CHAPTER 65

AIR POLLUTION-CONTROL TECHNOLOGIES

C. A. Miller
United States Environmental Protection Agency
Research Triangle Park, North Carolina

Air pollution and its control have played an increasingly important role in modern activities since the advent of the Industrial Revolution, particularly relative to industrial activities. Most industries engage in one or more activities that result in the release of pollutants into the atmosphere, and in the last 40 years, steps have been taken to reduce these emissions through the application of process modifications or the installation and use of air pollution control technologies. Air pollution sources are typically divided into two major categories, *mobile* and *stationary*. This chapter will discuss the use of technologies for reducing air pollution emissions from stationary sources, with an emphasis on the control of combustion-generated air pollution. Major stationary sources include utility power boilers, industrial boilers and heaters, metal smelting and processing plants, and chemical and other manufacturing plants.

Pollutants that are of primary concern are those that, in sufficient ambient concentrations, adversely impact human health and/or the quality of the environment. Those pollutants for which health criteria define specific acceptable levels of ambient concentrations are known in the United States as "criteria pollutants." The major criteria pollutants are carbon monoxide (CO), nitrogen dioxide (NO_2), ozone, particulate matter less than 10 μm in diameter (PM_{10}), sulfur dioxide (SO_2), and lead (Pb). Ambient concentrations of NO_2 are usually controlled by limiting emissions of both nitrogen oxide (NO) and NO_2, which combined are referred to as oxides of nitrogen (NO_x). NO_x and SO_2 are

---

Mechanical Engineers' Handbook, 2nd ed., Edited by Myer Kutz.
ISBN 0-471-13007-9

important in the formation of acid precipitation, and NO_x and volatile organic compounds (VOCs) can react in the lower atmosphere to form ozone, which can cause damage to lungs as well as to property.

Other compounds, such as benzene, polycyclic aromatic hydrocarbons (PAHs), other trace organics, and mercury and other metals, are emitted in much smaller quantities, but are more toxic and in some cases accumulate in biological tissue over time. These compounds have been grouped together as hazardous air pollutants (HAPs) or "air toxics," and have recently been the subject of increased regulatory control.[1] Also of increasing interest are emissions of compounds such as carbon dioxide (CO_2), methane (CH_4), or nitrous oxide (N_2O) that have the potential to affect the global climate by increasing the level of solar radiation trapped in the Earth's atmosphere, and compounds such as chlorofluorocarbons (CFCs) that react with and destroy ozone in the stratosphere, reducing the atmosphere's ability to screen out harmful ultraviolet radiation from the sun.

The primary method of addressing emissions of air pollutants in the United States has been the enactment of laws requiring sources of those pollutants to reduce emission rates to acceptable levels determined by the U.S. Environmental Protection Agency (EPA) and air pollution regulatory agencies at the state, regional, and local levels. Current standards vary between states and localities, depending upon the need to reduce ambient levels of pollutants. EPA typically sets "national ambient air quality standards" (NAAQS) for the criteria pollutants, and the states and localities then determine the appropriate methods to achieve and maintain those standards. EPA also sets minimum pollution performance requirements for new pollution sources, known as the "new source performance standards" or NSPS. For some pollutants (such as HAPs), EPA is required to set limits on the annual mass of emissions to reduce the total health risk associated with exposure to these pollutants. Other approaches include the limiting of the total national mass emissions of pollutants such as SO_2; this allows emissions trading to occur between different plants and between different regions of the country while ensuring that a limited level of SO_2 is available in the atmosphere for the formation of acid precipitation.

Combustion processes are a major anthropogenic source of air pollution in the United States, responsible for 24% of the total emissions of CO, NO_x, SO_2, VOCs, and particulates.[2] In 1992, 146 million tonnes (161 million tons) of these pollutants were emitted in the United States. Of these pollutants, stationary combustion processes emit 91% of the total U.S. SO_2 emissions, and 50% of the total U.S. NO_x emissions. The major combustion-generated pollutants (not including CO_2) by tonnage are CO, NO_x, PM, SO_2, and VOCs. Table 65.1 presents total estimated anthropogenic and combustion-generated emissions of selected air pollutants in the United States.

Combustion-generated air pollution can be viewed as originating through two major methods, although some overlap occurs between the two. The first of these methods is origination of pollution primarily from constituents in the fuel. Examples of these "fuel-borne" pollutants are SO_2 and trace metals. The second is the origination of pollutants through modification or reaction of constituents that are normally nonpolluting. CO, NO_x, and volatile organics are examples of "process-derived" pollutants. In the case of NO_x, fuel-borne nitrogen such as that in coal plays a major role in the formation of the pollutant; however, even such clean fuels as natural gas (which contains no appreciable nitrogen) can emit NO_x when combusted in nitrogen-containing air.

Major stationary sources of combustion-generated air pollution include steam electric generating stations, metal processing facilities, industrial boilers, and refinery and other process heaters. Table 65.2 shows the total U.S. emissions of criteria pollutants from these and other sources.

Given the wide variety of sources and pollutants, it is no surprise that there is a correspondingly wide variety of approaches to air pollution control. The three primary approaches are preprocess control, process modification, and postprocess control. Preprocess control usually involves cleaning of the fuel prior to introducing it into the combustion process, as in the case of coal cleaning. Process modifications are applied when the pollutant of interest is "process-derived," and such modifications do not adversely alter the product. Low-NO_x burners fall into this category. In the postprocess control approach, the pollution-forming process itself is not altered, and a completely separate pollution-cleaning process is added to clean up the pollutant after it has been formed. Flue gas desulfurization systems are an example of this approach.

Early work in the field of air pollution control technology focused on SO_2, NO_x, and particulates. Control technologies for these pollutants have been refined and tested extensively in service, and have in most cases reached the status of mature technologies. Nevertheless, work continues to improve performance, as measured by pollutant-reduction efficiency and operating and maintenance cost. These mature technologies are also being evaluated for their performance as control devices for HAPs, and as the bases for new hybrid technologies that seek to achieve pollutant emission reductions of 90% or more with minimal increase in capital or operating costs.

65.1 SULFUR DIOXIDE CONTROL

SO_2 emissions are controlled to a large degree by the use of flue gas desulfurization (FGD) systems. Although furnace sorbent injection has been demonstrated to provide some degree of SO_2 emission

Table 65.1 Anthropogenic Emissions of Selected Air Pollutants[a]

Pollutant	Anthropogenic Emissions, Tons/Year	Combustion Emissions, Tons/Year	Principal Source(s)	Reference
NO_x	2.3×10^7	2.2×10^7	Electric utilities/highway vehicles	16
N_2O	7.8×10^6	2.6×10^6	Biomass, mobile	17
SO_2	2.2×10^7	2.0×10^7	Electric utilities, industrial combustion	16
Total PM	1.1×10^7	2.1×10^6	Residential wood, off-highway vehicles	16
Metal PM	1.4×10^5	7.0×10^2	Metals same as listed below	16
Hg	3.3×10^2	2.1×10^2	MedWI, MWC, utility boilers	18
CO_2	5.5×10^9	5.4×10^9	Steam boilers, space heat, highway vehicles	16
CO	9.7×10^7	9.2×10^7	Highway and off-highway vehicles	16
PAH	3.6×10^4	1.8×10^4	Residential wood, open burning (16 PAHs)	16
CH_4	3.0×10^7	7.0×10^5	Stationary combustion	16
VOC	2.3×10^7	1.2×10^7	Highway and off-highway vehicles, wildfires	16
Organic HAPs	9.4×10^6	N/A		19
Pb	4.9×10^3	2.6×10^3	Highway vehicles, waste disposal	18

[a] Emission figures are for 1993 (CH_4 and CO_2 emission figures are for 1992 and HAPs are for 1991). Non-combustion HAPs reported through Toxic Release Inventory and do not include hydrogen chloride.

reductions, by far the most common FGD systems are wet or dry scrubbers. Other methods of reducing emissions of SO_2 include fuel desulfurization to remove at least a portion of the sulfur prior to burning, or switching to a lower-sulfur fuel.

65.1.1 Control Technologies

Wet scrubbers use a variety of means to ensure adequate mixing of the scrubber liquor and the flue gas. A venturi scrubber uses a narrowing of the flue gas flow path to confine the gas path. At the narrowest point, the scrubber liquor is sprayed into the flue gas, allowing the spray to cover as great a volume of gas as possible. Packed tower scrubbers utilize chemical reactor packing to create porous beds through which the flue gas and scrubber liquor pass, ensuring good contact between the two phases. The packing material is often plastic, but may be other materials as well. The primary

Table 65.2 Annual Combustion-Generated Emissions of Selected Pollutants by Stationary Source Category[a]

	Stationary Fuel Combustion Emissions			
Pollutant	Utility	Industrial	Other	% of Total
CO	311	714	5,154	6.4
NO_x	7,468	3,523	734	50.7
Total particulate	454	1,030	493	18.0
SO_2	15,841	3,090	589	88.7
VOC	32	279	394	3.1

[a] In thousand tons/year. Emissions values are for 1992.

requirements for the packing are to evenly distribute the gas and liquid across the tower cross section, provide adequate surface area for the reactions to occur, and allow the gas to pass through the bed without excessive pressure drop.

Perforated plate scrubbers usually are designed with the gas flowing upward and the liquid flowing in the opposite direction. The flow of the gas through the perforations is sufficiently high to retard the counterflow of the liquid, creating a liquid layer on the plate through which the gas must pass. This ensures good contact between the liquid and gas phases. Bubble cap designs also rely on a layer of liquid on the plate, but create the contact of the two phases through the design of the caps. Gas passes up into the cap and back down through narrow openings into the liquid. The liquid level is regulated by overflow weirs, through which the liquid passes to the next lower level. The gas pressure drop in this type of system increases with the height of the liquid and the gas flow rate.

