iron oxide fumes. A gas-cleaning system for the effluent must, therefore, be provided. These systems utilize high-energy scrubbers or electrostatic precipitators as the final collecting device.

The fume collecting hoods are of two types—closed hoods and open hoods. The closed hoods are designed to reduce infiltrated air to a minimum. After cleaning, the gas enters a gas-collecting and -holding system and is subsequently used for fuel or as a raw material for chemical manufacturing. A diagram of the system is shown in Figure 4–1.

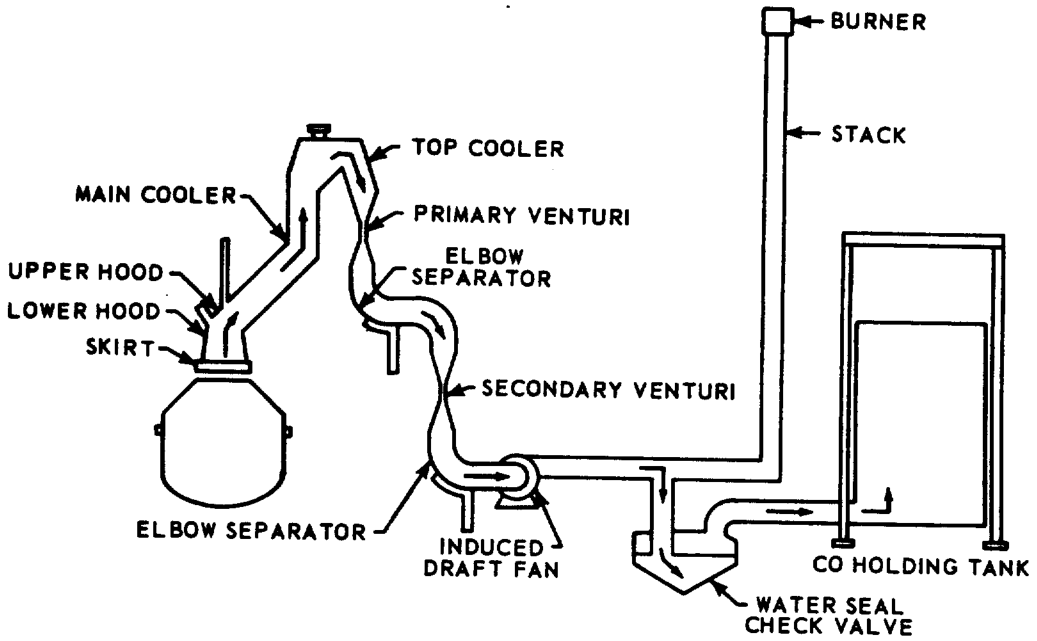

Figure 4-1. Basic oxygen furnace with closed hood and gas-cleaning and storage system.

In open-hood systems, sufficient air is admitted to completely burn the CO in the hood. An excess of air is usually provided, for safety reasons, and the effluent volume is as much as 25 times the volume of the oxygen used. The length of the hood should be sufficient to assure complete combustion of the CO before the gas is cooled below the ignition temperature in the quench chamber, which precedes the dust-collection equipment. Figure 4–2 illustrates an open-hood system.

In this diagram, gases generated at the furnace are burned with excess air and cooled with water sprays in a water-jacketed hood and chamber. The spray header acts as a baffle and causes some of the large particles in the gas stream to fall into the spark box and, from there, to a settling tank. The gas is further cooled by radiation in the flue con-

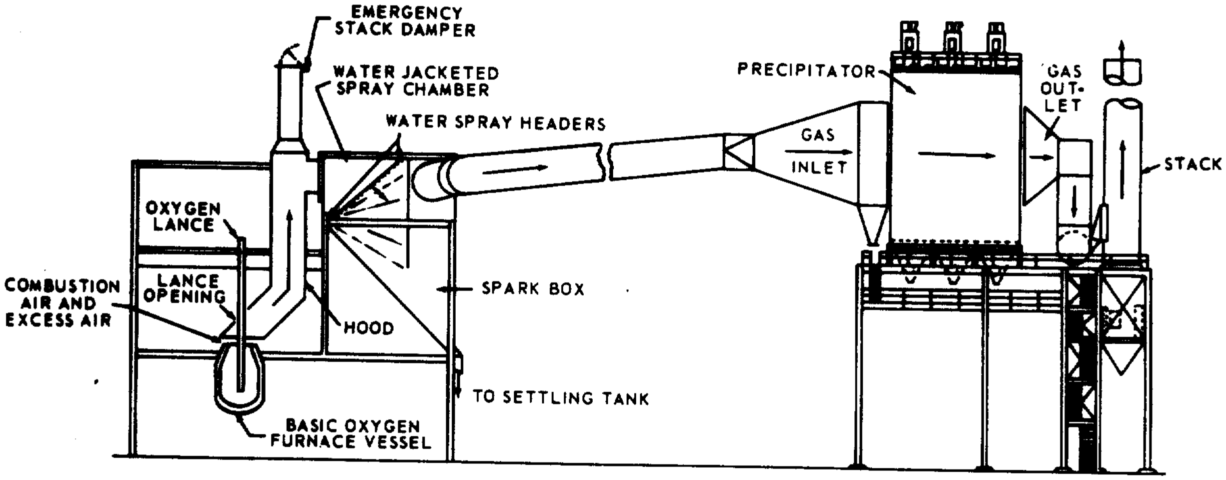

Figure 4-2. Basic oxygen furnace with open hood and gas-cleaning system.

necting the spray chamber to the gas inlet of the precipitator. This inlet decreases the gas flow, permitting more of the large particles to drop into the expansion chamber before the gas enters a plate precipitator for final cleaning.

Hoods are water-cooled because satisfactory refactory linings for this type of application have not been developed to date.[8] They may use cold water, hot water, or steam. Cold-water hoods are usually of parallel wall-panel construction, and operate at low pressures and high-flow rates. The water temperature rise is kept low to prevent scale deposits. Hot-water hoods are normally of a tubular design and use high-pressure water and high water-temperature differentials. Steam hoods are designed to take advantage of the latent heat of vaporization, and are normally constructed to tubular-membrane wall panels.[8] Figure 4–3 is a diagram of a system with a steam-generating hood.

Cold-water hoods require copious amounts of water; and, if water is recirculated, large water-cooling towers must be installed. If recirculation is not necessary, cold-water hoods are usually lowest in capital cost. Hot-water or steam hoods should be supplied with treated boiler feedwater. Hot-water hoods may serve as a source of hot water for other uses, or the water may be recirculated through a water-cooling tower or some type of heat exchanger. In view of the large quantity of heat available, the use of steam generated in a steam hood should be considered. Steam is generated on a cyclical basis, however, and the demand for it does not coincide with these cycles. Therefore, the steam is normally stored in accumulators and recovered as saturated steam. If there is no demand for saturated steam, super heaters can be installed after the accumulators. Air-cooled condensors are used with steam hoods if there is no demand for the steam.

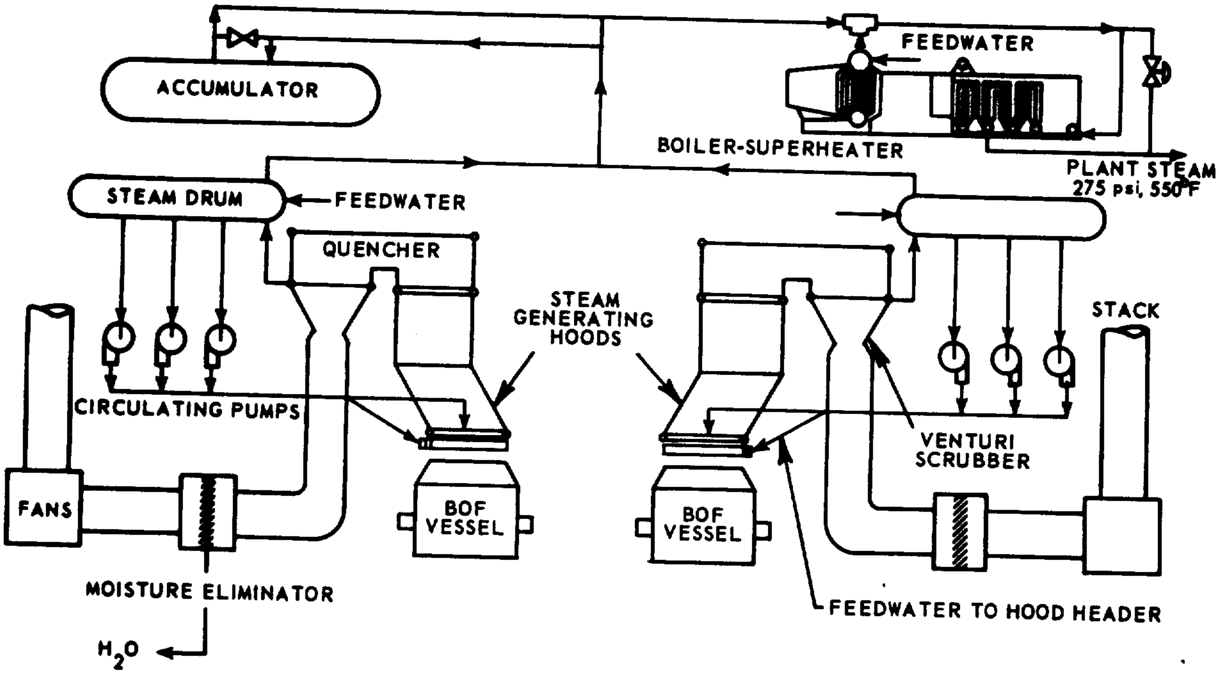

Figure 4-3. Open-hood system with steam-generating hoods.

4.1.4 Iron Cupolas

A cupola is a vertical refractory-lined cylinder, open at the top, and equipped with air nozzles (known as tuyeres) at the bottom. Air is supplied from a forced-draft blower. Alternate charges of metal, coke, and limestone are placed on top of the burning coke bed. The heat generated melts the metal, which is drawn off through the tap hole.

4.1.4.1 *Emissions*

As in the blast furnace, blowing air into an incandescent bed of coke results in the formation of a considerable amount of CO. The gases from cupolas contain from 10 to 13 percent CO.[9] On the basis of iron melted, this is from 220 to 370 pounds of CO generated per ton of iron.

A questionnaire survey of the 1,680 United States foundries has been completed by the National Air Pollution Control Administration and the Department of Commerce. Results show that the 14.6 million tons of iron castings shipments produced by cupolas in 1966 required 32.4 million tons of melt. Based on this survey, approximately 10 to 20 percent of this production was subject to flame afterburner control, which was about 90 percent efficient for CO reduction. With an emission factor of 250 pounds of CO per ton of melt for uncontrolled cupolas and 10 pounds of CO per ton of melt (or charge), for controlled cupolas, an estimated 3.467 million tons of CO was emitted from iron cupolas in 1966.

4.1.4.2 *Control Techniques*

Many cupolas operate without any effluent control measures; they emit CO, dust, and fumes directly to the atmosphere. Cupolas equipped with efficient particulate collecting systems have afterburners for burning CO in order to avoid handling explosive gas mixtures. The afterburner also burns the combustible particulates, such as coke breeze and any smoke and oil vapors, that may originate from oily scrap in the charge.

While afterburners may be installed as separate units, the common practice is to use the upper portion of the cupola above the charging door as the afterburner. When this is done, the height of the standard cupola must be increased to provide adequate retention time to complete the combustion in the afterburner.

An afterburner should be designed with adequate capacity to raise the temperature of the combustibles, inspirated air, and cupola gases to at least 1,200°F.[9] The geometry of the secondary combustion zone should be such that the products to be incinerated have a retention time of at least 1/4 second. Enough turbulence must be created in the gas stream for thorough mixing of combustibles and air. In large-diameter cupola furnaces, stratification of the gas stream may make this a major problem. One device, proved to be successful in promoting mixing in large-diameter cupolas, is the inverted cone[10] shown in Figure 4–4. The combustion air is inspirated through the charging door.

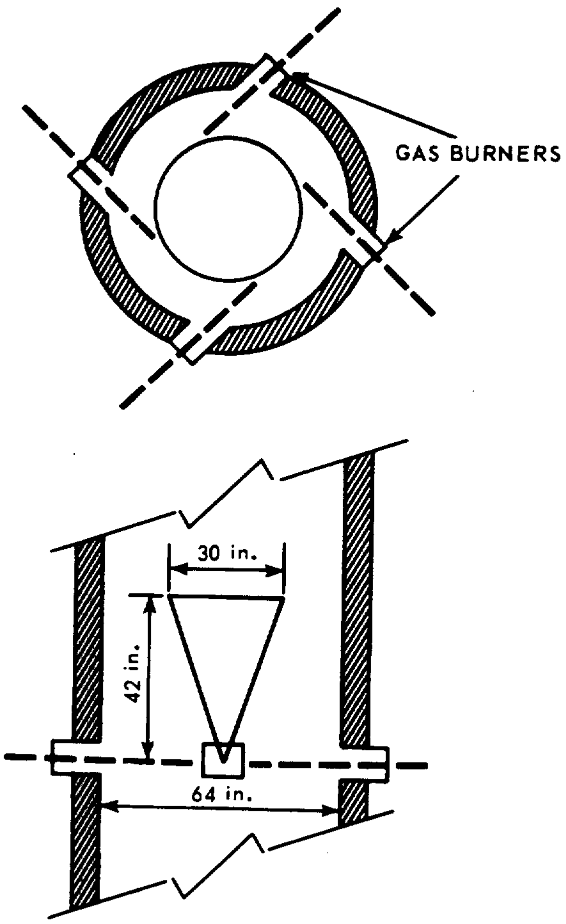

Figure 4-4. Integral afterburner with inverted cone installed in top part of cupola to create turbulence to ensure complete combustion.

Other necessary afterburner design features are:

1. A steady flame that does not go out and is not affected by the cupola charge. If the flame is extinguished, it relights automatically.
2. An automatic modulating control system of the main burners, controlled from a thermocouple in the stack, which cuts off the main burner flame, but not the pilot, if cupola gases have sufficient CO to affect the control temperature.
3. No interference with the cupola charging system or melting process.

These features are illustrated in Figures 4–5 and 4–6.

