

Control of Volatile Organic Compound (VOC) Air Pollutants

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(ABSTRACT)

A variety of methods exist to remove volatile organic compound (VOC) air pollutants from contaminated gas streams. As regulatory and public opinion pressures increase, companies are searching for more effective methods to control these emissions. This document is intended as a guide to help determine if existing systems are adequate and to provide additional information to improve the efficiency of the systems. It explores conventional methods of controlling VOC emissions, as well as innovative technologies including membrane separation, plasma destruction, and ozone catalytic oxidation. The conventional technologies covered include condensation, adsorption, absorption (or scrubbing), thermal incineration, flaring, catalytic incineration, and biofiltration. Each chapter includes a description of the technology, a discussion of the types of systems available, notes on the design of the system, economic estimates, an explanation of potential problems, and a list of considerations for installation and maintenance concerns. The final chapter is dedicated to the preparation and characterization of metal catalysts which were developed to improve the reaction rate of VOCs using ozone as an oxidant.

For family and friends who have supported, encouraged, and tolerated me
through this project.

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Chapter 1

Introduction

Over the last fifteen years, public awareness has been raised significantly about the effects of air pollution on the environment and society. Reports of the amount of pollutants emitted into the atmosphere have made headlines as the requirements of community right-to-know laws came into force and companies began to report the amount of pollution released to the air, water, and land. In addition, the 1990 Clean Air Act established annual fees for larger industries based on the amount of pollution emitted into the air from the facilities. These factors have encouraged industries to consider installing additional air pollution controls, even on sources where the controls are not required by regulation. For some companies, this action is regarded as a method to protect a corporate image based on improving public health. For others, it may be a method to appease neighbors or to appeal to a "greener" market.

Whatever the motivation, the result on the air pollution control industry is the same. The increased interest in controlling emissions, including low concentrations of emissions, is driving the industry toward creative problem solving, innovative controls, and combining control methods to achieve more efficient processes. As the demand for controls with higher removal efficiency increases, the market for innovative control technologies also improves. This thesis explores the technologies that are currently available, along with an additional section on the potential use of ozone to improve catalytic incineration performance. Ozone is recognized as a strong oxidant for VOCs. Therefore, the potential for improving the destruction efficiency of VOCs in catalytic incinerators or reducing the required combustion temperature is promising by the use of ozone. Such a process could substantially reduce the energy requirements to control VOCs. Research is continuing to refine the process for using ozone in catalytic incineration. The details of recent research to manufacture catalysts and characterize them is the subject of the last chapter.

Chapter 2

Overview of Technologies for Reduction of VOCs

Various strategies exist to control VOC release. The most desirable is to improve processes so that emissions are minimized at the outset. This is the idea behind “environmentally conscious manufacturing” [1], “green engineering” [2], and “benign by design” [3] initiatives in various industries. These initiatives may be applied in two ways: improvements or redesign of processes. *Improvements* include alteration of unit operations, such as increasing reactor yields, raising separation levels, or simply cutting down on fugitive emissions. *Redesign* involves more fundamental changes in processes such as switching from an organic phase to an aqueous phase, converting from stoichiometric to catalytic chemistry, or going from batch to continuous operation. In all these cases the concept is to eliminate emissions at the point of creation and avoid “end of the pipe” treatment.

An effective technology for waste minimization which is extremely broad in scope is catalysis. Its use in a wide variety of environmental applications has been reviewed [4]. For example, catalysis can be used to manufacture environmentally safer products like hydrofluorocarbons as replacements for the problematic chlorofluorocarbons (CFCs). It can be used as an alternative to hazardous and toxic chemicals like HCN, HF, HCl, phosgene in a variety of processes. It can be used to improve yields, reduce side-products, and produce unique molecules in a variety of chemical and energy applications.

There are many situations where it is impractical or impossible to avoid production of some waste. This can be due to inherent limitations in selectivity of reactions, or unavoidable inefficiencies in separations. Both kinetic and thermodynamic factors may be involved in these cases. Airborne contaminants may also be generated by the nature of the process itself. For example, manufacturing, painting, cooking, dry-cleaning, and animal rendering operations represent situations in which activities are carried out in relatively open spaces with release of volatile species into the immediate environment. Such operations usually require ventilation to sweep away any noxious substance. Treatment of this air stream containing low concentrations of contaminants now becomes the objective. Again, in this situation catalysis can be very effective [4]. Catalysis is used for the elimination of pollutants from fixed sources like power plants, mobile sources like vehicles, and increasingly in everyday environments like office, home, and retailing outlets.

Methods of VOC Control

A number of options are available for the elimination of VOCs [5]. These are described in a number of books and monographs [6,7,8,9,10,11,12,13,14,15] and are summarized in Table 2-1.

Table 2-1. Methods of VOC Abatement

Methods	References
Condensation	6,16
Adsorption	15,17,18,19
Absorption / Scrubbing	6,15,20,21
Thermal incineration	9,22,23
Catalytic incineration	9,24
Flaring	25, 26
Biological treatment	27,28,29
Odor modification	5,30
Air dilution	6,31,32
Membrane separation	33
UV treatment	34
Ozone catalytic oxidation	This thesis

The use of these methods depends on the precise nature of the VOCs, the concentration levels, and the conditions (temperature, pressure, flow rate). These have been described in a general manner in a number of articles and books. They are briefly described below and will be covered in more detail in subsequent chapters with particular emphasis on their applications to VOCs.

Condensation

Condensation is the liquefaction of condensable contaminants by the use of low temperatures. Specifically, the compounds to be removed from the gaseous phase are cooled to a temperature at which their partial pressure (fugacity) in the gas stream exceeds their dew point, so that they transform to liquids. Conventional condensers are shell and tube heat exchangers [35], used because they contain a relatively large amount of surface area for heat transfer, but are fairly compact. Critical parameters which establish the requirements and efficiency of the condenser include: the overall heat transfer coefficient (a function of the hot and cool stream composition, flow characteristics, and the construction material), the difference in temperature between the streams, and the operating pressure [36].

Condensation is most effective for compounds with high boiling points [37]. However, if a significant portion of the organic material is composed of compounds which solidify at the condenser operating temperature, a standard shell and tube design condenser will not be effective, as these will quickly foul the heat transfer area, plugging the condenser. For those cases, a contact condenser, in which the hot and cool streams come directly into contact with each other would be more appropriate.

Adsorption

Adsorption refers to the trapping of pollutants on a high-surface area material. The process is typically used to remove contaminants in fairly low concentrations from a gas stream. The pollutants are adsorbed onto the surface or interstitial areas of a material such as activated carbon or a molecular sieve by physical or chemical attraction. Once the carbon or adsorbent material is saturated, that is, it can no longer adsorb any more pollutant, the material is regenerated, typically by introducing steam to drive off the pollutants [38]. The vent stream is condensed, decanted if necessary to separate the

aqueous layer from the organic layer, and in some cases, further treated. For example, one of the layers may require distillation to further separate the constituents from the aqueous phase or from each other [39]. Because of the subsequent separation required to reuse the solvents, carbon adsorption is not well suited to streams which have a large number of VOCs, nor does it work effectively on streams that have constituents which are difficult to separate. In those circumstances, as well as situations where the adsorbed species has a large molecular weight and is therefore difficult to desorb, or in cases of low flows [40], the carbon can be used and then disposed of. This creates a similar dilemma to that of incineration, though, in that it treats a symptom (VOC emissions) but causes other problems such as waste disposal.

Absorption / Scrubbing

Absorption is a physical process consisting of the dissolution of a pollutant in a liquid. In absorbers (or scrubbers), the vapor stream is introduced into a chamber where it is intimately mixed with the liquid. The amount of pollutants remaining in the gas stream as it leaves the scrubber is governed by Henry's law, which establishes the amounts of a component in equilibrium in the gas and water streams for dilute mixtures [41]. By using counter current gas and water flows, the mass transfer between the vapor and liquid phases is maximized. If the vapor and liquid have adequate contact, the gaseous components that are soluble in the liquid are absorbed, where they may react or be removed by discharging the liquid. Some additional removal is accomplished by the evaporative cooling that occurs in the scrubber; some components condense out and are removed as the liquid is removed. Absorption, however, is not effective on constituents which are not soluble in the liquid medium. Therefore, it, too, is not well suited to vapor streams which have a large variety of constituents.

There is a variation of absorption known as *wet scrubbing* where the gas-phase component undergoes a chemical reaction [42] with a component in the liquid phase. The reactions can be of an acid-base nature, or an oxidation type. The reaction of the liquid phase compound results in a lower concentration of the liquid phase compound than would otherwise exist at equilibrium. Thus, the driving force for removal of the gas-phase component is higher than in simple adsorption. However, a drawback is that the scrubbing agent is consumed in the process, and hence the method is more costly than adsorption where the liquid phase can be reused. Also, in some cases, the process generates a by-product which must be separated and disposed [43].

Thermal Incineration

Incineration is basically the burning of combustible wastes [44]. For many years, thermal incinerators have been considered to be one of the most effective control devices for VOCs. They are relatively easy to operate, not likely to foul, and do not require additional processes to remove the pollutant. They are sometimes coupled with recuperative heat exchangers for energy efficiency or, more recently, with more efficient regenerative heat exchangers. Operating costs can be further minimized by ensuring that the gas stream is as concentrated as possible so that energy is not expended to heat excess air. The concentration is usually limited to approximately 25% of the Lower Explosive Limit (or *LEL*) by fire insurance regulations [45]. Incinerators are ideal candidates for gas streams which contain a variety of pollutants and where any solvent that is recovered is not viable for reuse. Under proper

conditions, the design efficiencies are typically in excess of 98%, and depend primarily on the gaseous components combusted, the residence time, the amount of mixing, and the combustion temperature [46]. Costs associated with incineration processes are typically higher than those associated with solvent recovery processes like carbon adsorption or condensation due to the cost of the natural gas and increased solvent cost. In addition, incineration can be perceived as a “Band-Aid” approach to VOC control, since it treats the major problem of VOC emissions but generates smaller problems like NO_x and CO₂ generation.

Catalytic Incineration

Catalytic incineration or combustion refers to the burning of combustible wastes with the aid of a catalyst [47,48,49,50]. The catalyst opens up a different reaction pathway with a lower activation energy than gas-phase combustion and allows oxidation to proceed at a lower temperature. Advantages of catalytic combustion are lower energy requirements and lower production of NO_x. However, caution must be exercised with catalytic units to avoid the introduction of particulate matter or metal fumes which can foul the catalyst [24]. The catalyst is usually a noble metal like platinum or palladium dispersed on an inert oxide support. To avoid pressure drop problems the support is usually deposited on the surface of a monolith carrier.

Flaring

Flaring is another combustion technique which involves the direct burning of an organic stream in an open flame. It is carried out at the tip of a burner, usually with the addition of extra fuel and, sometimes, steam [26]. There is no combustion chamber, so flame temperature and proper mixing of the combustible mixture with air are critical design aspects [51]. Flaring can tolerate large variations in flow rate, so is commonly employed in transient situations such as startup and shutdown. It is routinely used in refining as a method of disposing of VOCs in that industry.

Biological Treatment

Biological treatment consists of using microorganisms to biologically degrade contaminants [34]. Biological purification is a relatively new technology in the field of air pollution control, although the same concept has been used for years to treat wastewater streams. Microorganisms are grown on a substrate (*biofiltration*) or are suspended in a liquid scrubber media (*bio-scrubbers*) [52]. The scrubber liquid or substrate may also serve as an adsorbent for the pollutants, so that the microbes have a constant food supply, even if the process is not operating. In less variable processes, the microbes are contained in compost, peat, or a similar soil and the air stream is passed through the bed for treatment. Just as in water treatment operations, the microorganisms break down the large organic molecules into smaller, less harmful molecules, consuming a portion of the molecules for energy to sustain their microbial activity. Although this technology is still not well accepted in the US, there are several hundred installations operating worldwide [53]. Like adsorption, bio-purification is a good alternative for streams which have relatively low concentrations of organic constituents and is most effective for systems containing alcohols, ethers, aldehydes, and ketones.

Biofiltration offers excellent VOC removal, even from dilute gas streams with relatively low maintenance and operating costs. However, care must be exercised to remove particulates, ensure adequate moisture is present, avoid gas channeling, and maintain a fairly constant temperature

[29]. As with wastewater treatment systems, the microbes are susceptible to significant changes in the nature or concentration of pollutants and can be killed by sudden changes. Therefore, highly variable processes, or batch systems in which products change daily or weekly are not well-suited to biofiltration. In addition, design of a biofiltration system generally requires a pilot unit to determine the treatability of the gas stream and the residence time required for effective removal.

Membrane Separation

Membrane technology involves the use of semipermeable membranes to separate VOCs from a process stream [33]. The technology has been used in water purification, and has been adapted for use with gaseous media. Basically, the separation is based on preferential diffusion of VOCs across thin polymer layers wrapped around a perforated central tube. The driving force is a pressure differential between the inner and outer portions of the tube. The method is effective for recovering VOCs such as chlorinated hydrocarbons, chlorofluorocarbons, and hydrofluorocarbons that have been traditionally difficult to separate because of their high volatility.

UV Treatment

UV treatment is another emerging technology in which ultraviolet light is used to oxidize organic compounds. The oxidation reaction is promoted by the photocatalytic effect of the UV light and is conducted in the presence of a catalyst to activate the oxygen into highly reactive species including ozone. After reaction, the air stream is scrubbed to perform additional oxidation, dried, and remaining VOC compounds are adsorbed in activated carbon. The technique has been reported to be up to 99% effective in the destruction of organic compounds [34, 54]. Problems are activity at high flow rates and the low photoefficiencies of the catalytic process, which results in high costs [55].

Catalytic Ozone Oxidation

Ozone catalytic oxidation technology is already seeing commercialization in a number of household applications such as the deodorization of refrigerators and toilets and the purification of room air. A contaminated gas stream is mixed with ozone and passed over a catalyst bed to carry out a low-temperature catalytic combustion reaction. The process utilizes the oxidizing power of ozone together with the activity and selectivity of oxidation catalysts to convert VOCs to CO₂ and H₂O. The process works at high and low VOC concentrations, and at high flow rates. Because of the use of ozone the air stream does not require appreciable heating. Improvements in generation equipment have decreased the cost of the ozone substantially, and this promises to become a broadly used technology.

Comparison of Technologies

Figures 2-1 and 2-2 [Adapted from ref. 14, with permission] illustrate the ranges of concentration and flow rate that are generally suitable for different technologies. These, in combination with required control efficiency and the availability of utilities, labor, and capital form the basis for a control technology choice. In most cases where a VOC control is desired or required, one immediate and easy solution is incineration. Incineration is a very effective, flexible control technology that allows for changes in pollutants, concentration, and flow. In addition, thermal incineration devices are available today with greater than 95% heat recovery which minimizes the amount of supplemental fuel required. Catalytic incineration is also capable of high removal efficiencies with minimal natural gas requirements, but is more susceptible to

fouling from particulates and metal fumes.

The other technology which is recognized as capable of high efficiencies (greater than 99% in some cases [56]) is adsorption. Adsorption has additional advantages, as well, since the pollutants can be recovered for reuse. Not all VOCs are suitable for adsorption, and a source of steam or heat must be available for regenerative systems. Non-regenerative systems result in additional waste for disposal.

Biofiltration has also been reported to be capable of efficiencies greater than 90% [57], but are susceptible to sudden changes in temperature, concentration, and humidity. Condensation is generally considered to be less effective than the other technologies, but is capable of approximately 90% efficiency in cases where refrigerants are used to cool the gas stream [58].

Membrane separation, UV treatment, and ozone catalytic oxidation are all emerging technologies which should be further investigated to determine their suitability to the situation, as well as to assess the efficiency of commercial units. This book provides an in depth coverage of the topic of catalytic ozone oxidation of VOCs. As will be seen, this is a versatile technology that is effective for both large scale industrial pollution abatement as well as for low concentration indoor air treatment. Already, household appliances fitted with catalytic ozone devices have been commercialized for the elimination of odors in toilets and refrigerators.

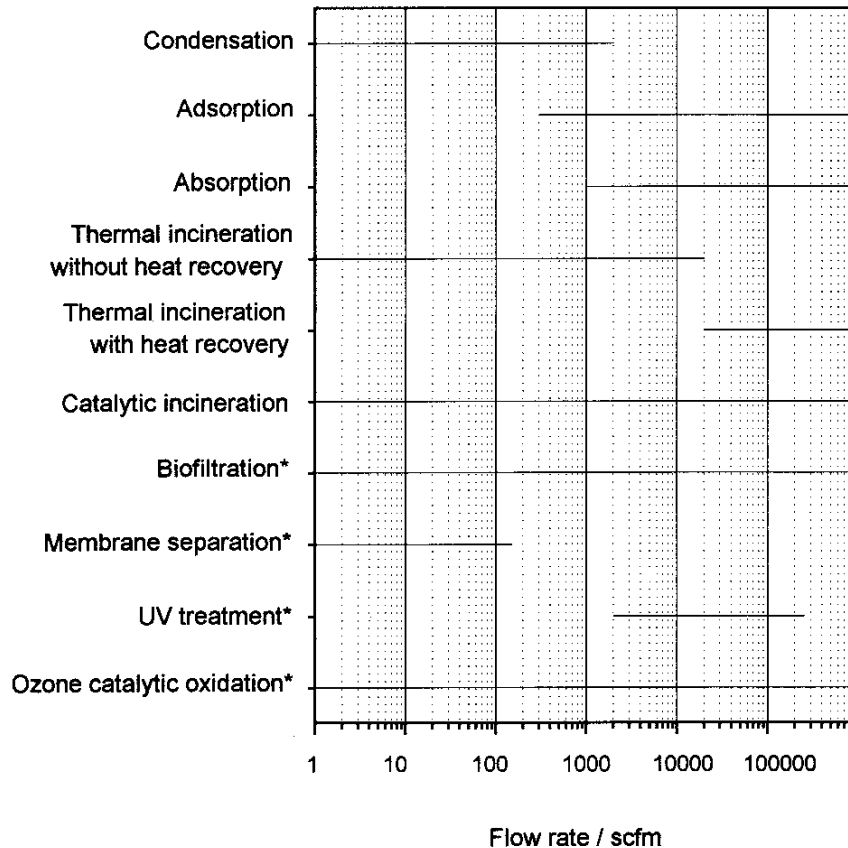


Figure 2-1. Range of Flow Rates for Various VOC Treatment Technologies

It is not likely that any of these technologies will be exactly suited to a given process. The choice of a control strategy is almost always a choice of lesser evils. However, one option that can be very beneficial in the long run is a process change to reduce or eliminate organic compounds, i.e. *reduction at the source*. Operational changes may have initial costs greater than the expenses associated with control equipment, and are frequently ruled out on that basis. Savings in operating costs, though, can frequently pay for the changes in a relatively short period of time. If new equipment is installed, the updated equipment usually also has better process control and results in improved quality and efficiency as well as reduced emissions. When coupled with the fact that fewer manhours are dedicated to complying with permits, regulations, and laws, process changes are frequently the optimum solution. Although they can be difficult initially, the rewards make operational changes well worth serious consideration as a control strategy.

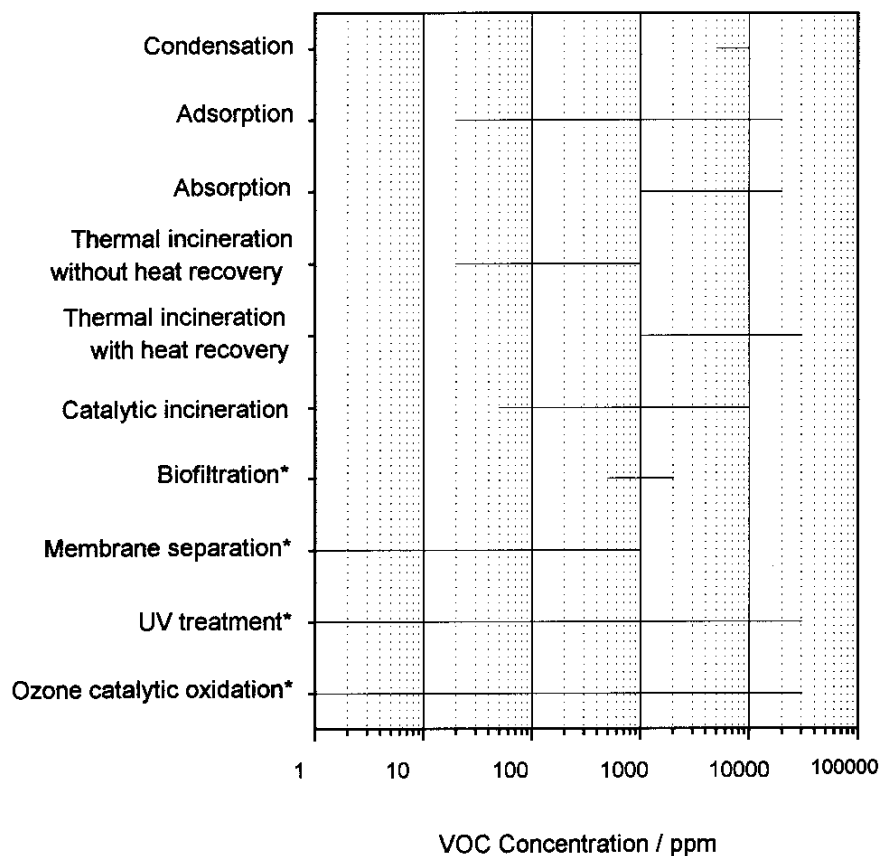


Figure 2-2. Range of Concentrations for Various VOC Treatment Technologies

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Chapter 3

Condensation

Technology Description

Condensation is a process used to separate compounds by either cooling the gas stream or pressurizing a gas stream to conditions where one or more of the components separates from the mixture as a liquid. This occurs when the partial pressure (fugacity) of the constituent in the gas phase equals or exceeds the vapor pressure of the pure component in liquid form under the same conditions [1]. The efficiency of removing VOCs from a gas stream by condensation depends on the vapor pressure of the component to be separated, the pressure and temperature that can be achieved during condensation, and the concentration of the constituent in the gas stream [2]. A typical flow diagram of a condensation system for air pollution control is shown in Figure 3-1.

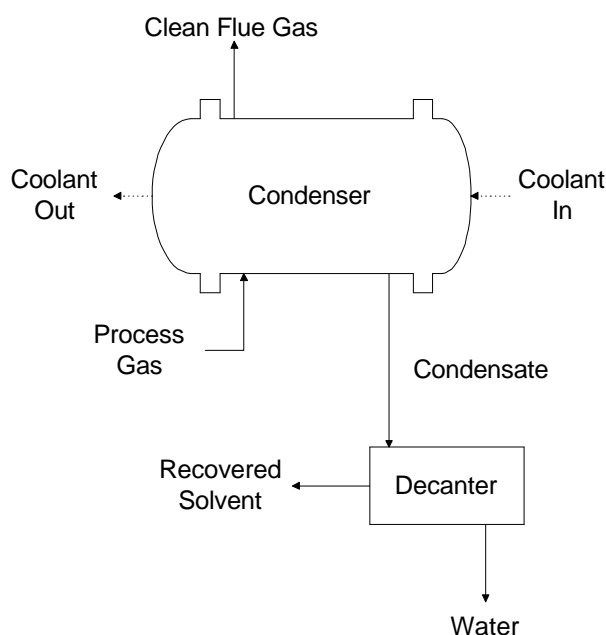


Figure 3-1. Typical Condensation Process

Water-cooled condensers are commonplace in industry [3]; they are used to prevent the escape of raw materials from the process, to liquefy components separated by distillation columns, and to liquefy steam to reuse it as boiler feedwater. Condensation is generally assumed to be considerably less efficient than other technologies for removing pollutants from the low concentration gas streams encountered in air pollution control [2]. However, an alternative coolant [4] such as calcium chloride, Freons, or methylene chloride may yield condensing systems with 90 percent [2, 5] or better efficiency. The increased efficiency, which results from outlet gas temperatures of 194 to 277 K (-79 to 4 °C, -110 to 40 °F) [6], comes at the cost of increased maintenance and system complexity, though. A refrigerant must be selected carefully to ensure that potential leakage of the coolant does not result in a more severe

environmental threat than that posed by the original gas stream. The potential danger from refrigerant leaks and the energy consumed by the refrigeration cycle should be weighed against the toxicity and impact of the untreated gaseous stream.

Condensers, particularly water-cooled condensers, are frequently used in combination with other control technologies [7]. In carbon adsorption systems, condensers are used to liquefy the concentrated plume of steam and pollutant that are removed during the desorption stage. They are also used for pretreatment of a gas stream, such as in a rendering plant where as much as 95% of the gas volume may be reduced by condensation [8]. Since cooling of the gas stream is inherent in a condensing system, the system reduces the volume and pollutant loading of a gas stream before it enters a final "polishing" control device, such as an absorber, adsorber, or incinerator. This enables the final control device to be smaller and to achieve lower emissions. Condensers may be used to reduce the loading to a level below the Lower Explosive Limit (LEL) of the gas stream. When placed in front of a destructive control device such as an incinerator or absorber, a condenser provides for partial recovery of raw materials prior to the final destruction necessary to achieve low emission rates. However, such a system requires that the gas stream be cooled, only to be heated up again to reach the combustion temperature. Condensation systems are more effective on compounds which have low vapor pressures at the achievable outlet gas temperature; typically higher molecular weight compounds are most suited to recovery by condensation. Table 3-1 gives several applications of condenser systems for VOC control [9, 10, 11].

Table 3-1. Typical Industrial Applications of Condensers [9, 10, 11]

Storage tanks
Petroleum refining
Phthalic anhydride manufacturing
Ammonia manufacturing
Dry cleaning
Styrene manufacturing
Rendering plants
Vapor degreasers
Kraft pulp mills

Types of Condensers

There are two primary types of condensers, *contact* and *non-contact* [12, 13]. The most common is the non-contact or surface condenser [14], in which heat is transferred across a barrier (usually a metal pipe or plate) which separates the gas stream from the coolant. Examples of non-contact condensers include shell-and-tube heat exchangers (Figure 3-2, redrawn from [8]) and plate-and-frame heat exchangers (Figure 3-3, [15]). In shell-and-tube heat exchangers, the coolant normally flows through the tubes [16]; the gas stream flows through the shell outside the tubes, and the condensible constituents form a film on the outside surface of the tubes. If there is little moisture in the gas stream, non-contact condensing systems can provide for pure product recovery [17] in situations where only one condensible compound is present in the gas stream. Even with moisture in the gas stream, the recovery

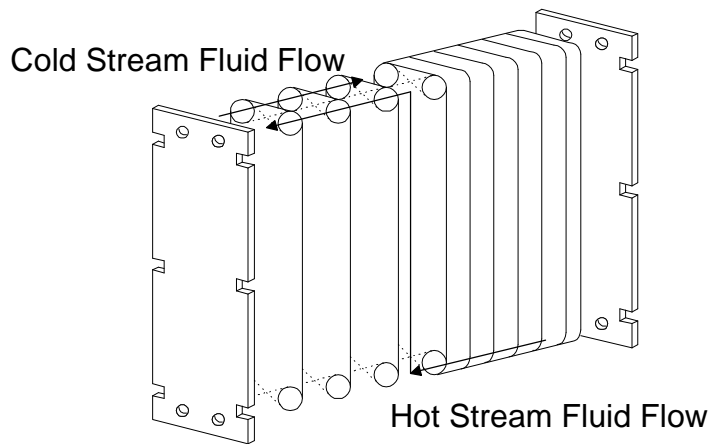


Figure 3-3. Plate and Frame Heat Exchanger [modified from 15]

is fairly simple: the organic is separated from the water either by decanting (if it is not soluble in the water) or by distillation [18].

In a contact condensing system, the coolant is sprayed directly into the gas stream to obtain the maximum heat transfer. These systems, while they are usually less complicated and less expensive [19], create additional difficulties since the coolant must be separated from the condensed vapor if either one is to be reused. If the condensate is not reused, the liquid stream must be discarded, usually through a wastewater treatment plant. Thus, an air pollution problem is simply converted to a wastewater problem [16]. However, contact condensers also have the advantage that the liquid absorbs any soluble compounds, acting as both a condenser and an absorber [20, 21], at least until the liquid becomes saturated with the pollutant.

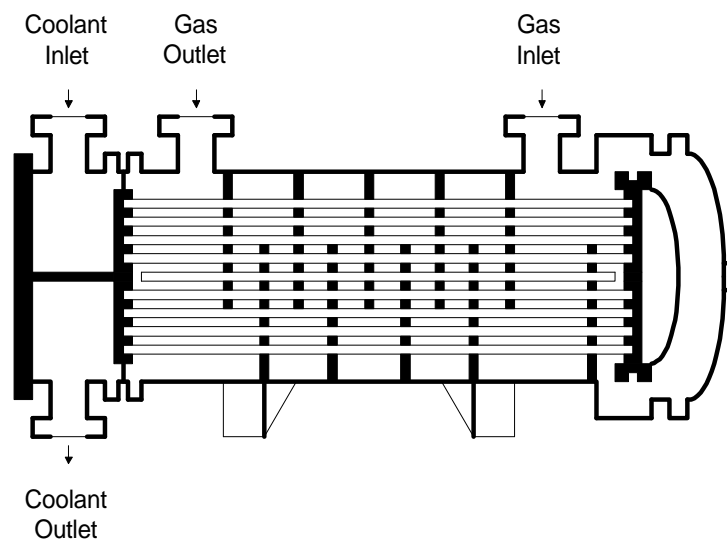


Figure 3-2. Shell-and-Tube Condenser [modified from 8]

Contact condensers come in a variety of designs [16], including simple spray chambers [8] (see Figure 3-4) and venturi scrubbers [8] (in which the velocity of the gas is accelerated to increase the contact, Figure 3-5). These types of vessels are also effective particulate collection devices [22, 23], an important consideration if the gas stream also contains particulate which might foul a shell-and-tube condenser.

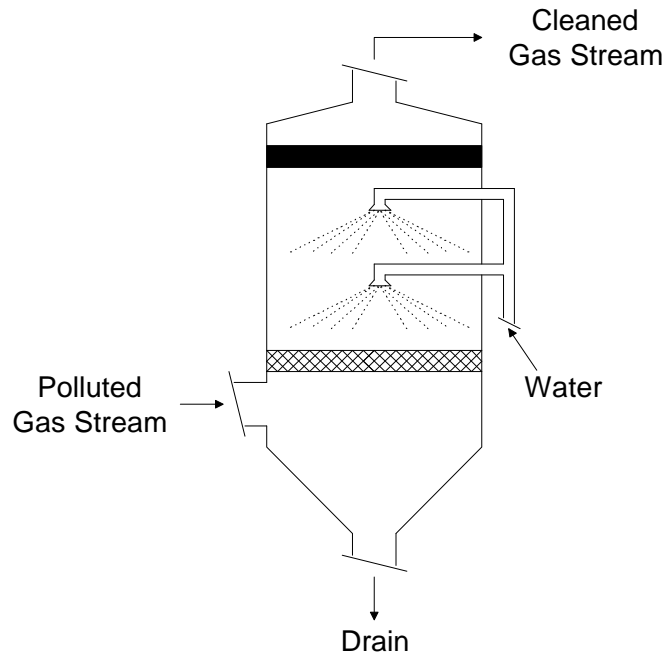


Figure 3-4. Spray Chamber [modified from 8]

Some contact condensing systems cool the condensate further than normally required and use the chilled condensate as the recirculating coolant [24]. While this method is only effective with pollutants which have a relatively low vapor pressure, it provides a good solution to the wastewater disposal problem encountered with miscible coolant and condensate systems.

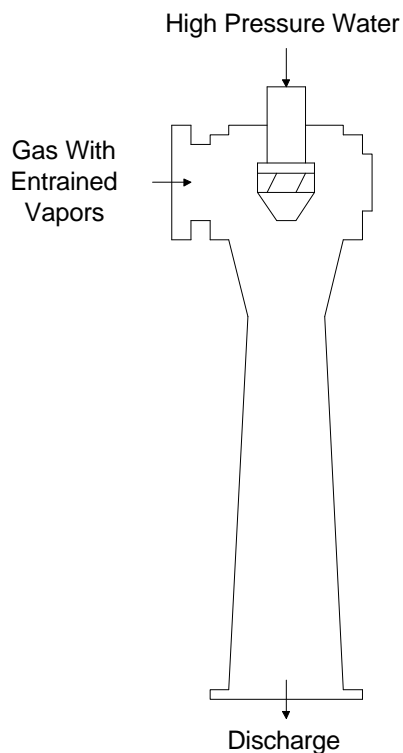


Figure 3-5. Venturi Scrubber (or Condenser) [modified from 8]

Condenser System Design

Choosing and specifying a condensation system for air pollution control involves several considerations. In addition to evaluating whether the technology is appropriate, the designer must also consider safety, efficiency, economics, and maintenance requirements. An important aspect of the safety considerations is designing the system to fail safe. Assuming that every condenser will eventually leak, at least for a short while, the designer should determine whether the coolant should leak into the gas stream or vice versa. The stream under the most pressure will inevitably make its way into the other stream once the vessel begins to leak, so the condenser should be designed for pressures that ensure that the leakage is safe and easy to detect.

The efficiency of the condensation system depends on adequate heat transfer and the concentration of the pollutant in the gas stream. The gas stream should therefore be as concentrated as possible, since additional air consumes cooling capacity [25] that would otherwise be used for condensing the pollutant. Excess air also dilutes the concentration of the pollutant, making it more difficult to achieve the partial pressure necessary for removal. As with the other control devices, unnecessary air flow should be eliminated [13] by reducing the airflow at pickup points if possible, properly maintaining the seals in the ductwork, eliminating unnecessary pickup points, and maintaining valves and valve seats in excellent condition. The concentration in the ductwork should never exceed fire safety levels. This is of particular importance in cases in which storage tanks are vented to a condenser, since the exhaust stream from the tank is saturated with solvent vapor.

Because of the strong influence of adequate heat transfer on the overall operation of the condenser,

ensuring an adequate supply of coolant at as low a temperature as possible and minimizing potential fouling are important aspects of the system design. It is important to ensure that adequate heat transfer surface is available. However, overdesigning the heat transfer area can actually be detrimental to the condenser operation [3] if the overdesign results in less air velocity and less liquid washing per unit of condensing surface so that more fouling occurs.

A rough estimate of the surface area required for condensation in a simple countercurrent heat exchanger can be obtained by determining the total amount of heat, q (J hr^{-1} or Btu hr^{-1}) that must be transferred out of the gas stream to achieve the desired outlet temperature. The specific heat of the vapor, the specific heat of the liquids, and the latent heat of vaporization of the condensable compounds must be known. The required surface area is then estimated by the equation [4]:

$$A_c = q / (U \Delta T_{lm}) \quad 3-1$$

where

A_c	=	Amount of heat transfer area required, m^2 or ft^2
q	=	Amount of heat to be transferred, J h^{-1} or Btu h^{-1}
U	=	Overall heat transfer coefficient, $\text{J m}^{-2} \text{h}^{-1} \text{K}^{-1}$ or $\text{Btu ft}^{-2} \text{h}^{-1} \text{R}^{-1}$
ΔT_{lm}	=	The log-mean temperature difference is calculated by the formula:

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln (\Delta T_1 / \Delta T_2)} \quad 3-2$$

where

ΔT_1	=	Temperature difference between the hot fluid and the cold fluid at the entrance of the hot fluid to the heat exchanger, K or $^{\circ}\text{R}$
ΔT_2	=	Temperature difference between the hot fluid and the cold fluid at the entrance of the cold fluid to the heat exchanger, K or $^{\circ}\text{R}$

Some typical overall heat transfer coefficients are given in Table 3-2. These values are intended as a general guide only and are not intended as the sole source of information for heat transfer. A more rigorous estimation such as that given in Perry's Handbook [26], Bejan [27], Sherwood and Reed [28], McAdams [29], or Jakob [30] should be used for design. Heat transfer equipment vendors are also excellent sources for precise information regarding the heat transfer coefficient for a given situation.

Table 3-2. Typical Overall Heat Transfer Coefficients [3, 11, 20, 31, 32, 33, 34]

Vapor	Coolant	U (J K ⁻¹ m ⁻² s ⁻¹)	U (Btu oF ⁻¹ ft ⁻² h ⁻¹)
Ammonia	Water	260-880	150-500
Alcohol	Water	80-350	45-200
Methanol	Water	440-880	250-500
Kerosene	Water	50-110	30-65
Light Organics (viscosity <0.5 cP), benzene, toluene, acetone, ethanol, gasoline)	Water	130-260	75-150
Heavy Organics	Heavy Organics	50-200	30-110
Heavy Organics	Light Organics	150-300	85-170
Heavy Organics	Water	25-370	15-210
Light Organics	Heavy Organics	50-200	30-110
Light Organics	Light Organics	200-400	110-230
High Boiling Hydrocarbons	Water	35-90	20-50
Low Boiling Hydrocarbons	Water	140-350	80-200
Organic Solvents (with large amount of noncondensibles)	Water or brine	35-140	20-80
Naphtha	Water	90-130	50-75
Vegetable oil vapors	Water	35-90	20-50
Steam	Water	350-1400	200-800
Gases (in general)	Water	4-90	2-50
Light organics	Brine	70-200	40-100
Gases	Air	4-15	2-8

Adequate provisions must also be made for subcooling the condensed liquid [8] so that the vapor is not simply re-evaporated from the warm liquid once the liquid reaches a storage tank or open vessel. This may be accomplished by maintaining a pool of condensate covering a small portion of the heat transfer surface. If this method is used, adjustments in the amount of heat transfer area should be made in the design of the condenser to ensure that adequate heat transfer area exists above the liquid pool to achieve the desired removal rate. Alternatively, a separate liquid-to-liquid heat exchanger or subcooler can be

installed to maintain the desired condensate temperature. Separate subcoolers are typically much smaller than the condenser. A list of instrumentation that should be considered for condenser systems is given in Table 3-3.

Table 3-3. Recommended Instrumentation

Gas stream temperature and pressure (inlet and outlet)
Pollutant concentration
Fan speed
Coolant flow and temperature (inlet and outlet)
Condensate flow
Refrigerant pressure (inlet and outlet), if applicable

Economic Estimates

The cost of a standard shell-and-tube heat exchanger can be estimated using the method published by Cowie [35]. If necessary, the cost of auxiliary equipment such as pumps and fans can be estimated using the equations given by Vatauvuk [4, 6]. The amount of heat transfer area per meter length of the exchanger is given in Table 3-4. Figures 3-6 and 3-7 give two components of the heat exchanger cost: a component that represents the cost of the heat exchanger per meter of length, and the additional cost that must be added to account for tube length.

These factors are based on the cost of a standard split ring floating head heat exchanger made of carbon steel shell and 19.05 mm (3/4 inch) tubes. Additional allowance must be made for other materials of construction, heat exchanger design, temperatures above 343 °C, or different tube or baffle configurations [35]. The costs should be scaled to current values using the methods given by Vatauvuk [4]. In addition to the cost of the heat exchanger and associated equipment, the installation costs must be included in the estimate. Installation costs associated with heat exchangers are typically 30-60 % of the cost of the equipment alone [33].

Table 3-4. Heat Exchange Area per Unit Length of Exchanger [modified from 35]

Shell Diameter		Area/ Tube Length	
mm	in	m ² /m	ft ² /ft
203 OD	8	1.67	5.48
254 OD	10	3.1	10
305 OD	12	4.54	14.9
356 OD	14	5.6	18
406 OD	16	7.89	25.9
457 OD	18	10.6	34.9
508 OD	20	15	49
560 OD	22	18.2	59.7
610 OD	24	22.2	72.8
635 OD	25	24.3	79.6
688 OD	27	28.0	91.9
737 OD	29	33.1	109
787 OD	31	38.2	125
838 OD	33	43.5	143
890 OD	35	49.5	162
940 OD	37	55.3	182
991 OD	39	62.2	204
1067 OD	42	72.7	238
1143 OD	45	84	276
1219 OD	48	96.2	316
1295 OD	51	108	353
1372 OD	54	121	396
1524 OD	60	149	490
OD – Shell diameter is outside diameter. ID - Shell diameter is inside diameter.			

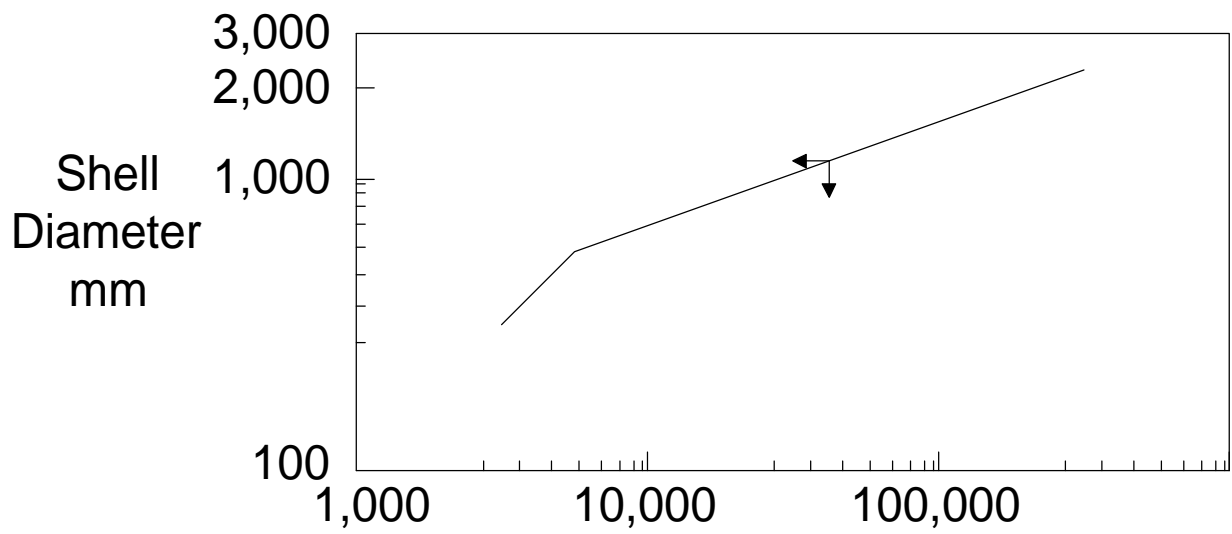


Figure 3-6. Cost of Heat Exchanger per Meter of Length in Dollars [redrawn from 35]

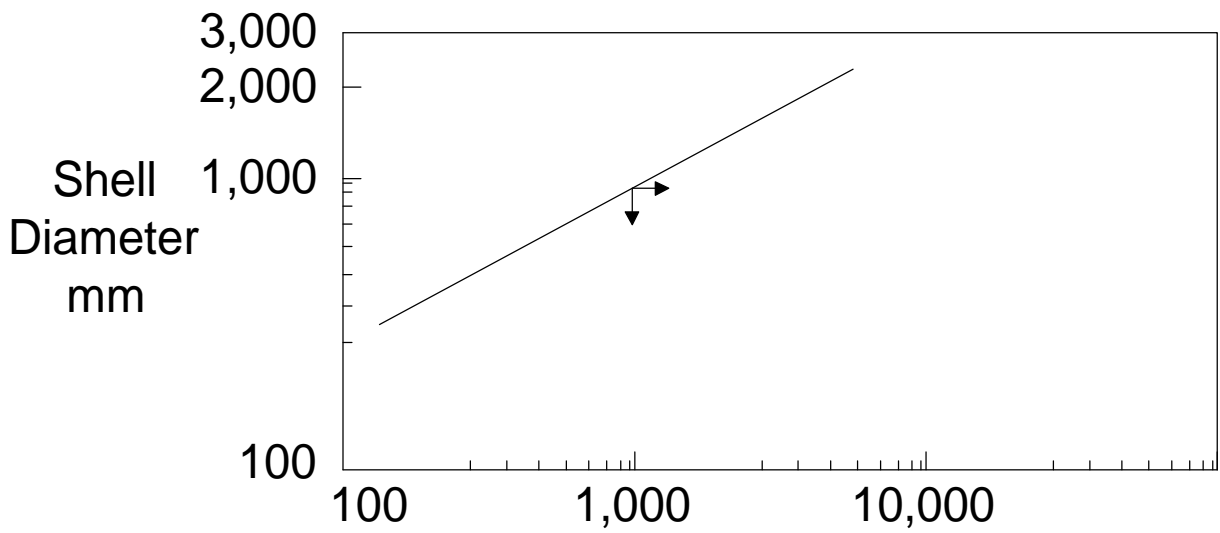


Figure 3-7. Additional Cost of Heat Exchanger per Meter of Length in Dollars [redrawn from 35]

Potential Problems

Fouling of the heat transfer area is one of the most prevalent concerns with non-contact heat exchangers [12]. Fouling refers to the build up of a layer of foreign material on the heat transfer surface [3] which reduces the rate of heat transfer. This may occur due to particulates in the incoming gas stream, contaminants in the cooling stream, organic growth in the cooling stream, or a variety of other factors. When river water is used as a coolant, special care must be taken to ensure that seeds from living organisms do not reach the heat exchanger tubes. For example, in the case of river mussels, the condenser tubes provide a relatively warm spot and the mussels can multiply quickly, choking off the cooling water flow [36].