Wet scrubbers for utility applications typically use either lime (CaO) or limestone (primarily calcium carbonate, $CaCO_3$) in an aqueous slurry, which is then sprayed into the flue gas flow in such a way as to maximize the contact between the SO_2-containing flue gas and the slurry. The reaction of the slurry and the SO_2 creates calcium sulfite ($CaSO_3$) or calcium sulfate ($CaSo_4$) in an aqueous solution. Because both these compounds have low water solubility, they may precipitate out of solution and create scale in the system piping and other components. Care must be taken during operation to minimize scale deposition by keeping the concentrations of $CaSo_3$ and $CaSO_4$ below the saturation point during operation. Wet scrubbers typically have high SO_2 removal efficiencies (90% or greater) and require relatively low flue gas energy requirements. In some cases, however, capital and operating costs may be higher than for dry scrubbers (see below) due to higher fan power requirements or increased maintenance due to excessive scaling.

Smaller industrial scrubbers typically use a clean liquor reagent, such as sodium carbonate or sodium hydroxide. Alkali compounds other than lime or limestone can also be used. Magnesium oxide (MgO) is used to form a slurry of magnesium hydroxide [$Mg(OH)_2$] to absorb the SO_2 and form magnesium sulfite or sulfate. The solid can be separated from the slurry, allowing the regeneration of the MgO and producing a relatively high concentration (10–15%) stream of SO_2. The SO_2 stream is then used to produce sulfuric acid.

Dual alkali scrubbing systems use two chemicals in a two-loop arrangement. A typical arrangement uses a more expensive sodium oxide or sodium hydroxide scrubbing liquor, which forms principally sodium sulfite (Na_2SO_3) when sprayed into the SO_2-containing flue gases. The spent liquor is then sent to the secondary loop, where a less expensive alkali, such as lime, is added. The calcium sulfate or sulfite precipitates out of the liquor, and the sodium-based liquor is regenerated for reuse in the scrubber. The calcium sulfate/sulfite is separated from the liquor and dried, and the solids are usually sent to a landfill for disposal. SO_2 removal efficiencies for such systems are typically 75% and higher, with many systems capable of reductions greater than 90%.

Dry scrubbers, or spray dryer absorbers (SDAs), also use an aqueous slurry of lime to capture the SO_2 in the flue gas. However, SDAs create a much finer spray, resulting in rapid evaporation of the water droplets and leaving the lime particles suspended in the flue gas flow. As SO_2 contacts these particles, reactions occur to create $CaSO_4$. The suspended particulate is then captured by a particle removal system, often a fabric filter (see below). An advantage of the dry scrubber is its lower capital and operating cost compared to the wet scrubber, and the production of a dry, rather than wet, waste material for disposal. In some cases, the dry slurry solids can be recycled and reused. Dry systems are typically less efficient than wet scrubbers, providing removal efficiencies of 70–90%.

Furnace sorbent injection is the direct injection of a solid calcium-based material, such as hydrated lime, limestone, or dolomite, into the furnace for the purpose of SO_2 capture. Depending upon the amount of SO_2 removal required, furnace sorbent injection can remove the need for FGD. SO_2 removal efficiencies of up to 70% have been demonstrated,[3] although 50% reductions are more typical. The effectiveness of furnace sorbent injection is dependent upon the calcium to sulfur ratio (Ca/S), furnace temperature, and humidity in the flue gas. A Ca/S of 2 is typically used. Furnace sorbent injection effectiveness decreases with increasing furnace temperature and increases as flue gas humidity levels decrease.

While the need for an SO_2 scrubbing system is eliminated, systems that use furnace sorbent injection require adequate capacity in their particulate removal equipment to remove the additional solid material injected into the furnace. In addition, increased soot blowing is also required to maintain clean heat transfer surfaces and prevent reduced heat-transfer efficiencies when furnace sorbent injection is used.

Fluid bed combustion (FBC) is another technology that allows the removal of SO_2 in a similar manner to furnace sorbent injection. In such systems, the fluidized bed contains a calcium-based solid that removes the sulfur as the coal is burned in the bed. FBC is limited to new plant designs, since it is an alternative design significantly different from conventional steam generation systems, and is not a retrofit technology. FBC systems typically remove 70–90% of the SO_2 generated in the combustion reactions.

65.1.2 Alternative Control Strategies

Coal cleaning (or fuel desulfurization) is also an option for removing a portion of the sulfur in the as-mined fuel. A significant portion of Eastern and Midwestern bituminous coals are currently cleaned to some degree to remove both sulfur and mineral matter. Cleaning may be done by crushing and screening the coal or by washing with water or a dense medium consisting of a slurry of water and magnetite. Washing is typically done by taking advantage of the different specific gravities of the different coal constituents. The sulfur in coal is typically in the form of iron pyrite (pyritic sulfur) or organic sulfur contained in the carbon structure of the coal.* The sulfur-reduction potential (or washability) of a coal depends on the relative amount and distribution of pyritic sulfur. The washability of U.S. coals varies from region to region and ranges from less than 10% to greater than 50%. For most Eastern U.S. high-sulfur coals, the sulfur reduction potential normally does not exceed 30%, limiting the use of physical coal cleaning for compliance coal production. Cleaning usually results in the generation of a solid or liquid waste that must be either disposed of or recycled.

Fuel switching is a further option for the reduction of SO_2 emissions. Fuel switching most often involves the change from a high-sulfur fuel to a lower-sulfur fuel of the same type. For coal, this change most commonly involves a change from a higher-sulfur Eastern coal to low-sulfur Western coals. In some instances, the change of coals may also result in restrictions to plant operability, usually due to changes in the slagging and fouling characteristics of the coal. However, many plants have found that the costs of compliance using a fuel-switching approach outweigh the operational changes. In some instances, fuel switching can also involve a change from high-sulfur coal to natural gas. In this case, not only are SO_2 emissions reduced, but the lack of nitrogen in natural gas also yields a reduction in NO_x emissions. Particulate emissions are also significantly reduced, as are emissions of trace metals.

65.1.3 Residue Disposal and Utilization

Flue gas desulfurization results in significant quantities of solid and/or liquid material that must be removed from the plant process. In some cases, the residues can be used as is, or processed to produce higher-quality materials for a number of applications. The cost of residue disposal can account for a significant portion of the total cost of SO_2 removal, particularly where landfilling costs are high. Early waste management approaches focussed on landfilling and, as such costs increased, more attention was given to utilization options.

For sludges from wet scrubbers, the use of forced oxidation of the spent scrubbing slurry produces $CaSO_4$ from the $CaSO_3$ in the slurry, which can then be processed to form a salable gypsum product. Some impurities can be removed by means of filtration and removal of the smaller particles, followed by the hydration of the $CaSO_4$ to form gypsum ($CaSO_4 \cdot 2H_2O$) and dewatering of the final solids. Depending upon the quality of the final product, the resulting solids can be used in building materials, soil stabilization and road base, aggregate products, or in agricultural applications. Spray dryer byproducts have a higher free lime content, making them less acceptable as a building material. The most likely end use of these residues is as a road-base stabilization material.

65.1.4 Costs of Control

Many factors are involved in the costs of applying SO_2 control technologies, including the amount of sulfur in the coal, the level of control required, and the plant size and configuration (particularly for retrofit applications). However, there have been several studies conducted to compare the costs of SO_2 controls in terms of capital cost per kilowatt of plant capacity, annual cost in mills per kilowatt-hour, and dollars per ton of SO_2 removed. Table 65.3 shows ranges of estimated costs[4,5] and indicates that, although the capital and annual costs can vary significantly between the different approaches, the costs in dollars per ton of SO_2 removed are much more comparable. This is due in large part to the fact that the lower-cost SO_2 control strategies tend to result in lower SO_2 reductions compared to the more expensive control options.

65.2 OXIDES OF NITROGEN—FORMATION AND CONTROL

65.2.1 NO_x Formation Chemistry

NO_x formed by the combustion of fuel in air is typically composed of greater than 90% NO, with NO_2 making up the remainder. Unfortunately, NO is not amenable to flue gas scrubbing processes, as SO_2 is. An understanding of the chemistry of NO_x formation and destruction is helpful in understanding emission-control technologies for NO_x.

*Sulfur in coal may also be in the form of sulfates, particularly in weathered coal. Pyritic and organic sulfur are the two most common forms of sulfur in coal.

Table 65.3 Emission Reductions and Costs of Different SO_2 Control Technologies

Control Technology	SO_2 Reduction, %	Capital Cost, $/kW	Annual Cost, mils/kW-hr	Cost, $/tonne SO_2 ($/ton SO_2) Ref. 5	Cost, $/tonne SO_2 ($/ton SO_2) Ref. 6
Wet scrubber	75–90+	150–180	16	385–660 (350–600)	1200 (1100)
Lime spray dryer	70–90	110–210	10	395–595 (360–540)	990 (900)
Furnace sorbent injection	50–70	50–120	6	460–825 (420–750)	825 (750)
Coal switching	60–70	27	4	NA	880 (800)

There are three major pathways to formation of NO in combustion systems: thermal NO_x, fuel NO_x, and prompt NO_x. Thermal NO_x is created when the oxygen (O_2) and nitrogen (N_2) present in the air are exposed to the high temperatures of a flame, leading to a dissociation of O_2 and N_2 molecules and their recombination into NO. The rate of this reaction is highly temperature-dependent; therefore, a reduction in peak flame temperature can significantly reduce the level of NO_x emissions. Thermal NO_x is important in all combustion processes that rely on air as the oxidizer.