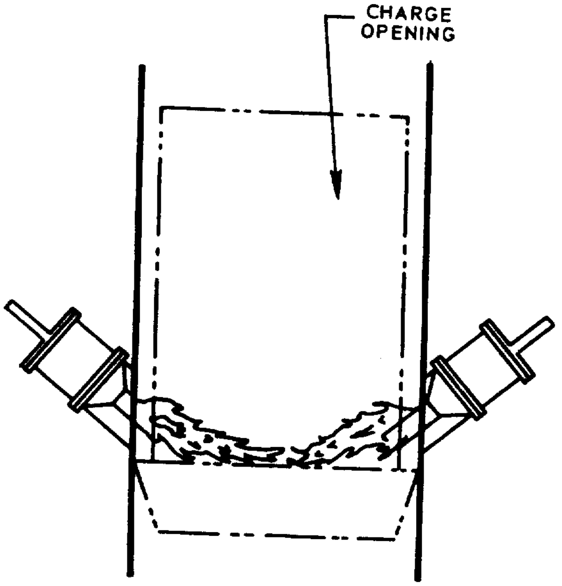

Figure 4-5. Diagram of afterburner system showing flame introduced at most favorable location to ignite cupola gases.
(Courtesy of American Foundryman's Society

The balanced-blast cupola represents a design that is capable of reducing CO in the exit gas from the cupola preheat zone. This cupola differs from the conventional cupola, mainly, in having three or more rows of tuyeres to admit air at several levels, instead of at only one or two levels.[11] By proper adjustment of air to the individual tuyeres, CO can be maximized in the bottom of the cupola where needed, and minimized at the top preheat zone. Uniform melting and reduction in bridging can be obtained; also, freezing near a tuyere can be prevented by temporary shutoff of air at that tuyere. These factors decrease both coke consumption and CO emissions. The conventional cold-blast cupola is fed with ambient blast air. The hot-blast cupola is fed with preheated blast air.[11] The airfeed is preheated to about 1,000°F before going to the tuyeres. The resultant increase in heat input to the cupola decreases the amount of coke required for melting, decreases the amount of combustion products, and tends to decrease CO emissions.

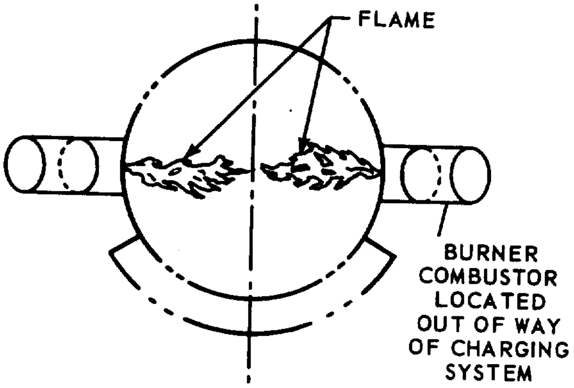

Figure 4-6. Diagram of flame in afterburner system that is neither extinguished nor affected by cupola charge.
(Courtesy of American Foundryman's Society)

4.1.5 Electric Furnaces

In 1967, 15 million tons or 11.8 percent of the U. S. annual steel production was made in electric-arc furnaces.[12] The electric furnace is particularly well adapted to the production of steel from cold scrap. Since the basic oxygen process has a limited scrap-handling capacity, and a plentiful supply of inexpensive scrap is available, the production rate of steel from electric furnaces continues to increase.

4.1.5.1 *Emissions*

When steel is made in the electric furnace, excess carbon is added to the charge to create a carbon boil, which serves to stir and purge the metal bath. The excess carbon rarely exceeds 0.5 percent. This amount of carbon, when oxidized, yields 18 pounds of CO per ton. Perhaps half of the oxygen in the CO reacts to CO_2 within the furnace.[13] Essentially all of the remainder oxidizes to CO_2 at the electrode ports.

4.1.6 Coke Ovens

Coke is produced by carbonization, the destructive distillation of coal. This process is carried out in either beehive or by-product ovens, both of which are carefully heated to coking temperature, then kept hot for the 20- to 30-year lifetime of the oven. A battery is made up of as many as 100 individual coke ovens side by side in a continuous structural unit. Coke production figures are given in Table 4–2.

The use of beehive ovens has declined to the extent that only about 1.2 percent of the annual U. S. coke supply is produced in them.[12] These ovens are far worse air polluters than are by-product ovens. About 6.5 tons of coal per batch is charged through an opening in the dome-like roof. Products of distillation and combustion escape through the same opening. A door in the front is used to regulate the amount of air admitted during coking and to discharge the finished coke.

Enough heat is retained by the oven between charges to drive off volatile gases from a new charge of coal. The gases ignite at the surface of the charge to provide heat for the coking process. As heat builds up, the coal is transformed into a pasty, semifused state, and expands appreciably. When coking is finished, the bricks placed in the door are torn away and the coke is sprayed with water. The rapid cooling causes the charge to break into irregular pieces having a column-like structure, a characteristic of beehive coke. When cooled, the coke is screened.

In by-product ovens, coal is heated in the absence of air. Volatile matter is ducted to equipment that extracts valuable ingredients, such as tar, ammonia liquor, and light oil, from the gas. Approximately 36 percent of the coke oven gas (heating value, 550 Btu/ft^3) produced during coking is used to heat the coke ovens.[12] The remainder of the gas is usually used for heat in other processes in the steel plant.

From 16 to 20 tons of coal is charged from ports in the top of the rectangular oven. The ports are sealed, and the coal begins to fuse, starting at the oven walls, which are heated by coal gas combustion. The fusing works toward

Table 4–2. HISTORICAL STATISTICS OF COKE INDUSTRY IN UNITED STATES[14]

	Coke production, 10^6 net tons				
Year	By-product ovens	Beehive ovens	Total	Production from by-product ovens, %	Yield of coke from coal, %
1880		3.3	3.3		63.7
1890		11.5	11.5		63.9
1900	1.1	19.4	20.5	5.2	63.9
1910	7.1	34.6	41.7	17.1	66.1
1920	30.8	20.5	51.3	60.0	67.4
1930	45.2	2.8	48.0	94.2	68.7
1940	54.0	3.1	57.1	94.6	70.1
1944	67.0	7.0	74.0	90.6	70.3
1950	66.9	5.8	72.7	92.0	69.9
1955	73.6	1.7	75.3	97.7	69.9
1960	56.2	1.0	57.2	98.2	70.3
1966[a]	66.0	1.4	67.4	97.9	69.9
1967[a]	63.8	0.8	64.6	98.8	69.6
1968	63.3	0.8	64.1	98.8	70.2

[a] Data are from Reference 12, p. 400

the center from both walls; a crack forms down the middle of the charge when the two fused zones meet. In about 20 hours, when carbonization is finished, the charge is shoved out into quench cars, cooled, and screened. The high-temperature process, during which the coal is heated to temperatures ranging from 1,650° to 2,150°F, is used almost exclusively in the United States.

The hot coal gas is first cooled with an aqueous solution of ammonia. Condensed tar and fixed salts, such as ammonium chloride, are removed. Further cooling and an electrostatic precipitator remove any remaining tar. The ammonia is recovered by a weak solution of sulfuric acid; an acid separator then removes sulfuric acid mist. Liquid oil, removed in a series of scrubbing towers, is distilled and treated to yield benzene, toluene, and other products.

4.1.6.1 *Emissions*

About 15,000 cubic feet of coal gas is recovered from the production of a ton of coke in a by-product oven.[14] Carbon monoxide makes up about 6 percent, by volume, of this gas.[15] Efficient combustion of the gas, to provide heat for coking or other processes, oxidizes the CO to CO_2. Some CO emissions occur during charging and discharging of the by-product ovens. No data are available, but the quantity is probably insignificant.

Coal gas formed during beehive-oven operations is burned inefficiently inside the ovens to provide the heat required for coking. Combustion products and unburned coal gas are allowed to escape to the atmosphere. If the figures cited above for by-product ovens are assumed to apply to the gases escaping from beehive ovens, then CO emissions (based on 1967 coke production figures) from all beehive ovens in the United States would total 5.4×10^8 cubic feet, or 20,000 tons, per year.

4.1.6.2 *Control Techniques*

Carbon monoxide emissions can be reduced by the same methods that can be used to reduce particulate emissions, as detailed in a companion NAPCA volume, AP–51, *Control Techniques for Particulate Air Pollutants.* These methods consist of techniques used to reduce emissions during charging of coal into the ovens, and of methods to minimize leaks.

Emissions during charging can be reduced by steam-jet aspirators in by-product header ducts, charging-car volumetric sleeves, mechanical removal of charging-hole lids, and sealing sleeves for levelling bars. Leaks can be minimized by gas-tight, self-sealing oven doors, which require a minimum of manual sealing with clay; mechanical cleaners or self-sealers for doors and charging-hole covers; and improved refractories, with less spalling and cracking, which cause warping of metal parts and gas leaks into flue systems and chimneys.

4.1.7 Cost of Controls

Afterburners are usually installed on cupolas to burn CO. Their cost is insignificant when compared to dust-collector costs. For example, 1968 installed costs for afterburners, with necessary controls and air blower for a typical-size cupola (54-inch, inside diameter) amounted to $2,400.[16] The cost for a venturi-scrubber system for dust collection, on the other hand, amounted to approximately $200,000.[10] Fuel for the afterburner cost approximately $5,000 for the 54-inch cupola (assuming a cost of 60¢ per 10^6 Btu for the fuel) in 1968.

A gas-cleaning system for a basic oxygen furnace must be considered as a multiple-pollutant-control system, i.e., for collection of particulates as well as CO. The components of such a system include the hood, gas cooler, duct work, collectors, fans, instrumentation, and collected-waste-handling equipment. Several distinct fume-hood schemes could be considered, based on whether CO is burned or collected, and the degree of heat recovery employed. In the United States, collection of CO as fuel is rare, and, therefore, the cost of CO control is rarely separable from that of dust abatement.

A very good discussion on costs of control equipment for the steel industry is given in *A Systems Analysis Study of the Integrated Iron* *and Steel Industry.*[7] The general points covered on cost derivation are helpful, but, for reasons already given, no costs in the study apply to CO emission abatement.

4.2 PETROLEUM REFINERIES

The sources of CO in a petroleum refinery include: catalyst regenerators, coking operations, blanketing gas generators, flares, boilers, and process heaters. Only moving-bed catalyst regenerators and fluid cokers emit significant amounts of CO.

4.2.1 Catalytic Operations

In petroleum processing, catalysts are employed in the operations of cracking, reforming, hydrotreating, isomerization, hydrocracking, alkylation, and polymerization. Most of the catalysts used are in the form of solid beads, pellets, and powders, which become coated with carbon from coking reactions of the feed materials. To maintain catalyst activity, these carbon deposits must be periodically burned off the catalyst surface. Burning carbon at a controlled temperature and at a set combustion air rate leads to the formation of CO. In some processes, the catalyst particles circulate continuously between the reaction zone and the regeneration zone, resulting in the regeneration process being continuous. Sulfur and nitrogen compounds are also removed in the regeneration process. Cracking catalysts are the only types that require regeneration frequently enough to produce significant amounts of CO.

Catalytic cracking units are of two types: fluid catalytic cracking (FCC) units and Thermofor catalytic cracking (TCC) units. FCC units utilize a powdered catalyst, and TCC units utilize bead or pelleted catalysts.

The reactor of an FCC unit is a large verticle cylinder in which a bed of powdered catalyst is kept in a fluidized state by the flow of vaporized feed material. The regenerator is a similar vessel, which may be placed above, below, or beside the reactor. The catalyst circulates continuously between the reactor and regenerator. The catalyst stream from the reactor is stripped of hydrocarbon vapors by steam and is conveyed to the regenerator by airflow. Additional air is injected into the regenerator to burn off the carbon deposits. The temperature is maintained in the range of 1,050° to 1,100°F. Coke-burnoff rates vary with the size of the unit from 5,000 to 34,000 pounds per hour. A stream of regenerated catalyst is continuously returned to the reactor. Its sensible heat furnishes the required heat for the cracking reactions.

Thermofor catalytic cracking and Houdriflow units utilize beaded or pelleted catalyst. Regenerated catalyst and vaporized feed enter the top of the reactor chamber and travel concurrently downward through the vessel. The catalyst is purged with steam at the base of the reactor and travels by gravity into the regenerator chamber. Combustion air is admitted at a controlled rate to burn off carbon deposits. From the bottom of the regenerator, the catalyst is returned by an airlift to a surge hopper above the reactor. Older units utilized a bucket elevator for catalyst return. An average-sized TCC unit regenerator has a coke-burnoff rate of 3,500 pounds per hour.

4.2.1.1 *Emissions*

When the carbon deposits are burned off the cracking catalyst, the temperature must be kept below about 1,100°F to avoid heat deactivation of the catalyst and to preserve the structural integrity of the equipment. Temperature is regulated by control of the combustion-air-flow rate. Large amounts of CO are formed in this process. The emission rates from different units show considerable variation, but average emission factors have been determined as follows: from FCC units, 13,700 pounds of CO per 1,000 barrels of fresh feed; and for TCC units, 3,800 pounds of CO per 1,000 barrels of fresh feed.[17]

A recent study gave the total 1967 rated capacity of the catalytic cracking units in the United States, as shown in Table 4–3.

