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Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products

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16. ABSTRACT

This report provides the necessary guidance for development of regulations to limit emissions of volatile organic compounds (VOC) from manufacture of synthesized pharmaceutical products. The report includes a characterization of manufacturing operations, emissions from these operations, applicable controls and costs of controls. General emission control guidelines are provided which represent application of reasonably available control technology (RACT).

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Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products

Emission Standards and Engineering Division
Chemical and Petroleum Branch

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
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OAQPS GUIDELINE SERIES

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PREFACE

This is one in a series of reports which provide guidance on air pollution control techniques for limiting emissions of volatile organic compounds (VOC) from existing sources in specific industries. These reports are designed to assist States in the development of air pollution control regulations for VOC which contribute to the formation of photochemical oxidants. This report deals with volatile organic emissions from the production of synthesized pharmaceutical products.

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements in agency documents in metric units. Listed below are abbreviations and conversion factors for British equivalents of metric units for the use of engineers and scientists accustomed to using the British system.

Abbreviations

Mg - Megagrams

kg - kilograms

m^3 - cubic meters

Conversion Factors

liters X .264 = gallons

gallon X 3.785 = liters

gram X 1 X 10^6 = 1 Megagram = 1 metric ton

1 pound = 0.454 kilograms

^oC = .5555 (^oF - 32)

Mg/yr X 0.907 = tons/yr

1 psi = 6,895 pascals (Pa)

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1.0 INTRODUCTION AND SUMMARY

This report is intended to assist State and local air pollution control agencies develop regulations to reduce emissions of volatile organic compounds (VOC) from existing sources within the pharmaceutical industry. Methodology described in this document represents the presumptive norm or reasonably available control technology (RACT) that can be applied to existing plants synthesizing pharmaceutical products. RACT is defined as the lowest emission limit that a particular source is capable of meeting by the application of control technology that is reasonably available considering technological and economic feasibility. It may require technology that has been applied to similar, but not necessarily identical, source categories. It is not intended that extensive research and development be conducted before a given control technology can be applied to the source. This does not, however, preclude requiring a short-term evaluation program to permit the application of a given technology to a particular source. This latter effort is an appropriate technology-forcing aspect of RACT.

1.1 INDUSTRY CHARACTERIZATION

Production activities of the pharmaceutical industry can be divided into the following categories:

1. Chemical Synthesis - The manufacture of pharmaceutical products by chemical synthesis.

2. Fermentation - The production and separation of medicinal chemicals such as antibiotics and vitamins from microorganisms.

3. Extraction - The manufacture of botanical and biological products by the extraction of organic chemicals from vegetative materials or animal tissues.

4. Formulation and Packaging - The formulation of bulk pharmaceuticals into various dosage forms such as tablets, capsules, injectable solutions, ointments, etc. that can be taken by the patient immediately and in accurate amount.

There are approximately 800 pharmaceutical plants producing drugs in the United States and its territories. Five States have nearly 50 percent of all plants: New York, 12 percent; California, 12; New Jersey, 10; Illinois, 5; and Pennsylvania, 6. These States also contain the largest plants in the industry. Puerto Rico has had the greatest growth in the past 15 years, during which 40 plants have located there; it now contains 90 plants or about 7.5 percent of the total. Most pharmaceutical plants are small and have less than 25 employees. EPA's Region II (New Jersey, New York, Puerto Rico, Virgin Islands) has 340 plants (28 percent of the total); Region V (Illinois, Minnesota, Michigan, Ohio, Indiana, Wisconsin) 215 plants (20 percent); and Region IX (Arizona, California, Hawaii, Guam, American Samoa) 143 plants (13 percent).

1.2 NEED TO REGULATE

The pharmaceutical industry uses many volatile organic compounds either as raw materials or as solvents. The Pharmaceutical Manufacturers Association (PMA) obtained estimates from 26 member companies of the ten largest volume volatile organic compounds that each company purchased and the mechanism by which they leave the plant, i.e., sold as product, sent to the sewer, or emitted as an air pollutant. Twenty-five of the 26 reporting companies indicated that their ten largest volume solvents accounted for 80 to 100 percent of their VOC purchases. (The other company said only 50 percent of their purchases were represented by their ten high VOC.) Overall, PMA estimates that these 26 reporting companies identified 85-90 percent of the total VOC's they used. These companies represented 53 percent of the domestic sales of ethical pharmaceuticals in 1975.* The results of the industry's estimates (which were developed by material balance and are not measured values) are presented in Appendix A, Table A-1.

According to the data submitted by pharmaceutical manufacturers, about 73 percent of all emissions reported by the industry are from the division referred to as "Synthesized Pharmaceutical Products" and only it is covered in this guideline.

1.3 SOURCES AND CONTROL OF VOLATILE ORGANIC COMPOUNDS FROM MANUFACTURE OF SYNTHESIZED PHARMACEUTICAL PRODUCTS

Synthesized pharmaceuticals are normally manufactured in a series of batch operations according to the following sequence: (a) reaction (sometimes more than one), (b) product separation, (c) purification, and (d) drying.

*Drugs are marketed in two categories, ethical and proprietary. Ethical drugs can be purchased only by prescription whereas proprietary drugs can be purchased "over the counter."

Each operation of the series may be a source of VOC emissions. The magnitude of emissions varies widely within and among operation categories and depends on the amount and type of VOC used, the type of equipment performing the operation, and the frequency of performing the operation. The wide variation prevents calculating typical emission rates for each operation; however, an approximate ranking of emission sources has been established and is presented below in order of decreasing emission significance. The first four sources generally will account for the majority of emissions from a plant.

1. Dryers
2. Reactors
3. Distillation units
4. Storage and transfer
5. Filters
6. Extractors
7. Centrifuges
8. Crystallizers

Applicable controls for all the above emission sources except storage and transfer are: condensers, scrubbers, and carbon adsorbers. Incinerators are expected to have limited application but may be useful for certain situations. Storage and transfer emissions can be controlled by vapor return lines, vent condensers, conservation vents, vent scrubbers, pressure tanks, and carbon adsorbers. Floating roofs may be feasible controls for large, vertical storage tanks. Emission reduction efficiencies for these controls are discussed in Chapter 4.

Since many of these individual vents are likely to be small in any given plant, it may often be reasonable to regulate on a plant by plant basis.

This approach involves determining which synthesized pharmaceutical manufacturing facilities emit large amounts of VOC and within such plants which operations are significant sources. Control requirements would then be imposed after considering local air quality, the mass rate of emissions, control cost estimates, and plant safety effects. Further information is given in Chapter 2 and Appendix B for determining emissions from various operations and equipment.

Where this approach is not practical, the following guidelines will serve as a generalized control program:

1. (a) For each vent from reactors, distillation operations, crystallizers, centrifuges, and vacuum dryers that emit 6.8 kg/day (15 lb/day) or more of VOC, require surface condensers or equivalent controls.

(b) If surface condensers are used, the condenser outlet gas temperature should not exceed:

(i) -25°C when condensing VOC of vapor pressure greater than 40 kPa (5.8 psi),*

(ii) -15°C when condensing VOC of vapor pressure greater than 20 kPa (2.9 psi),*

(iii) 0°C when condensing VOC of vapor pressure greater than 10 kPa (1.5 psi),*

(iv) 10°C when condensing VOC of vapor pressure greater than 7 kPa (1.0 psi),* and

(v) 25°C when condensing VOC of vapor pressure greater than 3.5 kPa (0.5 psi).*

(c) Equivalent control results when emissions are reduced at least as much as they would have been by using a surface condenser according to 1(b).

*vapor pressures as measured at 20°C

2. (a) For air dryers and production equipment exhaust systems that emit 150 kg/day (330 lbs/day) or more of VOC, require 90 percent emission reduction.

(b) For air dryers and production equipment exhaust systems that emit less than 150 kg/day (330 lbs/day), require emission reduction to 15 kg/day (33 lbs/day).

3. (a) For storage tanks storing VOC with a vapor pressure greater than 28 kPa (4.1 psi) at 20°C, allow one liter of displaced vapor to be released to the atmosphere for every ten liters transferred (i.e., a 90 percent effective vapor balance or equivalent), on truck/rail car delivery to all tanks greater than 7,500 liters (2000 gallons) capacity except where tanks are equipped with floating roofs, vapor recovery, or equivalent. This guideline does not apply to transfer of VOC from one in-plant location to another.

(b) For tanks storing VOC with a vapor pressure greater than 10 kPa (1.5 psi) at 20°C, require pressure/vacuum conservation vents set at ± 0.2 kPa, except where more effective air pollution control is used.

4. Enclose all centrifuges containing VOC, rotary vacuum filters processing liquid containing VOC, and any other filters having an exposed liquid surface where the liquid contains VOC. This applies to liquids exerting a total VOC vapor pressure of 3.5 kPa (0.5 psi) or more at 20°C.

5. All in-process tanks shall have covers. Covers should be closed when possible.

6. For liquids containing VOC, all leaks in which liquid can be observed to be running or dripping from vessels and equipment (for example: pumps, valves, flanges) should be repaired as soon as is practical.

2.0 PLANT CHARACTERIZATION AND REGULATORY APPROACH

2.1 SYNTHESIZED PHARMACEUTICAL MANUFACTURING PLANTS

The synthesis of medicinal chemicals may be done in a very small facility producing only one chemical or in a large integrated facility producing many chemicals by various processes. Most of the estimated 1200 plants are relatively small. Organic chemicals are used as raw materials and as solvents, and solvents constitute the predominant VOC emission from production. Plants differ in the amount of organics used; this results in widely varying VOC emission rates. Therefore, some plants may be negligible VOC sources while others are highly significant.

Nearly all products are made using batch operations. In addition, several different products or intermediates are likely to be made in the same equipment at different times during the year; these products, then, are made in "campaigned" equipment. Equipment dedicated to the manufacture of a single product is rare, unless the product is made in large volume.

Basically, production of a synthesized drug consists of one or more chemical reactions followed by a series of purifying operations. Production lines may contain reactors, filters, centrifuges, stills, dryers, process tanks, and crystallizers piped together in a specific arrangement. Arrangements can be varied in some instances to accommodate production of several compounds. A very small plant may have only a few pieces of process equipment but a large plant can contain literally hundreds of pieces, many of which are potential VOC emission sources.

Figure 2-1 shows a typical flow diagram for a batch synthesis operation. To begin a production cycle, the reactor may be water washed and perhaps dried with a solvent. Air or nitrogen is usually used to purge the tank after it is cleaned. In this example, solid reactants and solvent are charged to a 3,785 liter glass batch reactor equipped with a condenser (which is usually water-cooled). Still other volatile compounds may be produced as product or by-products. Any remaining unreacted VOC is distilled off. After the reaction and solvent removal are complete, the pharmaceutical product is transferred to a holding tank. After each batch is placed in the holding tank, three to four washes of water or solvent may be used to remove any remaining reactants and by-products. The solvent used to wash may also be evaporated from the reaction product. The crude product may then be dissolved in another solvent and transferred to a crystallizer for purification. After crystallization, the solid material is separated from the remaining solvent by centrifugation. While in the centrifuge, the product cake may be washed several times with water or solvent. Tray, rotary, or fluid-bed dryers may then be employed for final product finishing.

2.2 REGULATORY APPROACH

The plant characterization in the preceding section reveals the complexities of synthesized pharmaceutical manufacture. Each plant is unique, differing from other plants in size, types of products manufactured, amounts and types of VOC used, and air pollution control problems encountered. The dissimilarities make it impossible to define typical emission levels or emission factors for an average plant. This in turn prevents identifying in this document which sources definitely need to be controlled and how much overall emission reduction can be effected.

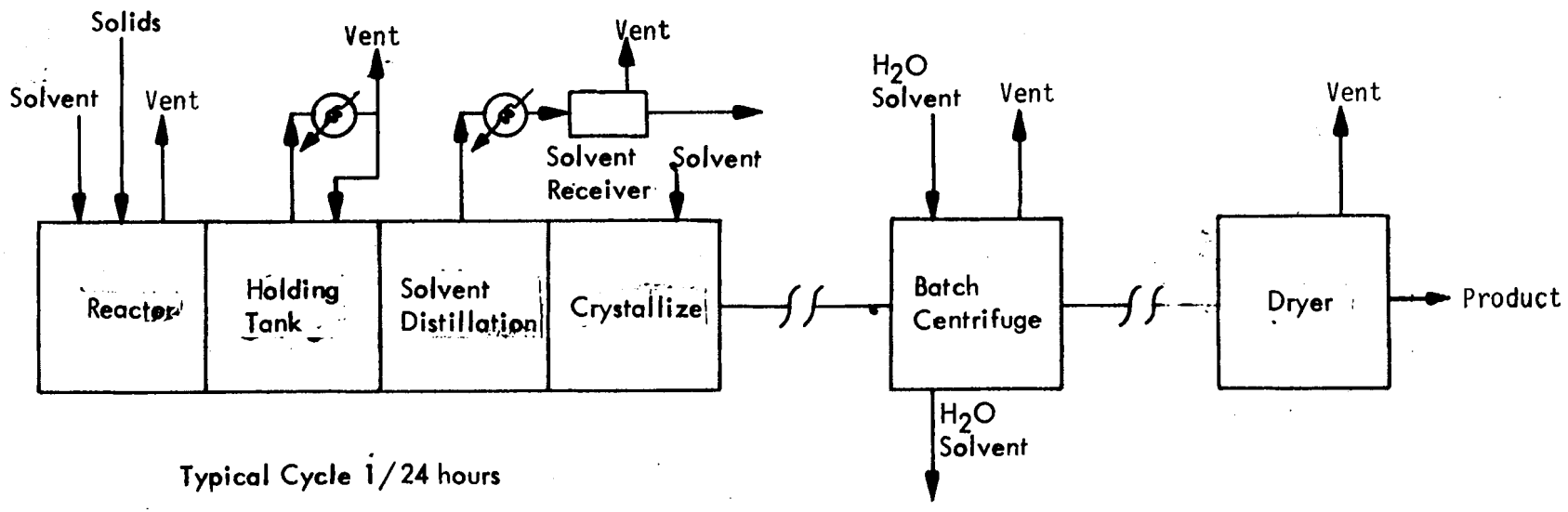

Figure 2-1 Typical Synthetic Organic Medicinal Chemical Process

With this in mind, it appears that a reasonable approach to regulation is to investigate emission levels and control options for a given plant on a plant by plant basis. The individual investigations would be begun by first determining which plants are significant VOC emitters and within such plants which process emission points are largest.

Emission data for pharmaceutical plants are scarce. Therefore, emission estimates will have to be obtained through other means. One way is to have plants submit solvent purchase and use information similar to that tabulated in Appendix A. The information in the Appendix resulted from a survey of 26 pharmaceutical manufacturers concerning amounts and types of VOC used and the ultimate disposition for each. As shown in the tables, estimates for air emissions were provided. It is acknowledged that these are only material balance estimates; nonetheless, they should be of sufficient accuracy to answer the question of whether or not the plant is a significant source.