Fuel NO_x is due to the presence of nitrogen in the fuel and is the greatest contributor to total NO_x emissions in uncontrolled coal flames. By limiting the presence of O_2 in the region where the nitrogen devolatilizes from the solid fuel, the formation of fuel NO_x can be greatly diminished. NO formation reactions depend upon the presence of hydrocarbon radicals and O_2, and since the hydrocarbon–oxygen reactions are much faster than the nitrogen–oxygen reactions, a controlled introduction of air into the devolatilization zone leads to the oxygen preferentially reacting with the hydrocarbon radicals (rather than with the nitrogen) to form water and CO. Finally, the combustion of CO is completed, and since this reaction does not promote NO production, the total rate of NO_x production is reduced in comparison with uncontrolled flames. This staged combustion can be designed to take place within a single burner flame or within the entire furnace, depending on the type of control applied (see below). Fuel NO_x is important primarily in coal combustion systems, although it is important in systems that use heavy oils, since both fuels contain significant amounts of fuel nitrogen.

Prompt NO_x forms at a rate faster than equilibrium would predict for thermal NO_x formation. Prompt NO_x forms from nonequilibrium levels of oxide (O) and hydroxide (OH) radicals, through reactions initiated by hydrocarbon radicals with molecular nitrogen, and the reactions of O atoms with N_2 to form N_2O and finally the subsequent reaction of N_2O with O to form NO. Prompt NO_x can account for more than 50% of NO_x formed in fuel-rich hydrocarbon flames;[6] however, prompt NO does not typically account for a significant portion of the total NO emissions from combustion sources.

65.2.2 Combustion Modification NO_x Controls

Because the rate of NO_x formation is so highly dependent upon temperature as well as local chemistry within the combustion environment, NO_x is ideally suited to control by means of modifying the combustion conditions. There are several methods of applying these combustion modification NO_x controls, ranging from reducing the overall excess air levels in the combustor to burners specifically designed for low NO_x emissions.

Low excess air (LEA) operation is the simplest form of NO_x control, and relies on reducing the amount of combustion air fed into the furnace. LEA can also improve combustion efficiency where excess air levels are much too high. The drawbacks to this method are the relatively low NO_x reduction and the potential for increased emissions of CO and unburned hydrocarbons if excess air levels are dropped too far. NO_x emission reductions using LEA range between 5 and 20%, at relatively minimal cost if the reduction of combustion air does not also lead to incomplete combustion of fuel. Incomplete combustion significantly reduces combustion efficiency, increasing operating costs, and may result in high levels of CO or even carbonaceous soot emissions.[7]

Overfire air (OFA) is a simple method of staged combustion in which the burners are operated with very low excess air or at substoichiometric (fuel-rich) conditions, and the remaining combustion air is introduced above the primary flame zone to complete the combustion process and achieve the required overall stoichiometric ratio. The LEA or fuel-rich conditions result in lower peak flame temperatures and reduced levels of oxygen in the regions where the fuel-bound nitrogen devolatilizes from the solid fuel. These two effects result in lower NO_x formation in the flame zone, and therefore lower emissions. Recent field studies showed approximately 20% reductions of NO_x emissions using advanced OFA in a coal-fired boiler.[8] OFA can be used for coal, oil, and natural gas, and to some degree for solid fuels such as municipal solid waste and biomass when combusted on stoker-grate units.

OFA typically requires special air-injection ports above the burners, as well as the associated combustion air ducting to the ports. In some cases, additional fan capability is required in order to ensure that the OFA is injected with enough momentum to penetrate the flue gases. Emissions of CO are usually not adversely affected by operation with OFA. Use of OFA can result in higher levels of carbon in fly ash when used in coal-fired applications, but proper design and operating may minimize this disadvantage. Another disadvantage to the application of OFA is the often corrosive nature of the flue gases in the fuel rich zone. If adequate precautions are not taken, this can lead to increased corrosion of boiler tubes.

Flue gas recirculation is a combustion-modification technique used to reduce the peak flame temperature by mixing some of the combustion gases back into the flame zone. This method is especially effective for fuels with little or no nitrogen, such as natural gas combustion systems. However, in many instances, the recirculation system requires a separate fan to compress the hot gases, and the fan capital and operating costs can be substantial. The resulting NO_x reductions can be significant, however, and emission reductions as high as 50% have been achieved.[9]

In the past 15 years, burners for both natural gas and coal have undergone major design improvements intended to incorporate the principles of staging and flue gas recirculation into the flow patterns of the fuel and air injected by the burner. These burners are generically referred to as *low NO_x burners* (LNBs), and are the most widely used NO_x control technology. Staging of fuel and air that is the basis for combustion modification NO_x control is achieved in LNBs by creating separate flow paths for the air and fuel. This is in contrast to earlier burner designs, in which the fuel and air flows were designed to mix as quickly and as turbulently as possible. While these highly turbulent flames were very successful in achieving rapid and complete combustion, they also resulted in very high peak flame temperatures and high levels of oxygen in the fuel devolatilization region, with correspondingly high levels of NO_x emissions. The controlled mixing of fuel and air flows typical of LNBs significantly reduced the rates of fuel and air mixing, leading to lower flame temperatures and considerable reductions of oxygen in the devolatilization regions of the flame, thereby reducing the production and emission of NO_x.

Low-NO_x burners may further reduce the formation of NO_x by inducing flue gases into the flame zone through recirculation. Careful design of the fluid dynamics of the air and fuel flows acts to recirculate the partially burned fuel and products of combustion back into the flame zone, further reducing the peak flame temperature and thus the rate of NO_x production. In some burner designs, this use of recirculated flue gas is taken a step further by using flue gas that has been extracted from the furnace, compressed, and fed back into the burner along with the fuel and air. These burners are typically used in natural gas-fired applications, and are among the "ultra-low NO_x burners" that can achieve emission levels as low as 5 ppm.

LNBs are standard on most new facilities. Some difficulties may be encountered during retrofit applications if the furnace dimensions do not allow for the longer flame lengths typical of these burners. The flame lengths can increase considerably due to the more controlled mixing of the fuel and air and, if adequate furnace lengths are not available, impingement of the flame on the opposite wall can lead to rapid cooling of the flame and therefore increased emissions of CO and organic compounds, as well as reduced heat transfer efficiency from the flame zone to the heat transfer fluid.

More precise control of air and fuel flows is often required for LNBs compared to conventional burners due to the reliance of many LNB designs on fluid dynamics to stage the air and fuel flows in particular patterns. Slight changes in the flow patterns can lead to significant drops in burner and boiler efficiencies, higher CO and organic compound emissions, and even damage to the burner from excessive coking of the fuel on the burner. In addition, the more strict operating conditions may impact the burners' ability to properly operate using fuels with different properties, primarily for coal-fired units. Coals with lower volatility or higher fuel nitrogen content may hamper NO_x reduction, and changes in the coals' slagging properties may lead to fouling of the burner ports. Further, improper air distribution within the burner may result in high levels of erosion within the burner, degrading performance and reducing operating life. An example of a typical pulverized coal LNB design is shown in Fig. 65.1

A further, relatively new method of controlling NO_x emissions by means of combustion modification is the application of *reburning*. Reburning is applied by injecting a portion of the fuel downstream of the primary burner zone, thereby creating a fuel-rich reburn zone in which high levels of hydrocarbon radicals react with the NO formed in the primary combustion zone to create H_2O, CO, and N_2. This is quite different from the other combustion modification techniques, which reduce NO_x emissions by preventing its formation. Reburning can use coal, oil, or natural gas as the reburn fuel, regardless of the fuel used in the main burners. Natural gas is an ideal reburn fuel, as it does not contain any fuel-bound nitrogen. Coals that exhibit rapid devolatilization and char burnout are also suitable for use as reburn fuels.

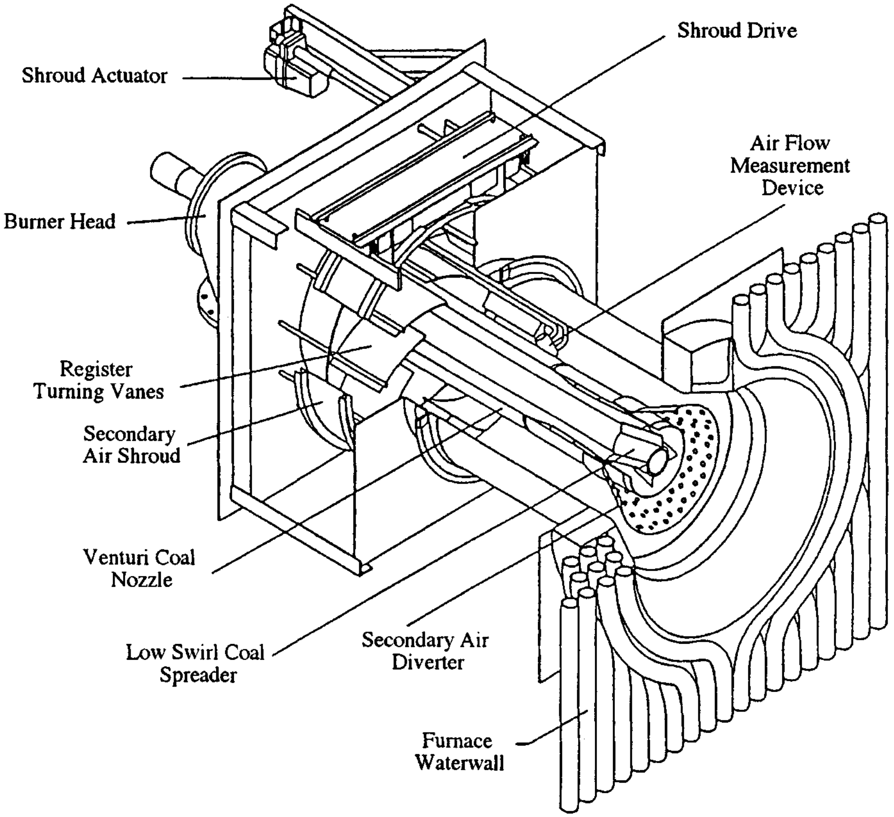

Fig. 65.1 Low-NO_x burner.

