EMISSION CONTROL, INDUSTRIAL

1. Introduction

Limits for exhaust emissions from industry, transportation, power generation (qv), and other sources are increasingly legislated (see also EXHAUST CONTROL, AUTOMOTIVE) (1,2). One of the principal factors driving research and development in the petroleum (qv) and chemical processing industries in the 1990s is control of industrial exhaust releases. Much of the growth of environmental control technology is expected to come from new or improved products that reduce such air pollutants as carbon monoxide [630-08-0] (qv), CO, volatile organic compounds (VOCs), nitrogen oxides (NO_x, or other hazardous air pollutants (see AIR POLLUTION). The mandates set forth in the 1990 amendments to the Clean Air Act (CAAA) push pollution control methodology well beyond what, as of this writing, is in general practice, stimulating research in many areas associated with exhaust system control (see AIR POLLUTION CONTROL METHODS). In all, these amendments set specific limits for 189 air toxics, as well as control limits for VOCs, nitrogen oxides, and the so-called criteria pollutants. An estimated 40,000 facilities, including establishments as diverse as bakeries and chemical plants are affected by the CAAA (3).

There are 10 potential sources of industrial exhaust pollutants which may be generated in a production facility (4): (*1*) unreacted raw materials; (*2*) impurities in the reactants; (*3*) undesirable by-products; (*4*) spent auxiliary materials such as catalysts, oils, solvents, etc; (*5*) off-spec product; (*6*) maintenance, ie, wastes and materials; (*7*) exhausts generated during start-up and shutdown; (*8*) exhausts generated from process upsets and spills; (*9*) exhausts generated from product and waste handling, sampling, storage, and treatment; and (*10*) fugitive sources.

Exhaust streams generally fall into two general categories, intrinsic and extrinsic. The intrinsic wastes represent impurities present in the reactants, by-products, coproducts, and residues as well as spent materials used as part of the process, ie, sources (*1–5*). These materials must be removed from the system if the process is to continue to operate safely. Extrinsic wastes are generated during operation of the unit, but are more functional in nature. These are generic to the process industries overall and not necessarily inherent to a specific process configuration, ie, sources (*6–10*). Waste generation may occur as a result of unit upsets, selection of auxiliary equipment, fugitive leaks, process shutdown, sample collection and handling, solvent selection, or waste handling practices (see also WASTES, INDUSTRIAL).

2. Control Strategy Evaluation

There are two broad strategies for reducing volatile organic compound (VOC) emissions from a production facility: (*1*) altering the design, operation, maintenance, or manufacturing strategy so as to reduce the quantity or toxicity of air emissions produced, or (*2*) installing after-treatment controls to destroy the pollutants in the generated air emission stream (5). Whether the exhaust stream contains a specific hazardous air pollutant, a VOC, a nitrogen oxide, or carbon monoxide, the best way to control the pollutant is to prevent its formation in the first place. Many technologies are being developed that seek to minimize the generation of undesirable by-products by modifying specific process materials or operating conditions. Whereas process economics or product quality may restrict the general applicability of these approaches, an increased understanding of the mechanisms and conditions by which a pollutant is created is leading to significant breakthroughs in burner design and operation (for nitrogen oxide control), equipment design, maintenance, and operation for fugitive and vent VOC emission control, and product and waste storage and handling design and operation (for VOC emission control). One source category of increasing importance is that associated with fugitive emissions from equipment leaks.

3. Fugitive Emissions from Equipment Leaks

Emissions can occur from process equipment whenever there is contact between the process chemicals and the atmosphere. Fugitive emissions represent this category of emissions associated with the unplanned or unmanaged, continuing or intermittent emissions of chemicals to the atmosphere, typically due to leakage from general plant equipment such as pumps, valves, pressure relief valves, flanges, agitators, and compressors (6). A leaking pump might lose >10 lb of product/day; a leaking compressor nearly 10 times this amount (see Table 1)

Fugitive emissions from chemical plants in the United States have been estimated to total >300,000 tons every year; about a one-third of the total organic emissions from U.S. chemical plants (7). Other studies indicate that as much as 72% of the total VOC emissions from a facility were attributable to equipment leaks (2). Controlling such emissions can also reduce employee exposure to hazardous chemicals, and enhance the safety of a unit.

Table 1. **Fugitive Emissions—Sources and Control Effectiveness**[a]

Equipment type	Number in an typical petrochemical unit	Average emission rate, lb/day	"Leaker" emission rate, lb/day	Modification	Approximate control efficiency, %	LDAR Program control effectiveness, %		
						Monthly monitoring, 10,000 ppmv leak definition	Quarterly monitoring, 10,000 ppmv leak definition	MACT requirements
pumps	5–20	1.1	12.8	sealless design	100	69	45	75
				closed-vent system	90			
				dual mechanical seal with barrier fluid	100			
valves	150–600	0.32	4.1	sealless design, bellows	100	87	67	92
compressors	1–3	12	85	closed-vent system	90			93
				dual mechanical seal with barrier fluid	100			
open-ended lines	7–30	0.11	0.63	blind, cap, plug, or second valve	100			
flanges and connectors	700–3000	0.10	0.60	weld or replace	100		33	

[a] Based upon information provided in Refs. 9 and 10.

Because these emissions generally occur randomly and may vary in intensity over time, they are difficult to predict, much less manage. Since a chemical process unit may contain anywhere from 5000 to 100,000 such components, measurements of equipment leak emissions actually represent a "snapshot" of the leaking process. Predicting whether any one component will leak is difficult, but the statistical predictability over large numbers of components in any one facility produces a fairly consistent picture of the distribution of leak rates. The distribution of loss rates varies predictably, with only a few components leaking significantly, (often defined as "leakers") many components leaking notably, and most others leaking a little. At 17 refineries investigated by the EPA, it was found that significant equipment leaks approached 5% of the equipment inspected (8,9).

Considering that these losses generally represent valuable raw materials or final products lost, controlling such emissions can represent a substantial increase in performance to the operating facility.

Rates of product loss from individual components at facilities depend on factors such as (5,6):

- Equipment design and standard of installation.
- Age of components.
- Access to component by operators.
- Time since last major maintenance turnaround.
- Specific inspection and maintenance procedures.
- External environmental variability (temperature, pressure) and stress.
- Specific process temperatures and pressures.
- Nature of chemicals in process unit.
- Rates and variability of production operation.

The approaches used to reduce equipment leak emissions fall into two categories: (*1*) modifying or replacing existing equipment with a more effective design, and (*2*) implementing a leak detection and repair (LDAR) program. The focus of such a program will vary depending on component type, the service (gas, light liquid or heavy liquid) and previous leak history (10,11) (see Table 1).

3.1. Pumps. Chemicals transferred by pumps can leak at the point of contact between the moving shaft and the stationary casing. Thus, pumps generally require a seal at the point where the shaft penetrates the housing in order to isolate the pumped fluid from the environment.

Equipment modifications for pumps include (*1*) routing leaking vapors to a closed-vent system, (*2*) installing a dual mechanical seal containing a barrier fluid, or (*3*) replacing the existing pump with a sealless type (canned-motor, magnetic drive, and diaphragm pumps). The control efficiency of sealless pumps and a dual mechanical seal is essentially 100%, assuming both the inner and outer seal do not fail simultaneously.

3.2. Valves. Most common valve designs contain a valve stem that operates to restrict or limit fluid flow. Typically, the stem is sealed by a packing gland or O-ring to prevent leakage of process fluid to the atmosphere. Emissions from valves occur at the stem or gland area of the valve body.

Emissions from process valves can be eliminated when the valve stem can be isolated from the process fluid, (ie, using sealless valves). Two types of sealless valves, diaphragm valves and sealed bellows, have been developed. The control efficiency of both types is essentially 100%.

3.3. Compressors. Compressors transport gases through a process unit in much the same way that pumps transport liquids. Compressors are typically driven with rotating or reciprocating shafts. The sealing mechanisms for compressors are similar to those for pumps.

Emissions from compressors may be reduced by collecting and controlling the emissions from the seal using a closed-vent system or by improving seal performance by using a dual mechanical seal system similar to pumps. The dual mechanical seal system has an emissions control efficiency of 100%, assuming both the inner and outer seal do not fail simultaneously.

3.4. Pressure Relief Devices. Pressure relief devices are safety devices commonly used in chemical facilities to prevent operating pressures from exceeding the maximum allowable working pressures of the process equipment. Equipment leaks from pressure relief devices occur when material escapes from the pressure relief device during normal operation, either because the device does not properly reseat after a release, from general deterioration of the seal, or when the process pressure is operating too close to the set pressure of the PRV.

There are two primary equipment modifications that can be used for controlling equipment leaks from pressure relief devices: (*1*) a closed-vent system, or (*2*) use of a rupture disk in conjunction with the PRV. The control efficiency of the closed vent system is dependent upon a number of operational factors. When Rupture disks can be installed upstream of a PRV they can prevent fugitive emissions through the PRV seat. The control efficiency of a rupture disk/PRV combination is essentially 100% when operated and maintained properly. Rupture disks cannot be used on processes where solids or polymers might collect around the disk, reducing its ability to release at the design pressure.

3.5. Flanges and Connectors. Connectors and flanges are the most common pieces of equipment in a chemical process unit. They are used to join sections of piping and equipment wherever pipes may require isolation or removal, such as at a valve or pump. Flanges are bolted, gasket-sealed connectors and are normally used for pipes with diameters of 2.0 in. or greater. The primary causes of flange leakage are poor installation, aging and deterioration of the sealant, and thermal stress. Flanges can also leak if improper gasket material is chosen. Threaded fittings (connectors) are normally used to connect piping and equipment having diameters of 2.0 in. or less. Seals for threaded fittings are made by coating the male threads with a sealant before joining it to the female piece. Leakage can also occur as the result of poor assembly or sealant application, or from thermal stress on the piping and fittings.

In cases where connectors are not required for safety, maintenance, process modification, or periodic equipment removal, emissions can be eliminated by removing the connector and welding the pipe or piece together.

3.6. Leak Detection and Repair Program. The LDAR program is a structured program to monitor the equipment on a regular schedule and repair the equipment identified as leaking (10). A LDAR program is more effective on valves and pumps than it is for flanges and connectors, because these sources have a greater leak potential relative to their fewer numbers.

In a typical LDAR program, a portable screening device is used to identify (monitor) pieces of equipment that have the potential to emit amounts of material at levels that warrant reduction of the emissions through simple repair techniques. Odors, area monitoring or remote sensing has also been used to identify significant leakers. These programs are best applied to equipment types that can be repaired on-line, resulting in immediate emissions reduction. The control efficiency of an LDAR program is dependent on three factors: (*1*) the leak definition, (*2*) the monitoring frequency of the LDAR program, and (*3*) the final leak frequency after the LDAR program is implemented. The leak definition is the screening value measured by a portable screening device above which a leak is indicated Screening values are measured as concentrations in parts per million by volume (ppmv).

The monitoring frequency is the schedule at which the piece of equipment must be monitored. It may vary from as short as a week for components that have a propensity to leak (pumps) and to the initial period during installation and testing to several years for low leaking components such as flanges (12). The leak frequency is the percentage of components found to be leakers. It has been shown that with implementation of a LDAR program, the leak frequency will decrease substantially, as defective or worn out components are identified and replaced.

Once an undesirable material is created, the most widely used approach to exhaust emission control is the application of add-on control devices (13). For organic vapors, these devices can be one of two types, combustion or capture. Applicable combustion devices include thermal incinerators (qv), ie, rotary kilns, liquid injection combusters, fixed hearths, and fluidized-bed combustors; catalytic oxidization devices; flares; or boilers/process heaters. Primary applicable capture devices include condensers, adsorbers, and absorbers, although such techniques as precipitation and membrane filtration are finding increased application. A comparison of the primary control alternatives is shown in Table 2 (see also ADSORPTION; MEMBERAME TECHNOLOGY).

The most desirable of the control alternatives is capture of the emitted materials followed by recycle back into the process. However, the removal efficiencies of the capture techniques generally depend strongly on the physical and chemical characteristics of the exhaust gas and the pollutants considered. Combustion devices are the more commonly applied control devices, because these are capable of a high level of removal efficiencies, ie, destruction for a variety of chemical compounds under a range of conditions. Although installation of emission control devices requires capital expenditures, these may generate useful materials and be net consumers or producers of energy. The selection of an emission control technology is affected by nine interrelated parameters: (*1*) temperature, T, of the inlet stream to be treated; (*2*) residence time; (*3*) process exhaust flow rate; (*4*) auxiliary fuel needs; (*5*) optimum energy use; (*6*) primary chemical composition of exhaust stream; (*7*) regulations governing destruction requirements; (*8*) the gas stream's explosive properties or heat of combustion; and (*9*) impurities in the gas stream. A process flow diagram for the consideration of these parameters is shown in Figure 1. Given the many fac-

Table 2. **Emission Control Technologies**

Technology	Reduction effectiveness	Recovery	Waste generation	Advantages	Disadvantages
activated carbon adsorption	90–98%	chemical recovery possible with regeneration	spent carbon or regenerant	good for wide variety of VOCs	carbon replacement, regeneration costs, potential for bed fires
adsorption in wet scrubbers	75–90% +	chemical recovery possible through decanting/distillation	spent solvent or regenerant	simple operation	not efficient at low concentration
vapor condensation	50–80%	chemical recovery possible through decanting/treatment	liquid wastes, needs off-gas treatment	simple operation, effective for high VOC concentration	low removals applicability limits to some VOCs, high power costs
thermal oxidation	99%	heat recovery	NO_x generation, CO_2 generation	handles any VOC concentration	high operating costs, capital costs, temperatures, and maintenance
catalytic oxidation	95–99%	heat recovery	spent catalyst regeneration acids and alkalines	simple systems, lower T than thermal economical operation	fouling of catalysts, temperature limits
biofiltration	65–99%	none	some contaminated water and inert solids	low installation and operating cost. Minimal waste and air pollutant generation. Particularly suited for odor reduction.	large area required for installation. Low removals for heavy organics. Some pretreatment required. potential for upsets with variable exhaust stream.