Plants concluded to be significant VOC emitters would be candidates for a control program. The next step is to account for the bulk of total plant emissions by determining emissions from individual pieces of process equipment. Common methods are sampling and analysis of vent streams, material balance, and theoretical calculation. Many vents are neither easily nor inexpensively sampled, and in some instances material balances will not be satisfactory. Therefore, theoretical evaluations may have to be conducted. Equations are presented in Appendix B that will aid in calculating potential emissions from process operations. Because of the assumptions underlying the equations, calculated values will tend to represent maximum possible emissions from an operation.

Especially in larger plants, attempts to sample, perform material balances, or calculate emissions from all plant vents would be an expensive and time consuming task. It would be better to concentrate on the larger vents, which are

the most likely to be controlled anyway. Plant personnel may be able to indicate the major emission points. By using the limited emission data accumulated for this document, a ranking has been established to illustrate relative expected VOC emissions from process sources. The ranking is presented below in order of decreasing relative emissions.

1. Dryers
2. Reactors
3. Distillation systems
4. Storage tanks and transfer operations
5. Filters
6. Extractors
7. Centrifuges
8. Crystallizers

The list is not intended to represent every plant; a single list could not possibly fit all situations. It is intended to convey that for many plants, emissions from dryers will be the largest source of VOC emissions, reactors the second largest, and so on. For most plants, the first four listed process sources will account for the great majority of total plant VOC emissions. However, this does not preclude the last four from being significant emitters.

Once the emission profile for a plant is established, this document can be used to select control measures or emission limits for the major emission points. Information is provided in Chapters 3-5 concerning control system application, performance, and costs. The decision to require control of specific exhaust streams will be determined based on local air quality, the mass emission rate of volatile organics, and the cost to the operator to control the streams.

3.0 EMISSION SOURCES AND APPLICABLE SYSTEMS OF EMISSION REDUCTION

Compounds typically emitted during pharmaceutical manufacture are listed in the tables in Appendix A. The list is not exhaustive but does account for the great majority of VOC emissions from plants reporting. These compounds are commonly used as solvents, although at times they may be used as raw materials. Emissions of VOC's formed during reaction are estimated to contribute only a small fraction to total emissions.

Volatile organic compounds may be emitted from a variety of sources within plants synthesizing pharmaceutical products. Because of the number of sources, the discussion of emissions and applicable controls is organized by process component. The following process components have been identified as VOC sources and are discussed in this chapter: reactors, distillation units, dryers, crystallizers, filters, centrifuges, extractors, and tanks.

3.1 REACTORS

3.1.1 Reactor Description and Operation

The typical batch reactor is glass lined or stainless steel and has a capacity of 2,000 to 11,000 liters (500-3000 gallons). For maximum flexibility, the tanks are usually jacketed to permit temperature control of reactions. Generally, each is equipped with a vent which may discharge through a condenser. They can be operated at atmospheric pressure, elevated pressure, or under vacuum. Because of their flexibility, reactors may be used in a variety of ways. Besides hosting chemical reactions, they can act as mixers, heaters, holding tanks, crystallizers, and evaporators.

Like almost all equipment in the pharmaceutical industry, reactors are used on a batch basis and may be used to produce several different products during a year. When changing from one product to another, special care must be taken in cleaning the equipment. Cleaning procedures vary. Sometimes a detergent and water wash is followed by a solvent wash (to aid in drying). Often, a solvent wash alone is sufficient. One procedure is to add the cleaning solution, raise the reactor temperature (to improve the cleaning efficiency), and then agitate or circulate the mixture. The vessel is then drained, flushed with solvent (or water), and dried by raising the temperature again.

A typical reaction cycle takes place as follows. After the reactor is clean and dry, the appropriate raw materials, usually including some solvent(s), are charged for the next product run. Liquids are normally added first, then solid reactants are charged through the manhole. After charging is complete, the vessel is closed and the temperature raised if necessary via reactor jacket heating. The purpose of heating may be to increase the speed of reaction or to reflux the contents for a period which may vary from 15 minutes to 24 hours. During refluxing, the liquid phase may be "blanketed" by an inert gas, such as nitrogen, to prevent oxidation or other undesirable side reactions. Upon completion of the reaction, the vessel may be used as a distillation pot to vaporize the liquid phase (solvent), or the reaction products may be pumped out so the vessel can be cooled to begin the next cycle.

3.1.2 Reactor Emissions

Reactor emissions stem from the following causes: (a) displacement of air containing VOC during reactor charging, (b) solvent evaporation during the reaction cycle (often VOC's are emitted along with reaction by-product gases which act as carriers), (c) overhead condenser venting uncondensed VOC during refluxing, (d) purging vaporized VOC remaining from a solvent wash, and (e) opening reactors during a reaction cycle to take samples, determine reaction end-points, etc.

Emissions may be greater when a reactor is operated under pressure because the pressure must be relieved between cycles. This may be done by venting directly to the atmosphere or through a condenser. When the reactor is vented through an overhead condenser, care must be taken not to overload the condenser by relieving reactor pressure too rapidly.

As with all VOC sources in pharmaceutical plants, reactor emissions vary tremendously. One would expect the greatest emissions from uncontrolled vessels reacting chemicals at elevated temperatures in the presence of volatile solvents. On the other hand, few emissions will result from low temperature and pressure, or water based reactions. Emissions also depend on the number of batches or annual throughput for a reactor. Below are reactor emission estimates from four companies.

Table 3-1. REACTOR EMISSION ESTIMATES[1,2,3,4]

Company	Number of Reactors	Emissions (per reactor) Mg/yr Uncontrolled	Controlled	Emission Control
1	4	-	5.0-6.4	vent condensers
2	18	0.2-9.5	-	none
3	8	0.6-8.7	0.06-1.3	vent condensers
4	4	2.2*	0.043*	carbon adsorber
	1	0.001	-	none
	1	-	0.05	vent condenser
	1	-	0.13	vent condenser

*Total emissions for all four reactors

3.1.3 Control Technology

Equipment options available to control emissions from reactors are condensers, adsorbers, and liquid scrubbers. Condensers are often included on reactor systems as normal process control equipment.

Surface condensers are the most prevalent form of control for reactor emissions. Water is the usual cooling medium. Barometric condensers are seldom used since they contaminate and dilute condensed VOC. Refrigerated cooling systems also are widely used to control lower boiling VOC's. Sometimes two condensers in series are used to effect greater VOC removal. One plant[5] has installed a double condenser system to a batch reactor operation where an inert gas is sparged into the reaction vessel at $0.057m^3$ (2 cubic ft) per minute to prevent decomposition of the reaction product. Previously, this inert gas was vented to a water cooled condenser to remove VOC and discharged to the atmosphere at a temperature of 30-35°C. Toluene is one of the materials being removed. If assumed to be in equilibrium with the inert gas, toluene was being emitted at a rate of about 0.9 kg (2 lbs) per hour. A brine-cooled condenser was installed in series to further reduce the exit gas temperature to 2-3°C and toluene emissions to 0.09 kg (0.2 lbs) per hour. An additional emission reduction was achieved by putting a conservation vent on the brine condenser vent and by regulating nitrogen pad pressure (maintained at 3-5 in. H_2O).

As is seen from Table 3.1, carbon adsorbers can be used to treat reactor offgases; although in some cases, safety factors or Food and Drug Administration requirements may preclude their use. Normally, the emissions from a single reactor would not be large enough to warrant installing an adsorber; rather, the emissions from several reactors or several VOC sources within the plant would be ducted together and treated by a common control system. Manifolding sources to a common control device is most easily done on process equipment dedicated to the production of a single product.

Liquid scrubbers are used to treat a variety of pharmaceutical plant emission sources, including reactor emissions.[6,7] Most are low pressure drop scrubbers which handle several sources, although special purpose units such as venturi scrubbers may control a single vent. A high degree of control can be obtained for water soluble VOC with smaller reductions

for slightly soluble or insoluble compounds. In two plants visited, emissions from reactor opening and charging were ducted through hoses to scrubber systems.[8,9] This control was installed principally to protect the workers.

Vapor incinerators will be feasible control options in certain instances. They are sometimes used in the industry to control odors from fermentation operations. Incineration technology has also been applied to VOC emissions from reactors. In one plant, VOC emissions from reactors, storage tanks, evaporators, and distillation apparatus are collected in a single ventilation header and fed to an incinerator.[10]

Emissions which result from solvents used to clean and dry reactors may be reduced by good housekeeping practices such as sealing reactors during the cleaning operation and purging cleaned reactors to a control device.

3.2 DISTILLATION UNITS

3.2.1 Distillation Operations

Distillation may be performed by either of two principal methods. The first method is based on the production of a vapor by boiling the liquid mixture to be separated and condensing the vapors without allowing any liquid to return to the still. The second method is based on the return of part of the condensate to the still so that the returning liquid is brought into intimate contact with the vapors on the way to the condenser. Either of these methods may be conducted as a batch or continuous operation.

Distillation may be performed in batch reactors, in small stills attendant to reactors, or in larger distillation columns such as may be used for waste solvent recovery operations. Most distillation equipment is small compared to that used in refineries and petrochemical plants. The largest distillation columns in pharmaceutical plants process around 3200 kg/hr (7000 lbs/hr) of feed material.[11]

3.2.2 Distillation Emissions

Volatile organic compounds may be emitted from the distillation condensers used to recover evaporated solvents. The magnitude of emissions depends on the operating parameters of the condenser, the type and quantity of organic being condensed, and the quantity of inerts entrained in the organic. Table 3-2 lists reported emission estimates for several distillation operations; VOC losses range from less than one to more than 23 Mg/yr. Since emissions vary widely among different distillation units, no typical emission factors can be established.

3.2.3 Control Technology

Emissions from distillation condensers can be controlled through use of aftercondensers, scrubbers, and carbon adsorbers.

The main condenser efficiency can be increased by lowering the coolant temperature or can be augmented by installing another condenser in series. The second condenser would utilize a circulating fluid cooler than that for the main condenser. The improvement in control can be estimated using the information in Section 4.1 of this document.

In existing plants, there are examples of distillation condenser emissions being ducted to carbon adsorbers and liquid scrubbers.[18,19] No examples of the use of incinerators were found, although incineration may be feasible in some instances. Refer to Sections 4.2, 4.3, and 4.4 for more information on the performance of liquid scrubbers, carbon adsorbers, and incinerators, respectively.

3.3 SEPARATION OPERATIONS

Several separation mechanisms are employed by the industry including extraction, centrifugation, filtration, and crystallization. These are discussed in the same section because of similarities in emissions and applicable controls. Distillation and drying are discussed in separate sections.

Table 3-2. EMISSION ESTIMATES
FOR DISTILLATION OPERATIONS[12,13,14,15,16,17]

Unit Number	Distilled Material(s)	Throughput Mg/yr	Throughput tons/yr	Emissions Mg/yr	Emissions tons/yr	Control (other than main condenser
1	Acetone	392.6	432.9	5.9	6.5	
	Chloroform	37.6	41.5	1.1	1.2	
	Ethyl Acetate	223.8	246.8	6.7	7.4	
	Methanol	906	999.0	14.4	15.9	
	Xylene	450.3	496.5	3.4	3.7	
2	Isopropanol	212	234.0	16.0	17.6	
	Methylene Chloride	176	194.2	6.6	7.3	
	Ethylene Dichloride	68.8	75.8	1.0	1.1	
3	Benzene	368.4	406.2	7.3	8.1	
	Dimethylformamide	452.2	498.6	7.9	8.7	
	Heptane	274.9	303.1	4.1	4.5	
	Isopropyl Ether	70.0	77.2	1.7	1.9	
	MIBK	14.3	15.8	0.36	0.4	
	Toluene	7.4	8.2	0.09	0.1	
4	Methanol	2352	2593	23.6	26	
5	Isopropanol	4671	5150	3.4	3.8	
	Mineral Oil	1166	1286		-	
6	Toluene	15.0	16.6	0.80	0.88	aftercondenser (brine), after-condenser vented to liquid ring vacuum pump
7	Isopropanol	0.12	0.13	0.05	0.06	
	Methanol	0.12	0.13	0.05	0.06	
	Toluene	0.12	0.13	0.05	0.06	
	Ethanol	0.12	0.13	0.05	0.06	
	Methylamine	0.01	0.01	0.01	0.01	
8	Acetone	590 kg/hr	1300 lbs/hr	2.3 kg/hr	5 lbs/hr	aftercondensers
9	Acetone	90	99	0.80	0.88	aftercondensers
10	Benzene	4.4	4.8	0.44	0.48	aftercondensers
	Methylene Chloride	1.5	1.7	0.15	0.17	

3.3.1 Extraction

Extraction is used to separate components of liquid mixtures or solutions. This process utilizes differences in solubilities of the components rather than differences in volatilities (as in distillation), i.e., solvent is used that will preferentially combine with one of the components. The resulting mixture to be separated is made up of the extract which contains the preferentially dissolved material and the raffinate which is the residual phase.

The pharmaceutical industry generally utilizes two kinds of solvent extraction. In the first, the extraction takes place within the reactor itself. Solvent is introduced into the vessel and agitated until the material to be extracted is dissolved. The two phases are then allowed to separate and the lower, denser layer is drawn off and transferred to a second vessel.

The second type of extraction takes place in a vertical cylinder. A solvent is made to flow upward or downward through the liquid mixture. Either the solvent or the mixture is dispersed before entering the column; this increases contact and promotes the extraction process. Further extraction efficiency may be gained by using a packed column. The packing enhances contact between liquids. Extraction columns are normally run continuously for extended periods of time. Surge tanks or receivers may be used to collect extract and raffinate.

3.3.2 Extraction Emissions

Emissions from batch extraction stem mainly from displacement of vapor while pumping solvent into the extractor and while purging or cleaning the vessel after extraction. Some VOC also may be emitted while the liquids are being agitated. Column extractors may emit VOC while the column is being filled, during extraction, or when it is emptied after extraction. Emissions not only occur at the extractor itself, but also through associated surge tanks. These tanks may emit significant amounts of solvent due to working losses as the tank is repeatedly filled and emptied during the extraction process.

Emission estimates were available from only one plant.[20] One extraction column emitted 2.86 Mg/yr before control, and 0.29 Mg/yr after a condenser was installed. The other extractor had uncontrolled emissions of 10.8 Mg/yr and controlled emissions of 1.6 Mg/yr. Again, the control was provided by a condenser.

3.3.3 Centrifugation Description

Centrifuges are used to remove intermediate or product solids from a liquid stream. Center-slung, stainless steel, basket centrifuges are most commonly used in the industry. To begin the process, the centrifuge is started and the liquid slurry is pumped into it. An inert gas, such as nitrogen, is sometimes introduced into the centrifuge to avoid the buildup of an explosive atmosphere. The spinning centrifuge strains the liquid through small basket perforations. Solids retained in the basket are then scraped from the sides of the basket and unloaded by scooping them out from a hatch on the top of the centrifuge or by dropping them through the centrifuge bottom into receiving carts.

3.3.4 Centrifuge Emissions

A large potential source is open type centrifuges which permit large quantities of air to contact and evaporate solvents. The industry trend is toward completely enclosed centrifuges and, in fact, many plants have no open type centrifuges. If an inert gas blanket is used, it will be a transport vehicle for solvent vapor. This vapor may be vented directly from the centrifuge or from a process tank receiving the mother liquor. However, this emission source is likely to be small because the inert gas flow is only a few cfm.