In most applications, between 10 and 20% of the total heat input to the furnace is introduced in the reburn zone in the form of reburn fuel. The main burners are operated at slightly fuel-lean stoichiometries. This usually results in lower NO_x levels leaving the primary zone, since the low excess air and lower flame temperatures produce lower NO_x. Above the primary zone, but far enough to allow for the combustion process to be nearly completed, the reburn fuel is introduced, and a reburn zone stoichiometry of 0.8 to 0.9 is created. Finally, sufficient air is injected downstream to burn out the remaining combustible materials (primarily CO) and reach the desired overall furnace stoichiometry (normally near 1.2). Reburning requires adequate furnace volume to allow the injection of the reburn fuel and the overfire air, as well as time for the combustion reactions to be completed.[10] Advanced reburning systems may utilize the injection of chemical reagents in addition to the reburn fuel to provide additional NO_x reductions or to reduce the amounts of reburn fuel required for a given NO_x reduction level. Reburning applied to full scale utility boilers has resulted in NO_x emissions ranging from 50 to 65%.

65.2.3 Postcombustion NO_x Controls

In some cases, either it is not possible to modify the combustion process or the levels of NO_x reduction are beyond the capabilities of combustion modifications alone. In these instances, postcombustion controls must be used. There are two primary postcombustion NO_x control technologies, *selective noncatalytic reduction* (SNCR) and *selective catalytic reduction* (SCR). Several systems have also been developed for scrubbing NO_x; however, since these remove only NO_2, they are not in broad commercial operation.

SNCR systems inject a nitrogen-based reagent into a relatively high temperature zone of the furnace, and rely on the chemical reaction of the reagent with the NO to produce N_2, N_2O, and H_2O. Removal efficiencies of up to 75% can be achieved with SNCR systems, but lower removal rates are typical. The SNCR reaction is highly temperature-dependent and, if not conducted properly, can result in either increased NO_x emissions or considerable emissions of ammonia. The reagents most commonly used are ammonia (NH_3) and urea (NH_2CONH_2), although other chemicals have also been used, including cyanuric acid, ammonium sulfate, ammonium carbamate, and hydrazine hydrate. A number of proprietary reagents are also offered by several vendors, but all rely on similar chemical reaction processes. Proprietary reagents are used to vary the location and width of the temperature window, and to reduce the amount of ammonia slip to acceptable levels (typically less than 10–20 ppm).

The optimum temperature for SNCR systems will vary depending upon the reagent used, but ranges between 870 and 1150°C (1600 and 2100°F). Increased NO_x reductions can be obtained by using increasing amounts of reagent, although excessive use of reagent can lead to emissions of ammonia or, in some cases, conversion of the nitrogen in the ammonia to NO. Reduction efficiencies increase as the base NO level increases and, for systems with a low baseline NO level, removal efficiencies of less than 30% are not unusual. Adequate mixing of the reagent into the flue gases is also important in maximizing the performance of the SNCR process, and can be accomplished by the use of a grid of small nozzles across the gas path, adjusting the spray atomization to control droplet trajectories, or of an agent such as steam or air to transport the reagent into the flue gas.

Where the reagent is injected in larger amounts than the available NO, or where it is injected into a temperature too low to permit rapid reaction, the ammonia will pass through to the stack in the form of "ammonia slip." Where chlorine is present, a detached visible plume of ammonium chloride (NH_4Cl) may be formed if it is present in high enough levels. As plume temperature drops as it mixes in the atmosphere, the NH_4Cl changes from a liquid to a solid, resulting in a visible white plume. While these plumes may not indicate excessive NO_x or particulate emissions, they can result in perceptions of uncontrolled pollutant emissions.

SNCR systems typically have low capital cost, but much higher operating cost compared to low-NO_x burners due to the use of reagents. In some applications that have wide variations in load, additional injection locations may be required to ensure that the reagent is being injected into the proper temperature zone. In this case, more complex control and piping arrangements are also required.

SCR systems similarly rely on the use of an injected reagent (usually ammonia or urea) to convert the NO to N_2 and H_2O in the presence of a catalyst, and at lower temperatures (usually around 315–370°C [600–700°F]) than SNCR systems. Catalysts are typically titanium- and/or vanadium-based, and are installed in the flue gas streams at various locations in the gas path, depending upon the available volume, desired temperatures, and potential for solid particle plugging of the catalyst. SCR systems have not been installed in U.S. pulverized-coal-fired systems due to difficulties associated with plugging and fouling of the catalyst by the fly ash, poisoning of the catalyst by arsenic, and similar difficulties. However, recent tests have indicated the ability of SCR catalysts to maintain their performance over an extended period in U.S. pulverized-coal-fired applications.

Parameters of importance to SCR systems include the space velocity (volumetric gas flow per hour, per volume of catalyst), linear gas flow velocity, operating temperature, and baseline NO_x level. System designs must balance the increasing NO_x reductions with operating considerations such as catalyst cost, pressure drops across the catalyst bed, increased rate of catalyst deactivation, and increased NH_3 requirements. As NO_x reductions increase, the life of the catalyst decreases and the required amount of NH_3 injected increases. NO_x emissions can be reduced by over 90% if adequate catalyst and reagent are present and injection temperatures are optimized. For such reduction levels, catalysts may require replacement in as little as two years. It is possible to increase catalyst life where lower reductions are suitable.

Operational problems such as catalyst plugging and fouling can significantly reduce the effectiveness of SCR systems. Plugging can be a problem where the fuel used (e.g., coal) has a high particulate content. Interactions between sulfur and the injected reagent can lead to ammonium sulfate or bisulfate formation, which can result in fouling of the catalyst. In addition, the catalyst can convert SO_2 into sulfur trioxide (SO_3), which has a much higher dewpoint and can condense onto equipment and lead to excessive corrosion.

SCR systems are often more expensive to install than other NO_x removal systems due to the relatively high catalyst cost (10,600–14,100 \$/m^3 [300–400 \$/ft^3]). However, SCR systems can also remove higher levels of NO_x, resulting in costs in terms of \$/ton of NO_x removed that are often competitive with other methods. Where very low NO_x emissions are required, SCR systems may be the only method of achieving the emission standard. SCR capital costs can be significant, particularly if large NO_x reductions are desired. In most cases, the largest portion of the cost is for the catalyst, which must be replaced periodically (approximately every three to four years). Costs for NH_3 must also be considered, but these costs are typically lower than for SNCR systems.

Hybrid systems combine SCR and SNCR by injecting a reagent into the furnace sections as the appropriate temperatures to take advantage of the SNCR NO_x reduction reactions, then passing the flue gases through a catalyst section to further reduce NO_x and provide some control of ammonia slip. Emissions of over 80% have been demonstrated on small-scale boilers using the hybrid approach.

Typical NO_x control performance and costs are shown in Table 65.4.

Table 65.4 Emission Reductions from Different NO_x Control Technologies

Control Technology	Application	NO_x Emission Reduction, %	Cost, \$/tonne NO_x (\$/ton NO_x) Removed
Low excess air (LEA)	Boilers and furnaces	5–20	
Overfire air (OFA)	Pulverized-coal-fired-boilers Stoker-fired coal boilers	5–20	
Flue gas recirculation (FGR)	Natural-gas-fired boilers	20–50	
Low-NO_x burners (LNB)	Natural-gas-fired boilers	40–60	
	Oil-fired boilers	20–40	
	Pulverized-coal, tangentially fired boilers	35–45	\$130–\$1300
	Pulverized-coal, wall fired boilers	40–65	(\$120–\$1200)
LNB + FGR	Natural-gas-fired boilers	75–90	
LNB + OFA	Natural-gas-fired boilers	40–60	
	Oil-fired boilers	40–60	
	Pulverized-coal-fired boilers	45–65	\$140–\$1400 (\$130–\$1300)
Reburning	Natural gas reburn fuel with pulverized-coal main fuel	50–60	\$420–\$800 (\$380–\$730)
	Coal reburn fuel with pulverized-coal main fuel	40–60	\$330–\$990 (\$300–\$900)
Selective noncatalytic reduction (SNCR)	Combustion sources	30–75	\$385–\$1500 (\$350–\$1400)
Selective catalytic reduction (SCR)	Combustion sources	80–90	\$420–\$990 (\$380–\$900)

65.3 CONTROL OF PARTICULATE MATTER

Particulate matter (PM) control technologies can employ one or more of several techniques for removing particles from the gas stream in which they are suspended. These techniques are mechanical collection, wet scrubbing, electrostatic precipitation, and filtration. Large industrial and utility sources generally use electrostatic precipitators or fabric filters to remove fine particles from high-volume gas streams. Particulate removal efficiencies are shown in Table 65.5 for multiclones, electrostatic precipitators, fabric filters, and wet scrubbers.