Corrosion is also a consideration in condensation equipment [18]. Appropriate materials are critical for maintaining the structural integrity of the condenser and ensuring that leaks do not occur. The durability of several materials of construction in corrosive atmospheres are given in Perry's [37]. Table 3-5 gives the relative costs of several materials. Although a titanium or hastelloy condenser has a much higher initial cost, it may easily pay for itself in maintenance, lost production, and replacement costs in a corrosive environment.

Table 3-5. Cost Ratio of Various Materials of Construction Relative to Carbon Steel [33]

304 Stainless Steel	7
316 Stainless Steel	10
Copper	7
Monel	10
Nickel	12
Hastelloy C	40
Inconel	13

Effective removal of the pollutant from the gas stream is dependent on the movement of gas molecules to the cold surface [38]. If the gas is cooled by more than 40 or 50 K (75 to 95 °F), there is the possibility that fog will form in the condenser. This happens when the rate of heat transfer exceeds the rate of mass transfer, thereby cooling the gas before the gas molecules disperse to the cold surface and condense. The resulting condensate fog is comprised of relatively small droplets (approximately one micron in diameter or smaller) which are difficult to collect [7].

Installation, Operation, and Maintenance Considerations

It is important to minimize thermal and mechanical stress and vibration [3] to reduce the opportunity for cracks and leaks [12]. Due to the shape and connections on a shell-and-tube condenser, it is very tempting to install it wherever it can be squeezed in and to force piping into place around it. It is, however, critical that the piping be designed and constructed to fit properly with adequate support for

the condenser so that the connections and condenser shell are not stressed unnecessarily. To avoid unnecessary thermal stress, the condenser should be warmed up slowly and uniformly by starting the coolant flow, then allowing the warm vapor in gradually [3]. Adequate venting is also a key to avoiding thermal stress during start-up, since it minimizes any cold spots [39].

Ample space must be maintained near the end of a shell-and-tube condenser to provide access and allow the tubes to be pulled from the shell for cleaning. Such routine maintenance should include a thorough cleaning of tubes on the inside and outside surfaces. Any cleaning methods must be used with care to avoid loosening seals between the tube and the tubesheet; steaming individual tubes is of particular concern [14]. During the outage, any tubes which have developed thin spots or leaks should be plugged to prevent loss of coolant or vapor. Careful documentation of tube failures will assist later in assessing erosion or stress problems in tubes. Similarly, proper instrumentation is essential to identifying malfunctions of a condenser. If measurements are made once the condenser is operational, but before fouling occurs, conditions can later be compared to the initial conditions to determine if the condenser is working properly or and to identify problems. A summary of the advantages/ disadvantages of condensation is given in 3-6.

Table 3-6. Advantages and Disadvantages of Condensation Systems

Advantages	Disadvantages
Allows for recovery / concentration of the pollutant	Effectiveness is pollutant-specific, depends on vapor pressure of compound
No additional pollutants formed	Potential corrosion of ductwork due to moisture in gas stream
	Generally less efficient than other alternatives
	Potential for wastewater problems [40]

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Chapter 4

Adsorption

Technology Description

Adsorption is a technique commonly used to remove relatively low concentrations of pollutants from a gas stream by trapping them on a solid with a large surface area. The solid is typically an activated carbon or a crystalline material with high internal porosity whose surface holds (adsorbs) the pollutant through intermolecular forces. The pore structure includes macropores (diameters larger than 50 nm), micropores (diameters less than 2 nm), and mesopores (transitional sizes between micropores and macropores) [1]. As shown in Figure 4-1 [2], for micropores, adsorbed molecules can actually block access to internal surfaces. Diffusion and mass transfer rates govern the movement of the pollutant from the air stream to the exterior surface of the solid, and then from the exterior into the pore structure. The efficiency of removing VOCs from a gas stream by adsorption depends on the type and concentration of pollutant, the pressure, temperature, and humidity of the gas stream as well as the pore structure, quantity of active sites, and nature of adsorbent material.

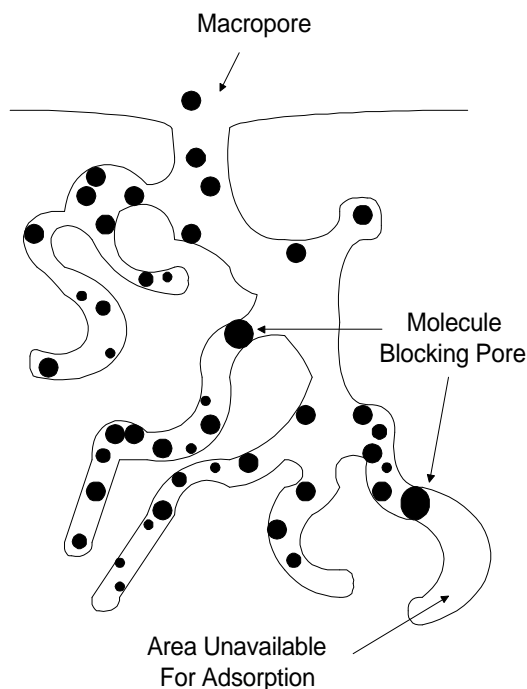


Figure 4-1. Pore Structure (redrawn from [2])

There are two types of adsorption. The first is physical adsorption, where the pollutant molecules are held in place in the pores by relatively weak physical attraction forces of a dipole or van der Waals nature. These forces are the same intermolecular attractive forces which cause condensation of gases [3] and are typically of low energy (1-15 kcal/gmol or 4-50 kJ/gmol). The second type of adsorption is chemical adsorption (or chemisorption), in which chemical bonding forces are also present. The bonds formed by chemical adsorption are much stronger (10-100 kcal/gmol or 40-400 kJ/gmol) and the process of desorption is therefore more energy intensive. The process of removing mercury from a gas stream by using a carbon impregnated with sulfur is an example of chemisorption [4]. Table 4-1 summarizes the characteristics of physisorption and chemisorption.

Table 4-1. Summary of Types of Adsorption [5]

	Physisorption	Chemisorption
Adsorbent	All solids	Some solids
Adsorbate	All gases below critical point	Some gases that are chemically reactive
Temperature Range	Low temperature	Generally high temperature
Heat of Adsorption	Low, 1-15 kcal/gmol	High, 10-100 kcal/gmol
Rate	Very rapid	
Activation Energy	Low	Ranges from low for nonactivated adsorption to high for activated adsorption
Coverage	Multiple layers	Monolayer or less
Reversibility	Reversible	Frequently not reversible
Uses	Determination of pore sizes and surface area	Determination of surface concentration, estimates of active center area, and adsorption/desorption rates

Adsorption systems like the one shown in Figure 4-2 [2] have been used since 1920 [6] to recover solvents in industries which use large quantities of organic liquids, such as synthetic fiber manufacturing, pharmaceuticals, munitions, and printing and coating. While incineration is also capable of very high efficiencies, one primary advantage of adsorption systems is the ability to recover pollutants for sale or reuse. This advantage is frequently a governing factor in the cost effectiveness evaluation, since the cost of solvent can be a significant portion of the manufacturing cost for some processes. One example is cellulose acetate manufacturing [7].

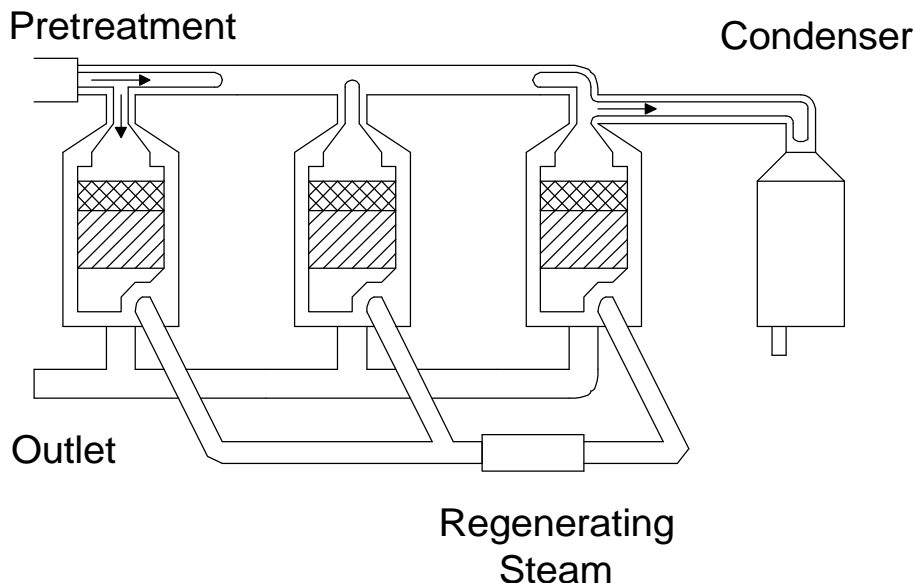


Figure 4-2. Typical Process Flow Diagram of an Adsorption System (redrawn from [2])

Another advantage of adsorption systems is that they work well with a wide range of adsorbate concentrations. If designed and operated properly, the removal efficiencies, which can exceed 98% [8], result in low outlet concentrations consistently, even with inlet concentrations exceeding 10,000 ppm.

Once the pollutant (or adsorbate) is adsorbed onto the surface of the solid (or adsorbent), the pollutant is held in place by van der Waals forces or by capillary condensation [3, 9, 10, 11]. Eventually, the pores are full or entry of additional molecules is blocked, and the solid is unable to adsorb any more pollutant. At this point, the solid is said to be “saturated” and is removed from service. It may be discarded or sent back to the manufacturer to be “cleaned out”, or it may be *regenerated* in place. *Regeneration* or *desorption* is the process of using heat or lower pressure to reverse the adsorption process. Direct steam injection is the most widely used method of providing heat for regeneration [12]. However, heating coils, hot air, microwave radiation and infrared radiation have also been used or investigated [13, 14]. A technique called *pressure swing adsorption* or “PSA” [15] may also be used, in which the adsorption cycle is under high pressure and the desorption is accomplished by operating the adsorber at a lower pressure [16].

Although it may seem somewhat pointless to adsorb the pollutant onto the surface of a solid only to drive it off again, the amount of air present during the desorption process is considerably less than that in the original gas stream, and a vapor stream with a much higher concentration is produced. The vapor stream is usually condensed to recover the pollutant [17]. If the pollutant is not water soluble, the condensed liquid stream can be decanted to produce a stream of relatively pure organic liquid. If the pollutant is water soluble, the condensed liquid stream is typically distilled from the condensed steam to recover the organic liquid [18] or the entire stream is sent to a wastewater treatment plant for disposal.

Adsorbers are frequently paired with other control systems, such as condensers used after the desorption cycle to cool and liquify the steam/pollutant mixture. Condensers may also be used

before the adsorption equipment to reduce the concentration of a pollutant to a safer level, such as one that is below the *lower explosive limit* of the gas stream (LEL) or to a level where the heat of adsorption is not sufficient to start a fire in the adsorber. Adsorption is an exothermic process and the heat that results from adsorption of large concentrations of a pollutant can be dangerous if not properly dissipated or controlled with relative humidity [19]. Having water present in the bed or as humidity in the gas stream provides a heat sink and allows better control of the exothermic process. However, water must be used with caution, since it competes to some degree with the pollutant for sites on the adsorbent. This effect is much less evident with activated carbon (a non-polar adsorbent) than with other adsorbents such as zeolites and aluminosilicates (which are polar).

Adsorption is also used in conjunction with incinerators, providing a means of concentrating the gas stream prior to destruction and lowering the overall amount of energy required for combustion. For example, a pollutant in dilute concentrations can be adsorbed onto carbon, then desorbed using hot air. By the adsorption/desorption cycle, the concentration of pollutant in the air can be increased significantly, decreasing the volume of air that must be heated to the combustion temperature [20].

Adsorption is well suited for organic compounds which have molecular weights in the range of 40 to 130 [21, 22] and boiling points in the range of approximately 290 to 420 K (21 to 150 °C, 70 to 300 °F) [10]. These compounds have high enough boiling points to be adsorbed (compounds that are gases at room temperature are not adsorbed to a substantial amount) [23] and low enough boiling points to be removed from the adsorbent. Adsorption is similar to the process of distillation [3] in that heavier compounds are retained better than lower boiling compounds and remain in the carbon, much as they would remain on the lower trays of a distillation column. By this process, the heavier, higher-boiling compounds replace the lighter weight, lower boiling compounds that are adsorbed. The higher boiling compounds are also more difficult to displace during regeneration, so they tend to accumulate in the bed. The presence of such compounds occupies active space in the pores and decreases the efficiency of the carbon bed. This is particularly a problem in processes where lubricating oils are used; even very small concentrations of lubricant can significantly affect the performance of a carbon bed [7]. It is generally accepted that adsorption in the carbon bed occurs only within a fairly small zone called the mass transfer zone or MTZ [13, 24]. The size of the MTZ depends on the velocity of air through the carbon bed, the pollutant characteristics, the temperature and pressure, and the humidity. Air is usually fed down through the carbon in the adsorber to avoid fluidizing the bed, to avoid creating channels for the air to bypass the carbon, and to avoid abrading the carbon any more than necessary. As vapor first enters the top surface of the carbon, the majority of the pollutant is removed from the gas stream before the gas travels very far into the bed. Mass transfer may actually only occur in the top three or four inches of carbon [9]. In the active adsorption zone, an equilibrium is reached between the gaseous molecules which impinge and are retained on the surface and those which are in the gas phase. There is a constant process of adsorption and desorption as molecules move. The equilibrium ratio of the amount of pollutant adsorbed to the partial pressure of pollutant in the gas stream at a constant temperature is represented by an *isotherm*. Isotherms of some typical pollutants are shown in Figure 4-3 [25, 26].

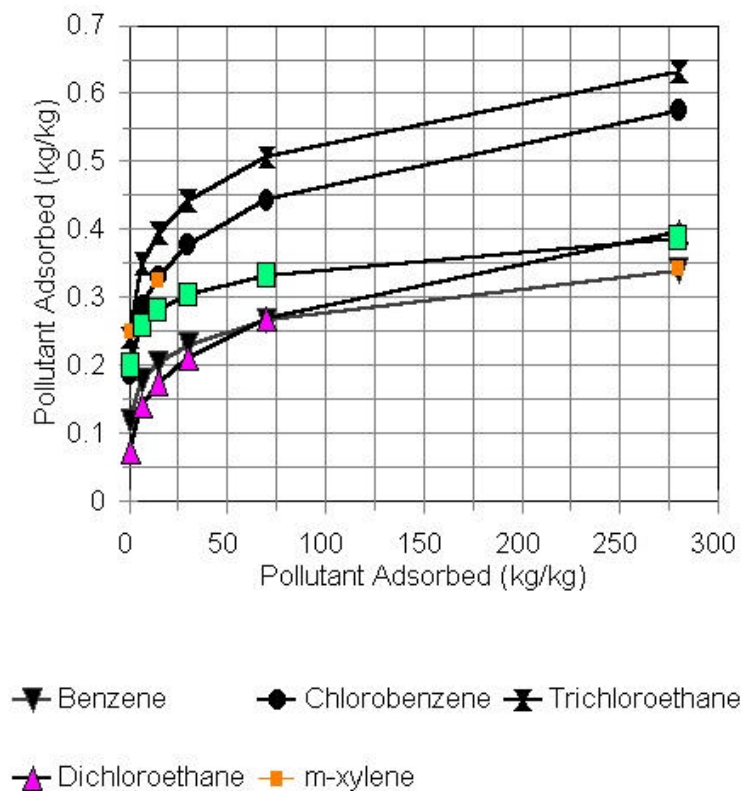


Figure 4-3. Isotherms of Typical Pollutants at 298 K (25 °C, 77 °F) [25, 26]

Figure 4-4 [25] depicts the change that occurs in the pollutant concentration at various depths in the bed as time progresses. At the beginning of the adsorption cycle (curve “a”), the bed immediately starts adsorbing pollutant, and the concentration declines rapidly over a very shallow portion of the bed (the *critical bed depth*, L_c). As the top layers become saturated, the concentration of pollutant in those layers becomes the same as the incoming gas. But there is relatively fresh carbon which has not been exposed to high concentrations of pollutant below the saturated layer. The mass transfer zone (represented by T_c in the diagram) shifts down, and the adsorption continues (the same process is depicted in Figure 4-5 [13]). By this process, the mass transfer zone works its way down the bed until its leading edge comes to the bottom of the carbon bed (curve “b” in Figure 4-4). This point, at which the concentration of organic in the exhaust stream begins to rise rapidly, is referred to as the *breakthrough point*. That is, the point at which the mass transfer zone is exiting the carbon bed, and (virtually) complete adsorption of the pollutant is no longer occurring.

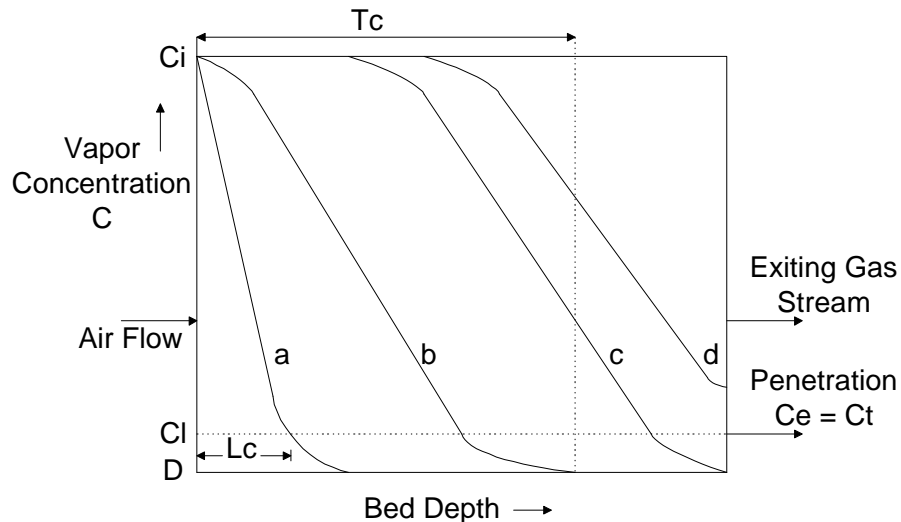


Figure 4-4. Progress of Adsorption Mass Transfer Rate Through the Bed (adapted from [25])

The mass transfer zone concept makes it evident that, at any given time, only a small portion of the carbon is actually being used in the adsorption process; there is carbon which has not yet encountered the mass transfer zone and carbon which is saturated, but only a few inches of the carbon may actually be in use. Since stationary carbon beds can be several feet deep [27], there is a substantial amount of carbon which is needed to maintain a reasonable adsorption cycle time, but is not in active use.

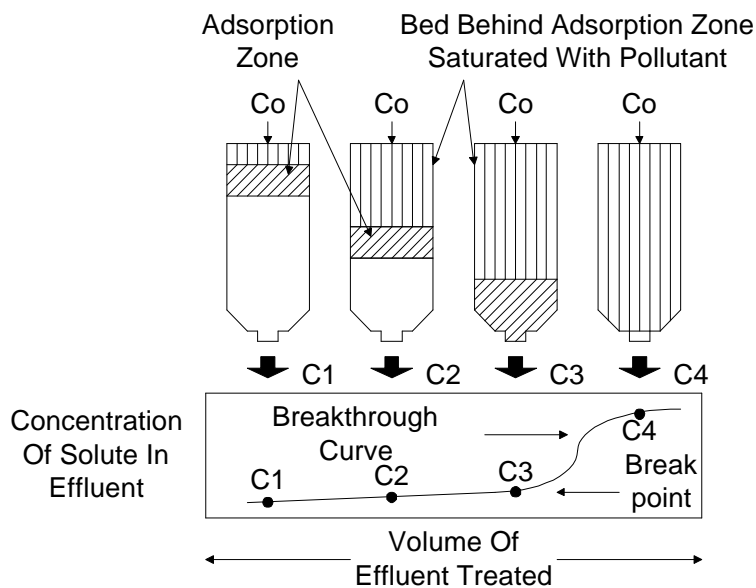


Figure 4-5. Flow of the Mass Transfer Zone Through the Bed [13]

The length of the mass transfer zone is determined by the pollutant characteristics, inlet concentration, and velocity through the bed. The amount of time that the bed can adsorb before reaching the “breakthrough” point can be calculated from the following equation [25]:

$$t_p = \left[\frac{w_p w_c}{C_m Q} - \frac{\rho Q}{K} \ln \left(\frac{C_m}{C_t} \right) \right] \quad 4-1$$

where: t_p = breakthrough time, min

w_p = capacity of carbon to adsorb pollutant, kg pollutant/ kg carbon (lb pollutant/lb carbon)

w_c = weight of carbon, kg (lb)

C_m = inlet concentration, kg/m³ (lb/ft³)

Q = actual flowrate, m³/min (ft³/min)

ρ = density of activated carbon, kg/m³ (lb/ft³)

K = pseudo first order reaction rate constant derived experimentally

C_t = breakthrough concentration kg/m³ (lb/ft³)

Operation of the carbon bed can be optimized using the amount of carbon, type of carbon, carbon replacement schedule, and bed depth to diameter ratio as variables. For large installations, collection of experimental data and pilot studies are essential to optimize these variables.

Types of Adsorption Systems

The conventional adsorber vessel (Figure 4-6) is a fairly long cylinder which may be installed in either a vertical or horizontal position [23]. The bed of adsorbent material is several feet thick and is suspended on a screen. Vapor laden air flows down through the bed.

Regeneration steam is frequently introduced from the bottom of the vessel. Several other types of adsorber vessels have been developed to maximize contact of the adsorbent with the gas stream and to minimize the amount of carbon in the system.

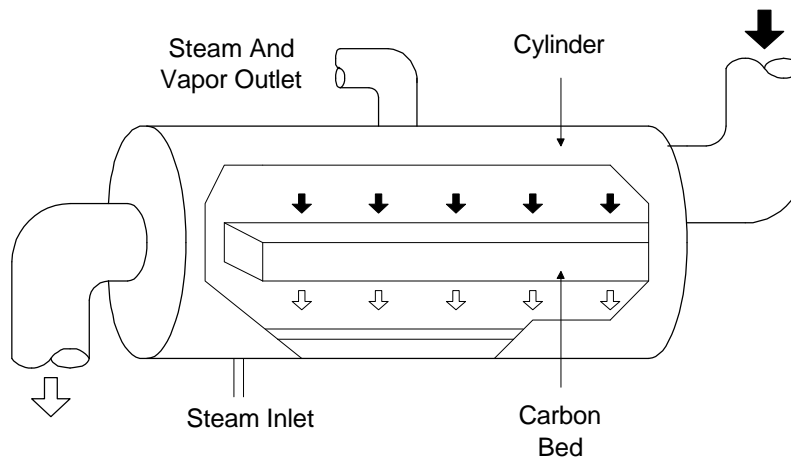


Figure 4-6. Conventional Adsorber Bed (adapted from [2])

Moving bed adsorbers are similar to fixed bed adsorbers, but the carbon is usually contained in a hollow cylinder or a disk-shaped packed bed (see Figure 4-7) [2, 28]. While one section of the carbon is adsorbing, another section is being steamed.

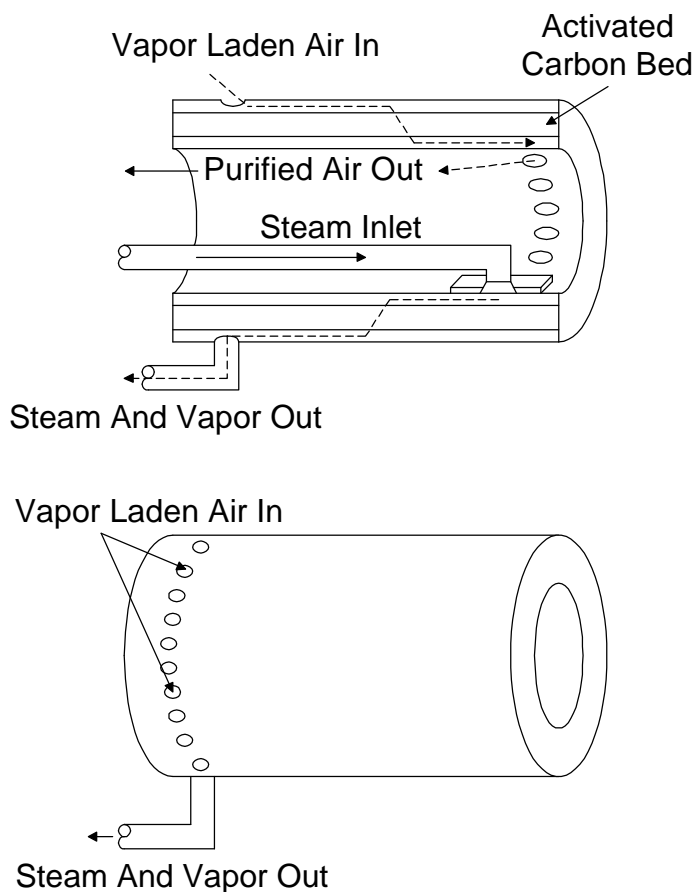


Figure 4-7. Moving Bed Adsorber [redrawn from 2]

Another type of adsorber designed to minimize the amount of carbon is the fluidized bed adsorber, (Figure 4-8 [11]). In a fluidized bed adsorber, the gas flows up through the carbon and suspends it. The carbon, which is in intimate contact with the gas stream, adsorbs the pollutants and works its way down the column and is replaced by recycled carbon introduced at the top of the adsorber. A regenerative section is also included in the fluidized bed; it may be at the top of the fluidized bed so that carbon is regenerated immediately before entering the adsorbing section [29], or it may be at the bottom of the adsorption section [3]. Table 4-2 gives a list of instrumentation that should be considered for adsorption systems.

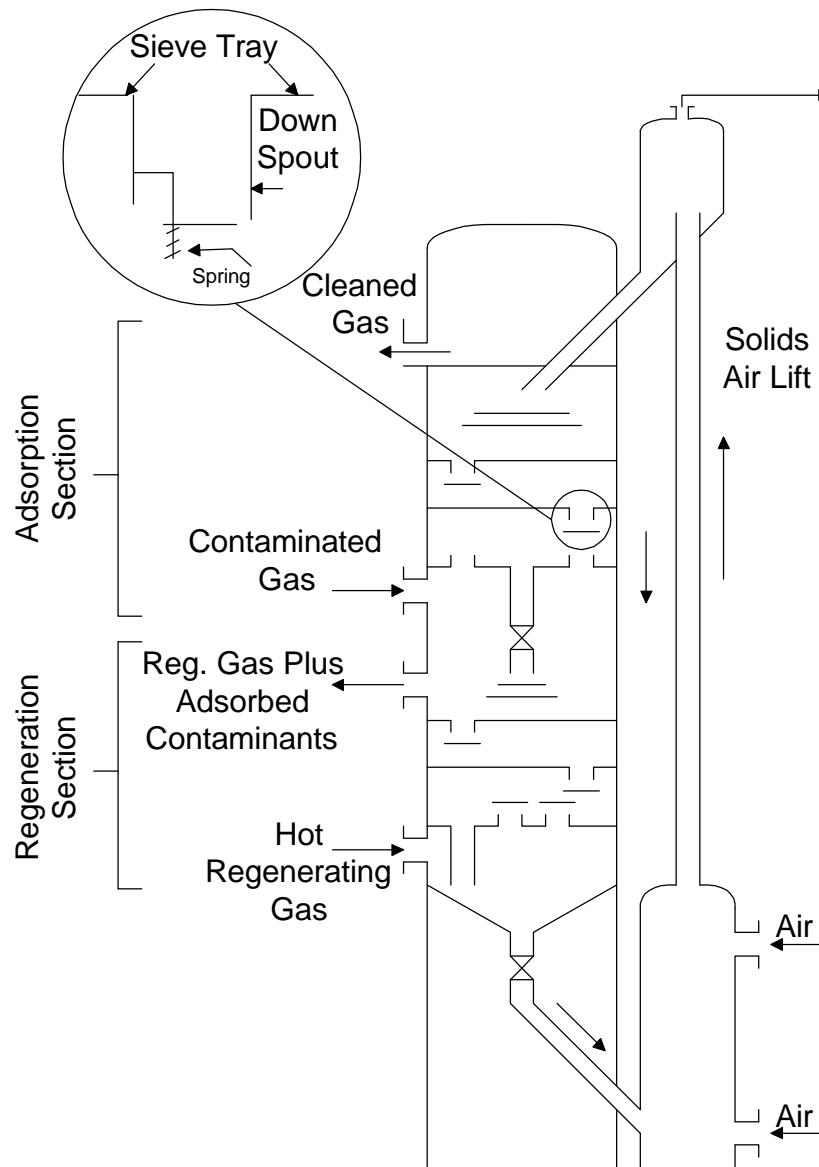


Figure 4-8. Fluidized Bed Adsorber (adapted from [11])

Table 4-2. Instrumentation to Consider for Adsorption Systems

Gas stream temperature and pressure (inlet and outlet)
Fan speed
Outlet concentration
Bed temperature
Humidity

Adsorption System Design

For continuous processes in which regenerative adsorption is used, several adsorbers are installed in parallel so that one or more are always available for adsorption while used ones are

regenerating (see Figure 4-9). It is also advantageous to operate the system in a “cooling” mode [30] in which the adsorber that has just finished steaming is not put directly on line, but takes the exhaust gas from an active adsorber. Routing the exhaust gas from the primary adsorbing bed through the “cooling” bed accomplishes two things. First, the relatively cool air serves to remove the heat from the steamed bed and dries it out, so that sites are available for organic vapor adsorption instead of being occupied by water molecules. Second, as the primary adsorbing bed becomes saturated and the exhaust concentration starts to rise, the exhaust gas is still being routed through the “cooling” bed. Since the cooling bed by this point in the cycle, is cooled and almost dry, it provides a clean bed to adsorb any residual organics before they are exhausted. Once the adsorbing bed reaches the breakthrough point (the point at which the concentration of organic compounds in the exhaust begins to increase dramatically), it is taken off line and steamed. Similarly, the bed that was in the “cooling” mode switches to be the primary bed for adsorption and the bed that was steaming begins the cooling cycle.

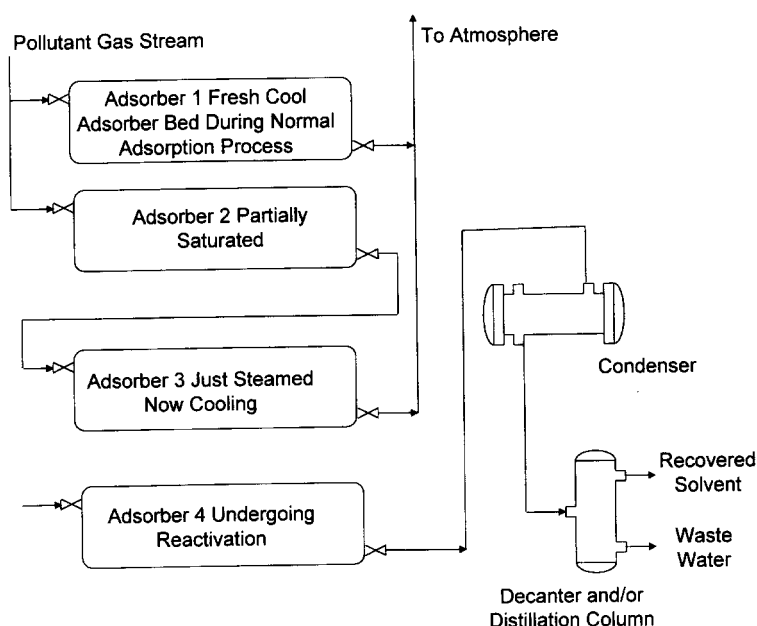


Figure 4-9. Schematic Diagram of the Cooling Cycle (adapted from [20])

In any regenerative adsorption system, some amount of pollutant remains in the adsorbent after regeneration is complete. This leftover portion is referred to as the “heel.” The magnitude of the heel can be changed by adjusting the temperature, pressure, length of the regeneration step, or by using activated carbon from a different source, but it is economically unfeasible to eliminate it altogether. A balance must be struck between the amount of heel left in the solid and the amount of steam used for the desorption. It is not cost effective nor possible under normal time constraints to continue the steaming past an optimum time at which the vast majority of the adsorbate has been removed.

In addition to the amount of adsorbent available, the type of adsorbent also significantly impacts the effectiveness of the system. A wide variety of solids are available for use in adsorption systems. The most common is activated carbon, also referred to as activated charcoal. Due to its non-polar nature, it is the adsorbent best suited for most VOC abatement systems, and is the only

one discussed in the remainder of this section. Other adsorbents include silica gel; zeolites (or molecular sieves), which have a very precise crystal structure and pore size; and carbon molecular sieves [31], an activated carbon made from polymeric materials which also has uniform pores.

The phenomenon in which higher boiling compounds replace low-boiling compounds has led to the development of “sacrificial” or “suicidal” carbon beds. These are beds which are placed in front of another control device to remove heavier compounds which might otherwise destroy the final control equipment [6]. The sacrificial bed is replaced or regenerated well before breakthrough of the heavier compound occurs. One potential application for such a system is in the manufacture of ammunitions containing nitroglycerine. Organic solvents used in the production of propellants are driven off by evaporation. In propellant formulas which also contain nitroglycerine, the nitroglycerine is also emitted, making it unsafe to collect or control the solvent emissions. It has been suggested that a sacrificial bed could be used to collect the heavier nitroglycerine vapors. This would be followed by a separate carbon bed to recover the other solvents. Such a system would also have to include an acid bath or other means of destroying the nitroglycerine once it accumulates in the carbon, but the sacrificial bed offers an alternative to the current method of exhausting the vapors without control [32].

There are several methods to determine the appropriate size of a carbon bed. One of the simplest methods, given by Vatauvuk [26], uses Freundlich isotherms to predict the amount of carbon necessary to accomplish the desired removal. The following equation is used to determine the maximum amount of pollutant which can be adsorbed onto the carbon under a given set of conditions:

$$w_e = k(C_F P)^m \quad 4-2$$

where w_e = the maximum amount of pollutant that is adsorbed under the given conditions, expressed as kg (or lb) of adsorbate/ kg (or lb) of adsorbent,
 C_F = conversion factor equal to 1.45×10^{-4} for pressures in Pa (1 for pressures in psia)
 P = partial pressure of the pollutant in kPa (or psia), and
 k, m = pollutant specific isotherm parameters (see Table 4-3 [26, 33]). Values should not be extrapolated outside of the applicable range listed in the table.

The total amount of pollutant to be removed from the gas stream is calculated by the following equation:

$$M = C * A * MW / F \quad 4-3$$

where:

M = Mass of pollutant to be adsorbed, kg/hr (lb/hr),
 C = Concentration of pollutant, ppmv (ppmv)
 A = Air Flow, Nm³/hr, corrected to 0 °C, (scfm, the air flow corrected to 70 °F), and
 MW = Molecular weight of pollutant, kg/kg-mole (lb/lb-mole)
 F = Conversion factor of 2.24×10^7 (6.42×10^6)

Once the amount of pollutant to be adsorbed is determined, the required amount of carbon is calculated by dividing the mass of pollutant (M) by the mass loading (w_e). Since the resulting carbon requirement represents the amount needed to adsorb the pollutant under ideal equilibrium

conditions, a safety factor of 100% is customary [26]. Therefore, the total amount of carbon in the system is generally twice that which would be required under ideal conditions.

Other design equations and procedures are given by LeVan, Carta, and Yon in Perry's Chemical Engineers' Handbook [34], and Buonicore and Theodore [11, 35]. Although these procedures can be used for initial cost estimates and to estimate the size of the adsorbers, empirical data is essential to proper design of a carbon adsorption system [36]. Any potential application should be tested on a lab scale, not only to determine the feasibility and efficiency which can be achieved, but also to evaluate the effectiveness of various carbons for the given application. Two carbons of the same size, even if produced from the same raw material using the same process, but at different plants, will behave differently in the same recovery system [7]. For the best performance, different types of carbons should be tested with the VOC of interest to determine not only the efficiency with which each adsorbs the compound, but also the degree of desorption that can be accomplished, the susceptibility of the carbon to abrasion, and the incremental pressure drop through the carbon.

Table 4-3. Isotherm Parameters [26]

Adsorbate	Ads.Temp			Isotherm Parameters		Applicable Partial Pressure Range	
	K	°C	°F	k	m	Pa	psia
Benzene	298	25	77	0.597	0.176	0.7-340	0.0001-0.05
Chlorobenzene	298	25	77	1.05	0.188	0.7-70	0.0001-0.01
Cyclohexane	311	38	100	0.508	0.210	0.7-340	0.0001-0.05
Dichloroethane	298	25	77	0.976	0.281	0.7-280	0.0001-0.04
Phenol	313	40	104	0.855	0.153	0.7-210	0.0001-0.03
Trichloroethane	298	25	77	1.06	0.161	0.7-280	0.0001-0.04
Vinyl Chloride	311	38	100	0.200	0.477	0.7-340	0.0001-0.05
m-Xylene	298	25	77	0.708	0.113	0.7-7	0.0001-0.001
	298	25	77	0.527	0.0703	7-340	0.001-0.05
Acrylonitrile	311	38	100	0.935	0.424	0.7-100	0.0001-0.015
Acetone	311	38	100	0.412	0.389	0.7-340	0.0001-0.05
Toluene	298	25	77	0.551	0.110	0.7-340	0.0001-0.05

Economic Estimates

Capital costs of the adsorption system are dependent on the gas flow, concentration, and the required efficiency. A procedure for estimating the installed capital cost of an adsorption system is given in the OAQPS Control Cost Manual [26]. Any estimates derived from these calculations should be checked with a vendor for confirmation. The estimates also need to be scaled up to current values. Scaling factors can be found on the EPA CATC website at <http://www.epa.gov/ttn/catc>. Once the total amount of carbon that is required and the number of adsorbers to be used in the system is determined, the capital cost of each adsorber vessel can be calculated based on the surface area of each vessel, according to the equations given below. Note that the equations are based on the amount of carbon in each vessel and the gas flow rate through each actively adsorbing vessel. In SI units, the vessel diameter is calculated from:

$$D = 7.93 \times 10^{-3} M_{CA} v_b / Q_A \quad 4-4$$

In English units, the equation is:

$$D = 0.127 M_{CA} v_b / Q_A \quad 4-5$$

where: D = diameter of the required adsorber vessel, (or ft)

M_{CA} = mass of carbon in each adsorber, kg (or lb)

v_b = superficial velocity through the bed, m/min (ft/min)

Q_A = actual flowrate of gas through each adsorber that is on-line, m³/min (acfm)

The adsorber length is calculated in SI units from the equation:

$$L = 126 Q_A^2 / (M_{CA} v_b^2) \quad 4-6$$

In English units, the equation is:

$$L = 7.87 Q_A^2 / (M_{CA} v_b^2) \quad 4-7$$

where: L = length of the adsorber vessel, m (or ft)

Once the diameter and length of the vessel are determined, the surface area is calculated from the following equation:

$$S = \pi D (L + D/2) \quad 4-8$$

where: S = surface area, m² (or ft²)

Then the vessel cost is estimated from:

$$C_V = 9.71 S^{0.778} \text{ for SI units} \quad 4-9$$

$$C_V = 271 S^{0.778} \text{ for English units} \quad 4-10$$

where C_V is the cost of each vessel in fall, 1989 dollars

These estimates are valid for horizontal adsorbers made of 304 stainless steel which are larger than approximately 0.7 to 1 meters (2 to 3 feet) in diameter, with surface areas between 9 and 196 m² (97 and 2110 ft²). Other materials of construction may significantly alter the cost. See Chapter 3 for factors for other metals. The cost of ductwork, stacks, pumps, fans, condensers, instrumentation, piping, and a decanter are not included in this cost. The ratio of the total system cost (with the exception of instrumentation and site specific requirements such as long ductwork) to the vessel costs are estimated from the following formulas.

In SI units:

$$R_C = 3.62 Q^{-0.133} \quad 4-11$$

In English units:

$$R_C = 5.82 Q^{-0.133} \quad 4-12$$

where R_C = ratio of total equipment cost to adsorber cost
 Q = actual flowrate of entire system, m^3/min (or ft^3/min)

The total system cost can then be estimated from:

$$CC = R_C (N C_C M_{CA} + N C_V) \quad 4-13$$

where CC = capital cost of adsorption equipment
 N = number of vessels required
 C_C = Cost of carbon, approximately \$4.40 / kg (\$2/lb) in fall 1989 dollars

The total capital investment can be estimated from the factors in Table 4-4. Particulate removal devices and site-specific construction requirements are not included. If the adsorption system is to be placed a long distance from the generation site, both the cost of additional ductwork and the cost of additional booster fans should be included in the cost estimate. As with the other chapters in this book, the cost estimates are to indicate a general order of magnitude. They are not specific enough to use as construction costs and should be confirmed with actual prices from vendors. Annual costs may be approximated using the guidelines in the OAQPS Cost Control Manual [26], as given in Table 4-5. Expected pressure drop through a bed of 4 x 10 mesh Calgon "PCB" carbon can be estimated as [26, 33]:

In SI units:

$$\Delta P_b = (2.12 \times 10^{-4} v_b + 2.03 \times 10^{-6} v_b^2) 0.0333 M_{AC} / (L D) \quad 4-14$$

in English units:

$$\Delta P_b = (0.03679 v_b + 1.107 \times 10^{-4} v_b^2) 0.0333 M_{AC} / (L D) \quad 4-15$$

where ΔP_b = pressure drop through the adsorber bed, kPa (or in of water column)

Table 4-4. Factors for Estimating the Total Installed Capital Cost of Adsorption Systems
[26]

<i>Cost Element</i>	<i>Estimated Cost</i>
<i>Direct Costs</i>	
Purchased Equipment Cost	
Adsorber system and Auxiliary Equipment	CC, Estimated from equation
Instrumentation	0.10 CC
Taxes	0.03 CC
Freight	0.05 CC
Total Purchased Equipment Cost, PEC	1.18 CC
Installation Costs	
Foundations and Supports	0.08 PEC
Erection and Handling	0.14 PEC
Electrical	0.04 PEC
Piping, Insulation, and Painting	0.04 PEC
Total Installation Cost	0.30 PEC
Site Preparation	As required for specific site, SP
Buildings	As required for specific site, BLDG
<i>Total Direct Costs</i>	<i>1.30 PEC + SP + BLDG</i>
<i>Indirect Costs</i>	
Engineering and Supervision	0.10 PEC
Construction, Field Expenses, and Fees	0.15 PEC
Start-up and Performance Test	0.03 PEC
Contingency	0.03 PEC
<i>Total Indirect Costs</i>	<i>0.31 PEC</i>
<i>TOTAL INSTALLED CAPITAL COSTS, TCC</i>	<i>1.61 PEC + SP + BLDG</i>

In addition to the pressure drop calculated above, 0.25 kPa (1 in of water column) should be included to account for losses through the ductwork. If long or complex ductwork is used, the miscellaneous pressure drop could be much higher. Electricity requirements can then be estimated from the following formulas.

In SI units:

$$\text{Power} = 1.65 \times 10^{-2} Q \Delta P / \eta \quad 4-16$$

In English units:

$$\text{Power} = 1.17 \times 10^{-4} Q \Delta P / \eta \quad 4-17$$

where: ΔP = pressure drop across the entire system, kPa (in of water column)
 η = combined efficiency of motor and fan, usually 35-65%

Operating and maintenance labor requirements are usually minimal, at approximately one half hour per shift each.

Table 4-5. Annual Operating Costs for Adsorption Systems [26]

Direct Annual Costs	Unit Cost	Estimated Requirement
Utilities:		
Electricity	\$0.05/ kWh	Calculated above
Steam	\$13/1000 kg \$6/1000 lb	3 to 4 kg steam /kg of VOC adsorbed (lb steam /lb VOC adsorbed)
Cooling Water	\$40 to 80/1000 m ³ \$0.15 to 0.30/ 1000 gallons	3.43 times the steam requirement
Operating Labor	\$12.96/h	½ hour per shift
Maintenance Labor	\$14.26/h	½ hour per shift
Maintenance Materials	Equal to maintenance labor	
Supervisory Labor	15% of Operating Labor	
Replacement Carbon	\$4.40/kg * 1.08 (shipping and taxes) * CRF ₅ (see below for calculation, assuming a five year life) \$2.00/ lb* 1.08* CRF ₅	Carbon requirement calculated above
Replacement Carbon Labor	CRF ₅ * \$0.11/kg CRF ₅ * \$0.05/lb	Carbon requirement calculated above
<i>Indirect Annual Costs</i>		
Overhead	60% of Maintenance Costs	
Property Tax	1% of TCC	
Insurance	1% of TCC	
Administrative Costs	2% of TCC	
Capital Recovery (CRF = $i(1+i)^n/[(1+i)^n-1]$ where i = pretax marginal rate of return n = economic life of equipment, usually 10 to 20 years)	CRF * TCC	
<i>Total Annual Operating Costs</i>	<i>Direct + Indirect Operating Costs</i>	

Potential Problems

Proper operation of an adsorption system depends on adequate contact between the adsorbent and the adsorbate. Sudden changes in air velocity or poor provisions for air distribution in a carbon bed can result in turbulent air flow patterns in which the adsorbent is physically moved and a hollowed spot in the bed results. Air flows more readily through the thin spot in the bed, so that portion of the carbon quickly becomes saturated and the overall capacity of the adsorption system is decreased significantly. Such a problem can be detected if the system is equipped with an analyzer and recorder of the organic vapor concentration in the exhaust from the adsorber. Normally, such analyzers are used to monitor exhaust concentration from each bed at the very end of the cycle. However, for suspected problems, the analyzer should be capable of

continuously measuring the exhaust concentration from any one bed, so that problems can be identified and isolated as quickly as possible. The normal exhaust concentration curve will start high when the bed is wet, but will quickly decrease as the bed dries out and begins to adsorb. It will reach a minimum where it should remain until just before the adsorber is removed from service for regeneration. At that point, the curve will increase very sharply as breakthrough occurs. By comparing the shape of the concentration curve in a troublesome adsorber with the anticipated shape, conclusions about what might be wrong can be made without having to remove the adsorber from service. For example, if the curve comes down steeply when the adsorption is initiated but starts back up gradually, it may indicate that there is a thin spot in the bed, allowing the polluted gas to bypass the majority of the bed. Once the carbon in the thin spot becomes saturated, the removal efficiency starts to decline. If the curve never reaches the anticipated minimum, it may indicate that there are leaking steam valves so the bed is remaining wet all of the time or that there are leaking isolation valves that allow untreated air to be directly exhausted instead of traveling through the adsorber bed.