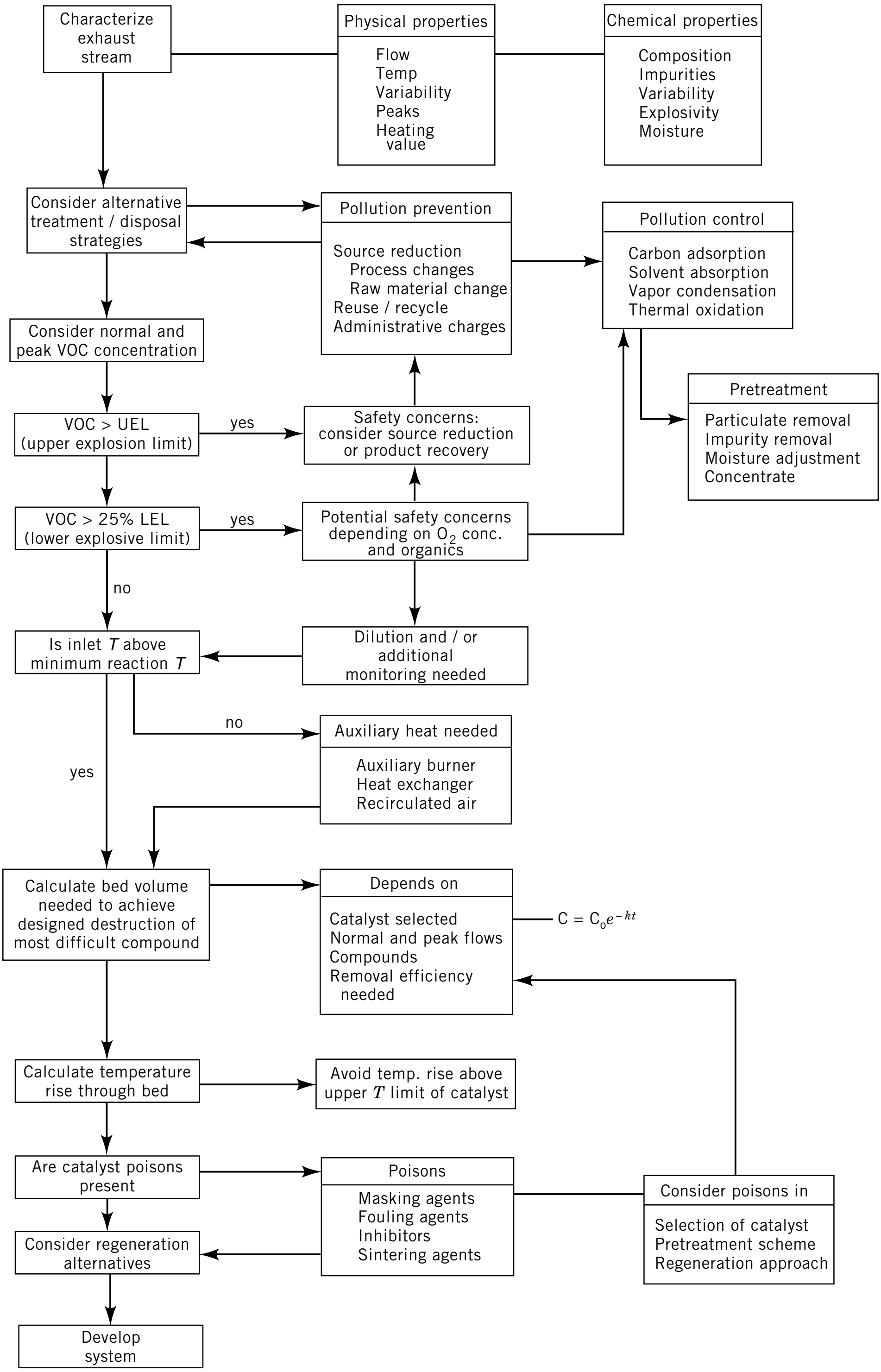

Fig. 1. Process flow diagram for the selection of an exhaust control system.

tors involved, an economic analysis is often needed to select the best control option for a given application (see ECONOMIC EVALUATION).

Capture devices are discussed extensively elsewhere (see AIR POLLUTION CONTROL METHOD). Oxidation devices are either thermal units that use heat alone or catalytic units in which the exhaust gas is passed over a catalyst usually at an elevated temperature. These latter speed oxidation and are able to operate at temperatures well below those of thermal systems. One developing technology that is a combination of the capture and oxidaton approaches is known as biofiltration.

4. Biofiltration Systems

Because control efficiencies of 90–98% or above are often required in emission control applications, the use of well-known add-on control technologies such as thermal and catalytic oxidizers are often favored over new technologies (14).

However, biofiltration is a new technology that is being increasingly considered for use in certain chemical process industries. A biofiltration system uses microbes to remove and consume the pollutants from a contaminated exhaust air stream. The term Biofiltration can apply to a variety of such systems, which include bioreactors, biotrickling filters, bioscrubbers, biomembranes and bioadsorption systems (15,16). These systems vary in the design of the beds, and the amount and type of auxiliary equipment.

Almost any substance, with the help of microbes, will decompose given the proper environment. This is especially true for organic compounds, but certain microbes also can consume inorganic compounds such as hydrogen sulfide and nitrogen oxides. The most common usage is in addressing odor nuisance where it is not necessary to meet the high control efficiencies. Although destruction efficiencies as high as 99% (17) have been reported for hydrogen sulfide, In some cases it may be enough to maintain destruction efficiencies as low as 65%. The biofiltration systems, have been widely used in the early 1990s in Europe, which required controlling nuisance from odorous compounds at concentrations <50 ppmv. Unfortunately, not all organics are degraded at the same rate. For that reason, the destruction efficiency of a bioreactor depends heavily on the composition of the organic feed stream. Large quantities of heavier organics can depress the average VOC destruction efficiency even while the oxidation efficiency of simpler compounds remains very high (18).

The EPA has indicated that where applicable, both the capital cost of a biofilter installation and its operating costs can be just a fraction of the cost of a traditional emission control devices.

An efficient Biofiltration system should only use small amounts of electrical power and some micronutrients in order to operate, and will generate water and CO_2 as by-products. Material that is indigestible becomes residue. However, because microbes are sensitive to environmental conditions (temperature, humidity, pH) as well as to the pollutant concentration and type, a biofiltration system is only suitable for selected applications (15).

Biofilters, usually use beds (media on which microbes live) made from naturally occurring organic materials (yard cuttings, peat, bark, wood chips or

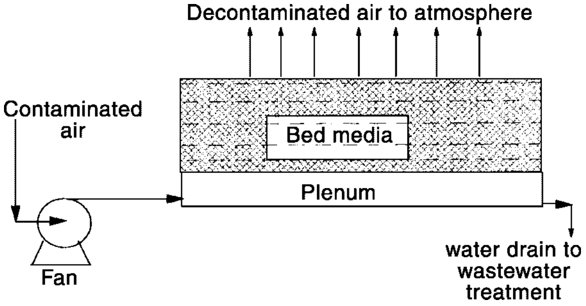

Fig. 2. Basic biofilter.

compost) that are slowly consumed by the microbes. Sometimes oyster shells (for neutralizing acid build-up) and fertilizer (for macronutrients) are mixed with bed media (see Fig. 2). These organic beds usually can supply most of the macronutrients needed to sustain the microbial activity. Under normal operating conditions, the beds must be replaced every 2–5 years (16), depending on the choice of bed material. However, in handling excessively moist exhaust streams, sloughing of the beds may clog the discharge system and require replacement of the beds more often (19).

A fan is used to collect contaminated air from a building or process, but if the air is too hot, too cold, too dry, or too dirty, it may be necessary to pretreat the contaminated air stream to obtain optimum conditions before introducing it into a biofiltration system.

Variables that effect the operation and efficiency of a biofiltration system include: temperature, pH, moisture, pollutant mix, pollutant concentration, macronutrient feeding, residence time, compacted-bed media, and gas channeling. These are crucial variables for which optimum conditions must be determined, controlled and maintained. Below are variables and limitations that affect the performance of all biofiltration systems, regardless of process type.

4.1. Temperature. Probably the most important variable effecting biofiltration operations is temperature. Most microbes can survive and flourish in a temperature range of 60–105°F (18). However, a short flow of hot air can totally destroy the system, while cold air can slow down and reduce the efficiency of the system. Where hot gases may be treated, the emissions would need to be cooled, often by passing them through a humidifier that can cool the gases and add moisture to the vapor stream.

4.2. Moisture. Microbes need moisture to survive and moisture creates the film that absorbs pollutants from an air stream where they can be assimilated by microbes. Low moisture problems can be corrected by passing emissions through a humidifier. Low moisture, for short periods, while not killing the microbes, will reduce efficiency (15). As water is removed or produced as a byproduct, water may accumulate in the biofiltration system. Excess water needs to be removed to reduce pressure loss and minimize load on the bed. Sloughing of the organic filter media has also been observed (19).

4.3. Acidity. Most biofiltration systems perform best when the bed pH is near 7, or neutral. Some pollutants form acids when they decompose. Examples of these compounds are: hydrogen sulfide, organic sulfur compounds, and halogens (chlorine, fluoride, bromine, and iodine). The Biofiltration systems that treat emissions that contain sulfur or sulfur compounds perform best when the pH is in the range 1–2 pH (20). But, in most cases, if the operation will lower the pH, it will eventually destroy the microbes. There are several techniques available to neutralize beds. One of the simplest techniques is to mix oyster shells with bed media. The shells will eventually dissolve and have to be replaced (16). Other solutions may be to introduce a dilute solution of soda ash into the bed either through the top of the bed or through hoses inside the bed.

4.4. Microbe Population. It takes some time for the microbial population to acclimate to the contaminated air stream and achieve optimum removal efficiency. Similarly, if the system is left idle, the population of microbes will change and efficiency will be reduced (21). A microbial population treating a variable exhaust stream will also have reduced efficiency since fewer microbes favoring any particular organic compound will be developed.

Biofilter Advantages:

- Installation and operation costs are usually low.
- Secondary waste generation (spent solvents, contaminated water, or carbon), pollutants (NO_x, CO etc) and other greenhouse gases are minimal.
- Natural-bed media used in biofilters usually need only to be replaced every 2–5 years.
- High destruction efficiencies for problematic odorous compounds such aldehydes, organic acids, nitrous oxide, sulfur dioxide, and hydrogen sulfide.

Biofilter Disadvantages:

- Large land requirement for traditional design.
- No continuous internal liquid flow in which to adjust bed pH or to add nutrients.
- Excessive conditions of the exhaust stream may require pretreatment to remove water, solids or alter temperature.
- Bed replacement can take 2–6 weeks, depending on bed size.
- Information on recovery of the system after an upset remains limited.
- Low destruction efficiencies for some organic compounds.
- Exhaust organic concentrations in excess of 500 ppmv may overtax the system (19).

5. Oxidization Devices

5.1. Thermal Oxidation. Thermal oxidation is one of the best known methods for industrial waste gas disposal. Unlike capture methods, eg, carbon adsorption, thermal oxidation is an ultimate disposal method destroying the objectionable combustible compounds in the waste gas rather than collecting them. There is no solvent or adsorbent of which to dispose or regenerate. On the other hand, there is no product to recover. A primary advantage of thermal oxidation is that virtually any gaseous organic stream can be safely and cleanly incinerated, provided proper engineering design is used (see INCINERATORS) (22).

A thermal oxidizer is a chemical reactor in which the reaction is activated by heat and is characterized by a specific rate of reactant consumption. There are at least two chemical reactants, an oxidizing agent and a reducing agent. The rate of reaction is related both to the nature and to the concentration of reactants, and to the conditions of activation, ie, the temperature (activation), turbulence (mixing of reactants), and time of interaction.

Thermal oxidation relies on a homogenous gas-phase reaction condition. Exhaust emissions from industrial sources usually contain organic compounds (the reducing agents) well mixed with oxygen (the oxidizing agent). Imparting the necessary, uniform temperature for reaction within this mixture is of primary importance in the design of the oxidizer and related equipment. Proper activation requires establishing the minimum required temperature (650–800°C) for an adequate time (0.1–0.3 s). General design consideration is given to minimizing heat input and reactor size under the constraints of time, turbulence, and temperature.

Thermal oxidization devices are widely used, and generally provide a high degree of assurance that the process oxidizes the material in the exhaust gas. The high temperature operation causes other problems, however, especially compared to alternatives such as catalytic oxidation. The thermal oxidation devices often incur higher fuel costs because of the higher temperatures necessary, and require exotic high temperature materials (see HIGH TEMPERATURE ALLOYS; REFRACTORIES), because the high temperatures entailed can bring about serious mechanical design problems as a result of operating in the temperature range in which metal creep takes place (1,23). In addition, equipment durability is reduced by the extent of thermal cycling. Thermal oxidation systems are susceptible to thermal stress effects which result in distortion of the ductwork and heat-exchange surfaces, creating the potential for cracks and leaks. A further consequence of these high temperatures is that a thermal oxidizer may produce nitrogen oxides (NO_x), and sometimes yield undesirable by-products such as dioxins from chlorinated materials (5).

Some of the problems associated with thermal oxidizers have been attributed to the necessary coupling of the mixing, the reaction chemistry, and the heat release in the burning zone of the system. These limitations can reportedly be avoided by using a packed-bed flameless thermal oxidizer that is under development. This system relies on radiant heat from a large heat sink to raise the temperature of the exhaust gas to its ignition temperature. The heat sink, a ceramic matrix, is preheated radiatively using an electric preheating element, or a natural gas preheater, prior to introducing the exhaust gas. Because the system temperature is reasonably constant, NO_x generation within the flame is minimized. High (99.99%) VOC reductions at low contact times were reported (24). However, as with all thermal oxidation systems, this system is most effective for higher concentration exhaust streams, and requires significant auxiliary heat to treat low concentration streams.

5.2. Catalytic Oxidization. A principal technology for control of exhaust gas pollutants is the catalyzed conversion of these substances into innocuous chemical species, such as water and carbon dioxide. This is typically a thermally activated process commonly called catalytic oxidation, and is a proven method for reducing VOC concentrations to the levels mandated by the CAAA (see CATALYSIS). Catalytic oxidation is also used for treatment of industrial exhausts containing halogenated compounds.

As an exhaust control technology, catalytic oxidation enjoys some significant advantages over thermal oxidation. The former often occurs at temperatures that are less than half those required for the latter, consequently saving fuel and maintenance costs. Lower temperatures allow use of exhaust stream heat exchangers of a low grade stainless steel rather than the expensive high temperature alloy steels. Furthermore, these lower temperatures tend to avoid the emissions problems arising from the thermal oxidation processes (25,26).