The solids removed from the basket are still "wet" with solvent and will be a source of emissions while being unloaded and transported to the next process step. Bottom unloaders can minimize this problem if the solids are transferred to a receiving cart through a closed chute and the receiving cart is covered while

transporting solids. It could be difficult to replace an existing top unloading centrifuge with a bottom unloading type because many centrifuges are on the ground floor and there is little room for raising or lowering.

Few data were found on centrifuge emissions. Emissions from two enclosed centrifuges averaged less than a megagram per year (<1.1 tons/yr) at one plant.[21] Although emissions from an open-type centrifuge could be significantly greater, no estimates were available.

3.3.5 Filter Descriptions

Generally, filtration is used to remove solids from a liquid, whether these solids be product, process intermediates, catalysts, or carbon particles (e.g., from a decoloring step). Pressure filters, such as shell and leaf filters, cartridge filters, and plate and frame filters are usually used. Atmospheric and vacuum filters have their applications, too.

The normal filtration procedure is simply to force or draw the mother liquor through a filtering medium. Following filtration, the retained solids are removed from the filter medium for further processing.

3.3.6 Filter Emissions

Enclosed pressure filters normally do not emit VOC during a filtering operation. The filtered liquid is sent to a receiving tank. Emissions can occur, however, when a filter is opened to remove collected solids. Emissions can also occur if the filter is purged (possibly with nitrogen or steam) before cleaning. The purge gas will entrain evaporated solvent and probably be vented through the receiving tank. Emissions from filter steam purging at one plant were estimated about 5 Mg/yr before control. After a condenser was put in, controlled emissions were about 0.55 Mg/yr.[22]

Largest VOC emissions are from vacuum drum filters which are operated by pulling solvent through a precoated filter drum. Potential emissions are significant both at or near the surface of the drum and from the ensuing waste stream. These filters can be shrouded or enclosed for control purposes.

3.3.7 Crystallization Operations

Crystallization is a means of separating an intermediate or final product from a liquid solution. This is done by creating a supersaturated solution, one in which the desired compound will form crystals. If performed properly and in the absence of competing crystals, crystallization can produce a highly pure product.

Supersaturation may be achieved in one or more of three ways. If solubility of the solute increases strongly with temperature, a saturated solution becomes supersaturated by simple cooling. If solubility is relatively independent of temperature, supersaturation may be generated by evaporating a portion of the solvent. If neither cooling nor evaporation is desirable, supersaturation may be induced by adding a third component. The third component forms a mix with the original solvent in which the solute is considerably less soluble.

3.3.8 Crystallization Emissions

If crystallization is done mainly through cooling of a solution, there will be little VOC emission. In fact the equipment may be completely enclosed. However, when the crystallization is done by solvent evaporation, there is greater potential for emissions. Emissions will be significant if evaporated solvent is vented directly to the atmosphere. More likely the solvent will be passed through a condenser or from a vacuum jet (if the crystallization is done under vacuum).

Emission estimates were available from only one plant. These are presented in the table below. They are not intended to establish an emission factor for crystallization but only to give an idea of the range and variability of emissions to be expected.

Table 3-3. EMISSION ESTIMATES FOR CRYSTALLIZATION OPERATIONS AT ONE PLANT[23]

Number of Crystallizers	Solvent Emitted	Solvent Throughput	Emissions**	Control Equipment
4	MIBK*	32,578 Mg/yr	1.6 Mg/yr	none
2	MIBK	22,500 Mg/yr	0.68 Mg/yr	none
1	n-butanol	429 Mg/yr	0.018 Mg/yr	none
	acetone	90 Mg/yr	0.072 Mg/yr	
1	MIBK	215 Mg/yr	<0.01 Mg/yr	none
	acetone	18 Mg/yr	<0.01 Mg/yr	

*Methyl isobutyl ketone
**All emissions estimated by vapor pressure calculation.

3.3.9 Separation Operations Control Technology

The most direct method of control for separation operations is to contain VOC vapors and minimize their opportunity to escape. Some equipment designs are inherently lower emitters than others. For example, it will be much easier to control vapors in a closed-feed centrifuge than one that is manually loaded or open faced. Operators should be encouraged to use equipment in which VOC vapors can be contained and required to maintain good operating practices; this will help minimize the capital and operating cost of any control system selected to capture or destroy the VOC.

Several add-on control technologies may be used on the separation equipment described in this section. Condensers certainly would be applicable and may be the least costly option. They can be applied to individual systems. Water scrubbers also have found wide usage in the industry.[24,25] They are versatile and capable of handling a variety of VOC having an appreciable water solubility. Scrubbers can be either small or quite large; thus, they can be designed to handle emissions from a single source or from many sources (via a manifold system).

Carbon adsorbers can be and have been employed on vents from separation operations.[26,27] Several vents may be ducted to an adsorber because it is likely that emissions from a single source would not warrant the expense of a carbon adsorption unit. Recently, small carbon canisters have been used to handle a single, relatively small, emission source; however, this is usually done to alleviate an odor problem. Finally, in some instances, incinerators may be applicable. They will not always be a good choice because the expected variability from these emission sources might make continuous incinerator operation difficult.

3.4 DRYERS

3.4.1 Dryer Description and Operation

Dryers are used to remove most of the remaining solvent in a centrifuged or filtered product. This is done by evaporating solvent until an acceptable level of "dryness" is reached. Evaporation is accelerated by applying heat and/or vacuum to the solvent laden product or by blowing warm air around or through it. Because a product may degrade under severe drying conditions, the amount of heat, vacuum, or warm air flow is carefully controlled.

Several types of dryers are used in synthetic drug manufacture. Some of the most widely used are: tray dryers, rotary dryers, and fluid bed dryers.

A typical batch tray dryer consists of a rectangular chamber containing two carts which support racks. Each rack carries a number of shallow trays that are loaded with the product to be dried. Heated air is circulated within the chamber.

A rotary dryer or tumbler dryer consists of a revolving cylindrical or conical shell supported in a horizontal or slightly inclined position. Rotary dryers may be vacuum type or hot air circulation type. The rotation of the dryer tumbles the product to enhance solvent evaporation and may also perform a blending function.

Fluid bed dryers evaporate solvent by forcing heated air through the wet material. Typically, a large pan loaded with product is placed inside the dryer where air is blown through the bottom of the pan. The air agitates or fluidizes the product. Some product particles may be entrained in the gas stream. They are captured by a fabric filter and returned to the dryer.

3.4.2 Dryer Emissions

Dryers are potentially large emission sources. Emission rates vary during a drying cycle and are greatest at the beginning of the cycle and least at the end of the cycle. Drying cycle times can range from several hours to several days.

Table 3-4 shows reported emissions for drying operations at several manufacturing facilities. In most cases the estimates are based on theoretical calculations or equipment vendor efficiency claims.

As the data in the table indicate, emissions vary considerably. The variations arise from differences in: dryer sizes, number of drying cycles per year, and amount and type of solvent evaporated per cycle. Emissions from air dryers are normally greater than those from vacuum dryers, mainly because air dryer emissions are dilute and more difficult to control.

3.4.3 Control Technology

Table 3-4 contains some of the control devices currently used on dryers. Control options include condensation, wet scrubbing, adsorption, and incineration.

Condensers are often the first devices selected when dealing with air pollution from vacuum dryers. They can be used by themselves or in series with another device. The first two examples in Table 3-4 indicate use of a condenser followed by a carbon adsorber. In these specific instances, total removal efficiency is estimated at greater than 99 percent. Condensers are not typically used on air dryers because the emissions are dilute. For information on condenser performance see Section 4.1.

Table 3-4. EMISSION ESTIMATES FOR DRYING OPERATIONS[28,29,30,31,32,33]

# of Dryers	Solvents Emitted	Uncontrolled Emissions	Controlled Emissions	Control Equipment	Remarks
1	MIBK* Isopropanol	1295 Mg/yr	0.8 Mg/yr	condenser & carbon adsorber	operates continuously
2	MIBK Isopropanol	1295 Mg/yr (per dryer)	5.2 Mg/yr (per dryer)	condenser & carbon adsorber	operates continuously
1	Isopropanol	52.6 Mg/yr	52.6 Mg/yr	none	blender-dryer
1	Methanol	77 Mg/yr	negligible	wet scrubber	
1	Ethanol	2.7 Mg/yr	2.7 Mg/yr	none	
1	Ethanol	1.2 Mg/yr	1.2 Mg/yr	none	
1	Acetone	46 Mg/yr	0.93 Mg/yr	carbon adsorber	tray dryer
2	Ethyl acetate	3.2 kg/hr	negligible	vacuum pump	pump acts as a contact condenser
1	Acetone	3.2 kg/hr	negligible	vacuum pump	pump acts as a contact condenser
2	Methanol	6.5 kg/hr (per dryer)	6.5 kg/hr (per dryer)	none	air transport type dryers, maximum emission rate
3	Unknown	52.2 Mg/yr (total three dryers)	52.2 Mg/yr	none	tray dryer

*MIBK - methyl isobutyl ketone

Wet scrubbers have also been used to control many plant sources, including dryers. They can also remove particulates generated during drying. The scrubber cited in Table 3-4 removes both methanol and particulates. For water soluble compounds, VOC absorption efficiencies can be quite high (i.e. 98-99 percent). See Section 4.2 for a discussion of the performance of scrubbers.

Several examples of the use of carbon adsorption are in the table. As was noted above, an adsorber can be used following a condenser. Not only will overall efficiency increase but a longer regeneration cycle can be used in the adsorber. Carbon adsorbers are discussed more fully in Section 4.3.

Vapor incinerators may be viable controls although no installations were found during our investigations. Varying VOC flows to the incinerator may present operating problems.

3.5 STORAGE AND TRANSFER

3.5.1 Storage and Transfer Description

Volatile organic compounds are stored in tank farms, 55 gallon drums, and sometimes in process holding tanks. Storage tanks in tank farms range in size from about 20,000-110,000 liters (5,000-30,000 gallons). Most are horizontal tanks, although vertical tanks also are used. Process holding tanks are smaller and range in size from 2,000-20,000 liters (500-5,000 gallons).

In plant transfer of VOC is done mainly by pipeline, but also may be done manually (e.g., loading or unloading 55 gallon drums). Raw materials are delivered to the plant by tank truck, rail car, or in 55 gallon drums.

3.5.2 Storage and Transfer Emissions

The vapor space in a tank will in time become saturated with the stored organics. During tank filling, vapors are displaced causing an emission or a "working loss." Some vapors also are displaced as the temperature of the stored

VOC rises, such as from solar radiation, or as atmospheric pressure drops; these are "breathing losses." The amount of loss depends on several factors: type of VOC stored, size of tank, type of tank, diurnal temperature changes, and tank throughput. Working and breathing losses can be estimated from equations found in an EPA publication entitled "Compilation of Air Pollutant Emission Factors, Supplement No. 7" printed in April, 1977. Although technically the equations are for vertical tanks storing petroleum liquids, they will provide reasonable approximations for horizontal tanks and pure chemicals. The equations are reproduced below:

Fixed Roof Breathing Losses

$$L_B = 2.21 \times 10^{-4} M \left(\frac{P}{14.7\ P}\right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_p C K_c$$

where L_B = Fixed roof breathing loss (lb/day)

M = Molecular weight of vapor in storage tank (lb/lb mole)

P = True vapor pressure at bulk liquid conditions (psia)

D = Tank diameter (ft)

H = Average vapor space height, including roof volume correction (ft)

ΔT = Average ambient temperature change from day to night (^oF)

F_p = Paint factor (dimensionless)

C = Adjustment factor for small diameter tanks (dimensionless)

K_c = Crude oil factor (dimensionless)

Fixed Roof Working Losses

$$L_W = 2.40 \times 10^{-2} M P K_N K_c$$

where: L_W = Fixed roof working loss (lb/10^3 gal throughput)

M = Molecular weight of vapor in storage tank (lb/lb mole)

P = True vapor pressure at bulk liquid conditions (psia)

K_N = Turnover factor (dimensionless)

K_c = Crude oil factor (dimensionless)

To illustrate the magnitude of storage emissions from tanks typical of the industry, several calculated emission rates are presented in Table 3-5. Four sizes of tanks are represented (4,000 liters; 20,000 liters; 50,000 liters; and 100,000 liters). The three largest tanks were assumed to be filled once per month. The smallest tank, representing a process tank, was assumed to be filled 200 times per year. Three organic chemicals have also been selected to represent compounds of lower volatility (toluene), medium volatility (acetone), and high volatility (methylene chloride). The following values were used for equation variables:

M = 58 lb/lb-mole (acetone) = 92 lb/lb-mole (toluene) = 85 lb/lb-mole (methylene chloride)	
P = 2.9 psia (acetone) = 0.3 psia (toluene) = 5.4 psia (methylene chloride)	assuming an average ambient temperature of 60°F
D = 4.9 ft. (4,000 liter tank) = 8.5 ft. (20,000 liter tank) = 11.5 ft. (50,000 liter tank) = 14.4 ft. (100,000 liter tank)	assuming tank height equals ≈ 1.5 times diameter
H = 3.6 ft. (4,000 liter tank) = 6.3 ft. (20,000 liter tank) = 8.6 ft. (50,000 liter tank) = 10.8 ft. (100,000 liter tank)	assuming H equals 1/2 tank height
ΔT = 20°F	
F_p = 1.0	assumes tank painted white
K_c = 1.0	different from 1.0 only when storing crude oil
C = 0.25 (4,000 liter tank) = 0.45 (20,000 liter tank) = 0.60 (50,000 liter tank) = 0.70 (100,000 liter tank)	see Appendix C for values for other tank sizes
K_N = 0.32 for 4,000 liter tank (200 turnovers/year) = 1.0 all other tanks (12 turnovers/year)	see Appendix C for values for other tank turnover numbers

As can be seen from the table, yearly emission rates for individual storage or process tanks are not great. However, a manufacturing facility may have ten

Table 3-5. CALCULATED STORAGE TANK LOSSES*

Tank Size	Chemical Stored	Breathing Losses lbs/day	Breathing Losses Mg/yr	Working Losses lbs/10^3 gal	Working Losses Mg/yr	Total Losses Mg/yr
4,000 liters (1060 gal)	toluene	0.049	0.008	0.212	0.02	0.028
	acetone	0.166	0.03	1.29	0.12	0.15
	methylene chloride	0.436	0.07	3.53	0.34	0.41
20,000 liters (5,280 gal)	toluene	0.305	0.05	0.662	0.02	0.07
	acetone	1.03	0.17	4.04	0.12	0.29
	methylene chloride	2.71	0.45	11.0	0.32	0.77
50,000 liters (13,200 gal)	toluene	0.804	0.13	0.662	0.048	0.18
	acetone	2.71	0.45	4.04	0.29	0.74
	methylene chloride	7.14	1.2	11.0	0.79	2.0
100,000 liters (26,400 gal)	toluene	1.55	0.26	0.662	0.095	0.35
	acetone	5.25	0.87	4.04	0.58	1.4
	methylene chloride	13.8	2.3	11.0	1.6	3.9

*For horizontal and vertical tanks with no control.

or more large tanks and several smaller tanks. Therfore, aggregate storage emissions from such a facility would be significant.