Mechanical collection systems rely on the difference in inertial forces between the particles and the gas to separate the two. Examples of mechanical collection systems include cyclones and multiclones, rotary fan collectors, and settling chambers. Settling chambers use gravity to force the particles to "fall" out of the gas. Cyclones and multicyclones induce a spinning motion in the gas, forcing the heavier particles to the outside of the gas stream and against the inner cyclone wall. As the gas passes up through the cyclone, the particles strike the wall and fall to the bottom of the cylinder, where they are collected. Mechanical collection systems are primarily useful only in applications in which the particulate matter is relatively large (> 10 μm in diameter). Other applications include the initial stage of a multiprocess cleaning, where they remove the larger particles before the gas enters a higher-efficiency control device.

Table 65.5 Emission Reductions from Different PM Control Technologies[20]

Control Technology	Total Mass Emission Reduction, %	Mass Emission Reduction for Particles ≤ 0.3 μm, %
Multicyclone	50–70	0–15
Wet scrubber	95–99	30–85
Electrostatic precipitator	90–99.7	80–95
Fabric filter	99–99.9	99–99.8

Electrostatic precipitators (ESPs) operate by inducing an electrical charge onto the particles and then passing them through an electric field. This exerts a force on the charged particles, forcing them toward an electrode, where they are collected. The basic configuration of an ESP consists of one or more high-voltage electrodes that produce an ion-generating corona, in combination with a grounded collecting electrode. The generated ions charge the particles, and the high voltage between the electrodes results in an electric field that forces the particles toward the collecting electrode (see Fig. 65.2). The particles are removed from the collecting electrode by periodic rapping of the electrode, causing the particles to fall into a collection hopper below.

ESP performance can be significantly affected by the resistivity of the incoming particles. Particles of high resistivity are less easily charged, reducing the performance of the unit. Chemical additives can be introduced to the flue gas to reduce the effect of the high resistivity in a practice referred to as *gas conditioning*. Pulsing the electrodes with intense periodic high-voltage direct current can also improve performance with high-resistivity particles.

Performance can be improved by using separate charging and collection stages, which allows optimization of each process. Flushing the collected particles with continuous application of water can also provide collection of some of the gaseous pollutants in the flue gas, although this approach is likely to require the treatment of the resulting waste water.

Industrial-scale ESPs may have collecting electrodes 7.6–13.7 m (25–45 ft) high and 1.5–4.6 m (5–15 ft) long, with 60 or more gas flow lanes per section. Large units may have eight consecutive

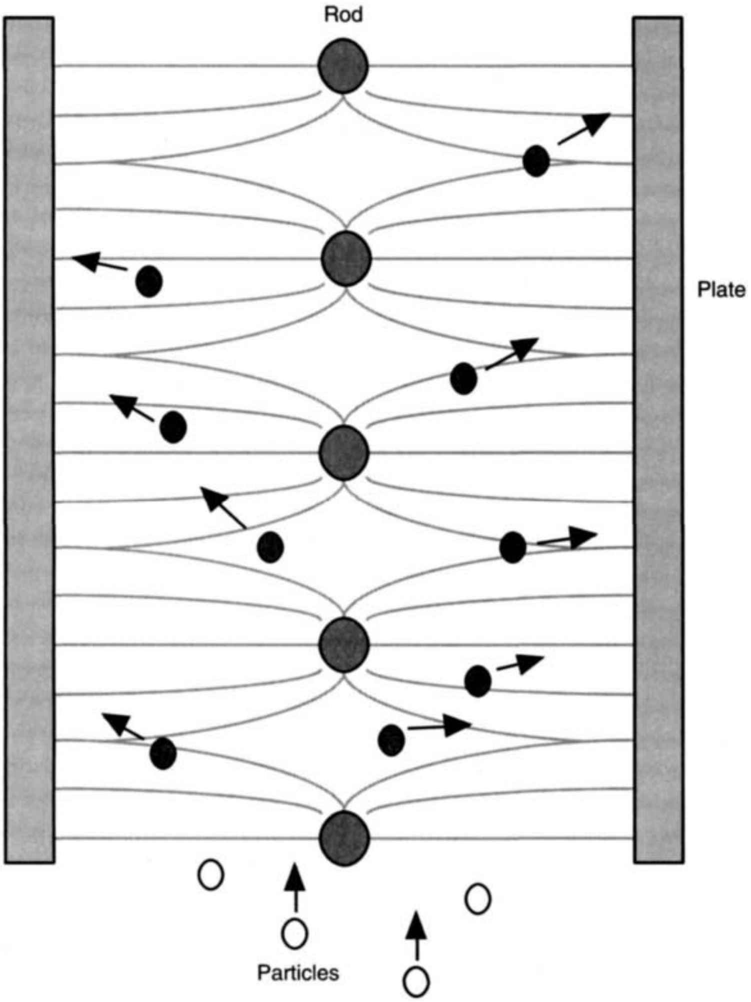

Fig. 65.2 Schematic of electrostatic precipitator operation.

sections, and gas flows of up to 85,000 m^3/min (3,000,000 ft^3/min). Voltages applied to the corona-generating electrode in industrial scale ESPs may range from 30 to 80 kV.

Pressure drops in ESPs are less than those of other particulate control devices, but they require significant amounts of electrical energy input to the electrodes. ESPs can remove 90–99.5% of the total particulate mass in the gas stream. However, particles are collected at lower efficiencies as their size decreases. In some applications, the combination of temperature and gas composition can lead to formation of trace organics, including polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the ESP. Proper control of temperatures can significantly reduce or eliminate this problem.

In addition to large-scale industrial applications, ESPs have also been used for control of particulates in indoor air handling systems.

Fabric filters can also be used for industrial-scale removal of particulates. There are several filter configurations, including bags, envelopes, and cartridges. Bags are most common for large-volume gas streams, and are distributed in a baghouse. Industrial-scale baghouses may contain from less than 100 to several thousand individual bags, depending upon the gas flow rate, particle concentration, and allowable pressure drop.

Filter bags can be operated with gas flowing from inside to outside the bags, or with the gas flowing from outside to inside. In the inside-to-outside configuration, the particles are collected on the inner bag surface and the bags are cleaned periodically by reversing the gas flow intermittently for a short time, mechanically shaking the bags, or a combination of the two. For outside-to-inside bag configurations, a short pulse of air is injected down the inside of the bag to remove the particles that have collected on the outer bag surface. An internal cage is used to prevent the collapse of the outside-to-inside bags due to the pressure of the flue gas flow. Inside-to-outside bags are up to 11 m (36 ft) long and 30 cm (12 in.) in diameter, while outside-to-inside bags are smaller, with lengths up to 7.3 m (24 ft) and diameters up to 20 cm (8 in.).

Fabric filters require higher fan power to overcome the resulting pressure drop of the flue gases than do ESPs, but little additional power is required to operate the cleaning systems. Filter materials are chosen based on the temperature and gas composition characteristic of the flue gas to be cleaned. Inside-to-outside bags are typically made of woven fibers, while outside-to-inside bags are usually felted fibers. Filter fabrics that are coated with a catalyst to improve reduction of VOCs or NO_x have been developed, but these systems require additional improvements before they are ready for large-scale commercial use. Overall mass removal efficiencies of fabric filters range from 95–99.9%.

Both ESPs and fabric filters can require heaters in the hoppers to maintain proper collection conditions. The energy required for heating to maintain these conditions may be a major part of the total energy requirement for the systems.

Particulates can also be removed by *wet scrubbing*. In some cases, wet scrubbing of particulates is done by creating a fine spray of liquid droplets which enhance the collection of small particles in the gas stream. This is known as *diffusion capture*, since it relies on the Brownian motion of the particles and droplets to lead to capture of the particles. Other methods include direct interception or inertial impaction, similar to mechanical collectors, but in the presence of a liquid (usually water) to assist in removing additional particles from the gas stream. Wet scrubbers typically require significant energy inputs to decrease liquid droplet sizes, increase the momentum of the gas stream, or a combination. Some particles can be captured by wet flue gas desulfurization systems; however, wet scrubbing does not usually perform as well as ESPs or fabric filters in the capture of small particles. ESP or fabric filter systems are often required in addition to adequately control particulate emissions in applications where high-ash-content fuels are used. Nevertheless, ESPs, fabric filters, and wet scrubbers can give equivalent particulate removal efficiencies if the systems are properly designed for the specific source and collection efficiency desired.

65.4 CARBON MONOXIDE

Carbon monoxide emissions are typically the result of poor combustion, although there are several processes in which CO is formed as a natural byproduct of the process (such as the refining of oil). In combustion processes, the most effective method of dealing with CO is to ensure that adequate combustion air is available in the combustion zone and that the air and fuel are well mixed at high temperatures. Where large amounts of CO are emitted in relatively high concentration streams, dedicated CO boilers or thermal oxidation systems may be used to burn out the CO to CO_2. CO boilers use the waste CO as the primary fuel and extract useful heat from the combustion of the waste gas. An auxiliary fuel, usually natural gas, is used to maintain combustion temperatures and as a start-up fuel.