Critical factors that need to be considered when selecting an oxidation system include (27) (*1*) waste stream heating value and explosive properties. Low heating values resulting from low VOC concentration make catalytic systems more attractive, because low concentrations increase fuel usage in thermal systems; (*2*) waste gas components that might affect catalyst performance. Catalyst formulations have overcome many problems owing to contaminants, and a guard bed can be used in catalytic systems to protect the catalyst; (*3*) the type of fuel available and optimum energy use. Natural gas and No. 2 fuel oil can work well in catalytic systems, although sulfur in the fuel oil may be a problem in some applications (28). Other fuels should be evaluated on a case-by-case basis; and (*4*) space and weight limitations on the control technology. Catalysts are favored for small, light systems.

There are situations where thermal oxidation may be preferred over catalytic oxidation: for exhaust streams that contain significant amounts of catalyst poisons and/or fouling agents, thermal oxidation may be the only technically feasible control; where extremely high VOC destruction efficiencies of difficult to control VOC species are required, thermal oxidation may attain higher performance; and for relatively rich VOC waste gas streams, ie, having 20–25% lower explosive limit (LEL), the gas stream's explosive properties and the potential for catalyst overheating may require the addition of dilution air to the waste gas stream (27).

Whereas the catalytic converter has been used in automobiles to control air pollutants only since 1975 (5), catalytic oxidation of industrial exhaust emissions began in the late 1940s, and is a reasonably mature technology (29). Initially it was used only in circumstances where an extremely serious odor problem was associated with an industrial system, or where the concentration of organic solvents in the gases to be discharged to the air was high enough that these could be burned and the heat utilized in the process (23). By the mid-1950s there were several dozen catalytic incinerators in California, primarily in Los Angeles county, the first sizable area within the United States to experience a serious air pollution problem. Early applications of this technology involved some serious odor, eye irritation, or visible organic emission problems resulting from halogen poisoning and catalyst fouling (30).

The chemical industry was the first to utilize catalytic oxidation extensively for emission control, building units capable of treating up to 50 m^3/s

(100,000 scfm) of exhaust gas containing VOCs. Catalytic systems accounted for roughly one-fourth of the $200 million market for VOC control systems in 1992, and over one thousand catalytic oxidization devices were in place by the end of that year (5).

Catalysts. A catalyst has been defined as a substance that increases the rate at which a chemical reaction approaches equilibrium without becoming permanently involved in the reaction (31). Thus a catalyst accelerates the kinetics of the reaction by lowering the reaction's activation energy (5), ie, by introducing a less difficult path for the reactants to follow. For VOC oxidation, a catalyst decreases the temperature, or time required for oxidation, and hence also decreases the capital, maintenance, and operating costs of the system (see CATALYSIS).

A key feature of a catalyst is that the catalytic material is not consumed by the chemical oxidation reactions, rather it remains unaltered by the reactions that occur generally on its surface and thus remains available for an infinite number of successive oxidation reactions.

Many chemical elements exhibit catalytic activity (5) which, within limits, is inversely related to the strength of chemisorption of the VOCs and oxygen, provided that adsorption is sufficiently strong to achieve a high surface coverage (32). If the chemisorption is too strong, the catalyst is quickly deactivated as the active sites become irreversibly covered. If the chemisorption is too weak, only a small fraction of the surface is covered and the activity is very low (32) (Fig. 3).

Catalysts vary both in terms of compositional material and physical structure (33). The catalyst basically consists of the catalyst itself, which is a finely divided metal (29,32,34); a high surface area carrier; and a support structure (see CATALYSIS, SUPPORTED). Three types of conventional metal catalysts are used for oxidation reactions: single- or mixed-metal oxides, noble (precious) metals, or a combination of the two (34).

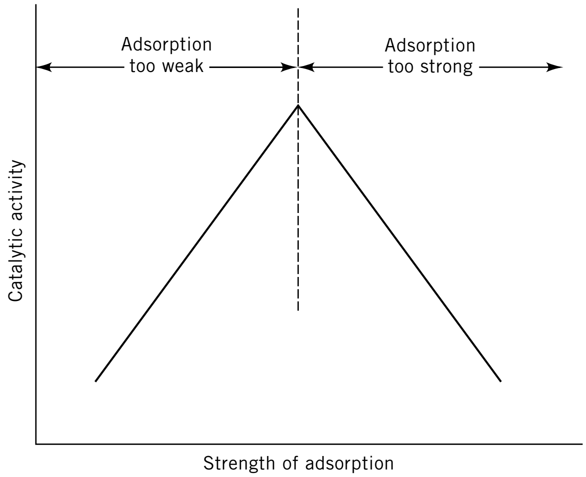

Fig. 3. Catalytic activity as a function of adsorption strength (32). (Courtesy of Oxford University Press.)

The precious metal or metal oxide imparts high intrinsic activity, the carrier provides a stable, high surface area for catalyst dispersion, and the mechanical support gives a high geometric surface area for physical support and engineering design features (35). Only the correct combination of these components provides suitable performance and long catalyst life of a properly designed catalytic system (36).

Metal Oxides. The metal oxides are defined as oxides of the metals occurring in Groups 3–12 (IIIB–IIB) of the periodic table. These oxides, characterized by high electron mobility and the positive oxidation state of the metal, are generally less active as catalysts than are the supported nobel metals, but the oxides are somewhat more resistant to poisoning. The most active single-metal oxide catalysts for complete oxidation of a variety of oxidation reactions are usually found to be the oxides of the first-row transition metals, V, Cr, Mn, Fe, Co, Ni, and Cu.

Noble Metals. Noble or precious metals, ie, Pt, Pd, Ag, and Au, are frequently alloyed with the closely related metals, Ru, Rh, Os, and Ir (see PLATINUM-GROUP METALS, COMPOUNDS). These are usually supported on a metal oxide such as α-alumina, α-Al_2O_3, or silica, SiO_2. The most frequently used precious metal components are platinum [7440-06-4], Pt, palladium [7440-05-3], Pd, and rhodium [7440-16-6], Rh. The precious metals are more commonly used because of the ability to operate at lower temperatures. As a general rule, platinum is more active for the oxidation of paraffinic hydrocarbons; palladium is more active for the oxidation of unsaturated hydrocarbons and CO (34).

Each precious metal or base metal oxide has unique characteristics, and the correct metal or combination of metals must be selected for each exhaust control application. The metal loading of the supported metal oxide catalysts is typically much greater than for nobel metals, because of the lower inherent activity per exposed atom of catalyst. This higher overall metal loading, however, can make the system more tolerant of catalyst poisons. Some compounds can quickly poison the limited sites available on the noble metal catalysts (34).

Carrier. The metal catalyst is generally dispersed on a high surface area carrier, ie, the carrier is given a washcoat of catalyst, such that very small (2–3-nm diameter) precious metal crystallites are widely dispersed over the surface area, serving two basic functions. It maximizes the use of the costly precious metal, and provides a large surface area thereby increasing gas contact and associated catalytic reactions (33).

Proper selection of the carrier is critical (35). For example, in most cases, the carrier of a precious metal catalyst is a high surface area alumina having an effective surface area in the order of 120 m^2/g of material. Alumina is often used because of its unique phase transformation properties. Various phases of the aluminum hydroxides exist as a function of temperature and starting phase. For a catalyst to be stable, the correct starting phase of alumina must be selected for the projected commercial operating temperature. Otherwise the alumina may undergo a transition during operation resulting in a carrier of less surface area, and hence less catalytic activity (1).

Efforts to redesign catalyst formulations involve both catalyst and washcoat. One thrust of this research is to manipulate the catalytic surface so that it can handle larger quantities of catalyst poisons and to incorporate more

Table 3. **Conventional Catalyst Bed Geometries**[a]

Geometry	Advantages	Disadvantages
metal ribbons	low pressure drop; high surface-to-volume	less active than ceramic-supported catalysts
spherical pellets	can be used in both fixed and fluidized beds	high pressure drop; attrition problem
ceramic rods	low pressure drop	low surface-to-volume ratio
ceramic honeycomb	low pressure drop; high surface-to-volume ratio	may have nonuniform catalyst coating
metal honeycomb	low pressure drop; high surface-to-volume ratio; high mechanical strength	less active than ceramic-supported catalysts

[a] Ref. 29.

catalytic sites, redistributed within the washcoat to make them more accessible to exhaust molecules. Altering the composition of the alumina washcoat by including various nonprecious metal oxides, such as oxides of barium, cerium, and lanthanum as stabilizers, is being looked at to promote catalyst activity before sintering and stabilize precious metal dispersion (33). Reformulation efforts are aided by use of computer controls and cleaner reactants and continuous monitoring, all of which help make exhaust composition more predictable (1).

The Support Structure. After the catalytic element is placed on the high surface area carrier, it is deposited on a mechanical support structure which determines the form of the catalyst. The support structure may have many forms, such as spheres, pellets, woven mesh, screen, honeycomb, or other ceramic matrix structures designed to maximize catalyst surface area (13). Some of the advantages of these different supports are listed in Table 3.

The pelleted and honeycomb support structures are most widely used; honeycombs are the most commonly employed. Pelleted structures are generally spherical beads or cylinders having diameters ranging from 0.16–0.64 cm. The pellets are assembled into a packed bed containing large numbers of these pellets through which the exhaust passes. The honeycomb supports are monolithic structures having numerous parallel channels through which the exhaust passes, the channel sizes ranging from ~8–50 cells/cm^2 of catalyst frontal area. Each cell has a width opening ranging from 0.29 to 0.13 cm, respectively. Some commercial honeycombs are available from 1.6 to 100 cells/cm^2 (35). The shape in the individual honeycomb channel is unlimited, eg, circle, square, and triangle.

Although more expensive to fabricate than the pelleted catalyst, and usually more difficult to replace or regenerate, the honeycomb catalyst is more widely used because it affords lower pressure losses from gas flow; it is less likely to collect particulates (fixed bed) or has no losses of catalyst through attrition, compared to fluidized bed; and it allows a more versatile catalyst bed design (33), having a well-defined flow pattern (no channeling) and a reactor that can be oriented in any direction.

The honeycomb structure is either fabricated of ceramic or stainless steel. The high surface area carrier and catalytic precious metal crystallites are coated onto the walls of the channels in the honeycomb. The honeycomb catalyst blocks

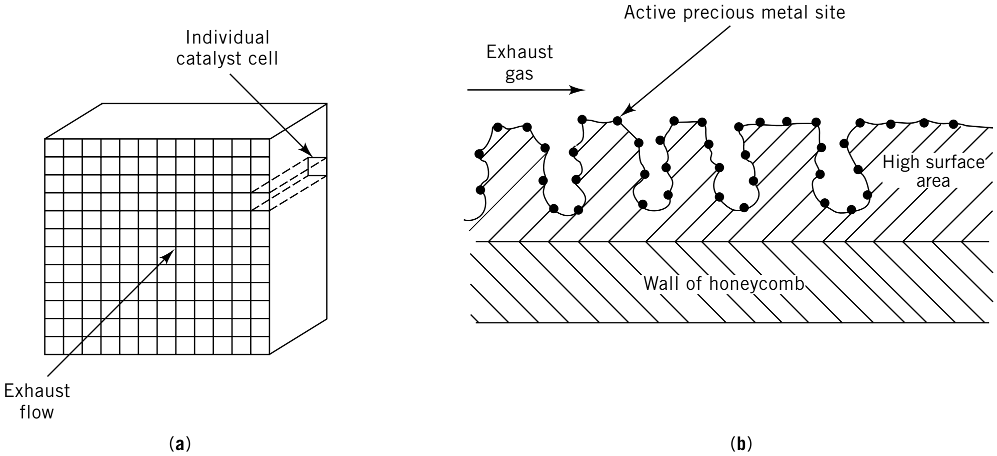

Fig. 4. Schematic of the flow through (**a**) a honeycomb catalyst structure and (**b**) a cross-section of a honeycomb channel.

generally range form 15 to 30-cm square at depths from 5 to 10 cm. These blocks are packed into larger modules containing many catalyst blocks. Flow through a honeycomb catalyst structure is shown in Figure 4 (33,37). A typical 30 cells/cm^2 honeycomb structure has about 4600 m^2 of geometric wall area per cubic meter of catalyst volume (33). The actual shape of the individual honeycomb channel is unlimited, eg, it may be circular, square, triangular, etc. In addition, the channel density can be varied. Commercial honeycombs are available that range from 1.5 to 100 cells/cm^2 (10 to 600 cells(in.^{2}) (35).

Only by using the carrier can the catalyst be sufficiently active because the majority of applications require 10–100 m^2/g of surface area (35). Surface areas for a typical monolith support structure and a carrier are given (35).

Mechanistic Models. A general theory of the mechanism for the complete heterogeneous catalytic oxidation of low molecular weight vapors at trace concentrations in air does not exist. As with many catalytic reactions, however, certain observations have led to a general hypothesis (32).

The overall process of any catalytic reaction is a combination of mass-transfer, describing transport of reactants and products to and from the interior of a solid catalyst, and chemical reaction kinetics, describing chemical reaction sequences on the catalyst surface. The most cost-effective catalytic oxidation systems require use of a solid catalyst material having a high specific surface area, ie, high surface area per net weight of catalyst. The presence of many small pores necessarily introduces pore transport diffusion resistance as a factor in the overall, or global, kinetics. The overall process consists of (32,38): (*1*) transport of reactants from the bulk fluid through the gas film boundary layer to the surface of the catalytic particle; (*2*) transport of reactants into the catalyst particle by diffusion through the catalyst pores; (*3*) chemisorption of at least one reactant on the catalyst surface; (*4*) chemical reaction between chemisorbed species or between a chemisorbed species and a physisorbed or fluid-phase reactant; (*5*) desorption of reaction products from the catalyst surface; (*6*) diffusive

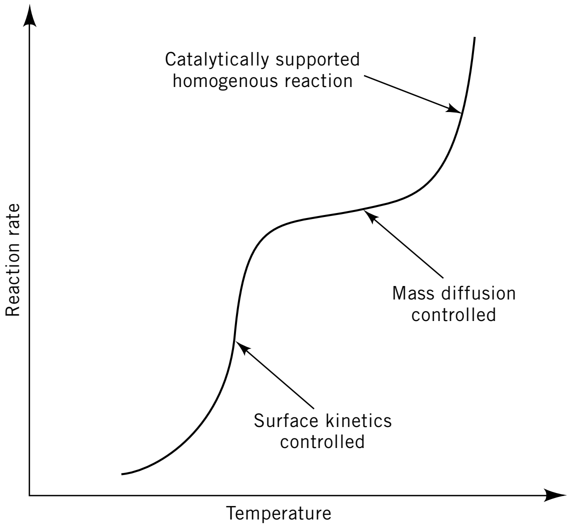

Fig. 5. Reaction rate profile as a function of temperature (20).

transport of products through the catalyst pores to the surface of the catalyst particle; and (*7*) mass transfer of products through the exterior gas film to the bulk fluid.