Chemical transfer operations also contribute to plant VOC emissions. Common sources of transfer emissions and other "fugitive" emissions are:

a) manual transfer of chemicals from 55 gallon drums to receiving vessels;

b) pump seals, flanges, valve seals, agitator seals;

c) hose connections or couplings;

d) head gaskets and seals on filters;

e) pressure relief devices;

f) and opening reactors for charging or cleaning.

Some chemicals are stored in 55 gallon drums. Transfer of chemicals from drums to process vessels is occasionally done through permanent piping; however, more commonly it is done by opening the drum and manually pouring the contents. The manual pouring is a source of emissions, although a relatively small one on a "per drum" basis.

Pump seals, valves, flanges, and agitator seals may begin to leak VOC during the course of normal use. Some leaks may be the result of poor or infrequent maintenance. Pressure relief devices do not normally leak. Liquid losses can usually be detected by sight and vapor leaks can be detected reliably by hydrocarbon detectors.

There are no known studies of the magnitude of fugitive emissions within pharmaceutical plants, although studies have been completed for petroleum refineries and petrochemical plants. Although these industries use similar processing equipment, there are significant differences. Pharmaceutical plant process equipment is much smaller and, for the most part, is not subjected to the elevated temperatures and pressures often used in refineries and chemical plants. High temperatures and pressures contribute to higher leak rates. In addition, the batch process

nature of pharmaceuticals leads to intermittent use of equipment and corresponding intermittent leaks. Refinery and chemical plant processes are continuous. Finally, pharmaceutical plant process equipment is usually enclosed in buildings. Inside the buildings, leaks are repaired quickly to protect workers from toxic chemical exposure. For the above reasons, pharmaceutical plant fugitive emissions are thought to be lower than those for refineries and petrochemical plants.

3.5.3 Control Technology

Emissions from storage or process holding vessels may be reduced with varying efficiency through use of vapor balance systems, conservation vents, vent condensers, pressurized tanks, and carbon adsorption. Good housekeeping practices can also assist in reducing emissions. For example, operating procedures should require that covers and ports be closed when a tank contains solvents or is being cleaned and dried with solvents. Covers should be open for only short periods when solid materials are charged or samples taken out.

When storage tanks are being filled, displaced vapors can be ducted to the delivery tank truck or rail car. Such vapor return lines are in common use in the pharmaceutical industry.[34] Emissions from filling are essentially eliminated; however, to complete the cycle, vapor recovery should be practiced when the tank truck or rail car is refilled or cleaned at the terminal.

Conservation vents are devices that seal a tank vent against small pressure changes. During the day, a conservation vent prevents tank emissions due to vapor warming and expansion until the internal tank pressure exceeds the vent set pressure. Similarly, at night the vapor inside a tank cools causing a decrease in internal tank pressure. Outside air is prevented from entering the tank until the vacuum setting of the vent is exceeded. Conservation vents will provide small reductions in breathing losses. Increasing the pressure/vacuum

setting will increase the amount of breathing loss control; however, the settings cannot be increased indiscriminately or the internal pressure/vacuum developed may damage the tank. Conservation vents may begin to reseat improperly through mechanical malfunction, freezing rain, corrosion, etc., thereby reducing effectiveness. A regular inspection and maintenance program can ensure that they remain in good operating condition. Working losses are not affected by conservation vents.

Fixed roof tank emissions may be controlled by use of refrigerated vent condensers. Condensers should be sized to handle the maximum vapor rate expected at any given time, which normally occurs during tank filling. Condensers also may have to be designed to handle freezing of moisture. The moisture gets into the tank along with ambient air during breathing. This problem can be solved by defrosting the condenser and separating the recovered water-VOC mixture. Vent condenser removal efficiency depends on the vapor concentration of VOC in the vapor space and on the refrigeration temperature. See Section 4.1 for a discussion of condenser efficiencies.

Internal floating roofs have been retrofitted on storage tanks to achieve 80-97 percent control of VOC emissions.[35] The floating roof is an internal cover using a closure device to seal the gap between tank wall and the floating roof around the roof internal perimeter. To retrofit an existing tank, an opening has to be made through which components of the floating roof are introduced. Other tank modifications may be needed. For example, the tank shell may require corrections for deformation and obstruction or special modifications for bracing, reinforcing, and vertical plumbing. Because of these retrofit problems, installation can be relatively expensive. This expense is justified for large storage tanks because of the amount of VOC kept from evaporating.

Floating roofs are widely used in refineries and petrochemical plants; however, their applicability to pharmaceutical plant storage tanks is less certain. This control option is usually reasonable only for vertical tanks of at least 76,000 liter capacity (20,000 gallons). Final guidance on the feasibility of applying a floating roof to this size range tank is forthcoming from EPA.

Another alternative for reducing storage losses is utilizing pressurized storage tanks. Pressure tanks are designed to withstand the internal pressure built up through rising stored VOC temperatures during the daytime, thereby eliminating breathing losses. A practical pressure tank system would use an inert gas to occupy the vapor space during emptying; this gas, containing VOC, would have to be purged during refilling operations. Thus, working losses will not be eliminated. Because of their high cost, pressure tanks are feasible only for storage of highly volatile VOC.

Carbon adsorbers have been used to control many different process emission sources, including process tanks in pharmaceutical plants.[36] Control of similar emission sources also has been achieved through scrubbing.[37] In each of these systems, one control device can handle the manifolded emissions from many sources. Control efficiencies claimed are 98+ percent. These technologies are also feasible for controlling emissions from larger tanks in the tank farm. One problem is that the systems handle all input VOC and the recovered mixed solvents have little value; therefore, recovery would be difficult. Scrubber effluent and adsorber regeneration condensate will (or generally will) have to be sent to the sewer or the plant's wastewater treatment system.

Breathing losses can be substantially reduced through use of underground storage tanks. Underground tanks are insulated from daily temperature fluctuations and, therefore, do not undergo the vapor space expansion/contraction cycles characteristic of above ground tanks. This control option is suggested mainly for new tank installations since in most cases it will be impractical to convert existing tanks to underground tanks.

Plant fugitive emissions are best dealt with through an active inspection and maintenance program. Leaking components should be replaced or repaired as soon as is practical.

Emissions from reactor or other vessel opening are controlled in some plants by drawing vapors through flexible hoses to scrubbing systems.[38,39] This control was installed principally to protect workers from VOC exposure rather than to reduce plant emissions.

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4.0 PERFORMANCE OF CONTROL SYSTEMS

This chapter contains information on expected control efficiencies for four major control techniques: condensation, scrubbing, carbon adsorption, and incineration. The information can be used to estimate potential emission reductions for significant VOC sources within pharmaceutical plants.

4.1 CONDENSATION

Condensers are widely used in the pharmaceutical industry to recover evaporated solvent from process operations and as air pollution control devices to remove VOC contaminants from vented gases. Most operate by extracting enough heat from the VOC vapor to cause condensation. In the most common type, surface condensers, the coolant does not directly contact condensable vapors, rather heat is transferred across a surface (usually a tube wall) separating vapor and coolant. In this way the coolant is not contaminated with condensed VOC and may be directly reused.

The type of coolant used depends on the degree of cooling needed for a particular situation. Coolants in common use are water, chilled water, and brine. The circulating temperature of these three coolants varies from plant to plant but typically will be around 17°C for water (yearly average), 5°C for chilled water[1], and -5°C for brine.[2] Freon coolant may be used when lower cooling temperatures are required; freon can be circulated at -40°C.[3]

Since most pharmaceutical process equipment is used for manufacturing several different products during the year, it is possible that varying VOC loads will be

put on a condenser. To handle this situation most modern reactors or distillation units have condenser/receiver systems which are manifolded to permit using alternate coolants.[4]

4.1.1 Condenser Performance

Any component of any vapor mixture can be condensed if brought to equilibrium at a low enough temperature. The temperature necessary to achieve a given solvent vapor concentration is dependent on the vapor pressure of the compound.

When cooling a two-component vapor where one component can be considered noncondensable, for example, a solvent-air mixture, condensation will begin when the temperature is reached where the vapor pressure of the volatile component is equal to its partial pressure. The point where condensation first occurs is called the dew point. As the vapor is cooled further, condensation continues and the partial pressure stays equal to the vapor pressure. The less volatile a compound, that is, the higher the normal boiling point, the lower will be the amount that can remain vapor at a given temperature.

In cases where the solvent vapor concentration is high, for example, from the desorption cycle of a carbon adsorber, condensation is relatively easy. However, for sources where concentrations are typically below 25 percent of the lower explosive limit (LEL), condensation is economically infeasible.

If the relationship between VOC vapor pressure and temperature is known, the removal efficiency of a condenser can be estimated. The following method may be used to estimate removal efficiency. This method is applicable to gas streams containing a single condensable VOC component.

Emission Reduction Calculation Method

1. Make up a Cox chart for the VOC using vapor pressure and temperature data from a suitable reference book and specially designed graph paper.[5] An example

of a Cox chart made up for four solvents widely used in the pharmaceutical industry is shown in Figure 4-1.

2. Determine the amount of VOC (mole fraction) in the condenser inlet stream, if unknown. This can be done by chemical analysis or by dew point. To use the dew point method, direct a sample of the condenser inlet stream into a dew point device and cool the cup till condensation occurs. The intersection of the dew point temperature line and the vapor pressure line for the VOC will give the partial pressure of the VOC in the stream in mmHg. The VOC mole fraction can be determined by dividing the partial pressure of the VOC by the condenser operating pressure (usually 760 mmHg). The volume percent of VOC is equal to the mole fraction solvent times 100.

3. If a number of different inlet compositions and condenser exit temperatures are to be evaluated, it is convenient to plot a second graph showing temperature vs. the mole fraction of VOC in the vapor. This is simply done by plotting temperature versus the VOC vapor pressure divided by the system pressure (usually 760 mmHg) on semi-logarithmic paper. An example of this type of graph is shown in Figure 4-2 for the same four solvents shown on the Cox chart.

4. Determine the mole fraction of VOC in the condenser outlet stream. To do this select a temperature for the outlet gas stream and from the intersection of this temperature and the vapor pressure line for the VOC read the final partial pressure of the VOC. Calculate the mole fraction as before.

5. The percent VOC condensed can then be calculated:

$$PC = \frac{MFS_1 - \left(\frac{1-MFS_1}{1-MFS_2} \cdot MFS_2\right)}{MFS_1} \times 100$$

where PC = percent of VOC condensed;
MFS_1 = mole fraction VOC into condenser;
MFS_2 = mole fraction VOC out of condenser.

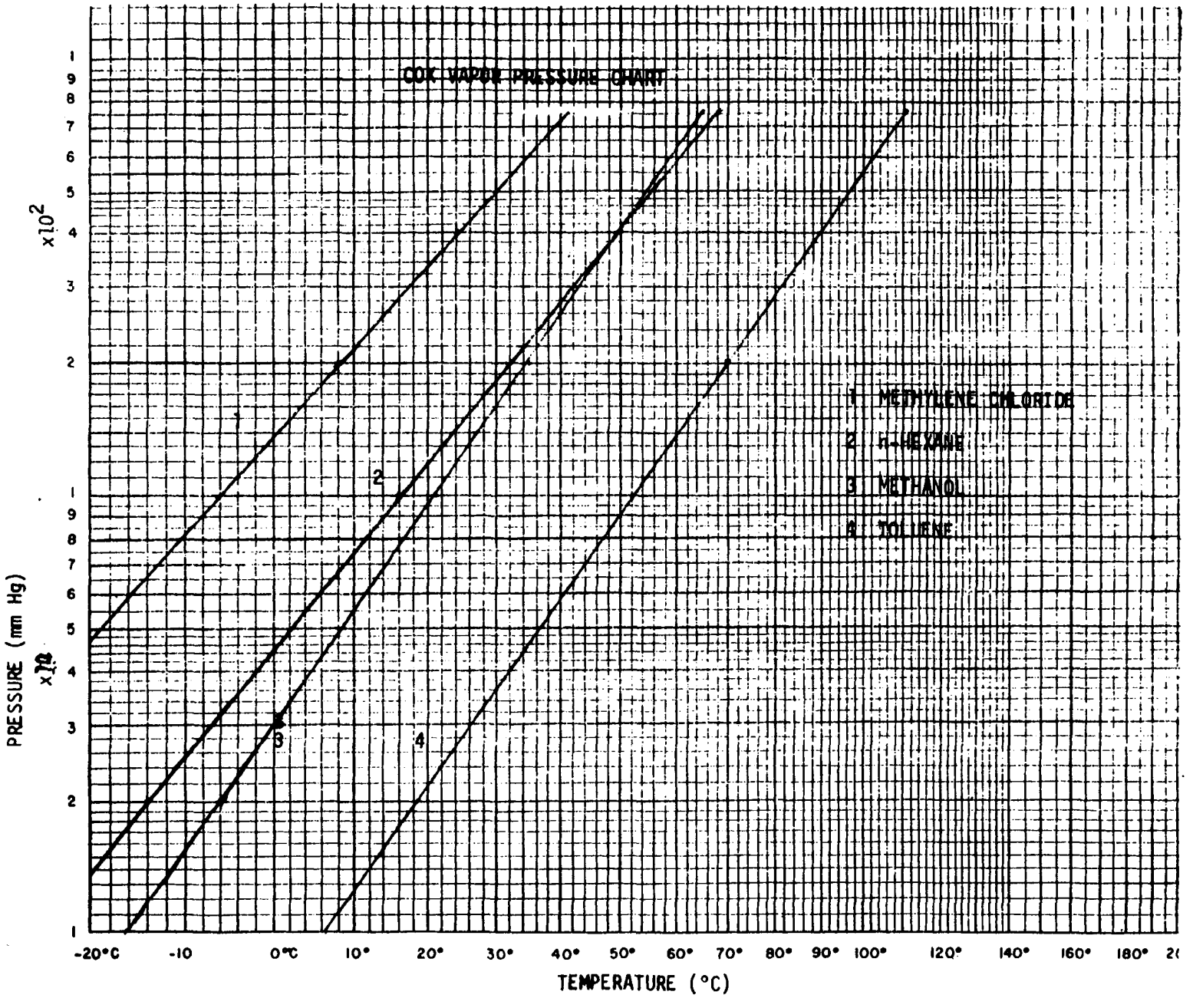
COX VAPOR PRESSURE CHART
1 METHYLENE CHLORIDE
2 n-HEXANE
3 METHANOL
4 TOLUENE
PRESSURE (mm Hg)
x10^2
x10
TEMPERATURE (°C)
-20°C
-10
0°C
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
120°
140°
160°
180°

Figure 4-1.