The potential for fouling due to lubricant oils or other heavy organic contaminants has already been discussed. Another source of problems is particulate matter in the gas stream. Particulates also block access of the gases to the pores and cause a gradual increase in pressure drop as they accumulate in the bed. In gas streams where solids are likely to be present, a simple particulate filter should be installed prior to the adsorbers [37].

As noted earlier, the presence of organic vapors, carbon, oxygen, and heat from regeneration raise concerns about the possibility of fires in the adsorption beds. It is advisable to ensure that anytime steam is used to regenerate carbon, the bed is adequately cooled before it is exposed to air. This is particularly important if high pressure steam is used to revitalize the carbon. The temperatures achieved in such a scenario are adequate to cause spontaneous combustion of the carbon if oxygen is available [38].

The heat and presence of the carbon can cause some compounds such as acrylic acid, phenol, 2-ethylhexanol, and toluene diisocyanate [6] to polymerize. Polymerized compounds are heavier than the original chemical and hence, more difficult to desorb from the carbon. As with other contaminants, the polymeric substance occupies available sites on the carbon and decreases overall effectiveness.

Installation, Operation, and Maintenance Considerations

Perhaps the most important detail in maintaining the efficiency of an adsorber unit is to eliminate any duct leakage or unnecessary dilution air. An equilibrium is established in the carbon as the gas makes its way through the bed. The equilibrium is concentration dependent, so if the pollutant is more dilute, not as much adsorbate will be retained on the carbon. Additional air also means that the gas must travel faster through the bed, and the retention time is decreased. This combination of factors makes the daily or weekly check for duct damage critical. In addition to the typical inspection for obvious holes or creases, old ducting should also be checked for structural integrity, since the duct can be abraded to only a very thin porous shell without noticeable damage [7]. The concentration in the ductwork should be routinely checked to ensure that it never approaches unsafe levels.

Temperature is another important factor in maintaining the equilibrium. The lower the temperature, the more pollutant is adsorbed in a given system [2]. Table 4-6 gives the overall advantages and disadvantages of adsorption systems.

Table 4-6. Advantages and Disadvantages of Adsorption Systems

Advantages	Disadvantages
Allows for recovery / concentration of the pollutant	Effectiveness is pollutant-specific, depends on vapor pressure of compound
Usually no additional pollutants formed	Potential corrosion with some organic solvents (ketones, halogenated compounds)
High efficiency over a wide range of concentrations and pollutants	Treatment of wastewater stream required

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Chapter 5

Absorption

Technology Description

Absorption (also known as *scrubbing*) is a process in which pollutants in a contaminated gas stream are dissolved into a solvent liquid stream by mass transfer [1]. The driving force is the difference in the partial pressure of the pollutant in the gas stream and the vapor pressure (or solubility) of the same component in the liquid. A low vapor pressure of the component in the liquid stream indicates that the component is less likely to come out of the liquid, and is therefore soluble [2]. Because this equilibrium establishes the effectiveness and size of the absorption equipment, it is very important that a solvent be chosen in which the organic contaminant is as soluble as possible. The size of absorption systems can also be minimized by using a liquid which results in a reaction with the pollutant. This process, called chemical absorption, reduces the concentration of pollutant in the liquid and drives the absorption toward completion [3]. The process which does not use a chemical reaction but relies on the solubility to remove the pollutant is called physical absorption.

Absorption systems are capable of removal efficiencies greater than 98% [3]. Because of their high efficiencies, they are frequently used to remove odorous compounds from gaseous streams. Applications for indoor air treatment have also been described in the literature [4]. Water is commonly used as the scrubbing liquid [5] or *sorbent*. For example, scrubbers are used at rendering plants to remove contaminants in the plant exhaust before it is released into the atmosphere [6]. In some cases, sea water, chlorine, hypochlorite, hydrochloric acid, sodium hydroxide, or sodium bicarbonate are added to enhance the scrubbing efficiency [7, 8]. Absorption systems are most suited to plants that already have an oversized wastewater treatment plant or pollutants which can be removed by simple chemical reaction with little effect on the chemical composition of the liquid stream. Simple absorber designs are also useful for streams that contain large amounts of particulate, since the particulate can more easily foul a packed bed. It is not usually possible to optimize removal of both particulate and gaseous components in the same vessel [9]. Table 5-1 lists some typical applications of absorption systems for air pollution control [7, 10, 11].

Table 5-1. Typical Applications of Absorption [7, 10, 11]

Odor Control in Rendering Plants or Fish Processing
Light Hydrocarbon Absorption at Petroleum Refineries
Plating Operations
Sewage Treatment Odor Removal
Organic Binder Emissions from Foundries

There are some significant disadvantages to absorption systems. The primary disadvantage is that absorption usually eliminates a problem with a contaminated gas stream only to create a contaminated liquid stream. The liquid must then be treated, either to recover the pollutant and reuse the liquid, or to dispose of the spent solvent.

Types of Absorption Systems

There are many types of absorber designs, each with unique methods of increasing the contact between the liquid and vapor phases. Some are vertical columns with packing (packed towers) or trays (sieve-plate, bubble cap, float-valve or impingement plate columns, all similar to those used for distillation or extraction columns), others are horizontal chambers with packing (cross-flow), open vessels (spray chambers), or agitated tanks with sparge pipes [12]. Packed columns can be further divided according to the direction of liquid flow: countercurrent or cocurrent.

A typical flow diagram of a countercurrent packed tower absorber is shown in Figure 5-1 (adapted from [13]). Countercurrent flow columns are similar to distillation columns; the vapor flows upward while the liquid flows down through the column. This provides for the longest contact time and therefore highest efficiencies. However, the columns are prone to fouling and have higher pressure drops than columns in which the gas and liquid flow in the same direction [14]. Even with pressure drops approximately twice that of a cross-flow absorber [15], the countercurrent packed tower is the most common type of absorber used in air pollution control applications because it is efficient, versatile, has a broad range of operability with relatively low pressure drop, and can be designed to handle corrosive fluids relatively inexpensively [2, 14, 16]. In this type of system, the vapor and liquid flow in opposite directions, so that the treated vapor exiting the absorber contacts the cleanest liquid [17]. This results in the greatest concentration difference between the vapor and liquid states that can be achieved in an absorber. The primary component in the system is a vertical cylindrical tower which contains ceramic, plastic, or metal packing. The tower itself may be metal or reinforced plastic. The packing is supported by a plastic or metal plate which allows for proper distribution of air. A “hold-down” plate or packing restrainer may also be at the top of the packing to keep packing in place during periods of high gas flow [17]. The liquid distribution system above the top of the packing consists of one or more spray nozzles, designed to spread liquid over the entire cross sectional area of the tower as evenly as possible. Liquid is collected at the bottom of the tower and may be recirculated to the tower with a pump. There may also be a demister at the top of the tower to remove droplets of liquid from the gas stream before it exits the scrubber. Some tall towers contain more than one section of packing, each with its own support plate and liquid distribution system. Multiple sections are used to reduce liquid channeling that can occur if the packing gets too high (above three meters or ten feet as a general guide) [18]. In addition to these components, it may be advantageous to have a particulate collector upstream of a packed tower scrubber to eliminate potential problems of poor liquid or gas distribution and elevated pressure drop which can be caused by buildup of particulate in the column. Packed columns can typically accommodate approximately 11.4 g/m^3 (5 grains/ft³ where 7000 grains equal one pound) of particulate if the particulate dissolves in the scrubbing liquor [19].

Countercurrent columns are designed to ensure that there is plenty of space for the gas stream and liquid stream to pass in the column. As the gas stream velocity increases through the column, it reaches a point where the liquid is actually prevented from flowing down the column in any significant amount. Instead the liquid builds up in the column. This phenomenon is referred to as “flooding” and must be avoided to ensure safe and effective column operation.

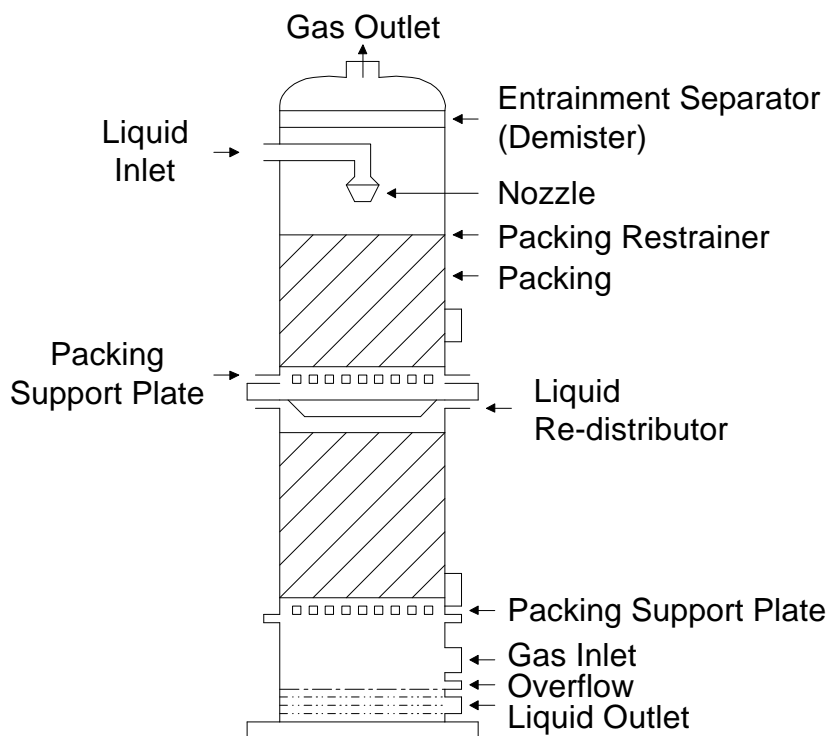


Figure 5-1. Countercurrent Packed Tower Absorber (adapted from [13])

In some countercurrent packed columns, a lightweight packing is used that is partially or completely fluidized by the gas stream. This type of scrubber is referred to as a mobile packing scrubber. In each stage, the plastic packing spheres are contained between two grids, approximately 0.6 to 1.5 m (2 to 5 feet) apart. For difficult separations, as many as five or more stages may be used. The movement of the spheres allows for solids to be flushed through the system and also permits the use of more viscous scrubbing liquids [15]. At air flows of 120 to 150 m/min (400 to 500 ft/min), the design has air flow capacities approximately 5-6 times that of a conventional packed or plate scrubber [7]. The associated pressure drop is approximately 0.5 to 0.75 kPa (2 to 3 inches of water) per stage [7].

Countercurrent columns may also have sieve plate or bubble cap trays instead of packing to provide for gas-liquid contact. Scrubbers containing sieve plate or bubble cap trays generally have a more narrow operating range than packed towers [20]. Sieve plates are horizontal disks that fit tightly in the tower. The liquid and gas pass through holes (typically 3 mm or 1/8 in diameter, placed about 10 mm or 3/8 in apart [21]) in the plates. The column may also have downcomers to allow the liquid to flow from plate to plate more easily. The plates are typically placed about 0.3 m (12 in) apart if there are no downcomers, 0.38 m (15 in) apart if the column has downcomers [18]. Sieve plates can be placed closer together in the column than bubble cap trays, since sieve plates normally only have about one third as much entrainment [22].

A bubble cap tray has a more complex structure which collect the gas coming up through a tray and

forces it back down into the liquid to establish good gas-liquid contact. Bubble cap trays are usually set about 0.46 m (18 in) apart [22]. It is important to maintain an even liquid level on both sieve plates and bubble cap trays so that there is equal resistance to gas flow across the entire cross sectional area of the absorber. Therefore, the plates should be level and bubble cap columns should have an adequate number of downcomers to ensure that the liquid head across each plate is even [21]. Typical pressure drops through these columns are approximately 0.5 to 1 kPa (2 to 4 in of water column) per plate or tray [16]. These absorbers are better suited to processes in which heat is evolved during solution of the pollutant in the liquid (ammonia in water, for example), since they can be designed with cooling coils between the plates. They are also better suited to gas streams with fouling tendencies or particulate matter, since they can be cleaned easier [23]. However, they are less suitable than packed columns for foaming liquids [12]. Additional information comparing high performance trays with structured packings is available [24].

In cocurrent columns, the gas and liquid flow in the same direction, usually downward through a packed column [14]. The amount of contaminant that can be removed from the vapor stream with this method is limited, since there is no supply of fresh liquid toward the end of the contact time to drive the equilibrium further toward removal of the contaminant from the gas stream. However, these vessels can handle more gas flow than countercurrent columns, since increased gas flow facilitates liquid flow through the column, and there is no possibility of flooding [25].

The gas in cross-flow vessels flows horizontally while the liquid flows downward through the packing as shown in Figure 5-2 [23]. It has both a low pressure drop and improved solids handling capability. Cross-flow vessels are currently used for pollutants with moderate - to high- solubility [14]. This type of scrubber effectively removes particulate which is 5 microns and larger from the gas stream [25].

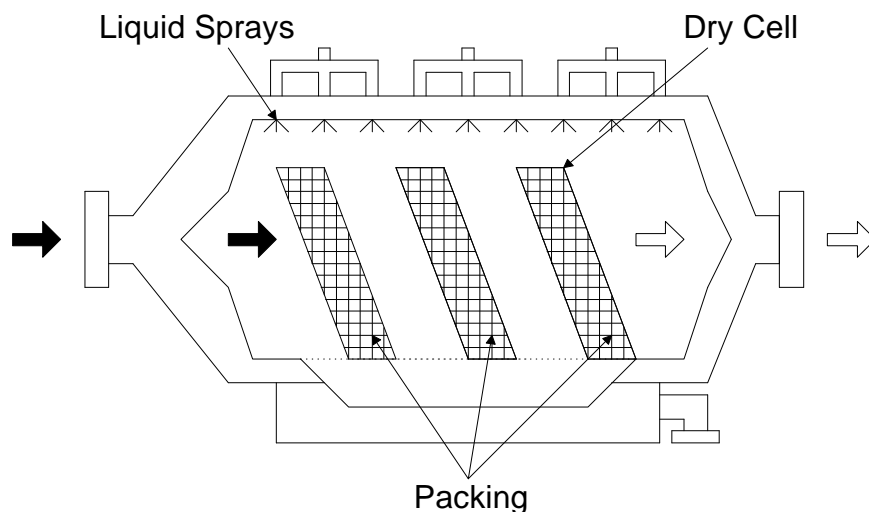


Figure 5-2. Cross-Flow Absorber [23]

Baffle towers are not common, but are a type of scrubber with simple contact mechanisms between the gas and liquid. The liquid cascades down through the column, flowing from one plate to the other as shown in Figure 5-3 [19]. The gas must pass through the liquid cascade as it makes its way up the column. Very little information is available on designing these types of columns [19].

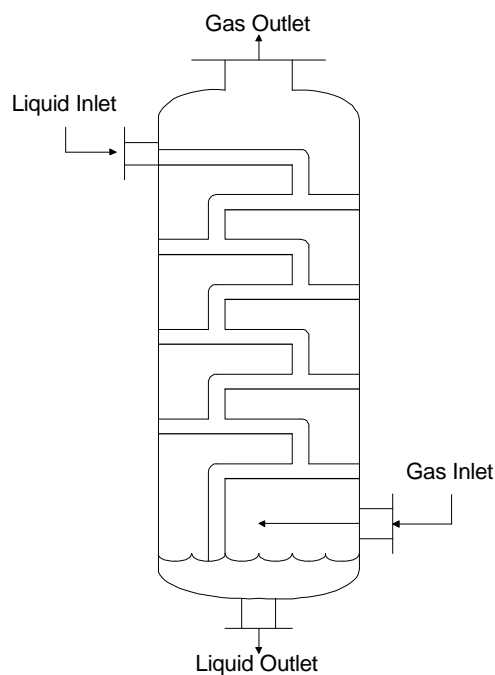


Figure 5-3. Baffle Tower [19]

Some equipment which has historically been used to remove particulate from gas streams is also occasionally used to remove very soluble organic compounds. Spray chambers may be vertical (as shown in Figure 5-4, adapted from [23]) or horizontal vessels which contain multiple levels of spray nozzles to provide a liquid mist or fog through which the gas passes. Figure 5-5 shows a venturi scrubber (redrawn from [23]), which operates by injecting liquid into gas stream. The liquid may be injected at a venturi, or it may be injected upstream of the venturi. The difference in velocity between the gas stream and the liquid droplets provide for contact between the phases. Although venturi scrubbers are well-suited for gaseous streams which contain a significant amount of particulate, they do not provide for long contact times and are therefore only suitable for use with very soluble compounds [26]. The venturi scrubber must be followed by a gas-liquid separation device; most installations have a cyclonic separator in which liquid droplets are removed by inertia.

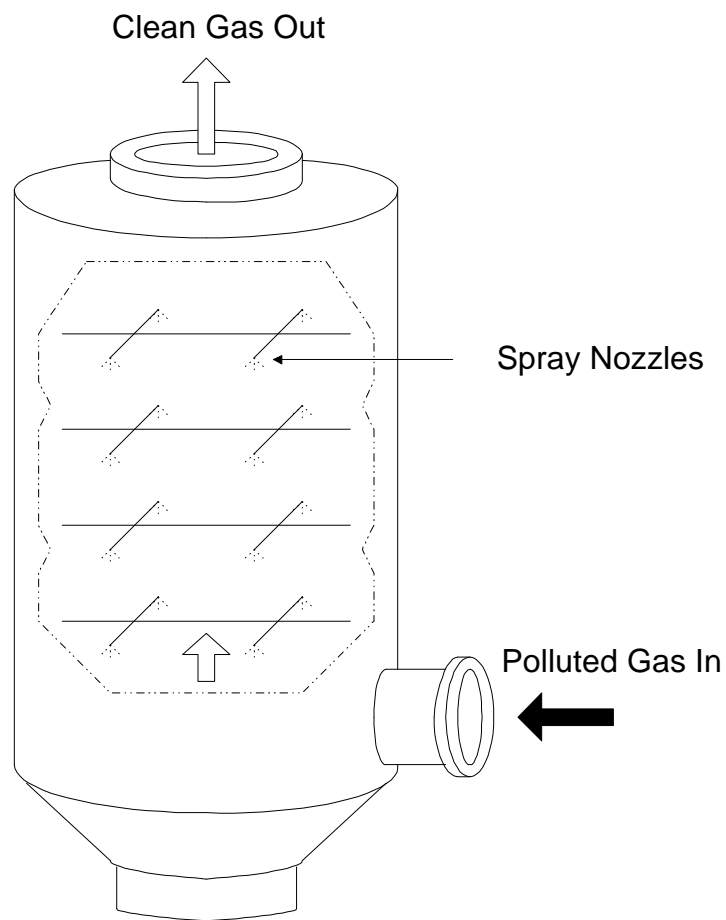


Figure 5-4. Vertical Spray Chamber (adapted from [23])

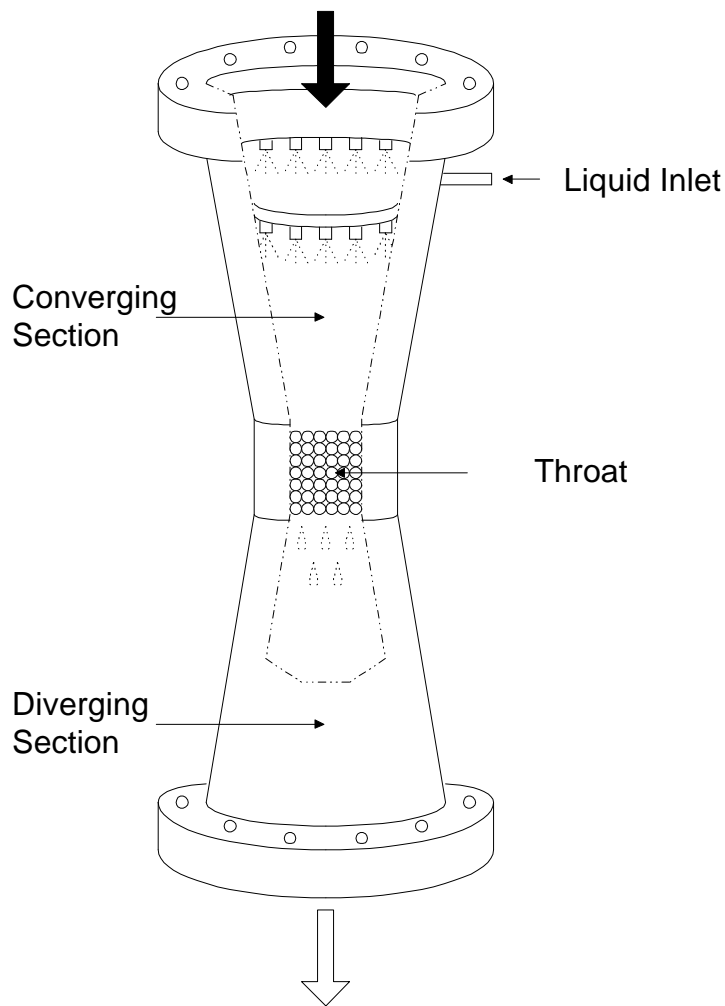


Figure 5-5. Venturi Scrubber (redrawn from [23])

Agitated tanks are also sometimes used as absorption vessels when the gas stream contains significant amounts of particulate [12]. The contact between the gas and liquid is enhanced by an agitator and baffle plates in the tank. Centrifugal absorbers, such as the one shown in Figure 5-6, have been used in Europe to remove contaminants from gas streams. These units contain a disk in the middle that spins at high velocity. The rotation of the disk forces liquid to spray into the gas stream, resulting in contact between the vapor and liquid gas streams [19].

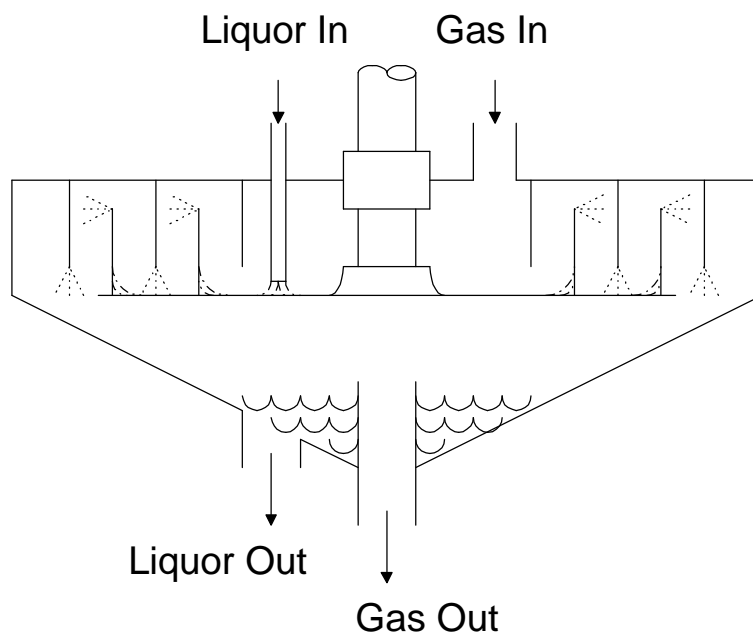


Figure 5-6. Centrifugal Absorber (redrawn from [19])

Absorption System Design

The design methods given here are for packed bed absorbers, since the majority of scrubbers are packed beds. They are included as general guides to facilitate understanding of absorption systems, to enable quick cost estimates, and to assist in identifying problems with existing absorption systems. Detailed design considerations are given in *Perry's Chemical Engineer's Handbook* [1, 27], *Indoor Air Quality and Control* [4], *Air Pollution Control Equipment, Volume II* [13], *Air Pollution Control and Design Handbook, Part II* [8], *Industrial Control Equipment for Gaseous Pollutants, Volume I* [22], *Odor and VOC Control Handbook* [28, 29, 30], *Kirk-Othmer Encyclopedia of Chemical Technology* [31], and the *OAQPS Control Cost Manual* [17], available on the internet at <http://www.epa.gov/ttn/catc/products.html>. Additional information useful in estimating tray efficiencies can be found in *Bubble Tray Design Manual* [32] and *Equilibrium-Stage Separation Operations in Chemical Engineering* [33]. Additional information on designing cross flow units can be found in "The Crossflow Scrubber – A Digital Model for Absorption" [34]. Formulas for calculating removal efficiencies of particulate in spray towers are given by Hesketh [35]. It is also advantageous to consult manufacturers in the design of any absorption system, since they can frequently offer specific experience with similar applications.

The efficiency of a given absorber is usually predicted using Henry's Law which relates the concentration of a compound in the liquid stream to the concentration (or partial pressure) of the compound in the gas stream at equilibrium [23]:

$$p_A = H x_A$$

5-1

where: A is the pollutant to be absorbed
 p_A = partial pressure of A in the vapor stream (molar concentration, mol/l or M),
 x_A = concentration of A in the liquid (molar concentration, mol/l or M), and
 H = Henry's Law Constant (molar concentration in gas/molar concentration in liquid, M/M)

Several Henry's law coefficients are given in Table 5-2 [36]. Additional information is given by Schwartz and White [37] and Martin [38]. A more comprehensive list of values is contained in *Sources and Control of Air Pollution* [39] and on the world wide web under <http://chemfinder.camsoft.com>. Various equations for Henry's law are used. When using Henry's law coefficients from other sources, care must be exercised to identify the units [21]. Some texts define a Henry's law coefficient which is the inverse of the one given here. Henry's law applies when the partial pressure of the pollutant does not exceed one atmosphere of pressure [40] and when compounds do not react during absorption. The coefficients are temperature dependent; they may be adjusted by van't Hoff's equation [41, 42] which simplifies to:

$$\ln \frac{H(T_2)}{H(T_1)} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad 5-2$$

where: ΔH = heat of solution of the gaseous pollutant, kJ/kmol
 R = Gas constant, 8.314 kJ/kmol K
 $H(T_1)$ and $H(T_2)$ = Henry's law coefficient at two different temperatures, and
 T_1 and T_2 = absolute temperatures.

This approximation is only valid when ΔH is relatively constant, that is, over relatively small temperature ranges.

Table 5-2. Henry's Law Coefficients [36]

Pollutant	Solvent	H, M (gas)/M (liquid)	Temp (K)
Acetylene (C ₂ H ₂)	Water	0.823	288
Ammonia (NH ₃)	Water	4.71 x 10 ⁻⁴	288
Ethane (C ₂ H ₆)	Water	17.2	288
Ethylene (C ₂ H ₄)	Water	6.82	288
Hydrogen Chloride (HCl)	Water	2.82 x 10 ⁻⁹	288
Hydrogen Sulfide (H ₂ S)	Water	0.322	288
Methane	Water	25.7	288
Ozone (O ₃)	Water	2.19	298
Propylene (C ₃ H ₆)	Water	3.86	288
Sulfur Dioxide (SO ₂)	Water	7.85 x 10 ⁻³	288

Lower Henry's law coefficients indicate improved solubility, since the pollutant is less likely to evaporate into the gas stream. The absorption efficiency is enhanced if the pollutant reacts with the liquid, thereby

decreasing the concentration of pollutant in the liquid and driving the absorption reaction toward completion. For this reason, weak acid solutions, caustic solutions, and ozone are sometimes used in scrubbers to improve the removal of organic compounds from a gas stream.

The selection of solvent is generally the first step in absorption design [13, 27]. Other important considerations in determining an appropriate solvent are [7, 13, 19, 26, 43]:

1. Solubility. The pollutant should be as soluble as possible in the liquid at the expected operating temperature to enhance the mass transfer rate [44].
2. Low volatility. The solvent should generally have a volatility less than approximately 0.1 mm Hg at the outlet temperature to avoid excessive evaporation of the solvent from the column [19]. Evaporation of the solvent can cause unnecessary operating expense, in addition to creating a different air pollution problem. The prominent exception to this is water, which is used in most absorption systems [5] because evaporation of water is not generally a significant cost or pollution issue, and other design considerations such as solubility and disposal outweigh the concerns.
3. Corrosivity. The solvent selected should have a low corrosivity if possible so that less expensive materials of construction can be utilized. In addition, the corrosivity of the pollutant and any reaction products between the pollutant and the solvent should be considered in determining appropriate construction materials.
4. Cost. Cost is an obvious concern for systems where the liquid is only used once. In some absorption systems, the solvent is continuously regenerated and reused by distilling the pollutant, by reacting it to form a removable solid, or by liquid-liquid extraction. Even though the liquid is recycled, there are inevitably losses through equipment leaks, cleaning, equipment blowdown, and degradation.
5. Availability. The liquid should be easy to obtain in a relatively short time period so that the equipment is not out of service if a column is accidentally released to a sewer or in case of a malfunction. For solvents which may have a long delivery time, it may be feasible to use an additional storage tank to ensure that there is always an adequate supply available.
6. Safety. To simplify the operating procedures and protect workers, the liquid should have as low a toxicity and flammability as possible.
7. Low viscosity. A low viscosity reduces electrical demands for pumping the liquid, reduces the column pressure drop which results in lower electrical demands for moving the gas stream, decreases the likelihood of exceeding the capacity of the column during periods of high gas flow (flooding), and increases the efficiency of the column by improving liquid distribution.
8. Stability. The liquid should not degrade with use or expected temperature.
9. Low melting point. A low melting point is desirable to keep the column from freezing in cold weather, particularly if the column is taken out of service.

Mineral oil, heavy hydrocarbon oils, and aqueous solutions are also used as sorbents in absorption systems [3, 45].

Before the overall size of the absorber can be determined, the packing material must be identified. The packing material will affect the degree of contact that can be achieved in the scrubber, and will affect the weight of the scrubber and the materials of construction. Packing may be “dumped” or structured. Despite the name, “dumped” packing is not randomly thrown into the absorber. It must be installed carefully to avoid breaking the packing and ensure that it is spread uniformly. Structured packing is generally stacked in the vessel. In addition to sophisticated dumped or structured packing material,

simple materials such as broken rock, coke, broken bottles, aggregate, marbles, and wood slats have also been used [8, 9, 15, 21]. The selected packing should provide for: maximum amount of wetted area per volume of packing, reasonable weight, chemical resistance to the gas stream and liquid stream constituents, good distribution of liquid and gas phases, minimal amount of liquid retained on the packing (holdup), low gas pressure drop through the packing, structural strength, design flexibility (to allow changes in operation without substantial effects on the removal efficiency), and low cost [21, 46]. The chosen packing should have a diameter less than about 1/30th of the column diameter [2], and it should not force the gas stream to contract or expand, since that would increase the pressure drop through the column unnecessarily [8].

The packing supports must have the physical strength to support the weight of the packing and liquid, they must be able to withstand the expected temperature and corrosivity of the gas and liquid streams, and they must provide adequate passage of the gas and liquid so that there is not a significant pressure drop. The support plates may be as simple as a grid or expanded metal plate, or they may be designed to separate the gas and liquid flows as in “gas-injection” support plates (see Figure 5-7) [8].

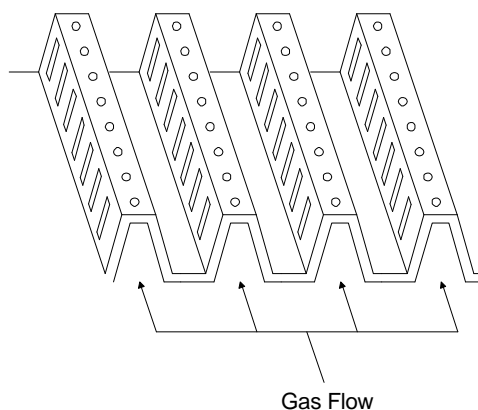


Figure 5-7. “Gas-Injection” Support Plate (adapted from [8])

An estimate of the absorber size can be obtained using US Stoneware’s correlation [9, 22, 47] once the liquid and gas mass flow rates have been determined. It is assumed that the gas flow rate, initial concentration, and required removal efficiencies are specified by the application. The concentration of pollutant in the liquid stream and exiting the column can then be determined from the Henry’s law correlation. It is usually assumed that the concentration of pollutant in the entering liquid stream is zero, although this can also be estimated from Henry’s law if the liquid is reused after recovery of the pollutant. Furthermore, the required liquid flowrate can be calculated by an overall mass balance from the overall amount of pollutant that must be removed and the final concentration of that pollutant in the gas stream. Assuming that the pollutant is the only constituent of the gas stream that is soluble in the liquid and that the solvent is nonvolatile, the minimum liquid to gas ratio can be determined from the following equations [17]. If the concentration of pollutant is more than a few percent of the volume, these assumptions are no longer valid.

$$Y_o = Y_i(1-100)$$

5-3

where Y_o = pollutant concentration in gas stream leaving adsorber, kg-mol pollutant/kg-mol pollutant free gas (lb-mol/lb-mol)

Y_i = pollutant concentration in gas stream entering adsorber, kg-mol pollutant/kg-mol pollutant free gas (lb-mol/lb-mol)

= removal efficiency, %

X_o^e = maximum concentration of pollutant in the liquid stream leaving the absorber, assuming that the liquid is in equilibrium with the gas stream entering the absorber, kg-mol pollutant/kg-mol pollutant free solvent (lb-mol/lb-mol)

X_i = concentration of pollutant in liquid stream entering the absorber kg-mol pollutant/kg-mol pollutant free solvent (lb-mol/lb-mol). Henry's law is generally valid for determining this value for small concentrations of pollutant.

The minimum liquid to gas ratio is then:

$$\left(\frac{L}{G}\right)_{\min} = \frac{Y_i - Y_o}{X_o^e - X_i} \quad 5-4$$

and the actual liquid to gas ratio can be calculated from:

$$\left(\frac{L}{G}\right)_{\text{act}} = \left(\frac{L}{G}\right)_{\min} AF \quad 5-5$$

where: L = molar flow rate of pollutant-free solvent, kgmol/h (lbmol/h)

G = molar flow rate of pollutant-free gas, kgmol/h (lbmol/h)

AF = adjustment factor to compensate for the fact that true equilibrium is not realistic, typically between 1.2 and 1.5 [48]

Once the pollutant-free liquid and gas flows are known, the total molar flowrate of the liquid and gas streams are calculated by the following equations:

$$G_{\text{mol}, T} = G(1+Y_i) \quad 5-6$$

$$L_{\text{mol}, T} = L(1+X_i) \quad 5-7$$

and the cross sectional area that is required for the expected gas and liquid flowrates is determined. The value of the following expression is calculated and located on the x-axis of the chart given in Figure 5-8.

$$\frac{L_m}{G_m} \left(\frac{\rho_G}{\rho_L} \right)^{0.5} \quad 5-8$$

where: L_m = Liquid Flowrate, mass per hour units

- G_m = Gaseous Flowrate, mass units per hour units, must correspond with those for the liquid flowrate [9].
- [23] ρ_G = density of gas stream, 1.17 kg/m³ (0.073 lb/ft³) for air at 303 K (30 °C, 86 °F)
- ρ_L = density of liquid stream, 1000 kg/m³ (62.4 lb/ft³) for water at 303 K (30 °C, 86 °F), units must correspond to those of ρ_G .

The point on the flooding line in Figure 5-8 is then located that corresponds to the abscissa value calculated above. The value on the y-axis which results is ϵ . Using this value, the following equation can be solved for G'_{flood} [23], using packing factors given in Table 5-3.

Using a packing factor in SI units:

$$G'_{\text{flood}} = \frac{1.81[\epsilon \rho_G \rho_L g_c]^{0.5}}{(F \phi \mu_L^{0.2})^{0.5}} \quad 5-9$$

With a packing factor in English units:

$$G'_{\text{flood}} = \frac{[\epsilon \rho_G \rho_L g_c]^{0.5}}{(F \phi \mu_L^{0.2})^{0.5}} \quad 5-10$$

- where: G'_{flood} = the mass flow rate of gas per unit of column cross sectional area which will just cause the column to flood, g s⁻¹m⁻² (lb s⁻¹ft⁻²)
- ϵ = the y-axis value from Figure 5-8.
- g_c = the gravitational constant, 9.82 m/s² (32.2 ft/s²)
- F = Packing Factor, m²/m³ (ft²/ft³)
- ϕ = ratio of liquid specific gravity to that of water
- μ_L = liquid viscosity, cP, 0.8 cP for water

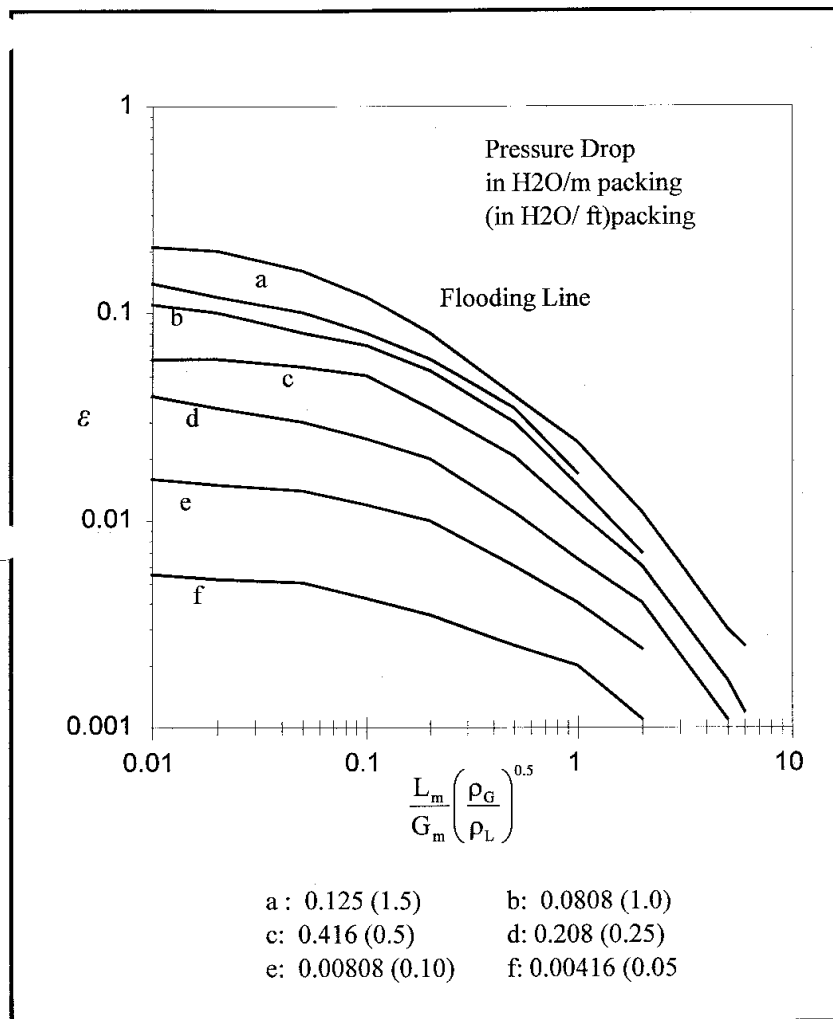


Figure 5-8. US Stoneware's Pressure Drop Correlation [23]

Table 5-3. Packing Data [17, 23, 46]

Packing	Size (in)	Weight		Surface Area		Void Fract.(%)	Packing Factor, F		Price (1990 \$)	
		(lb/ft ³)	(kg/m ³)	(ft ² /ft ³)	(m ² /m ³)		ft ² /ft ³	(m ² /m ³)	(\$/ft ³)	(\$/m ³)
Raschig Rings (Ceramic or porcelain)	½	52	833	114	374	65	580	1903		
	1	44	705	58	190	70	155	509	12.8	452
	1 ½	42	673	36	118	72	95	312	10.3	364
	2	38	609	28	92	75	65	213	9.4	332
	3	34	545	19	62	77	37	121	7.8	275
Raschig Rings (Carbon Steel)	½ x 1/32	77	1233	128	420	84	300	984		
	1 x 1/32	40	641	63	207	92	115	377	36.5	1289
	2 x 1/16	38	609	31	102	92	57	187	20.5	724
Raschig Rings (Stainless Steel)	1								155	5474
	1.5								117	4132
	2								87.8	3101
Raschig Rings (Carbon Steel)	1								52.0	1836
	1.5								46.2	1631
	2								33.9	1197
	3								31.0	1095
Berl Saddles (Ceramic or porcelain) prices given for porcelain	¼	55	881	274	899	63	900	2953		
	½	54	865	155	509	64	240	787		
	1	48	769	79	259	68	110	361	33.5	1183
	1.5	40	641	46	151	71	65	213	21.5	759
	2	38	609	32	105	75	45	148	15.6	551

Packing	Size (in)	Weight		Surface Area		Void Fract.(%)	Packing Factor, F		Price (1990 \$)	
		(lb/ft ³)	(kg/m ³)	(ft ² /ft ³)	(m ² /m ³)		ft ² /ft ³)	(m ² /m ³)	(\$/ft ³)	(\$/m ³)
Intalox Saddles (Ceramic)	¼	54	865	300	984	75	725	2379		
	½	45	721	190	623	78	200	656		
	1	44	705	78	256	77	98	322	17.6	622
	1.5	39	625	59	194	76	52	171	13.0	459
	2	42	673	36	118	79	40	131	11.8	417
	3	36	577	28	92	79	22	72	10.7	378
Intalox Saddles (Plastic) Prices given for polypropylene	1	6.00	96	63	207	91	30	98	21.2	749
	2	3.75	60	33	108	93	20	66	13.1	463
	3	3.25	52	27	89	94	15	49	7.0	247
Pall Rings (Plastic) prices given for polypropylene	5/8	7.0	112	104	341	87	97	318		
	1	5.5	88	63	207	90	52	171	21.2	749
	1.5	4.8	77	39	128	91	40	131	14.4	509
	2	4.5	72	31	102	92	25	82	13.1	463
Pall Rings (Steel)	5/8 x 0.018 thick	38	609	104	341	93	73	239		
	1	30	481	63	207	94	48	157		
	1 ½ x 0.03 thick	24	384	39	128	95	28	92		
	2	22	352	31	102	96	20	66		
Tellerettes	1	7.5	120	55	180	87	40	131		
	2	3.9	62	38	125	93	20	66	11.5	406
	3	5	80	30	98	92	15	49		
Tellerette pricing given is an average of prices from \$100 to 700/m ³ (\$3 to 20/ft ³)										

It is usually assumed that the column will operate at a gas flow between 50 and 75% of the flooding velocity [13, 22], although well-designed columns can operate at flows up to 90% of flooding [19]. The gas flow per unit area through the column under normal operating conditions can be estimated from the following equation [9]:

$$G'_{\text{oper}} = f G'_{\text{flood}} \quad 5-11$$

where G'_{oper} = mass flow of gas stream per unit area of column under normal operation, $\text{g s}^{-1}\text{m}^{-2}$ ($\text{lb s}^{-1}\text{ft}^{-2}$)
 f = acceptable fraction of flooding for normal operation, typically 0.6 [2, 22]

The required column cross sectional area can be obtained by [9]:

$$A = G / G'_{\text{oper}} \quad 5-12$$

where: A = Column cross sectional area, m^2 (ft^2)

Since absorption columns are usually round, the diameter is calculated from the formula for the cross sectional area of a circle [1]:

$$D = \sqrt{\frac{4A}{\pi}} \quad 5-13$$

where: D = Column diameter, m (ft)

The calculated column diameter should be rounded up to a readily available diameter. Increments of 0.15 m (or 1/2 foot) are common.

Typical liquid flow rates are approximately 0.04 to 2 m^3/min per square meter (1-50 gal/min per square foot) of column area. Superficial gas velocity through a packed tower is generally about 30 to 150 m/min (100-500 ft/min) [15].