In principle, any of these steps or some combination can be rate controlling. In practice, temperature plays a primary role in determining the rate-controlling stage. Any comprehensive analysis of actual catalytic oxidation systems of practical interest must include a quantitative understanding of the relative effects of mass transfer (steps *1,2,6,7*) and surface reaction (steps *3–5*). The temperature relationship of these two mechanisms is shown in Figure 5 (32,33,35). As a catalyst is heated, conversion of the pollutant is negligible until a critical temperature is reached, then the rate of conversion increases rapidly with rising temperature. This is referred to as the kinetically limited region. Conversion increases in this region because catalytic reaction rates increase with temperature, until the catalyst's normal operating temperature is achieved. Then the conversion rate increases only slightly with further temperature rise in the mass-transfer limited region. At some advanced temperature, the conditions reach a point where thermal oxidation begins to play a role, and the rate of conversion again increases rapidly.

In the mass-transfer limited region, conversion is most commonly increased by using more catalyst volume or by increasing cell density, which increases the catalytic wall area per volume of catalyst. When the temperature reaches a point where thermal oxidation begins to play a role, catalyst deactivation may become a concern.

Reaction Rate. The kinetics for a single catalytic reaction can be modeled as

$$-r_m = k(T)f(C)n \qquad (1)$$

where $-r_\mathrm{m}$ is the rate of the main reaction; $k(T)$ is the rate constant, a function of temperature, T; $f(C)$ is the function of reactant and product concentration, C;

and n is the effectiveness factor, which accounts for pore-diffusional resistance (39). The form of the terms *k(T)* and *f(C)* depends on the kinetic model for the system. Kinetic models for the catalytic oxidation can either be empirical or mechanistic.

Empirical Models. In the case of an empirical equation, the model is a power law rate equation that expresses the rate as a product of a rate constant and the reactant concentrations raised to a power (32), such as

$$r_m = kC_1^a C_2^b \tag{2}$$

where r_m is the rate constant; C_1 is the concentration of reactant 1; C_2 is the concentration of reactant 2; and a and b are empirically determined reaction orders.

For combustion of simple hydrocarbons, the oxidation reactions appear to follow classical first-order reaction kinetics sufficiently closely that practical designs can be established by application of the empirical theory (23). For example, the general reaction for a hydrocarbon:

$$\mathrm{C}_x\mathrm{H}_y + (x + y/2)\ \mathrm{O}_2 \longrightarrow x\ \mathrm{CO}_2 + (y/2)\ \mathrm{H}_2\mathrm{O} \tag{3}$$

can be represented by the rate equation

$$r_m = (dC/dt) = -kC \tag{4}$$

where C = hydrocarbon concentration, r_m = rate of change of contaminant concentration, t = time, and k = reaction rate constant, which must be determined experimentally from the burning of various organic materials. The pattern of variation with t is predictable from kinetic theory and follows the Arrhenius equation,

$$k = A\exp(-\Delta E/RT) \tag{5}$$

where A is the Arrhenius collision constant, ΔE the activation energy, and R is the universal gas constant. A catalyst increases the rate of reaction by adsorbing gas molecules on catalytically active sites. The catalyst may function simply to bring about a higher concentration of reactive materials at the surface than is present in the bulk gas phase, which has the effect of increasing the collision constant, A, or the catalyst may modify a molecule of adsorbed gas by adding or removing an electron or by physically opening a bond. This has the effect of decreasing the activation energy, ΔE, in the Arrhenius equation. In either circumstance, it is necessary for the reactive materials to reach the active catalyst surface by diffusion through the gas phase, and for the reaction products to leave the surface. For the conditions encountered in most hydrocarbon emission control applications, the oxygen partial pressure is much larger than the organic reactant partial pressure, and can be treated as a constant.

Mechanistic kinetic expressions are often used to represent the rate data obtained in laboratory studies, and to explain quantitatively the effects observed in the field. Several types of mechanisms have been proposed. These differ primarily in complexity, and on whether the mechanism assumes that one compound that is adsorbed on the catalyst surface reacts with the other compound in the gas phase, eg, the Eley-Rideal mechanism (38); or that both compounds are adsorbed on the catalyst surface before they react, eg, the Langmuir-Hinshelwood mechanism (40).

The volatile organic compounds on the list of hazardous air pollutants under the CAAA have been classified into four main categories: (*1*) pure hydrocarbons (qv), (*2*) halogenated hydrocarbons (see CHLOROCARBONS AND CHLOROHYDROCARBONS SURVEY), (*3*) nitrogenated hydrocarbons (see CYANIDES), and (*4*) oxygenated hydrocarbons (see ALDEHYDES; ETHERS; KETONES). The compounds in these groups are characterized by the following oxidation reactions (41):

Hydrocarbons

$$C_6H_6 + 9\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O \qquad (6)$$

Halogenated hydrocarbons

$$CCl_4 + O_2 + 2\,H_2O \longrightarrow CO_2 + 4\,HCl + O_2 \qquad (7)$$

Nitrogenated hydrocarbons

$$2\,HCN + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O + 2\,N_2 \qquad (8)$$

Oxygenated hydrocarbons

$$C_4H_8O + 5\frac{1}{2}\,O_2 \longrightarrow 4\,CO_2 + 4\,H_2O \qquad (9)$$

Temperature reaction rate profiles for representatives compounds are available (36,41). Particularly important are the operating temperatures required before destruction is initiated. Chemical reactivity by compound class from high to low is (42) alcohols > cellsolves/dioxane > aldehydes > aromatics > ketones > acetates > alkanes > chlorinated hydrocarbons. In general, within a class the higher the molecular weight, the higher the relative destructibility. All of these compound classes, except chlorinated hydrocarbons, can be destroyed with 98–99% efficiency at sufficiently low space velocities and/or high enough inlet temperatures (43). Table 4 (37) presents oxidation temperatures for a number of hydrocarbons.

Historically, the destruction efficiency for chlorinated hydrocarbons is quite low. In addition, tests conducted after the chlorinated hydrocarbon is treated show that the catalyst is partially deactivated. More recent advancements in catalyst technology have resulted in the development of a number of catalysts and catalytic systems capable of handling most chlorinated hydrocarbons under a variety of conditions (34).

Mixture Effects. Care must be taken in determining the oxidation kinetics for a mixture of chemicals (44). In principle, given one set of conditions and a two-component mixture, the overall conversion of one component A may be controlled by mass transfer to the catalyst surface and the conversion of another component B by surface-reaction kinetics. Of course, the controlling regime

Table 4. **Ignition Temperatures for 90% Conversion**

Component	Temp, °C
hydrogen	93
acetylene	177
carbon monoxide	218
cyclohexanone	218
propylene	232
toluene	232
2-propanol	260
ethylene	260
benzene	260
xylene	260
ethanol	260
methyl ethyl ketone	274
ethyl acetate	288
cyclohexane	288
n-hexane	316
methyl isobutyl ketone	316
propane	399
methane	427[a]

[a] Ref. 22.

(mass transfer or reaction) can change with temperature. Thus for two independent parallel reactions the combined effect of diffusional and reaction rate resistances can have a considerable influence on the relative rate of the two reactions. Additionally, a third, fourth, or *n*th component can conceivably affect the other components by, eg, competing more successfully for active surface sites than B while simultaneously influencing the mass transfer of A. Thus even for a simple two- or three-component mixture, interpretation of observed results can be difficult. Extrapolation of mixture behavior from single-component data is ill-advised.

In a mixture of *n*-hexane and benzene (44), the deep catalytic oxidation rates of benzene and *n*-hexane in the binary mixture are lower than when these compounds are singly present. The kinetics of the individual compounds can be adequately represented by the Mars-VanKrevelen mechanism. This model needs refinements to predict the kinetics for the mixture.

One important consideration in any catalyst oxidation process for a complex mixture in the exhaust stream is the possible formation of hazardous incomplete oxidation products. Whereas the concentration in the effluent may be reduced to acceptable levels by mild basic aqueous scrubbing or additional vent gas treatment, studying the kinetics of the mixture and optimizing the destruction cycle can drastically reduce the potential for such emissions.

Design and Operation. The destruction efficiency of a catalytic oxidation system is determined by the system design. It is impossible to predict *a priori* the temperature and residence time needed to obtain a given level of conversion of a mixture in a catalytic oxidation system. Control efficiency is determined by process characteristics such as concentration of VOCs emitted, flow rate, process fluctuations that may occur in flow rate, temperature, concentrations of other materials in the process stream, and the governing permit regulation, such as the mass-emission limit. Design and operational characteristics that can affect the destruction efficiency include inlet temperature to the catalyst bed, volume of catalyst, and quantity and type of noble metal or metal oxide used.

Catalytic oxidation systems are normally designed for destruction efficiencies that range from 90 to 98% (42). In the early 1980s, typical design requirements were for 90% or higher VOC conversions. More recently, however, an increasing number of applications require 95 to 98% conversions to meet the more stringent emission standards (35).

Operational Considerations. The performance of catalytic incinerators (43) is affected by catalyst inlet temperature, space velocity, superficial gas velocity (at the catalyst inlet), bed geometry, species present and concentration, mixture composition, and waste contaminants. Catalyst inlet temperatures strongly affect destruction efficiency. Mixture compositions, air/gas (fuel) ratio, space velocity, and inlet concentration all show marginal or statistically insignificant effects (45).

Operating Temperature. The operating temperature needed to achieve a particular VOC destruction efficiency depends primarily on the species of pollutants contained in the waste stream, the concentration of the pollutants, and the catalyst type (29). One of the most important factors is the hydrocarbon species. Each has a catalytic initiation temperature that is also dependent on the type of catalyst used (29).

For a given inlet temperature, the quantity of supplied heat may be provided by (13) the heat supplied from the combustion of supplemental fuel, the sensible heat contained in the emission stream as it enters the catalytic system, and the sensible heat gained by the emission stream through heat exchange with hot flue gas (13). Three types of systems for catalytic oxidation of VOCs are shown in Figure 6 (26). The simplest (Fig. 5**a**) uses a direct contact open flame to preheat the gas stream upstream of the catalyst. The second (Fig. 5**b**) involves only a catalyst bed over which the gas stream passes, usually after some indirect preheating. The third (Fig. 5**c**) involves more extensive indirect preheating and heat exchange. The difference in the three configurations is the method for preheating the gas.

There are two general temperature policies: increasing the temperature over time to compensate for loss of catalyst activity, or operating at the maximum allowable temperature. These temperature approaches tend to maximize destruction, yet may also lead to loss of product selectivity. Selectivity typically decreases with increasing temperature; faster deactivation; and increased costs for reactor materials, fabrication, and temperature controls.

Reactor Design. The catalytic reactor is designed to be operated in the masstransfer controlled catalytic region. The prime design parameter is the geometric surface area. The honeycomb catalyst shows substantial advantage over other forms because of the high geometric surface areas obtainable with low pressure drop (35).

Catalyst Selection. The choice of catalyst is one of the most important design decisions. Selection is usually based on activity, selectivity, stability, mechanical strength, and cost (46). Stability and mechanical strength, which make for steady, long-term performance, are the key characteristics. The basic strategy in process design is to minimize catalyst deactivation, while optimizing pollutant destruction.

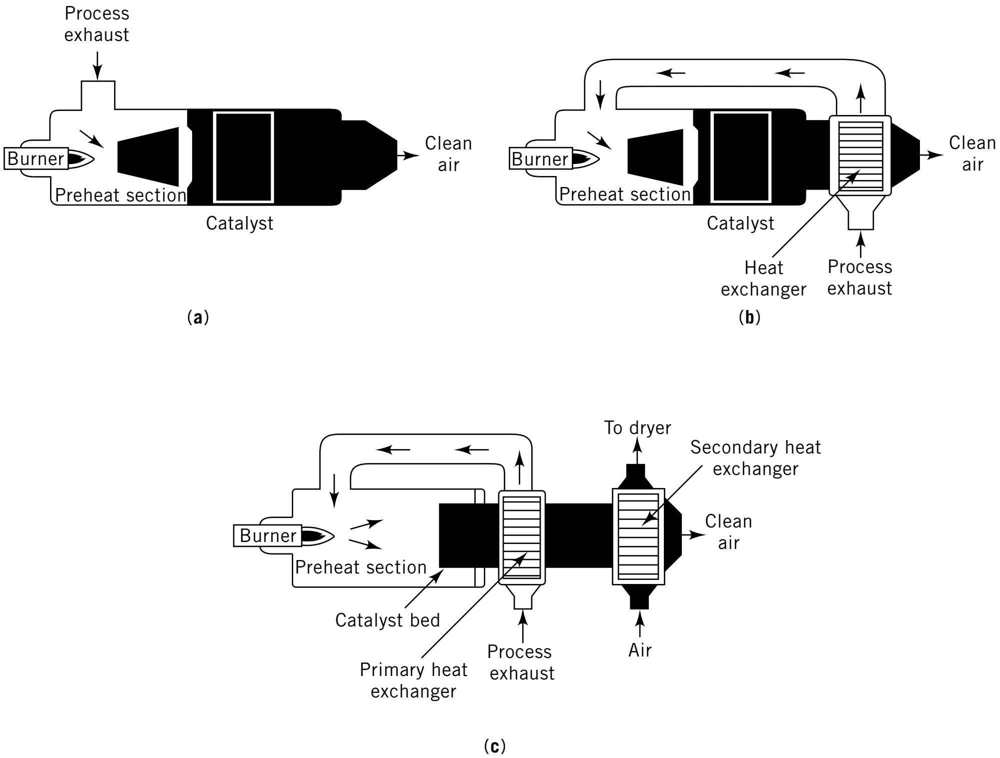

Fig. 6. Catalytic system designs (26) of (**a**) basic VOC catalytic converter containing a preheater section, a reactor housing the catalyst, and essential controls, ducting, instrumentation, and other elements; (**b**) a heat exchanger using the cleaned air exiting the reactor to raise the temperature of the incoming process exhaust; and (**c**) extracting additional heat from the exit gases by a secondary heat exchanger.

Both catalyst space velocity and bed geometry play a role. The gas hourly space velocity (GHSV) is used to relate the volumetric flow rate to the catalyst volume. GHSV has units of inverse hour and is defined as the volume flow rate per catalyst volume.