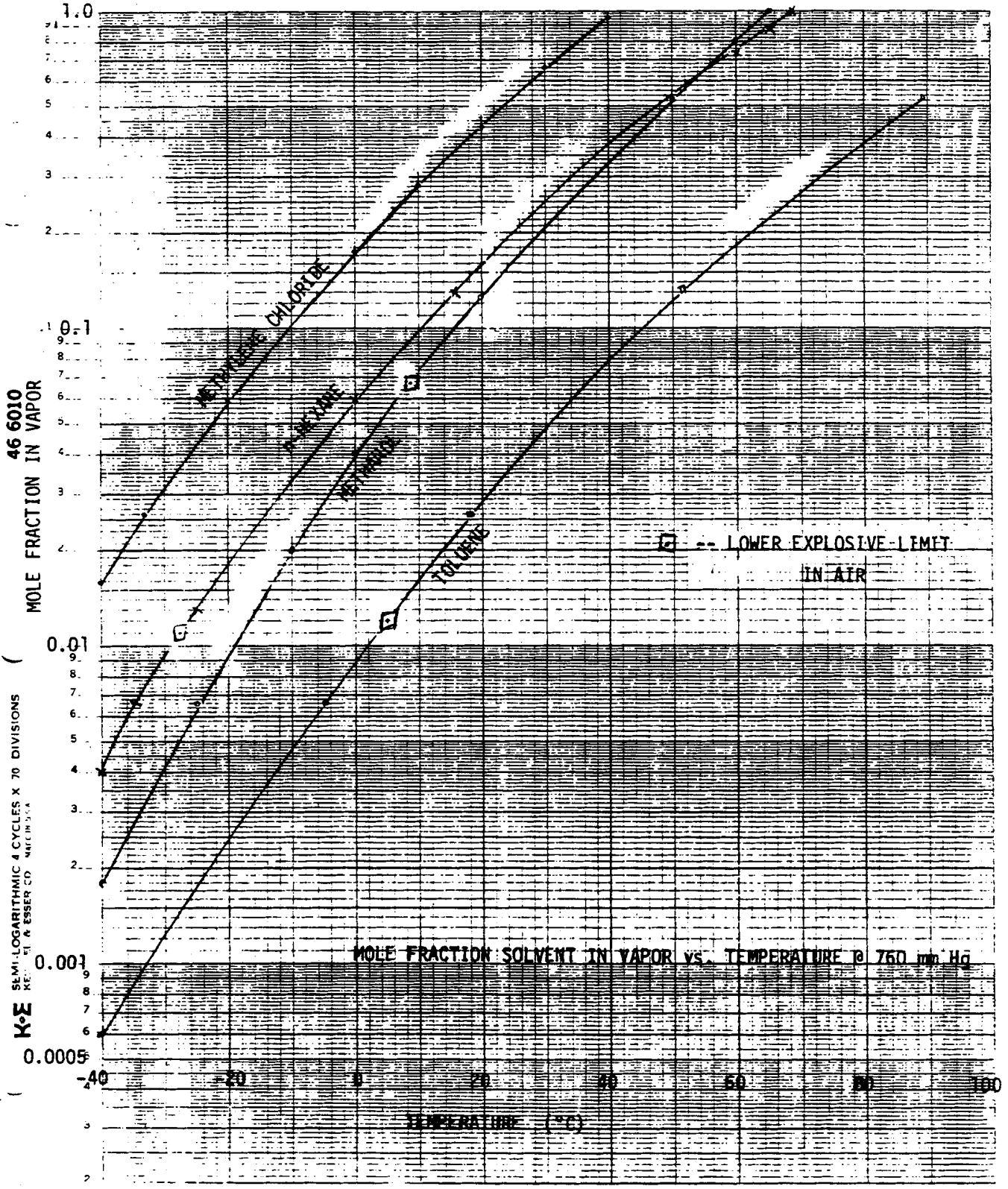
MOLE FRACTION IN VAPOR
1.0
0.1
0.01
0.001
0.0005
METHYLENE CHLORIDE
P-XYLENE
METHANOL
TOLUENE
-- LOWER EXPLOSIVE LIMIT IN AIR
MOLE FRACTION SOLVENT IN VAPOR vs. TEMPERATURE @ 760 mm Hg
-40
-20
0
20
40
60
80
100
TEMPERATURE (°C)
K+E SEMI-LOGARITHMIC 4 CYCLES X 70 DIVISIONS
46 6010

Figure 4-2.

It is sometimes simpler to calculate the vapor pressure of a VOC at one temperature, rather than plotting a Cox chart. This can be done by the use of Antoine's equation:

$$\text{Log}_{10} Pi = a - \left(\frac{b}{c + Ti}\right)$$

where Pi = vapor pressure of the VOC;
Ti = temperature of the system, ^{o}C;
a,b,c = Antoine equation constant from Lange's Handbook of Chemistry.[6]

The calculation methods for gases containing more than one condensable component are complex, particularly if there are significant departures from ideal behavior of the gases and liquids. As a simplification, the temperature necessary for control by condensation can be roughly approximated by the weighted average of the temperatures necessary for condensation of each VOC considered separately but at concentrations equal to the total organic concentration.

4.1.2 Applicability

Condensers work best on gas streams that are or nearly are saturated with the condensable VOC. Many streams in synthesized pharmaceutical manufacturing facilities fit this description. Condensers are less attractive control options when the gas stream is dilute or far from saturation. In this case considerable cooling would be required just to bring the stream to the saturation point, and additional cooling would be required to actually condense the VOC. In these situations, other control techniques may be better choices.

Sometimes condenser performance may be limited by characteristics of condensable components. For example, the lower temperature limit for condenser operation will be the point where one of the condensables first freezes. Operating below that point would result in freezing water or VOC (as the case may be) to condenser tubes or walls rendering them ineffective as heat transfer surfaces.

4.2 SCRUBBERS OR ABSORBERS

Absorption is a gas-liquid contacting process for gas separation which utilizes the preferential solubility of the pollutant gas or gases in the liquid. It is one of the major chemical engineering unit operations and is treated extensively in the chemical engineering literature. Absorption is important in the pharmaceutical industry because many VOC's and other chemicals being used are soluble in water or aqueous solutions. Therefore, water, caustic, or acidic scrubbers can be applied to a variety of air pollution problems. In recognition of this fact, many examples of scrubbing are found in the industry today.

The main types of scrubbers are the venturi, packed tower, plate or tray tower, and spray tower. Each is designed for the same purpose - to provide intimate contact between the scrubbing liquid and the gaseous pollutant so that mass transfer between phases is promoted. Each type has advantages and disadvantages and may be best suited to a particular emission problem.

4.2.1 Control Performance

Theoretically, the lowest possible concentration of VOC pollutant(s) in a scrubber exhaust is equal to the equilibrium partial pressure of the pollutant(s) above the scrubbing medium at scrubber exit conditions. Absorption systems do not operate exactly at equilibrium conditons but do approach this state. For a given unit, overall scrubber efficiencies are influenced by a number of factors, including intimacy of contact developed between gas and liquid, operating temperature of the unit, concentration of pollutant in gas stream, concentration of pollutant in the liquid scrubbing medium, and flow rates of gas and liquid.

At one manufacturing facility two sets of scrubbers were employed. The first set (two scrubbers) handled acid and VOC emissions from various process sources in two main production lines. The scrubbing medium is a circulating 20 percent caustic solution and design efficiency is 99 percent. The other two scrubbers remove acids and organics ducted to them from storage vessels, hoods, centrifuges, filters, etc. Again design efficiency is 99 percent.[7]

In a second plant, emissions from dimethylamine storage tanks are scrubbed with a 10 percent sulfuric acid solution. Estimated removal efficiency is in excess of 99 percent.[8] A third plant uses wet scrubbers to control emissions from a reactor and a dryer. The reactor offgas contains 15-20 volume percent of organics at 113 scfm. The company estimates negligible amounts of organic are emitted from the scrubber exit. The dryer exhaust contains 0.37-0.72 volume percent of organic and again scrubbing results in negligible emissions.[9]

As a final example, a manufacturer directs benzene and isopropyl alcohol emissions from a distillation column to a water scrubber. Essentially 100 percent of the alcohol is scrubbed out but only about 85 percent of the benzene.[10] The variance can be attributed to differences in water solubility; isopropyl alcohol is infinitely soluble in water while benzene is only slightly soluble.

The above examples indicate very high removal efficiencies can be attained through use of scrubbing. In some situations, system characteristics may be such that somewhat lower performance is realized. Nonetheless, efficiencies in excess of 90 percent should be expected.

4.2.2 Applicability

Scrubbers are widely used emission control devices at pharmaceutical plants. They can be successfully applied to VOC emissions soluble in water or whatever scrubbing medium is used. Compounds of medium to low solubility can also be treated, but scrubber sizes and liquid flow rates would have to be correspondingly

larger to attain removal efficiencies comparable to those attained when scrubbing soluble compounds.

Examples of emission control by scrubbing have been found for all sources within plants synthesizing pharmaceuticals; these include emissions from reactors, distillation equipment, process tanks, centrifuges, filters, crystallizers, storage tanks, dryers, and fugitive sources. Most often the emissions from more than one source are ducted together and treated in a common control system.

4.3 CARBON ADSORPTION

Adsorption is the phenomenon in which molecules of a fluid contact and adhere to the surface of a solid. Adsorption is important in controlling VOC emissions because many organics are easily adsorbed onto activated carbon. Because the adsorbed compounds have practically no vapor pressure at ambient temperatures, a carbon adsorption system is particularly suited to recovering VOC in small concentrations.[11]

In operation, a carbon adsorption system initially removes a VOC contaminant; however, a stage is reached in which the carbon continues to adsorb but at a decreasing rate. At this stage, VOC will begin to appear in the system exhaust; this is breakthrough. At or before breakthrough, the carbon is regenerated through desorption of collected VOC and another adsorption cycle is then begun.

4.3.1 Control Performance

The amount of material adsorbed on a carbon bed depends on the type of activated carbon used, the characteristics of the VOC, the VOC concentration and the system temperature, pressure, and humidity. Overall VOC removal efficiencies depend on the adsorption cycle time (i.e., how soon after breakthrough the carbon is regenerated), the completeness of regeneration, carbon bed depth, contact time, and the effectiveness of recovery of desorbed organics.

One pharmaceutical manufacturer uses two carbon adsorbers to control VOC emissions. One adsorber handles emissions from various reactor and condenser vents and the other unit cleans vented gases from centrifuges and dryers.[12] Both of the units are designed to remove 98 percent of the VOC emissions. Another manufacturer employs carbon adsorption to control emissions from rotary vacuum filters. The organics removed are methyl isobutyl ketone and isopropanol; reported removal is in excess of 99 percent.[13] At the same plant, emissions from several dryers are sent to a condenser followed by an adsorber. Overall control again is over 99 percent.[14]

Two adsorbers are also in use at another pharmaceutical plant. The first adsorber works in series with a scrubber and a condenser. The system is designed to remove ammonia, methanol, and methylene chloride vapors from amination reactions. Overall system efficiency is designed at 99.9 percent.[15] The second adsorber is a small unit controlling methyl bromide emissions from several sources in a minor production operation. Control efficiency is designed at 99.9 percent.[16]

These examples serve to illustrate that carbon adsorbers can be very effective VOC control devices. Units can be designed and operated at removal efficiencies well above 90 percent.

As with all adsorption equipment, careful attention has to be paid to regeneration timing. Instrumentation is needed to assure that breakthrough is detected. A common arrangement is two or more carbon beds in parallel. During regeneration VOC's are desorbed with steam, warm air or inert gas, or sometimes vacuum. Stripped vapors are usually condensed or absorbed and residual gases vented through one of the working carbon beds. Possible points of VOC re-emission are condensate receivers, water (condensed steam) drains, and wastewater treatment basins.

4.3.2 Applicability

While there will be exceptions, applicability of carbon control systems can be summarized as follows:[17] (a) controls organics with boiling points up to 250°C and 1 ppm to 40 volume percent, (b) handles air flow rates of 10 cfm to 200,000 cfm, and (c) adsorbs at temperatures up to 140°C. It is stressed that these limits of applicability represent extremes and operation near the the extremes may not be practical in some cases. For example, the Pharmaceutical Manufacturers Association estimates that VOC concentrations above 5 volume percent preclude normal use of carbon adsorption because of safety considerations. At high VOC concentrations, the carbon bed temperature may rise to the ignition point of the vapor stream unless an adequate cooling system is employed. Also, a few compounds present special hazards which make adsorption difficult or infeasible.

4.4 INCINERATION

Vapor incinerators, or afterburners, combust VOC in waste gases to carbon dioxide and water. The two types of vapor incinerators in use are (1) direct-fired, or thermal, and (2) catalytic.

Thermal incinerators depend upon flame contact and relatively high temperatures to burn the combustible materials. Since most waste streams contain dilute VOC concentrations, supplemental fuel is required to maintain the necessary combustion temperatures. In general, factors which influence the efficiency of combustion are: (1) temperature, (2) degree of mixing, (3) residence time in the combustion chamber, and (4) type of VOC combusted.

Catalytic incinerators operate by preheating a contaminated gas stream to a predetermined temperature (usually lower than in thermal incineration) and then promoting further oxidation by bringing contaminants into contact with a catalyst. The efficiency of catalytic incineration is a function of many variables. These include surface area of the catalyst, catalyst type,

uniformity of gas flow through the catalyst bed, type of VOC oxidized, oxygen concentration, volume of gases per unit of catalyst, and operating temperature of the unit. Efficiency decreases as the unit is used, and periodic catalyst replacement is required. Some compounds, such as chlorides and silicones, also may "poison" the catalyst and render it ineffective. At lower VOC concentrations, the catalytic incinerator efficiency decreases markedly even at relatively high discharge temperatures, such as 580°C (1100°F).[18]

4.4.1 Control Performance

The South Coast Air Quality Management District (formerly Los Angeles County Air Pollution Control District) provided to EPA data from their compliance testing program covering a period of several years. These data are shown in Figure 4.3 as a plot of incinerator efficiency versus inlet organic concentration. Most of the data are from incinerators on paint baking operations, although many other industries are represented. Only those units operating at or above 90 percent VOC destruction (on a mass basis) have been used in the graph. The cross hatched band is meant to show the upward trend in efficiency as concentration is increased. A general conclusion drawn from the plot is that control efficiencies greater than 90 percent can be and have been achieved on gas streams containing VOC concentrations of 200-20,000 ppm.[19]

The data were also plotted for incinerator efficiency as a function of operating temperature. In this instance, the data points were scattered and no trend was obvious. However, nearly all operating temperatures were between 690°C (1300°F) and 830°C (1550°F). At 690°C the average mass efficiency was 96 percent and at 775°C (1450°F) it was 98 percent.[20]

Case studies identified by four thermal incinerator manufacturers indicate that efficiencies of less than 95 percent were achieved, except in one case, at temperatures of 730°C or lower. Conversely, efficiencies of 99 plus percent were achieved at temperatures of 760°C or greater.[21]