For extremely soluble pollutants or pollutants which react with the scrubbing liquid, the number of theoretical stages (N_{OG}) can be estimated from [9, 17]:

$$N_{\text{OG}} = \ln (Y_1/Y_2) \quad 5-14$$

where Y_1 = mole fraction of pollutant in the entering gas
 Y_2 = mole fraction of pollutant in the exiting gas

The height of a theoretical transfer unit (H_{OG}) should be obtained from vendor information for the specific application, but it usually ranges between 0.3 and 1.2 m (1 and 4 ft). A rough estimate of 0.6 m (2 ft) can be used if necessary [9]. The total packing height is calculated from:

$$H_{\text{pack}} = N_{\text{OG}} * H_{\text{OG}} \quad 5-15$$

It may be necessary to install the packing in sections, each with a separate packing support plate and liquid distribution system in tall towers. Generally, packing is installed in sections three meters (ten feet) high. For columns packed with Raschig rings, the maximum depth of each section should be no more than approximately three column diameters, to a maximum of 3 to 5 m

(10 to 15 ft). For saddle packings, the depth of each section should be no more than approximately five to ten column diameters, to a maximum of 4 to 6 m (12 to 20 ft) [13].

Other important factors in designing an absorption system are to ensure that the liquid and gases are distributed evenly throughout the column. Otherwise, gas channeling can result, causing areas of low gas or liquid flow which cause losses in removal efficiency.

Two types of demisters are shown in Figure 5-9. While chevrons are frequently used, particularly in dirty gas streams, they are usually considered less efficient in removing small particles than mesh pads. The very small droplets (less than 5 μ m in diameter) are not captured as effectively as they are in a mesh pad, increasing the likelihood that water droplets will escape the collector. Demisters may be installed in horizontal or vertical piping; horizontal is preferred [21]. Figure 5-10 [8] gives a graphical representation of the range of droplet sizes and velocities that result in effective separation in a mesh pad.

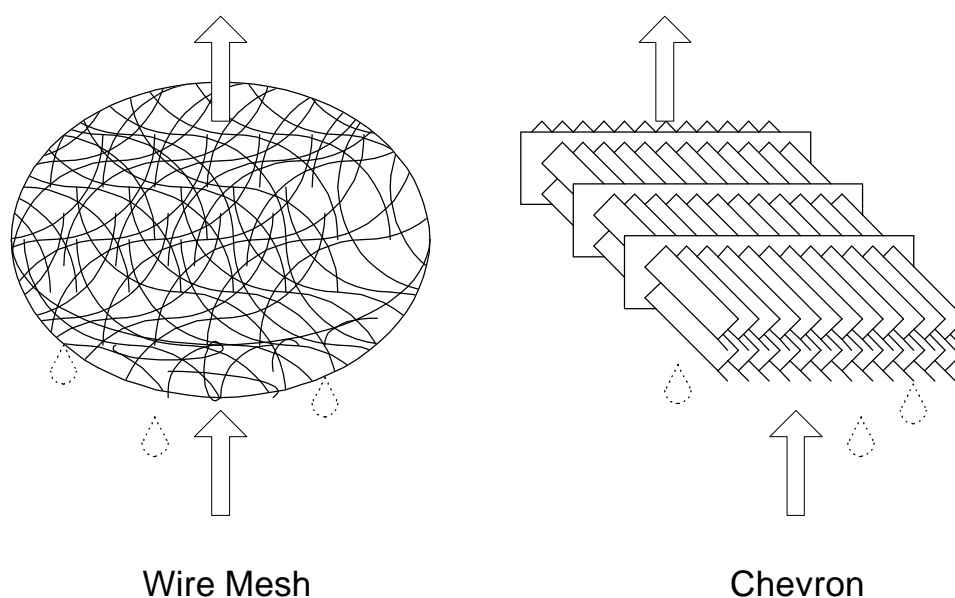


Figure 5-9. Two Types of Demisters (adapted from 23])

New developments in absorption techniques include cryogenic absorption [45], UV enhancement, and combinations of scrubbing columns and catalytic beds designed to destroy odorous compounds. In the Odorgard process from ICI Katalco, compounds are absorbed into a dilute hypochlorite solution, then the liquid is passed over a catalyst to oxidize the pollutants. The process is designed to reduce the amount of free chlorine emitted from scrubbers and achieve lower outlet concentrations of the pollutants [2]. Catenary grid scrubbers use suspended webs of wire mesh which are suspended from the column sides and fall in a hyperbolic shape. One design includes an ultraviolet lamp and hydrogen peroxide to destroy methanol in the wastewater from paper production [3]. Table 5-4 includes a list of instrumentation that should be considered for absorption systems [21].

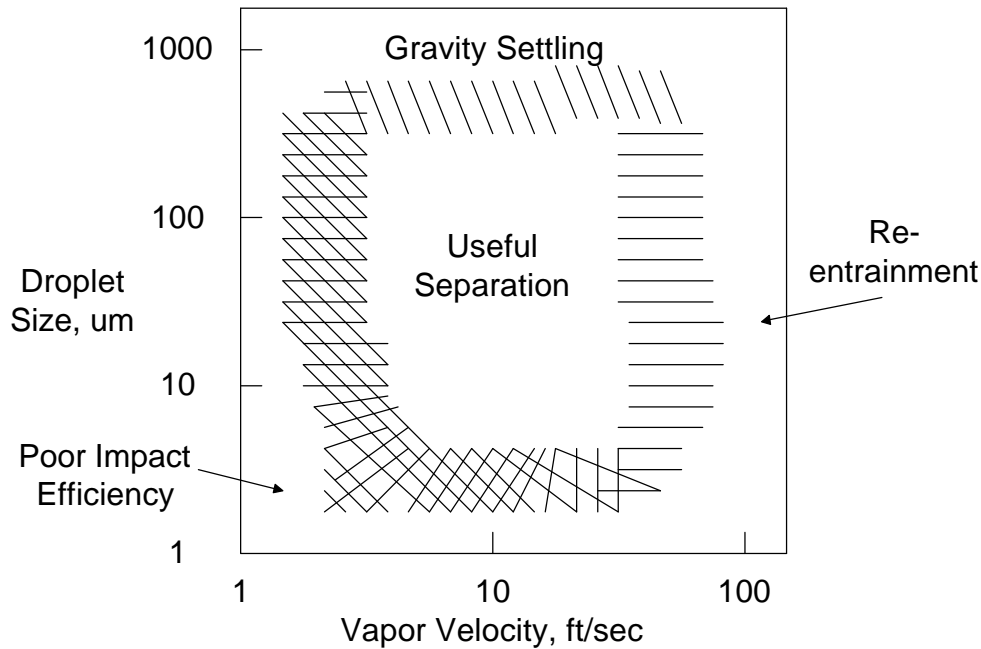


Figure 5-10. Range of Droplet Sizes and Velocities for Effective Separation [8]

Table 5-4. Recommended Instrumentation [21]

Gas stream temperature and pressure (inlet and outlet)
Liquid flowrate and pressure
Inlet gas stream relative humidity
Fan speed
pH of liquid effluent
Mist eliminator wash rate and frequency

Economic Estimates

One method of estimating the cost of an absorption system is given by the *OAQPS Control Cost Manual* and is considered to be accurate to within 30% [17]. The total column surface area is first calculated:

$$S = \pi D(1.4H_{\text{pack}} + 1.52D + 2.81) \quad 5-16$$

where: S = Surface area of column, ft^2 , valid for diameters between 0.6 and 3.7 m (2 and 12 feet) and packing heights between 1.2 and 3.7 m (4 and 12 ft)

Then the cost of the components of a fiberglass reinforced plastic column (in third quarter 1991 dollars) can be estimated by multiplying the surface area in m^2 (ft^2) by a factor of $\$1240/\text{m}^2$ ($\$115/\text{ft}^2$) [17]. This factor includes the cost of the column, inlet and outlet ports for gas and liquid, sump space, two liquid distributors, two packing supports, a mist eliminator, internal piping, and ladders and access platforms, but does not include packing, instrumentation, fans, or pumps. This cost estimate is valid for columns with surface areas from 6.4 to 140 m^2 (69 to 1507

ft²). For other materials of construction, the cost can be scaled by a factor of 0.8 to 1.1 for a polypropylene column, a factor of 0.5 to 0.9 for a polyvinyl chloride (PVC) column, and a factor of 1.1 to 1.75 for a stainless steel column (304) [17]. This, as well as any other costs, should be scaled up to current value using procedures given in the EPA's "Escalation Indexes for Air Pollution Control Costs", which can be found on the internet under <http://www.epa.gov/ttn/catc> [17].

In addition to the items included in the cost of the column, the cost of the packing, instrumentation, fans, and pumps must also be included in the total equipment cost (EC). Approximate packing costs are given in Table 5-3. The cost of instrumentation is estimated at 10% of the cost of the column, packing, and auxiliary equipment, following the method in the OAQPS Control Cost Manual. However, as noted there, the cost of instrumentation and controls varies depending on the complexity of the system [17].

General information on other types of scrubbers indicates that a bubble cap column costs about 2/3 as much as a packed tower with ceramic rings for the same application using the same materials of construction. A sieve plate tower is about 45% of the cost of the packed tower [21]. The total installed cost of the system can be estimated from the factors in Table 5-5.

Annual costs may be approximated using the same methodology as given in the OAQPS Cost Control Manual [17], as shown in Table 5-6. Total electricity requirements can be estimated from the formulas for the fan and pump requirements. A method for calculating the electricity requirement for the fan is given in Chapter 4. The electricity for required for the pumps can be estimated from the following equations.

$$E_{\text{pump}} = \frac{0.746 * 0.252 L_i P_L}{\text{eff}_{\text{pump}}} \quad 5-17$$

where: E_{pump} = electricity requirements for the liquid pump, kW
 L_i = Inlet liquid flow, gallons per minute
 P_L = Liquid pressure, feet of water
 eff_{pump} = efficiency of the pump and motor combined, approximately 0.4-0.7

Solvent requirements can be estimated from the liquid flowrates determined earlier. If the solvent is recycled, an estimate should be made of the amount of solvent that is evaporated during absorption or lost during the remaining processing steps. Operating and maintenance labor requirements vary depending on the complexity and dependability of the system, but can be estimated as one half hour per shift, following the suggestion in the OAQPS Control Cost Manual.

Table 5-5. Factors for Estimating the Total Installed Capital Cost of Absorption Systems
[Adapted from 17]

<i>Direct Costs</i>	
Purchased Equipment Cost	
Absorber, Packing, and Auxiliary Equipment	EC, Estimated from equation
Instrumentation and Controls	0.1 * EC
Taxes	0.03 * EC
Freight	0.05 * EC
Total Purchased Equipment Cost, PEC	1.18 * EC
Installation Costs	
Foundations and Supports	0.12 PEC
Erection and Handling	0.40 PEC
Electrical	0.01 PEC
Piping, Insulation, and Painting	0.32 PEC
Total Installation Cost	0.85 PEC
Site Preparation	As required for specific site, SP
Buildings	As required for specific site, BLDG
<i>Total Direct Costs</i>	<i>1.85 PEC + SP + BLDG</i>
<i>Indirect Costs</i>	
Engineering and Supervision	0.10 PEC
Construction, Field Expenses, and Fees	0.20 PEC
Start-up and Performance Test	0.02 PEC
Contingency	0.03 PEC
<i>Total Indirect Costs</i>	<i>0.35 PEC</i>
<i>TOTAL INSTALLED CAPITAL COSTS, TCC</i>	<i>2.2 PEC + SP + BLDG</i>

Potential Problems

The capital cost of the absorber depends on the volume of gas to be treated. Similarly, the efficiency of the absorption process depends on the concentration of the pollutant in the gas stream (the higher the concentration in the gas stream, the better the removal is expected). Therefore, it is critical that air infiltration be kept to a minimum by ensuring that seals in the ductwork remain air tight, eliminating unnecessary pickup points, maintaining valves and valve seats in excellent condition, and reducing the amount of air going into the capture system as much as possible. Care must be taken to ensure that the concentration in the ductwork does not exceed safe levels.

As with other gaseous control systems, corrosion can become a problem if the selection of construction materials is not deliberate. Since the absorption system saturates the gas stream with liquid, condensation in the remaining ductwork and fan can also lead to corrosion [18]. If a lining or plastic material is chosen to reduce corrosion, care must be taken to ensure that the temperature of the gas stream will not exceed the maximum allowable temperature of the material [4].

Table 5-6. Annual Operating Costs for Absorber Systems (adapted from [17])

Direct Annual Costs	Unit Cost	Estimated Requirement
Utilities:		
Electricity	\$0.05/ kWh	calculated above
Solvent	\$40 to 80/1000 m ³ \$0.15 to 0.30/ 1000 gallons	calculated above
Wastewater Treatment or solvent disposal	\$1000/1000 m ³ \$3.80/1000 gal	calculated above
Chemical Use for Regenerating Solvent	Application specific	Application specific
Operating Labor	\$12.96/h	½ hour per shift
Maintenance Labor	\$14.26/h	½ hour per shift
Maintenance Materials	100% of Maintenance Labor	
Supervisory Labor	15% of Operating Labor	
Indirect Annual Costs		
Overhead	60% of total operating and maintenance costs	
Property Tax	1% of TCC	
Insurance	1% of TCC	
Administrative Costs	2% of TCC	
Capital Recovery (from <i>Estimating Costs of Air Pollution Equipment</i> [5, 6])	CRF * TCC where $CRF = [i(1+i)^m]/[(1+i)^m - 1]$; i = interest rate m = control system economic life CRF = 0.1315 for 15 year equipment life and 10% interest rate	
Total Annual Operating Costs	Direct + Indirect Operating Costs	

Even if corrosion is not anticipated as a problem, the gas stream characteristics may require other considerations for the materials of construction. For example, if the gas or liquid stream contains high levels of particulate, organic linings or construction materials may be particularly susceptible to erosion [7].

For the column to be as effective as possible, the contact between the gas phase and the liquid phase must be excellent. Clogged liquid distribution systems, plugged air holes in plates, and bypassing must be avoided. Proper instrumentation can assist in diagnosing such problems; a relatively small amount of money spent for additional pressure or flow measurements when the system is installed can save a significant amount of time in trouble shooting later.

The column should also be designed with adequate turndown ratios which correspond to typical production levels in the process so that the column operates as efficiently as possible under various sets of operating conditions. However, adequate excess capacity should be included in the initial design to ensure that the capacity of the column can be increased if necessary without increasing the physical size [7]. This can be done by either providing a flanged connection on the

shell to allow for extra shell sections to be added, or the shell can be designed with extra height to allow for additional packing to be added [18]. If the shell is designed with extra height, the design should ensure that the liquid distribution system is never so high above the packing level that it makes the liquid distribution inefficient by allowing all of the liquid to reach the tower walls. Similarly, overpacking the column can result in poor distribution [8].

Installation, Operation, and Maintenance Considerations

During installation, it is critical that the tower be carefully levelled to ensure that the liquid and gas flow are not altered by a slight tilt. The liquid and gas lines should be traced to ensure that connections are correct and are leak tight and rotation of pumps should be checked. In lines which may have significant concentrations of solids, provisions may be needed for recirculation to prevent settling in the lines. Packing should be installed by carefully stacking if it is structured packing. In the case of dumped packing, liquid should be added to the column to protect the packing from damage [13, 21]. Any damage to the packing could result in liquid channeling or in increased pressure drop on the gas stream. A week or more may be required for polypropylene packings to become “conditioned”; because of the molding process, the surface may not be immediately wettable [8].

Approximately two weeks after the scrubber is put into operation, it should be inspected for pluggage and to determine if the packing has settled [18] or shifted. If the packing has settled, packing should be added to the design level, taking care to ensure that the packing is evenly distributed over the bed [21].

The warm, humid environment in wet scrubbers can be a preferred location for bacterial growth. Excessive bacteria can result in a soap bubble-like appearance and clogging of the column internals or mist eliminators. It is frequently necessary to add bacteriostats to ensure that this problem does not occur. When adding bacteriostats, however, the Material Safety Data Sheet should be reviewed to make sure that the ingredients in the bacteriostat are compatible with the construction materials of the column.

Proper operation of mist eliminators ensures that liquid droplets do not escape from the scrubber. If the demisters become clogged, the gas flow through the remaining demister area may speed up, and may carry over additional liquid with it. This possibility can be reduced in scrubbers with significant particulate loading in the gas stream by installing nozzles above the demisters to wash them in place. Washing is typically done while the absorber is off line to ensure that the washing liquid is not entrained in the exhaust gas [18].

Effective pollutant removal depends on establishing intimate contact between the gas phase and the liquid phase. If the scrubber is operating perfectly, the gas stream which leaves the scrubber is completely saturated with solvent. For scrubbers which use water as the solvent, the gas stream leaving the scrubber contains the maximum amount of moisture that it can hold under the existing temperature conditions. Depending on gas stream temperatures, the gas stream exiting the scrubber may begin to cool as it travels through the stack and into atmosphere. The gas can not continue to hold all of the moisture at lower temperatures, so the vapor begins to condense. Condensing liquid particles agglomerate into droplets. Therefore, on days in which the outdoor temperature is cooler than the operating temperature of the scrubber, it is typical to have droplets of water in the gas stream exiting the stack. Droplets in the gas stream on days in which the weather is warmer than the scrubber operating temperature indicate that there is carryover through the demisting system. Additional discussion of this phenomenon and potential methods

of addressing it are given in the *Electric Utility Users Manual* [9]. While the given article specifically addresses flue gas desulfurization systems, most of the concepts apply to other types of wet scrubbers as well, with the exception that flue gas desulfurization systems usually use a lime or limestone slurry as the scrubbing liquid. This concept is also documented in *Handbook of Air Pollution Control Engineering and Technology* which states "Conceivably, during wintertime operation some moisture due to condensation may be observed and considered a problem with the entrainment separator. However, it should be recognized that this is not uncommon, since the air off an absorber [scrubber] is saturated with water vapor, and any difference or lowering of the temperature will cause condensation to occur" [9]. Other methods of reducing condensation in the stack exhaust is to cool the gas stream to below the ambient temperature or to heat it to approximately 27 K (27°C, 50 °F) above saturation [15].

Carryover of droplets through the demisting system can be caused by several conditions:

1. Most packed bed scrubbers are designed for vertical velocities of approximately 1 to 2 m/s (3 to 6 ft/s) [10]. If the velocity of the gas stream approaches 2 m/s (6 ft/s) at the design flow rate, any clogging can cause the air to bypass the portions of the demisters which are clogging, increasing the linear velocity through the remainder of the demister. This can cause liquid to be entrained in the gas stream as it leaves the demisting zone.
2. If mesh pad demisters are used, they are typically installed on a slight angle to allow captured droplets to drain properly [23].
3. Velocities below approximately 1 m/s (3 ft/s) [7] or about 30% of the design velocity [21] can result in inefficient demister performance for droplets less than approximately 100 μ m in diameter, because the water droplets do not have sufficient inertial energy to impact on the scrubber demister material. Instead, they follow the streamlines of the gas flow and exit the scrubber with the gas.
4. Torn or misplaced mesh pads will allow bypassing of the gas stream, resulting in entrained liquid exiting with the gas stream. It is possible for demisters to be chemically degraded by the constituents of the liquid or gaseous streams. In the case of polypropylene mesh pads, the polypropylene can be attacked by strong oxidizing acids, peroxide, gasoline, benzene, carbon tetrachloride, acetone, alcohols, or wet chlorine [48] streams. Chemical damage to plastic material can be verified by examining one of the old mesh pads to determine the condition of the fiber. If either chemical or heat damage has occurred, the fiber should be brittle, maleable, or deformed.
5. Poorly functioning nozzles or liquid distribution systems can also result in carryover of liquid through the demister. The nozzles should be examined to identify small pieces of plastic or solids which can clog the distributors.

Increases and decreases in pressure drop through a column can indicate improper operation. Increases in pressure may be due to increased liquid flow, plugged or decomposing packing, plugging demister, blockages in the packing support plate or air distribution systems, or increased air flow through the scrubber [18]. Liquid and gas flow rates should be monitored during scrubber operation to detect any gradual changes in flow. To check for plugging, it is advantageous to take pressure drop readings without any liquid flow immediately after the packing and demisters are installed, cleaned, or replaced. This data will help determine whether future episodes of high pressure drop are associated with increased pressure drop in the vapor

stream (such as in the demisters or packing) or are the result of increased liquid flow. The dry pressure drop during periods of questionable operation can be compared with the dry pressure drop when the demisters and packing are known to be clean. If there is a significant difference between the two, it is an indication that the increase in overall pressure drop is due to clogging of the demisters or column [9]. If there is not a significant difference, then other factors should be examined to identify the reason for the excessive pressure drop. Other factors that affect the demister operation, pressure drop, and the overall operation of the scrubber are excessive vapor or liquid flow rates. Care should be taken to ensure that the gas flow is neither excessive nor so low that it results in an excessive liquid flow rate.

Decreases in pressure drop can indicate low liquid flows, low air flows, channeling of liquid through the scrubber which may be resulting from poor liquid distribution, collapsed packing support plates, or changes in the density of the gas [18, 21]. Changes in the pressure or flow of liquid may be attributable to plugged filters or pipes in the liquid system, plugged nozzles, low sump level (which may cause pump cavitation), a worn pump impeller, changes in valve position, internal piping leaks or breaks, or eroded spray nozzles [18]. Changes in gas flow may result from plugging in the packing or demister, changes in liquid flow, poor fan operation due to loose belts or worn impeller, partially plugged ductwork, changes in damper settings, leaks in the ductwork or scrubber, damage to the packing or packing support plates [18]. If the efficiency of an absorption system decreases, it may be attributable to low liquid flow, insufficient additive feed, pH probe malfunction, or liquid channeling due to pluggage in the scrubber or liquid distribution system [18].

It is also recommended that copies of the fan curves for the systems be retained, so that the gas flowrate can be determined as the pressure drop through the scrubber changes. The curves should be prepared at approximately the same temperature of the gas as it goes through the fan.

Particulate that builds up in the tower, demister, or distribution systems increases the pressure drop and hinders efficient operation, so any particulate collection devices before the scrubber should be maintained in good operating condition. Since it is possible that media replacement will be required, the system should be designed and constructed with adequate space and access for demisters and packing or trays to be removed as easily as possible.

Once the column is in place and operational, there are still changes that can be made to facilitate improved operation. If increased gas flows must be accommodated, it is possible to convert a countercurrent column into a cocurrent one, where the gas and liquid both travel down through the column. Cocurrent columns do not experience the same difficulties with flooding, but efficiency would be sacrificed [7]. Changes in packing material can also affect the pressure drop and efficiency achieved in the column for a cost significantly below that required to replace the column or install an additional unit.

If liquid is channeling through the column but the liquid distributors are working well, the problem may be due to poor liquid flow characteristics in the packing. It may help to replace a portion of the top packing layers with smaller size packing to improve liquid distribution [8]. Newer packing designs have been developed to reduce lateral flow [8]; these may also be advantageous in such a situation. These packings are also less likely to redistribute liquid flow, so proper liquid distribution is even more critical than with older style packings. An overall summary of the advantages and disadvantages of absorption systems is given in Table 5-7.

Table 5-7. Advantages and Disadvantages of Absorption

Advantages	Disadvantages
<p>Allows for recovery / concentration of the pollutant</p> <p>High efficiencies possible</p> <p>No additional pollutants formed</p>	<p>Effectiveness is pollutant-specific, depends on solubility of compound</p> <p>Transfers air pollution problem to liquid waste problem</p> <p>Potential corrosion of ductwork due to additional moisture in gas stream</p>

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Chapter 6

Thermal Incineration

Technology Description

Incinerators are relatively simple devices in which organic material in a gas stream is destroyed by combustion. Gaseous incinerators are also sometimes referred to as “*afterburners*”, particularly if they are installed downstream of a primary fuel combustion unit [1], like a medical waste incinerator. This name is indicative of the equipment’s function: to provide adequate time and temperature for compounds to finish burning. If designed and operated properly, the exhaust from gaseous incinerators consists primarily of carbon dioxide and water, along with inert gases from the atmosphere like nitrogen. Because of their capability for high destruction efficiency and their ability to destroy a wide variety of compounds, incinerators are very common control devices [2]. For situations which are particularly sensitive to emissions of nitrous oxides, other control devices should be considered, since there is inevitably some formation of nitrous oxides at combustion temperatures, although methods and equipment are available to minimize their formation.

Care must be taken to properly identify the constituents of a gas stream before incineration is selected as the control method. Sulfur compounds in the gas stream (including mercaptans which are added to natural gas and propane to make sure that leaks are detectable [3]) react to form sulfur dioxide, which may need to be removed before venting to the atmosphere. Likewise, halogenated compounds in the contaminated gas stream react to form acids which can severely corrode ductwork and downstream equipment if not removed immediately after the incineration process. The gas stream must also be relatively clean, that is, there should not be material present that would clog nozzles if the gas stream is used as primary combustion air. Metals present in the gas stream can also affect the combustion process, especially in units where combustion is promoted by the presence of a catalyst. Vaporized species from elements such as iron and silicon can bind to the catalyst and render it inactive. In addition, materials which might coat the surface of the catalyst without reacting must be avoided in catalytic incinerators.

There are two primary types of incinerators: *thermal incinerators* (or *thermal oxidizers*) and *catalytic incinerators* [4]. Thermal incinerators rely on a high operating temperature and usually a direct flame to ignite the pollutants. They generally operate in the range of 973-1073 K (700 to 800 °C, 1300-1500 °F) [5], but field testing has shown that most incinerators should maintain approximately 1143 K (870 °C, 1600 °F) for at least 0.75 seconds to achieve 98% reduction of non-halogenated compounds [6, 7, 8, 9]. Halogenated compounds are more difficult to destroy [10]. Incineration temperatures as high as 1477 K (1204 °C, 2200 °F) are required for effective destruction of some chlorinated compounds [11]. Catalytic incinerators, as described in Chapter 8, contain a surface of noble metal or other catalyst which brings the reactants together in close proximity or otherwise facilitates the oxidation reaction so that it occurs at a lower temperature. Catalytic units generally operate in the range of 620 to 870 K (340 to 590 °C, 650 °F to 1100 °F) [12]. Flares, which basically function as thermal incinerators with no combustion chamber, are discussed in Chapter 7.

In thermal incinerators, the organic removal efficiency that can be achieved is governed by the

“three T’s” [13]: time, temperature, and turbulence. In other words, the combustion reaction depends on maintaining the proper temperature for long enough for the combustion process to occur. In order to ensure that the temperature and reactants are distributed evenly, the incinerator must provide adequate velocity and turbulence to mix the combusted gases with the pollutants. The proper conditions are already present in many boiler or process heater fireboxes; these, too, can be used for incineration of gases if the gaseous stream introduction is properly positioned [14]. It is well documented that there is flexibility between the temperature and residence time requirements, that is, the required time can be shortened by elevating the temperature, and a lower temperature can be used if the mixture is allowed a longer time to react. Figure 6-1 [15] gives a typical correlation of the relationship between temperature and retention time. Well designed and maintained incineration units are capable of achieving efficiencies of 99% at pollutant concentrations greater than approximately 100 ppm [16].

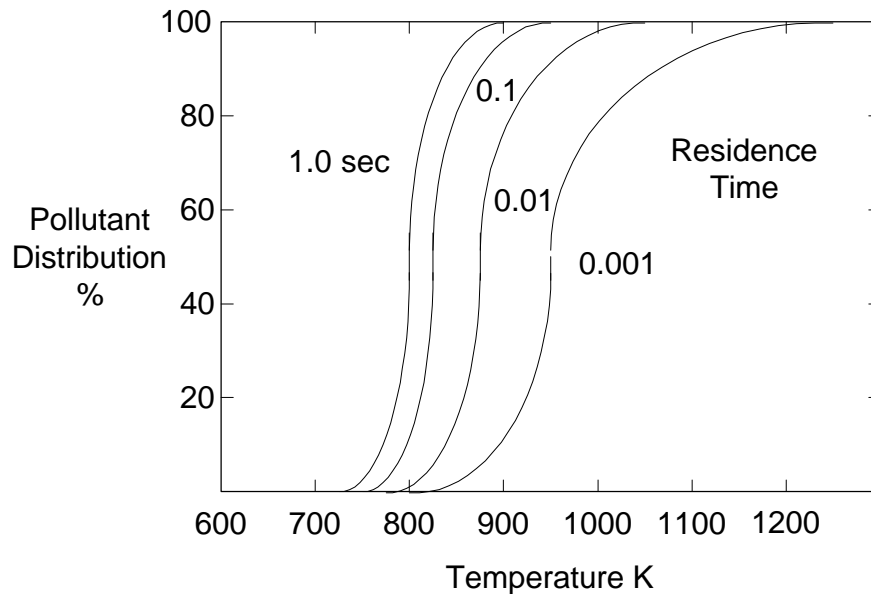


Figure 6-1. Effect of Temperature and Residence Time on Destruction Efficiency [adapted from 15]

Incineration is most appropriate for processes where there is no physical or economic benefit to recovering the organic material. Examples of typical uses for thermal incineration are given in Table 6-1 [17, 18, 19, 20, 21].

Table 6-1. Typical Applications of Thermal Incineration for VOC Removal
[17, 18, 19, 20, 21]

Landfill offgases
Printing operations
Medical waste incinerator exhaust
Bakeries
Paint bake ovens
Foundry core ovens
Paper operations
Coffee roasting
Sewage sludge incineration offgas
Rendering plants
Smokehouse operations
Textile drying
Asphalt blowing and asphalt paper manufacture

Types of Thermal Incineration Systems

Incinerators are further characterized by the method used to transfer heat from the gaseous exhaust to the incoming waste gas stream. Older thermal incinerator units and catalytic incinerators commonly use *recuperative* heat exchangers (as shown in Figure 6-2 [22] and 6-3 [23]), in which the exhaust gases from the incinerator pass through a shell-and-tube or plate-type heat exchanger to recover the heat of combustion and increase the fuel efficiency of the VOC destruction process. The incoming gases pass through the heat exchanger, too, but without directly contacting the exhaust gas. Recuperative units are generally only able to recover about 70% of the available heat [24], although at least one manufacturer reports primary heat recovery in a recuperative unit of up to 82% [25]. Some units are designed with a secondary heat recovery unit to preheat air, water, or heat transfer oil for other plant processes such as drying ovens [26].

More recently, *regenerative* systems have been introduced (see Figure 6-4 [27]) which use beds of rock or packed ceramic material as a heat sink. Regenerative incinerators allow for better heat recovery, meaning that dilute vapor streams can be incinerated at lower costs [28]. The post-combustion gases pass through one bed and heat up the ceramic material. Then the flow shifts, and the post-combustion gas stream is used to heat up a second bed of ceramic material while pre-combustion air flows through the first hot bed, gaining heat as it travels to the burner. Flow is shifted back and forth between the beds as they heat up and cool down. Heat transfer efficiencies of approximately 95% can be achieved with regenerative units [6]. The average number of cycles is between 15 and 60 per hour [24]. The alternating sequence decreases the removal efficiency which can be achieved in such a system; control efficiencies are usually below 99% [29, 30]. At least one manufacturer reports destruction efficiencies of 95 to 99% [31]. Depending on the required removal efficiencies, more than two beds may be needed. In some cases a third bed is used as a “purge” bed to capture the untreated gases that would normally be exhausted from the

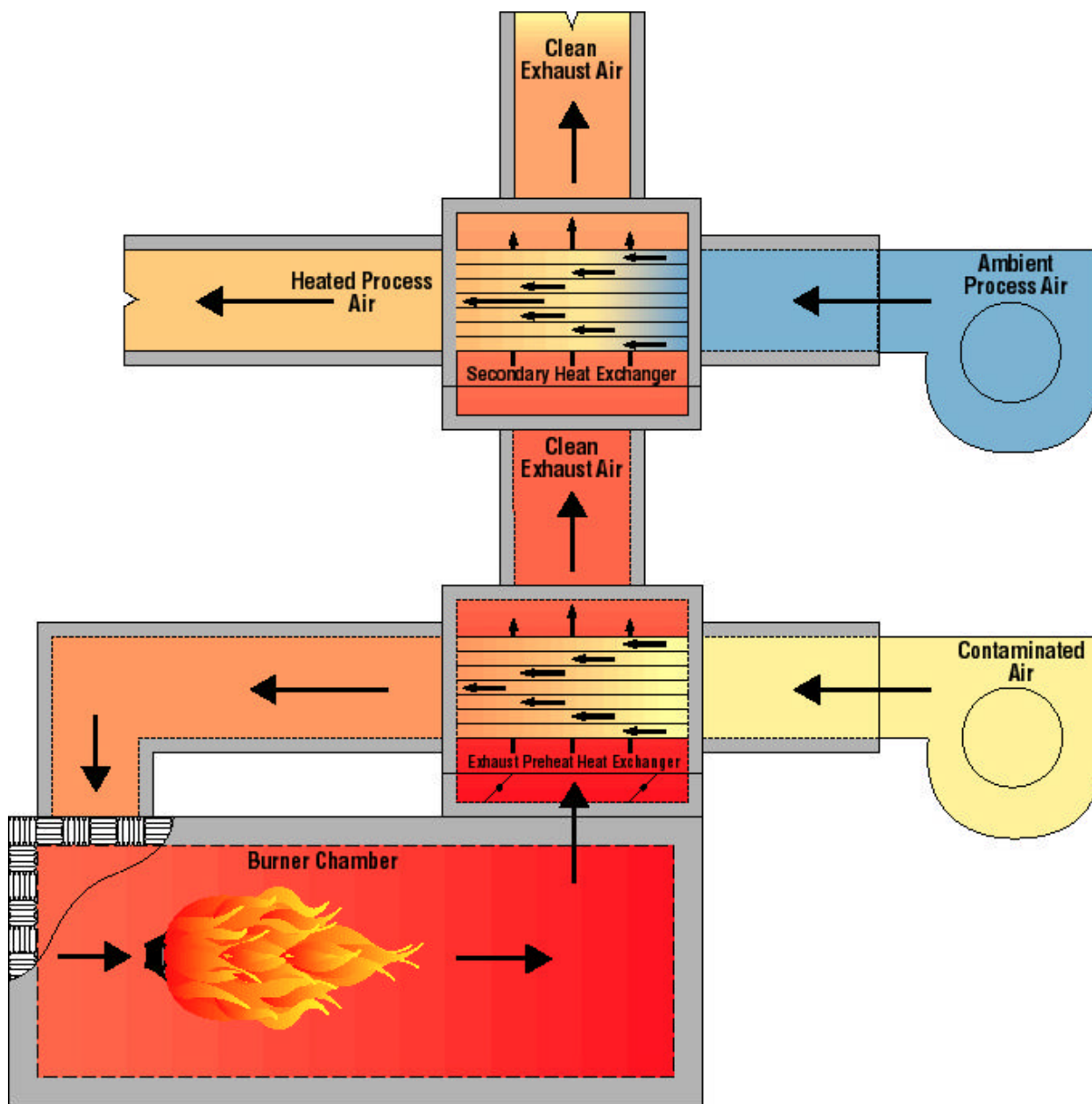


Figure 6-2. Glenro, Inc. Recuperative Oxidizer with Secondary Heat Recovery [22]

Anguil Thermal Oxidizer System

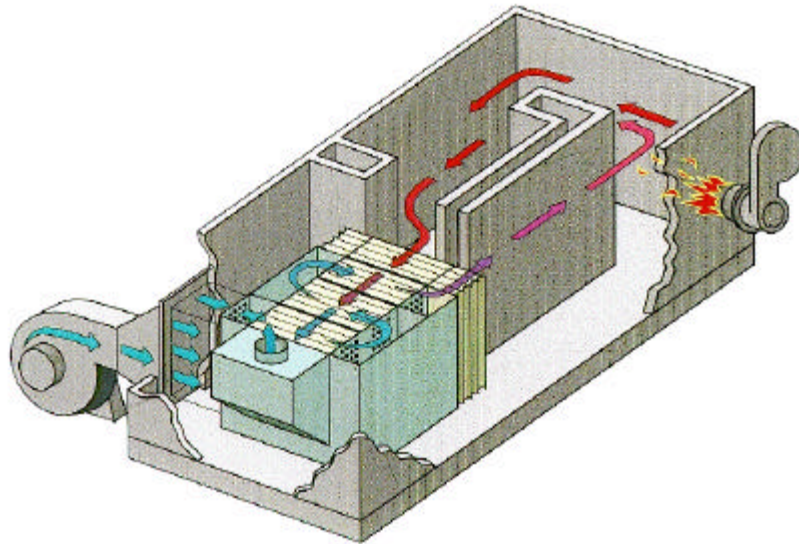


Figure 6-3. Anguil Recuperative Thermal Oxidizer [23]

ducting when the valves change position [24]. For systems demanding removal efficiencies above 98%, the valving mechanism becomes more complex, as double valves are used to reduce the opportunity for any leakage. The space between the valves is slightly pressurized with fresh air to ensure that no untreated gas is released to the stack [24].

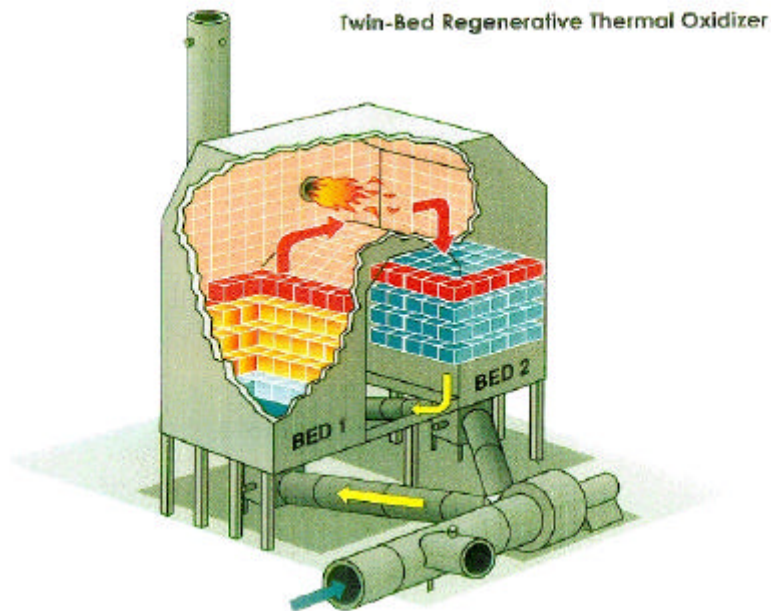


Figure 6-4. Anguil Environmental Systems, Inc. Regenerative Oxidizer [27]
Horizontal flow regenerative incinerators have been introduced recently which result in lower space requirements and make the technology more suitable for retrofit situations [29]. Figure 6-5 shows an example of the flow through a horizontal regenerative incinerator [29]. In addition,

some manufacturers have introduced a system which combines an adsorbing wheel with thermal or catalytic incineration so that the inlet gas to the incinerator is more concentrated. This results in better thermal efficiency, since the amount of air that must be heated to the combustion temperature is significantly decreased. An example is shown in Figure 6-6 [23].

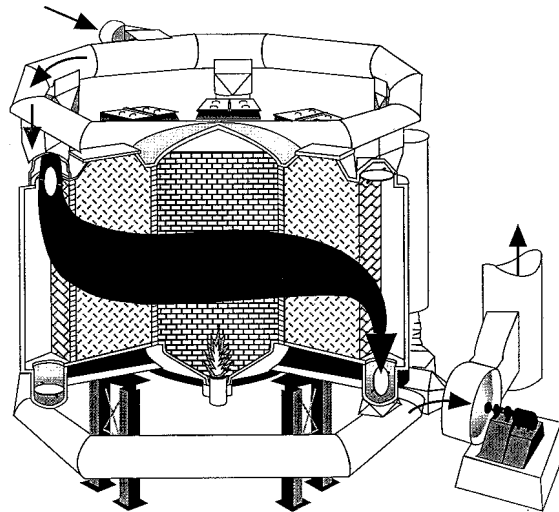


Figure 6-5. REECO Horizontal Flow Regenerative Incinerator [29]

Anguil Rotor Concentrator

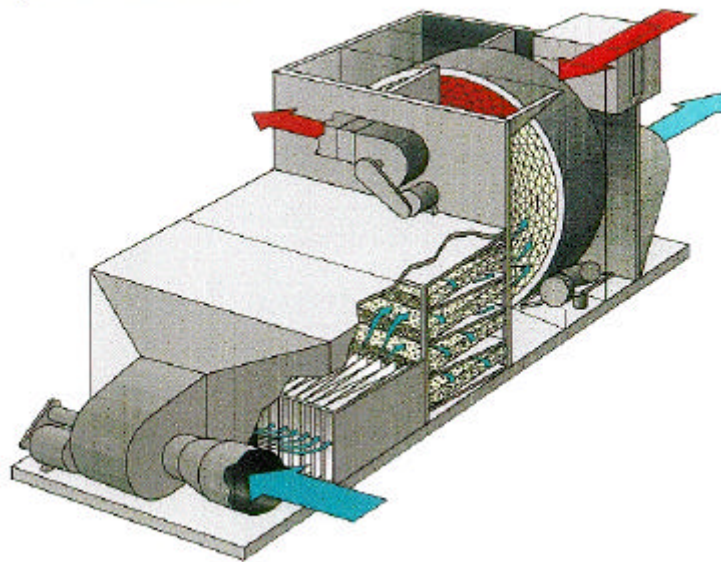


Figure 6-6. Anguil Environmental Systems, Inc Roto-Concentrator [23]

Thermal Incinerator System Design

It is a generally accepted practice to model the complex free radical reactions that occur during combustion as a single first order reaction for many compounds [32, 33, 34, 35], so that the final concentration (or the overall destruction efficiency) can be estimated if the temperature, T , and residence time, τ , are known:

$$\ln\left(\frac{C_B}{C_{B0}}\right) = -k\tau \quad 6-1$$

where: $k = Ae^{-E/RT}$ 6-2
 and: $A =$ Compound specific constant (s^{-1})
 $E =$ Apparent activation energy, kJ/mol (or Btu/lb-mol, if English units are used throughout the calculation)
 $R =$ Gas constant, 8.314 kJ/mol K (or 1.987 Btu/lb-mol °R)
 $\tau =$ Residence time, s
 $T =$ Absolute Temperature, K (or °R)

Values of the apparent activation energy and compound specific constants are given in Table 6-2. The average residence time of an incinerator can be estimated from knowledge of the outlet volumetric flow rate, Q , and the volume of the incinerator, V :

$$\tau = \left(\frac{V}{Q}\right) \quad 6-3$$

where: $V =$ Internal volume of the incinerator chamber, m^3 (or ft^3)
 $Q =$ Flowrate of gases out of the incinerator, m^3/s (or ft^3/s)

As with other VOC control devices, the amount of gas to be treated should be minimized to reduce the capital and operating costs of the incinerator. Care must be exercised, however, to ensure that the concentration of pollutant in the gas does not exceed a safe level in the ducting, even during process upsets or start up conditions. This is particularly important, since the incinerator itself provides a source of heat and ignition. Most insurance companies consider 25% of the *Lower Explosive Limit (LEL)* to be the maximum acceptable concentration of VOC in the ducting as a general guide. Although this value can be exceeded in some situations, it typically requires additional instrumentation to monitor the level of VOCs at all times and to instantaneously shut down the process or vent the contaminated gas to the atmosphere at a given threshold. Information regarding the LEL should be available from Material Safety Data Sheets or the chemical manufacturer. Additional information about the LEL is also available from the U.S. Bureau of Mines [36, 37]. The heating value of hydrocarbons at the LEL has been determined to be approximately 2 mJ/Nm³ (50 Btu/scf) [6].

To ensure an effective incinerator design, the operating temperature should be approximately 90-150 °C (200-300 °F) above the highest autoignition temperature of any of the components [38]. The autoignition temperature is the temperature at which a mixture of organics and air will ignite without a spark or flame [39]. Modulating controls should be used to regulate the flow of fuel to the burner [40]. In the past, units have been designed with on/off controls for the pilot ignition source. This type of control is ineffective because it allows short intervals of time where no flame is available for the combustion process. Although the intervals are short, they can substantially affect the overall performance of the incinerator. It is essential that the proper temperature and retention time be maintained so that contaminants are completely destroyed. Incomplete combustion can lead to compounds such as aldehydes, dioxins, and furans with more severe health effects than the original hydrocarbon gas components.[3, 41]

Table 6-2. Pre-Exponential Factors and Apparent Activation Energies [adapted from 32]

Pollutant	Pre-Exponential Factor, A (s ⁻¹)	Apparent Activation Energy, E (kJ/g-mol)
Acrolein	3.30x10 ¹⁰	150
Acrylonitrile	2.13x10 ¹²	218
Allyl Alcohol	1.75x10 ⁶	89.5
Allyl Chloride	3.89x10 ⁷	122
Benzene	7.43x10 ²¹	401
Butene –1	3.74x10 ¹⁴	244
Chlorobenzene	1.34x10 ¹⁷	320
Cyclohexane	5.13x10 ¹²	199
1,2 – Dichloroethane	4.82x10 ¹¹	191
Ethane	5.65x10 ¹⁴	266
Ethanol	5.37x10 ¹¹	201
Ethyl Acrylate	2.19x10 ¹²	192
Ethylene	1.37x10 ¹²	213
Ethyl Formate	4.39x10 ¹¹	187
Ethyl Mercaptan	5.20x10 ⁵	61.5
Hexane	6.02x10 ⁸	143
Methane	1.68x10 ¹¹	218
Methyl Chloride	7.34x10 ⁸	171
Methyl Ethyl Ketone	1.45x10 ¹⁴	244
Natural Gas	1.65x10 ¹²	206
Propane	5.25x10 ¹⁹	356
Propylene	4.63x10 ⁸	143
Toluene	2.28x10 ¹³	236
Triethylamine	8.10x10 ¹¹	181
Vinyl Acetate	2.54x10 ⁹	150
Vinyl Chloride	3.57x10 ¹⁴	265

Most of the gas streams treated with incinerators have fairly low loadings of VOCs. For more concentrated gas streams, a regenerative system may not be advantageous. Depending on the heat content of the vapor, heat recovery above 90% may not be necessary and may actually be detrimental, since too high a temperature in the combustion air can reduce the efficiency of the incinerator [42].