The size of the catalyst bed depends mainly on the degree of VOC reduction required (29). VOC destruction efficiencies up to 95% can usually be attained using reasonable space velocities (29). However, the low GHSVs, and subsequently high catalyst volumes required to achieve extremely high (eg, 99%) conversions, can sometimes make catalytic oxidation uneconomical. Conventional bed geometries may be found in the literature (29).

Process Conditions. To effectively design a catalytic control system, the Manufacturers of Emissions Controls Association recommends the following data be obtained (5): list of all VOCs present and range of concentration of each, flow rate of exhaust and expected variability, oxygen concentration in exhaust and expected variability, temperature of exhaust and expected variability, static pressure, potential uses for heat recovery, particular performance criteria and/or regulations to be met, capture efficiency, ie, fraction of all organic vapors generated by the processes that are directed to the control device, presence of hydrocarbon aerosols in the effluent exhaust, identity and quantity of all inorganic and organic particulate, amount of noncombustibles, presence of possible catalyst deactivators, and anticipated start-up/shutdown frequency of the system.

Pilot Studies. Applications requiring the reduction of VOC emissions have increased dramatically. On-site pilot tests are beneficial in providing useful information regarding VOC emission reduction applications. Information that can be obtained includes optimum catalyst operating conditions, the presence of contaminants in the gas stream, and the effects of these contaminants.

Catalyst Inhibition. A number of potential applications for catalytic oxidation of organic materials have resulted in serious odor or eye irritation, or visible emission problems (23). Some of these failures are a result of fouling of the catalyst surface. Others occur because materials such as halogens in the gas stream interfere with or suppress the activity of the catalyst, or because the substances react with the precious metals, rendering them permanently inactive. Finally, all catalysts eventually deteriorate by aging or thermal processes (23).

Many of the exhaust streams that must be purified contain significant amounts of halogenated organics, such as polychlorinated ethanes and ethylenes vented in the manufacture of vinyl chloride monomer or released in usage solvents (47) (see SOLVENTS, INDUSTRIAL). However, the catalysts used in the conventional catalytic oxidation are severely inhibited by the halogen atoms in these compounds (47). Other trace contaminants of concern in air streams may include phosphorus-, nitrogen-, and sulfur-containing compounds. Whereas gases containing chlorine, sulfur, and other atoms can deactivate supported noble metal catalysts such as platinum, chlorinated VOC can be treated by certain supported metal oxide catalysts (22).

The four basic mechanisms of catalyst decay are shown in Figure 7 (5,33,39). These are fouling or masking, poisoning, thermal degradation through aging or sintering, and loss of catalyst material through formation and escape of vapors. Poisoning and vapor transport are basically chemical phenomena, whereas fouling is mechanical. Table 5 lists substances that inhibit catalyst activity (5).

Masking or Fouling. Masking or fouling is a physical deposition of species from the fluid phase onto the catalyst surface (Fig. 6**a**) that results in blockage of reaction sites or pores (39). Masking or fouling is caused by a gradual accumulation of noncombusted, solid material that mechanically coats the catalyst's surface and prevents or slows down the diffusion of reactants to the catalyst.

Typical masking or fouling agents include (5,23,36,39) airborne dust or dirt; metal oxides formed from materials in the process, such as silicon dioxide ash remaining when silicone compounds are oxidized; aggregate compound formation on the catalyst surface, ie, phosphorus for lubricating oils; corrosion products from the duct system; and organic char or tars formation from incomplete combustion products, often caused by too low a reactor operating temperature.

Low levels of particulates or potential poisons can sometimes be tolerated without a dramatic decrease in performance. Generally, it has been recommended that the maximum particulate concentration not exceed 115 mg/m^2

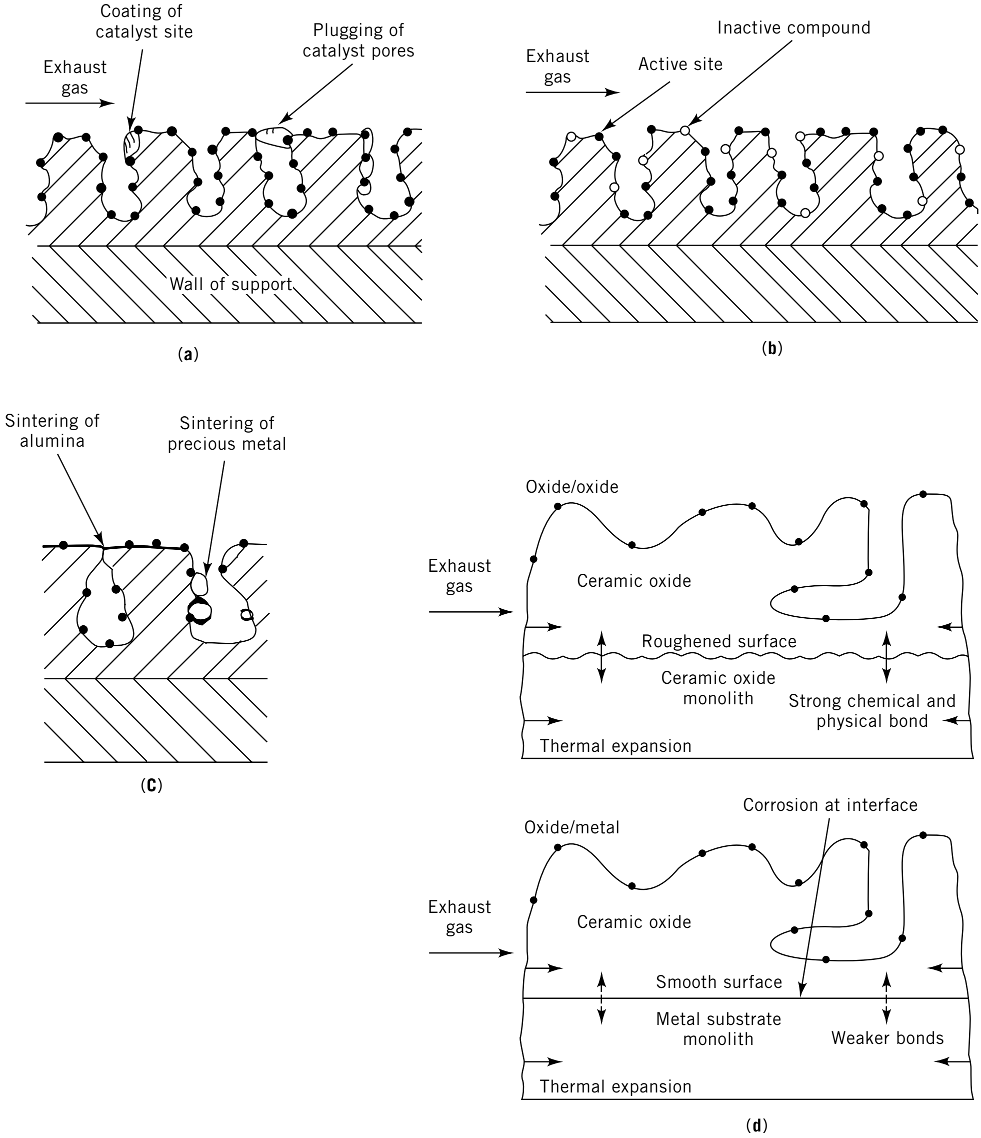

Fig. 7. Catalyst inhibition mechanisms where (•) are active catalyst sites; ⧄, the catalyst carrier; and ⧅ the catalytic support: (**a**) masking of catalyst; (**b**) poisoning of catalyst; (**c**) thermal aging of catalyst; and (**d**) attrition of ceramic oxide metal substrate monolith system, which causes the loss of active catalytic material resulting in less catalyst in the reactor unit and eventual loss in performance.

and that the maximum poison concentration not exceed 25 ppm (29). In addition, every effort should be made to avoid flow over a cold catalyst bed for any extended period of time, as a process stream containing volatile organics may condense on a cold catalyst bed (5).

Combustible masking materials such as organic char may be partially or completely removed by periodic elevations of the catalyst bed temperature.

Table 5. **Substances that Inhibit Catalyst Activity**[a]

Type of inhibitor	Effect	Examples	Regeneration
fast-acting inhibitors	reduction of catalyst activity at rate depending on concentration and temperature	phosphorus, bismuth, lead, arsenic, antimony, mercury	catalyst regeneration is sometimes difficult or impossible
slow-acting inhibitors	reduction of catalyst activity; higher concentrations than those of fast-acting catalyst inhibitors may be tolerated	iron, tin, silicon	catalyst regeneration remains difficult or impossible
reversible inhibitors/ maskers	surface coating of catalyst active area; rate also dependent on concentration and temperature	sulfur, halogens, silicon, zinc, phosphorus	regeneration is possible
surface maskers	surface coating of catalyst active areas	organic solids	removed by increasing catalyst temperature or by acid and alkaline washing
surface eroders and maskers	surface coating of catalyst active area, or erosion of catalyst surface; both result in loss of catalyst activity; rate dependent on particle size, grain loading, and gas stream velocity	inert particulates	surface coating is easily removed by washing
thermal degradation and sintering	loss of catalyst surface area because of catalyst dispersion and crystal growth, or catalyst support collapse through sintering	higher temperature for extended time, temperature excursions, hot spots in bed	regeneration generally very difficult; best avoided by operating in optimum temperature range and avoiding temperature excursions
vapor transport and attrition	loss of catalytic material through formation of metal carbonyl oxides, sulfides, and halides, or surface shear effects resulting from exhaust gas velocity, particulates, or thermal shock	CO, NO, hydrogen sulfide, halogens, and particulates	must replace lost catalytic material; vaporization generally not a factor; attrition particularly important in fluidized beds

[a] Refs. 5 and 37.

Noncombustible masking materials may be removed by air lancing or aqueous washing generally with a leaching solution (35,36).

Poisons Halogens, sulfur dioxide [7446-09-5], SO_2, nitrogen dioxide [10102-44-0], NO_2, and numbered other materials act as catalyst suppressants for precious-metal oxidation catalysts. These compounds tend to adsorb strongly on the catalytic surface, preventing the reactants from doing so. The strength of adsorption is ordinarily such that the suppressant materials can gradually be stripped off after there is no longer a concentration of suppressant materials in the gas stream passing through the catalyst (23). In other cases, the adsorption is irreversible. A poison blocks the catalytic sites, and may also induce changes in the surface to result in formation of compounds (39). Active precious-metal sites become inactive, reducing catalyst performance (see Fig. 6**b**).

At low ($>450°C$) temperatures, the presence of these materials, particularly the oxides, leads to simple masking or fouling. In some cases, a catalyst that shows reduced activity believed to be from poisoning may simply be masked, and activity can be rejuvenated by cleaning with aqueous leaching solutions (36).

Poisoning is operationally defined. Often catalysts believed to be permanently poisoned can be regenerated (5) (see CATALYSTS, REGENERATION). A species may be a poison in some reactions, but not in others, depending on its adsorption strength relative to that of other species competing for catalytic sites (39), and the temperature of the system. Catalysis poisons have been classified according to chemical species, types of reactions poisoned, and selectivity for active catalyst sites (39).

Groups 14 and 15 (VA and VIA) elements act as poisons. The interaction depends on the poison's oxidation state and chemical structure. For sulfur, the order of decreasing poisoning activity is $H_2S > SO_2 > SO_4^{2-}$. Adsorption studies indicate that H_2S adsorbs strongly and dissociates on nickel surfaces. The sulfur adsorbs essentially irreversibly and over most of the catalyst–metal surface. It has been observed that SO_2 and SO_3 also poison catalysts differently (28); SO_2 selectively adsorbs on Pt or Pd in an oxidation catalyst, whereas SO_3 reacts with the Al_2O_3 carrier, forming $Al_2(SO_4)_3$, which destroys the structure of the catalyst. The latter can be prevented by using a more inert support such as SiO_2 or TiO_2. The former requires a change in operating conditions such as a higher temperature. When No. 2 fuel oil is used in some gas turbines, the sulfur compound in the fuel oil can be converted to SO_2 at levels of 40–150 ppm in the exhaust. For such applications, the presence of 100–200 ppm SO_2 can require 150–200°C higher temperature for the catalyst to give the same CO conversion as without SO_2.

Toxic heavy metals and ions, eg, Pb, Hg, Bi, Sn, Zn, Cd, Cu, and Fe, may form alloys with catalytic metals (39). Materials such as metallic lead, zinc, and arsenic react irreversibly with precious metals and make the surface unavailable for catalytic reactions. Poisoning by heavy metals ordinarily destroys the activity of a precious-metal catalyst (23).

Molecules having unsaturated bonds, eg, CO, NO, HCN, and benzene, may chemisorb through multiple bonds (39).

Catalysts having improved poison resistance have been developed. Catalysts are available that can destroy chlorine-, fluorine-, or bromine-containing organic compounds (5).

Thermal Degradation and Sintering. Thermally induced deactivation of catalysts may result from redispersion, ie, loss of catalytic surface area because of crystal growth in the catalyst phase (36,39,48) or from sintering, ie, loss of catalyst-support area because of support collapse (39). Sintering processes generally take place at high (>500°C) temperatures and are generally accelerated by the presence of water vapor (see Fig. 6**c**). Another thermal effect is the transformation of catalytic phases to noncatalytic ones, eg, the reaction of nickel and alumina to form nickel aluminate (39). Each catalyst has a recommended temperature window of operation. At temperatures above this window (usually ~760°C), sintering can occur.

Loss of Catalyst by Vapor Transport. The direct volatilization of catalytic metals is generally not a factor in catalytic processes, but catalytic metal can be lost through formation of metal carbonyl oxides, sulfides, and halides in environments containing CO, NO, O_2, and H_2S, and halogens (39).

The ceramic oxide carrier is bonded to the monolith by both chemical and physical means. The bonding differs for a ceramic monolith and a metallic monolith. Attrition is a physical loss of the carrier from the monolith from the surface shear effects caused by the exhaust gas, a sudden start-up or shutdown causing a thermal shock as a result of different coefficients of thermal expansion at the boundary between the carrier and the monolith, physical vibration of the catalyzed honeycomb, or abrasion from particulates in the exhaust air (36) (see Fig. 6**d**).

Avoiding Catalyst Deactivation. Catalyst deactivation is more easily prevented than cured. Poisoning by impurities may be prevented by removing impurities from the reactants. Carbon deposition and coking may be prevented by minimizing formation of precursors and manipulating mass-transfer regimes so as to minimize the carbon's or coke's effect on activity. Most sintering is irreversible, or reversible only with great difficulty, so it is important to choose reaction, ie, lower temperatures, that do not sinter the catalyst. Additionally, when process upsets that could release inhibitors or cause small fluctuations in the heating value of the oxidizer are highly probable a thermal system is favored over a catalytic one (22).