Using the preceding emission factors, the above capacity figures, and a factor of 0.9 to relate capacity per stream day to charge per calendar day, the CO generated is calculated to be:

FCC units: 7.4 million tons per year of CO

Table 4–3. CATALYTIC CRACKING CAPACITY IN UNITED STATES[18]

Type unit	Total feed, bbl/stream day	Recycle, %
FCC	4,655,570	29.9
TCC	748,600	29.0
Houdriflow	199,000	29.2

TCC and Houdriflow units: 422,000 tons per year of CO

4.2.1.2 *Control Techniques*

The CO waste-heat boiler affords a means of utilizing the heat of combustion of CO and the sensible heat of the regeneration gases. The CO and other combustibles, mainly hydrocarbons, are oxidized to CO_2 and water,

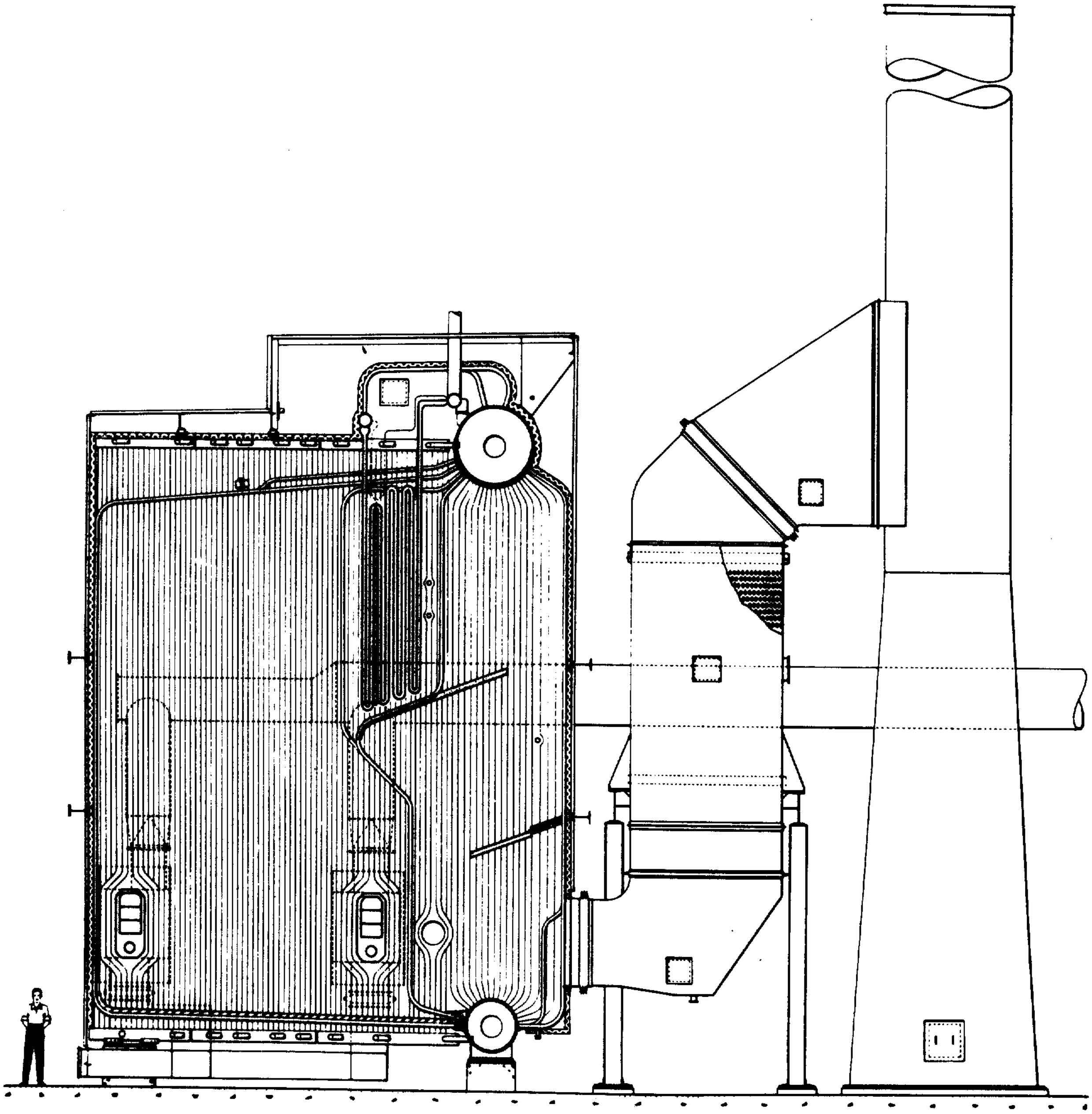

Figure 4-7. Water-cooled, carbon monoxide waste-heat boiler.
(Courtesy of Combustion Engineering, Inc., Windsor, Conn.)

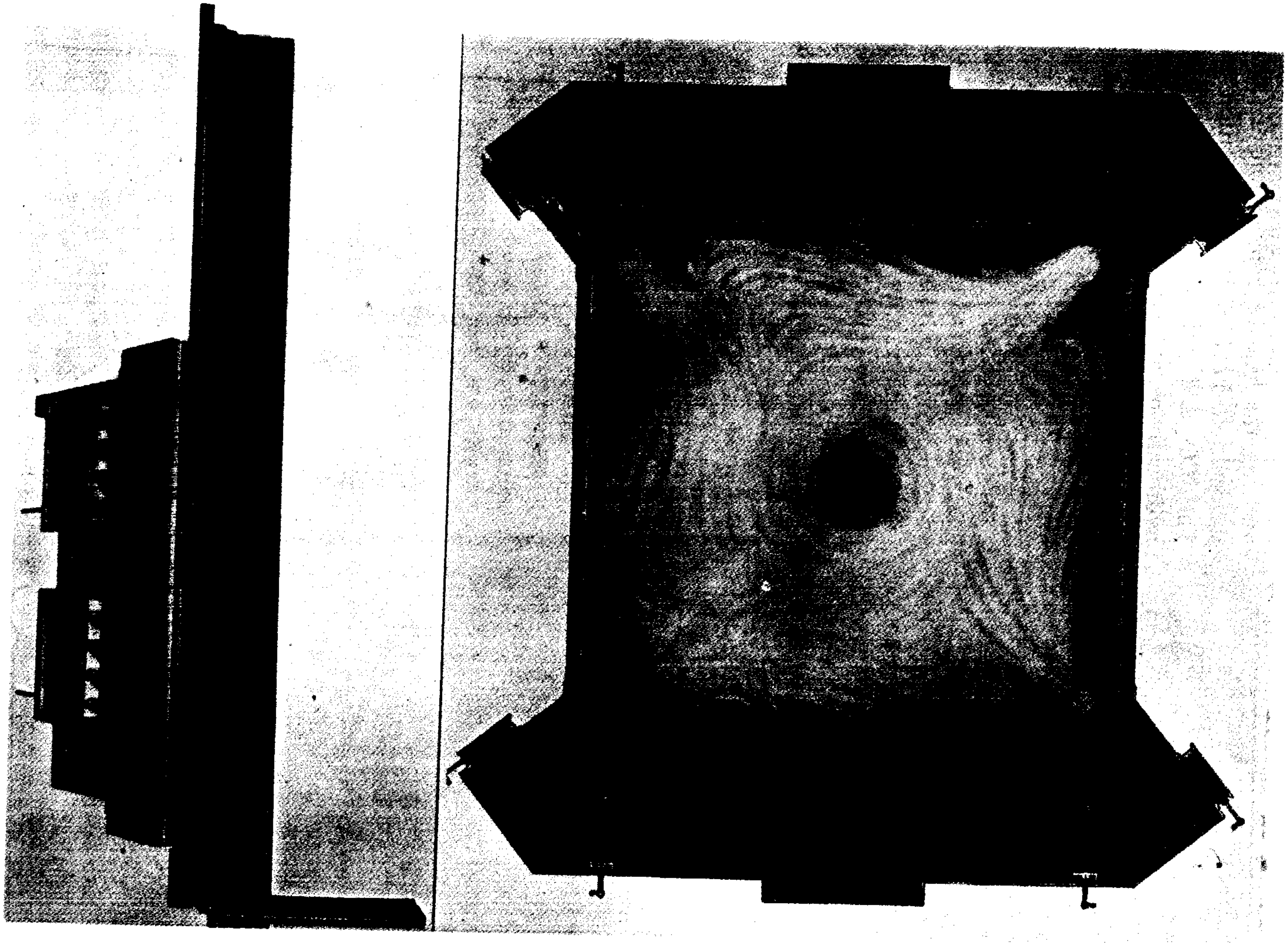

Figure 4-8. Corner-fired burners of a carbon monoxide waste-heat boiler: (left, Elevation view showing a typical set of burners for one corner; (right) plan view of firebox showing location of the four sets of burners.

(Courtesy of Combustion Engineering, Inc., Windsor, Conn.)

and are, thereby, eliminated as air pollutants. Thus, regenerator gas from catalytic cracking is commonly burned to recover its heating value.

In most cases, supplementary fuel is required to insure stable operation. This fuel may be fuel oil, refinery process gas, or natural gas. The boiler does not contain an oxidation catalyst chamber for conversion of the CO to CO_2. It depends, instead, upon the maintenance of a minimum CO gas-combustion temperature of 1,800°F within the primary furnace section, provided by the introduction of supplementary fuel.[19]

The CO boiler may be a vertical structure with either a rectangular or circular cross section with water-cooled walls, as shown in Figure 4–7. The outer dimensions of a typical rectangular boiler are 32 feet wide by 44 feet deep by 64 feet high, with a 200-foot-high stack.[20] The boiler is equipped with a forced-draft fan and four sets of fixed, tangential-type burners (one set for each corner). A typical set of burners includes two CO compartments, four fuel gas nozzles, and two steam-atomized oil burners, as shown in Figure 4–8. The burners are approximately 1-1/2 feet wide by 6 feet high. A tangential-type mixing of the gases for more nearly complete combustion is achieved by arranging the burners slightly off center.

Regeneration gases from the FCC unit are normally delivered to the inlet of the CO boiler duct work at about 1,100°F and 2 pounds per square inch (gauge). Whenever the regenerator gases first pass through an electrical precipitator, the inlet gas to the precipitator must be cooled below 500°F. The CO boiler would then receive regeneration flue gas at a temperature between 450° and 500°F.

4.2.2 Fluid Cokers

A fluid-coking unit resembles an FCC unit in that a bed of fluidized solids is used to transfer heat to the partially vaporized feed material. It differs in that the solid particles are coke, which is a product of the cracking reaction. Coking occurs in a thin, liquid film on circulating, fluidized, seed coke agitated by rising gaseous products in the reactor.[21] Reactor temperature is 900° to 1,050°F.

A stream of coke particles is continuously withdrawn, steam-stripped, and transported to another vessel called a burner. A controlled amount of air is injected into the burner, and sufficient coke is burned to maintain the coke bed at a temperature of 1,110° to 1,200°F. A stream of coke at this temperature is returned to the reactor. More coke is formed in the reactor than is burned; consequently, a coke-product stream is withdrawn.

4.2.2.1 *Emissions*

In the burner, coke is burned under conditions of limited air with respect to the amount of carbon present. Hence, the flue gas is very rich in CO. It is estimated that CO emissions average 30 pounds per barrel of fresh feed.[22] In 1960, the total capacity of the fluid-coking plants in the United States was 100,000 barrels per day.[23] On this basis, the total CO generated in 1960 from fluid-coking units was 550,000 tons per year. Estimated CO emissions (shown in Table 2–1) indicate that CO boilers are often used to burn the CO generated in fluid coking.

4.2.2.2 *Control Techniques*

The flue gas from the burner can be burned in CO boilers similar to those used for catalyst regenerator flue gas.

4.2.3 Cost of Controls

The economics of a CO boiler installation in conjunction with a catalytic-cracking unit are specific for a given refinery. The economics may be generalized sufficiently, however, to determine a range of catalytic-cracking unit sizes that can pay out a CO boiler.[19] The basic variable used in determining the size of the catalytic-cracking unit is coke-burning rate. Other variables that affect payout include the following in the order of decreasing importance: (1) fuel value, (2) CO_2/CO ratio, (3) flue gas temperatures, (4) excess oxygen in CO gas, and (5) hydrogen content of regenerator coke.

On the assumption that additional steam is required in the refinery, a coke-burning rate of 10,000 pounds per hour or more can be economically attractive for installation of a CO boiler when fuel has a value of 20¢ per 10^6 Btu. If additional steam is not required, the minimum coke-burning rate to provide a reasonable payout for a CO boiler is about 18,000 pounds per hour. A payout of 6 years after taxes is assumed.[19] In some areas, the reduction in air contaminants is sufficiently important to justify a payout longer than 6 years.

No figures are available for a CO boiler for a fluid-coking unit, but economic considerations would be similar to those given above for the catalytic cracking unit CO boiler. This would be true, however, only for a new fluid coking unit when the CO boiler is built integral with the unit during construction. The installation of duct work, blower, and other accessories for adding a CO boiler to an existing unit usually cannot be economically justified.

4.3 CHEMICAL INDUSTRY

Carbon monoxide is used directly in the chemical industry as a raw material for synthesizing other chemicals, such as methanol and phosgene. It is also produced, and has a transitory existence, as one of the gaseous products of the reformer, where hydrogen or a mixture of hydrogen and nitrogen is desired. In these cases, CO is removed as such or, more commonly, is oxidized to CO_2 or reduced to methane.

The production of CO by the chemical industry of the United States is estimated at somewhat greater than 6.6 million tons per year. This includes the CO that has only a transitory existence in the vessels and pipelines of the reforming plants. This production does not loom large, by comparison, with the 60 million tons per year emitted to the atmosphere from gasoline engines (Table 2–1), or with the 90 million tons per year produced in pig-iron blast furnaces and mostly used as fuel therein.

4.3.1 Synthesis Gases

Most of the hydrogen used by the chemical industry in the United States is made by the steam-reforming process. Hydrocarbons furnish the source of hydrogen, and the basic reaction is:

$$C_nH_m + n\,H_2O \longrightarrow n\,CO + \frac{2n+m}{2}\,H_2$$

Natural gas is the hydrocarbon most often used in this country:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

These reactions, the main sources of CO within the chemical industry, are used extensively to generate synthesis gases, which are used to make such products as methanol and ammonia. The manufacture of hydrogen by this method always involves, therefore, the generation and handling of CO. The above reaction is favored by higher temperature and lower pressure, but modern plants operate at pressures of 450 pounds per square inch (gauge) or more, for economic reasons.

The gas reformer is a furnace having alloy tubes containing a nickel-base catalyst. The reforming process requires heat, and temperatures of 1,400° to 1,800°F are commonly used.[24]

The gases most often needed are hydrogen, or a mixture of hydrogen and nitrogen for ammonia synthesis. For these uses, the water gas shift reaction is employed to remove CO:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

This reaction is not affected by pressure, but is favored by lower temperatues, which, however, reduce the reaction rate. Highly active low-temperature catalysts of recent development allow operation under 500°F and remove most of the CO at a reasonable rate in one shift stage. The CO_2 formed is removed by scrubbing.

Small residual amounts of CO and CO_2 can be removed by methanation:

$$3H_2 + CO \longrightarrow CH_4 + H_2O$$

This reaction is carried out at elevated temperatures over a nickel catalyst and can reduce CO to less than 10 ppm.[24]

Another type of reforming is partial oxidation, for which there are several processes. Hydrocarbons are burned under reducing conditions:

$$C_nH_m + \frac{n}{2}O_2 \longrightarrow n\,CO + \frac{m}{2}H_2$$

Naphtha or natural gas are the hydrocarbons generally fed. The percentage of CO in the raw synthesis gas increases with the C/H ratio in the feed hydrocarbon. Typical results for conversion of the hydrocarbon, using 95 percent oxygen as oxidant, are given in Table 4–4.

Table 4–4. SYNTHESIS GAS COMPONENTS[25]
(vol. %)

Synthesis gas	H_2	CO
Natural gas	60.9	34.5
Naphtha	51.6	41.8
Heavy fuel oil	46.1	46.9

Table 4–5 compares various industrial gases according to their typical contents of CO and hydrogen. The last three gases listed in Table 4–5 are the raw unpurified synthesis gases. Steam-reforming of methane tends to be favored where there is a plentiful supply of cheap natural gas, as in the United States.[24] Partial oxidation is more often used in Europe.