Halogenated or sulfur compounds in the gas stream form acidic gases upon combustion and the incinerator system must be designed to handle the corrosion which may result. Chlorinated compounds may also form dioxins when they are treated by thermal incineration [2, 43]. A scrubber following the incinerator is necessary under most circumstances to remove the acid gases before the gas stream is released to the atmosphere. The scrubber should be considered as an integral part of the incinerator system and should not be overlooked even in preparing rough cost estimates, since the cost of the scrubber can be a significant portion of the overall system cost.

Some heavy metals such as mercury and cadmium may become vapors during high temperature incineration [3]. Special considerations are required for process streams containing metals which may be released into the atmosphere during incineration; additional heat recovery and particulate

control may be warranted in these circumstances.

Procedures for calculating the total flue gas flow (that is, the flowrate of gases leaving the incinerator) are given in the *OAQPS Control Cost Manual* [6] and by Vatauvuk [44]:

$$Q = Q_w + Q_f \quad 6-4$$

where: Q = Total flue gas flowrate, normal m^3/min abbreviated Nm^3/min (in English units, standard ft^3/min abbreviated scfm)

Q_w = Waste gas flowrate at inlet to incinerator, Nm^3/min (scfm)

Q_f = Flowrate of auxiliary fuel, Nm^3/min (scfm)

The flowrate of auxiliary fuel is calculated from the equation:

$$Q_f = Q_w X/Y \quad 6-5$$

where: $X = 1.1 C_{po} (T_c - T_r) - C_{pi} (T_i - T_r) - h_w \quad 6-6$

$Y = h_f - 1.1 C_{po} (T_c - T_r) \quad 6-7$

C_{po} = Mean heat capacity of exhaust stream from the incinerator, $\text{kJ min}/\text{Nm}^3$ ($\text{Btu scf}^{-1} \text{ } ^\circ\text{F}^{-1}$). The heat capacity of air is typically used, since most of the gas stream is air. At 1144 K (871°C , 1600°F), the heat capacity of air is $1.50 \text{ kJ}/\text{Nm}^3 \text{ } ^\circ\text{C}$ ($0.0194 \text{ Btu}/\text{scf } ^\circ\text{F}$).

T_c = Combustion temperature, $^\circ\text{C}$ (or $^\circ\text{F}$)

T_r = Reference temperature, 21°C (70°F) is typical

C_{pi} = Mean heat capacity of inlet streams to the incinerator, $\text{kJ min}/\text{Nm}^3$ ($\text{Btu scf}^{-1} \text{ } ^\circ\text{F}^{-1}$). Again, the heat capacity of air is typically used, since most of the incoming stream is air. At 311K (38°C , 100°F), the heat capacity of air is $1.4 \text{ kJ}/\text{Nm}^3 \text{ } ^\circ\text{C}$ ($0.018 \text{ Btu}/\text{scf } ^\circ\text{F}$).

T_i = Inlet gas stream temperature, after preheating, $^\circ\text{C}$ ($^\circ\text{F}$). T_i may be calculated from the equation $T_i = T_w + \text{Eff} (T_c - T_w)$

T_w = Temperature of waste gas stream before preheating, $^\circ\text{C}$ ($^\circ\text{F}$).

Eff = Anticipated fractional thermal efficiency of the incinerator (usually between 0.5 and 0.95)

h_w = Heat content of waste gas stream, kJ/Nm^3 (Btu/scf)

h_f = Heat content of fuel, kJ/Nm^3 (Btu/scf). For natural gas, h_f is approximately $37,000 \text{ kJ}/\text{Nm}^3$ ($900 \text{ Btu}/\text{scf}$).

h_f may be calculated in SI units from the following equation if the heat content is known in kJ/kg :

$$h_f = \text{heat content in kJ/kg} \times \text{fuel molecular weight in kg/kg-mole} / 22.4 \text{ Nm}^3 \text{ per kg-mole} \quad 6-8$$

In English units, h_f can be calculated from the known heat content in Btu/lb :

$$h_f = \text{heat content in Btu/lb} \times \text{fuel molecular weight in lb/lb-mole} / 386.5 \text{ ft}^3 \text{ per lb-mole} \quad 6-9$$

These equations are considered valid for gas streams with an oxygen content above 16% that contain VOCs at a concentration less than 25% of the LEL. They assume a 10% loss of energy from the incinerator [44]. Note that no allowance is included for volume changes due to changes in the total number of moles in the system which may occur during reaction. Additional

correction may be needed for gas streams which contain large concentrations of organic compounds, particularly if the organic compounds contain significant amounts of oxygen.

Additional capital cost can sometimes be avoided if an existing boiler or furnace can be used to control VOCs in addition to its original function [17]. Using a VOC-containing gas stream as combustion air can benefit the overall process, since the organic compounds serve as fuel when the gas stream is combusted. The following criteria must be satisfied before a boiler or process heater is used as an incinerator for waste gases [17, 45, 46]:

There should be very few particles present in the waste gas stream or formed during combustion, since any particulate may build up on heat exchanger surfaces, decreasing the overall fuel efficiency which can be achieved. If this occurs, the additional cleaning required to return the boiler or furnace to peak efficiency may be extremely expensive and may require significant equipment outage time. In addition, solids which make it beyond the heat exchanger can contribute to the overall particulate loading in the exhaust stream and may make it more difficult for the combustion device to meet any air pollution control requirements.

1. The gas stream should be only a small part of the total amount of air required for combustion. If the gas stream represents a significant amount of the combustion air for the boiler or process furnace, additional design is required to ensure that the oxygen balance is maintained, that mixing is adequate, and that there is an alternative source of combustion air if the VOC process is not operating.
2. The contaminated gas stream should have an oxygen content similar to that of air. If the oxygen content is insufficient, incomplete combustion could occur. The products of incomplete combustion can be more toxic than the original VOC contaminant. Products of incomplete combustion may also be sticky material which fouls heat exchanger surfaces.
3. Using a boiler or process furnace to control VOC emissions may inadvertently tie the VOC emitting process and the boiler operation together, since the boiler needs to be operating whenever the emissions are required to be controlled. This may have significant impacts on the VOC emitting process when a boiler is taken off-line for annual or bi-annual maintenance.
4. There should be no compounds in the waste gas stream which will damage the boiler. Halogenated compounds in the gas stream should be avoided, since they may contribute to corrosion in the boiler or flue gas equipment.
5. Additional design changes may be needed to the boiler to ensure adequate mixing. For example, baffling may be necessary to ensure that the waste gas does not bypass the flame. Changes to the flame patterns and radiation should be avoided.
6. It is preferable to use a base-loaded boiler to combust the waste gas. A base-loaded boiler is one that operates at a consistent rate for long periods of time. Base-loaded boilers are normally accompanied by swing-load boilers, which alter the fuel input to respond to changing steam or energy demands.
7. The concentration of the organic compound should be less than 25% of the LEL. For more concentrated streams, the waste gas stream may need to be treated as an auxiliary fuel, particularly if the concentration is above the LEL.

Any type of thermal combustion device generally results in the formation of some nitrous oxides (NO_x). In some cases, the formation of NO_x compounds is more of a concern than the presence of VOCs. Therefore, careful examination of the NO_x emissions and applicable requirements should be conducted before selecting incineration as the control method. A packed bed flameless thermal oxidizer is reportedly being developed which has a relatively low combustion

temperature, resulting in minimal NO_x formation [2, 47]. The concentration of NO_x that results from the combustion process is highly dependent on the peak temperature of combustion, since the NO_x is formed relatively quickly at high temperatures but does not readily degrade at lower temperatures. Therefore, the NO_x concentration in the exhaust gases from combustion devices are generally the same magnitude as equilibrium concentrations at the peak combustion temperature [48]. The formation of NO_x from the nitrogen and oxygen in the air is very fast when the combustion temperature is above approximately 1920 K (1650 °C, 3000 °F) [49]. Most thermal incinerators operate at temperatures lower than the combustion chambers in boilers and NO_x formation is minimal [50].

A list of instrumentation that should be considered is given in Table 6-3. While the amount of instrumentation may seem excessive during the design phase, it is often helpful for monitoring any deterioration in performance and for troubleshooting.

Table 6-3. Recommended Instrumentation

Combustion temperature
Inlet / outlet concentration
Fan speed
Pressure
Auxiliary fuel rate
Pressure drop across any particulate collection devices

Economic Estimates

Estimates of the capital cost of a package recuperative thermal incineration system are given by Vatavuk [44]. In SI units, the equation is:

$$CC = a (Q/0.026)^b \quad 6-10$$

In English units, the equation is:

$$CC = a Q^b \quad 6-11$$

where: CC = Purchased Price, in 1988 dollars

Q = Flowrate of gases after combustion, Nm³/min (scfm)

a and b are parameters dependent on the amount of heat recovery required.

For 0% heat recovery, a = 3,120 and b= 0.360. For 50% heat recovery, a = 4,920 and b= 0.389. At 70% heat recovery, a = 5,690 and b=0.408 [51].

These estimates are valid for incinerators between 130 and 1300 Nm³/min (5,000 and 50,000 scfm) operating at approximately 1090 K (820 °C, 1500 °F). In addition to the combustion chamber and burner, the price includes a heat exchanger, fan, motor, instrumentation and controls, and a ten foot stack. Ductwork, particulate removal devices, and site-specific construction requirements are not included. If the incinerator is to be placed a long distance from the generation site, both the cost of ductwork and the cost of additional booster fans should be considered. As with the other chapters in this book, the cost estimates are to indicate a general order of magnitude. They are not

specific enough to use as construction costs and should be confirmed with actual prices from vendors.

For comparison, Ruddy and Carroll give estimates of capital costs for recuperative incinerators as \$35.3–7060 per cubic meter per minute (\$10-200 /cfm). The capital cost for regenerative systems is estimated as \$1060-16,000/(m³/min) (\$30-450 /cfm)[52]. It is not specified whether these costs are for actual or standard flowrates.

For a regenerative incinerator with 95% thermal efficiency, the *installed* cost may be estimated based on the inlet gas flow according to the following equations [44].

In SI units:

$$C = 383,000 + 589 Q_w \quad 6-12$$

In English units,

$$C = 383,000 + 15.3 Q_w \quad 6-13$$

This equation is valid for waste gas stream flows between 130 and 1300 Nm³/min (5,000 and 50,000 scfm). The cost of foundations, freight, taxes, and ductwork are not included, but the labor to install the incinerator is. Approximately 20% additional cost is required for the foundations, freight, taxes, and ductwork [53]. To estimate the total installed capital expenditure, the factors in Table 6-4 may be used, which follow the methodology of EPA's *OAQPS Cost Control Manual*.

Annual costs may be approximated using the guidelines in the OAQPS Cost Control Manual [6], as given in Table 6-5. Electricity requirements can be estimated from the formulas given in Chapter 4, assuming a pressure drop of 1 kPa (4 inches of water column) for the combustion chamber itself. The heat exchanger adds another 1-3.7 kPa (4-15 inches of water column), corresponding to heat recoveries of 35 to 70 percent [6]. Operating and maintenance labor requirements are usually minimal with thermal incinerators, at approximately one half hour per shift.

Rough estimates of annual operating costs range from \$530-3200 per m³/min (\$15-90 /cfm) for recuperative units to \$710 – 5300 per m³/min (\$20-150 /cfm) for regenerative systems according to Ruddy and Carroll [52].

Potential Problems

Like any equipment, incinerators are susceptible to damage caused by severe temperature changes. Although they are designed to be operated at high temperature, large fluctuations in temperature can cause thermal stress and lead to premature failure of the refractory lining. Therefore, incinerators are best suited to operations which maintain a fairly constant emission rate [29] and those that operate continuously instead of those that operate for only a few hours each day. The manufacturer's start-up procedure normally specifies a warm-up sequence in which the incinerator is brought to operating temperature gradually. Following this procedure lengthens the life of the refractory, but also uses additional fuel and may take longer than is feasible for the process. It is not unusual for maintenance or operating staff to develop a shorter start-up procedure. Using such a shortcut lowers the overall gas usage but is likely to result in considerably higher maintenance requirements. For cyclical processes, a regenerative incinerator should be considered which can be maintained at operating temperature with minimal natural gas consumption. Some of these units can even be put on an "idle" mode, in which little or no gas is pulled from the process, but the incinerator recycles exhaust air to the inlet to conserve heat [54].

If a dilute waste gas stream is mixed with the required amount of fuel to achieve the flame temperature, it is possible that the resulting mixture will not have adequate energy concentration to propagate a flame. This can result in flame quenching in the incinerator, which produces additional contaminants due to the partial oxidation of the fuel and pollutant gas. Therefore, usually about one-half of the waste gas stream is mixed with the fuel and the remaining waste gas stream is introduced after the initial flame and mixed with the products of combustion [55].

Table 6-4. Factors for Estimating the Total Installed Capital Cost of Thermal Incineration Systems [6]

<i>Cost Element</i>	<i>Estimated Cost</i>
<i>Direct Costs</i>	
Purchased Equipment Cost	
Incinerator and Auxiliary Equipment	CC, Estimated from equation
Taxes	0.03 CC
Freight	0.05 CC
Total Purchased Equipment Cost, PEC	1.08 CC
Installation Costs	
Foundations and Supports	0.08 PEC
Erection and Handling	0.14 PEC
Electrical	0.04 PEC
Piping, Insulation, and Painting	0.04 PEC
Total Installation Cost	0.30 PEC
Site Preparation	As required for specific site, SP
Buildings	As required for specific site, BLDG
<i>Total Direct Costs</i>	<i>1.30 PEC + SP + BLDG</i>
<i>Indirect Costs</i>	
Engineering and Supervision	0.10 PEC
Construction, Field Expenses, and Fees	0.15 PEC
Start-up and Performance Test	0.03 PEC
Contingency	0.03 PEC
<i>Total Indirect Costs</i>	<i>0.31 PEC</i>
<i>TOTAL INSTALLED CAPITAL COSTS, TCC</i>	<i>1.61 PEC + SP + BLDG</i>

Table 6-5. Annual Operating Costs for Incinerator Systems [6]

<i>Direct Annual Costs</i>	Unit Cost	Estimated Requirement
Utilities:		
Electricity	\$0.05/ kWh	See Chapter 4
Natural Gas	\$3.30/1000 ft ³	Calculated above
Operating Labor	\$12.96/h	½ hour per shift
Maintenance Labor	\$14.26/h	½ hour per shift
Maintenance Materials	Equal to maintenance labor	
Supervisory Labor	15% of Operating Labor	
<i>Indirect Annual Costs</i>		
Overhead	60% of Maintenance Costs	
Property Tax	1% of TCC	
Insurance	1% of TCC	
Administrative Costs	2% of TCC	
Capital Recovery (see Chapter 4 for formula to calculate capital recovery factor)	CRF * TCC	
<i>Total Annual Operating Costs</i>	<i>Direct + Indirect Operating Costs</i>	

Installation, Operation, and Maintenance Considerations

The main problem with recuperative incinerators tends to be ensuring that the heat exchange surface remains clean and that the heat exchanger does not develop cracks [56]. In addition to difficulties with the refractory linings in the incinerator, heat stress can take a toll on the heat recovery equipment. At best, heat stress or buildup of material may keep butterfly valves on regenerative units from seating properly, a common problem which allows leakage of the contaminated gas stream into the outlet gas stream, decreasing efficiency. At worst, heat stress can crack metal joints in heat exchangers, so that gas is allowed to escape from the clean side to the dirty side or vice versa, depending on the position of the fan. Such cracks can be difficult to locate, since the metal contracts as it cools to room temperature. The incinerator system should be designed considering the potential leakage of material. An additional fan is usually required to move the air from the process into the incinerator. This fan may be installed either before or after the heat exchangers and incinerator. By careful analysis of the system and fan placement, it can be ensured that any leakage occurs in an acceptable direction. Any inorganic particulate that may block nozzles, interfere with the combustion flame, or foul heat transfer surfaces should be removed prior to the incineration system. A list of advantages and disadvantages of thermal incineration is given in Table 6-6 for comparison with other technologies during a technical and economic evaluation [57, 58].

Table 6-6. Advantages and Disadvantages of Thermal Incineration [57, 58]

Advantages	Disadvantages
Simple, straightforward operation	Some NO _x formation, although it can be minimized
Heat recovery for other processes is feasible	Explosion potential
High efficiencies possible with proper design	Fuel consumption can be significant
Technology is applicable for a wide variety of gas concentrations and constituents.	No ability to reuse pollutants
Useful for multi-component streams	Approximately 3 times higher fuel usage than in catalytic incinerators

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Chapter 7

Flaring

Technology Description

Flaring is another type of combustion process, referred to as “complete combustion”, in which the combustion reaction occurs instantaneously at the burner tip [1], with the air diffusing across the combustion boundary toward the core of fuel gas [2]. The operating temperature is generally between 1370 and 1920 K (1090 and 1650 °C, 2000 and 3000 °F) [3, 4]. Flares are frequently used to control emergency venting of pollutants during process upsets [5]. While the mechanisms are similar to thermal oxidation, flares have historically been treated separately from thermal oxidizers because it is often extremely difficult to sample the emissions from a flare. Instead, emissions are frequently calculated from emission factors developed in the early 1980’s [6]. Mixing and temperature are the critical parameters of properly designed flares, since there is no residence chamber to continue the combustion reaction [7]. While flares constitute relatively simple control devices, there are many concerns in their operation, including noise, smoke, energy consumption, and safety [8]. Safety concerns encompass both the large amounts of heat released and the potential for releasing combustion by-products [9]. A typical flow diagram of a flare is given in Figure 7-1 [10].

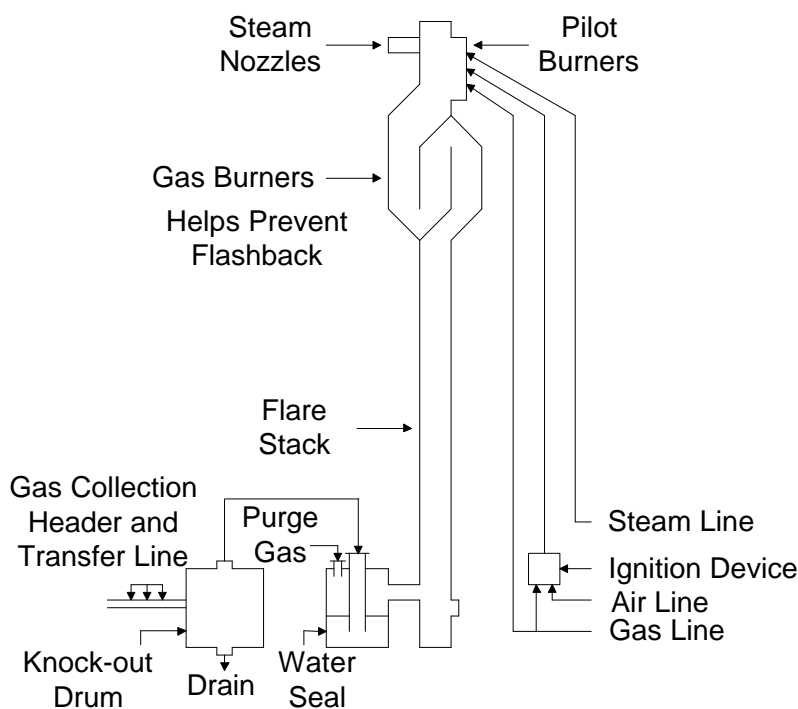


Figure 7-1. Typical Flare Diagram [10]

Flares are prevalent in the petrochemical industry [11, 12] both for control of emissions at steady state, and for destroying pollutants during unstable operating conditions such as start-ups and shutdowns [13]. They are particularly well-suited to processes with variable gas flow, because

they can be designed to operate over a wide range of flow. Flares can handle a gas stream with a maximum flow rate 1000 times as high as the minimum flow rate [7]. In addition, they can handle gas flows at least as high as two million pounds per hour [13]. If properly designed, flares are capable of efficiencies rivaling those of incinerators and absorbers. On gas streams with heat contents of 12.2 MJ/Nm³ (300 Btu/scf) or higher, 98% destruction is feasible. In fact, this is required by EPA regulations for some flares [2, 14].

The color of the flare flame indicates the mechanisms by which combustion is occurring. A blue flame indicates that the fuel and air mixture is being heated gradually to form aldehydes and ketones which are then reacted to form carbon dioxide and water. By contrast, a yellow-orange flame indicates that cracking of the fuel is occurring, and that the hydrocarbons have not had adequate opportunity to react with available oxygen, so that elemental carbon and hydrogen are formed. The carbon particles cause the flame to glow yellow. If the flame is not adequately mixed or of sufficient temperature, the carbon particles cool below the carbon ignition temperature and form black smoke or soot [2, 7].

As with other combustion techniques, the application of flaring is limited to situations in which the pollutants are not valuable enough to make recovery economically viable. Furthermore, it is generally also limited to gas streams with relatively concentrated organic constituents, although less concentrated streams can be flared if the additional cost of auxiliary fuel can be justified due to the toxicity of the pollutant or the sensitivity of local citizens.

In general, flaring is not a suitable control technology for halogenated compounds, since these compounds require longer residence time to achieve complete combustion and accelerate corrosion of the nozzle [15]. In addition, it is impossible to treat the acid by-products which result from burning halogenated compounds. If thermal incineration is employed instead, the off-gases can be treated by a scrubber before being released to the atmosphere.

Table 7-1. Typical Applications of Flaring [7, 16, 17, 18, 19]

Acrylonitrile product loading
Refineries
Dangerous gases such as hydrogen cyanide and ammonia
Landfills
Sewage treatment plants
Dimethylamine odors from soap manufacturing

Types of Flares

There are four types of flares, classified according to the method used to provide for adequate contact at the burner tip. The most common is the steam assisted flare, which is commonly used in chemical processes and refinery operations [2, 20, 21]. Steam injected into the flame provides mixing between the air and the gas for better combustion and helps to pull air into the combustion zone [2, 14]. The steam also assists in the combustion efficiency by reacting with intermediate combustion products to form oxygenated compounds which combust at lower temperatures [2, 7]. It also helps maintain a lower temperature in the flame to reduce thermal cracking [2]. The type and concentration of pollutants determine the amount of steam needed for good combustion; the mass ratio of steam to air is usually in the range of 0.01-0.6 [2, 7, 11]. Steam assisted or smokeless flares are used to control emissions of organic compounds that have a lower ratio of hydrogen to carbon [19]

Other types of flares are air-assisted, in which air is blown into the combustion zone to improve mixing and provide oxygen for combustion; non-assisted, in which a gas stream with low heat content and easily combustible gases that are resistant to thermal cracking is burned without any mixing enhancement; and pressure-assisted flares, in which the gas stream itself is pressurized to enhance the mixing. Air- and pressure-assisted flares are advantageous, in that they can be used in areas without available steam. [2]

Flare Design

A flaring system generally includes a collection header for the waste gas, followed by a knock-out pot (if necessary) to remove liquid droplets. A water seal is used to prevent the flame from propagating back down the stack and into the process if the velocity of the gas is reduced. As the gas travels through the flare, pilot burners ignite the gas stream to destroy the VOCs [22]. The diameter of the flare stack and nozzle must be sized appropriately so that the flame does not propagate back into the stack because of too low a stack gas velocity nor get extinguished because of too high a flow rate. EPA has developed regulations to ensure that flares are designed to achieve high destruction efficiencies [23]. EPA guidelines for steam-assisted flares include the following [2]:

1. For gas streams with heat contents greater than 41 MJ/Nm^3 (1000 Btu/scf), the maximum exit velocity is 122 m/s (400 ft/s). For other gas streams, the maximum exit velocity is determined from the net heating value (Bv) by the following equation:

In SI units:

$$V_{\max} = 10^{(Bv/0.0404 + 1214)/852}$$

or in English units:

$$V_{\max} = 10^{(Bv+1,214)/852}$$

where : V_{\max} = maximum exit velocity, m/s (or ft/s for English units)

Bv = net heating value, MJ/Nm^3 (or Btu/scf)

2. The net heating value of the gas must be at least 12.2 MJ/Nm^3 (300 Btu/scf).
3. A flame must be present at any time emissions may be vented.
4. No visible emissions (smoke) is allowed from the flare.

The minimum nozzle diameter (D_{\min}) can be calculated from the volumetric flowrate (Q) and the maximum velocity. The diameter is normally sized so that the maximum volumetric flow rate is conveyed through the nozzle at approximately 80% of the allowable velocity, V_{\max} [2]:

In SI Units:

$$D_{\min} = 162.5 (Q_{\min}/V_{\max})^{1/2}$$

In English Units:

$$D_{\min} = 1.95 \left(\frac{Q}{V_{\max}} \right)^{1/2}$$

where D_{\min} = Minimum nozzle diameter, (mm or in.)

Q = Outlet maximum volumetric flowrate (actual m^3/min or actual ft^3/min).

Safety concerns associated with flares are obvious: since flares are usually installed on streams where the gas exceeds the Lower Explosive Limit (or LEL), a flame will propagate very quickly through the ducting if adequate suppression systems are not installed. Explosive limits for several compounds are given in Table 7-2. The flare must also be installed at a safe elevation. A conservative calculation of the required distance from exposed objects can be made from the following equations[2]:

In SI units:

$$L = 0.02078 \left(\frac{mB_m}{K} \right)^{1/2}$$

In English units:

$$L = \left(\frac{0.2mB_m}{4K} \right)^{1/2}$$

where L = the required distance, meters (or feet)

m = mass flow rate, kg/h (or lb/h)

B_m = heat content of the gas stream, kJ/kg (or Btu/lb)

K = allowable radiation, assumed to be $49 \text{ kJ h}^{-1} \text{ m}^{-2}$ ($500 \text{ Btu h}^{-1} \text{ ft}^{-2}$)

Table 7-2. Flammability Limits in Air [7]

Pollutant	Lower Explosive Limit (Volume %)	Upper Explosive Limit (Volume %)
Hydrogen	4.00	74.20
Carbon Monoxide	12.50	74.20
Methane	5.00	15.00
Ethane	3.00	12.50
Propane	2.12	9.35
n-Butane	1.86	8.41
Isobutane	1.80	8.44
n-Hexane	1.18	7.4
Ethylene	2.75	28.60
Propylene	2.00	11.10
n-Butene	1.75	9.70
Benzene	1.40	7.10
Toluene	1.27	6.75
Xylene	1.00	6.00
Methyl Alcohol	6.72	36.50
Ethyl Alcohol	3.28	18.95
Ammonia	15.50	27.00
Hydrogen Sulfide	4.3	45.50
Gasoline	1.40	7.60

Specifications in the state of Texas for steam-assisted flares include guidance that at least 0.4 kilograms (or pounds) of steam be used per kilogram (or pound) of waste gas when the H/C ratio is less than 0.3. In addition, the guidance recommends that an H/C ratio higher than of 1 be avoided, since the VOC destruction efficiency may be decreased [6]. Additional design information is given by Swithenbank [24]. Instrumentation that should be considered when installing a flare system is given in Table 7-3.

Table 7-3. Instrumentation to Consider for Flare Systems

Gas stream pressure and flow (particularly if flow is variable)
Concentration or % LEL
Fan speed
Auxilliary fuel flow

Economic Estimates

As shown in the following equations, the type of support required for the flare stack can substantially affect the cost of the system. Three types of flare structures are included: self-supported flares, derrick-supported flares, and flares supported by guy wires. Figures 7-2 [2], 7-3 [2], and 7-4 [2] show examples of types of support structures which can be used for flares. Operating costs are governed primarily by the amount of auxiliary fuel, steam and electricity needed.

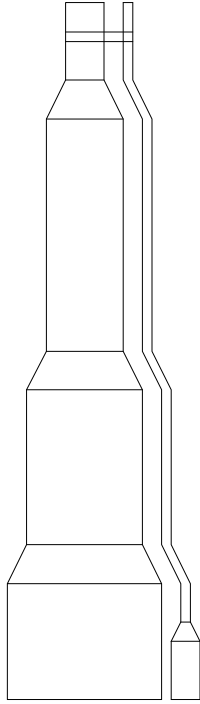


Figure 7-2. Self-Supported Flare

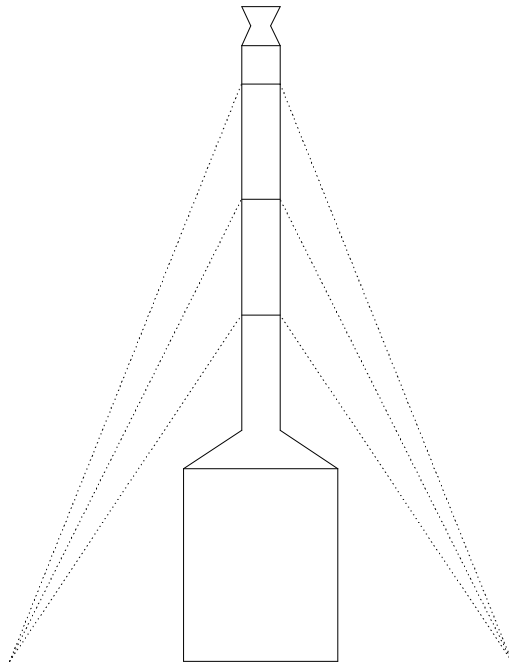


Figure 7-3. Guyed Supported Flare

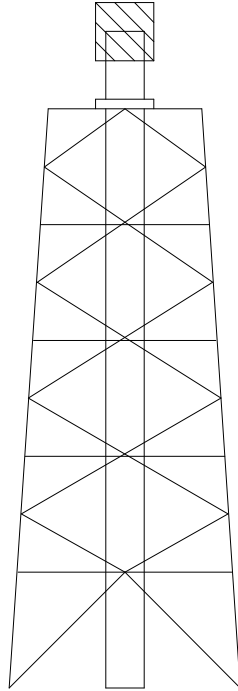


Figure 7-4. Derrick Supported Flare

Estimates of the capital cost of the flare can be obtained from the following equations [2]. The figures given are in 1990 dollars and should be scaled up to the current year using escalation factors available on the Clean Air Technology Center website (<http://www.epa.gov/ttn/catc>).

In SI units,

$$C_F = a + bD/25.4 + cL/3.2808$$

In English Units,

$$C_F = (a + b D + c L)^2$$

where:

D = tip diameter, mm (or in)

L = Height of flare stack, m, 9.14 m at a minimum (or ft, 30 feet at a minimum).

Factors a, b, and c are specific to the type of support structure, given in Table 7-4:

Table 7-4. Factors for Capital Cost Equation

Type of Support	a	b	c
Self supported	78.0	9.14	0.749
Guy wires	103	8.68	0.470
Derrick Supported	76.4	2.72	1.64

These cost estimates include a carbon steel flare stack with the upper 1.2 m (four feet) made of 310 stainless steel, 310 stainless steel burner tip, pilot lights, liquid and gas seals, access ladders and platforms as required. They also include utility piping from the base of the stack, metering and control. The equations are generally valid for tip diameters from 25 to 1520 mm (1 to 60

inches) and for stacks from 9.1 m to 152 m (30 to 500 feet).

In addition to the cost of the flare itself, costs for vent piping and a knock out pot must also be included in the overall estimate of equipment cost. The approximate size of a vertical knock out pot on a relatively constant flow vent stream can be estimated from the following equations:

In SI Units:

$$A = \frac{Q_a}{197G \left(\frac{\rho_l - \rho_v}{\rho_v} \right)^{1/2}}$$

In English Units:

$$A = \frac{Q_a}{60G \left(\frac{\rho_l - \rho_v}{\rho_v} \right)^{1/2}}$$

where A = cross sectional area of the knock out vessel, m² (or ft²)
 Q_a = actual flow rate of vent stream, m³/min (or ft³/min)
 G = vapor velocity factor, usually 0.15 –0.25
 ρ_l = density of the liquid to be removed in the knock out pot, kg/m³ (or lb/ft³)
 ρ_g = density of the gas stream, kg/m³ (or lb/ft³)

Once the cross sectional area of the vessel is known, the diameter can be calculated from the following equations [2].

In SI units:

$$d_{\min} = \sqrt{\frac{4}{\pi} A}$$

In English units:

$$d_{\min} = 13.5\sqrt{A}$$

where: d_{min} = minimum diameter of the vessel, m (or ft)

For an actual diameter, d_k, the minimum should be rounded to the next highest standard size. Vessels are usually available in 0.152 m (0.5 ft) increments. The thickness of the vessel, t, is determined from Table 7-5 .

Table 7-5. Determination of Knock Out Pot Wall Thickness [2]

Diameter		Thickness, t	
m	ft	mm	in
Less than 0.914	Less than 3	6.4	0.25
At least 0.914 and less than 1.83	At least 3 and less than 6	9.4	0.37
At least 1.83 and less than 2.74	At least 6 and less than 9	12.7	0.5
At least 2.74 and less than 3.66	At least 9 and less than 12	19.1	0.75
3.66 or over	12 or over	25.4	1

The height of the knock out drum, h (m or ft), is estimated as three times the actual diameter [2]. With the diameter and height of the knock out drum, the cost of the knock out drum, C_K is estimated as [2, 25, 26]:

In SI units:

$$C_K = 2.1 [d_K t (h + 0.812 d_K)]^{0.737}$$

In English Units:

$$C_K = 0.364 [d_K t (h + 0.812 d_K)]^{0.737}$$

The cost of piping the vent stream to the flare stack, C_P , is calculated separately from the following equation [2], assuming that that 31 m (100 feet) of piping is required that has the same diameter as the tip of the flare [27]:

In SI units:

$$C_P = 2.53 D^{1.21} \text{ for diameters between 25 and 610 mm}$$

$$C_P = 4.36 D^{1.07} \text{ for diameters between 760 and 1520 inches}$$

In English units:

$$C_P = 127 D^{1.21} \text{ for diameters between 1 and 24 inches}$$

$$C_P = 139 D^{1.07} \text{ for diameters between 30 and 60 inches}$$

Piping costs are based on Schedule 40 carbon steel pipe.

The total purchased equipment cost includes the cost of the flare, the knock-out pot, and the piping, plus instrumentation, sales taxes, and freight. Additional fans or blowers are not included in these calculations, but may be required due to the significant pressure drop in some systems. Instrumentation is estimated as 10% of the equipment cost, sales taxes as 3%, and freight as 5% for a total of [2]:

$$PEC = 1.18 (C_F + C_K + C_P)$$

As shown in Table 7-6, the total capital investment is estimated as 192% of the purchased equipment price [19] .

Annual costs may be approximated as given in Table 7-7. Electricity requirements can be estimated from the formulas given in Chapter 4. The pressure drop for flare systems can be as high as 60 inches of water [28], depending on the configuration of the equipment and the length of the gas piping. Steam costs can be estimated as 0.6 lb/lb of waste gas [28].

Table 7-6. Factors for Estimating the Total Installed Capital Cost of Flares [2]

<i>Cost Element</i>	<i>Estimated Cost</i>
<i>Direct Costs</i>	
Purchased Equipment Cost	
Flare and Auxiliary Equipment (EC)	$EC = C_F + C_K + C_P$
Instrumentation	0.10 EC
Taxes	0.03 EC
Freight	0.05 EC
Total Purchased Equipment Cost, PEC	1.18 EC
Installation Costs	
Foundations and Supports	0.12 PEC
Erection and Handling	0.40 PEC
Electrical	0.01 PEC
Piping, Insulation, and Painting	0.04 PEC
Total Installation Cost	0.57 PEC
Site Preparation	As required for specific site, SP
Buildings	As required for specific site, BLDG
<i>Total Direct Costs</i>	$1.30 PEC + SP + BLDG$
<i>Indirect Costs</i>	
Engineering and Supervision	0.10 PEC
Construction, Field Expenses, and Fees	0.20 PEC
Start-up Performance Test	0.02 PEC
Contingency	0.03 PEC
<i>Total Indirect Costs</i>	$0.35 PEC$
<i>TOTAL INSTALLED CAPITAL COSTS, TCC</i>	$1.92 PEC + SP + BLDG$

Table 7-7. Annual Operating Costs for Flare Systems [2, 19]

<i>Direct Annual Costs</i>	Unit Cost	Estimated Requirement
Utilities:		
Electricity	\$0.05/ kWh	See Chapter 4
Steam	\$10.25/1000 kg \$4.65/ 1000 lb	0.6 kg/kg 0.6 lb/lb
Natural Gas (equation is for elevated flares)	\$127/1000 Nm ³ \$3.30/ 1000 scf	SI units: $2.03 \times 10^{-6} Q_A^{0.934} \text{ Nm}^3/\text{h}$ English units: $0.00218 Q_a^{0.934} \text{ scf/h}$ [19, 29]
Operating Labor	\$12.96/h	½ hour per shift
Maintenance Labor	\$14.26/h	½ hour per shift
Maintenance Materials	100% of Main. Labor	
Supervisory Labor	15% of Operating Labor	
<i>Indirect Annual Costs</i>		
Overhead	60% of Maintenance Costs	
Property Tax	1% of TCC	
Insurance	1% of TCC	
Administrative Costs	2% of TCC	
Capital Recovery (see Chapter 4 for the formula to calculate capital recovery)	CRF * TCC	
<i>Total Annual Operating Costs</i>	<i>Direct + Indirect Operating Costs</i>	

Potential Problems

It is helpful to enclose the sides of the flare with a fibrous insulating material held in place by a lightweight shroud. Such protection reduces the impact of wind turbulence which can make the flare less effective. The enclosure also reduces heat losses [30, 31]. An open-ended refractory chamber can also be used to increase the residence time of the flare to improve destruction efficiency [32].

The pilot flames need to be designed in such a way that they can be relit, even in severe weather such as high wind and hard rain [32]. Precautions must also be taken to ensure that gas streams which are normally above the explosive limit do not become explosive due to increased temperature, pressure or increased air infiltration.

Liquid droplets must be carefully removed from the gas stream to eliminate the possibility that water will cool the flame or that organic droplets will pass through the flare nozzle and fall out in the atmosphere as flaming particles [22]. Solid particulate may also serve to erode the nozzle and should be removed from the gas stream. If inert material is present, it may be necessary to preheat the gas stream by installing a ring burner in addition to the pilot burners [31].

Installation, Operation, and Maintenance Considerations

Corrosion is a potential problem with any control device. In flares, it is usually a problem with high concentrations of sulfur compounds or high concentrations of halogenated compounds. These compounds are better suited to incineration followed by scrubbing to remove the corrosive compounds [29].

Texas requires that all proposed flare systems include a continuous pilot ignition system so that process and emergency flares are relit immediately. In addition, it is recommended that a remote infrared monitor be used to monitor the flame [6]. A summary of the advantages and disadvantages of using flaring systems to control VOCs is given in Table 7-8.

Table 7-8. Advantages and Disadvantages of Flares

Advantages	Disadvantages
Relatively simple equipment and operation	No recovery of contaminant
Capable of high efficiency	Potential corrosion of ductwork due to moisture in gas stream

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Chapter 8

Catalytic Incineration

Technology Description

Like thermal incinerators, *catalytic incinerators* destroy organic pollutants by combustion to produce a mixture of carbon dioxide and water. Catalytic incinerators utilize a noble metal or metal oxide solid catalyst material. The catalyst itself does not react, but it enables the combustion reaction to occur at a lower temperature than normal, generally without the presence of a flame. This allows for virtually complete combustion of the pollutants with very little NO_x formation. Although the mechanism of the catalyzed reaction for most organics is not well understood [1], the presence of the catalyst makes a new reaction pathway possible that has a lower activation energy than the uncatalyzed reaction. It is believed that the catalyst promotes the reaction by forming reactive intermediates and bringing them into close proximity on its surface [2, 3]. The catalyst is usually impregnated over a high surface area washcoat like alumina on a porous matrix as shown in Figure 8-1 [4]. As the gas flows through the matrix, the pollutants and oxygen diffuse to the surface of the catalyst, where probably both species (oxygen and the pollutant) adsorb onto the catalyst surface. The type of catalyst and the type of pollutant determine how the species adsorb [1]. At higher temperatures, the combustion reaction can also propagate into the gas phase, initiating homogeneous chain reactions [5]. Catalytic incinerators operate at a lower temperature, usually 620 to 870 K (340 to 590 °C, 650 °F to 1100 °F) [6], than thermal incinerators, but if properly applied, are capable of destruction efficiencies similar to those for thermal incinerators if properly applied. The lower operating temperature results in less NO_x formation [4] (generally less than 15 ppm [7]) and significantly smaller fuel consumption (reported to be as low as one third) [8, 9, 10] than most thermal incinerators.

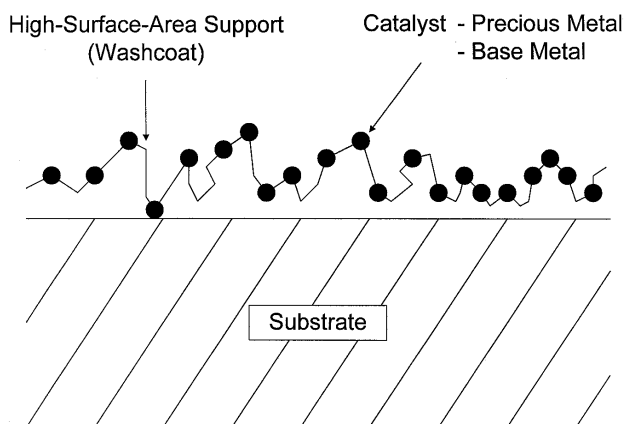


Figure 8-1. Cross Sectional Diagram of Catalyst Composition [4]

A typical flow diagram for a catalytic incinerator is shown in Figure 8-2 [11, 12]. The pollutant-laden gas flows through a heat exchanger to preheat the incoming gas with the heat of the exhaust gases. The incinerator may or may not have a supplemental burner to further preheat the pollutant-laden gas stream. As the preheated gases react going through the catalyst bed, the temperature of the gas stream increases. The reaction generates the same amount of heat as the heat of combustion that is generated in a thermal incinerator [13]. The reacted gas stream then passes back through the heat exchanger and is released to the atmosphere.

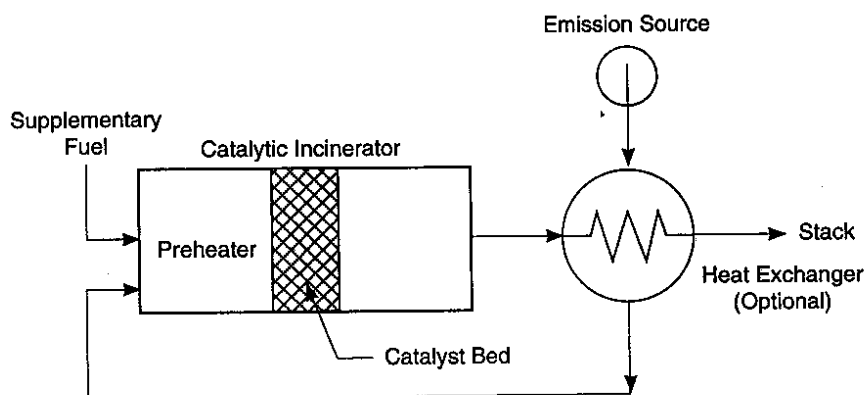


Figure 8-2. Catalytic Oxidizer Flow Diagram [11, 12]

Care must be taken to properly identify the constituents of a gas stream before either thermal or catalytic incineration is selected as the control method. Some compounds interfere with the action of the catalyst, either by chemically binding to the surface or by adsorbing on to the surface and deactivating sites for future reaction. Compounds that bind chemically to the catalyst are referred to as poisons and may be classified as either fast- or slow-acting. Fast-acting poisons include phosphorus, bismuth, arsenic, antimony, chlorine, fluorine, bromine, and mercury. Zinc, lead, and tin are slow-acting poisons [14, 15]. The portion of the surface that is bound to the poison is not available for reaction, so the overall reaction rate decreases due to a decrease in the amount of available surface area. Other compounds, such as heavy oils, dust, and silica [16] may coat the surface of the catalyst. If the operating temperature is not high enough to promote combustion of the oily compounds, the surface area will be reduced. Sulfur compounds in the gas stream (including mercaptans which are added to natural gas and propane to make sure that leaks are detectable [17]) may bind to components in the washcoat to form sulfates (*e.g.*, aluminum sulfate) [4], rendering a portion of the surface unusable. At a minimum, sulfur reacts to form sulfur dioxide, which may need to be removed before venting to the atmosphere. Halogenated compounds in the contaminated gas stream may also interfere with the catalyst action, either by binding to the catalyst or reacting to form acids which can severely corrode the catalyst supports, ductwork and downstream equipment. Special attention must be given to the catalyst selection to ensure that halogenated compounds do not react to form molecular halogen species like Cl_2 [18]. Catalysts have been developed recently which are resistant to poisoning by halogen compounds [19, 20]. Particulates, oils, sulfur, and halogens are all compounds which can poison the catalyst but which are reversible inhibitors. Once the compound is removed, the activity of the catalyst is restored. Generally, superheated steam is adequate to remove the compounds from the catalyst

surface [21].