Except for No. 2, fuel oil should not be considered as auxiliary fuel when using a catalytic system because of the sulfur and vanadium the fuel oil may contain (22). In some cases even the sulfur in No. 2 fuel oil can present a problem. Galvanized metal should not be used in process ovens or ductwork because zinc is a catalyst poison.

Proper system design and catalyst maintenance are key to minimizing deactivation and providing long-term catalyst service. For example, control of air dilution, use of temperature control loops, and use of catalysts having high intrinsic thermal stability can provide necessary protection against high temperature damage caused by reaction exotherms and from operational upsets (35).

Experimental Evaluation. Often the deactivation kinetics for a catalytic oxidation system can be evaluated in a series of laboratory studies (39). Reactors should be gradientless with respect to reactant poison concentration and temperature. Heat- and mass-transfer effects should be avoided because these disguise the intrinsic kinetics. Experiments should be designed to study one deactivation process at a time, and accelerated targets must be representative of the process. Deactivation can be accelerated by using smaller amounts of catalyst, operating at higher temperatures or different pressures, at greater residence times, or at different gas compositions.

Whereas changing catalyst volume or residence time rarely yields complications, changing temperature or pressure could introduce sintering. The properties of the catalyst should be measured both before and after deactivation and inlet and outlet streams should be analyzed by chromatography (qv) or spectrometry.

Around 1972, it was reasoned that the problem of catalyst deactivation could not always be entirely eliminated, but that continuous replacement of a portion of the catalyst bed during normal operation would allow continuing operation at high efficiency even in the presence of poisoning agents. Hence, the fluidized bed was born (23). In some applications, fluidized-bed oxidation processes overcame poisoning, masking, and thermal aging. A process in which performance depends on the continuous attrition of the external surface of the catalyst particles, however, has many unattractive features, including the effort required for trapping, collecting, and disposing of the fine particulate released from the reactor (47).

At least one printer using catalytic oxidation has experienced relatively rapid catalyst deactivation, requiring replacement after useful lives as short as 3–6 months, when producing high quality printed matter using some of the most desirable lithographic printing plates and materials (49). It was observed that the use of phosphorus additives caused rapid deactivation of the conventional catalyst used to destroy the hydrocarbons in the solvent-laden air (SLA) discharged from the press dryer. A precious-metal catalyst containing platinum and palladium was being used in this application. It had replaced an earlier base metal catalyst, which showed rapid deactivation as a result of sulfur in the SLA, presumably introduced in the fuel used to fire the heatset dryer. It was found that the P concentration in the SLA might be as high as 0.16 ppm. The phosphorus concentration on the deactivated catalyst was found to be 1.4% of the catalyst. The printer was urged by the supplier to find and eliminate the cause of the phosphorus contamination of the waste gas entering the catalyst bed. However, after it was determined that use of phosphorus-containing additives was crucial to many of the high quality printing jobs, attention was directed at the catalyst bed itself.

A catalyst with a substantially improved resistance to poisoning by phosphorus in catalytic oxidation applications was developed. In part, the catalyst in this program permitted printers to use photolighographic technology without paying an unreasonable cost in terms of frequent replacement of oxidation catalysts.

Catalyst Reactivation. Some catalytic systems are reported to have operted continuously for >10 years with little or no loss in control efficiency (5). In most processes catalysts inevitably lose activity, and when the activity has declined to a critical level, the catalyst needs to be discarded or regenerated (39). Regeneration is only possible when the deactivation is reversible by chemical washing or heat treatment or oxidation (36,39).

Thermal Treatment. A thermal treatment for catalyst regeneration is usually effective when deactivation is a result of coking or masking of the catalyst surface. Thermal treatment can usually be done on-site, by elevating the temperature of the catalyst bed by 50–100°C above the normal operating point and running at this oxidizing condition for a specified limited period of time (35). The elevated temperature vaporizes or oxidizes the organic compounds or char that may be masking the catalyst surface.

Physical Treatment. If inspection of the catalyst indicates deposits again, or if an excessive pressure drop across the catalyst is noted, then the catalytic bed may be lanced, on-site, using compressed air or water until the deposits are removed. Abrasion by contact with excessively high pressure from the compressed air should be avoided (35). If this treatment is combined with heating, hot spots or overtemperatures that could further deactivate the catalyst should be avoided (39). In many cases, periodic maintenance, removing the catalyst bed and blowing or washing off residues, has restored catalyst to original or near-original activity levels (5).

Chemical Treatment. The most involved regeneration technique is chemical treatment (35) which often follows thermal or physical treatment, after the char and particulate matter has been removed. Acid solution soaks, glacial acetic acid, and oxalic acid are often used. The bed is then rinsed with water, lanced with air, and dried in air. More involved is use of an alkaline solution such as potassium hydroxide, or the combination of acid washes and alkaline washes. The most complex treatment is a combination of water, alkaline, and acid washes followed by air lancing and drying. The catalyst should not be appreciably degraded by the particular chemical treatment used.

Analyses of a catalyst used in a process involving cloaning products and pigments and achieving a hydrocarbon destruction capacity of only 13% showed deposition of P, Sn, Pb, and Na contaminants (35). Initial acid treatment increased the hydrocarbon destruction capacity from 13 to 63%. Alkaline treatment increased the capacity to 90% of that new.

6. Exhaust Control Technologies

In addition to VOCs, specific industrial exhaust control technologies are available for nitrogen oxides, NO_x, carbon monoxide, CO, halogenated hydrocarbon, and sulfur and sulfur oxides, SO_x.

6.1. Nitrogen Oxides.

Annual releases of nitrogen oxides (NO_x) into the atmosphere amounted to $\sim 550 \times 10^6$ t in the early 1990s. A number of states, in addition to California, regulate NO_x emissions (50). New atmospheric modeling analysis has indicated that in many cases, NO_x has a significant role in the formation of tropospheric ozone, a heavily regulated atomospheric pollutant (51,52). The production of nitrogen oxides can be controlled to some degree by reducing formation in the combustion system. The rate of NO_x formation for any given fuel and combuster design are controlled by the local oxygen concentration, temperature, and time history of the combustion products. Techniques employed to reduce NO_x formation are collectively referred to as combustion controls and U.S. power plants have shown that furnace modifications can be a cost-effective approach to reducing NO_x emissions. Combustion control technologies include operational modifications, such as low excess air, biased firing, and burners-out-of-service, which can achieve 20–30% NO_x reduction; and equipment modifications such as low NO_x burners, overfire air, and reburning, which can achieve 40–60% reduction (53,54) As of the early 1990s, ~600 boilers having 10,000 MW of capacity use combustion modifications to comply with the New Source Performance Standards (NSPS) for NO_x emissions (55). Since then, such modifications have become standard practice (52).

When NO_x destruction efficiencies approaching 90% are required, some form of postcombustion technology applied downstream of the combustion zone is needed to reduce the NO_x formed during the combustion process. Three postcombustion NO_x control technologies are utilized: selective catalytic reduction (SCR); nonselective catalytic reduction (NSCR); and selective noncatalytic reduction (SNCR).

Selective Catalytic Reduction. Selective catalytic reduction (SCR) is widely used in Japan and Europe to control NO_x emissions (1). SCR converts the NO_x in an oxygen-containing exhaust stream to molecular N_2 and H_2O using ammonia as the reducing agent in the presence of a catalyst. NO_x removals of 90% are achievable. The primary variable is temperature, which depends on catalyst type (56). The principal components of an SCR system include the catalyst, the SCR reactor, the ammonia injection grid (AIG), the ammonia—air dilution system, the ammonia storage—vaporization system, the ammonia addition control system, and a continuous emissions monitoring system (57).

The AIG is used to uniformly inject diluted ammonia into the reactor. Uniform mixing of the ammonia into the flue gas is necessary to maintain catalyst performance at its highest level and to minimize ammonia leakage (ammonia slip) past the catalyst.

The ammonia—air dilution system dilutes the vaporized ammonia by a factor of 20–25 with air for better admixing through the AIG and to prevent explosive ammonia—air mixtures. Once the catalyst volume is selected, the NO_x removal is set by the NH_3/NO_x mole ratio at the inlet of the SCR system (57).

SCR was first developed in the United States in the late 1950s, targeted at nitric acid tail-gas exhausts, using precious-metal catalysts. In the mid-1970s, SCR entered widespread commercial use in Japan using base metal catalysts. The first SCR systems in Germany started up in 1986 (57), and German utilities are committed to installing SCR systems on the majority of oil- and coal-fired boilers to achieve between 60 and 90% NO_x reductions (57). By the end of 1992, there were ~120 SCR plants in service in Germany alone (58). An increasing amount of experience has been documented in the United States (59–61), although commercial service began in 1985 and has continued to increase (62,63) in those areas where NO_x remains a concern.

Performance criteria for SCR are analogous to those for other catalytic oxidation systems: NO_x conversion, pressure drop, catalyst/system life, cost, and minimum SO_2 oxidations to SO_3. An optimum SCR catalyst is one that meets both the pressure drop and NO_x conversion targets with the minimum catalyst volume. Because of the interrelationship between cell density, pressure drop, and catalyst volume, a wide range of optional catalyst cell densities are needed for optimizing SCR system performance.

Reactions. The SCR process is termed selective because the ammonia reacts selectively with NO_x at temperatures >232°C in the presence of excess oxygen (64). The optimum temperature range for the SCR catalyst is determined by balancing the needs of the redox reactions.

SCR reactions

$$4\,\mathrm{NO} + 4\,\mathrm{NH_3} + \mathrm{O_2} \longrightarrow 4\,\mathrm{N_2} + 6\,\mathrm{H_2O} \tag{10}$$

$$2\,\mathrm{NO_2} + 4\,\mathrm{NH_3} + \mathrm{O_2} \longrightarrow 3\,\mathrm{N_2} + 6\,\mathrm{H_2O} \tag{11}$$

The NO reduction is the most important because NO_2 accounts for only 5–10% of the NO_x in most exhaust gases.

Ammonia oxidation reactions

$$4\,\mathrm{NH_3} + 5\,\mathrm{O_2} \longrightarrow 4\,\mathrm{NO} + 6\,\mathrm{H_2O} \tag{12}$$

$$4\,\mathrm{NH_3} + 3\,\mathrm{O_2} \longrightarrow 4\,\mathrm{N_2} + 6\,\mathrm{H_2O} \tag{13}$$

When sulfur dioxide is also present there are important side reactions in which SO_2 is oxidized to SO_3. The main side reaction in the SCR catalyst is the conversion of SO_2 to SO_3, thus facilitating the reaction above. The SO_3 in turn reacts with ammonia to form ammonium sulfates.

$$\mathrm{NH_3} + \mathrm{SO_3} + \mathrm{H_2O} \longrightarrow \mathrm{NH_4HSO_4} \tag{14}$$

$$\mathrm{NH_3} + \mathrm{SO_3} + \mathrm{H_2O} \longrightarrow \mathrm{(NH_4)_2SO_4} \tag{15}$$

The formation of ammonium bisulfate is strongly temperature dependent. Formation is favored at the lower temperatures. The temperature at which ammonium bisulfate is not formed depends strongly on the SO_3 concentration in the exhaust gas. The temperature needed to minimize bisulfate formation has been reported to increase by ∼15°C (around ∼350°C) when the SO_3 concentration increases from 5 to 15 ppm (38). The formation of the bisulfate is reversible, ie, if the temperature is raised to 20°C above the minimum temperature, the reaction is shifted to result in the decomposition of the bisulfate formed. When chlorides are present, ammonium chlorides can be formed:

$$\mathrm{NH_3} + \mathrm{HCl} \longrightarrow \mathrm{NH_4Cl} \tag{16}$$

When sulfuric acid is present, ammonium bisulfate can be formed:

$$\mathrm{NH_3} + \mathrm{H_2SO_4} \longrightarrow \mathrm{NH_4HSO_4} \tag{17}$$

These various reactions should be minimized to avoid plugging the catalyst and to prevent fouling of the downstream air preheaters, when these components condense from the gas at the lower temperatures.

The SCR Process.The first step in the SCR reaction is the adsorption of the ammonia on the catalyst. SCR catalysts can adsorb considerable amounts of ammonia (65). However, the adsorption must be selective and high enough to yield reasonable cycle times for typical industrial catalyst loadings, ie, uptakes in excess of 0.1% by weight. The rate of adsorption must be comparable to the

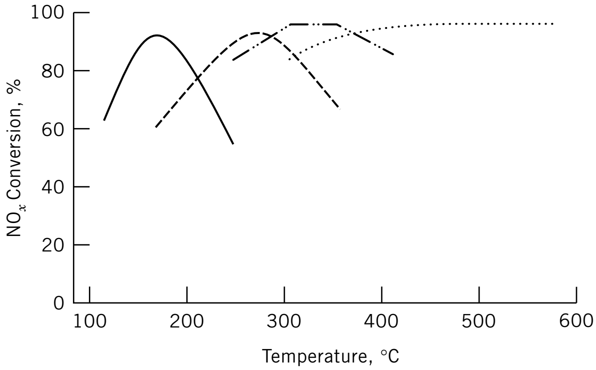

Fig. 8. NO$_x$ reduction versus temperature for SCR catalysts: (——) CAT LT-1, (- - -) CAT LT-2, (—··—) CAT VNX, and (······) CAT 2NX (59).

rate of reaction to ensure that suitable fronts are formed. The rate of desorption must be slow. Ideally the adsorption isotherm is rectangular. For optimum performance, the reaction must be irreversible and free of side reactions.

It has been suggested that the first step, weak coadsorption of NO and O_2 on a reduced vanadium site, may represent the slow step in the mechanism. Subsequent formation of a N_2O_3-like intermediate could be a fast step, because it is known that in the gas phase the equilibrium of $NO-NO_2$ and N_2O_3 is established within microseconds (52).

At low temperatures the SCR reactions dominate and nitrogen oxide conversion increases with increasing temperature. But as temperature increases, the ammonia oxidation reactions become relatively more important. As the temperature increases further, the destruction of ammonia and generation of nitrogen oxides by the oxidation reactions causes overall nitrogen oxide conversion to reach a plateau then decreases with increasing temperatures. Examples are shown in Figure 8 (64) .