Table 4–5. CARBON MONOXIDE AND HYDROGEN CONTENT IN SOME INDUSTRIAL GASES[26]
(vol. %)

Gas	CO	H_2
Coke oven	6.3	53
Blast furnace	27.5	
Water gas	42.8	49.8
Methane reformer	15.5	75.7
Methane partial combustion	35.6	61.5
Oil partial combustion	47	47

4.3.2 Methanol

The production of synthetic methanol in the United States in 1968 was about 3.750 billion pounds.[27] Theoretically, this production would require a feed of 1.65 million tons of CO, which represents the minimum known requirement for this production. Methanol is synthesized as follows:

$$CO + 2H_2 \longrightarrow CH_3OH.$$

This reaction is favored by high pressure and by lower temperatures, and it is exothermic. In practice, pressures of 4,500 pounds per square inch (gauge) and temperatures up to 700°F have been used in the presence of a suitable catalyst. Temperature control of the methanol converter is by dilution with quench gas or CO_2. The methanol produced contains some impurities, which must be removed by flashing on pressure letdown, followed by distillation. The unreacted gas is recycled by the recycle compressor and combined with fresh feed; inert gases are prevented from building up in the system by purging. The methanol converters of some recent methanol plants utilize new copper-based catalysts permitting operation at pressures and temperatures as low as 700 pounds per square inch (gauge) and 500°F, respectively.[28]

Synthesis gas can be produced for use directly in methanol synthesis, without the separations or adjustments required for making phosgene, ammonia, and other products.

4.3.3 Ammonia

The production of ammonia in the United States in 1968 was about 12.5 million tons.[27] From the data given in Table 4–5 for the methane reformer, the CO associated with the production of this amount of ammonia can be calculated to be over 4 million tons, if the ammonia synthesis gas were made by the steam-methane reforming process. For ammonia manufacture, the CO is removed to a residue of less than 20 parts per million, since it poisons the catalyst. This removal is done by the gas shift and methanation reactions described previously.

Ammonia is synthesized by the following reaction:

$$N_2 + 3H_2 \longrightarrow 2\,NH_3$$

This reaction is favored by high pressure and by lower temperatures. Pressures of 100 to 1,000 atmospheres and temperatures of 750° to 900°F have been used. In order to secure the required nitrogen-hydrogen mixture, a hydrocarbon gas is reacted in two stages. In the first stage, part of the hydrocarbon is reformed with steam; in the second stage, the unreacted hydrocarbon is partially oxidized with sufficient air to yield the proper hydrogen-nitrogen ratios.

4.3.4 Phosgene

Phosgene is made from CO and chlorine by the reaction:

$$CO + Cl_2 \longrightarrow COCL_2.$$

This exothermic reaction is carried out in water-cooled tubes filled with activated-carbon catalyst. Only a slight excess of CO is used to insure complete reaction of the chlorine, and the yield is over 99 percent.

In 1967 there were 17 phosgene-manufacturing establishments in the United States[29] having a combined annual capacity of over 400,000 tons, much of which was for in-plant use only. Theoretically, 114,000 tons of CO is required to make the above quantity of phosgene. Phosgene itself is such a dangerous material and is so hazardous to life, that leaks anywhere in the phosgene system are made improbable by careful design and watchful operation.

The CO manufacturing system employing phosgene is similar to that required for making methanol, in that it has a reformer; it differs, however, in having the requirement for relatively pure hydrogen-free CO. The CO in raw synthesis gas is therefore purified by absorption and desorption or by cryogenic methods. A commonly used purification method involves high-pressure absorption of CO in a special copper liquor containing cuprous and cupric chlorides and ammonium carbonate:

$$Cu_2(NH_3)_4^{--} + 2\,CO + 2NH_3 \longrightarrow Cu_2(NH_3)_6(CO)_2^{--}$$

The CO is liberated on release of pressure. Absorption is carried out at near ambient temperatures, and the temperature is raised to aid desorption. This is quite a complicated system; the ratio of cupric to cuprous copper must be held within a certain range, and CO_2 and sulfides should be removed.[30] This removal is done ahead of the copper-liquor system by, first, passing the gas through an ethanolamine absorber-stripper system. Cool mono- or diethanolamine absorbs the acidic hydrogen sulfide and CO_2, and these are both driven off later by heating the amine solution in a stripping tower, which regenerates the amine. In the following copper-liquor system, the separation and purification of the CO takes place.

There may be three CO-handling units in phosgene manufacture: the reformer, the ethanolamine absorber-stripper unit, and the copper liquor CO absorption-purification equipment. Nevertheless, the relatively small usage of phsogene relegates this industry to one of minor potential CO emissions.

4.3.5 Organic Acids[31]

Carbon monoxide can be made to react with certain alcohols and unsaturated hydrocarbons to form organic acids. Perhaps the most important of such processes is the synthesis of acetic acid from CO and methanol as shown by the following reaction:

$$CH_3OH + CO \longrightarrow CH_3COOH$$

The synthesis takes place in the presence of aqueous cobaltous iodide at about 250°C and 10,000 pounds per square inch.[25] Published yield figures show that at one large plant, CO requirements are 21,000 tons per year, exclusive of that required for making methanol.[25] The vent gases are expanded to about 150 pounds per square inch (gauge) and washed with methanol feed before being piped to the fuel supply. By-products other than gas are also formed in the reaction and are separated from the acetic acid by distillation.

Other types of organic acids can be synthesized in accordance with the following general equation:

$$RCH{=}CH_2 + CO + H_2O \longrightarrow RCH_2CH_2COOH$$

Acrylic,[25] pivalic,[32] succinic,[33,34] and monobasic unsaturated acids[25] are among those that may be made.

4.3.6 Aldehydes

Carbon monoxide can be made to react with certain olefins to form aldehydes. Among patented processes are the following:

$$C_2H_4 + CO + H_2 \longrightarrow C_2H_5CHO$$

This reaction takes place at 600 pounds per square inch and 130°C with a catalyst of cobalt on kieselguhr, and the yield of propionaldehyde is over 75 percent.[35] Normal butyraldehyde is formed in the presence of cobalt naphthenate catalyst at 150°C and 500 pounds per square inch in accordance with the following reaction:[36]

$$C_3H_6 + CO + H_2 \longrightarrow C_3H_7CHO$$

The Oxo process is of commercial importance, expecially in Europe; with this process, aldehydes can be made from olefins, CO, and hydrogen.[25] The Oxo process is illustrated by the following reaction:

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO$$

This reaction is carried out at about 150°C and 250 atmospheres with a cobalt catalyst. There are some by-products, which are separated by distillation. If alcohols are desired, they are made by hydrogenation in a separate process step. Olefin conversion is over 95 percent.

Formaldehyde (HCHO) manufacture consumes about 40 percent of all the methanol produced annually in the United States.[27] Methanol vapor and air are passed over a hot catalyst at 1 atmosphere, and the gases are absorbed in water. The following reactions may occur, depending on the type of catalyst used:

$$CH_3OH \longrightarrow HCHO + H_2$$

$$CH_3OH + 1/2\,O_2 \longrightarrow HCHO + H_2O$$

Since HCHO is thermodynamically unstable and tends to decompose under the reaction conditions into CO and H_2, some CO is always formed by partial decomposition of HCHO. The product gases go directly to the scrubbers, and CO leaves in the scrubber off-gas.

4.3.7 Other Organic Compounds

A number of miscellaneous organic syntheses involving CO have been worked out or patented.

At least one plant abroad makes butanol as follows:[25]

$$C_3H_6 + 3CO + 2H_2O \longrightarrow C_4H_9OH + 2\,CO_2$$

This reaction is carried out at 100°C and 220 pounds per square inch (gauge) with a catalyst mixture containing iron pentacarbonyl. By-products include propane, CO_2, and hydrogen; these are bled off, along with some CO, through a scrubber. Most of the CO is recycled back to the reactor.

The versatile and powerful solvent, dimethyl formamide, can be made by the following reaction involving CO[37]

$$(CH_3)_2NH + CO \longrightarrow (CH_3)_2NO\,CH$$

This reaction is carried out at a temperature of about 60°C and a pressure of 90 pounds per square inch in the presence of sodium methylate catalyst.

Diethyl ketone can be made by a reaction involving CO:[38]

$$2C_2H_4 + CO + H_2 \longrightarrow C_2H_5\,CO\,C_2H_5$$

The yield given for this particular synthesis was rather low, at only 20 percent.[31]

The preceding discussion has indicated that CO is an important petrochemical feedstock; its use may greatly increase at some future time. It is available in enormous amounts in the steel industry at a current rate of about 90 million tons per year from pig iron blast furnaces, and 2.3 million tons per year from basic oxygen furnaces. A variety of synthesis gases could be made from these gases, using steam and hot coke.

4.3.8 Emissions

All CO emissions in the chemical process industry come directly or indirectly from processes involving synthesis gas. The various synthesis gases always contain some inert gases. As the reactive gases are consumed, inert gases build up. They are commonly purged from the system by continuously bleeding off a small percentage of the total gas stream. The reacting gas forms a considerable percentage of this purge stream; and if the reacting gas is CO, the purge represents a potential emission of CO. One leading manufacturer of methanol, for instance, estimates that emissions—including those from purging—range from 0.2 pound of CO per ton of methanol produced in a modern single-line plant, to 15 pounds of CO per ton produced in a relatively old multiple-line plant.[39] If 70 percent of the 1968 methanol was produced in modern, single-line plants, the CO emission from all plants would have been less than 4,000 tons. In addition to the above emissions, methanol plants may vent CO from high stacks during periods of startup, shutdown, or circuit upset. A 600-ton-per-day methanol plant may vent a mixture of the H_2 and CO containing about 10,000 standard cubic feet per minute of CO, under such conditions, for periods up to several hours.

Carbon monoxide emissions from formaldehyde manufacture are about 0.05 pound for each pound of formaldehyde produced.[39] Based on production figures, CO emissions amounted to 34,000 tons in 1967.

Carbon monoxide is not one of the easiest materials to burn; thus, emissions often are released when it is used as fuel, or is incinerated.[40,41] The lower and upper flammability limits are 12.5 and 74 percent by volume.

Leaks, a source of emissions and a source of economic loss to the industry, are a continuous problem to engineering and maintenance personnel.[42] Leaks occur from shaft seals, such as the stuffing boxes for agitators and pumps, and at fan and compressor shafts. Valves can leak from stem-packing or faulty seating. Flanges and gaskets are prone to develop leaks, especially if all of the loading conditions were not recognized and investigated during design.

Operation of safety valves may release large amounts of CO for a short time, and poor reseating of the blown valve can prolong the emission. Rupture discs, sometimes installed to protect equipment from overpressure, release all the gas in a given system, if ruptured. Safety valves and rupture discs are usually manifolded to a relief system having a flare or stack. In the event of a line break, gas is released just as in the case of a rupture disc, except that this release is directly to the atmosphere.

Operating areas and compressor houses are often monitored continuously for CO. Unscheduled shutdowns, such as those caused by power failures, sometimes result in sudden releases of gases.

On high-pressure systems, these gases operate the safety valves, as just noted. Systems operating near atmospheric pressure may release CO and other gases at a temporarily high rate through water seal pots.

4.3.9 Control Techniques

Although significant amounts of CO are generated and handled by the chemical industry of the United States, the emissions are minor. This is because any appreciable emission would cause loss of the desired raw material, regardless of whether the material is CO itself, or hydrogen. Emission of these gases would also constitute a toxic or fire hazard.

The chemical industry adapted earlier refinery and oil-processing know-how in making equipment adaptations to satisfy its own special needs. The result is that syntheses of the type described herein are generally made in continuous, automatically controlled process plants. Such plants feature seamless pipe and welded pressure vessels—made, assembled, and tested strictly according to code.[43,44] Piping and pressure vessel codes still reflect the historic technical interdependence between the two industries. Continuous processing was not developed to reduce air pollution; but, as an incidental benefit, emissions of all kinds tend to be less from continuous processes than they are from batch processes.

Design codes are mainly responsible for low CO emissions in the chemical process industries.[45,46] The code followed for piping has been the United States of America Standards Institute Code B 31.3 for Petroleum Refinery Piping. This code gives minimum standards, but acts as a guide to chemical construction firms and engineering staffs of the chemical industry. A piping code for the chemical industry is now nearing completion, and publication[45] is planned for 1970. This will be Code B 31.6 for Chemical Plant Piping.[46] It differs from the old Code B 31.3, mainly, in that it includes provision for handling lethal fluids (such as HCN gas) and design rules for piping items that are damageable mechanically, such as glass.

Another important code is the American Society of Mechanical Engineers (ASME) Code for Unfired Pressure Vessels, Section VIII. Vessels are an important part of most chemical plants and include reactors, surge tanks, separators, and many other kinds of equipment. Approximately 25 of the states currently require compliance with this code. The code is long and complicated: in addition to many details of design and strength of materials, it considers such things as pneumatic and hydrostatic tests, inspection of welds, and qualification and testing of welders. For these reasons, vessel failures are extremely rare when vessels are used as designed in accordance with this code. In the case of synthesis gas, the hydrogen, not the CO, is the difficult component to contain. The type of steel used retains the hydrogen. The steel is specified for the process conditions expected.[47]

Purge gas composition depends upon the use to which the original synthesis gas was put, and may be high in CO. One methanol manufacturer reports that he sends methanol synthesis purge gas to the reformers that make ammonia synthesis gas. A common method of control for purge gas is to send it to the plant fuel system[48] or to pipe it directly to a boiler.[24] It may also be burned in a flare.

Flaring is often used to burn miscellaneous waste vapors, and, also, to control emergency vapor releases. A flare is a flame maintained out of doors at the end of a waste-gas-collection system; it burns both regular and emergency emissions.

Pressure vessels, heat exchangers, and pipelines are commonly protected against overpressure by safety (or relief) valves or rupture discs.[49,50] These devices are specified in a manner consistent with the requirements of the piping and pressure-vessel codes mentioned above. The spring-loaded safety valve opens to relieve pressure in the system and then reseats itself. The rupture disc is a thin metal diaphragm installed between flanges and carefully designed to rupture at a certain difference in pressure on the two sides. Normally, the outside pressure on the disc is atmospheric. Rupture discs are available in many metals, from aluminum to platinum, and in many alloys. Discs must be made of corrosion-resistant materials because the rupture strength is altered by only slight metal attack.

Safety valves are normally required to protect individual vessels, heat exchangers, and even sections of piping that can be blocked off for any reason. To specify safety-valve protection, each equipment piece or plant section to be protected is carefully examined with respect to what can go wrong. Typical of conditions investigated would be: (1) chemical reaction out of control, (2) failure of cooling water, (3) bursting of an exchanger tube, (4) blocking off a vessel or line, and (5) fire. These conditions may all give rise to gas evolution and overpressure. Fire is often the governing condition through which the most vapor is generated. Fire is often, therefore, the basis of design of the safety valve or rupture disc.