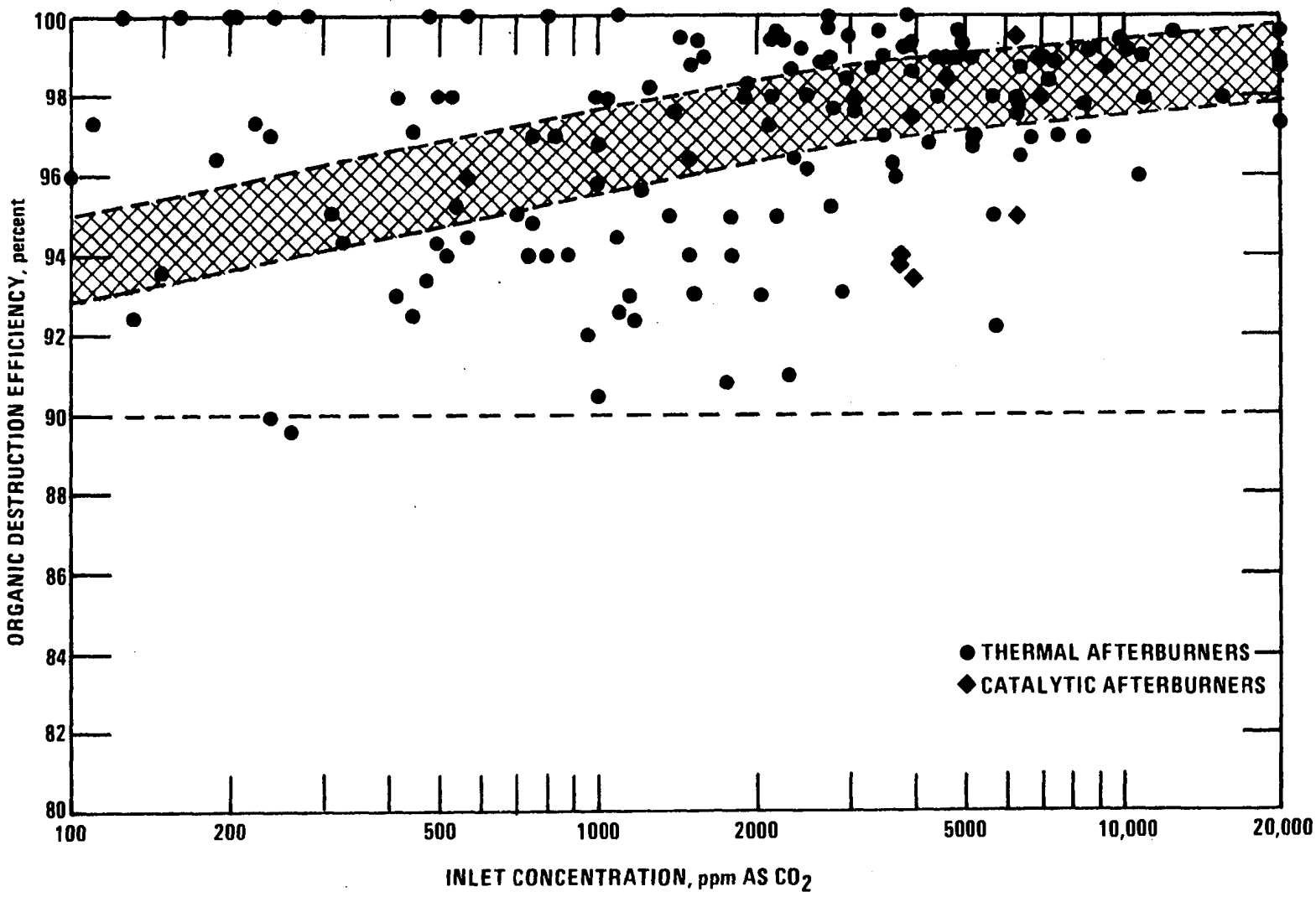

Figure 1. Afterburner efficiency as a function of inlet concentration. From compliance test data of southern California AQMD.

Figure 4-3.

Although destruction efficiencies in thermal incinerators are influenced by a number of variables, a review of literature and actual case studies mentioned above allow the following generalizations to be made:

(1) 90 + percent VOC destruction can be achieved at an operating temperature of 745°C (1400°F) and residence time of 0.5 seconds,

(2) 98 percent efficiency can be achieved at 800°C (1500°F) and 0.5 seconds, and

(3) 99 percent can be achieved at 860°C (1600°F) and 0.5 seconds residence time.[22]

Concerning performance of catalytic incinerators, the fractional reduction in pollutant concentration depends strongly on the amount of catalyst in a unit. This dependence is such that conversions up to 90-95 percent can be attained with reasonable catalyst volumes (i.e. 0.5-2.0 m^3 catalyst per 1000 m^3 of waste gases). However, the catalyst volume required for very high conversion (e.g. > 98 percent) generally makes catalytic incineration uneconomical.[23]

4.4.2 Applicability

Incinerators are not currently widely used to control vapor phase organic emissions from synthesized drug production facilities. Part of the lack of use may be due to the variability of waste gases that would be ducted to an incinerator and the batch nature of the processes. Fluctuating flows and pollutant concentrations may hamper safe and efficient operation. Therefore, incinerators would most likely find application where relatively stable waste gas flows can be established. Stability may be enhanced by ducting emissions from several sources to a common control device.

Another potential disadvantage with incinerators is that heat recovery is likely to be uneconomical because at pharmaceutical plants incinerators will be relatively small and the potential energy recovery correspondingly small, especially when viewed in light of the costs for installing heat recovery

equipment. In addition, the incinerator would generally run less than 24 hours a day. In this case, heat recovery would be intermittent, thus decreasing its utility.

A final consideration is that some compounds such as chlorinated organics, amines, and sulfinated organics can cause corrosion in incinerators. Because of this, these compounds are neither easily nor inexpensively incinerated.

To summarize, application of incineration is likely to be limited to those situations which a number of different vents can be controlled or plant operation is more or less continuous.

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Section 5

COST ANALYSIS

5.1 INTRODUCTION

5.1.1 Purpose

This chapter presents capital and annualized cost estimates for equipment to control VOC emissions from plants manufacturing synthesized pharmaceutical products. Because the amount and type of emissions vary widely from plant to plant, each control application will be unique. Therefore, in some situations, control system construction materials, operating conditions, installation expenses, etc. will be different from those assumed in calculating costs for this chapter. In instances where regulatory decisions hinge on the cost of control, it would be proper to consider additional information that may more accurately reflect control costs for the plant in question.

5.1.2. Scope

The preceding section described systems for controlling emissions from the following sources in this industry: storage and transfer operations, reactors, crystallizers, centrifuges, filters, dryers, and distillation condensers. Table 5-1 lists the 14 techniques for controlling these sources that are analyzed in terms of capital and operating costs in this section. The table presents the emission sources and appropriate control techniques and their expected VOC control efficiencies.

The control costs are developed for typical pharmaceutical operations within typical size ranges. In practice, however, it may be possible for one device to control more than one emission source.

Annualized emissions and their reductions cannot presently be quantified because of the variety of pharmaceutical manufacturing operations, the many kinds and concentrations of organic compounds, and the frequent use of batch

TABLE 5-1. VOC EMISSION CONTROL OPTIONS IN THE PHARMACEUTICAL INDUSTRY, PERCENTAGE OF EFFICIENCY

Control technique	Emission source				
	Storage and transfer	Reactors	Separation operations[a]	Dryers	Distillers
Conservation vent	5 - 20	N.A.	N.A.	N.A.	N.A.
Pressure tank vessel	50-95	N.A.	N.A.	N.A.	N.A.
Floating roof	90	N.A.	N.A.	N.A.	N.A.
Carbon adsorption	95	95	95	95	95
Thermal incinerator	90 - 99	90 - 99	90 - 99	90 - 99	90 - 99
Thermal incinerator with heat recovery	90 - 99	90 - 99	90 - 99	90 - 99	90 - 99
Catalytic incinerator	90 - 95	90 - 95	90 - 95	90 - 95	90 - 95
Catalytic incinerator with heat recovery	90 - 95	90 - 95	90 - 95	90 - 95	90 - 95
Water-cooled condenser	30 - 70	70 - 90	70 - 90	70 - 90	70 - 90
Chilled-water-cooled condenser	50 - 90	70 - 99	70 - 99	70 - 99	70 - 99
Chilled-brine-cooled condenser	70 - 99	90 - 99	90 - 99	90 - 99	90 - 99
Freon-cooled condenser	70 - 99	95 - 99	95 - 99	95 - 99	95 - 99
Packed-bed scrubber	90 - 99	90 - 99	90 - 99	90 - 99	90 - 99
Venturi scrubber	90 - 99	90 - 99	90 - 99	90 - 99	90 - 99

[a] Includes crystallizers, filters, and centrifuges.
N.A. - Not applicable.

processing. As a consequence, cost-effectiveness ratios have not been developed. These limitations do not preclude the costing of control options based upon their size and operating capabilities. The estimates are given for retrofit installations, and all cost figures reflect mid-1978 dollars.

5.1.3 Bases for Capital Cost Estimates

Capital costs represent the initial investment required for retrofitting a control system: equipment; materials and labor for installation, including foundations, structural steel, instruments, piping, ducting, insulation, and painting; and associated costs. Indirect expenses, such as contingencies, contractor's fees, and tax allowances, are also included. The bases for capital cost estimates are presented in Table 5-2. Additionally, capital cost factors are presented in Table 5-4. Actual cost information has been derived from sources in the literature;[1-11] and from equipment vendors.[12-21]

5.1.4 Bases for Annualized Costs

Annualized costs represent the cost of operating and maintaining the emission control system, including materials, utilities, and normal maintenance; as well as costs associated with capital recovery over the depreciable life of the system. Table 5-3 presents the cost factors and methods that have been used to estimate annualized costs for each control system. In general, credits for VOC recovery have not been included for each control because they cannot be defined on an annualized basis. The amounts of these credits depend upon the value of the specific organic compound in use. However, in some instances it was necessary in developing the annualized costs to quantify and qualify the emissions.

TABLE 5-2. BASES FOR CAPITAL COST ESTIMATES

- All costs are expressed in mid-1978 dollars.
- All costs include:

  Basic control equipment

  Auxiliaries, such as hoods and ducts

  Installation and other labor

  Contingencies

  Contractor's fee

  General tax allowance

  Other indirect costs.
- Carbon adsorption systems have two carbon beds to allow for continuous operation. One bed operates while the other is regenerated. The initial carbon bedding is included as a capital cost.
- Initial catalyst is included in the capital cost of catalytic incineration equipment.
- The materials of construction for equipment, ducts, piping, etc. are carbon steels, except for the packed bed and venturi scrubbers which are fiberglass reinforced plastic and cast iron, respectively.

TABLE 5-3. BASES FOR ANNUALIZED COST ESTIMATES

Description	Unit cost	Basis for costs and other comments
Annualized costs		One-year period commencing mid-1978
Installation type		Retrofit
Yearly operating times		8 h/day, 5 days/wk, 50 wk/yr 16 h/day, 7 days/wk, 48 wk/yr 24 h/day, 7 days/wk, 48 wk/yr
Utilities:		
No. 2 fuel oil[a]	\$0.105/liter (\$0.396/gal)	Based on transport lots of 27,250 liters (7200 gal) delivered from Midwest terminal
Electricity	\$0.0266/kWh	EPA-230/3-77-015b report cost for iron and steel industry
Water	\$8.50/1000 m^3 (\$0.24/1000 ft^3	For municipal water plus an equal amount for standard sewage. Where applicable, a BOD_5 surcharge of \$0.02/kg (\$0.045/lb)
Steam	\$8.99/Mg (\$4.07/10^3 lb)	Based on 80% efficiency; includes 16% for facilities, maintenance, depreciation, etc.
Operating labor	\$8.66/h	Includes 20% for fringes
Maintenance:		
Labor	\$9.53/h	At 10% premium over operating labor
Material	\$9.53/h	Average (over life of equipment) material costs equal to labor costs
Misc. maint., parts, and material	10% of capital cost for carbon bed; 10% of capital cost for catalyst; 35% of capital cost for floating-cover seal	Based on 5-year life
Capital recovery factor	16.275% of capital cost	10% interest rate and 10 years equipment life
Taxes and insurance	2% of capital cost	
Administration and permits	2% of capital cost	
Adjustment credit[b]	\$0.105/liter (\$0.396/gal)	Reclaimed solvent for use of diesel or fuel oil; value of VOC saved due to preventive measures on the basis of ethanol \$0.29/liter (\$1.12/gal)

[a] Assumed to be the only fuel used by all systems.

[b] Where applicable.

5.2 VOC EMISSION CONTROL IN PHARMACEUTICAL OPERATIONS

5.2.1 Plant Parameters

The control efficiencies of the add-on systems analyzed range from 5 to 99 percent, and each control device may show different efficiencies with different applications. This variation is minor for carbon adsorption and incineration, but is significant for control by pressure, cooling/condensing, and scrubbing. The ability of carbon to adsorb various VOC is generally between 6 to 8 kg (13 to 18 lb) of VOC per 100 kg (221 lb) of carbon; as a result, carbon adsorption systems have a fairly uniform control efficiency of 95 percent. On the other hand, a brine-cooled cooler/condenser having brine at -10°C (14°F) can control 99 percent of an ethanol VOC, but less than 25 percent of a methyl chloride VOC.

5.2.2 Capital Costs for VOC Emission Controls

Capital costs of various sizes of the 14 types of control systems are presented graphically. These figures, which appear after the text, are referenced by number in the discussion that follows.

Capital costs of conservation vents with flame arresters are depicted in Figure 5-1. The analysis is based upon 6.9 kPa (1.0 psi) pressure, 3.45 kPa (0.5 psi) vacuum, typical tank dimensions, and a pumping rate of 6.3 liter/s (100 gal/min). The vent, with the flame arrester, is the equipment item.

The costs of floating roofs for storage tanks, as shown in Figure 5-3, are based upon the tank diameter. The floating roof with its seals is the equipment item.

The costs of pressure vessels vary with the diameter and height of the tank, as well as the wall thickness. Figure 5-5 presents the cost of pressure vessels, based on tank size. For this analysis, it was assumed that average

tank height equals two diameters, and that the shell and heads are 1.27 cm (0.5 inch) thick. The vessel is the equipment item.

Carbon adsorption systems are sized according to volumetric gas flow rate. Significant dilution is sometimes necessary for adequate recovery of specific solvents.[11] To allow for these large dilution requirements and for the widely varying VOC concentrations considered in this study, costs of carbon adsorption systems are presented for a large range of sizes. Figure 5-7 presents costs of carbon adsorption units having the capacity to treat VOC rates from 40 to 1500 kg/h (88 to 3300 lb/h).

All of the systems are standard packages and are fully automatic, with twin carbon beds. They will cycle through adsorption and desorption, and will reclaim solvent from the desorbing steam by condensation followed by water separation. The regenerative mode (desorption) takes less time than the adsorption mode, to provide for continuous operation.

Incinerators are sized according to the volume of emissions controlled in units of Nm^3/h (scfm). Both thermal (Figure 5-9) and catalytic incinerators (Figure 5-11) are analyzed on the basis of No. 2 oil being the only fuel. Thermal incinerators are designed for 816°C (1500°F) operation. Catalytic incinerators are designed for gas streams at 316°C (600°F) into the catalyst and 704°C (1300°F) out of the catalyst. Thermal incinerators are sized for 65 percent primary heat recovery and catalytic incinerators for 38 percent primary heat recovery, to minimize the fuel requirements for emissions at 25 percent of lower explosive limit (LEL).[22] The equipment is a package unit complete with burner, controls, stack, and (where applicable) modular gas heat exchangers.

Cooling/condensing systems are sized for tons of cooling. Ethanol was assumed as the VOC for purposes of heat exchanger sizing. Costs

of water-cooled condensers are depicted in Figure 5-13. Their sizes range from 1 to 30 tons of cooling at the condenser. A cooling tower, not included in the capital cost, provides the water coolant. The condenser, which is of carbon steel construction, is the only equipment item.