65.5 VOLATILE ORGANIC COMPOUNDS AND ORGANIC HAZARDOUS AIR POLLUTANTS

Volatile organic compounds (VOCs) are emitted from a broad variety of stationary sources, primarily manufacturing processes, and are of concern for two primary reasons. First, VOCs react in the atmosphere in the presence of sunlight to form photochemical oxidants (including ozone) that are harmful to human health. Second, many of these compounds are harmful to human health at relatively low concentrations. This second group of VOCs is referred to as *hazardous air pollutants* (HAPs) and is included for potential regulation under Title III of the Clean Air Act Amendments of 1990.[1]

Total VOC emissions in the U.S. have been declining over the past 10 years, primarily due to significant improvements in vehicle emission levels. During the same period, VOC emissions from industrial sources, solvent utilization, and chemical manufacturing have increased slightly, making these sources more important from a control perspective. In addition to VOCs, heavier organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), nitrogenated PAHs, polychlorinated biphenyls (PCBs), and polychlorinated dibenzodioxins (PCDDs), are also important HAPs that may be emitted from a variety of sources. Combustion processes in general can form PAHs; however, proper equipment operation and maintenance typically results in PAH emissions from combustion sources on the order of parts per billion or less. Chlorinated organics emissions are characteristic of incineration processes in which chlorine is present; these compounds are discussed further below.

Control of VOCs and organic HAPs is less straightforward than for criteria pollutants due to the wide range of sources and the large number of different compounds that fall into this category. Much of the emissions of these compounds are due to fugitive emissions from process equipment such as valves, pumps, and transport systems, and emissions can be reduced considerably by proper maintenance and operation of existing equipment. Pump and valve seals and transfer equipment specially designed to reduce fugitive emissions can also provide significant reductions in such emissions. In other instances, alternative solvents or process modifications can eliminate the use of VOCs in manufacturing processes, thereby eliminating emissions. Often, these approaches can also reduce operating expenses by improving process efficiencies. In some cases, where the emission stream is relatively concentrated and characterized by a fixed pollutant or mixture of pollutants, several technologies are available that may allow recovery of the compound(s).

For process streams which cannot take advantage of these approaches, the emission stream often contains very dilute concentrations of the pollutant or pollutants, or the characteristics of the stream change significantly in composition and/or concentration. This makes generic prediction of control efficiencies and economics impossible for the broad category of VOCs and organic HAPs.

65.5.1 Conventional Control Technologies

Thermal oxidizers destroy organic compounds by passing them through high-temperature environments in the presence of oxygen. In practice, thermal oxidizers or incinerators typically operate by directing the pollutant stream into the combustion air stream, which is then mixed with a supplementary fuel (usually natural gas or fuel oil) and burned. Where the organic concentration is high enough to support combustion without a supplementary fuel, the organics are used as the fuel for incineration. Thermal incinerators are usually applied to emission streams containing dilute (less than 1000 ppm) of VOCs and organic HAPs. Destruction efficiencies can exceed 99%, but the effectiveness of the incinerator is a function of the temperature of the combustion chamber, the level of oxygen, and the degree of mixing of the air, supplementary fuel, and emission stream.

Boilers or industrial furnaces that are already present on a plant site can also be used as thermal incineration systems for appropriate streams of VOCs and organic HAPs. If the emission streams are of relatively low concentration, they can be added to the combustion air of the boiler or furnace and fed into the combustion environment for destruction. Where there is a very large emissions stream of relatively high concentration, the emission stream may be suitable as the primary fuel source for the boiler or furnace, with some supplemental fuel to maintain stable operation. Because these units are used to provide power or steam for plant processes, it is essential to maintain proper operation of these systems. The dual function of these units makes adequate monitoring and control essential to maintaining stable operation for both pollution control and process quality.

Flares are a simple form of thermal oxidation that do not use a confined combustion chamber. As with other forms of thermal oxidation, flares often require supplemental fuel. Flares are often used when the emission stream is intermittent or uncertain, such as the result of a process upset or emergency.

Catalytic oxidizers use a catalyst to promote the reaction of the organic compounds with oxygen, thereby requiring lower operating temperatures and reducing the need for supplemental fuel. Destruction efficiencies are typically near 95%, but can be increased by using additional catalyst or higher temperatures (and thus more supplemental fuel). The catalyst may be either fixed or mobile (fluid bed). Because catalysts may be poisoned by contacting improper compounds, catalytic oxidizers are neither as flexible nor as widely applied as thermal oxidation systems. Periodic replacement of the catalyst is necessary, even with proper usage.

Adsorption systems rely on a packed bed containing an adsorbent material to capture the VOC or organic HAP compound(s). Activated carbon is the most common adsorbent material for these systems, but alumina, silica gel, and polymers are also used. Adsorbers can achieve removal efficiencies of up to 99%, and in many cases allow for the recovery of the emitted compound. Organic compounds such as benzene, methyl ethyl ketone, and toluene are examples of compounds that are effectively captured by carbon bed adsorption systems. Adsorption beds must be regenerated or replaced periodically to maintain the bed's effectiveness. If absorbers are exposed to high-temperature gases (over 130°C), high humidity, or excessive organic concentrations, the organic compound will not be captured and "breakthrough" of the bed will occur. Monitoring of process conditions is therefore important to maintain the effectiveness of the adsorber performance.

Absorbers are similar to wet scrubbers in that they expose the emission stream to a solvent which removes the VOC or organic HAP. The solvent is selected to remove one or more particular compounds. Periodically, the solvent must be regenerated or replaced as it becomes saturated with the pollutant(s). Replacement of the solvent results in the need for disposal of the used solvent, often increasing potential for contamination of ground or surface water. Absorbers are therefore often used in conjunction with thermal oxidation systems in which the waste solvent can be destroyed.

Condensers are used to reduce the concentrations of VOCs and organic HAPs by lowering the temperature of the emission stream, thereby condensing these compounds. Condensers are most often used to reduce pollutant concentrations before the emission stream passes into other emission-reduction systems such as thermal or catalytic oxidizers, adsorbers, or absorbers.

65.5.2 Alternative VOC Control Technologies

Other technologies have been developed for the removal of VOCs and organic HAPs from emission streams that are not as widely applied as the control technologies noted above. In some cases, these alternatives are still under development, and hold promise for improving the capabilities of organic compound removal beyond conventional systems.

Biofilters rely on microorganisms to feed on and thus destroy the VOCs and organic HAPs. In these systems, the emission stream must come into direct contact with a filter containing the microorganism for sufficient time for the bioreaction to occur. Although biofilters can have lower overall costs than other technologies, technical problems, such as proper matching of the emission stream and the microorganisms, long-term operational stability, and disposal of the resulting solid wastes, may prevent their use in particular situations.

Corona destruction units use high-energy electric fields to destroy VOCs and organic HAPS as they pass through the corona. Two types of corona destruction units have been developed: packed bed corona and pulsed corona. In the packed bed system, the bed is packed with a high dielectric material and high voltage (15,000–20,000 V) is applied to electrodes at both ends of the bed. The resulting high-energy electric field fills the spaces between the packing material. As the emission stream passes through the bed, the organic compounds in the emission stream are destroyed. A pulsed corona system uses a single wire as one electrode and the walls of the reactor as the other. High voltages are intermittently applied across the electrodes at nanosecond intervals. The organic compounds passing through this electric field are destroyed. Disadvantages of the corona discharge systems include their high energy consumption and their potential for creating high levels of NO_x in the corona.

Plasma destruction systems rely on high temperatures generated by streams of ions to destroy the organic compounds. Plasma are incineration systems typically use an inert gas electrically heated to such high temperatures that the gas dissociates into a stream of ions. This high-temperature stream is then used to thermally break down organic materials into their simpler atomic constituents, which then recombine at lower temperatures into nontoxic products. The high temperatures result in high organic destruction efficiency; disadvantages include the high electrical energy requirement and the need to ensure that the entire waste gas stream adequately contacts the plasma.

Separation systems include membranes, hydrophobic molecular sieves, superactivated carbons, and improved absorption technologies. *Membranes* are used to separate and recover organics from an emission stream, particularly if the stream is consistent in composition. These systems can be used as control devices if high enough removals are achieved. High pressure drops in the emission stream and high sensitivity to contaminants are disadvantages of membrane systems.

Ultraviolet (UV) oxidizers use UV radiation as the basis for destruction of VOCs and organic HAPs. Absorption of UV light activates organic compounds, leading to photodissociation (or decomposition) or increased reactivity with other compounds. Reaction rates are sometimes increased by using a catalyst (typically titanium dioxide) in conjunction with UV radiation.

65.6 METAL HAZARDOUS AIR POLLUTANTS

Along with organic compounds, metals have risen in importance as pollutants of concern. Although the total mass of metal emissions is small compared to SO_2, NO_x, and total particulates, many metals have been shown to be toxic when people are exposed to even relatively small quantities over a long period of time.[11] In addition, some metals bioaccumulate, and people can be exposed to these metals through ingestion of contaminated food.

For the most part, metal emissions are in the form of particulate, although more volatile metals such as mercury can be emitted in the form of a vapor. In combustion systems, metal emissions are the result of the metals' being introduced into the combustion environment via the fuel. This is true for coal and heavy oils in particular. In other systems, such as metal-processing facilities, metal emissions are usually significantly higher in concentration, and are also more difficult to collect due to the lack of a single exit stream, as with coal-fired boilers.

If the metal particulate or vapor exits the plant via a single gas stream, most metal emissions can be reduced by installation of particulate removal equipment (see Section 65.3, above). For more volatile metals such as mercury, additional steps may be necessary to control emissions. One approach to mercury control has been injecting activated carbon into the flue gas downstream of the furnace and subsequently collecting the carbon with either a fabric filter or ESP. For systems with high uncontrolled mercury emissions, reductions of up to 90% can be achieved when using carbon injection in combination with fabric filters or ESPs. The level of reduction is dependent upon several factors, including the mercury species being removed, the temperature of the flue gases, and the amount and type of carbon being injected.