After the safety valves are sized and specified, the vapor-collection system is designed. This system receives gas and liquid from the discharge side of the safety valves and rupture discs, and conveys the gases to a flare or stack. At least one knockout drum[51] is commonly furnished to separate liquid from the gas stream. The flare itself is commonly an elevated stack having a pilot burner to ignite the discharged gas. In designing the collection system, allowance is made for the variation from normal to emergency flow: a small bypass can take care of normal gas flow and a water seal can accommodate very large gas flows. Actually, water seal pots have been used in reformer plants to limit pressure in the system and to release sudden gas accumulations.

Figure 4–9 illustrates a typical blowdown and relief-collection system and flare, such as may be used in a chemical plant or complex. The collection header for blowdown and relief, discharges into a separator drum[51] to remove liquid droplets before going to the stack. Separated liquid is pumped off to disposal. An inert purge gas, such as nitrogen, prevents flame flashback. Safe operation can be obtained by purging at such a rate that the oxygen concentration in the stack 25 feet from the top is less than 6 percent.[52] Purging is costly, and molecular seals[53] are now commonly used to reduce purge-gas requirements and reduce emissions to the atmosphere. During startup, the headers may be purged with fuel gas, prior to igniting the flare; the flare is ignited by a pilot gas flame at the flare tip. The flame arrester, shown at the base of the flare stack in Figure 4–9 is included for added insurance against flame flashback. The flare can be extinguished by flame blowout due to too-high-flare-gas velocity. This would release CO, but blowout is prevented by designing within certain stack velocities. If blowout occurs, remote reignition is accomplished by the pilot burner.

Safety and the effect of heat radiation are important considerations in flare design.[54] Because a large flare may radiate enormous amounts of heat, it may have to be elevated and distant from structures and personnel. Many flare stacks are 200 feet high or more.

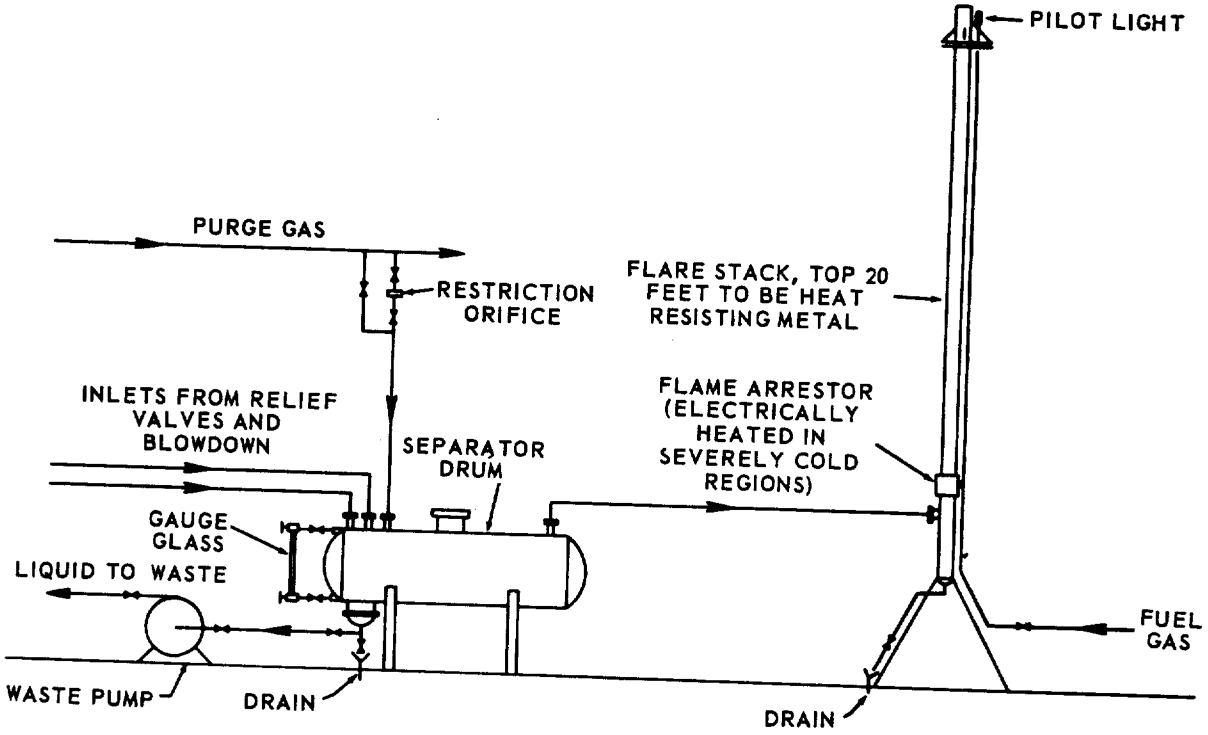

Figure 4-9. Blowdown and relief collection system.

4.3.10 Cost of Control

The following installed costs of flares 100 feet high, presented in Table 4–6, include: guying, caged ladder, pilot and ignition system, and engineering. They do not include separator drum, flare piping, gas piping, electric lighting, and real estate. The given costs are for smoking-type flares, suitable for disposing of the CO-containing gases previously discussed; by contrast, oil refinery flares should be the smokeless type, because they so often burn smoke-producing material. Operating costs estimates are based on a natural gas cost of $0.35 per 1,000 cubic feet. Flares are low-mainteance items, with replacements most commonly being in the ignition system. Flares suitable for upset conditions in ammonia and methanol plants will be closer to the 24-inch-diameter size. The above capital costs do not take into account the piping runs to the flare; for remote flare locations, the capital costs of these piping runs can be substantial.

Table 4–6 COST OF FLARES[55]

Flare-stack diameter, inches	Costs		
	Capital	Annual operating	
		Pilot gas	Purge gas
12	$48,000	$1,000	$1,000
24	60,000	1,000	4,000

Control of CO emissions from all of the processes described in this section is inherent in the design and construction of the plants. Capital cost of control would be a sum subjectively arrived at by allocation of facilities. The difficulties in allocation are obvious, and it is perhaps for this reason that there is no information in the literature about costs of control for the plants described above.

4.4 CARBON BLACK MANUFACTURING PLANTS

The carbon black industry in the United States has grown at a rate of 4 percent per year[56] from 1945 through 1965. At the end of 1967, the industry's nine producers had 35 plants whose yearly production capability totaled 3.102 billion pounds.[57] Actual total production in 1967 was 2.484 billion pounds of carbon black. In 1968, two more large plants were put in operation; each has a capacity of 100 million pounds per year.[58,59]

Most of the carbon black produced (93 percent) is used in the rubber industry to reinforce rubber. Essentially, it provides abrasion resistance to retard wear in products such as tires. In the paint and ink industries, carbon black is used as a colorant. It is also used in the food, plastics, and paper industries.

Carbon monoxide is evolved in the production of carbon black. Carbon black is produced by the partial breakdown of certain hydrocarbons to elemental carbon and other by-products, including CO. This hydrocarbon breakdown is usually accomplished by thermal cracking (thermal process) or by incomplete combustion (furnace and channel processes). All of these methods can produce CO.

In the United States, 6 percent of the carbon black is produced by the channel process, 12 percent by the thermal process, and 82 percent by the furnace process. Figure 4–10 is a flow diagram of a typical carbon black plant. As shown in Figure 4–10, CO is produced in the carbon black process. CO can be emitted from leaks in the cyclones, bag filter, exhaust system after the fan, or from connecting duct work. Some CO, trapped between carbon black particles, might escape in the grinder or in storage, but this amount would probably be very minor, compared to that from the exhaust system.

4.4.1 Channel Black

Channel black is produced by impinging a natural gas flame on a relatively cool iron plate or channel. Because the distance between the gas tip and the channel is too short to allow complete combustion, the unburned carbon is deposited on the channel as carbon black. Channel black is made on a continuous basis in buildings called "hot houses," containing 2,000 to 4,000 flames, which impinge

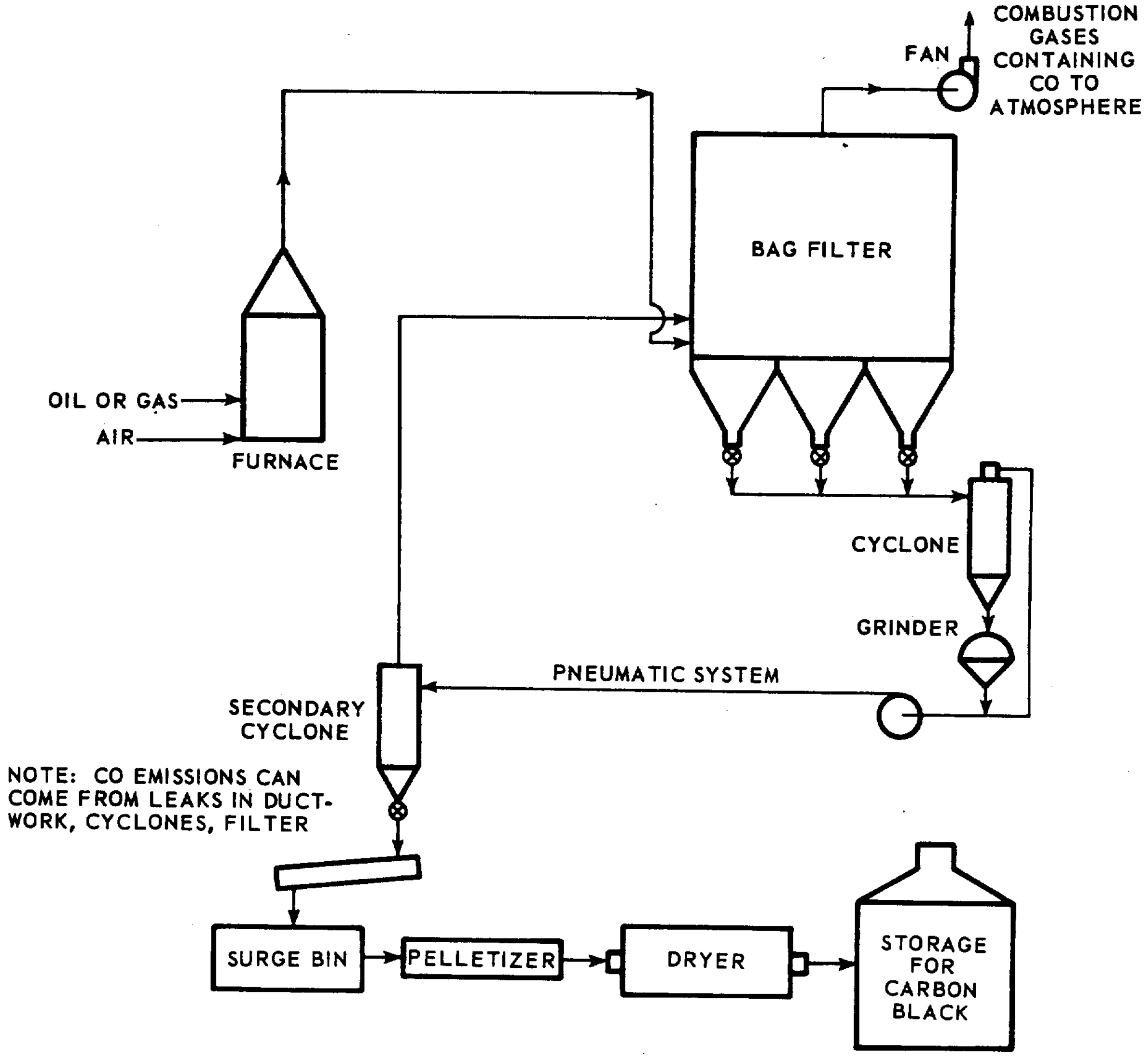

Figure 4-10. Typical diagram for carbon black manufacture.

on moving channels. The black is then automatically scraped from the channels and conveyed to the product-handling system. Each hot house uses 150,000 to 260,000 cubic feet of natural gas per day.[60] The temperature of the hot house is kept at about 1,000°F by the natural draft created in the building. The yield of carbon black in the channel process is about 2.5 pounds per 1,000 cubic feet of gas.[60] Recently, because of the rising cost of natural gas, the gas has been enriched with cracked recycle and cracked distillate oil. The yield from these oils is about 2.5 pounds of black per gallon.

4.4.1.1 *Emissions*

The channel black process emits CO directly to the atmosphere from the hot houses; therefore, there is no practical method for accurately determining the amount of CO emitted. All of the CO produced in this process goes to the atmosphere as CO because it does not oxidize readily at process conditions. A gross estimate of the CO emissions from the channel black process is 59,500 tons per year.[60]

4.4.1.2 *Control Techniques*

Channel black is used as the colorant in ink black[61] because its properties cannot be duplicated in the other two processes. The channel process must have a natural draft through the hot house. Any attempt to confine the emissions from these hot houses would disturb the natural draft and, thus, reduce the yield and quality of the black. The only control used is the moving of the entire plant if the problem gets too bad in a particular area. The particulate problems would probably necessitate a move before the CO would reach high enough levels to cause a problem.

4.4.2 Thermal Black

Thermal black is produced by the decomposition of natural gas in the absence of air or flame. This thermal-cracking process takes place in a checkerwork furnace or generator. First, the furnace is heated to 2,400° to 2,800°F; then, the flue is closed, and the natural gas is admitted to the generator. The gas is decomposed principally to carbon and hydrogen, with smaller quantities of CO, CO_2, methane, and nitrogen. The thermal carbon black passes from the furnace, is cooled, and is then collected. When the furnace becomes cool, the gas is shut off and the furnace is reheated with the gases (principally hydrogen) produced in the cracking process. The full cycle for this process takes about 10 minutes, with the time being divided about equally between heating and cracking.[60] Theoretically, if the natural gas were all methane, 31.82 pounds of carbon black and 2,000 cubic feet of hydrogen would be produced per thousand cubic feet of methane. The actual yield for the thermal process is 40 to 50 percent (up to 16 pounds of black per thousand cubic feet of natural gas).[60] Thermal black is coarse and does not have the reinforcing properties or color of channel black.

4.4.2.1 *Emissions*

Emissions from the thermal process are estimated at 47 pounds of CO per ton of thermal black or a yearly value of 3,500 tons of CO. Since the gas given off during the cracking process is used to reheat the checkerwork, however, much of this CO may be further oxidized to CO_2 during the reheating phase.

4.4.2.2 *Control Techniques*

The thermal process emits a comparatively small amount of CO when the exit gases are reused to heat the checkerwork. The amount is probably not enough to make it economically feasible to control the CO pollution.

4.4.3 Furnace Black

Furnace black, which can be divided into gas-furnace black and oil-furnace black, is produced by the incomplete combustion of fuel (oil or gas) in a specially designed furnace. To produce gas-furnace black, a turbulent mixture of air and natural gas is burned at 2,200°F. The ratio of air to gas (4.5:1) does not allow complete combustion, and results in the production of black. After the black leaves the furnace, it is cooled, agglomerated, and collected. The yield from the gas furnace is 25 to 30 percent for the larger-particle-size furnace black and 10 to 15 percent for the smaller-particle black.[60] Sometimes the gas is enriched with oil.