In the SCR process, ammonia, usually diluted with air or steam, is injected through a grid system into the flue/exhaust stream upstream of a catalyst bed (55). The effectiveness of the SCR process is also dependent on the NH_3 to NO_x ratio. The ammonia injection rate and distribution must be controlled to yield an ~1:1 molar ratio. At a given temperature and space velocity, as the molar ratio increases to approximately 1:1, the NO_x reduction increases. At operations above 1:1, however, the amount of ammonia passing through the system increases (56). This ammonia slip can be caused by catalyst deterioration, by poor velocity distribution, or inhomogeneous ammonia distribution in the bed.

Types of SCR Catalysts. The catalysts used in the SCR were initially formed into spherical shapes that were placed either in fixed-bed reactors for clean gas applications or moving-bed reactors where dust was present. The moving-bed reactors added complexity to the design and in some applications resulted in unacceptable catalyst abrasion. As of 1993 most SCR catalysts are either supported on a ceramic or metallic honeycomb or are directly extruded as a honeycomb (1). A typical honeycomb block has face dimensions of 150 by 150 mm and can be as long as one meter. The number of cells per block varies from 20 by 20 up to 45 by 45 (57).

No SCR catalyst can operate economically over the whole temperature range possible for combustion systems. As a result, three general classes of catalysts have evolved for commercial SCR systems (44): precious-metal catalysts for operation at low temperatures, base metals for operation at medium temperatures, and zeolites for operation at higher temperatures.

The precious-metal platinum catalysts were primarily developed in the 1960s for operation at temperatures between ∼200 and 300°C (1,56,64). However, because of sensitivity to poisons, these catalysts are unsuitable for many combustion applications. Variations in sulfur levels of as little as 0.4 ppm can shift the catalyst required temperature window completely out of a system's operating temperature range (64). Additionally, operation with liquid fuels is further complicated by the potential for deposition of ammonium sulfate salts within the pores of the catalyst (64). These low temperature catalysts exhibit NO_x conversion that rises with increasing temperature, then rapidly drops off, as oxidation of ammonia to nitrogen oxides begins to dominate the reaction (see Fig. 7).

The most popular SCR catalyst formulations are those that were developed in Japan in the late 1970s comprised of base metal oxides such as vanadium pentoxide [1314-62-1], V_2O_5, supported on titanium dioxide [13463-67-7], TiO_2 (1). As for low temperature catalysts, NO_x conversion rises with increasing temperatures to a plateau and then falls as ammonia oxidation begins to dominate the SCR reaction. However, peak conversion occurs in the temperature range between 300 and 450°C, and the fall-off in NO_x conversion is more gradual than for low temperature catalysis (64).

A family of zeolite catalysts has been developed, and is being increasingly used in the United States in SCR applications. Zeolites that can function at higher temperatures than the conventional catalysts, are claimed to be effective over the range of 300 to 600°C, having an optimum temperature range from 360 to 580°C (55,56). However, ammonia oxidation to NO_x begins ∼450°C and is predominant at temperatures in excess of 500°C. Zeolites suffer the same performance and potential damage problems as conventional catalysts when used outside the optimum temperature range. In particular, at ∼550°C the zeolite structure may be irreversibly degraded because of loss of pore density. Zeolite catalysts have not been continuously operated commercially at temperatures >500°C (55).

Using zeolite catalysts, the NO_x reduction takes place inside a molecular sieve ceramic body rather than on the surface of a metallic catalyst (see MOLECULAR SIEVES). This difference is reported to reduce the effect of particulates, soot, SO_2/SO_3 conversions, heavy metals, etc, which poison, plug, and mask metal catalysts. Zeolites have been in use in Europe since the mid-1980s and there are approximately 100 installations on stream. Process applications range from use of natural gas to coal as fuel. Typically, nitrogen oxide levels are reduced 80 to 90% (55).

Catalyst Selection. For an SCR application, catalyst selection depends largely on the temperature of the flue gas being treated. A given catalyst exhibits optimum performance within a temperature range of ∼30–50°C. Below this optimum temperature range, the catalyst activity is greatly reduced, allowing unreacted ammonia to slip through. Above this range, ammonia begins to be oxidized to form additional NO_x. Operations having adequate temperature controls are important, as are uniform flue gas temperatures (55,56).

Problems. A number of difficulties in utilizing SCR operations have been identified. Problems in European installations are of particular interest because SCR systems are subjected to conditions not experienced in Japan, but also encountered in the United States. Difficulties include matching the NH_3 injection pattern to the nonuniform flow of NO_x in the ductwork ahead of the SCR rector; inability to optimize the NH_3 injection rate by feedback control of slip ammonia for lack of a reliable NH_3 monitor; erosion and plugging on units retrofitted to boilers that fire high ash coal; catalyst deactivation caused by arsenic poisoning on wet-bottom units that recycle flyash; process control under load swings; and spent catalyst disposal. For medium to high sulfur coals, the potential exists for accelerated catalyst deactivation caused by sulfur poisoning and contamination by trace metals in flyash, and deposit buildup and corrosion of the air heater.

For boilers, SCR $DENO_x$ plants can be installed at the exhaust exit just before the air preheater. These are called high dust plants (17-g dust/m^3) (38) because the flue gas still contains volatile trace elements as well as flyash particles. When the SCR system is installed after the flue gas desulfurization (FGD) system, it is called a low dust or tail-end plant. The high dust plant has the advantages of not requiring any additional energy because of the high temperatures present. The low dust plant requires a regenerative heat exchanger, but requires less catalyst because (58): there is less dust to contaminate the bed, potential catalyst poisons are removed from the flue gas by the FGD system, and a high activity catalyst can be used when only low concentrations of poisons such as SO_2 remain after the flue gas system.

Other problems that can be associated with the high dust plant can include alkali deterioration from sodium or potassium in the stack gas deposition on the bed, calcium deposition, when calcium in the flue gas reacts with sulfur trioxide, or formation and deposition of ammonium bisulfate. In addition, plugging of the air preheater as well as contamination of flyash and FGD wastewater discharges by ammonia are avoided if the SCR system is located after the FGD (38).

A significant problem area for initial SCR systems has been the continuous emission monitoring (CEM) systems. In power plants, all sites equipped with CEM systems report the highest failure frequency. The CEM systems are the most labor intensive component, requiring as much as full-time attention from one technician. At one power plant CEM systems were responsible for 100% of 73 reported SCR system shutdowns (56). As CEM systems continue to improve, these concerns may disappear.

Nonselective Catalytic Reduction. Hydrocarbons, hydrogen, or carbon monoxide can be used as reducing agents for NO_x in applications where the exhaust oxygen concentration is low, as it is in fuel rich-burn reciprocating engines, where it is $<1\%$, and in nitric acid plants, when it is from 2 to 3%. This approach is called nonselective catalytic reduction (NSCR). In some applications, the oxygen must be removed from the feed stream prior to the catalyst (52). An oxygen sensor in the exhaust stream signals the air–fuel delivery system to adjust the air/fuel ratio so it is just slightly fuel-rich, having enough reducing agent present to react with all the oxygen and nitrogen oxides (1).

Nonselective catalytic reduction systems are often referred to as three-way conversions. These systems reduce NO_x, unburned hydrocarbon, and CO simultaneously. In the presence of the catalyst, the NO_x are reduced by the CO resulting in N_2 and CO_2 (55). A mixture of platinum and rhodium has been generally used to promote this reaction . It has also been reported that a catalyst using palladium has been used in this application (1). The catalyst operation temperature limits are 350–800°C, and 425–650°C are the most desirable. Temperatures >800°C result in catalyst sintering (55). Automotive exhaust control systems are generally NSCR systems, often shortened to NCR.

Typically NO_x conversion ranges from 80 to 95% and there are corresponding decreases in CO and hydrocarbon concentrations. Potential problems associated with NSCR applications include catalyst poisoning by oil additives, such as phosphorus and zinc, and inadequate control systems (37).

6.2. Carbon Monoxide. Carbon monoxide is emitted by gas turbine power plants, reciprocating engines, and coal-fired boilers and heaters. Carbon monoxide can be controlled by a precious-metal oxidation catalyst on a ceramic or metal honeycomb. The catalyst promotes reaction of the gas with oxygen to form CO_2 at efficiencies that can exceed 95%. Carbon monoxide oxidation catalyst technology is broadening to applications requiring better catalyst durability, such as the combustion of heavy oil, coal (qv), municipal solid waste (qv), and wood (qv). Research is underway to help cope with particulates and contaminants, such as flyash and lubricating oil, in gases generated by these fuels (1,66).

Carbon monoxide conversion is a function of both temperature and catalyst volume, and increases rapidly beginning at just under 100°C until it reaches a plateau at ~150°C. But, unlike NO_x catalysts, >150°C there is little benefit to further increasing the temperature (64). Above 150°C, the CO conversion is controlled by the bulk phase gas mass transfer of CO to the honeycomb surface. That is, the catalyst is highly active, and its intrinsic CO removal rate is exceedingly greater than the actual gas transport rate (36). When the activity falls to such an extent that the conversion is no longer controlled by gas mass transfer, a decline of CO conversion occurs, and a suitable regeneration technique is needed (36).

It has been reported that below ~370°C, sulfur oxides reversibly inhibit CO conversion activity. This inhibition is greater at lower temperatures. CO conversion activity returns to normal shortly after removal of the sulfur from the exhaust (64). Above ~315°C, sulfur oxides react with the high surface area oxides to disperse the precious-metal catalytic agents and irreversibly poison CO conversion activity.

Catalyst contamination from sources such as turbine lubricant and boiler feed water additives is usually much more severe than deactivation by sulfur compounds in the turbine exhaust. Catalyst formulation can be adjusted to improve poison tolerance, but no catalyst is immune to a contaminant that coats its surface and prevents access of CO to the active sites. Between 1986 and 1990 >25 commercial CO oxidation catalyst systems operated on gas turbine cogeneration systems, meeting both CO conversion (40–90%) and pressure drop requirements.

6.3. Halogenated Hydrocarbons. Destruction of halogenated hydrocarbons presents unique challenges to a catalytic oxidation system (65–72). The first step in any control strategy for halogenated hydrocarbons is recovery and recycling (65). However, even upon full implementation of economic recovery steps, significant halocarbon emissions can remain. In other cases, halogenated hydrocarbons are present as impurities in exhaust streams (65). Impurity sources are often intermittent and dispersed.

The principal advantage of a catalytic oxidation system for halogenated hydrocarbons is in operating cost savings. Catalytically stabilized combusters improve the incineration conditions, but still must employ very high temperatures as compared to VOC combustors; eg, carbon tetrachloride [56-23-5], CCl_4, has a 40-fold lower heat of combustion than a typical organic vapor such as toluene [108-88-3], thus CCl_4 requires much more supplemental fuel to burn than do typical organics (65). Alternatively, the low temperature catalytic oxidation process is typically designed for a maximum adiabatic temperature rise of only 200°C. This would correspond to only ~1500 ppm of an organic compound in the exhaust stream. But, with the lower heat of combustion, up to 40,000 ppm of carbon tetrachloride could be treated in the same temperature rise, or with less dilution air.

By-Product Formation. The presence of halogenated hydrocarbons dramatically increases the yield of aldehydes from the oxidation process (65). For example, in the partial oxidation of methane on a PdO sponge catalyst (34), methylene chloride, CH_2Cl_2, was added in pulses to the inlet gas, which also contained the methane. Methane oxidation was strongly inhibited and formaldehyde was formed. The formaldehyde production continued even after the methylene chloride addition was stopped, suggesting a strong interaction of chlorine with the catalyst. However, pulses of pure CH_4 plus oxygen gradually restored the original activity to the catalyst, indicating that the effect of this interaction was reversible.

Catalyst Deactivation. Catalyst deactivation (65) by halogen degradation is a very difficult problem particularly for platinum (PGM) catalysts, which make up ~75% of the catalysts used for VOC destruction (25). The problem may well lie with the catalyst carrier or washcoat. Alumina, eg, a common washcoat, can react with a chlorinated hydrocarbon in a gas stream to form aluminum chloride which can then interact with the metal. Fluid-bed reactors have been used to offset catalyst deactivation but these are large and costly (65).

Catalytic Reaction. The desired reaction of the chlorine group on a chlorinated hydrocarbon is

$$\mathrm{RCl} + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{HCl} + \mathrm{R'} \tag{18}$$

It is important to produce HCl rather than elemental chlorine, Cl_2, because HCl can be easily scrubbed out of the exhaust stream, whereas Cl_2 is very difficult to scrub from the reactor off-gas. If the halogenated hydrocarbon is deficient in hydrogen relative to that needed to produce HCl, low levels of water vapor may be needed in the entering stream (65) and an optional water injector may be utilized. For example, trichloroethylene [79-01-6], C_2HCl_3, and carbon tetrachloride require some water vapor as a source of hydrogen (65).

$$\mathrm{C_2HCl_3} + \mathrm{H_2O} + 1.5\ \mathrm{O_2} \longrightarrow 2\ \mathrm{CO_2} + 3\ \mathrm{HCl} \tag{19}$$

Groundwater contaminated with chlorinated hydrocarbons is being remediated by a conventional air stripper or a rotary stripper, producing an air stream

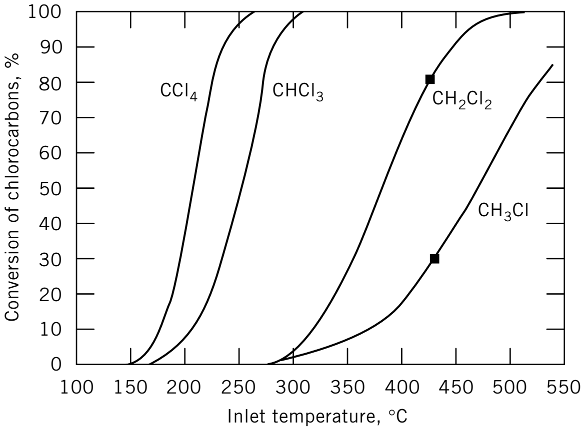

Fig. 9. Destruction of C1 chlorocarbons over HDC in the presence of 1.5% H_2O in air at 15,000 h^{-1} GHSV at STP. Chlorocarbon concentrations are CCl_4, 900 ppmv; $CHCl_3$, 500 ppmv; CH_2Cl_2, 800 ppmv; and CH_3Cl, 600 ppmv.

containing the halogenated hydrocarbon vapors and saturated with water vapor (65), which is then passed through a catalyst bed.

At least two catalytic processes have been used to purify halogenated streams. Both utilize fluidized beds of probably nonnoble metal catalyst particles. One has been estimated to oxidize >9000t/yr of chlorinated wastes from a vinyl chloride monomer plant (65). Several companies have commercialized catalysts which are reported to resist deactivation from a wider range of halogens. These newer catalysts may allow the required operating temperatures to be reduced, and still convert >95% of the halocarbon, such as trichlorethylene, from an exhaust stream. Conversions of C1 chlorocarbons utilizing an Englehardt HDC catalyst are shown in Figure 9. For this system, as the number of chlorine atoms increases, the temperatures required for destruction decreases.