For applications such as metal-smelting facilities, reduction of metal-bearing emissions is much less straightforward. In some cases, a complete redesign of the process may be necessary to have a significant impact on emissions. In other cases, enclosure of a large area may be required to allow the channelling of the gases to a single exit point, where existing control technologies, such as fabric filters or ESPs, can then be applied.

Recent work has focused on the injection of sorbent materials into the flame to capture the metal. Sorbent injection can also influence the size of metal-bearing particulate by capturing many of the smaller particles, leading to a shift in particle-size distribution toward larger, more easily collected particles. In addition, if the sorbent reacts chemically with the metal, the leachability of the collected solid is reduced, making disposal of the collected particulate much less expensive. Sorbents have not yet been found that are universally applicable to the range of metals present in many combustion systems.

65.7 INCINERATION

Waste incineration presents unique problems due to the characteristics of the fuels employed. Uncontrolled emissions from hazardous waste incineration (HWI), municipal waste combustion (MWC), or medical waste incineration (MWI) are typically much higher in metals and halogenated compounds than those from combustion of fossil or biomass fuels. This is due to the high contents of metals and halogens, particularly chlorine, in the wastes being burned. Metal emissions can be reduced using the methods outlined above, the HCI emissions are usually reduced using a spray dryer, dry sorbent injection, or wet scrubber.

In some instances, waste incineration has resulted in the emissions of products of incomplete combustion (PICs) that are either not destroyed in the incineration process or are formed during some phase of the incineration and/or gas cleaning process. Trace quantities of organic compounds are typically produced during the combustion of hydrocarbon fuels, although, when proper temperatures and mixing of the fuel and oxygen are maintained, these emissions are near the detection limits of modern measurement methods, which are often in the range of several parts per billion by volume (although some compounds, such as dioxins, can be measured in the parts per trillion range).

Of particular concern are PCDDs and PCDFs, which are highly toxic. Studies have shown that flue gases containing HCl and fly ash at temperatures between 200 and 600°C can form PCDDs/PCDFs in the presence of a catalytic metal, such as copper. Due to the use of copper in ESPs and the need to maintain the flue gases at temperatures above the acid gas dew point, these conditions were often present in the air pollution-control systems of MWC units. Modifying the operating conditions of these units eliminated or greatly reduced the PCDD/PCDF formation potential.

65.8 ALTERNATIVE POLLUTION-CONTROL APPROACHES

In recent years, there has been a growing emphasis on the prevention of pollution rather than the removal of pollutants following their formation. Pollution prevention is in many cases a much more cost-effective approach than the installation and operation of traditional control technologies. Not only can prevention lead to reduced emissions of one or more pollutants, it can also improve the efficiency of the overall process, leading to significant improvements in energy efficiency and/or material use. Such approaches are frequently very process- and/or site-specific, and depend upon the equipment currently in use and process parameter limitations. However, periodic inspection and replacement of items such as valve and pump seals and gaskets, and reduction of atmospheric venting, can have significant impacts on the annual emissions of pollutants.

Where new equipment is being considered, prevention approaches can be very attractive, since the initial specifications can be set with emission minimization as a key parameter in combination with the process requirements. Investment in pollution-minimizing systems and processes can in many cases significantly reduce the requirements for additional equipment specifically for pollution control. Pollution prevention is most cost-effective when the entire production process can be designed with pollution control in mind. For instance, the use of paints that do not rely on the evaporation of an organic solvent can eliminate fugitive emissions of the organic solvent without the need for VOC control equipment. While these approaches can be very cost-effective, they often are applicable only when new equipment or processes are being installed.

One method of pollution prevention that can be applied without extensive replacement of existing equipment is the use of computer-based controls. Many current processes are poorly instrumented and are often controlled manually based on operational "rules of thumb." The rapidly increasing capabilities of desktop computers and programmable controllers provide many opportunities to improve process efficiency and reduce emissions of many pollutants. Many of these process controls can be applied in a straightforward manner, using simple feedback systems that maintain a given process setpoint. In more complex systems where feedstocks may be rapidly and unpredictably changing, the use of artificial intelligence (AI) methods may provide considerable improvements in control. Some examples of AI-based systems are expert systems, fuzzy logic controls, and artificial neural networks.

Expert systems are based on expert rules developed by system designers and operators, and in their simplest forms use a series of yes–no questions to arrive at an operational diagnosis of the system's performance and recommendations of process changes to improve that performance. These systems can act either as an operational advisor, taking process information and providing control guidance to operators, or in a closed loop capacity making the appropriate process changes automatically. Expert systems can be applied to pollution-control problems by signalling operators when plant conditions require adjustment to maintain proper pollution-control performance.

Fuzzy logic is an AI-based method that uses similar expert rules as the basis for automatic controls. Fuzzy-logic controls have been successfully applied to household appliances, automobiles, and robotic mechanisms, and are likely to be used in an increasing number of applications in the future. Their advantage over traditional feedback control systems is their simple design and ease of modification. Fuzzy logic is likely to become increasingly common in automatic controls for combustors and pollution control equipment.

Artificial neural networks (ANNs) are a pattern-recognition technique based on the neurons of the brain. ANNs have been used to identify patterns in the stock market, in computer vision systems and in radar signal-processing equipment. In pollution-control applications, ANNs may allow computerized control systems to identify automatically modes of operation that will maintain production efficiency while minimizing pollutant emissions, or may be used to identify conditions that indicate incipient failures of equipment, thereby minimizing or eliminating transient emissions due to equipment failure.

65.9 GLOBAL CLIMATE CHANGE

In recent years, emissions of certain gases from industrial and other human activities have been the focus of concern over their impact on global climate. In particular, emissions of CO_2, CH_4, and N_2O have been identified as having the potential to increase the concentrations of these compounds in the atmosphere to such a degree that the average global temperature could increase. Climatologists have predicted that slight changes in the average global temperature could have broad detrimental effects on local climates, including large and extended drought, flooding of coastlines, and decreased production of food. Because of the far-reaching impacts of such climate changes, considerable attention has been directed toward reducing the emissions of these global warming gases.

In addition, other compounds have been identified as having severe impacts on the stratospheric ozone layer that protects the Earth's surface from harmful ultraviolet radiation generated by the sun. Some of the ozone-depletion substances (ODSs) that have been identified include the broad category of chlorofluorocarbons (CFCs), which have been widely used as refrigerants, solvents, aerosol propellants, and foam-blowing agents.

65.9.1 CO_2

A number of commercially available processes exist for the removal of CO_2 from flue gases, or *CO_2 scrubbing.* These processes have been developed primarily for use in cleaning impurities, including CO_2, from natural gas, and are based on the use of an absorption solvent to scrub out the CO_2. In most cases, the solvent also removes other compounds, including H_2S, SO_2, HCN, COS, CS_2, and NH_3.[12] To date, no large-scale demonstration of a CO_2 scrubbing system has been conducted on a fossil fuel boiler or furnace, although engineering studies have been made to assess the costs and performance associated with CO_2 scrubbing. Removal efficiencies have been estimated at up to 95% for commercial CO_2 scrubbing processes.[13] However, applications of CO_2 scrubbers will reduce the overall efficiency of a plant, requiring additional CO_2 to be emitted in order to overcome the losses, bringing the overall process efficiency down. A schematic of a CO_2 scrubbing system is shown in Fig. 65.3.

Additional control technologies include cryogenic separation, which produces CO_2 in liquid form, or membrane separation, which also results in liquid CO_2 as the end product. Both these technologies are more energy-intensive than the absorption-based technologies, and are therefore likely to be suitable only in special instances unless significant breakthroughs are achieved.

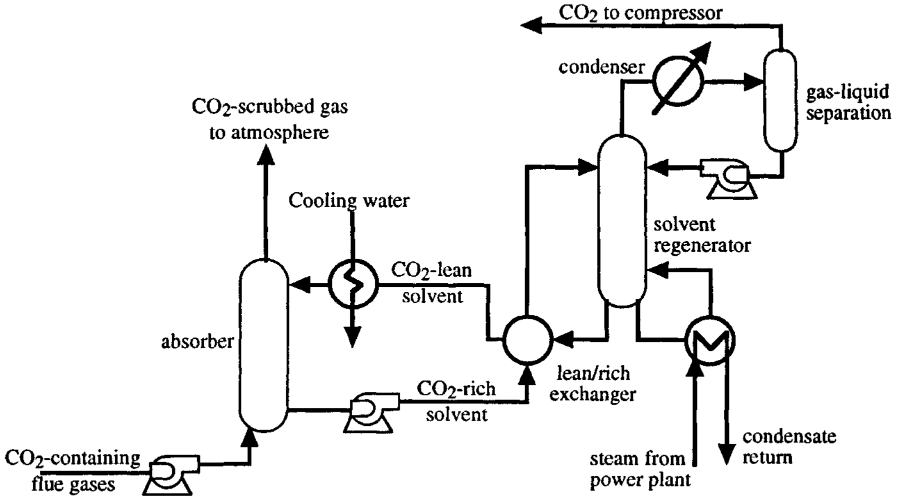

Fig. 65.3 Schematic of CO_2 scrubbing system.