Destruction efficiencies of 98% or greater are now common in catalytic incinerators [4]. Destruction efficiencies of 99% are achievable, but the increased temperature or large catalyst volume required may make the technology economically infeasible [22]. The removal efficiency is determined by the type of catalyst, the surface area of the catalyst, the pollutant species, the pollutant concentration, the residence time, the extent of mixing, the uniformity of gas flow through the catalyst, the oxygen concentration, and the temperature [2, 23, 24]. Examples of potential uses for catalytic incineration are given in Table 8-1 [2, 15, 24, 25, 26, 27, 28, 29, 30, 31].

Table 8-1. Potential Applications of Catalytic Incineration for VOC Removal [2, 15, 24, 25, 26, 27, 28, 29, 30, 31]

Odor control
Printing operations
Polymer processing
Bakeries
Paint bake ovens
Foundry core ovens
Tire manufacturing
Metal furniture coating
Wire enameling
Textile drying
Gasoline marketing

Types of Catalytic Incineration Systems

Catalytic incinerators can be classified in several different ways. They may be classified according to the type of heat recovery used, the type of catalyst (noble metal or metal oxide catalyst) used, or the shape of the catalyst substrate. Because most gas streams are dilute, heat recovery is normally used to help reduce the amount of supplemental fuel required. Catalytic incinerators may use either recuperative or regenerative heat exchangers (see the discussion in Chapter 6). Most systems use *recuperative* heat exchangers (as shown in Figure 8-3 [32]), in which the exhaust gases from the incinerator pass through a non-contact heat exchanger to recover the heat of combustion and increase the fuel efficiency of the VOC destruction process. A few *regenerative* systems have been introduced (see Figure 8-4 [33]) which use beds of inert ceramic material as a heat sink [34, 35]. Regenerative incinerators allow for better heat recovery, meaning that dilute vapor streams can be incinerated at lower costs [36]. The type of heat recovery system must be chosen carefully, both to avoid higher than necessary energy costs and also to make sure that efficient energy recovery does not result in too high a catalyst temperature.

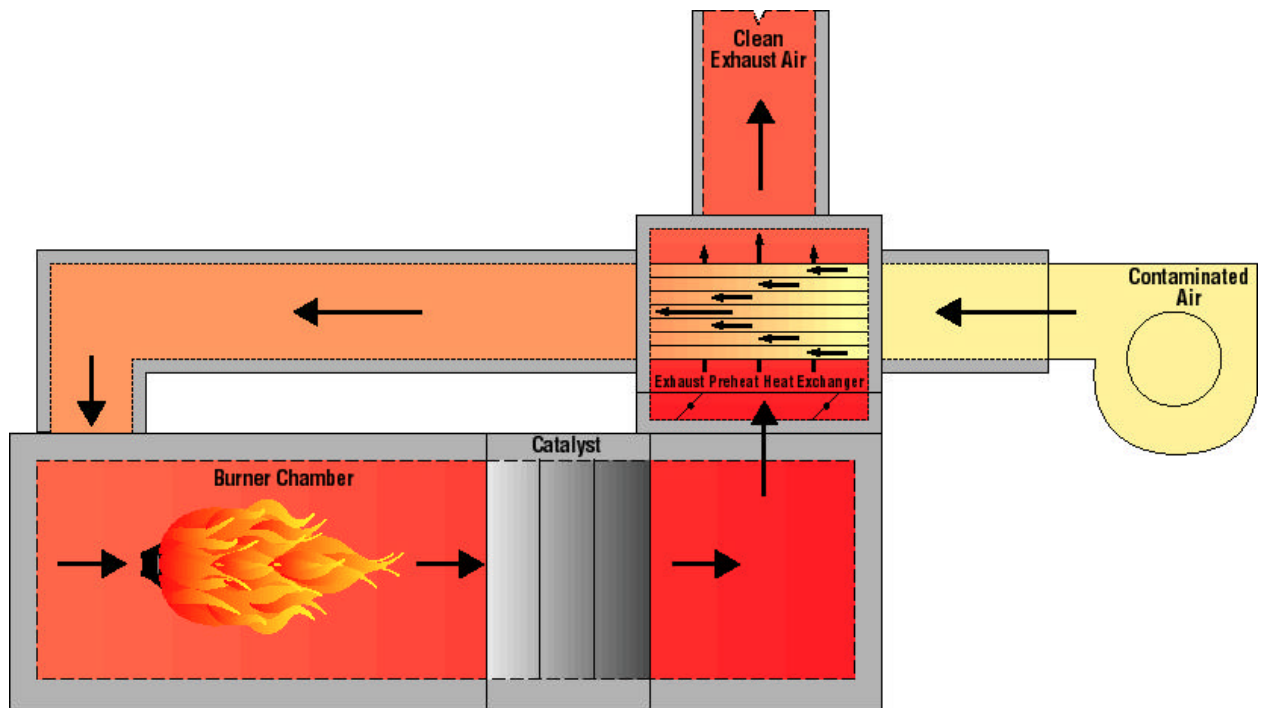


Figure 8-3. Catalytic System with Recuperative Heat Exchange, Glenro, Inc. [32]

Catalytic systems may also be classified according to the form of the catalyst material. The primary objective in design of a catalyst is to provide as much surface area as possible to promote the reaction with minimal pressure drop. Both fixed beds and fluid beds are used to accomplish this. A typical catalyst consists of a ceramic or metal substrate coated with an alumina washcoat to provide surface area, then a noble metal or metal oxide on the surfaces [35]. Precious metals such as platinum, palladium, and rhodium are frequently used; they usually allow for more reactivity which results in a lower operating temperature and shorter residence time [37, 38]. Substrates for fixed beds may be in the shape of honeycombs, rods, or metal ribbon [2]. Fixed beds may also contain catalysts in the form of beads or pellets. Fluid beds generally consist of a tray or chamber filled with spherical or pellet-shaped catalysts. While pellet-shaped catalysts are more susceptible to attrition, this can be a benefit for gas streams that contain more particulate [4]. The attritive action serves to clean off the surfaces of the catalyst beads.

Hybrid systems have also been introduced which combine adsorption with catalytic combustion, to increase the concentration of pollutants for the combustion process. The VOCs from the gas stream are adsorbed onto zeolite, then they are desorbed with a smaller gas stream. This results in lower energy usage, since less air must be heated to the combustion temperature. While the system is more complex, it does provide an alternative which uses less auxiliary fuel [39]. Chapter 6 contains a diagram of one such system [40].

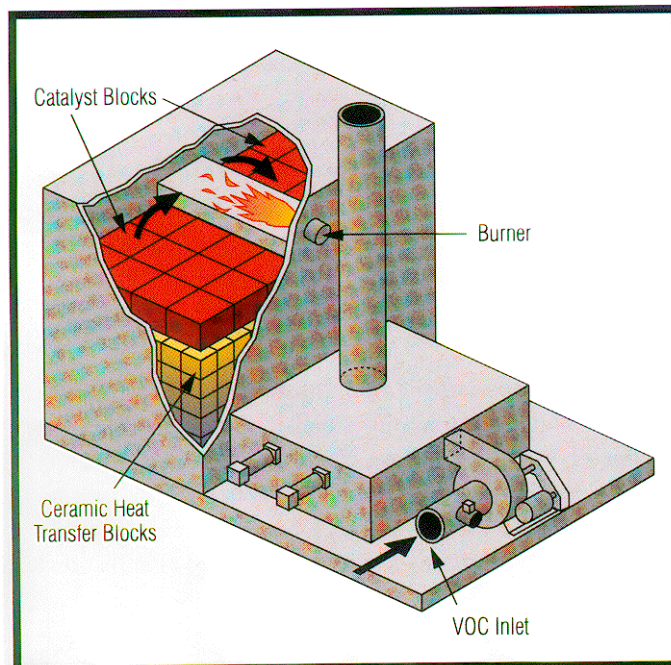


Figure 8-4. Anguil Regenerative Catalytic Oxidizer [33]

Catalytic Incinerator System Design

It is generally not feasible to empirically predict the action of a given catalyst and organic compound with the accuracy required for designing process equipment [13, 41]. Therefore, it is highly encouraged that a catalytic system vendor be contacted to determine an appropriate type and volume of catalyst for the specific VOC mixture in the gas stream. It may also be helpful to use a test unit, particularly if poisons or deactivators may be present in the gas stream [4].

The amount of gas to be treated should be minimized to reduce the capital and operating costs of the incinerator. Usually, the gas streams treated with catalytic incineration are so dilute that no additional combustion air is required. If the concentration of VOC is significant, care must be exercised to ensure that the catalyst does not overheat and that the concentration of pollutant in the gas does not exceed a safe level in the ducting, especially during process upsets or start up conditions. See Chapter 7 and the U.S. Bureau of Mines information [42, 43] for additional information about acceptable ductwork concentrations and LELs. The heating value of hydrocarbons at the LEL has been determined to be approximately 2030 kJ/Nm^3 (50 Btu/scf). For catalytic units, the heat of combustion should normally be less than approximately 400 kJ/Nm^3 (10 Btu/scf) so that the catalyst temperature does not become excessive. However, regenerative heat recovery would reduce this number further. Similarly, if the oxygen content of the gas stream is lower than approximately 20%, auxiliary air may be required for the combustion process [41].

The inlet temperature to the catalytic bed must be higher than the catalytic ignition temperature to ensure that the reaction occurs [41]. Incomplete combustion can lead to emissions of compounds with more severe health effects than the original hydrocarbon gas stream [1, 44]. Many catalytic incinerators use a preheat burner to raise the temperature of the gas stream higher than that

obtained in the heat exchanger. This direct combustion also has the effect of creating a high chemical activity [45].

If the gas stream contains halogenated or sulfur compounds, a scrubber may be required to remove acidic gases after treatment. Depending on the catalyst chosen, these compounds may need to be removed prior to the catalyst. In either case, the scrubber or removal mechanism should be considered as an integral part of the incinerator system and should not be overlooked even in preparing rough cost estimates, since the cost of the scrubber can be a significant portion of the overall system cost [46].

Procedures for the basic design of the heat exchange and fuel consumption for a catalytic incinerator are given in the *OAQPS Control Cost Manual* [41]. The procedures were developed to ensure that the catalyst temperature remains above the catalytic ignition temperature but below about 920 K (650 °C, 1200 °F), where damage to the catalyst may result. The first step is to determine the appropriate outlet temperature of the catalyst bed. Combustion Engineering suggests that this should be between approximately 420 and 760 K (150 and 480 °C, 300 and 900 °F) to achieve 90-95% destruction [47]. However, the exact value will depend on the constituents of the gas stream as well as the type of catalyst. Vendors should be consulted to accurately determine an appropriate outlet temperature. The temperature of the polluted gas stream exiting the heat exchanger is then determined from the equation:

$$T_i = T_w + \text{Eff} (T_c - T_w) \quad 8-1$$

where:

T_c = Catalyst outlet temperature, °C (or °F)

T_r = Reference temperature, 21°C (70°F) is typical

T_i = Inlet gas stream temperature, after heat exchanger, °C (or °F), generally 260-320 °C (500-600 °F) [48].

T_w = Temperature of inlet gas stream before heat exchanger, °C (or °F)

Eff = Anticipated fractional thermal efficiency of the incinerator (usually between 0.5 and 0.95)

Procedures for calculating the total flue gas flow (that is, the flowrate of gases leaving the incinerator) are given in the *OAQPS Control Cost Manual* [41] and by Vatauvuk [49]:

$$Q = Q_w + Q_f \quad 8-2$$

where: Q = Total flue gas flowrate, normal m^3/min abbreviated Nm^3/min (in English units, standard ft^3/min abbreviated scfm)

Q_w = Waste gas flowrate at inlet to incinerator, Nm^3/min (scfm)

Q_f = Flowrate of auxiliary fuel, Nm^3/min (scfm)

The flowrate of auxiliary fuel is calculated from the equation:

$$Q_f = Q_w X/Y \quad 8-3$$

where: $X = \frac{1.1 C_{po} (T_c - T_r) - C_{pi} (T_i - T_r) - h_w}{h_f - 1.1 C_{po} (T_c - T_r)}$

C_{po} = Mean heat capacity of exhaust stream from the incinerator, kJ min/Nm^3 ($\text{Btu scf}^{-1} \text{ } ^\circ\text{F}^{-1}$). The heat capacity of air is typically used, since

most of the gas stream is air. At approximately 670K (400°C, 750 °F), the heat capacity of air is 1.38 kJ/Nm³ °C (0.0181 Btu/scf °F).

C_{pi} = Mean heat capacity of inlet streams to the incinerator, kJ min/Nm³ (Btu scf⁻¹ °F⁻¹). Again, the heat capacity of air is typically used, since most of the incoming stream is air. At 311K (38 °C, 100 °F), the heat capacity of air is 1.30 kJ/Nm³ °C (0.017 Btu/scf °F).

h_w = Heat content of waste gas stream, kJ/Nm³ (Btu/scf)

h_f = Heat content of fuel, kJ/Nm³ (Btu/scf). For natural gas, h_f is approximately 40,200 kJ/Nm³ (1000 Btu/scf).

h_f may be calculated in SI units from the following equation if the heat content is known in kJ/kg:

$$h_f = \text{heat content in kJ/kg} \times \text{fuel molecular weight in kg/kg-mole} / 22.4 \text{ Nm}^3 \text{ per kg-mole}$$

In English units, h_f can be calculated from the known heat content in Btu/lb:

$$h_f = \text{heat content in Btu/lb} \times \text{fuel molecular weight in lb/lb-mole} / 386.5 \text{ ft}^3 \text{ per lb-mole}$$

This must result in a positive value for the fuel consumption, or the amount of heat that is being recovered is too great to maintain the outlet temperature at the desired value. In addition, if there is a preheater combustion chamber, the amount of auxiliary fuel should be at least 5% of the total energy to make sure that the burner flame is stable. If the required fuel consumption is less than 5% of the energy, a lower heat transfer efficiency should be used and the calculations should be repeated.

If a preheat burner is used, the temperature at the outlet of the preheat burner and the inlet to the catalyst is calculated from the equation:

$$T_{ci} = \frac{\rho_f Q_f [(-\Delta h_f) + 1.1 C_{pi} T_r] + \rho_w Q_w C_{pa} (T_i + 0.1 T_r)}{1.1 C_{pa} (\rho_f Q_f + \rho_w Q_w)} \quad 8-4$$

where: T_{ci} = catalyst inlet temperature (after the preheater combustion chamber), °C (°F)

ρ_f = density of fuel, 0.6533 kg/m³ (0.0408 lb/ft³) for methane at 298K (25 °C, 77 °F) and 1 atm

ρ_w = density of polluted gas stream which can usually be adequately represented by the density of air, 1.183 kg/m³ (0.0739 lb/scf) for air at 298K (25 °C, 77 °F) and 1 atm

The value of T_{ci} that is calculated should be checked against values of catalytic ignition temperatures to ensure that the preheat temperature is high enough to initiate the reaction. The catalytic ignition temperature should be available from the vendor.

The amount of catalyst required will depend on the type of catalyst, the required removal efficiency, the VOCs to be destroyed and the anticipated reaction temperature. If the required residence time and the percentage of void space in the reactor is known, the volume can be estimated. As an approximation, 0.043 - 0.057 m³ (1.5 – 2.0 ft³) of catalyst will be required for every thousand cubic feet of combusted gas to achieve 90-95% destruction [21]. Velocity of the gas is usually approximately 3 to 6 m/s (10-20 ft/s) through the incinerator [2].

These equations assume a 10% loss of energy from the incinerator. Note that no allowance is included for volume changes due to changes in the total number of moles in the system which may occur during reaction. Additional correction may be needed for gas streams that contain

large concentrations of organic compounds, particularly if the organic compounds contain significant amounts of oxygen.

Instrumentation to consider for monitoring the overall performance and temperature history of the catalytic combustor is given in Table 8-2.

Table 8-2. Recommended Instrumentation

Inlet and outlet temperature
Inlet / outlet concentration
Fan speed
Pressure drop
Auxiliary fuel rate

Economic Estimates

There is typically a trade-off between the higher capital cost associated with a catalytic incinerator and the higher operating cost associated with a thermal incinerator [41]. Estimates of the capital cost of a fixed bed catalytic incineration system are given by the OAQPS Manual [41] according to the following equations.

In SI units, the equation is:

$$CC = a (Q/0.026)^b \quad 8-5$$

In English units, the equation is:

$$CC = a Q^b \quad 8-6$$

where: CC = Purchased Price, in 1988 dollars

Q = Flowrate of gases after combustion, Nm³/min (scfm)

a and b are parameters dependent on the amount of heat recovery required. For 0% heat recovery, a = 1,105 and b = 0.5471. For 50% heat recovery, a = 1,215 and b = 0.5575. At 70% heat recovery, a = 1,443 and b = 0.5527.

These estimates are valid for incinerators with flowrates of approximately 50 and 1300 Nm³/min (2,000 and 50,000 scfm).

Estimates of the capital cost of a fluid bed catalytic incineration system are calculated from the following equations.

In SI units:

$$CC = c + dQ/0.026 \quad 8-7$$

In English units:

$$CC = c + dQ \quad 8-8$$

where: CC = Purchased Price, in 1988 dollars

Q = Flowrate of gases after combustion, Nm^3/min (or standard ft^3/min , scfm)

c and d are parameters dependent on the amount of heat recovery required. For 0% heat recovery, c = 84,800 and d = 13.2. For 50% heat recovery, c = 86,600 and d = 15.8. At 70% heat recovery, c = 83,900 and d = 19.2 [41].

These estimates are valid for incinerators with flowrates of approximately 50 to 650 Nm^3/min (2,000 to 25,000 scfm).

In addition to the catalyst and preheat burner, the price includes a heat exchanger, fan, motor, instrumentation and controls, insulation, structural supports, and a short stack. Ductwork, particulate removal devices, scrubbers, and site-specific construction requirements are not included. If the incinerator is to be placed a long distance from the generation site, both the cost of ductwork and the cost of additional booster fans should be considered. As with the other chapters in this book, the cost estimates are to indicate a general order of magnitude and must be scaled up to current dollars to get even an estimated cost. They are not specific enough to use as construction costs and should be confirmed with actual prices from vendors.

To estimate the total installed capital expenditure, the factors in Table 8-3 may be used, which generally follows the methodology of EPA's *OAQPS Cost Control Manual* [41, 50].

Annual costs may be approximated using the guidelines in the *OAQPS Cost Control Manual* [41], as given in Table 8-4. Site specific values for unit costs should be used wherever possible to accurately reflect the anticipated costs. Electricity requirements can be estimated from the *OAQPS* formula given in Chapter 4, assuming a pressure drop of 1.5 kPa (6 in of water column) for a monolith catalyst, 1.5 to 2.5 kPa (6 to 10 inches of water column) for a fluid bed catalytic chamber. Very high efficiency designs require additional catalyst volume and are likely to increase the pressure drop through the catalyst chamber. The heat exchanger adds another 1 to 3.7 kPa (4-15 inches of water column), corresponding to heat recoveries of 35 to 70 percent [41]. Operating and maintenance labor requirements are usually minimal, at approximately one half hour per shift. However, dirty gas streams that require frequent catalyst cleaning will increase the amount of maintenance required.

Table 8-3. Factors for Estimating the Total Installed Capital Cost of Incineration Systems [41, 50]

<i>Cost Element</i>	<i>Estimated Cost</i>
<i>Direct Costs</i>	
Purchased Equipment Cost	
Incinerator and Auxiliary Equipment	CC, Estimated from equation
Taxes	0.03 CC
Freight	0.05 CC
Total Purchased Equipment Cost, PEC	1.08 CC
Installation Costs	
Foundations and Supports	0.08 PEC
Erection and Handling	0.14 PEC
Electrical	0.04 PEC
Piping, Insulation, and Painting	0.04 PEC
Total Installation Cost	0.30 PEC
Site Preparation	As required for specific site, SP
Buildings	As required for specific site, BLDG
<i>Total Direct Costs</i>	<i>1.30 PEC + SP + BLDG</i>
<i>Indirect Costs</i>	
Engineering and Supervision	0.10 PEC
Construction, Field Expenses, and Fees	0.15 PEC
Start-up and Performance Test	0.03 PEC
Contingency	0.03 PEC
<i>Total Indirect Costs</i>	<i>0.31 PEC</i>
<i>TOTAL INSTALLED CAPITAL COSTS, TCC</i>	<i>1.61 PEC + SP + BLDG</i>

Table 8-4. Annual Operating Costs for Incinerator Systems [41]

<i>Direct Annual Costs</i>	Unit Cost	Estimated Requirement
Utilities:		
Electricity	\$0.059/ kWh	See Chapter 4
Natural Gas	\$127/1000 Nm ³ \$3.30/1000 scf	Calculated above
Catalyst Replacement	\$23,000/m ³ \$650/ft ³ (metal oxide)	100% replacement every 2 years
Operating Labor	\$12.95/h	½ hour per shift
Maintenance Labor	\$14.25/h	½ hour per shift
Maintenance Materials	Equal to maintenance labor	
Supervisory Labor	15% of Operating Labor	
<i>Indirect Annual Costs</i>		
Overhead	60% of Maintenance Costs	
Property Tax	1% of TCC	
Insurance	1% of TCC	
Administrative Costs	2% of TCC	
Capital Recovery (see Chapter 4 for formula to calculate capital recovery factor, CRF)	CRF * [TCC-1.08*Catalyst Cost]	
<i>Total Annual Operating Costs</i>	<i>Direct + Indirect Operating Costs</i>	

Potential Problems

As with thermal incinerators, catalytic incinerators are best suited to operations that maintain a fairly constant flow rate and emission rate. With catalytic incinerators, however, large fluctuations in concentration or flow may result in overheating of the catalyst, leading to premature catalyst aging. Temperatures above approximately 920 K (650 °C, 1200 °F) may volatilize the metal catalyst or cause recrystallization of the support or catalyst metal [2]. In addition, high temperature fluctuations increase the stress on seams as the material expands or contracts. For that reason, catalytic incinerators are more appropriate for facilities that operate continuously instead of those that operate for only a few hours each day. The manufacturer's start-up procedure normally specifies a warm-up sequence in which the incinerator is brought to operating temperature gradually. Following this procedure lengthens the life of the refractory, but also uses additional fuel and may take longer than is feasible for the process. It is not unusual for maintenance or operating staff to develop a shorter start-up procedure. Using such a shortcut lowers the overall gas usage but is likely to result in considerably higher maintenance requirements. For cyclical processes, a regenerative incinerator should be considered which can be maintained at operating temperature with minimal natural gas consumption. Some of these units can even be put on an "idle" mode, in which no gas is pulled from the process, but the incinerator recycles exhaust air to the inlet to conserve energy [51].

Installation, Operation, and Maintenance Considerations

Particulate concentrations in a gas stream treated by catalytic incineration should be kept below 0.12 grams/Nm³ (0.05 grains/scf). The concentration of catalytic poisons should not exceed 25 ppm [52].

The main problem with catalytic incinerators is that the catalyst must be kept in relatively good

condition to ensure that the reaction proceeds as anticipated. As particulate or other materials build up on the surface, the amount of surface area available for reaction is decreased and the efficiency is reduced. It is generally recommended that the surface of the catalyst be cleaned by blowing jets of air across it, steaming with superheated steam, vacuuming, or cleaning with a non-phosphorus detergent every three to twelve months [13]. For gas streams which contain deactivating compounds, an acid or alkaline wash may be required to restore the catalyst to a normal activity level [4, 53]. As the catalyst ages, pores become permanently blocked from particulate or inorganic compounds, the metal surfaces tend to erode, vaporize, or be lost by attrition [15, 41, 54, 55], eventually leading to the need to replace the catalyst. This aging process may take many years to occur in a relatively clean constant gas stream, or it may occur within a period of months or even hours if the catalyst temperature limits are exceeded. It is recommended that the temperature change across the catalyst bed be constantly monitored and recorded, since that allows for an assessment of the catalyst activity. A low temperature rise across the catalyst indicates that the catalyst may have become deactivated [19]. Recording the outlet temperature also provides a method for confirming whether the catalyst has been subjected to a period of elevated temperature that may have damaged it. If the catalyst is properly cared for and its activity decreases gradually, the life of the catalyst may be extended somewhat by increasing the preheat temperature so that the average reaction temperature is increased a small amount [2]. This may be particularly helpful in providing for continued VOC reduction while a new catalyst is ordered and delivered.

Catalytic incinerators can be designed to handle a small amount of organic particulate. However, operating such an incinerator below the design temperature can result in carbon or organics building up on the surface of the catalyst due to incomplete combustion [2].

Several other process considerations that can help avoid poisoning the catalyst are given by Jennings, Krohn, and Berry [24]. The use of galvanized metal in ovens or ductwork should be avoided because the zinc used for galvanizing is a catalyst poison. Temperature indicating devices should not include mercury components that could also contaminate the catalyst. Cleaning detergents should not include phosphorus. Lubricants should not contain silicones or other inorganic metal compounds.

The heat exchange surfaces should also be kept clean and free of cracks [56]. In addition to difficulties with the catalytic material in an incinerator, heat stress can take a toll on the heat recovery equipment. At best, heat stress or buildup of material may keep valves from seating properly, a common problem with thermal regenerative units that allows leakage from the contaminated gas stream into the outlet gas stream, decreasing efficiency. At worst, heat stress can crack metal joints in heat exchangers, so that gas is allowed to escape from the clean side to the dirty side or vice versa, depending on the position of the fan. Such cracks can be difficult to locate, since the metal contracts as it cools to room temperature. The incinerator system should be designed considering the potential leakage of material. By the position of the fan, it can be ensured that any leakage occurs in an acceptable direction.

Any particulate, oily substances, or catalytic inhibitors should be removed prior to the incineration system. An overall summary of the advantages and disadvantages of catalytic oxidation systems is given in Table 8-5.

Table 8-5. Advantages and Disadvantages of Catalytic Incineration [21, 57, 58]

Advantages	Disadvantages
Reduced fire hazards	High initial cost
Heat recovery for other processes is feasible	No ability to reuse pollutants
High efficiencies possible with proper design	Particulate removal may be necessary
Technology is applicable for a wide variety of gas concentrations and constituents.	Disposal of spent catalyst may be difficult
Approximately one third the fuel usage of thermal incinerators	
Useful for multi-component streams if the components are all compatible with the catalyst	

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Chapter 9

Biodegradation

Technology Description

Biodegradation is the process of using microorganisms to convert pollutants into simple compounds. In air pollution control devices, the pollutants are first absorbed into a water film that contains microbes. Then the microbes metabolize the contaminant to obtain energy and nutrients. When VOCs are treated by biodegradation, the principal products of this metabolic process are carbon dioxide, water, and microbe cell mass. This process is the same one that has been used for decades in wastewater treatment plants and landfills to treat organic material [1].

In the most common type of biodegradation system used for air pollution control, gas is passed through a moist solid media, where pollutants are absorbed into the liquid layer on the surface of the solids. The biological activity results from the high concentration of microorganisms in this layer, or biofilm. These biofilters are common air pollution control devices in Europe, with over 500 in place [2]; they are used to remove odorous compounds and VOCs from waste gases [3, 4]. These systems are particularly effective for pollutants which are easy to degrade such as toluene, xylene, alcohols, butanol, formaldehyde, trimethylamine, acetaldehyde, and butyric acid [3]. Biofilters can also be combined with carbon adsorption or condensation to treat higher concentrations of gases. Biofilters are also capable of degrading volatile inorganic compounds (VICs) [5].

A typical *biofiltration* system for air pollution consists of a humidification chamber and a reactor. In addition to these components, particulate collectors may be required upstream of the biofilter to remove solid matter from the gas stream that would otherwise plug the bed and hinder gas distribution, in addition to increasing the pressure drop through the bed. While the humidification system is controlled manually for many simpler units, automatic controls are sometimes used on more sophisticated biofiltration systems designed for low maintenance. The reactor itself contains solid media, usually compost, soil, or peat, which provides a surface on which the microorganisms can reside. Organic substrates also provide nutrients to sustain the organisms. Inorganic media may be used which is more expensive [6], but is also more resistant to compaction and maintains the porosity of the bed for longer bed life. The solids are approximately 1 meter (3 feet) deep. Gas enters the biofilter from either the top or the bottom of the bed. Incoming gas travels through a piping manifold system or molded concrete blocks designed to uniformly distribute the gas across the surface to obtain uniform residence time of the gas stream, as well as to keep from drying out portions of the bed with higher gas velocities. Moisture levels throughout the media must be maintained at a level adequate to prevent drying and cracking of the bed, but low enough to avoid liquid channeling and the development of areas in the bed where oxygen is not present. Any anaerobic zones which develop can result in significant odors being emitted from the bed. The optimum moisture content is generally considered to be approximately 35 % to 60% in compost biofilters for removing H₂S [7] and VOCs [8, 9, 10, 11]. For biofilters with inorganic substrate materials, the optimum moisture is approximately 40-50% [10].

Biofiltration is capable of efficiencies ranging from 80 to 99%, depending on the characteristics

of the pollutants [12]. The efficiency of removing VOCs from a gas stream by biodegradation depends on several factors: the degree of contact between the gas stream and the media, the moisture level, the pollutant concentration, the residence time, and specific physical characteristics of the pollutant. The physical characteristics of importance are the Henry' Law constant, the solubility in water, the molecular weight, and the presence of complex bonding structures which prevent microbial attack [1, 10, 13]. Additional information about biodegradation for air pollution control is given by Skladany, Deshusses, Devinny, Togna, and Webster [14], Bowker [15], and Heinsohn and Kabel [16]. Some typical applications for biodegradation systems are given in Table 9-1 [3, 4, 17, 18, 19].

Types of Biodegradation Systems

There are two types of biodegradation systems. In *bio-scrubbers*, the microbes are contained in a wash liquid which is contacted with the contaminated air as in an absorber [19]. This chapter will focus on *biofilters* (a typical diagram is in Figure 9-1 [20]), systems in which the microbes are contained on a solid material like compost, soil, granular activated carbon (GAC), diatomaceous earth, or inert synthetic packing material [1, 11, 21]. The microbes live in a water film around the solid particles. Gases are adsorbed into the water film and digested. Trickle bed air biofilters (TBAB) [22] or biotrickling filters [23] are a specific type of biofilter, in which a liquid stream of water (with or without additional nutrients) is constantly applied to the solid media. Recycling the liquid effluent from the bed results in microbe reseedling, better control of pH, and ultimately superior performance according to several articles [11, 24, 25, 26, 27, 28, 29]. In particular, the concentration of styrene or benzene that can be degraded with a 90% removal efficiency in a biotrickling filter has been shown to be more than twice as high as that which can be removed in a conventional biofilter [23, 30].

While the general configuration of biofiltration systems is similar, each system has specific design considerations. They vary according to the flue gas pretreatment equipment that is required, the number of beds, the solid media that is used, and the gas distribution system. Biofilters may be closed to the atmosphere with the exception of a vent stack, or they may have open tops, so that the gas flows up through the bed and directly into the atmosphere (see Figure 9-2 [31]).

Biofilter System Design

Because of the significant effect that the microbe activity can have on the efficiency of the operation, it is generally required that design parameters be developed from previous experience or from pilot testing [3, 6]. This testing can help determine the optimum solid media for the filter, an estimate of the required moisture addition rate, the appropriate microbes, and the appropriate residence time.

Table 9-1. Typical Applications of Biodegradation [3, 4, 17, 18, 19]

Pharmaceutical Processes
Solid Stabilization Processes for Landfills
Rendering Plants
Chemical Manufacturing Processes
Print Shops
Flavors and Fragrances
Coffee and Cocoa Roasting
Sewage Treatment Odor Removal
Coating Processes
Composting
Food Processing
Livestock Farms
Foundries

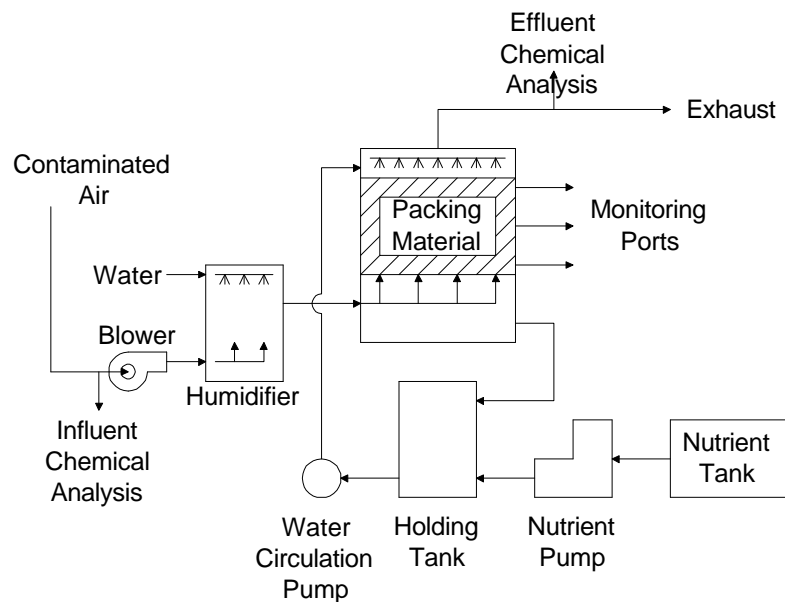


Figure 9-1. Typical Flow Diagram of a Biofilter [adapted from 20]



Figure 9-2. Open Type Biofilter [31]

Before the overall size of the biofilter is determined, it is helpful to identify an appropriate solid bed material, since the material of choice will affect the overall operating costs of the filter, as well as the required size. As mentioned earlier, the filter media may be organic or inert synthetic material [11]. Typical organic materials are compost, peat, leaves, soil, bark, wood chips, activated carbon, or clay [1, 32, 33, 34, 35]. Inert materials that are used include perlite, pelletized ceramics, ceramic monoliths, diatomaceous earth, and synthetic packing material [6, 21, 36]. While organic materials provide many nutrients needed by the microbes [6], they are also degraded at a faster rate than the VOCs themselves [37], resulting in additional compaction of the bed and a corresponding increase in pressure drop through the media [1]. After several years, maintenance is required to remove the material or mix it to reduce the pressure drop and improve overall performance. Cleaning of the air distribution system may also be needed to remove bed material which has collected there. The overall performance of the filter bed can be enhanced by adding inert solids like polystyrene beads to reduce compaction, extend bed life, and increase porosity [11, 38]. Or the entire bed can be constructed of inert media like pelletized ceramics, activated carbon or ceramic monoliths [6]. While inert media results in more uniform gas distribution [11] and less maintenance, it is also typically more expensive [6]. Additives such as lime are sometimes used to provide buffering capacity for the bed, particularly if the bed is used to treat chloride or sulfide compounds which can result in acidic decomposition products [39, 40]. Activated carbon can also be added to improve retention of the pollutants and maintain a consistent feed source for the microorganisms in cases where the process does not emit a constant level of pollutants [39, 41, 42].

The media should provide for even air distribution and pressure drop through the bed, high specific surface area, high porosity, adequate inorganic nutrients, efficient drainage, good mechanical strength to resist attrition, minimal pressure drop, and a surface that accommodates attachment of the microbes [11, 43, 44, 45].

Nutrients must be present for the microbes to grow. With organic media, the microbes get many of the inorganic nutrients required from the media itself. However, micronutrients are sometimes required and are available in forms which can be dissolved in water and spread onto the surface of the bed. The necessary nutrients include nitrogen, phosphorus, iron, calcium, and magnesium in addition to the carbon, hydrogen, and oxygen [39] that are available in the gas stream. The accepted ratio of carbon to nitrogen and phosphorus is approximately 100:10:1 [46]. If the essential nutrients and micronutrients are not present, samples of the bed material will have evidence of microbes which have encapsulated themselves [46].

Microorganisms typically found in biofilters are similar to those found in water treatment operations. They include both bacteria and fungi species. Bacterial species may include *actinomyces globisporus*, *micrococcus albus*, *micrmonospora vulgarus*, *proteus vulgarus*, *bacillus cereus*, and *streptomyces* species. Typical fungi are species of the genres *penicillium*, *cephalosporium*, *mucor*, *circinella*, *cephalotecium*, *ovularia*, and *stemphilium* [39].

Based on the work of Ottengraf [39, 47, 48], the reaction rate is generally assumed to follow the Monod (or Michaelis-Menten) relationship:

$$R = R_{\max} C_l / (C_l + K_m) \quad 9-1$$

where:

R = Biodegradation rate, units of mass per length cubed per time ($M L^{-3} T^{-1}$)

R_{\max} = Maximum biodegradation rate ($M L^{-3} T^{-1}$)

C_l = Concentration in the liquid biofilm ($M L^{-3}$)

K_m = Monod (or Michaelis – Menten) constant ($M L^{-3}$)

R_{\max} can be further described by the relationship:

$$R_{\max} = X \mu_m / y_i \quad 9-2$$

where :

X = active microorganism cell concentration ($M L^{-3}$)

μ_m = maximum rate of growth (T^{-1})

y_i = coefficient of cell yield

The reaction in biofilters is generally considered to be first-order at low VOC concentrations in which the biofilm is not completely saturated. Therefore, the rate of VOC destruction is controlled by the mass transfer rate of pollutant into the biofilm. [6, 39]. As the concentration in the gas stream increases, the concentration of pollutant in the liquid (C_l) is much larger than the Monod constant. At this point, the system is no longer limited by mass transfer, since the biofilm is saturated and the microorganisms have immediate access to the compounds. The point at which this transition from first order to zero order is pollutant specific and is determined empirically.

This biological model assumes that there is no interaction between multiple pollutants in the gas phase. In addition, it is based on the simplifying assumptions that the gas flow through the biofilter is plug flow and that equilibrium concentrations exist at the boundaries of the liquid and gas which can be described by Henry's law. Furthermore, the biofilm is considered to be adequately represented as flat, since the biofilm thickness is small compared to the particle size.

It is also assumed that the only biological reactions occur in the liquid phase [39]. Availability of oxygen has not been found to be rate limiting, even in gas streams with oxygen concentrations lower than ambient air [49].

The size of vessel required for a biofiltration system can be estimated from the following equation [50] when the concentration is less than 1 g/m³:

$$V = 0.0155 Q C^{0.5} \quad 9-3$$

where:

V = required volume of filter bed, m³

Q = flowrate of gas stream to be treated, m³/hr

C = VOC concentration, g/m³

For gas streams with concentrations higher than 1 g/m³, the required volume is predicted by:

$$V = 0.01 Q \{C + [3 - 0.1 * C^{0.5}]\} \quad 9-4$$

An alternative way to estimate the volume required in a biofilter is to predict it on the basis of removal rates which have been achieved in similar systems. A measure of the effectiveness of a biofilter is the elimination capacity (EC) for a given compound. The elimination capacity is the maximum amount of pollutant that the system can degrade, expressed in g/hr of the pollutant divided by the volume of the empty reactor (m³) [43]. Elimination capacities of several compounds which have been reported in the literature are given in Table 9-2 [4, 8].

The other important factor in designing a biofiltration system is to ensure adequate, even, distribution of moisture. If the media becomes too dry, it will shrink, causing cracks to develop which allow gas to pass through the bed untreated [51]. If the media is too wet, gas channeling can result, causing areas of low oxygen supply and creating anaerobic zones in the filter. Moisture is usually controlled by saturating the incoming gas stream to a level of 90-95% relative humidity. This, however, is not adequate to ensure that the bed does not dry out. Since the decomposition of VOCs is an exothermic process, the temperature in the biofilter is usually a few degrees higher than the inlet gas temperature. Therefore, even if the inlet gas stream is completely saturated, it will continue to remove moisture from the bed as the gas warms up in the biofilter and approaches saturation at the new temperature [39]. Approximately 10-20% of the moisture required to replace the water evaporated because of this temperature difference is produced in the biofilter as the VOCs are decomposed [45]. The moisture balance in a biofilter is also affected by the ambient temperature and the amount of heat exchanged with the surroundings. This can cause condensation in the biofilter, particularly as it is started up.

For simple systems with relatively low loadings of VOCs, the moisture balance may be fairly stable, so that water can be added manually to the biofilter, either with a hose, or with a spraying system which is controlled manually. For systems with high amounts of moisture evaporated (such as those with VOC concentrations greater than 0.5 g/m³ or elimination capacities exceeding 50 g/m³h), or with variable conditions, automatic monitoring and control of moisture are more critical [45]. The moisture can be monitored by measurement of electric conductivity or capacitance in given spots, but the most common method is to use load cells to determine the moisture content in a portion of the bed or in the entire bed. Load cells are devices which are installed in the support structure for the bed to monitor the "load" or weight of the bed. This type

Table 9-2. Maximum Elimination Capacities of Various Compounds [4, 8]

Compound	Media	EC (g/m ³ /h)	EC (lb/ft ³ /h)	Reference
Methyl Formiate	Unspecified	934.4	0.0583	[52]
Butyl Acetate	Peat	64.3	0.00401	[47]
Butanol	Peat	64.3	0.00401	[47]
N-Butanol	Compost	64.1	0.00400	[53]
BTEX (benzene, toluene, ethyl benzene, xylene)	Compost	20-30	0.0012-0.0019	[54]
BTX	Pelletized Biologically Active Media	55	0.0034	[55]
BTX	Peat Moss and Chicken Manure	5.8-63.6	0.00036-0.00397	[56]
Ethyl Acetate	Peat	54.2	0.00338	[47]
Ethyl Benzene	Perlite	85.2	0.00531	[36]
Ethanol	Peat	120	0.00749	[43], (inlet loading of 135 g/m ³ /hr)
Ethanol	Unspecified	175	0.0109	[23]
Toluene	Peat	42.2	0.00263	[47]
Toluene	Peat	70	0.0044	[43], (inlet loading of 100 g/m ³ /hr)
Toluene	Perlite	72.9	0.00455	[36]
Toluene	Compost and inerts	21	0.0013	[48]
Simulated JP-4 Fuel (85% kerosene, 15% gasoline)	Lawn compost, Composted sewage sludge, perlite, gypsum, activated sludge	At loadings of 25-1000 ppm m ³ /m ² min and residence times of 1 to 3 minutes, >99% removal		[57]
TEX (toluene, ethyl benzene, o-Xylene)	Perlite	70	0.0044	[36]
o-Xylene	Perlite	63.6	0.00397	[36]
Methanol	Unspecified	36.0	0.00225	[52]
Methanethiol (Methyl Mercaptans)	Peat	24	0.0015	[58]
Styrene	Unspecified	70	0.0044	[23]
Dimethyl Disulfide	Peat	18	0.0011	[58]
Dimethyl Sulfide	Peat	10	0.00063	[58]
Ammonia	Peat	4.3	0.00027	[59]
H ₂ S	Compost	130	0.00811	[7]

of system cannot be used with open-type biofilters, since any additional weight such as growth of vegetation or snow on the surface of the biofilter will affect the reading. The load cells may need to be recalibrated occasionally to compensate for media losses [45]. With VOC elimination capacities greater than 100 g/m³h, it may be difficult to maintain a proper moisture level in large systems, even with automated measurement and controls.

Using biofilters with gas flowing down through the media can assist in maintaining proper moisture levels, since water can be easily applied to the surface of the filter media. The majority of the media drying occurs at the entrance of the gas stream to the bed, so a downflow biofilter allows water to be directed more easily to the locations where it is needed. An exception to this is beds for treating feeds with chlorides or sulfides which can contain acidic decomposition products. Upflow filters may be preferable for such beds, because the more concentrated acidic byproducts are at the bottom of the bed and can be flushed out more completely [45]. Gas flow through biofilters is usually between 1 and 5 cubic feet per hour per square foot of media surface [4].

Other important factors in designing the system include adequate oxygen content of the gas stream [4] (although this is not usually a limiting factor in the system performance [49]), removal of decomposition products which inhibit biodegradation, supply of nutrients to the reactor, and adequate buffering capacity.

Studies [22, 60] have shown that supplying nitrogen to the reactor in the form of nitrates instead of ammonia reduces the amount of nitrifying bacteria which are believed to inhibit the effectiveness of the biofilter. Proper biofiltration operation requires the addition of vitamin solutions which contain macronutrients, micronutrients, and buffers [11, 36]. Buffering agents may be used to adjust the pH of the media or the liquid nutrient mixture.

In reactors used to treat gas streams with acidic decomposition products, providing adequate buffering capacity in the biofilter is important, since the biofilter performance may decline significantly once the buffering capacity is exhausted and the media must be replaced.

Instrumentation that should be considered for biofiltration systems is given in Table 9-3 [45].

Economic Estimates

Estimates of the total installed capital cost of a biofiltration system are given in Figure 9-3, in terms of dollars (1997) per cubic meter of media. At each filter volume, there is a range of costs. The low end of the range represents open biofilter systems, which frequently require longer residence times (and therefore larger vessels) to achieve a given level of control due to less efficient gas distribution, less precise moisture control, and non-optimized filter media. The upper end of the range represents the cost associated with installing an enclosed, controlled, multi-level biofilter system [45].