Systems that include air-cooled refrigeration units are represented in Figures 5-15, 5-17, and 5-19. The three variations are chilled-water-cooled condensers, chilled-brine condensers, and Freon-cooled condensers. As with water-cooled condensers, the sizing basis for costing is 1 to 30 tons; but in these cases, the tonnage of cooling is the nominal rating of the refrigerant system (10°C (50°F) chilled water leaving the VOC condenser and 27°C (80°F) air entering the refrigerant condenser). For the chilled-water-cooled condenser, the coolant temperature is limited to 4.4°C (40°F) to prevent freezing. The equipment items are a package refrigeration system (using a Freon refrigerant), a VOC cooler/condenser, and an emissions precooler. The cost of the VOC heat exchangers is small compared to the cost of refrigeration machinery.

Scrubber system capital costs are presented in Figures 5-21 and 5-23. Packed-bed scrubbers are sized from the emission rate and the degree of control. Ethanol VOC and 95 percent control were assumed. The liquid-to-gas ratio of 45 liters/28 Nm^3 (12 gal/1000 ft^3) required a 3.7 m (12 ft) bed depth. The scrubbing liquor containing ethanol is recirculated. The system includes a fiberglass scrubber, polypropylene packing, demister, fiberglass ducting, blower, and recirculating pump. No water treating equipment is included.

Venturi scrubbers were sized on the same basis as packed-bed scrubbers. Two scrubbers in series are required to achieve 95 percent control. The liquid-to-gas ratio for each stage is 284 liters/28 Nm^3 (75 gal/1000 ft^3).

The equipment includes two jet venturi scrubbers with separators and recirculating pumps.

5.2.3 Annualized Costs of VOC Emission Controls

Annualized costs of the 14 control systems are presented graphically. The costs are correlated with operating time and control system size. Credits for VOC recovery have not been included in the annualized costs (except for carbon adsorption systems), because they are not presently definable. However, the credits are significant for those controls--pressure systems, carbon adsorption, cooling/condensing systems--that recover VOC of a quality comparable to the organic liquid. Neither the scrubbing nor the incinerating systems recover VOC for reuse, because they destroy it by oxidation (combustion in incinerators, or water treatment of scrubber effluent for removal of organics). Figure 5-25 provides a guide for estimating VOC recovery credits where they apply.

The annualized cost of conservations vents, as depicted in Figure 5-2, is limited to maintenance and capital charges. As a consequence, annualized costs are constant for the tank sizes analyzed. If ethanol is assumed as the VOC stored, and if the conservation vent is set for 6.9 kPa (1.0 psi) pressure and 3.45 kPa (0.5 psi) vacuum, the standing losses at 27°C (80°F) are almost eliminated. Credits for the VOC not emitted are dependent upon tank diameter, but the credits may be significant enough to reduce the total annualized cost to a credit.

The annualized cost of pressure vessels, shown in Figure 5-6, increases with the size of the vessel. If recovery credits are considered, the annualized costs will be reduced by an amount determined by the type of VOC being stored.

The annualized cost of internal floating roofs increases with tank diameter (Figure 5-4). These control devices are usually applied to larger tanks where a pressure vessel would be too expensive. Although floating roofs do not eliminate VOC emissions, the recovery credits for a VOC (ethanol) could negate annualized costs.

The annualized cost of carbon adsorption systems is presented in Figures 5-8a and 5-8b. Values are based on the VOC emission rate, because adsorption rate determines carbon-bed regeneration frequency and associated operations. Adsorption of VOC to 8 weight percent of the carbon was assumed. It was further assumed that the VOC was not water soluble, and that it could be recovered from the desorbent steam by using process water. This recovered VOC may be realized as a fuel valued at \$0.11/kg (\$0.05/lb). Annualized costs increase with plant operating time. The value of reclaimed solvents cause annualized costs to decrease rapidly as emission rates increase, resulting in negative operating costs. If the VOC were not reclaimed but were discharged to an in-plant treating system, operating at a BOD_5 removal cost of less than the municipal rate of \$0.027/kg (\$0.06/lb) VOC, the cost would increase dramatically.

The annualized costs of incinerators with or without heat recovery, as depicted in Figures 5-10 and 5-12, increase with size and hours of operation. To determine the annualized costs, it was necessary to assume a VOC (ethanol) at the specified 25 percent LEL.[17] The fuel requirements are about equal for catalytic and thermal incinerators with 38 percent and 65 percent (respectively) primary heat recovery. The burner fuel requirements are also minimal. Fuel savings are insufficient to offset the additional cost of heat recovery on the following systems: thermal incinerators with 65 percent primary heat recovery

operating at less than 6800 Nm^3/h (4000 scfm) for fewer than 6000 h/yr; and catalytic incinerators with 38 percent primary heat recovery operating at more than 1500 Nm^3/h (885 scfm) for more than 3000 h/yr. When incineration systems without heat recovery are compared, the annualized costs of the catalytic system are slightly greater. As the LEL is lowered, however, this advantage declines.

Water-cooled condenser annualized costs are presented in Figure 5-14. The curves show that costs increase as capacity and annual operating hours increase; the increase mainly reflects the requirement for cooling water.

The annualized cost curves in Figure 5-16 for chilled-water-cooled condensers show a normal rise with increases in capacity and operating hours. If the VOC is ethanol, its recovery could more than offset the annual cost of operation.

Figures 5-18 and 5-20 present annualized costs of brine-cooled and Freon-cooled condensers. Both have a normal increase in annualized operating costs with increases in capacity and operating hours. Operating labor increases with hours, and utilities increase with hours and capacity. As with the chilled-water-cooled condenser, recovery credits from ethanol VOC could more than offset the annual cost of operation.

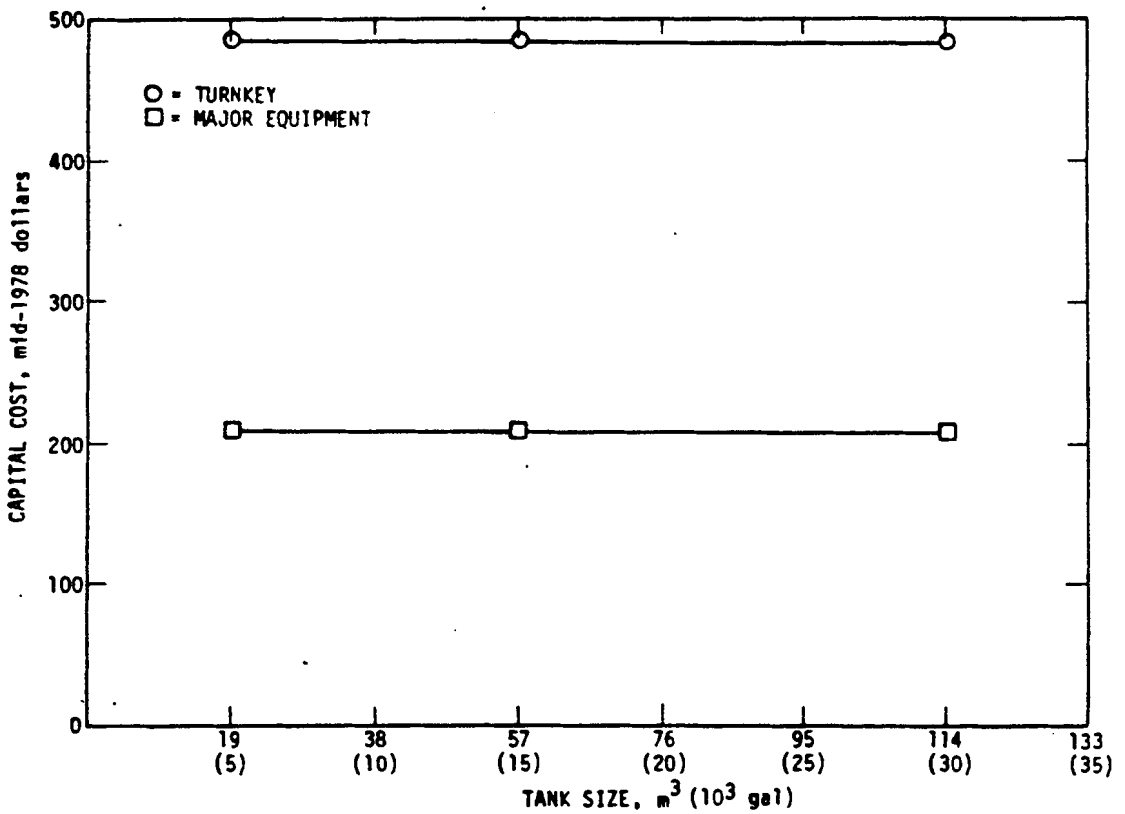
The annualized costs of packed-bed scrubbers (Figure 5-22) increase substantially with increases in operating hours and capacity; this is largely caused by the costs of wastewater treatment from the discharge of BOD.

Venturi scrubber costs also increase substantially with increases in operating hours and capacity. Compared with packed-bed scrubbers, the annualized costs are higher: much higher for the larger capacities, because

of larger volume costs for water and sewage. This larger volume is required because jet venturi scrubbers are, in effect, single-stage units; whereas packed-bed scrubbers use the more effective countercurrent contact.

5.3 COST-EFFECTIVENESS

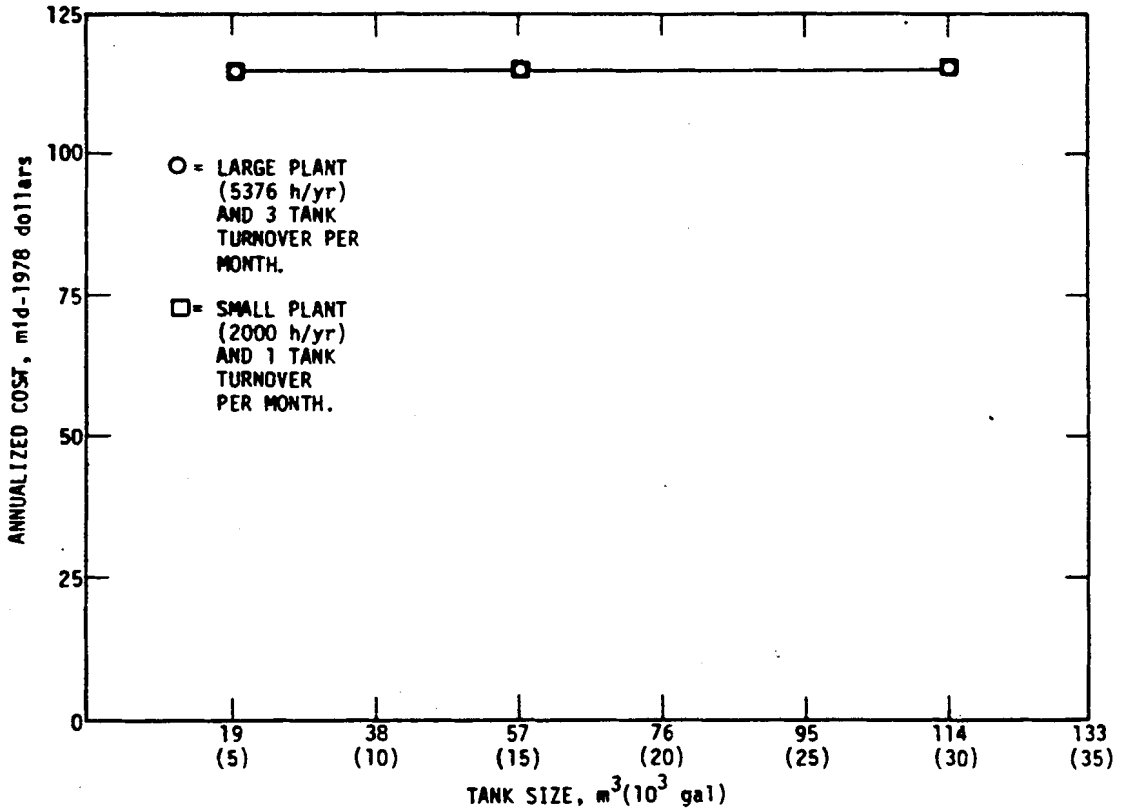
The cost relationships developed in this section represent a wide range of emission rates and pollutants. Emissions from pharmaceutical manufacture vary significantly by operating time and by the size and number of process operations. Because quantities of annual emissions cannot be estimated in a manner consistent with the costing techniques used in this analysis, cost-effectiveness was not measured for this industry.



NOTES: 1. BASED ON 6.3 m^3/s (100 gal/min) pumping rate.

2. BASED ON 6.9 kPa (16 oz) PRESSURE AND 3.45 kPa (8 oz) VACUUM.

Figure 5-1. Capital cost of conservation vents on storage tanks.



NOTES: 1. SEE FIGURE 5-25 FOR VOC RECOVERY CREDITS.

Figure 5-2. Annualized cost of conservation vents on storage tanks.

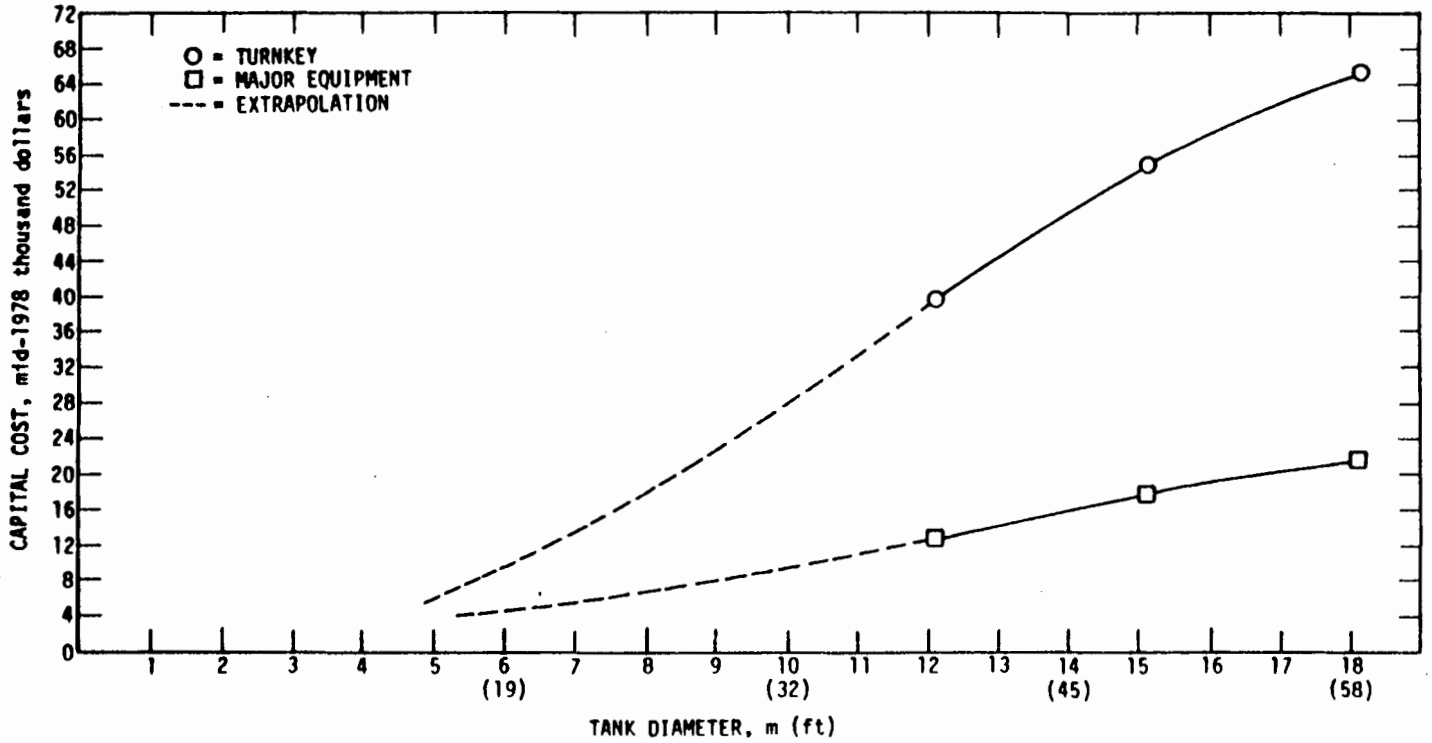


Figure 5-3. Capital cost of floating roof.