To produce oil-furnace black, the oil is first preheated to 550° to 700°F; then the air and gas are fed at a constant ratio while the weight of oil is varied to keep the furnace at 2,500°F. Different grades of black can be produced by varying the temperature and velocity in the furnace, or the geometry of the furnace. A yield of 55 percent can be expected from oil furnace black.[60] Oil furnace black tends to predominate in the industry because of advanced technology and the increasing cost of gas.[56]

4.4.3.1 *Emissions*

Carbon monoxide emissions from furnace-black production vary from 5 to 11 percent by volume in the exit gases.[60] On the average, 560 pounds of CO is emitted per ton of furnace black produced.[60] This gives an estimated yearly emission of 285,000 tons of CO from the production of furnace black.

4.4.3.2 *Control Techniques*

The furnace process may at some time have to be controlled in the United States. Two furnace plants in the United Kingdom are now required to control their CO emissions.[60] A flare on the stack is being used successfully to incinerate the CO.

Catalytic incineration is not practical for CO concentrations in the 5 to 10 percent range because the operating temperatures would exceed 1,000°F, which is well above the permissible operating temperature range of the catalysts.[62]

4.5 PULP AND PAPER INDUSTRY

Carbon monoxide emissions from kraft pulp mills are often overlooked. Potential sources of CO emissions from these mills are recovery furnaces and lime kilns. Bark-fired and fossil fuel-fired boilers are other potential sources of CO emissions. Carbon monoxide emissions from boilers and control techniques for boiler emissions are discussed in Section 3, "Industrial Stationary Combustion Sources."

4.5.1 Kraft Pulp Mill Recovery Furnaces

All kraft pulp mills use one or more recovery furnaces to recovery valuable chemicals and heat energy from the black liquor produced in the wood digestion process. The materials recovered or burned would otherwise create a waste disposal problem and represent an economic loss.

The kraft recovery furnace is a highly specialized unit. Design of these units and modification of design or modification of operating conditions, therefore, require extensive specialized knowledge and experience.

4.5.1.1 *Emissions*

Carbon monoxide emissions from United States kraft recovery furnaces are estimated at 700,000 tons per year.[63,64,65] CO emission rates are estimated at 60 pounds per ton of pulp produced.[63,65]

Emissions of CO from individual furnaces vary from as much as 2 percent when insufficient air is supplied, to a negligible level when sufficient air is admitted.[66]

The kraft recovery furnace recovers the salt content of waste cooking liquor. A reducing atmosphere must be maintained in the furnace to reduce the sodium sulfate content of the liquor to sodium sulfide.[67] This reduction must take place so that the sodium ion can remain soluble in the following lime causticization step. Reducing conditions form much CO in the furnace, which would escape as such were it not for the fact that additional air is admitted above the furnace reducing zone to oxidize CO. Thus, if the furnace is operated as designed, very little CO is emitted.

4.5.1.2 *Control Techniques*

With proper control of kraft-recovery furnace combustion, CO emission levels are below the range detectable with Orsat-type instruments (0.2 percent).[66] Combustion is controlled by adjustment of primary and secondary air and by monitoring the CO and oxygen content of the combustion gases. Many recovery furnaces operate with minimum CO emissions when the oxygen content of the combustion gases is adjusted to about 3 percent.

Since most kraft recovery furnaces are designed by experienced manufacturers, furnace design is seldom the cause of excessive CO emissions. Almost invariably, the cause of CO emissions is furnace operation well above rated capacity—a situation wherein it is impossible to maintain oxidizing conditions in the exit gas.

4.5.2 Lime Kilns

All kraft pulp mills use one or more lime kilns to regenerate lime from calcium carbonate produced in the causticizing process.

4.5.2.1 *Emissions*

Carbon monoxide emissions from kraft pulp mill lime kilns are estimated at 130,000 tons per year. Carbon monoxide emission rates are estimated at 10 pounds per ton of pulp produced.[64]

4.5.2.2 *Control Techniques*

Because of the specialized nature of the kraft pulp mill lime process, and the lack of accurate data on CO emissions from the lime kilns, no proved CO emissions control techniques are available for these specific sources.

These emissions could possibly be reduced, however, through variations in the kiln air supply, kiln temperatures, and increased turbulence and reaction time. Kiln design modification is a good possibility for new installations.

4.5.3 Costs

If CO emissions from kraft pulp mill recovery furnaces and lime kilns can be controlled solely by increasing the quantity of air admitted to the furnace or kiln, the cost of reduction would be the cost of developing the control technique and the cost of the heat energy lost with the increased volume of stack gases.

4.6 MISCELLANEOUS INDUSTRIAL SOURCES

4.6.1 Electrometallurgical Furnaces

The submerged arc electric furnace is used in the production of ferroalloys; Table 4–7 shows United States production in 1967.

Table 4–7. ELECTRIC FURNACE PRODUCTION OF FERROALLOYS IN THE UNITED STATES,[7] 1967. (tons/year)

Ferroalloy	Production
Ferromanganese	280,000
Ferrosilicon	528,000
Ferrochromium	263,000
Ferrochromsilicon	154,000
Ferrophosphorus	111,000
Silicomanganese	230,000
All others	259,000
Total	1,825,000

Ferroalloys are made by reduction of suitable oxides in the electric arc furnace. For example, in making ferrochromium the charge may consist of chrome ore, limestone, quartz (silica), coal and wood chips, along with scrap iron. In this case, the silica and lime form a slag. For ferrosilicon, the charge would consist mainly of iron scrap, silica, and coke. In every case, CO is formed copiously and escapes through the pores and channels in the charge. The escaping gas carries large quantities of particulates, which are essentially submicron in size (50 percent less than 0.1 micron), and which present a notoriously difficult control problem. Particulate abatement requires control equipment that bears little relation to that required for the comparatively minor control problem presented by CO.

The ferroalloy furnace may be hooded for collection of the off-gases, which will contain as much as 85 percent CO, 2.5 percent CO_2, 0.5 percent O_2, 10 percent H_2, and 2 to 2.5 percent each CH_4 and N_2. Utilization of this gas even as boiler fuel (approximate heating value, 340 Btu per cubic foot) requires scrubbing for removal of dust and is only marginally economical. Most furnaces operate with an open top and allow the CO to burn as it escapes through the charge. Temperature of the escaping CO is normally about 750°F, but may be as much as 1,500°F. Residual CO concentrations of several percent may be present because of incomplete combustion and the high equilibrium CO concentration at flame temperatures.

Adequate ventilation is necessary in the furnace areas to hold CO levels within safe limits. CO monitors are employed to warn of buildup of hazardous concentrations.

Figure 4–11 illustrates an electric arc furnace with dust control system typical of the ferroalloy industry. The fan draws dilution air into the system through the gap between furnace body and cover. If a baghouse is used instead of a wet scrubber, dilution air is even more necessary, to lower the temperature of the gas going to the bags. The CO burns inside the furnace cover when it mixes with the admitted air. Unburned CO goes through the particulate control device and up the stack. No emission factors are presently available for these furnaces. With a tight hood, the CO content of scrubbed gas will be 80 to 90 percent, and the gas can be used as boiler fuel if a user is nearby; otherwise, the gas would be flared.

Because these furnaces are extremely dusty, there will be increasing pressure in the future for particulate controls. Baghouses and other

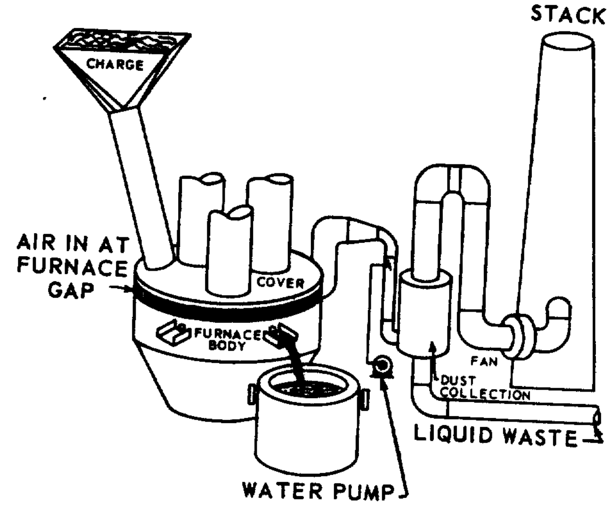

Figure 4-11. Electric furnace for ferroalloys industry.

control devices would be lower in cost if the furnace offgases could be cooled by radiation or other methods, instead of by air dilution, which increases the gas volume handled. This would mean the use of closed systems, handling and emitting relatively concentrated CO. Potential CO emissions would be greatly increased, but it might be possible to use the gas as fuel or to flare it.

4.6.2 Silicon Carbide Furnaces

Silicon carbide is an important abrasive manufactured by heating a mixture of sand (SiO_2) and coke to about 2,200°C in an electric resistance furnace. The heat is generated by the resistance of the charge to a flow of electric current passed through it. The silicon-carbide furnace is illustrated in Figure 4–12. At these temperatures the reaction proceeds as follows:

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

The walls of the furnace are temporary, so that they can be torn away from the charge after completion of heating. The gases that are formed work their way out of the porous charge and escape to the atmosphere. Because the surface of the charge is relatively cool, some CO may escape unburned.

For every pound of silicon carbide formed, 1.4 pounds, or about 18 cubic feet of CO, is formed. Although much of the released CO burns above the furnace, the combustion is uncontrolled and, undoubtedly, a considerable portion dissipates into the ambient atmosphere. Silicon carbide furnaces are not normally hooded for collecting CO or for providing excess air to dilute its concentration.

4.6.3 Calcium Carbide Furnaces

Calcium carbide is manufactured by heating a mixture of quicklime (CaO) and carbon in an electric arc furnace. The reaction proceeds at about 2,100°C as follows:

$$CaO + 3C \longrightarrow Ca\,C_2 + CO$$

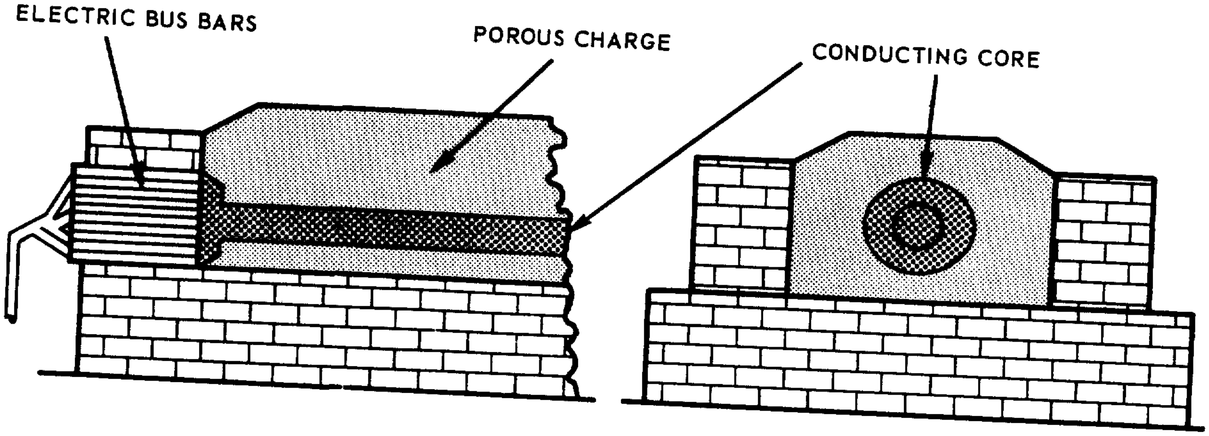

Figure 4-12. Electric furnace for production of silicon carbide.

The gases that are formed escape through the porous charge. The use of high-grade raw materials is necessary, because few impurities are eliminated in manufacture. Metallurgical coke, petroleum coke, or anthracite coal is used as the source of carbon. The actual reaction occurs between solid carbon and liquid lime in the melt below the electrode tips. The calcium carbide product is removed from the bottom of the furnace as a liquid.

Calcium carbide furnaces are essentially the same as ferroalloy furnaces, and may be hooded to collect the CO evolved. Because the offgas must be cleaned, even for utilization as boiler fuel, the economics of recovery is marginal. Adquate ventilation and monitoring are necessary to prevent hazardous concentrations of CO in operating areas.

Competitive combustion processes for manufacture of acetylene have largely supplanted calcium carbide as a source material for acetylene. The further burden of investment and expense for pollution control is probably not recoverable by increasing calcium carbide prices.

4.6.4 Elemental Phosphorus Furnaces

Elemental phosphorus is made entirely by an electric furnace process. A mixture of phosphate rock, sand, and coke is heated in a three-electrode (three phase) electric furnace to about 1,500°C. The following equation represents the overall reactions occurring:

$$4\,Ca_5\,F(PO_4)_3 + 18\,SiO_2 + 30C \longrightarrow$$

$$18\,[CaO \cdot SiO_2 \cdot 1/9\,CaF_2] + 30\,CO + 3P_4$$

Excess carbon is necessary to reduce iron, which may be present in the charge; a small fraction of the silicon is also reduced.[68]

The furnace (Figure 4–13) is operated at, or very slightly under, atmospheric pressure. The escaping gases are primarily CO, but they do contain all of the P_4 (gas), some dust, and some SiF_4 (gas). The dust is removed in an electrostatic precipitator, after which the P_4 is condensed as a liquid (m.p. 111°F) in a water condenser. The residual gas is about 90 percent CO, the balance being H_2, O_2, and CH_4. This gas is burned as fuel in phosphate-rock-drying kilns, or is flared if the kilns are out of service.

Escape of CO from the furnace involves simultaneous escape of P_4, which is very undesirable. CO emissions would, therefore, be either accidental and temporary in duration, or due to incomplete combustion of the washed gas.

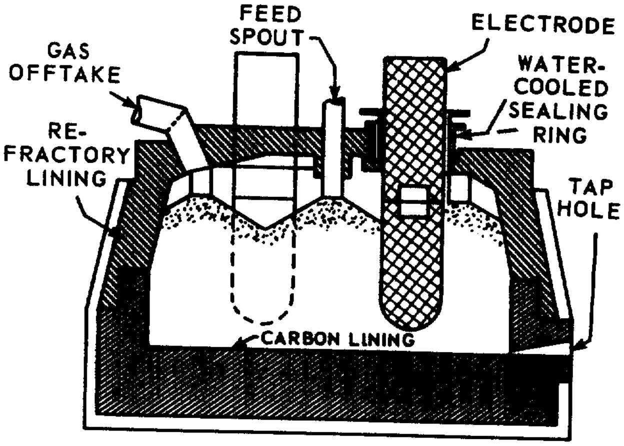

Figure 4-13. Diagram of electric furnace for production of elemental phosphorus.