Table 9-3. Recommended Instrumentation [45]

Gas stream temperature and pressure (inlet and outlet)
Inlet gas stream relative humidity
Fan speed
Moisture content of the inlet gas stream
Moisture content of the media (may be manual sample)
pH of liquid effluent

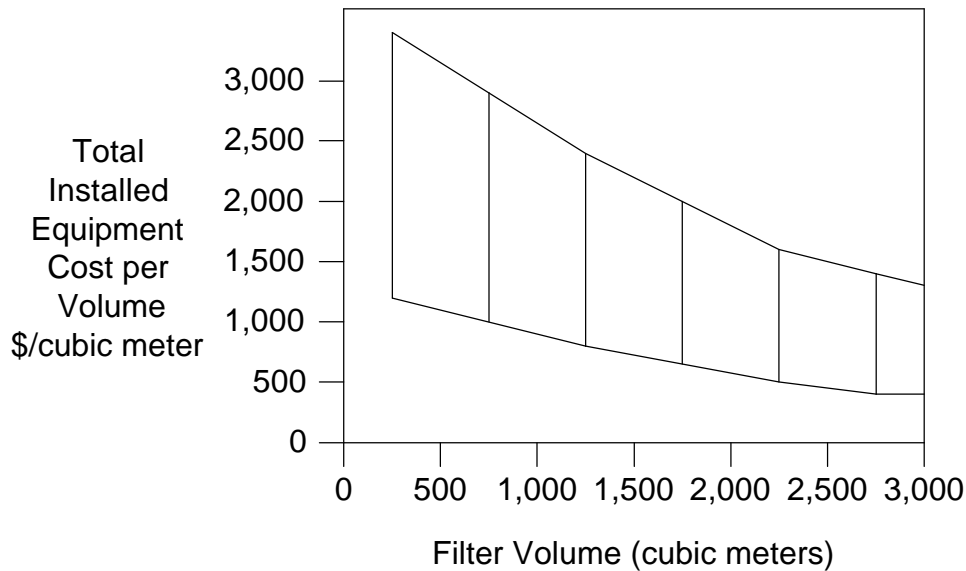


Figure 9-3. Installed Capital Cost Range for Biofilter Systems Greater than 100 m³ [45]

Alternatively, an estimate of the capital cost of the purchased equipment alone can be found from the following equations [50], then the cost scaled using standard factors to arrive at an estimate of the total installed capital cost. For a system which requires less than 200 m³ of media:

$$CC = 51315 V^{0.49} \quad 9-5$$

where: CC = Capital Cost in 1993 dollars

For a system which requires more than 200 m³ of media, the appropriate equation is:

$$CC = 231254 + 2285 V \quad 9-6$$

To estimate the total installed capital expenditure, the factors in Table 9-2 may be used [50], which generally follow the methodology of EPA's OAQPS Cost Control Manual [61] and HAP-PRO software[62] used for other technologies. The OAQPS Cost Control Manual and HAP-PRO software do not currently contain information for biofilters.

Annual costs may be approximated using the same methodology as given in the OAQPS Cost Control Manual [61] for other systems, as given in Table 9-3. Electricity requirements can be estimated from the formulas given in Chapter 4, assuming a pressure drop of 50 to 3,000 Pa (0.2-12 inches of water), depending on the media chosen, the velocity through the media, the media depth, and the number of beds. Water requirements can be estimated from the general guideline of 5-10 gallons of water required for every 100,000 standard cubic feet of gases treated [4]. Operating and maintenance labor requirements are also highly variable, ranging from a few minutes a day for a well controlled system treating relatively low concentrations of pollutants to a few hours a day for an open, uncontrolled system with high pollutant loadings and high moisture losses [45].

Potential Problems

As the solid media in a biofilter degrades, the bed compacts and pressure drop through the filter increases. The pressure drop through the bed should be monitored carefully so that

required replacement of media can be anticipated and the required outage time can be scheduled with the production facility. Monitoring the pressure drop through the bed also enables early detection of cracks in the bed which allow gas to pass through untreated [4].

Optimum temperature for microbial activity is approximately 30-40 °C [4, 7, 45]. At lower or higher temperatures, the removal of VOCs in the biofilter may be significantly reduced (by approximately 50% for each 10 °C drop in temperature [63]). However, due to the exothermic nature of the metabolic reactions, it is possible to maintain adequate VOC removal even in ambient temperatures which are significantly below the optimum [7, 64]. The most prevalent concerns with biofilter operation are maintaining adequate moisture, removing solids which build up in the media, “fluffing” or replacing of the solid media, and maintaining appropriate temperatures.

Table 9-4. Factors for Estimating the Total Installed Capital Cost of Biofiltration Systems[50]

<i>Cost Element</i>	<i>Estimated Cost</i>
<i>Direct Costs</i>	
Purchased Equipment Cost	
Biofilter and Auxiliary Equipment	CC, Estimated from equation
Taxes	0.03 CC:
Freight	0.05 CC:
Total Purchased Equipment Cost, PEC	1.08 CC:
Installation Costs	
Foundations and Supports	0.08 PEC
Erection and Handling	0.14 PEC
Electrical	0.04 PEC
Piping, Insulation, and Painting	0.04 PEC
Total Installation Cost	0.30 PEC
Site Preparation	As required for specific site, SP
Buildings	As required for specific site, BLDG
<i>Total Direct Costs</i>	<i>1.30 PEC + SP + BLDG</i>
<i>Indirect Costs</i>	
Engineering and Supervision	0.10 PEC
Construction, Field Expenses, and Fees	0.15 PEC
Start-up and Performance Test	0.03 PEC
Contingency	0.03 PEC
<i>Total Indirect Costs</i>	<i>0.31 PEC</i>
<i>TOTAL INSTALLED CAPITAL COSTS, TCC</i>	<i>1.61 PEC + SP + BLDG</i>

Optimum temperature for microbial activity is approximately 30-40 °C [4, 7, 45]. At lower or higher temperatures, the removal of VOCs in the biofilter may be significantly reduced (by approximately 50% for each 10 °C drop in temperature [65]). However, due to the exothermic

nature of the metabolic reactions, it is possible to maintain adequate VOC removal even in ambient temperatures which are significantly below the optimum [7, 66]. The most prevalent concerns with biofilter operation are maintaining adequate moisture, removing solids which build up in the media, “fluffing” or replacing of the solid media, and maintaining appropriate temperatures.

Table 9-5. Annual Operating Costs for Biofilter Systems [50]

Direct Annual Costs	Unit Cost	Estimated Requirement
Utilities:		
Electricity	\$0.05/ kWh	See Chapter 4
Water		5-10 gal/100,000 cf [4]
Operating Labor	\$12.96/h	½ hour per shift
Maintenance Labor	\$14.26/h	½ hour per shift
Maintenance Materials	2% of TCC	
Supervisory Labor	15% of Operating Labor	
Indirect Annual Costs		
Overhead	60% of Maintenance Costs	
Property Tax	1% of TCC	
Insurance	1% of TCC	
Administrative Costs	2% of TCC	
Capital Recovery (see Chapter 4 for formula to calculate capital recovery factor)	CRF * TCC	
Total Annual Operating Costs	Direct + Indirect Operating Costs	

Biofiltration should be used with some caution on gas streams that contain contaminants that are difficult to degrade, since the compound may not be broken down completely. In these cases, it is possible to form more toxic byproducts than the original pollutants [67]. For example, the aerobic degradation of trichloroethylene can form vinyl chloride as a byproduct [68].

Installation, Operation, and Maintenance Considerations

As discussed earlier, the moisture control in a biofilter is a key parameter in ensuring that the biofilter operates as designed. Therefore, the moisture distribution system including the humidification chamber and water distribution system in the bed are operating properly.

Likewise, particulate that builds up in the gas stream distribution system increases the pressure drop and hinders good distribution, so any particulate collection devices should also be checked periodically to ensure that they are in good operating condition.

Since media replacement is almost inevitable, the system must be designed and constructed with adequate space and access for the large equipment needed to “fluff” the biofilter contents or replace it. Studies have shown that periodic backflushing of the filter with water may be beneficial in reducing the amount of excess biomass which builds up in the filter over time, increasing the pressure drop [22, 69, 70].

Table 9-6. Advantages and Disadvantages of Biofiltration [51, 45]

Advantages	Disadvantages
Relatively simple equipment and operation	Effectiveness is pollutant-specific
Usually no additional pollutants formed other than carbon dioxide, water, biomass, and mineral salts	Potential corrosion of ductwork due to moisture in gas stream
Process is at ambient temperatures and is therefore inherently safer	Sensitivity to temperature, concentration, and moisture
Typically lower capital and operating costs than other technologies	Proper moisture control of streams with high loadings of organic compounds may be difficult
Low energy requirements	

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Chapter 10

Emerging Technologies

The need for better destruction efficiency and lower cost of air pollution control systems drives the development of new methods of VOC elimination [1]. The basic technology for some of these systems, such as membrane filtration and use of ozone for VOC oxidation, has been in existence for many years. However, as regulations become more stringent and as public awareness increases, the technologies are reconsidered and redesigned to address air pollution control issues. In addition, there are new technologies like plasma destruction that have recently been discovered as potential methods for controlling air pollutants. While many of these systems are available commercially, there is not much information available yet about costs, maintenance, and operational concerns. This chapter describes several of those innovative technologies.

Membrane Separation

Membrane separation processes are used to remove organic compounds from a polluted gas stream by establishing a partial pressure gradient across a semi-permeable glassy or rubbery surface that constitutes the membrane. The membrane is designed to allow either air molecules or pollutant molecules to pass preferentially, resulting in a more concentrated pollutant stream on one side of the membrane. One common system works by pressurizing the incoming gas stream, removing as much of the pollutant as possible by condensation, then exposing the resulting gas stream to a membrane which allows passage of organic molecules while limiting the passage of air molecules [2]. The organic *permeate* stream may also be under vacuum to increase the driving force for mass transfer. The permeate stream may be recycled to the compressor inlet. Once the concentration builds up sufficiently, the pollutant is removed by the condensation process [3]. Two membranes in series may be used if the gas stream is dilute to reduce the amount of permeate stream that must be recycled [4].

A typical flow diagram for a membrane separation system is shown in Figure 10-1 [5]. The pollutant-laden gas is compressed to 0.31-1.38 MPa gauge pressure (45-200 psig), then flows into a condenser. From the condenser, the gas flows through the membrane system where it is separated into an exhaust gas stream that has very low concentrations of organics, and a permeate gas stream which is a more concentrated VOC stream [6, 7, 8]. The permeate gas stream may be recycled to the compressor. In this system, a condenser is added between the compressor and the membrane system and the recycled vapor eventually reaches a state in which it is concentrated enough to condense. The permeate stream may also be treated by a conventional technology such as thermal or catalytic incineration. Membrane systems are also available in which the pollutant passes across the membrane into a scrubbing liquor, where it is presumably neutralized or destroyed [9].

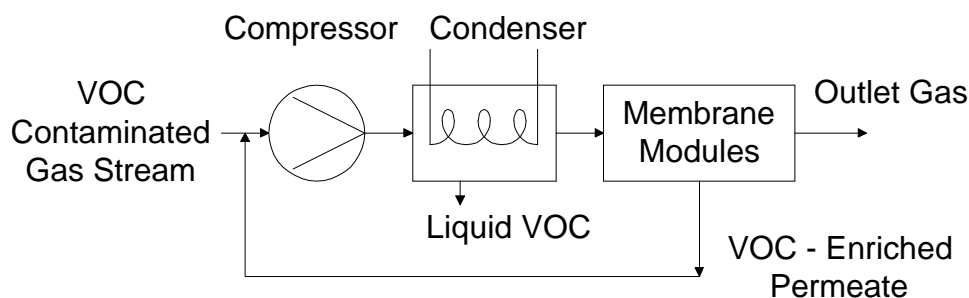


Figure 10-1. Flow Diagram for a Membrane Separation System [adapted from 5]

As with other technologies, the constituents of the gas stream should be well characterized before a membrane system is employed to ensure that the membrane is chemically compatible with the potential gas stream constituents. Membranes are susceptible to fouling, and it is advisable to remove any particulate or oily compounds prior to the membrane system. Efficiencies of membrane separation systems are reported to be as high as 90 to 99.99% [10, 11], although it is important to note that greater removal efficiencies result in lower permeate stream concentrations [2].

Membrane separation is perhaps the most developed of the technologies to be covered in this chapter. There are approximately 60 membrane filtration systems that have been installed for VOC recovery [3, 2, 12, 13]. The system is based on technology that was first envisioned in 1950 by Weller and Steiner [14]. The technology has been used for several decades in the Chemical Process Industry and in drinking water treatment plants [4, 15]. Typical and potential applications of membrane systems are given in Table 10-1 [3, 8, 12, 13, 16, 17, 18, 19]. The principles of gas permeation which are the foundation of membrane design work are given in the literature [3, 20, 21, 22, 23, 24, 25, 26, 27, 28].

Table 10-1. Applications of Membrane Separation Systems for VOC Removal [3, 8, 12, 13, 16, 17, 18, 19]

Vapor Recovery from Gasoline Loading and Unloading
Hospital sterilizer vents
Pharmaceutical plants
Polymer production
Industrial chiller purge streams
Film drying
Liquid ring vacuum pump exhaust
Tank and drum filling
Removal of higher hydrocarbons from natural gas

Membrane systems are convenient, in that they are continuous processes [9], they can be used with a large fluctuation in inlet concentration or flow [5], and they are normally modular in design [9], which simplifies installation and increases in capacity. They are usually cost competitive with carbon adsorption when the VOC concentration is above approximately 1000 ppm [2]. They are also applicable in situations where carbon adsorption is not appropriate, such

as low molecular weight compounds [6] or compounds that polymerize on activated carbon.

Membrane systems can be classified according to the type of membrane used. Glassy membranes (such as polyetherimide) are more permeable to air molecules than to organics [3]; rubbery membranes (such as natural rubber) are more permeable to organic compounds. Furthermore, glassy polymers in general allow substantially less material to flow through than rubbery membranes (about 1/1000 as much). Because glassy membranes are more resistant to flow, a much larger membrane is required than if a rubbery membrane is employed. This is aggravated by the fact that the air must pass through the glassy membrane to get an effective separation. Since the proportion of air is usually much higher than that of the pollutant, glassy membranes result in much larger amounts of material being transferred through the membrane. The amount of material that must pass through the membrane, in combination with the permeability of the membrane, determines the surface area of membrane required. Therefore, rubbery membranes are generally used in VOC separation, since the required surface area is significantly less than with glassy membranes [2]. Glassy membranes, though, can provide greater selectivity, resulting in a purer gas stream exiting the system [3]. The remainder of this chapter will deal with rubbery membranes, since they are generally the most cost effective for VOC removal.

Membrane systems can also be classified according to the design of the membrane unit. As shown in Figure 10-2 [29], plate and frame units are similar to filter presses, where the feed stream travels into a series of plates. The pollutant migrates from the plates through the membrane into a "frame". A frame is a space between the plates that direct the permeate out of the membrane module.

The spiral-wound module shown is similar to a stack of flat membranes and spacers that have been wound around a hollow center shaft. The feed flows into one end of the space created by the spacers, travels by the membrane, and the permeate goes through the membrane into another cavity which winds to the hollow center shaft. The permeate collects in the center shaft and is removed from the end of the shaft. The feed that does not go through the membrane is collected at the end of the membrane module.

The third type, which is not commonly used for air pollution applications, is similar to a shell-and-tube heat exchanger. There are "heads" on each end which hold the ends of hollow fibers or tubes. The feed stream can flow either in the "shell" side of the membrane module, in which the permeate is removed from the "tube" side, or the feed stream can flow in the "tube" side and the permeate is removed from the "shell" side.

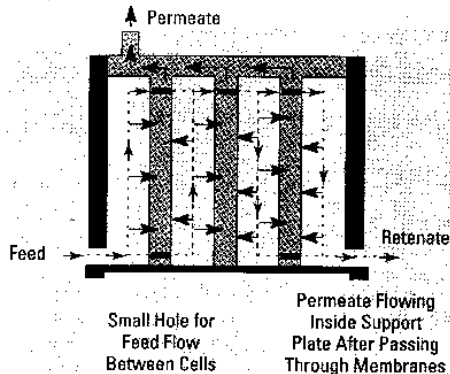
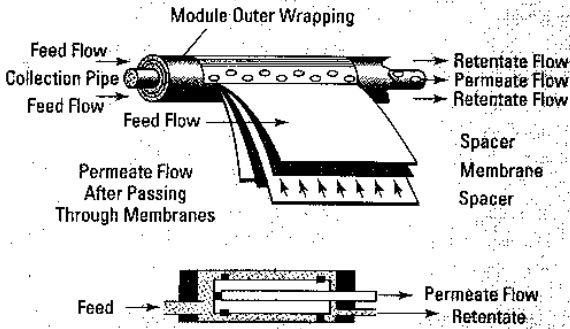
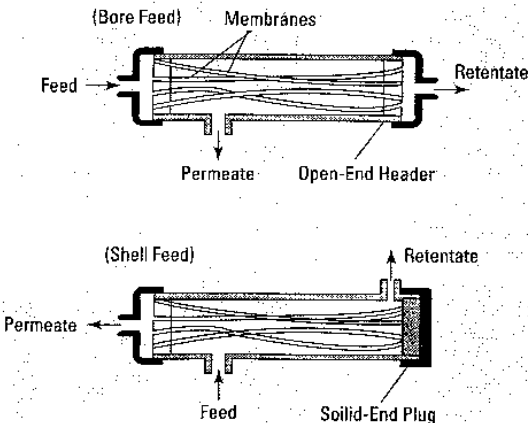
Configuration Type	Comments
<p>Plate and Frame</p>  <p>Small Hole for Feed Flow Between Cells</p> <p>Permeate Flowing Inside Support Plate After Passing Through Membranes</p>	<p>Arrows show the upstream and permeate paths. The upstream leaves as the retentate and is enriched in nonpermeate. Permeate is collected from channels in support plates and leaves enriched in the most-permeable component.</p> <p>Advantages: Easy to clean and replace membranes.</p> <p>Disadvantages: Low membrane area per volume — a problem. In high-pressure applications where pressure-vessel costs are significant.</p>
<p>Spiral-Wound Module</p>  <p>Module Outer Wrapping</p> <p>Feed Flow</p> <p>Collection Pipe</p> <p>Feed Flow</p> <p>Permeate Flow After Passing Through Membranes</p> <p>Spacer</p> <p>Membrane</p> <p>Spacer</p> <p>Feed</p> <p>Permeate Flow</p> <p>Retentate</p>	<p>The "unrolled" element shows the contact and flow patterns for feed, permeate, and retentate. The "sandwich" made of membrane, feed spacer, and permeate spacer is glued on three sides and terminates at its fourth side into the perforated pipe that collects permeate. This assembly is wrapped into a spiral and placed in a cylindrical shell.</p> <p>Advantage: Easy and inexpensive to adjust hydrodynamics by changing feed-spacer thickness to overcome concentration polarization and fouling.</p> <p>Disadvantages: 1. Rather low membrane area per volume. 2. Can become expensive for high pressures because extra-high-pressure shells must be purchased. 3. Bypassing of feed may occur due to nonuniform wrapping of module spiral.</p>
<p>Hollow-Fiber, Capillary and Tubular</p>  <p>(Bore Feed)</p> <p>Membranes</p> <p>Feed</p> <p>Permeate</p> <p>Open-End Header</p> <p>Retentate</p> <p>(Shell Feed)</p> <p>Permeate</p> <p>Feed</p> <p>Soiled-End Plug</p> <p>Retentate</p>	<p>Hollow fibers (<0.5 mm OD), capillaries (0.5–5 mm OD) and tubes (5–15 mm OD) can be configured in bore- or shell-feed modules. Packing densities can be as high as 50%. (Note: sketch shows low density for ease of visualization.) Position of feed and permeate ports affect flow in the module. High-pressure applications tend to use shell feed, and low pressures favor bore feeds.</p> <p>Advantages: 1. Eliminates bypassing when used in bore-feed mode. 2. Huge membrane area per volume possible with fibers.</p> <p>Disadvantages: 1. Membrane formation is more complex, because the support and the selecting layer are formed as an integral cylindrical unit during "spinning" for fibers and capillaries. 2. To avoid excessive pressure drop in bore for bore-feed mode, large diameter fibers may be required in some cases. 3. Bypassing of feed in shell-feed mode due to any nonuniformities in fiber packing. 4. Fouling due to high surface areas if feed contains particulates or other foulants.</p>

Figure 10-2. Various Configurations of Membrane Separators from W.J. Koros, "Membranes: Learning a Lesson from Nature", *Chemical Engineering Progress*, October, 1995, p. 68-81. Reproduced with permission of the American Institute of Chemical Engineers.

The degree of separation which can be achieved in a membrane module is governed by the selectivity of the membrane to the pollutant over the remaining components of the gas stream.

The selectivity of the membrane is given by the formula:

$$\alpha_{A/B} = P_A/P_B \quad 10-1$$

where: $\alpha_{A/B}$ = selectivity of the membrane to pass component A instead of component B

P_A = permeability of gas A through the membrane

P_B = permeability of gas B through the membrane

Usually, membranes have selectivities of approximately 20-100 [3], indicating that approximately 20 to 100 times as much organic material as air will pass through the membrane. Permeability is a measure of the volume of a compound that moves through a (1 cm thick) membrane at a standard pressure difference of 1 cm of mercury. The permeability is usually given in units of Barrers. One Barrer is equal to $1 \times 10^{-10} \text{ cm}^3 \text{ (STP)}/(\text{cm}^2 \text{ s cmHg})$. The permeability of a compound is related to the diffusion coefficient, a measure of the rate of transport the compound through the membrane material and the Henry's Law sorption coefficient, a measure of the condensability of the compound [2].

It is important that the relative permeabilities or selectivity be measured in experiments with the simulated gas composition as opposed to measuring the permeabilities of pure gases separately and comparing them. This technique is necessary because rubbery membranes swell in the presence of organic compounds, changing the diffusion of each compound through the membrane. This phenomenon results in a higher selectivity for the organic compound than would be predicted otherwise [3].

Likewise, temperature can affect the selectivity and permeability of the membrane. The selectivity usually improves as the temperature is decreased [3]. Polymer membranes are generally limited to 363 K (194 °F, 90 °C) [30]. The amount of membrane surface required will depend on the type of membrane, the permeability of the pollutant through the membrane, the required removal efficiency, and the difference in pressure across the membrane [3].

Little cost information is available for membrane systems. The cost for membranes which allow passage of organic compounds has been estimated at approximately \$71/1,000 standard m^3 of gas (\$2/1,000 scf of gas) [29] and at \$4-11/kg of VOC recovered (\$2-5/ lb of VOC recovered) [31]. The majority of the annual cost associated with a typical membrane system will be the cost to compress the gas stream. Annual energy consumption associated with compressing the gas may be approximated using the guidelines in the OAQPS Cost Control Manual [32]:

$$\text{Power (kW)} = A Q \Delta P / \eta \quad 10-2$$

where: A = Factor, 1.66×10^{-5} using SI units (use 1.17×10^{-4} with English units shown in parenthesis)

Q = Total flue gas flowrate, standard m^3/min or sccm (standard ft^3/min or scfm)

ΔP = pressure change, Pa (inches of water)

η = combined efficiency of motor and compressor

If a vacuum pump is used on the permeate stream, it would also need to be included in the electrical cost estimate.

There are few moving parts in membrane systems, so they are less likely to require maintenance [9]. Membrane systems are less susceptible to malfunction due to changes in concentration and flowrate than other pollution control systems, as long as the fluctuations were anticipated as part of the original design. However, the temperature must be maintained low enough to effectively separate the compounds and to ensure that the membrane is not damaged. Similarly, care must be taken to ensure that the gas stream constituents are compatible with the membrane material and other materials of construction, so that the membrane is not damaged by solvent action of the gas stream. Particulate or oils that could accumulate on the membrane or in the pores of the membrane should also be removed to extend the life of the membrane. High concentrations of organic compounds should also be avoided to minimize the risk of explosions. See the discussion of lower explosive limits in Chapter 6.

An overall summary of the advantages and disadvantages of membrane systems is given in Table 10-2 [5, 33, 34].

Table 10-2. Advantages and Disadvantages of Membrane Separation [5, 33, 34]

Advantages	Disadvantages
Solvent recovery	High energy costs
No secondary wastes	
Compact design	
High efficiencies possible with proper design	
Technology is applicable for variable pollutant concentrations.	

Ambient Oxidation Processes

Ultraviolet (UV) oxidation uses the same types of photochemical reactions that occur in the atmosphere [6, 35] to assist in the oxidation of organic compounds to form water and carbon dioxide. UV light and oxidants such as ozone, peroxide, hydroxyl radicals, or oxygen radicals are used to break down the VOCs into carbon dioxide and water [1]. The wavelength of light used is determined based on the VOCs to be destroyed. In one system, the incoming gas stream passes through a filter to remove particulate, then into a chamber where the reactions occur. Following the main reaction chamber, any residual VOCs may be scrubbed with water or adsorbed onto activated carbon. The scrubbing liquor and carbon regeneration may also include oxidants to further enhance removal efficiency [35].

Photocatalytic oxidation (PCO) or heterogeneous photocatalysis [36] is a similar process, but it includes a catalyst surface (usually titanium dioxide, although nickel and mixtures of titanium dioxide and platinum have also been used) [37, 38]. In PCO, the catalyst surface is a semiconductor material that becomes active in UV or near-UV light. The light source may be either the sun or a fluorescent bulb [39, 40]. The process operates by adsorption of the pollutant compound onto the surface of the catalyst, then decomposition of the compound in a manner similar to catalytic oxidation. Ozone, peroxide, hydroxyl radicals, or oxygen radicals may also be added to or generated within the process [41]. The process is applicable for aliphatic hydrocarbons, ethers, ketones, alcohols, and aldehydes [42]. It is particularly well suited to chlorinated hydrocarbons, since they are more reactive than non-chlorinated compounds. In

conventional technologies, such as thermal incinerators, the chlorinated compounds are more difficult to destroy than the non-chlorinated compounds [39]. Aromatics can also be treated; the addition of ozone or hydrogen peroxide increases the rate of reaction of aromatics substantially [43]. Microbes are also destroyed in the process [44].

One type of PCO reactor is shown in Figure 10-3 [45]. The reactor consists of two concentric tubes. Beads coated with catalyst are packed between the two tubes, and a UV light source is put in the center tube. The polluted gas stream flows through the beads. Alternatively, the reactor can be designed with the catalyst arranged on a series of disks over which the gas flows [46]. The goal of either design is to expose as much of the catalyst surface as possible to the light while maintaining a low pressure drop for the gas stream. The mechanism of the surface reaction is not well understood, although it is recognized that the excitation of the semiconductor catalyst material promotes the formation of electron-hole pairs in the solid [41].

The constituents of the gas stream must be identified in order to determine if a PCO system would be suitable. In addition, particulates, oily compounds, or compounds such as hexamethyldisilazane which could foul the surface of the catalyst must be removed prior to the reactor.

Efficiencies of laboratory PCO systems have been reported as high as 99% at high temperatures or residence times [47, 48]. Efficiencies at ambient temperatures and residence times which are more realistic for commercial systems have been reported as high as 95% for a 400 ppm gas stream [43]. Commercial systems are currently being designed to achieve 99+% destruction [49].

PCO technology is best suited for low concentration (<1000 ppm) gas streams at low to moderate flow rates (<567 m³/min or 20,000 cfm). At higher concentrations, larger catalyst area is required and the system becomes less cost competitive with other technologies [45]. Normal fluorescent lighting may be an adequate light source for destroying odors and very low concentrations of pollutants using TiO₂ as a photocatalyst [50]. Potential applications of PCO systems are given in Table 10-3 [40, 45, 49, 51, 52].

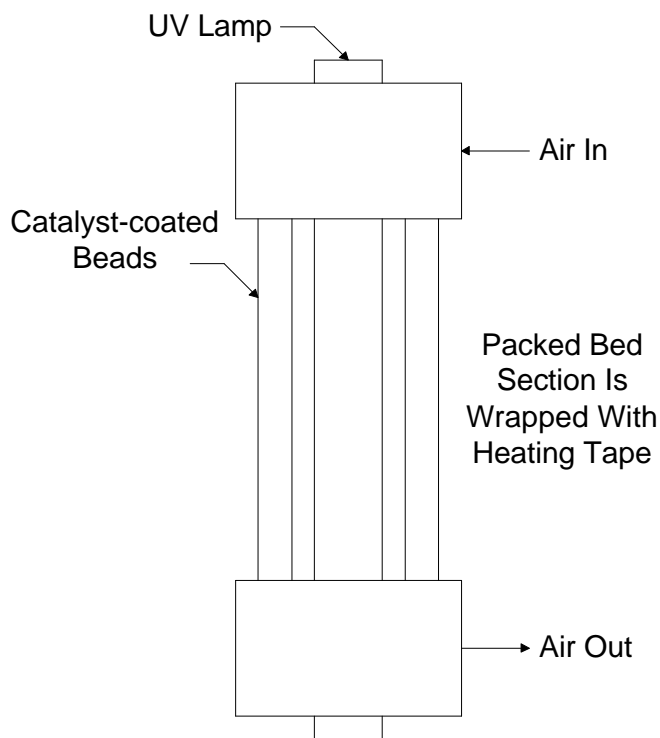


Figure 10-3. Flow Diagram of a Packed Bed PCO Reactor [45]

Table 10-3. Applications of PCO Systems for VOC Removal [40, 45, 49, 51, 52]

Soil or Groundwater Remediation Vent Streams
Contact Lens Degreasing
Lithography Equipment
Paint Spray Booths
Cleaning Equipment
Indoor Air Pollution from Paint and Solvents

For the reaction to occur, the organic species must first be adsorbed onto the catalyst surface. The rate of adsorption is governed by the concentration of the pollutant in the gas stream and the temperature. Increasing temperature generally increases the rate of destruction of the compound. However, increased temperature also reduces the speed of the adsorption process, so less compound is available for destruction. Care must be taken to ensure that adequate surface area is available for adsorption. Once the surface of the catalyst is saturated with compound, increases in concentration have little or no effect on the destruction rate of the pollutant, so the destruction efficiency declines rapidly [45]. It is also important, therefore, to ensure that adsorption sites are

not blinded by particulate or non-reactive compounds. The reaction also will not occur without light. The light can, however, be quickly turned off or on for an intermittent pollutant stream, resulting in lower energy consumption [49].

Little cost information is available for these oxidation systems. Cost estimates have been prepared for a photocatalytic oxidation system in the same manner as costs for other controls were estimated by Mukhopadhyay and Moretti [53], which generally follow the methodology of the OAQPS Cost Control Manual published by EPA [54]. The cost for a PCO system has been estimated at approximately \$883-1069 /standard m³ per min of gas (\$25-30 /scfm of gas), although the cost will depend on the relative reactivity of the compound to be treated. Unlike other control systems, the cost increases with the concentration of organic compound, but remains relatively stable with increasing flowrates [39].

There are not many moving parts in PCO systems, so it is anticipated that annual maintenance costs would be relatively low. Because of the low temperatures, simple materials of construction can be used like plastic piping [55] which reduce both capital and maintenance costs. An overall summary of the advantages and disadvantages of PCO systems is given in Table 10-4 [49].

Table 10-4. Advantages and Disadvantages of PCO [49]

Advantages	Disadvantages
Can be turned off with a switch to save energy between batches	May form additional pollutants if process is not properly designed
Compact design	Solvent recovery is not feasible
High efficiencies possible with proper design	
Technology is applicable for small or short fluctuations in pollutant concentrations.	

Corona Destruction

The *Corona Destruction* process also operates at ambient temperature. A high voltage/ low current electrical discharge is used to produce high energy electrons which collide with VOCs and decompose them into carbon dioxide and water [1, 56]. The basic process is described by Yamamoto [57]. It is believed that the technology may be eventually applicable for low concentration VOC streams, however, available information indicates that the energy requirements are currently too high to be competitive with other technologies. Packed bed systems which use a bed of dielectric beads (perovskite BaTiO₃) with an electrode connected on either end are being investigated. The beads store electrical energy and discharge it out of phase with the applied electric field, producing electrons which destroy the VOC. High destruction efficiencies are possible with the corona discharge processes, however, it has been demonstrated that ozone is formed in substantial concentrations (approximately 500 ppm, see Chapter 11). In addition, NO_x and incomplete products of combustion may also be formed [56]. The potential benefits of corona destruction are that it would not require auxilliary fuel, would operate at ambient temperatures, and would be able to treat both halogenated and non-halogenated compounds [1].

Plasma Destruction

Several types of plasma destruction are also being investigated to determine if they are applicable for controlling chlorinated or non-chlorinated compounds [6]. Plasma technologies can be divided into high and low temperature processes. In high temperature processes, the contaminated gas stream is mixed with oxygen or water vapor and passes into the reactor. A plasma or high temperature ionized gas state is maintained in the reactor by an electric discharge (arc) or by radio frequency energy. The plasma is extremely reactive and the gas reacts with the water or oxygen to form carbon dioxide [6]. One such system is used in Japan to destroy chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Destruction efficiencies have been measured at 99.99% and higher using 35-138 kW of electricity for a gas stream containing 36-100 kg/h [58].

Cold plasma techniques heat only the electrons in the plasma by a series of micro-arcs similar to tiny lightening bolts. The electron temperatures are typically 3 eV, approximately equal to 30,000 K (29,700 °C or 54,000 °F). However, the remainder of the gas is not heated. The reactions which occur are similar to the free radical reactions which occur in thermal oxidation, but the free radicals are produced by the collisions of the electrons and the gas molecules, not by the temperature. Efficiencies in the range of 90-99% have been demonstrated on laboratory scale units. However, ozone, carbon monoxide, nitrous oxides, and nitric acid may also be formed as byproducts of the reactions. Preliminary cost estimates are approximately \$1.18/ scmm (\$33.3/1000 scfm) [59].

Ozone Catalytic Oxidation

Catalytic oxidation of VOCs with ozone as the primary oxidant offers the advantage of low temperatures of reaction. This topic is currently being investigated by S. Ted Oyama's research group in the Chemical Engineering Department at Virginia Tech. The synthesis process for some of the catalysts being investigated is discussed in the next chapter.

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Chapter 11

Preparation and Characterization of Supported Manganese and Iron Oxide Catalysts

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Abstract

Catalysts based on manganese and iron oxide were prepared by the impregnation of an aluminum oxide washcoat deposited on alumina foam blocks. Samples contained Mn_3O_4 , Mn_2FeO_4 , MnFe_2O_4 , and Fe_3O_4 with a total loading of 0.35 to 0.66 mmol/g of Al_2O_3 washcoat (ranging from 12 to 15 wt % total oxide). The original foam blocks were approximately 5 cm by 5 cm with a thickness of approximately 1.3 cm. The specific surface area of the materials coated with the washcoat and catalyst ranged from 90 to 130 m^2g^{-1} . Temperature programmed reduction studies resulted in well defined peaks from approximately 360 to 970 K and indicated that the order of reducibility was $\text{Mn}_3\text{O}_4 < \text{Mn}_2\text{FeO}_4 < \text{MnFe}_2\text{O}_4 < \text{Fe}_3\text{O}_4$. Oxygen chemisorption on samples reduced at temperatures just below the bulk reduction temperature gave oxygen uptakes of 267 to 487 μmol per gram of applied coating, corresponding to dispersions of 27.4 to 51.6%.

Keywords: foam; manganese; iron; oxide; ozone; VOC

Introduction

There are increasing economic incentives to develop highly efficient methods of removing volatile organic compounds from industrial vent streams to reduce air pollution. One of the reasons for this increased interest is that large companies are now required to file annual reports which specify the amount of pollution emitted from each facility [1]. Not only are industries concerned about the impact of such information on their public image, but they have also become aware of the cost of raw materials which are being lost to the atmosphere. In addition, the Clean Air Act Amendments of 1990 require EPA to issue new regulations to limit the emissions of certain VOC compounds from targeted industrial categories [2]. Companies are currently evaluating the effects of the public scrutiny and the anticipated regulations. Many have concluded that it is in their best interest to install additional air pollution control equipment, even if it is not yet required by state or federal regulations. Many more will have to install controls to

meet the anticipated air pollutant emission standards that are currently being developed by EPA.

The recognition that many companies will need to develop additional controls has increased the interest in alternative or innovative air pollution control methods [3]. Some of these innovations result in new types of equipment; others increase the removal efficiency or the cost efficiency of existing technologies. This paper describes research to improve performance and reduce energy consumption associated with catalytic incineration by the use of ozone as an oxidizing agent.

The catalysts employed are oxides of manganese and oxides of iron, including mixtures of the two. These catalysts have been shown in previous work [4, 5] to be effective at reducing VOCs to simple compounds such as carbon dioxide and water. With VOCs, it is critical to completely destroy the pollutant, because incomplete oxidation can result in more harmful compounds being produced than present in the original gas stream [3].

Ozone is an extremely effective oxidant for destroying VOCs [6, 7, 8, 9]. It has been shown previously that ozone increases the catalytic rate by opening up new reaction channels [4, 7]. By improvements in catalysts and the presence of ozone, we anticipate that the temperature required for complete oxidation can be substantially reduced. Because the cost of ozone can be as low as \$2 /kg (\$1/lb) [3], this temperature reduction could result in significant savings for companies planning to install new catalytic incinerators.

Additional improvements in catalyst technology include the need for catalysts which are less susceptible to deactivation by impurities in the gas stream, which are lighter weight [10], and which result in lower pressure drops [11].

There are generally three types of substrate available for catalyst deposition. Pellets (see Figure 11-1 [11]) have been in use for many years in commercial systems, but generally result in a higher pressure drop than other substrates when compared on the basis of the same number of active sites (see Figure 11-2 [11]). Other substrates include monoliths (Figure 11-3 [11]) and ceramic foams (Figure 4 [11]). The current research uses foams as a substrate to provide good mixing while retaining a low pressure drop. As evident in Figure 4, the foam substrate has a random pattern which allows gas to flow in different directions, enhancing the mixing of the gas stream [10].



Figure 11-1. Pellets [11]

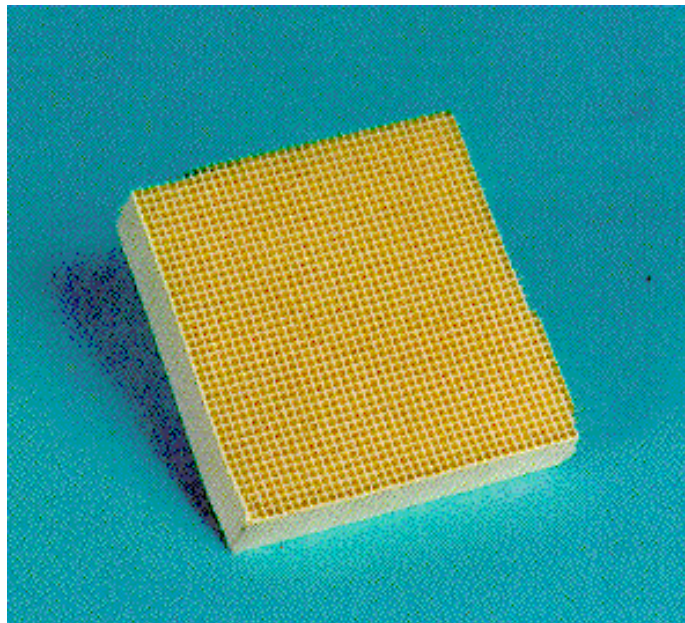


Figure 11-2. Cordierite Monolith [11]



Figure 11-3. Cordierite Foam [11].

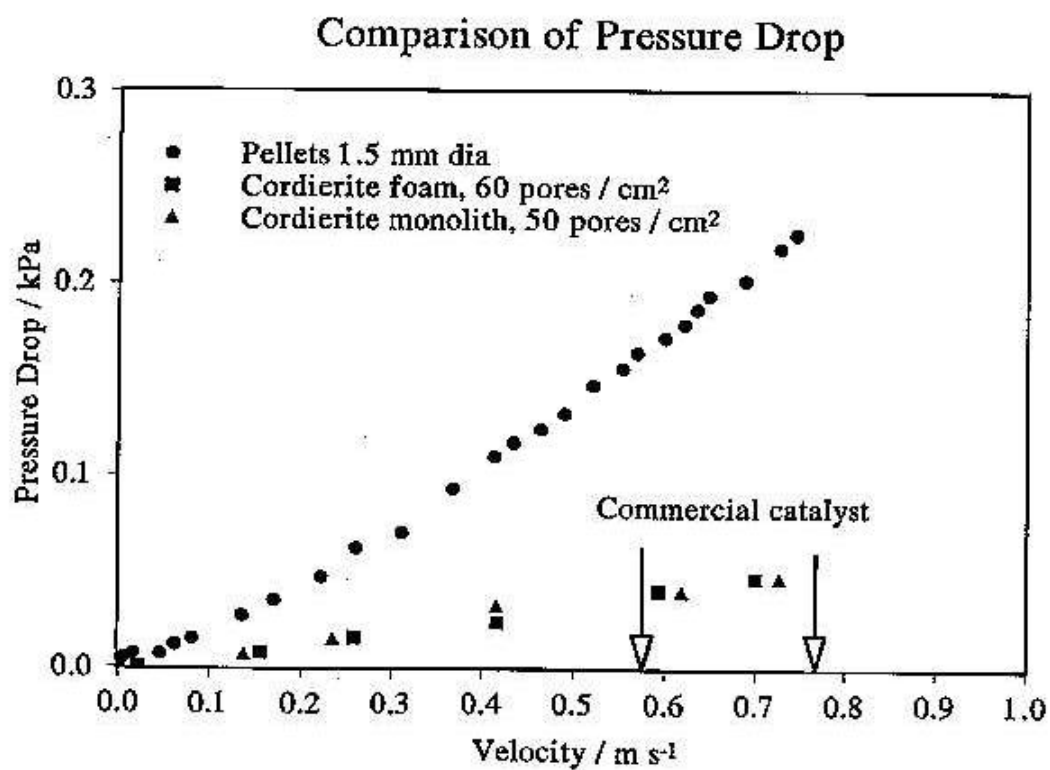


Figure 11-4. Pressure drop vs. Velocity for Various Types of Substrates [11]

The research described here includes the preparation of manganese and iron oxide catalysts on aluminum oxide foam substrates. An aluminum oxide washcoat is used to increase the surface area of the foam before the catalyst is deposited. Measurements of the BET surface area of the prepared catalyst have been carried out and the results are included. BET surface area analysis results for the foam and washcoated blanks are also presented.

Experimental Method

Samples of Amporex aluminum oxide foam manufactured by Fiber-Ceramics, Inc in Cincinnati, Ohio served as the substrate material for the catalyst deposition. The foam blocks are 5 cm x 5 cm x 1.3 cm. A picture of the foam substrate is shown in Figure 5. The pore density of the original foam material is a nominal 30 pores per cm² [12] compared to an actual measured density of 33 ±4 pores per cm².



Figure 11-5. Foam Substrate

The foam samples are treated with a washcoat to increase the surface area and to improve the bonding of the metal oxide catalysts. The foam samples were treated with a slurry of 15.03 g of alumina (Degussa Aluminumoxid C) in 100 ml of water. The aluminum oxide has a surface area of approximately 85 to 115 m²/g [13]. A single one-step application method of the aluminum oxide slurry resulted in agglomerated particles of alumina with poor adhesion to the foam substrate. Therefore, the final preparation method relied on a multiple impregnation process. The sample was placed in the aluminum oxide slurry for approximately 30 seconds, removed, then was shaken to remove as much residual liquid as possible. A jet of air was subsequently blown down through the large face areas of the block and the sample was moved from side to side and front to back to ensure that the jet of air was forced through all the areas of the sample. The coated sample was heated and calcined with a temperature profile consisting of an initial rate of 0.03 K s⁻¹ to a temperature of 373 K, where it was maintained for four hours. The second portion of the heating cycle increased the temperature by 0.08 K s⁻¹ to a final temperature of 673 K, where it was maintained for three hours. During the heating cycles, additional air was introduced through a 1/8" diameter tube pointed toward the oven floor in the middle of the oven. Previous work had used a similar air jet blowing directly on each sample. By dispersing the air evenly over multiple samples by directing the air jet toward the bottom of the oven and using a drying rack, the production capability was increased from one sample per cycle to eight samples per cycle. Three or more coating/heating cycles were required to achieve the same approximate

weight of washcoat. However, the samples appeared to be more uniformly coated without crystals forming in the interstitial spaces of the foam. Final weights of washcoats and original samples are given in Table 11-1.