7. Uses

Catalytic oxidation of exhaust streams is increasingly used in those industries involved in the following (28,30,32):

Surface coatings: aerospace, automobile, auto refinishing, can coating, coil coating, fabric coating, large appliances, marine vessels, metal furniture, paper coating, plastic parts coating, wire coating and enameling, wood furniture.

Printing inks: flexographic, lithographic, rotogravure, screen printing.

Solvent usage: adhesives, disk manufacture, dry cleaning, fiber glass manufacture, food tobacco manufacture, metal cleaning, pharmaceutical, photo finishing labs, semiconductor manufacture.

Chemical and petroleum processes: cumene manufacture, ethylene oxide manufacture, acrylonitrile manufacture, caprolactam manufacture, maleic anhydride manufacture, monomer venting, phthalic anhydride manufacture, paint and ink manufacture, petroleum product refining, petroleum marketing, resin manufacture, textile processing.

Industrial/commercial processes: aircraft manufacture, asceptic packaging, asphalt blowing, automotive parts manufacture, breweries/wineries, carbon fiber manufacture, catalyst regeneration, coffee roasting, commercial charbroiling, electronics manufacture, film coating, filter paper processing, food deep frying, gas purification, glove manufacture, hospital sterilizers, peanut and coffee roasting, plywood manufacture, rubber processing, spray painting, tire manufacture, wood treating.

Engines: diesel engines, lean burn internal combustion, natural gas compressors, oil field steam generation, rich burn internal combustion, gas turbine power generation,

Cross media transfer: air stripping, groundwater cleanup, soil remediation (landfills), hazardous waste treatment, odor removal from sewage gases

The most important factors affecting performance are operating temperature, surface velocity, contaminant concentration and composition, catalyst properties, and the presence or absence of poisons or inhibitors.

7.1. Air Stripping of Groundwater.

Treatment of exhaust streams from the air stripping of contaminated groundwater is a particular challenge, because the emissions from air stripping units may consist of a complex mixture of both fuel and solvent fractions (13). The catalytic oxidation of any given compound is generally negatively impacted by the presence of others in mixtures, and higher catalyst bed operating temperatures are required to achieve adequate destruction.

Some catalysts exposed to air stripping off-gas were subject to deactivation. However, using a catalytic oxidizer at a U.S. Coast Guard facility (Traverse City, Mich.) for the destruction of benzene, toluene, and xylene stripped from the groundwater, the catalytic oxidization unit operated at 260–315°C, and was able to achieve 90% destruction efficiency (see GROUNDDWATER MONITORING).

7.2. Printing and Graphic Arts.

In the graphic arts industry, the catalyst in the oxidizer needs to be monitored regularly because it is susceptible to contamination by phosphorus from fountain solutions, silica from silicone gloss enhancer sprays, and chlorides from chlorinated solvents or blanket wash solutions. Phosphorus and silica accumulate most rapidly on the leading edge of the catalyst bed, deactivating the catalyst by masking the precious metals. In a fluidized-bed configuration, the catalyst surface is continually renewed by abrasion and the problem of masking the catalyst surface with silicones is avoided.

7.3. Chemical Processing.

Terephthalic Acid Production. The control of exhaust from production of pure terephthalic acid (PTA) has been a challenge (see CARBOXYLIC ACIDS SURVEY) (73). Eight million metric tons of PTA are produced annually worldwide for use primarily in high grade polyester fiber production. Based on a *para*-xylene feedstock, vent gases from the process contain such by-products as methyl acetate, organic acids, and often methyl bromide. These exhausts have been estimated to total 34,000-m^3 worldwide. Historically, the presence of the methyl bromide limited the use of fixed-bed catalytic oxidation as a control technology using precious-metal catalysts. Thus base metal catalysts in fluidized-bed reactors have been the primary catalytic technology of choice. In this application, the continuous abrasion of the outer layer of the catalyst particles exposes a fresh surface of unpoisoned material to the reactants, allowing the catalyst to effectively treat the exhaust stream.

In the late 1980s, however, the discovery of a noble metal catalyst that could tolerate and destroy halogenated hydrocarbons such as methyl bromide in a fixed-bed system was reported (73,74). The products of the reaction were water, carbon dioxide, hydrogen bromide, and bromine. Generally, a scrubber would be needed to prevent downstream equipment corrosion. However, if the focus of the control is the VOCs and the CO rather than the methyl bromide, a modified catalyst formulation can be used that is able to tolerate the methyl bromide, but not destroy it. In this case the methyl bromide passes through the bed unaffected, and designing the system to avoid downstream effects is not necessary. Destruction efficiencies of hydrocarbons and CO of better than 95% have been reported, and methyl bromide destructions between 0 and 85% (73).

Latex Monomer Production. ARI Technologies, Inc. has introduced a catalyst system which, it is claimed, can operate at an average bed temperature of 370°C while achieving conversion efficiency in excess of 99.99% on exhaust streams from latex monomer production.

Acrylonitrile Manufacture. In the manufacture of acrylonitrile (qv), off-gases containing from 1–3% of CO plus various hydrocarbons are emitted. Catalytic beds of platinum-group metals are used to reduce the regulated compounds to acceptable levels. Close attention to bed design is required to prevent the formation of appreciable quantities of NO_x caused by the fixation of combustion-air nitrogen. Some NO_x also is produced from fuel nitrogen by oxidation. Because of the high thermal energy content of the off-gases, considerable heat recovery is possible in abating acrylonitrile plant emissions (see HEAT-EXCHANGE TECHNOLOGY).

Vinyl Monomer Manufacturing. Process vent gases containing small quantities of halogenated hydrocarbons and substantial quantities of nonhalogenated hydrocarbons have been successfully reduced to comply with regulatory objectives in large-scale laboratory–pilot catalytic fume abaters having satisfactory long-term catalyst performance. The design freedoms offered by precious metals on ceramic honeycomb support catalysts have been demonstrated in equipment that utilizes the heat energy resulting from the substantial exotherm of the nonhalogenated hydrocarbon oxidation to preheat the exhaust gases. Fuel consumption is thereby minimized.

7.4. Coatings Industries. Surface coating processes (qv) produce similar air pollution problems in a number of different industries (see also COATINGS).

Can Manufacturing. An internal coating is necessary to protect the purity and flavor of can contents for beverages or any edible product that might react with the container metal (see BEER; CARBONATED BEVERAGES; FOOD PACKAGING). Both the exterior decorative and interior sanitary coatings are applied to the metal surface by rolls or spray guns using a solvent vehicle. Catalytic oxidation systems are used by the principal can manufacturers to treat coatings exhaust streams. The can manufacturers' industry is estimated to utilize more catalysts than any of the other surface coating industries.

A large number of diverse solvents are used in exterior and interior coatings in plants for manufacturing both three-and two-piece cans. Most of the organic solvents are found in the cure-oven exhausts at concentrations of 2–16% of the lower explosive limit (LEL). The oven exhaust volumes are usually 1–35 m^3/s. When burned, these concentrations of combustibles provide an exotherm of 30–220°C. The heat that is released is used for preheating the incoming effluent and/or heating the cure oven by recycling the hot, cleaned gases to the supply blowers or by heating makeup air by heat exchange. A few plants use the heat of the cleaned exhaust to produce hot water for the two-piece can line washers, hot air for dry-off ovens, or building space heating. For example, one large can company utilizes the heat energy contained in the stream, leaving some of their catalytic fume abaters to supply all the heat energy required by the oven's heating zones, which have no burners. The fuel energy supplied to the catalytic fume abater is less than would be needed to heat the oven if the solvent fumes were exhausted directly to the atmosphere without use of the fume abater. The exhaust rate of the oven is adjusted to maintain a solvent concentration of at least 8% of the LEL, equivalent to a 110°C temperature differential (see ENERGY MANAGMENT).

The various reaction rate properties of the different solvents influence the design of a catalytic reactor. For example, for a specific catalyst bed design, an effluent stream containing a preponderance of monohydric alcohols, aromatic hydrocarbons, or propylene requires a lower catalyst operating temperature than that required for solvents such as isophorone and short-chain acetates.

Design considerations and costs of the catalyst, hardware, and a fume control system are directly proportional to the oven exhaust volume. The size of the catalyst bed often ranges from 1.0 m^3 at 0°C and 101 kPa/ 1000 m^3/min of exhaust, to 2 m^3 for 1000 m^3/min of exhaust. Catalyst performance at a number of can plant installations has been enhanced by proper maintenance. Annual analytical measurements show reduction of solvent hydrocarbons to be in excess of 90% for 3–6 years, the equivalent of 12,000–30,000 operating hours. When propane was the only available fuel, the catalyst cost was recovered by fuel savings (vs thermal incineration prior to the catalyst retrofit) in two to three months. In numerous cases the fuel savings paid for the catalyst in 6–12 months.

Can manufacturers often regenerate the catalyst beds on an annual or biannual basis during a weekend downtime. Both air lancing and an aqueous bath are utilized to remove noncombustible particulates that mask the active sites. Frequently, condensed organic material on the catalyst is removed by short-term (4–6 h) heating excursions to 370 or 430°C; the organic matter is removed much like a self-cleaning oven. The gaseous and organic smoke, which is usually evolved from the first few cm of catalyst bed depth, is oxidized in the latter part of the bed. If allowed to operate too long at temperatures that promote condensation, high boiling organic compounds, the subsequent carbon char that is formed, may require temperatures of 480–540°C to convert the carbon to carbon monoxide for subsequent oxidation. The higher temperatures required for burn-offs should be approached in small (0–30°C) increments to bring about slow evolution and partial oxidation; this prevents autogenous combustion of local high concentrations of combustible material.

Day-to-day operating techniques that are employed by one large can manufacturer and are intended to prevent organic condensation are dictated by the use of a low cost, well-established, sanitary coating for beer and beverage three-piece cans. Polybutadiene and other sanitary coatings may have volatile resin monomers entrained in the oven atmosphere as a result of rapid evaporation of solvent before polymerization takes place. A short (4–6 h) heating excursion up to a catalyst inlet temperature of 400°C after use of the coating usually burns off any condensed organic materials. It has become standard practice in some plants to turn the catalytic afterburner up to 370°C for these coatings versus the normal 315°C operating temperature for vinyls, acrylics, etc.

Coil Coating. Coil coating is the prefinishing of many sheet metal items with protective and decorative coatings that are applied by roll coating on one or both sides of a fast-moving metal strip. The metal strip (from 13 mm to 1.7 m in width) unwinding from a coil travels at rates of 30–150 m/min through the coating applicator rolls and bake ovens. It is rewound into a coil for transport to a forming operation for products that are to be used in cans, appliances, industrial and residential siding, shelving, cars, gutters, downspouts, etc. The source of hydrocarbon emissions in coil coating is the coating application area and the cure-oven exhaust. The coatings include primers, finishes, and metal protective (5 μm) films or backers.

The increasing use of siliconized coatings for weather durability caused severe masking problems for the all-metal, filter mesh-like catalyst elements available in the 1970s. Interest in catalytic afterburners increased when dispersed-phase precious metal-alumina-on-ceramic honeycomb catalysts offered economically attractive results.

The hot (260–370°C) oven exhaust can be oxidized catalytically without preheat, but when the coater-area exhaust (at room temperature) is combined with the oven exhaust, a preheat burner becomes necessary. The greatest energy savings potential having the least capital investment is obtained by recycling a portion of the hot, cleaned exhaust to the oven. This principle has been demonstrated at a number of can manufacturing plants and at least four coil coating facilities. One operator preheats oven make-up air that has been taken from the oven cooler section by means of a heat exchanger; whereas others recycle directly to the oven. In one case, the heat energy for the dry-off oven is supplied by the catalytic incinerator exhaust (482°C) remaining after supplying most of the heat energy to operate the four zones in the oven. The concentration of solvents in the exhaust is $\sim$12% LEL (167°C temperature differential). The net fuel energy consumption is $\sim$20% of that required to fire the paint, bake, and dry-off ovens without fume control.

Coil coaters operate equipment continuously and, in most cases, operate catalytic fume abaters 6000–7000 h/year. Under these conditions the anticipated catalyst life is years, with an annual aqueous solution cleaning. However, the catalyst may last no more than two years if frequent maintenance is needed, such as in-place air lancing every 60–90 days to remove noncombustible particulates. Frequent maintenance may be needed if coatings such as siliconized polyester (15–40% silicones) comprise 30% of the coatings put through the system.

Filter Paper Processing. In the fabrication of fuel oil and air filters for vehicles such as motorcycles and diesel locomotives, heat processing of the filter paper is required to cure the resin (usually phenolic) with which the paper (qv) is impregnated (see PHENOLIC RESINS). The cure-oven exhaust, which contains water vapor, alcohols, and dimers and trimers of phenol, produces a typical blue haze aerosol having a pungent odor. The concentration of organic substances in the exhaust is usually rather low.

The paper-impregnation drying oven exhausts contain high concentrations (10–20% LEL) of alcohols and some resin monomer. Vinyl resins and melamine resins, which sometimes also contain organic phosphate fire retardants, may be used for air filters. The organic phosphates could shorten catalyst life depending on the mechanism of reduction of catalyst activity. Mild acid leaching removes iron and phosphorus from partially deactivated catalyst and has restored activity in at least one known case.

Catalysis is utilized in the majority of new paper filter cure ovens as part of the oven recirculation/burner system that is designed to keep the oven interior free of condensed resins and provide an exhaust without opacity or odor. The application of catalytic fume control to the exhaust of paper-impregnation dryers permits a net fuel saving by oxidation of easy-to-burn methyl or isopropyl alcohol, or both, at adequate concentrations to achieve a 110–220°C exotherm.

8. Environmental Technology Verification

In 1995, the U. S. Environmental Protection Agency (EPA) established the Environmental Technology Verification (ETV) Program. This program was established to evaluate the truth of a commercially ready environmental technology's performance under specific, predetermined criteria and adequate quality assurance (QA) procedures. As of 2003, this program has five operational centers to evaluate the technologies organized around the critical technologies being reviewed (including greenhouse gas technology, air pollution control technology and pollution prevention processes). By mid 2003, >200 technologies were verified under the program with 140 applications for testing pending (75).

With active EPA participation, both vendors and users will be able to offer or select control equipment that would best fit their applications with a high degree of confidence.

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