4.6.5 Aluminum Reduction Cells

Aluminum is manufactured by the electrolysis of alumina (Al_2O_3) dissolved in a bath of molten cryolite (Na_3AlF_6). Impurities are removed from bauxite ore in the first step of the process to avoid deposition in the metallic aluminum. The cryolite renders the bath electrically conducting; small amounts of other fluorides are then added to lower the melting point so that the cell operating temperature is about 950°C. Both the cell anode and cathode are made of carbon. Metallic aluminum separates at the cathode, and oxygen is released at the anode. Depending on the operating conditions in the electrolytic cell, between 500 and 1,200 pounds of CO is formed per ton of aluminum produced.[65] For a 1968 production of about 3.2 million tons of aluminum, 0.8 to 1.9 million tons of CO was formed. Much of the CO burns upon exposure to the atmosphere or in the afterburner of cells so equipped.

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5. WASTE INCINERATION AND OTHER BURNING

5.1 EMISSIONS

Preliminary results of a survey conducted by the Public Health Service indicate that household, commercial, and industrial solid-waste production in the U. S. is about 10 pounds per capita per day, or 360 million tons per year. About 190 million tons per year (or 5.3 pounds per day per capita) is collected for disposal, the remainder being either disposed of onsite or handled by the household or establishment itself.[1]

An estimated 177 million tons of this material is burned in the open or in incinerators.[2] An additional 550 million tons of agriculture waste and 1.1 billion tons of mineral wastes are generated each year.[1] It is estimated that half of the agricultural wastes are burned in the open. Except for the estimated 48 million tons of coal refuse consumed by fire each year, no other mineral wastes are burned.[2] The quantity of material consumed by forest-burning and structural fires is estimated to total about 220 million and 8 million tons a year, respectively.[2]

Incineration and open-burning are used to reduce the weight and volume of solid waste. High-temperature incineration with excess air reduces emissions of particulates, CO, and smog-forming compounds such as aldehydes, hydrocarbons, and organic acids—which typify open burning—but tends to increase nitrogen oxides emissions.

Figures 5–1 through 5–7 show various basic types of incinerators. In a multiple-chamber design, as illustrated in Figure 5–3, combustion products are formed by contact between underfire air and waste on the grates in the primary chamber. Additional air (overfire air) is admitted above the burning waste to promote gas-phase combustion. Gases from

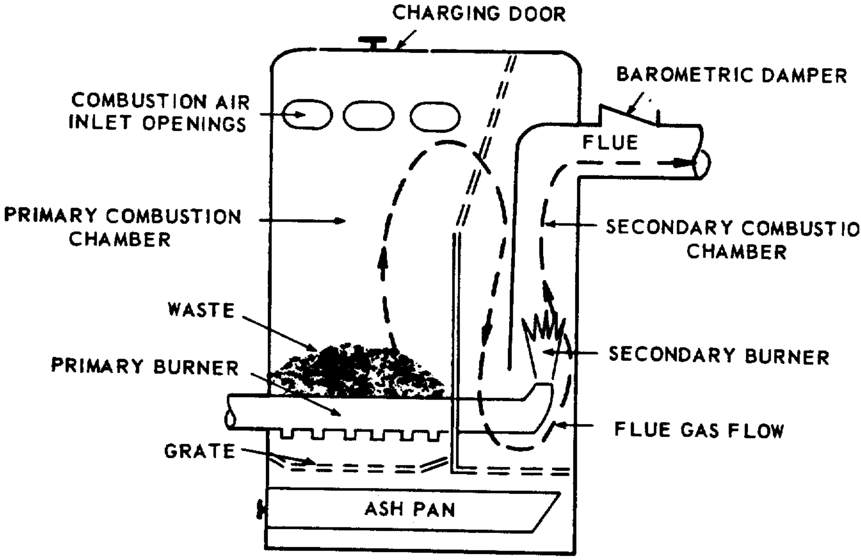

Figure 5-1. Domestic gas-fired incinerator.

the primary chamber flow to a small mixing chamber where more air is admitted, and then, to a larger, secondary chamber where more complete oxidation occurs. Auxiliary burners are sometimes installed in the mixing chamber to increase combustion temperature to about 1,400° to 1,800° F. As much as 150 percent excess air may be supplied in order to promote oxidation of combustibles. Sizes and configurations of incinerators vary with the service for which they are designed. References 3 and 4 contain information on design parameters for incinerators.

Estimated CO emissions from incineration and other burning are shown in Table 5–1.

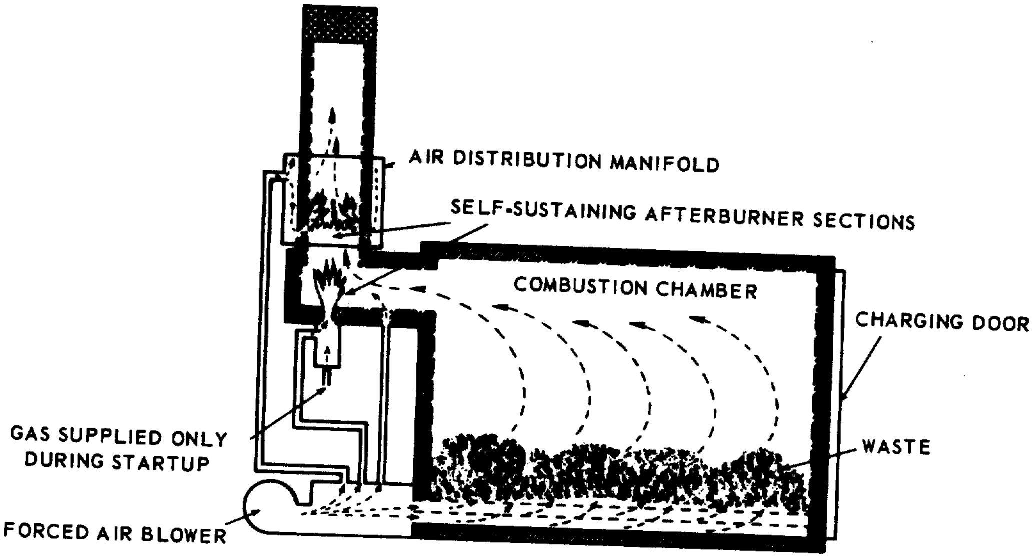

Figure 5-2. Single-chamber incinerator.

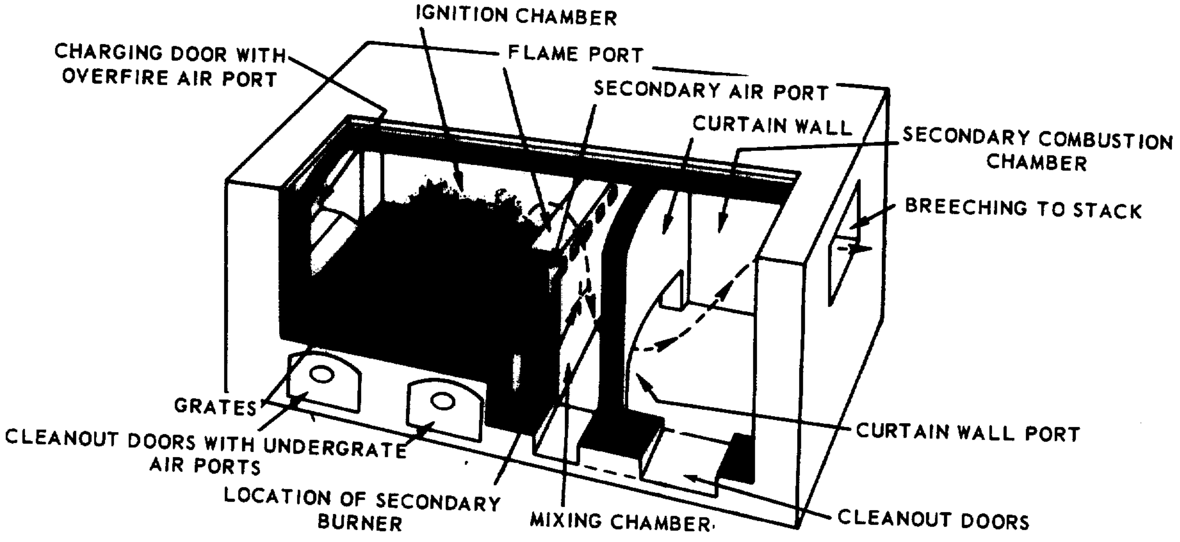

Figure 5-3. Cutaway of in-line multiple-chamber incinerator.

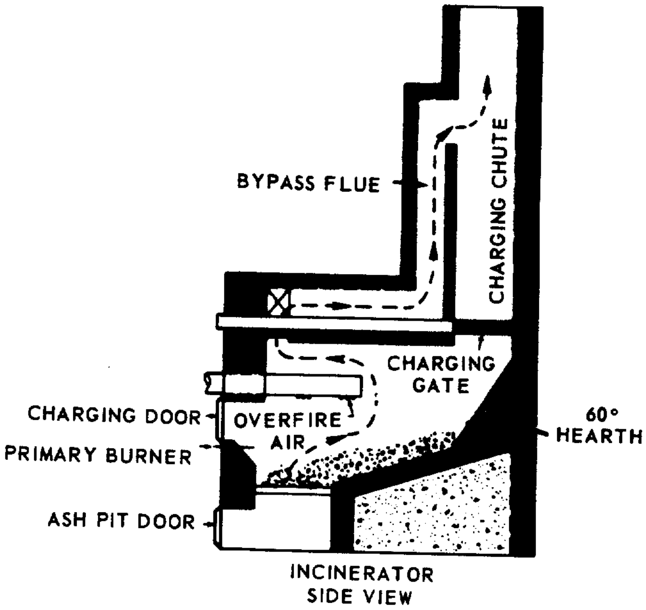

Figure 5-4. Section of flue-fed incinerator.

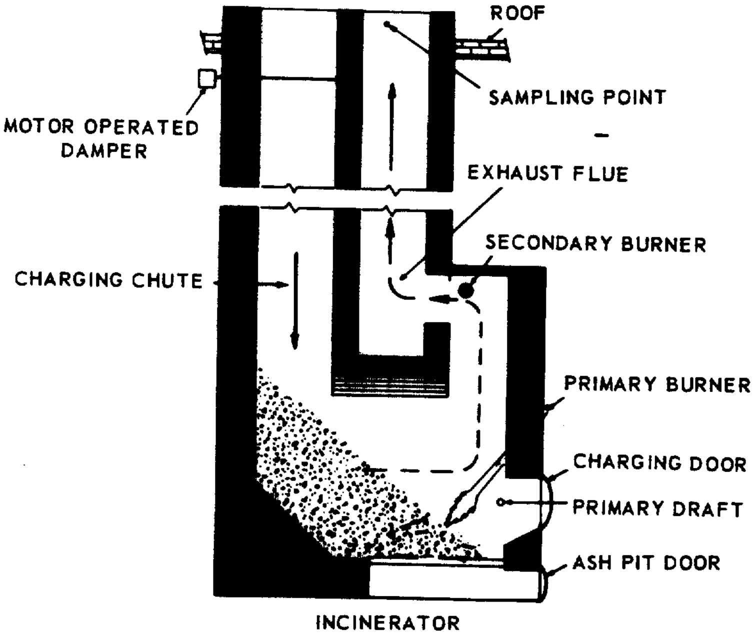

Figure 5-5. Section of chute-fed apartment incinerator.

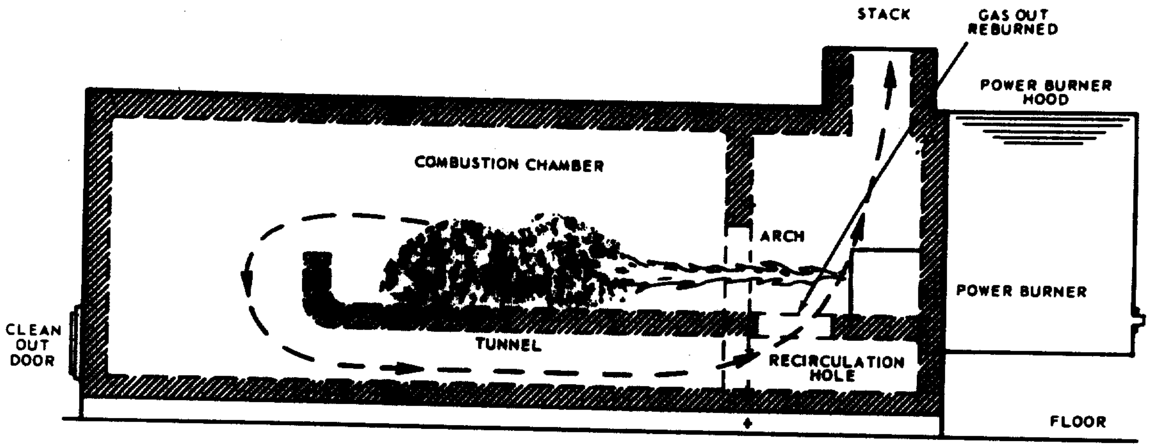

Figure 5-6. Section of pathological incinerator.
(Courtesy of Silent Glow Oil Burner Corp.)

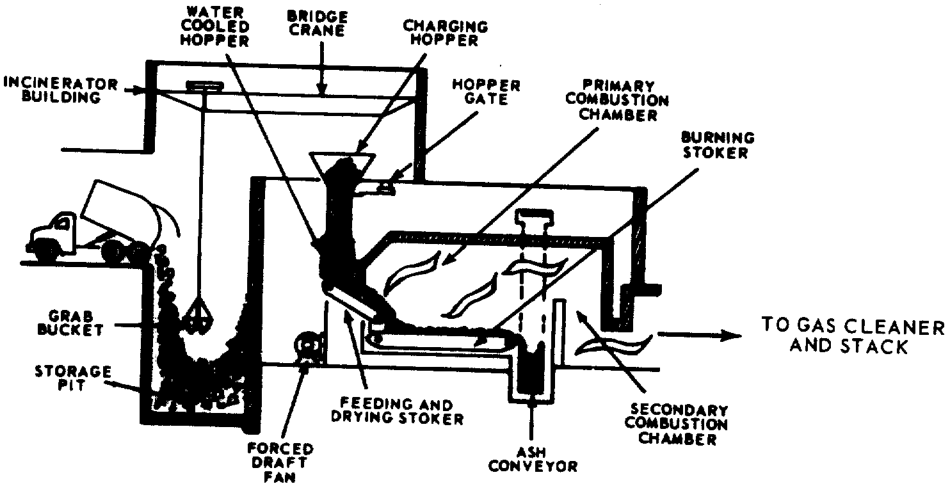

Figure 5-7. Section of municipal incinerator.