Table 11-1. Weights of Samples and Applied Coating

Sample ID	Foam Wt (g)	Washcoated Wt (g)	Wt of Washcoat (g)	Reagent	Wt of Sample and Catalyst Coating(g)	Catalyst Coating Wt (g)	Wt of Applied Coating (g)
phh01024a	20.269	22.958	2.689	Fe	23.451	0.493	3.182
phh01024b	18.393	20.666	2.273		21.070	0.404	2.677
phh01025c	19.786	22.160	2.374	Mn	22.703	0.543	2.917
phh01024d	19.430	22.805	3.375		23.438	0.633	4.008
phh01024e	20.108	22.989	2.881	Mn:2Fe	23.478	0.489	3.370
phh01024f	19.410	22.374	2.964		22.874	0.500	3.464
phh01024g	17.475	20.675	3.200	2Mn:Fe	21.160	0.485	3.685
phh01024h	18.723	21.531	2.808		21.974	0.443	3.251

After the washcoat application was complete, the active catalyst was deposited onto the samples by an impregnation method. The chemicals used in this experiment were manganese (II) acetate tetrahydrate (99.99% purity) and iron (III) nitrate nonahydrate (Aldrich, 99.99 % purity). Initially, the metal solutions were applied in the same one-step method as the original method for the washcoat. The solution concentrations were calculated by determining the amount of metal oxide that was needed on the final sample (15-20% by weight of the washcoat weight). Then the amount of reagent was determined based on the number of moles of metal that were required to result in the necessary deposition and the reagent was dissolved in 100 ml of water. The presence of high quantities of moisture during drying, though, resulted in uneven drying and a splotchy appearance, as evident in the iron oxide example shown in Figure 11-6. In addition, weights of the samples changed very little with the addition of the catalyst deposition due to several factors including removal of the washcoat component with long exposure to the metal solutions and low concentration of metal solutions. Therefore, the catalyst deposition method was modified by use of solutions that were approximately ten times as strong and by dipping the samples quickly into the solution, then shaking them to remove excess solution and blowing air across them in the same manner as with the washcoat. The air jet and sample rack were also used during the drying/calcining process to ensure even drying.



Figure 11-6. Iron Oxide Sample with Uneven Drying

The samples were analyzed for BET surface. Results of the surface area per gram of washcoat are given in Table 11-2. Surface area analyses were also performed for a typical foam block and a washcoated block as blanks.

Table 11-2. BET Surface Area Analysis Results

Sample ID	Foam Wt (g)	Washcoated Wt (g)	Wt of Washcoat (g)	Reagent	Wt of Sample and Catalyst Coating (g)	Wt of Catalyst Coating (g)	Wt of Applied Coating (g)	BET Surface Area (m ² /g sample)	Surface Area/g washcoat
phh01024b	18.393	20.666	2.273	Fe	21.070	0.404	2.677	11.8832	110.1536
phh01025c	19.786	22.160	2.374	Mn	22.703	0.543	2.917	13.6147	130.1999
phh01024e	20.108	22.989	2.881	Mn:2Fe	23.478	0.489	3.370	10.8075	88.07306
phh01024h	18.723	21.531	2.808	2Mn:Fe	21.974	0.443	3.251	14.8395	116.1265
phh01047a	Foam Blank							0.5004	NA
phh01046h	18.793	21.701	2.908	Washcoated Blank			2.908	10.4732	78.15644

The samples were analyzed by temperature programmed reduction (TPR) and oxygen chemisorption to determine the active surface area of the catalyst. Approximately 2 grams of the crushed sample was loaded into a reactor and held in place with glass wool. The samples were pretreated with oxygen and heat to ensure that the catalyst was fully converted to the oxide form. The pretreatment was performed using a temperature ramp of approximately 0.83 K s⁻¹ to a temperature of 773 K. The sample temperature remained at 773 K for two hours. During the heating cycle, oxygen was passed over the sample at a rate of approximately 40 μmol s⁻¹ (1 cm³ s⁻¹). Once the oxygen pretreatment was complete, the sample returned to room temperature and was purged briefly with helium to remove any oxygen from the system. Then, hydrogen was introduced at a rate of approximately 67 μmol s⁻¹ (1.3 cm³ s⁻¹) and a separate heating cycle was begun. The temperature was ramped to 1223 K at a rate of approximately 0.17 K s⁻¹ and

remained at the elevated temperature for approximately 300 s. During the temperature ramping, the exhaust stream was monitored with a mass spectrometer (Dycor Quadrupole Gas Analyzer) for concentrations of helium, hydrogen, water, and oxygen. The resulting temperature profile was used to determine the temperature at which reduction of the bulk material began. The oxygen chemisorption tests were then conducted by pretreating the sample in the same manner with oxygen. The pretreated sample was then reduced with hydrogen flowing over it for two hours at a temperature just below that at which reduction of the bulk material began. The objective was to reduce the surface sites without reducing the bulk material. Once the two hour reduction cycle was complete, 5.39 μmol pulses of oxygen were introduced. The first several pulses were completely adsorbed onto the surface of the sample. By comparing the size of subsequent oxygen peaks on the mass spectrometer, the total amount of oxygen uptake can be determined.

In addition to the standard TPRs, TPRs were conducted with the iron and manganese samples using helium as the carrier gas to eliminate any peaks in the TPR data due to dehydration of surface hydroxyl groups.

Results and Discussion

The original methods for applying the washcoat and the catalyst coating were unsuccessful, resulting in uneven deposition of catalyst. However, the modified methods, including use of the air jet in the oven and the sample rack, resulted in even deposition of the washcoat and metal coatings. In addition, the speed of producing samples was increased substantially. The uniformity of the metal coatings is evident, as shown in Figures 11-7, through 11-10. Foam weight, washcoat weight, solution concentration, and weight of catalyst coating for the final method are given in Table III.

One of each pair of samples was crushed and tested for BET surface area. Blanks of the foam material and the foam coated with the alumina washcoat were also analyzed. The results of those analysis are given in Table 11-2, in square meters of surface area per gram of washcoat. The manganese oxide sample has the largest surface area, with 130 m^2/g . The metal oxide coatings substantially increased the surface area of the block from the blank washcoated value of 78 m^2g^{-1} .

The surface area of the washcoat was somewhat reduced from the original value in the powder. This may be attributable to the binding of the catalyst on the washcoat, but it is more likely due to the multiple layers of washcoat that are applied to the sample which block micropores.

Figure 11-7. Manganese Impregnated Catalyst Sample

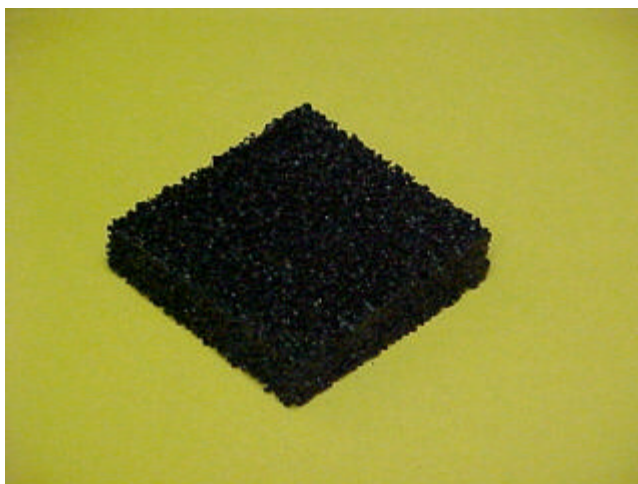
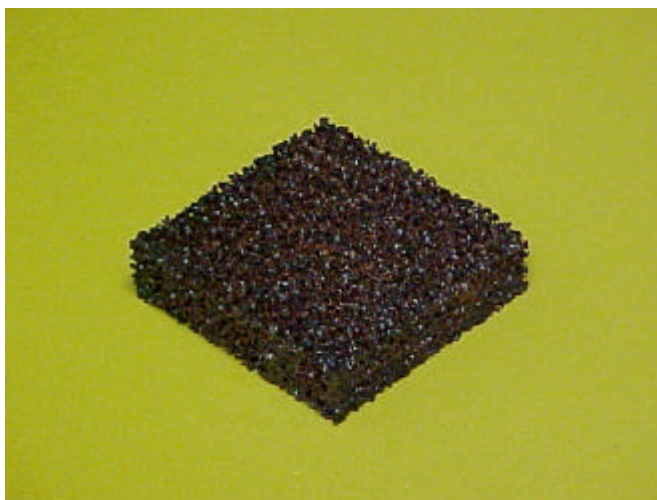


Figure 11-8. Iron Impregnated Catalyst Sample



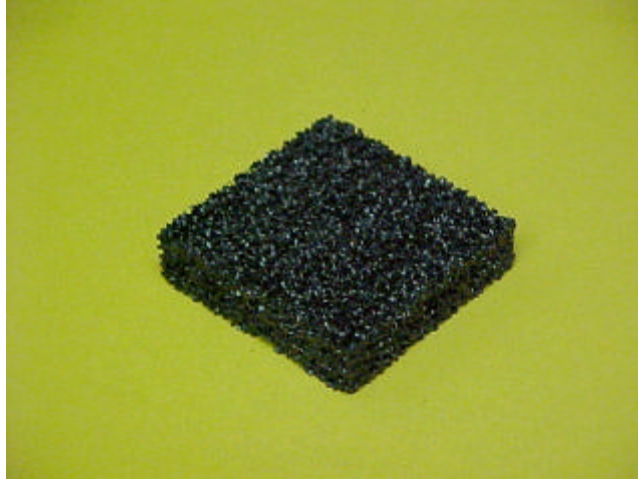


Figure 11-9. Sample Impregnated with a Mn:2 Fe Ratio

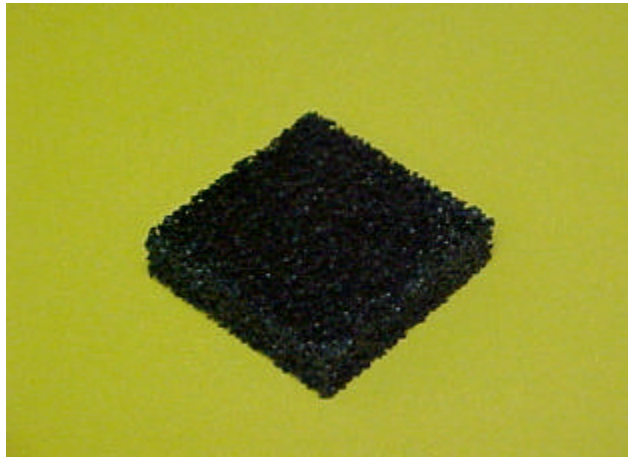


Figure 11-10. Sample Impregnated with a 2 Mn: Fe Ratio

Table 11-3. Experimental Data for Catalyst Preparation

Sample ID	Foam Wt (g)	Washcoated Wt (g)	Wt of Washcoat (g)	Reagent	Conc (g of reagent/100 ml of water)	Wt of Sample and Catalyst Coating (g)	Catalyst Coating Wt (g)	Wt of Applied Coating (g)
phh01024a	20.269	22.958	2.689	Fe	13.51	23.451	0.493	3.182
phh01024b	18.393	20.666	2.273			21.070	0.404	2.677
phh01025c	19.786	22.160	2.374	Mn	8.00	22.703	0.543	2.917
phh01024d	19.430	22.805	3.375			23.438	0.633	4.008
phh01024e	20.108	22.989	2.881	Mn:2Fe	5.37	23.478	0.489	3.370
phh01024f	19.410	22.374	2.964		17.70	22.874	0.500	3.464
phh01024g	17.475	20.675	3.200	2Mn:Fe	9.85	21.160	0.485	3.685
phh01024h	18.723	21.531	2.808		8.12	21.974	0.443	3.251

Temperature programmed reduction results indicated that bulk reduction begins at approximately 500 K for the iron sample, 475 K for the manganese sample, 487 K for the 2 Mn:Fe sample, and 506 K for the Mn:2 Fe sample. Graphs of the water signal vs. temperature for the samples and washcoated blank are given in figures 11-11 through 11-15. The washcoated blank resulted in a relatively consistent baseline with no significant reduction. The TPR tests done with only helium as a carrier gas resulted in no significant reduction, as shown in figures 11-16 and 11-17.

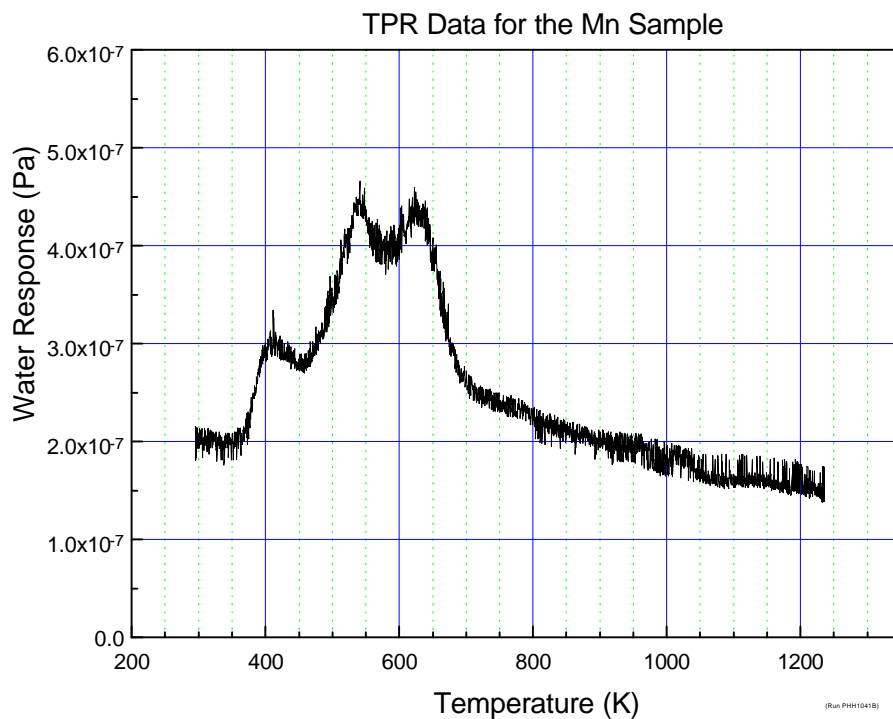


Figure 11-11. TPR Graph for Manganese Sample

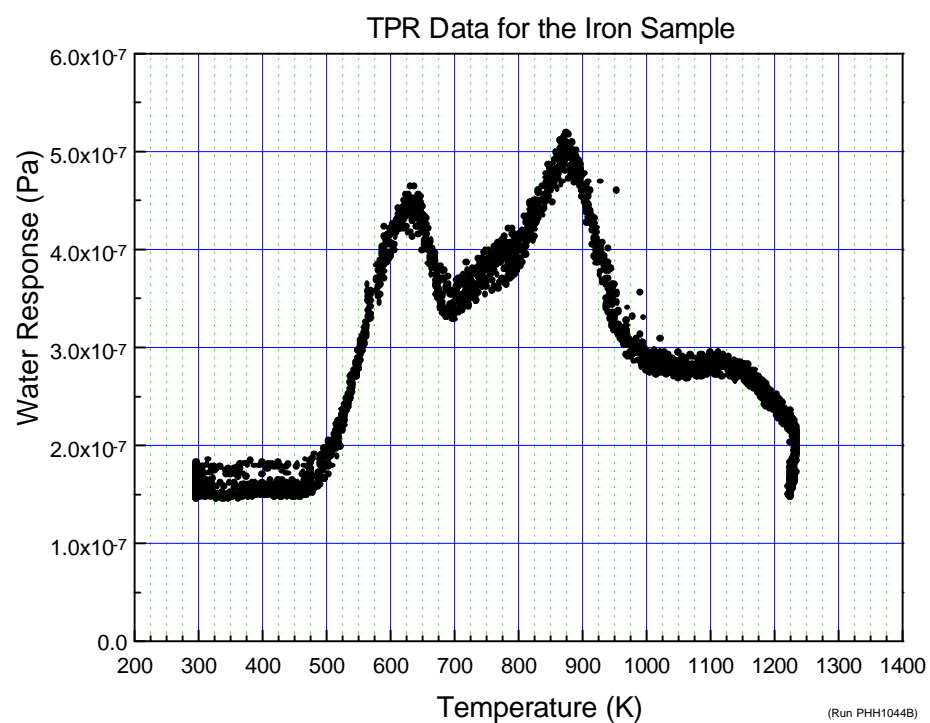


Figure 11-12. TPR Graph for Iron Sample

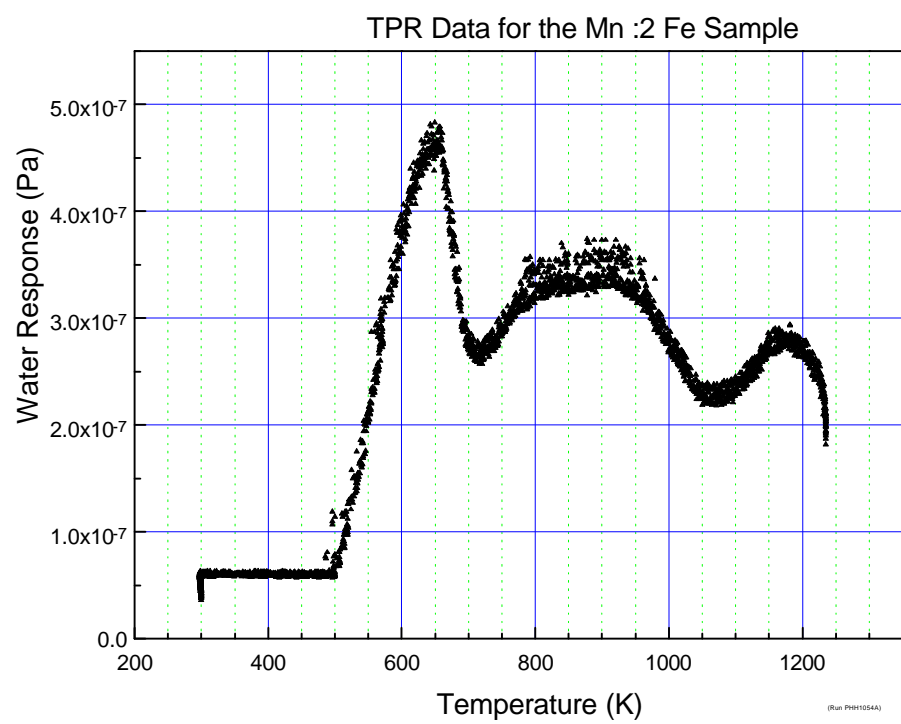


Figure 11-13. TPR Graph for the Mn:2 Fe Sample

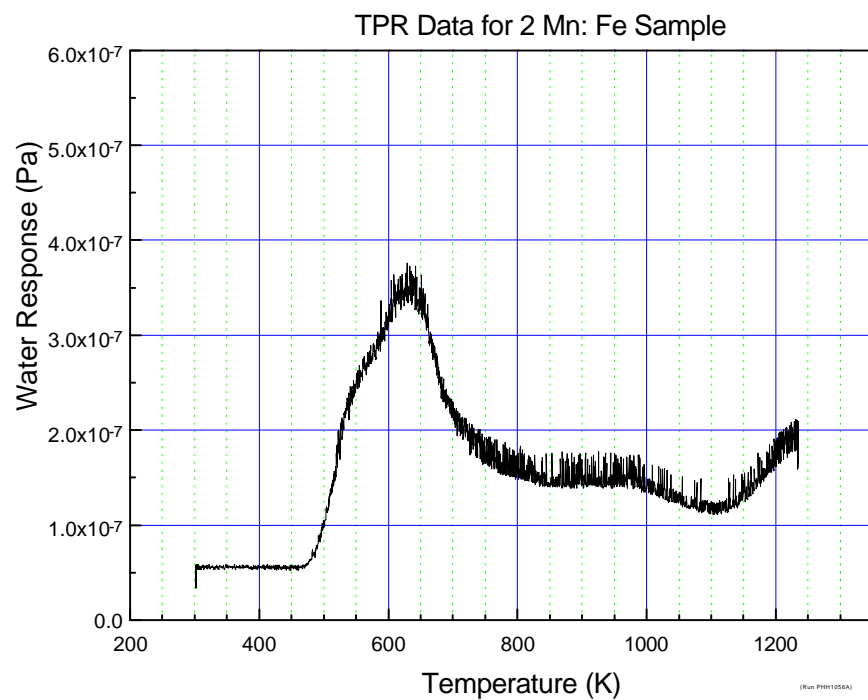


Figure 11-14. TPR Graph for 2 Mn: Fe Sample

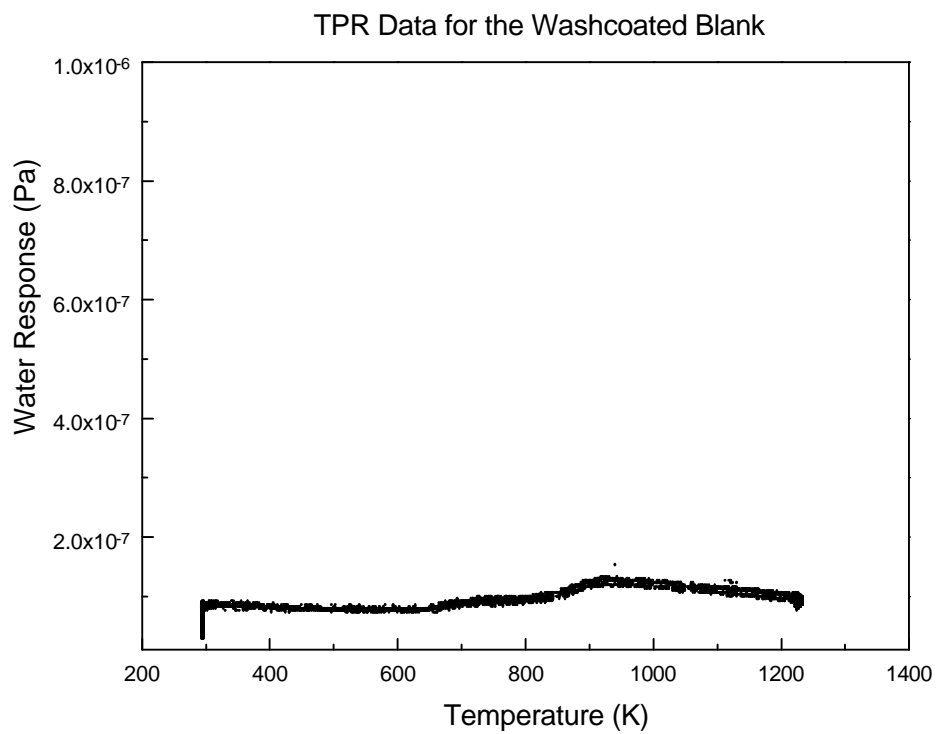


Figure 11-15. TPR Graph for the Washcoated Blank

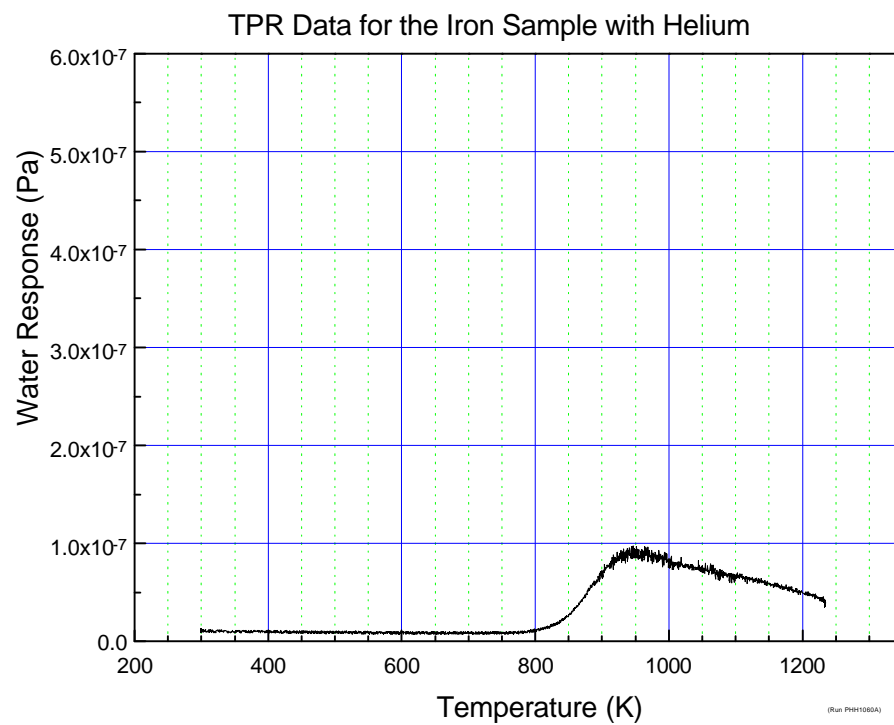


Figure 11-16. TPR Graph for Manganese with Helium Carrier Gas

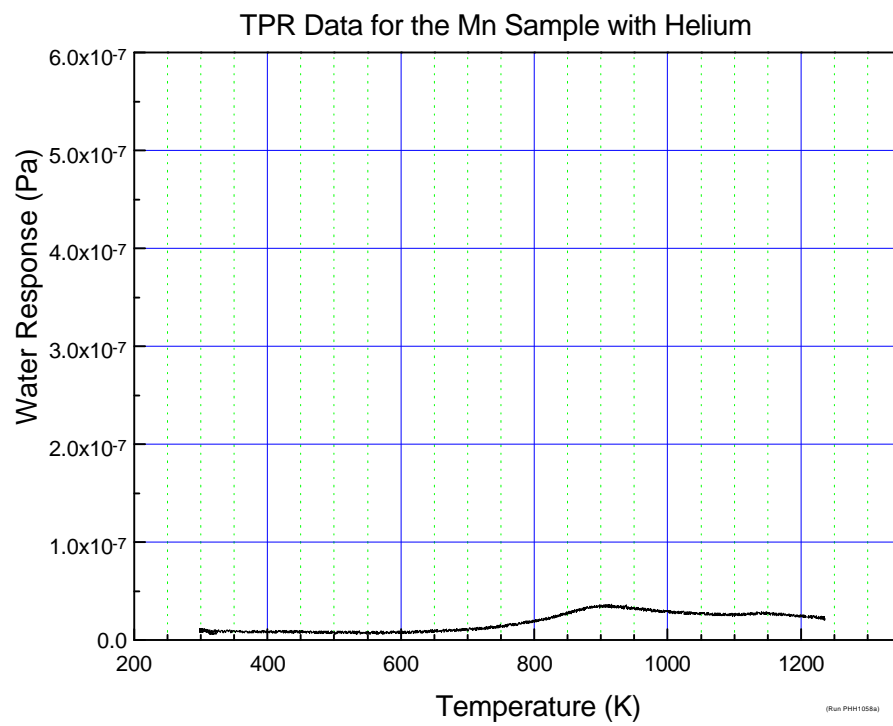


Figure 11-17. TPR Graph for Iron with Helium Carrier Gas

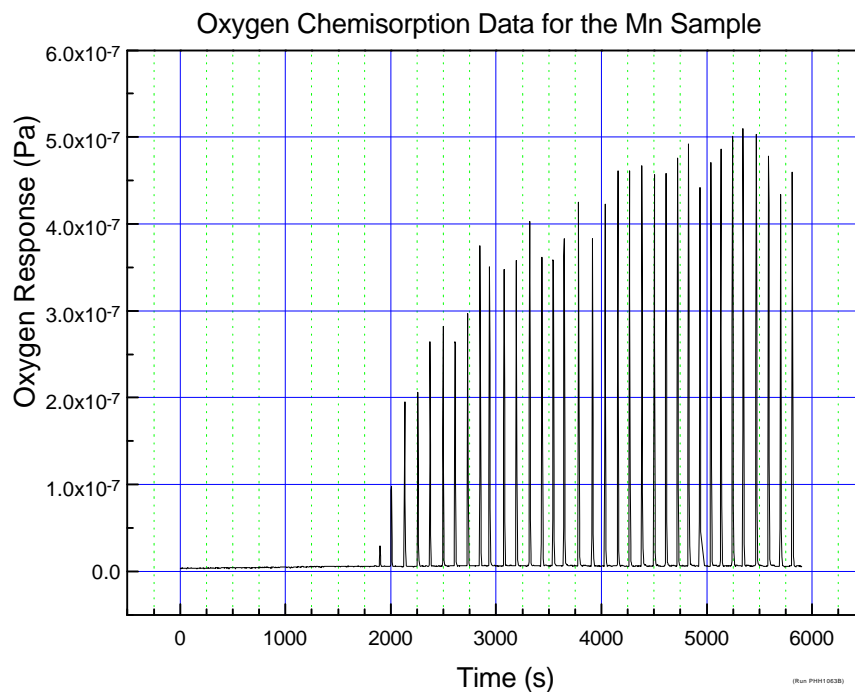


Figure 11-18. Oxygen Chemisorption Response for Mn Sample

The oxygen chemisorption tests were performed at approximately 500 K for the iron sample, 475 K for the manganese sample, 487 K for the 2 Mn:Fe sample, and 506 K for the Mn:2 Fe sample. The manganese sample was originally tested at 368 K, but the results were inconclusive, so the test was repeated at a temperature corresponding to the beginning of the second reduction temperature peak. Graphs of the mass spectrometer response during the oxygen pulsing process are shown in Figures 11-18 through 11-21. In Figure 11-21, the data for one peak was not automatically collected due to a failure of the data collection system, but the peak area was estimated from manual readings taken during the test. Results of the oxygen chemisorption testing are given in Figures 11-22 through 11-25 and Table 11-4. The highest oxygen chemisorption rate occurred in the Mn:2 Fe sample with an adsorption rate of 487 μmol per gram of applied coating (includes both the alumina washcoat and the active metal oxide).

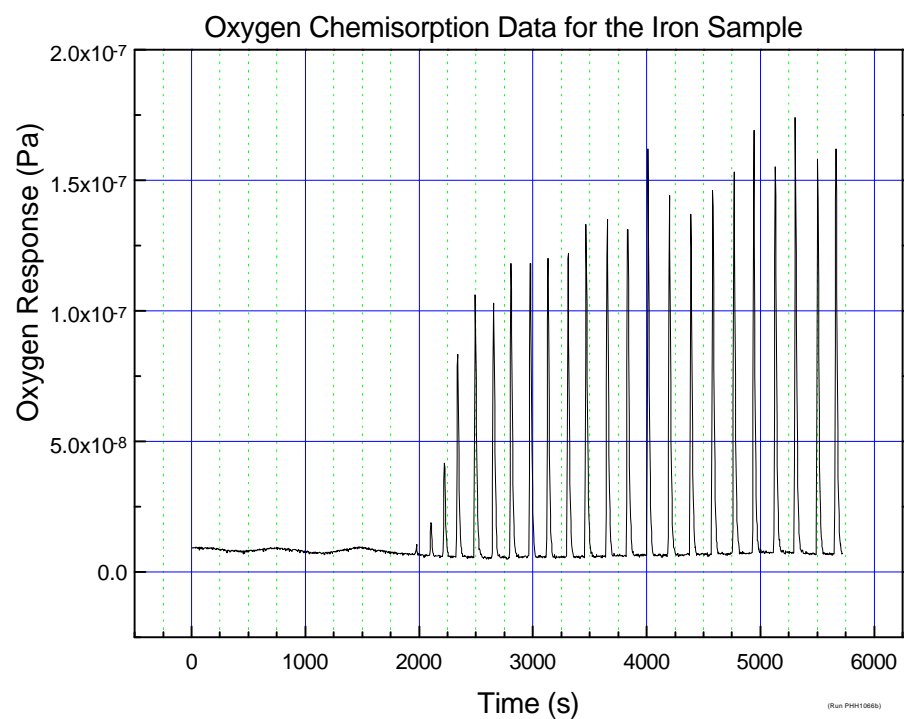


Figure 11-19. Oxygen Chemisorption Response for Iron Sample

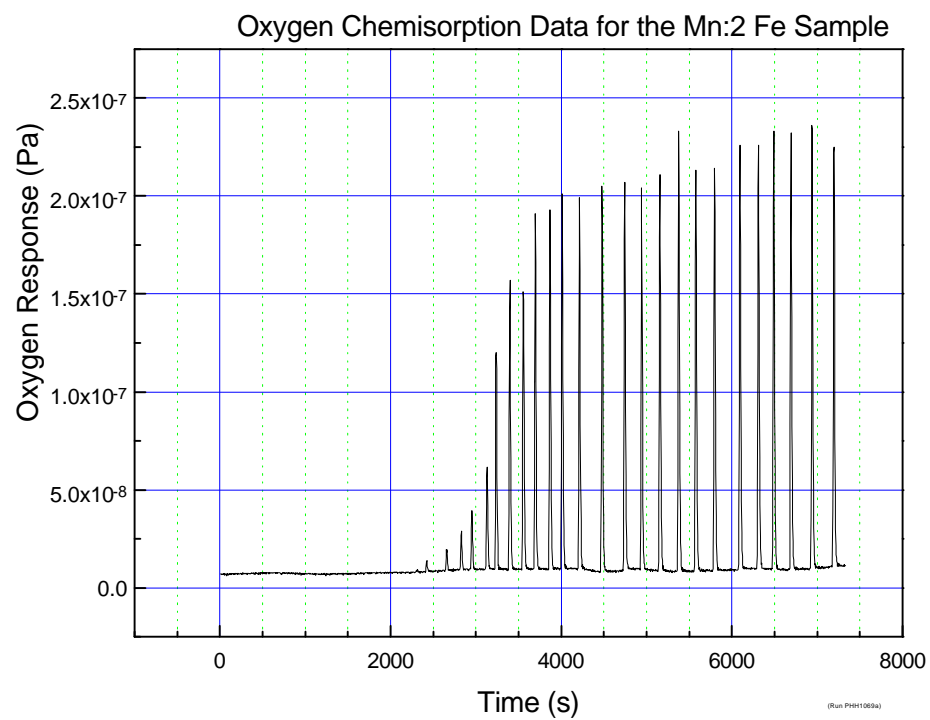


Figure 11-20. Oxygen Chemisorption Response for the Mn:2 Fe Sample

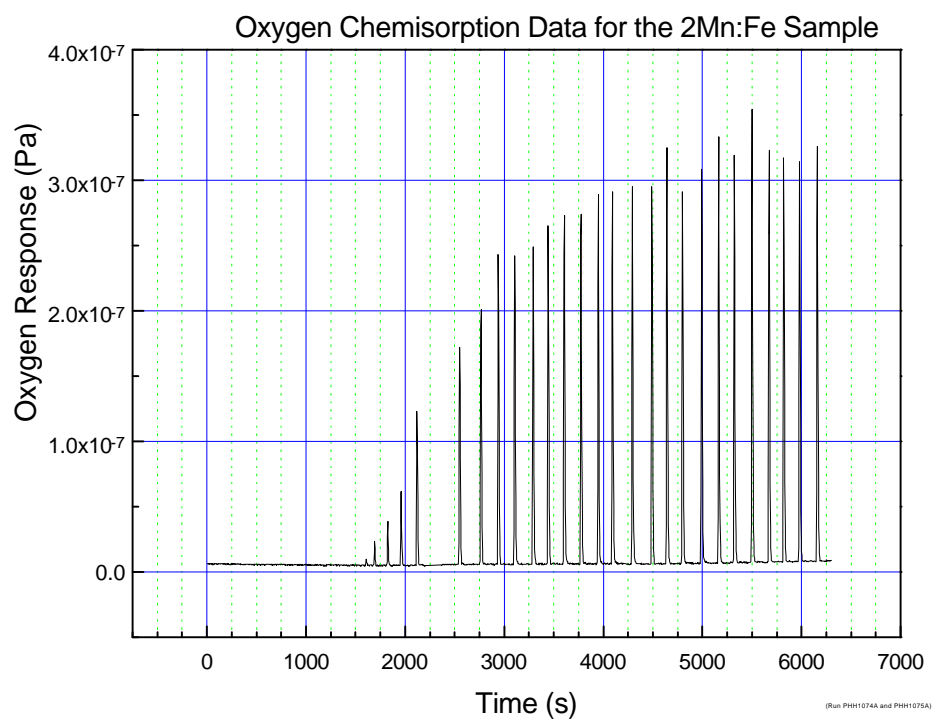


Figure 11-21. Oxygen Chemisorption Response for the 2 Mn: Fe Sample

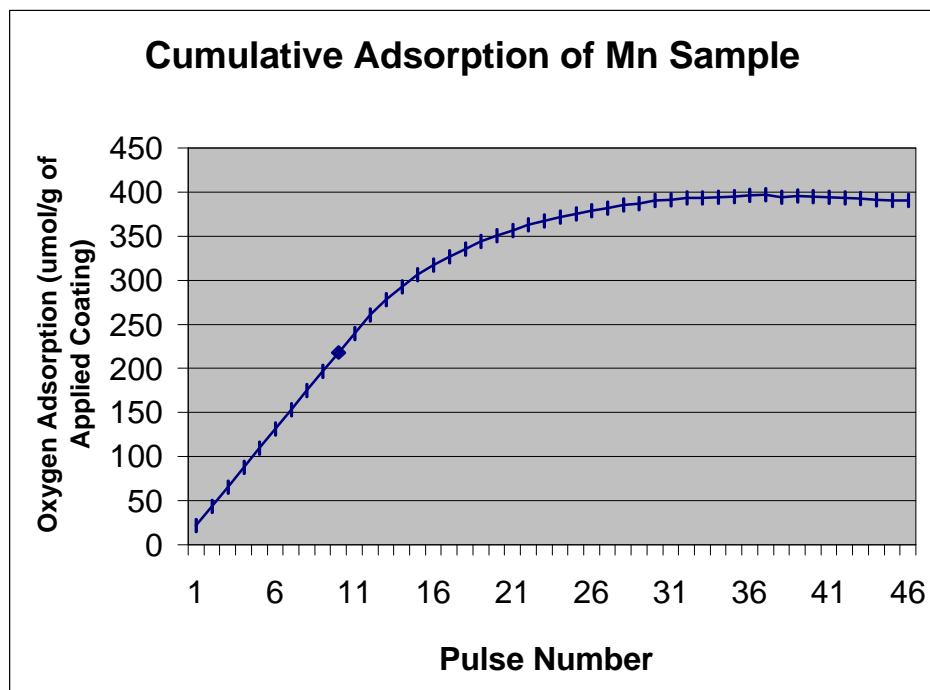


Figure 11-22 Cumulative Oxygen Adsorption for Mn Sample

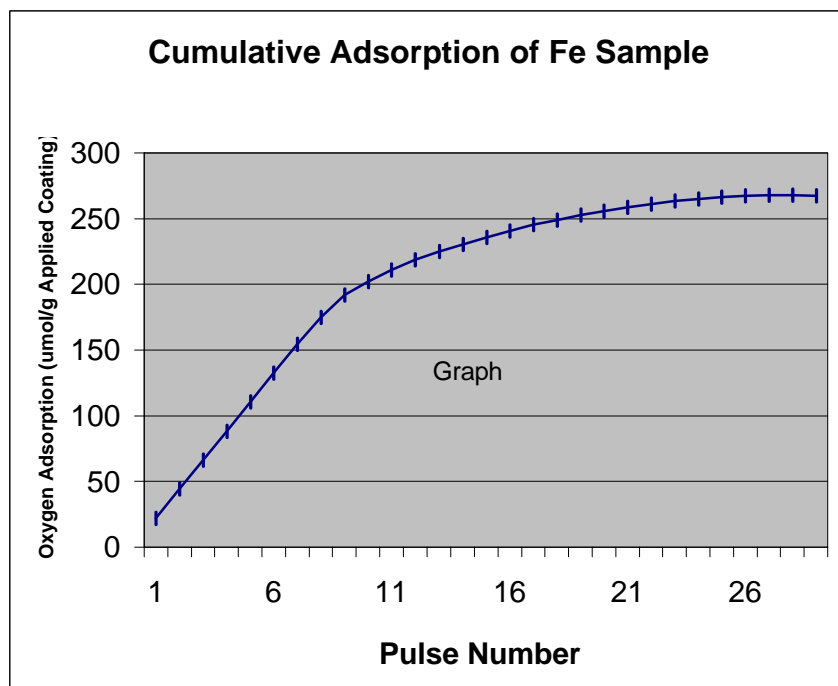


Figure 11-23. Cumulative Oxygen Adsorption for Fe Sample

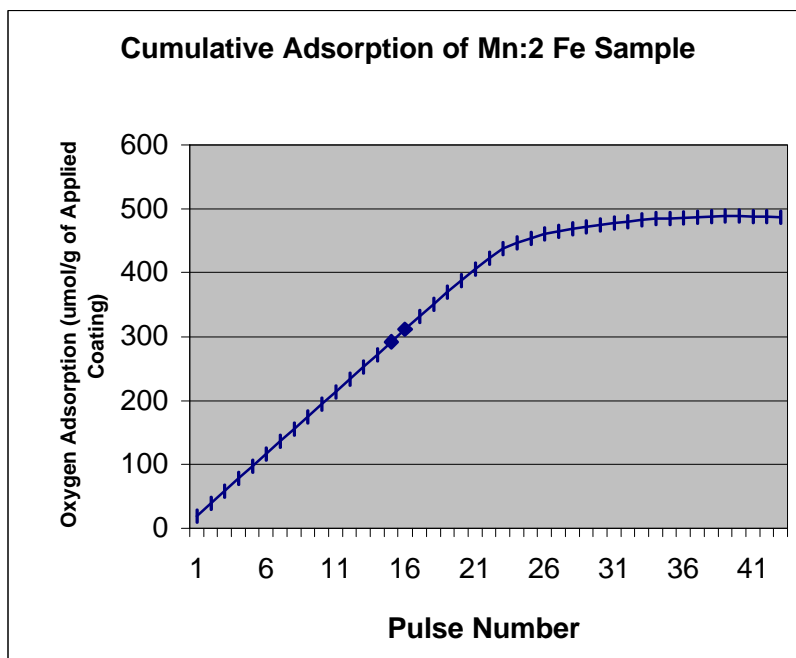


Figure 11-24. Cumulative Oxygen Adsorption for Mn:2 Fe Sample

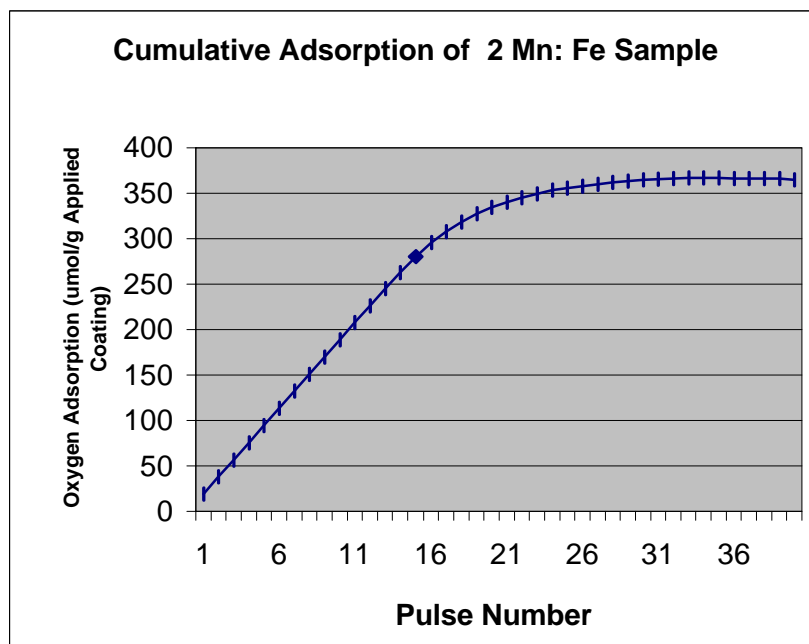


Figure 11-25. Cumulative Oxygen Adsorption for 2Mn:Fe Sample

Table 11-4. Results of Oxygen Chemisorption Testing

Sample ID	Wt of Washcoat (g)	Assumed Form of Catalyst	Wt of Sample and Catalyst Coating (g)	Catalyst Coating Wt (g)	% Catalyst on Alumina	% Alumina on Foam	Wt of Applied Coating (g)	Oxygen Adsorption (umol/g applied Coating)	MW of Catalyst	Fractional Dispersion
phh01024b	2.273	Fe ₃ O ₄	21.070	0.404	17.8	12.4	2.677	267.47	231.54	0.274
phh01025c	2.374	Mn ₃ O ₄	22.703	0.543	22.9	12.0	2.917	390.29	228.81	0.320
phh01024e	2.881	MnFe ₂ O ₄	23.478	0.489	17.0	14.3	3.370	487.01	230.63	0.516
phh01024h	2.808	Mn ₂ FeO ₄	21.974	0.443	15.8	15.0	3.251	365.12	229.72	0.410

Fractional dispersions were also calculated for each analyzed sample by ratioing the number of surface sites to the total number of moles of active metal oxide. Dispersions ranged from a low of 27.4% in the iron sample to 51.6% in the Mn:2Fe sample.

Conclusions

An improved sample preparation method was developed which resulted in uniform distribution of catalyst on the washcoat and a substantial increase in the production speed of the catalysts over previous methods. Bulk reduction of the samples was found to begin at approximately 500 K for the iron sample, 475 K for the manganese sample, 487 K for the 2 Mn:Fe sample, and 506 K for the Mn:2 Fe sample. The Mn:2 Fe sample resulted in the highest

amount of oxygen uptake on the surface of the catalyst per gram of combined washcoat and active metal oxide. The order of oxygen uptake during chemisorption was found to be $\text{Fe} < \text{Mn} < 2 \text{ Mn:Fe} < \text{Mn:2 Fe}$.

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Vita

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