Even if CO_2 control technologies can be shown to be cost-effective and technically feasible, CO_2 disposal is a critical issue that is as yet unresolved. Suggested options include injection of CO_2 into oil reservoirs to improve recovery, or injection into deep oceans. However, the technical uncertainties associated with these options are significant in terms of number and magnitude. Technical feasibility, environmental acceptability, cost, and safety of each of the proposed options are not yet understood to the degree that large-scale implementation is likely in the near term.

More feasible in the short term are CO_2 mitigation measures, such as increased efficiency and demand-side management to reduce the use of fossil fuels. These strategies are particularly important for controlling emissions from mobile sources, since removal technologies are not available for automotive or other sources in the transportation sector. A wider use of electrically powered vehicles will transfer the CO_2 emissions from the transportation to the utility sector, and may allow scrubbing technologies to be applied indirectly to the transportation sector. Biomass-derived or other non-fossil liquid fuels for transportation are another approach to mitigation of mobile source emissions. Ethanol, methanol, and hydrogen are three liquid fuels that have the potential to be used in mobile applications. However, supply, cost, and safety issues remain to be resolved before widespread use of these fuels is possible.

Other CO_2 mitigation approaches include increased use of biomass fuels, which are part of the global carbon cycle and do not add to the amounts of carbon that must be absorbed into the cycle, increased planting of forests, reduced destruction of existing forests, and increased efficiencies of energy use in developing countries.

65.9.2 Other Global Warming Gases

Sources of CH_4 emissions include the petroleum and natural gas production and processing industries, release of coal mine gases, escape of gases produced in solid waste landfills, and the raising of livestock. These emissions are often most efficiently reduced through stricter management of process releases and equipment leaks. In the cases of coal mine gas, landfill gas, and livestock releases, other approaches are necessary. Extraction and use of CH_4 from landfill gas as the feedstock for the generation of electricity from fuel cells has been demonstrated, and techniques for capturing emissions from cattle feedlots have been proposed.[14] Potential controls include improved nutrition, recovery of methane from covered waste lagoons, and the use of digesters. For coal mine CH_4 emissions, pre-mining degasification wells and capture and treatment of ventilation air are two possible control approaches.

Adipic acid plants produce an intermediary product in the production of nylon, and are major emitters of N_2O. Control technologies include thermal destruction in boilers, conversion to NO for recovery, and catalytic dissociation to molecular nitrogen and oxygen.[14] N_2O is also emitted by some combustion processes, particularly low-temperature combustion such as fluidized-bed combustors, but is not emitted in significant levels from conventional high-temperature combustion processes. Catalytic reduction can be applied to these systems with considerable success.

65.9.3 Ozone-Depleting Substances

Several substances have been identified as destroying ozone in the stratosphere, thereby reducing the atmosphere's ability to screen out harmful ultraviolet radiation from the sun. The most common of these ozone-depleting substances (ODSs) are chlorofluorocarbons (CFCs). CFCs are used as the working fluids in vapor-compression cycles, as solvents and leak-checking systems in industry, and in production of foams. Through venting and leakage, these compounds have been emitted into the atmosphere, where they are now playing a major role in the reduction of stratospheric ozone. Because of the potential adverse health impacts of increased UV radiation, an international agreement to eliminate the production and use of ODSs was established in 1990. New compounds have been, and are currently being, developed to replace existing CFCs, and methods of CFC replacement and destruction have been developed to minimize the amount of these compounds that reach the ozone layer.

CFC replacement chemicals include hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), and hydrocarbons (HCs). Many issues remain unresolved regarding the use of these compounds. HCFCs are also ODSs and are being phased out over the next 20–25 years and are therefore not long-term alternatives to CFCs. In addition, some HCFCs have their own unique markets such as heat pumps, which will require the development of replacement compounds. The use of "natural" refrigerants such as H_2O, CO_2, or NH_3 is being proposed for some cases, but these chemicals are not suitable for all applications where CFCs are now used.

In refrigeration applications, many replacement chemicals are not fully compatible with materials of construction in existing systems. In severe cases, the incompatibility can lead to a breakdown of the lubricant or other material, thus resulting in failure of the refrigeration unit. In such cases, changes in either the lubricant or the entire system are required for the replacement refrigerant to be used in a particular application. Additionally, steps are being taken with commercial refrigeration and vehicle air-conditioning systems to minimize CFC emissions by control of system leaks. Title VI of the 1990 Clean Air Act Amendments[1] now requires that motor vehicle air-conditioning system maintenance personnel be certified as having adequate training in the recovery and storage of CFCs. These substances must now be recycled and reused rather than being vented as in earlier practice.

Where CFCs are used as solvents, a dual approach is also being taken to reduce the emission of CFCs to the atmosphere. As with refrigeration applications, replacement chemicals are being used where possible. And in all processes where CFCs are being used, vapor-capture and recovery systems are being used to recycle and reuse as much of the chemical as possible. Vapor-capture and recovery systems are also being employed in the production of foams.

Destruction of CFCs once they have been recovered can be a difficult process, since many CFCs are also used as fire retardants and suppressants. However, studies have shown that CFCs can be incinerated, although incineration can produce high levels of hydrochloric and hydrofluoric acid (HCl and HF) gases in the exhaust. Due to the high levels of chlorine in the incineration flue gases, the production of PCDDs/PCDFs is also a concern, although sufficient flame temperatures and adequate gas-cleaning systems are usually sufficient to destroy any measurable levels of these compounds.[15]

REFERENCES

1. Public Law 101-549, Clean Air Act Amendments of 1990, November 15, 1990.
2. *National Air Pollutant Emission Trends Report,* 1990–1993, EPA-454/R-94-027 (NTIS PB95-171989), Office of Air Quality Planning and Standards, October 1994.
3. P. S. Nolan et al., "Results of the EPA LIMB Demonstration at Edgewater," in *Proceedings: 1990 SO_2 Control Symposium,* Vol. 1, EPA-600/9-91-015a (NTIS PB91-197210), Research Triangle Park, NC, May 1991.
4. R. J. Keeth, P. A. Ireland, and P. T. Radcliffe, "1990 Updated of FGD Economic Evaluations," in *Proceedings: 1990 SO_2 Control Symposium,* Vol. 1, EPA-600/9-91-015a (NTIS PB91-197210), Research Triangle Park, NC, May 1991.
5. T. E. Emmel, M. Maibodi, and N. Kaplan, "Retrofit Costs of SO_2 Controls in the United States and the Federal Republic of Germany," in *Proceedings: 1990 SO_2 Control Symposium,* Vol. 1, EPA-600/9-91-015a (NTIS PB91-197210), Research Triangle Park, NC, May 1991.
6. C. T. Bowman, "Control of Combustion-Generated Nitrogen Oxide Emissions: Technology Driven by Regulation," in XXIV Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1992, pp. 859–876.
7. K. J. Lim et al., *Environmental Assessment of Utility Boiler Combustion Modification NO_x Controls: Volume 1. Technical Results,* EPA-600/7-80-075a (NTIS PB80-220957), Research Triangle Park, NC, April 1980.
8. S. M. Wilson, J. N. Sorge, L. L. Smith, and L. L. Larsen, "Demonstration of Low NO_x Combustion Control Technologies on a 500 MWe Coal-Fired Utility Boiler," in *Proceedings: 1991 Joint Symposium on Stationary Combustion NO_x Control,* Vol. 1, EPA-600/R-92-093a (NTIS PB93-212843), Research Triangle Park, NC, July 1992.

9. B. de Volo et al., "NO_x Reduction and Operational Performance of Two Full-Scale Utility Gas/Oil Burner Retrofit Installations," in *Proceedings: 1991 Joint Symposium on Stationary Combustion NO_x Control,* Vol. 3, EPA-600/R-92-093c (NTIS PB93-212868), Research Triangle Park, NC, July 1992.

10. S. L. Chen et al., "Bench and Pilot Scale Process Evaluation of Reburning for In-Furnace NO_x Reduction," in XXI Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1986, pp. 1159–1169.

11. W. P. Linak and J. O. L. Wendt, "Toxic Metal Emissions from Incineration: Mechanisms and Control," *Progress in Energy and Combustion Science* **19**, 145–185 (1993).

12. I. M. Smith and K. V. Thambimuthu, *Greenhouse Gases, Abatement and Control: The Role of Coal,* IEACR/39, London UK, IEA Coal Research, June 1991.

13. I. M. Smith, C. Nilsson, and D. M. B. Adams, *Greenhouse Gases—Perspectives on Coal,* IEAPER/12, London, UK, IEA Coal Research, August 1994.

14. P. G. Finlay, P. H. Pinault, and R. P. Hangebrauck, "Climate Change Prevention Technologies: Current and Future Trends," presented at the First North American Conference and Exhibition on Emerging Clean Air Technologies, Toronto, Canada, September 26–29, 1994.

15. United Nations Environment Programme, "Ad-Hoc Technical Advisory Committee on ODS Destruction Technologies," May 1992.

16. *National Air Pollutant Emission Trends, 1900–1993,* EPA-454/R-94-027 (NTIS PB95-171989), October 1994.

17. M. A. K. Khalil and R. A. Rasmussen, "The Global Sources of Nitrous Oxide," *J. Geophys. Res.* **97**, 14,651 (1992).

18. *Mercury Study Report to Congress,* Book 2 of 2, EPA-600/P-94-002ab (NTIS PB95-167342), Cincinnati, OH, 1995.

19. *National Air Pollutant Emission Trends, 1900–1992,* EPA-454/R-93-032 (NTIS PB94-152097), October 1993.

20. *Control Techniques for Particulate Emissions from Stationary Sources—Volume 1,* EPA-450/3-81-005a (NTIS PB83-127498), Research Triangle Park, NC, 1982.