Table 5–1. ESTIMATED NATIONAL EMISSIONS IN 1968 FROM INCINERATION AND OTHER BURNING[2]
(tons/year)

Source	Quantity burned	Carbon monoxide emissions
Onsite incineration	57,000,000	780,000
Municipal incineration	16,000,000	20,000
Conical-burner incineration	27,000,000	3,600,000
Open burning	77,000,000	3,400,000
Agricultural burning	275,000,000	8,250,000
Prescribed forest burning	76,000,000	2,480,000
Forest wildfires	146,000,000	4,740,000
Structural fires	8,000,000	250,000
Coal-refuse fires	48,000,000	1,200,000
Total	730,000,000	24,720,000

5.2 CONTROL TECHNIQUES

High-temperature incineration using excess air, or alternative waste-disposal methods not involving burning, are the most likely means for reducing CO emissions. Some of these methods are discussed in the following sections.

5.2.1 Waste Disposal

From the standpoint of air pollution control, the most satisfactory methods of waste disposal are those that do not involve burning. Sanitary landfills are good alternatives if land for this purpose is available. Approximately 1.2 acre-feet of volume is required per 1,000 persons per year of operation when waste production is 5.3 pounds per day per capita.[5] In addition, cover material approximating 20 percent by volume, of the compacted waste is required. Availability of fill material limits the use of sanitary landfills.

Unusual local factors may ameliorate the landfill site problem. For example, reference 6 indicates that a project is under way in which the refuse is shredded and baled for loading on rail cars for shipment to abandoned strip-mine landfill sites. Noncombustion alternatives may have application in some localities. Composting has been considered and is being tested on a practical scale[7] for disposal of garbage. Dumping at sea has been practiced by some seacoast cities, but some of the garbage floats and returns to shore, unless dumped far out at sea or unless properly prepared. Such practices are now forbidden by the United States Government. A recent report[8] states that refuse has been ground and compressed into bales, which are wrapped in chicken wire and coated with asphalt. The high-density bales sink to the bottom in the deeper ocean areas and, reportedly, remain intact. The practice of grinding garbage in kitchen units and flushing it down the sewer has been increasing. This, in turn, increases the load on sewage-disposal plants and the amount of sewage sludge.

5.2.2 Incineration

Although no exact criteria are set for temperature, excess air, or residence time for incinerators, incineration temperatures greater than 1,600°F, excess air in a quantity of more than 150 percent, and heat-release rates less than 18,000 Btu per hour per cubic foot of total combustion space are sometimes used as design parameters for CO emission reduction. When these conditions are achieved, CO emission rates are less than 1 pound per ton of waste incinerated.[9]

Where the most effective CO emission control is desired, auxiliary burners are used to increase incineration temperature to 1,600° to 1,800° F. At temperatures above 1,800° F, slagging of refractories is often a problem. Even when dry, combustible wastes that will burn at temperatures exceeding 1,600°F are incinerated, auxiliary burners are useful for preheating the secondary combustion sections of the incinerator before the waste is ignited. Temperature-control systems promote consistent emission reduction. These usually consist of on-off type controls for smaller units, and modulating-type controls for larger incinerators.

Incineration air may be supplied by natural or mechanical draft. Recommended stack or chimney dimensions; barometric damper dimensions; and induced-draft-fan capacities for various incinerators, air flow, and wastes are published by the Incinerator Institute of America.[10] For the most effective control, air is passed through the grates (underfire air), admitted over the burning waste (overfire air), and admitted into chambers where auxiliary burners are located (secondary air). The ratio among these air supplies varies, depending upon the design of the incinerator. For small incinerators, combustion air is regulated by manual adjustment of air ports at the various points of entry. For larger incinerators, admission of air is automatically regulated and, at times, the ratio between air supply at various points is automatically controlled. For 150 percent excess air, the oxygen content of the undiluted gases at the incinerator outlet ranges between 12 and 14 percent, depending upon the type of waste incinerated and the type of auxiliary fuel used.

Sufficient residence time for oxidation of combustibles is provided by furnishing insulated combustion space. A maximum heat-release of 18,000 Btu per hour for each cubic foot of total combustion space is sometimes used as a design parameter for determining required combustion space. Contact between gaseous combustibles and air is promoted through the design by providing baffles, bridge walls, checkerwork, curtain walls, down passes, drop arches, and mixing chambers; by introducing air at strategic locations; and by locating auxiliary burners to promote mixing.

Differences among CO emissions from various types of incinerators are caused by differences in incineration conditions. Although insufficient air, combustion space, and mixing increase emission rates, the most common cause of increased CO emission rates is low incineration temperature. Estimates of emission factors from various types of incinerators are given in Section 6.

Another way of reducing total CO emissions from incineration and combustion is by recovering heat in a boiler, and thereby eliminating the need for combustion of some fossil fuels. This means of refuse disposal has already received considerable attention in Europe,[11-15] and has been tried in the United States.[16]

5.2.3 Forest Wildfires

About 4.7 million tons of CO is emitted annually from forest wildfires.[2] These fires are caused by natural elements such as lightning, or by careless practices. Considerable activity has been and is being directed toward reducing the frequency of occurrence and the severity of these fires. These activities include publishing and advertising information on fire prevention and control, surveillance of forest areas where fires are likely to occur, and various fire-fighting and control activities. Information on forest fire prevention and control is available from the U.S. Department of Interior and state and local agencies.

5.2.4 Controlled Vegetation-Burning

Forest debris, crop residues, scrub, brush, weeds, grass, and other vegetation are burned for one or more of the following purposes:

1. To control vegetation, insects, or organisms harmful to plant life.
2. To reduce the volume of waste.
3. To minimize fire hazards.
4. To improve land.

Carbon monoxide emissions from this burning are estimated at about 10.7 million tons per year.[2]

Collection and incineration of these wastes in properly controlled incinerators would reduce emission rates from an estimated 60 to 65 pounds per ton to as little as 1 pound per ton.[2]

Other alternatives to incineration are abandonment or onsite-burial, transport and disposal in remote areas, and utilization. Abandonment or onsite-burial is practical in cases where no other harmful effects will ensue. Since abandoned or buried vegetation can have harmful effects upon plant life—e.g., hosting harmful insects or organisms—agricultural agencies such as the U.S. Department of Agriculture, state, and local agencies should be consulted before these techniques are recommended. Other harmful aspects, such as odor or water pollution potential or fire hazards, should also be considered. Collection and transport of these materials for disposal in areas where harmful effects are avoided is possible, but not commonly practiced.

At times it is possible to use some of these waste materials. Large forest scraps are processed by chipping or crushing, and are used as raw materials for kraft pulp mills or processes producing fiberboard, charcoal briquettes, or synthetic firewood.[17] Composting or animal-feeding are other possible alternatives to burning.

5.2.5 Coal-Refuse Fires

An estimated 1.2 million tons of CO is emitted each year from 19 billion cubic feet of burning coal refuse.[2] Extinguishing or preventing such fires are the techniques used for eliminating these emissions. These methods involve cooling and repiling the refuse, sealing refuse with impervious material. injecting slurries of non-combustibles into the refuse, minimizing the quantity of combustibles in the refuse, and preventing ignition of the refuse. The above techniques and the status of future plans and research are described and discussed in AP–52, *Control Techniques for Sulfur Oxide Air Pollutants.*[18]

5.2.6 Structural Fires

Structural fires emit an estimated 250,000 tons of CO annually.[2] Fire prevention and control techniques are used to minimize these expensive sources of emissions. Some of the techniques used to prevent fires are: use of fireproof construction; proper handling, storage, and packaging of flammable materials; and publishing and advertising information on fire prevention. Fire control techniques include the various methods for promptly extinguishing fires, such as by the use of sprinklers, foam, and inert gas systems. Also included is the provision of adequate fire-fighting facilities, personnel, and alarm systems. Information on these and other techniques for fire prevention and control are available from agencies, such as:

1. Local fire departments.
2. National Fire Protection Association.
3. National Safety Council.
4. Insurance companies.

5.3 COSTS OF CONTROLS

Costs of controls are primarily a function of the relative costs of the various methods of incineration and the costs of non-combustion waste disposal. Because cost comparisons vary widely with locality, they should be made on an individual basis.

The average community budgets $5.39 per capita per year for waste collection. Communities operating their own facilities budget about $6.80 per capita per year for semiweekly collection and about $5.60 per capita per year for weekly collection.[1] Sanitary landfill costs–including amortization–have been reported as $1.05 per ton for 27,000 tons of waste per year, and $1.27 per ton for 11,000 tons per year.[1] Operating costs for municipal incinerators are estimated at $4 to $8 per ton of waste, and capital costs are estimated at $6,000 to $13,000 per ton per day capacity.[19] Estimated capital costs of smaller incinerators are given in AP–51, *Control Techniques for Particulate Air Pollutants.*[20]

Installed auxiliary burner costs range from $2 to $6 per pound per hour incinerator capacity.[21] Fuel requirements for increasing incineration temperatures to 1,600°F with 150 percent excess air range from none for dry combustible wastes, to an estimated 15,000 Btu per pound for a 3,500 Btu-per-pound-gross-heating-value waste containing 75 percent free moisture.

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6. CARBON MONOXIDE EMISSION FACTORS

For an accurate air pollution survey, whether for a single source or for a metropolitan area, pollutant emissions must be identified by type and quantity. This determination–together with meteorological, air quality and effects sampling programs, and strong enforcement actions–fulfills the requirements for local, state, and Federal air pollution control activities.

An adequate emission investigation will provide evidence of source emissions and define the location, magnitude, frequency, duration, and relative contribution of these emissions. This emission survey of pollutants will include emission rates from fuel combustion at stationary and mobile sources, solid waste disposal, and industrial process losses.

Ideally, to determine emission rates, a stack analysis of each source of interest would be necessary. This is impractical, of course, when an air pollution survey must cover a large land area that could contain many thousands of sources. Emissions must be estimated from sources that do not have accurate stack-gas analyses. Estimates are arrived at by the use of emission factors, which are estimates of pollutant emission rates based on past stack-sampling data, material balances, and engineering appraisals of sources that are similar to those in question.

Table 6–1 is a compilation of available emission factors for CO from various types of

Table 6–1. CARBON MONOXIDE EMISSION FACTORS

Source	Emission factor[a]	Reference
Stationary fuel combustion		1,2,3
Coal		
Less than 10 x 10^6 Btu/hr capacity	50 lb/ton of coal burned	
10 to 100 x 10^6 Btu/hr capacity	3 lb/ton of coal burned	
Greater than 100 x 10^6 Btu/hr capacity	0.5 lb/ton of coal burned	
Fuel oil		
Less than 100 x 10^6 Btu/hr capacity	2 lb/1,000 gal of oil burned	
More than 100 x 10^6 Btu/hr capacity	0.04 lb/1,000 gal of oil burned	
Natural gas		
Less than 100 x 10^6 Btu/hr capacity	0.4 lb/10^6 ft^3 of gas burned	
More than 100 x 10^6 Btu/hr capacity	Negligible lb/10^6 ft^3 of gas burned	
Wood	30–65 lb/ton of wood burned	
Solid waste disposal		
Open burning onsite of leaves, brush, paper, etc.	60 lb/ton of waste burned	
Open-burning dump	85 lb/ton of waste burned	
Municipal incinerator	1 lb/ton of waste burned[d]	

Table 6–1. CARBON MONOXIDE EMISSION FACTORS cont.

Source	Emission factor[a]	Reference
Commercial and industrial multiple chamber incinerator	10 lb/ton of waste burned	
Commercial and industrial single chamber incinerator	44 lb/ton of waste burned	
Flue-fed incinerator	27 lb/ton of waste burned	
Domestic incinerator	200 lb/ton of waste burned	
Process industries (specific examples)		
Gray iron foundry		
Cupola		
Uncontrolled	250 lb/ton of charge	
Controlled with afterburner	8 lb/ton of charge	
Iron and steel manufacture		
Blast furnace	1,700–250 lb/ton of pig iron produced[c]	5,6
Basic oxygen furnace	124–152 lb/ton of steel produced[d]	5,6,7
Petroleum refinery		
Fluid catalytic unit	13,700 lb/1,000 bbl fresh feed[e]	
Moving-bed catalytic cracking unit	3,800 lb/1,000 bbl fresh feed[e]	

[a] These emissions are from uncontrolled sources, unless otherwise noted.

[b] This represents excellent design and operation.

[c] Practically all of the CO is burned for heating purposes or in waste gas flares.

[d] Gases emitted from a basic oxygen furnace during the blowing period contain 87 percent CO. After ignition of the gases above the furnace, the CO amounts to 0.0–0.3 percent.

[e] These emissions are completely controlled when CO waste heat boilers are utilized.

sources. These emission rates represent uncontrolled sources, unless otherwise noted. These emission factors apply best to areas, rather than to specific sources; actual measurements are preferable when calculations are made for specific sources, but emission factors can be used when data are lacking. For a specific source where control equipment is utilized, the listed uncontrolled process source emission rates must be multiplied by 1 minus the percent efficiency of the equipment expressed in hundredths. Except where noted, emission factors are from a Public Health Service Publication.[1]

There are of course, many other process sources of CO emissions. Emission factors for other miscellaneous process sources can be found through literature searches, stack-gas testing, and material balances on the process in question. It must be remembered that the emission factors listed herein are average values and can vary, depending on operating conditions and other factors.

Examples of how to use emission factors are given below.

1. Fuel oil combustion:

   Given: Power plant burns 50,000,000 gallons of fuel oil per year

$$(50{,}000{,}000 \frac{\text{gal}}{\text{yr}})\ (0.04\ \frac{\text{lb of CO}}{1000\ \text{gal}})$$

$$=2{,}000\ \frac{\text{lb of CO}}{\text{yr}}$$

2. Petroleum refinery:

   Given: 50,000 bbl/day catalytic cracking unit operating 355 days/yr with CO boiler having 99.7% control.

$$(50{,}000 \frac{\text{bbl}}{\text{day}})\ (\frac{13700}{1000})\ \frac{\text{lb CO}}{\text{bbl}}\ (1-.997)$$

$$\text{x } 355\ \frac{\text{operating days}}{\text{yr}} = 730{,}000\ \frac{\text{lb CO}}{\text{yr}}$$

3. Solid waste disposal:

   Given: Apartment complex having flue-fed incinerator which burns 5,000 tons per year

$$(5{,}000\ \frac{\text{tons}}{\text{yr}})\ (27\ \frac{\text{lb of CO}}{\text{ton of waste}}) =$$

$$135{,}000\ \frac{\text{lb of CO}}{\text{yr}}$$

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