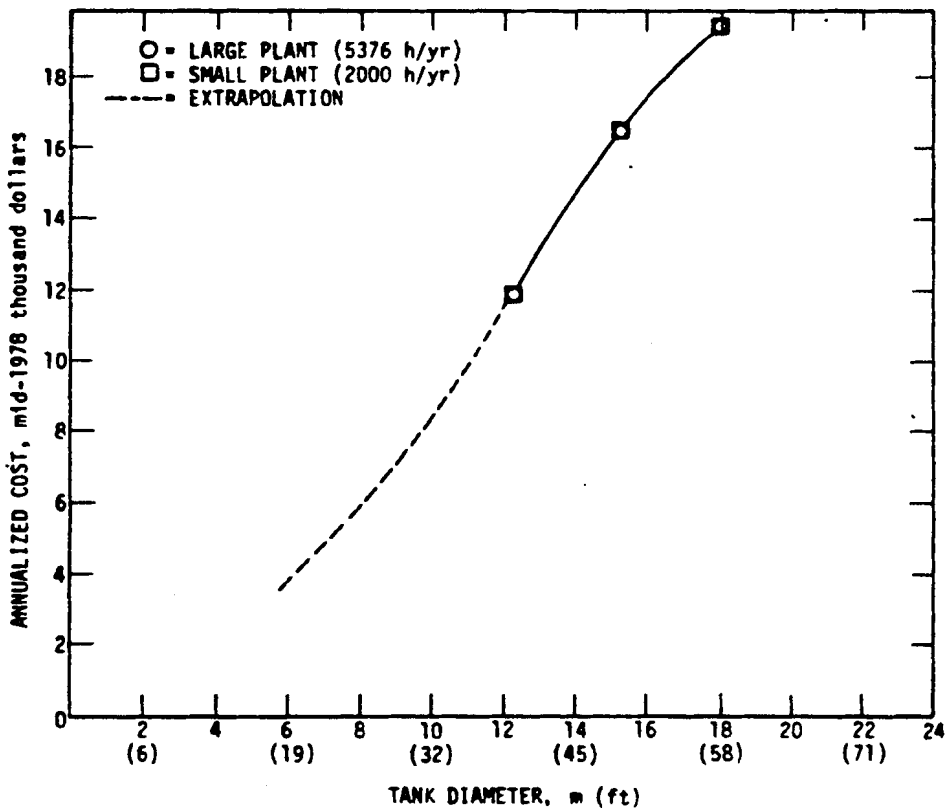
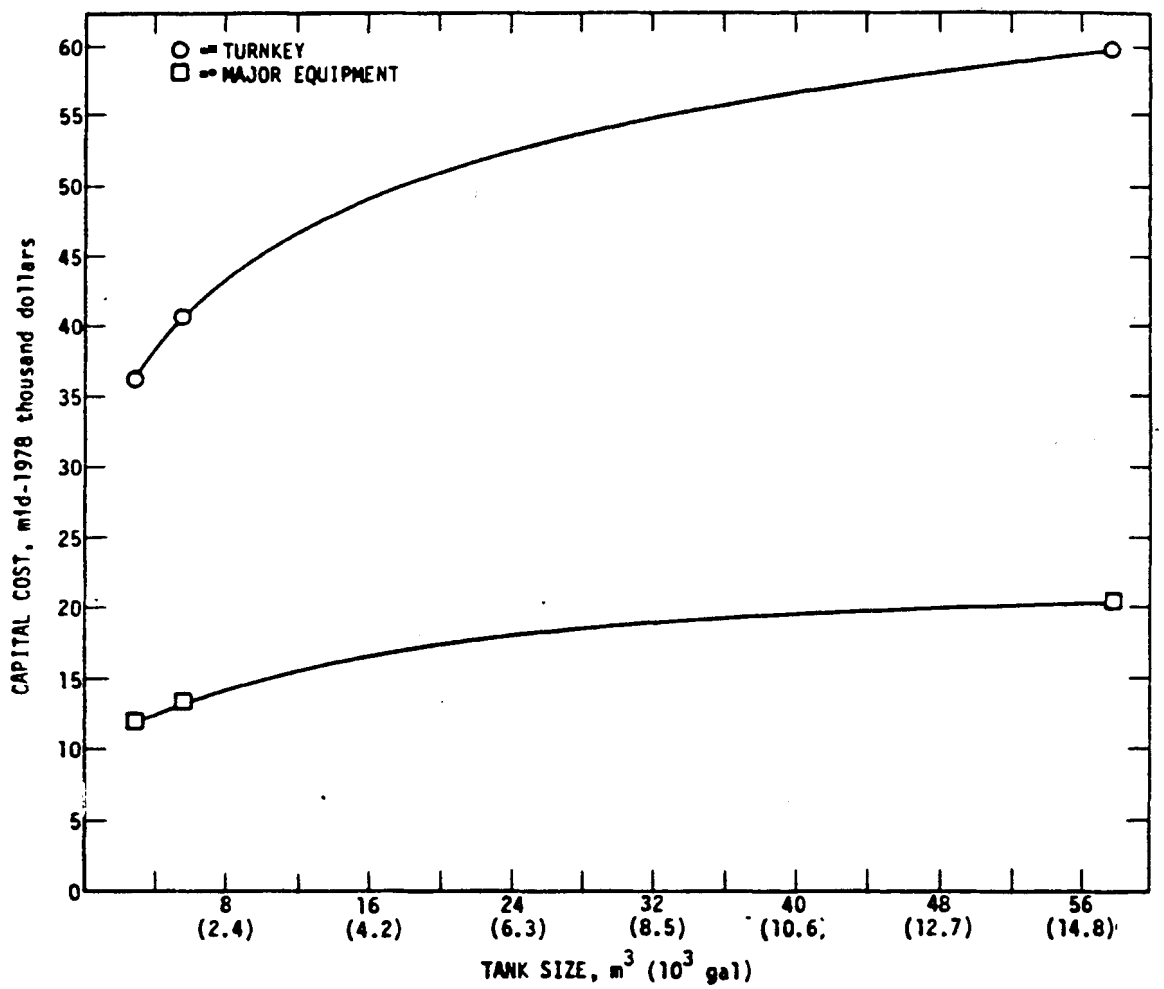


Figure 5-4. Annualized cost of floating roof.



NOTES: 1. CARBON STEEL VESSEL 1.27 cm (1/2 inch) SHELL AND HEMISPHERICAL HEADS, NOZZLES, AND SADDLES.

Figure 5-5. Capital cost of pressure vessels.

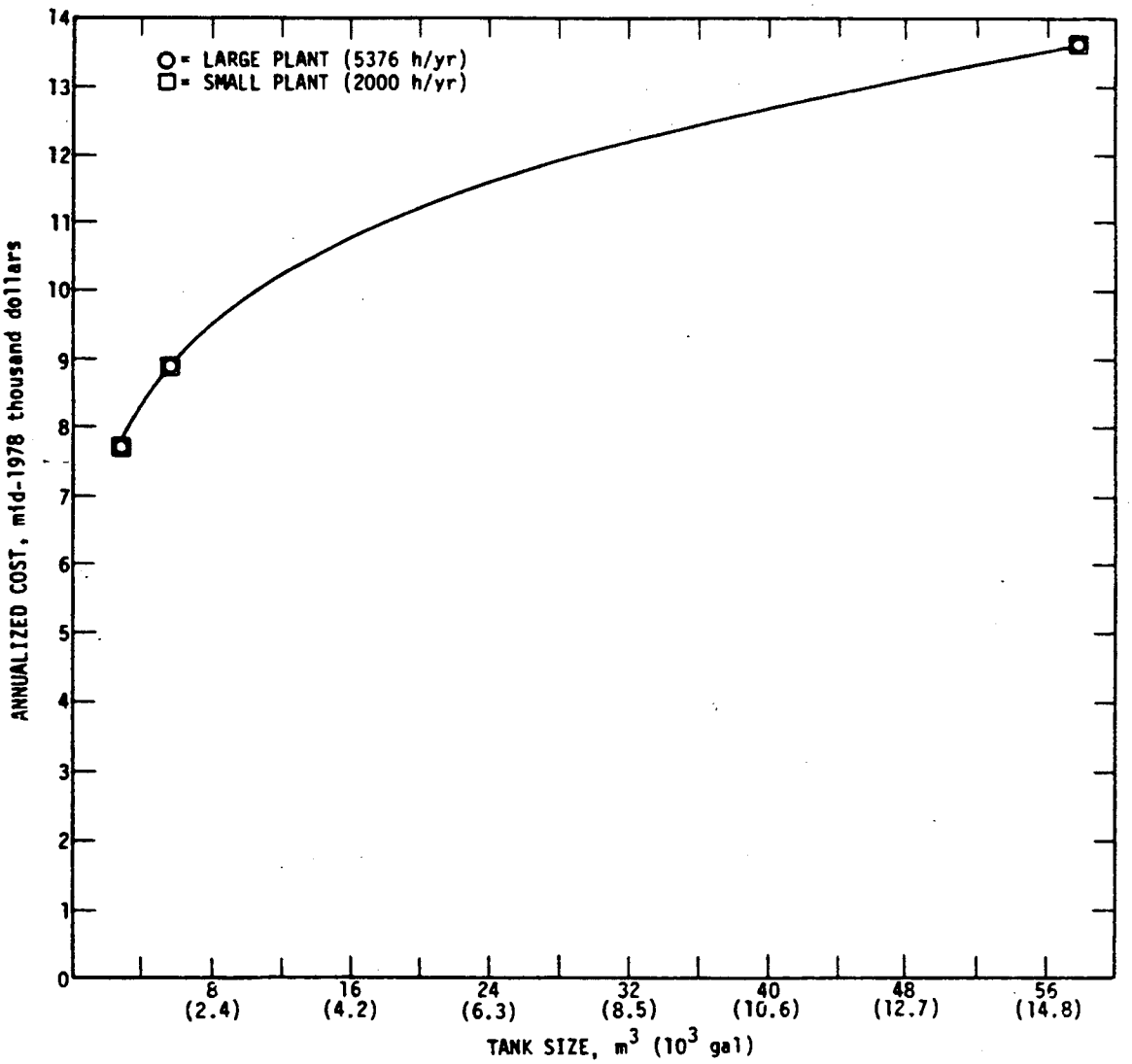
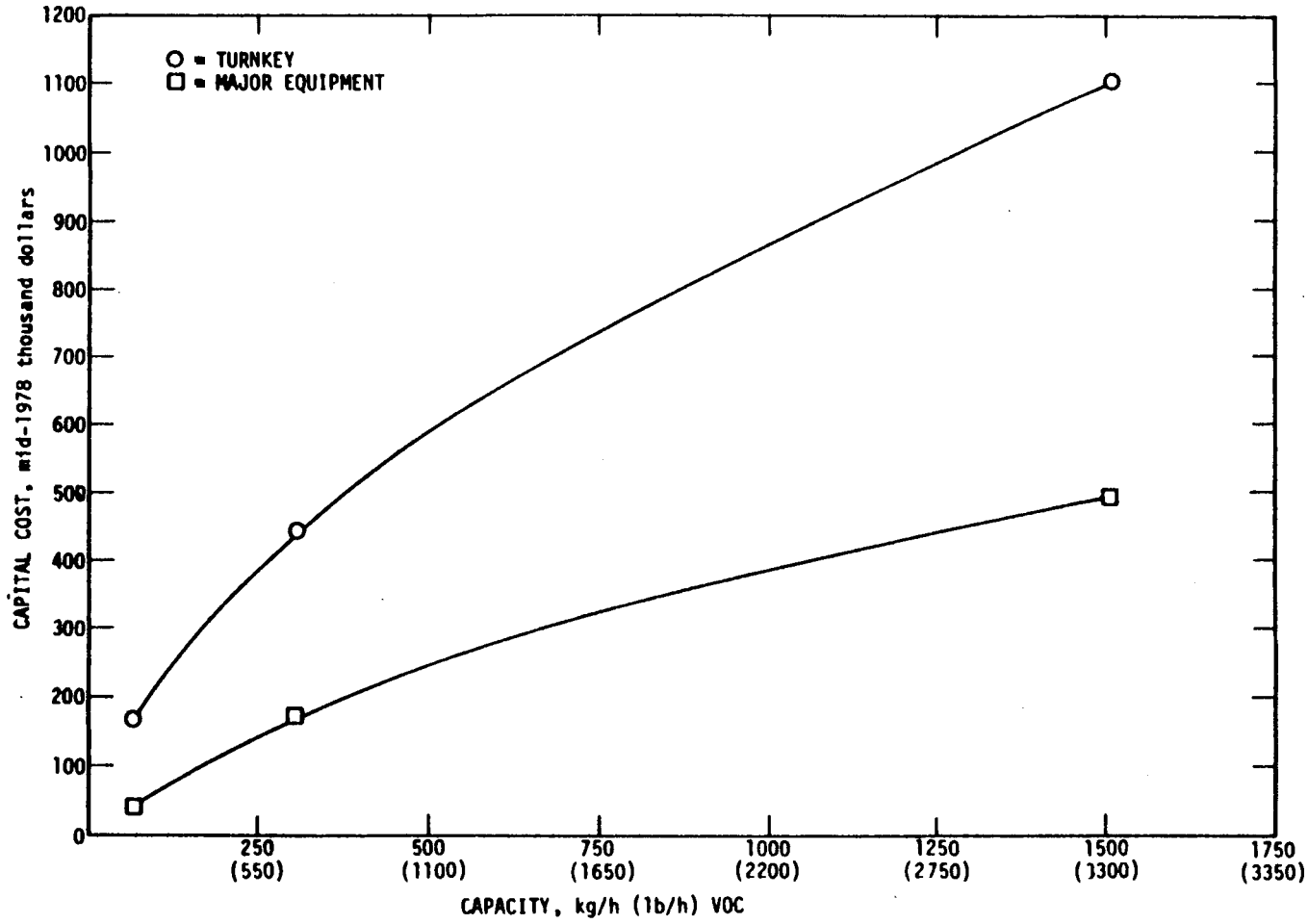
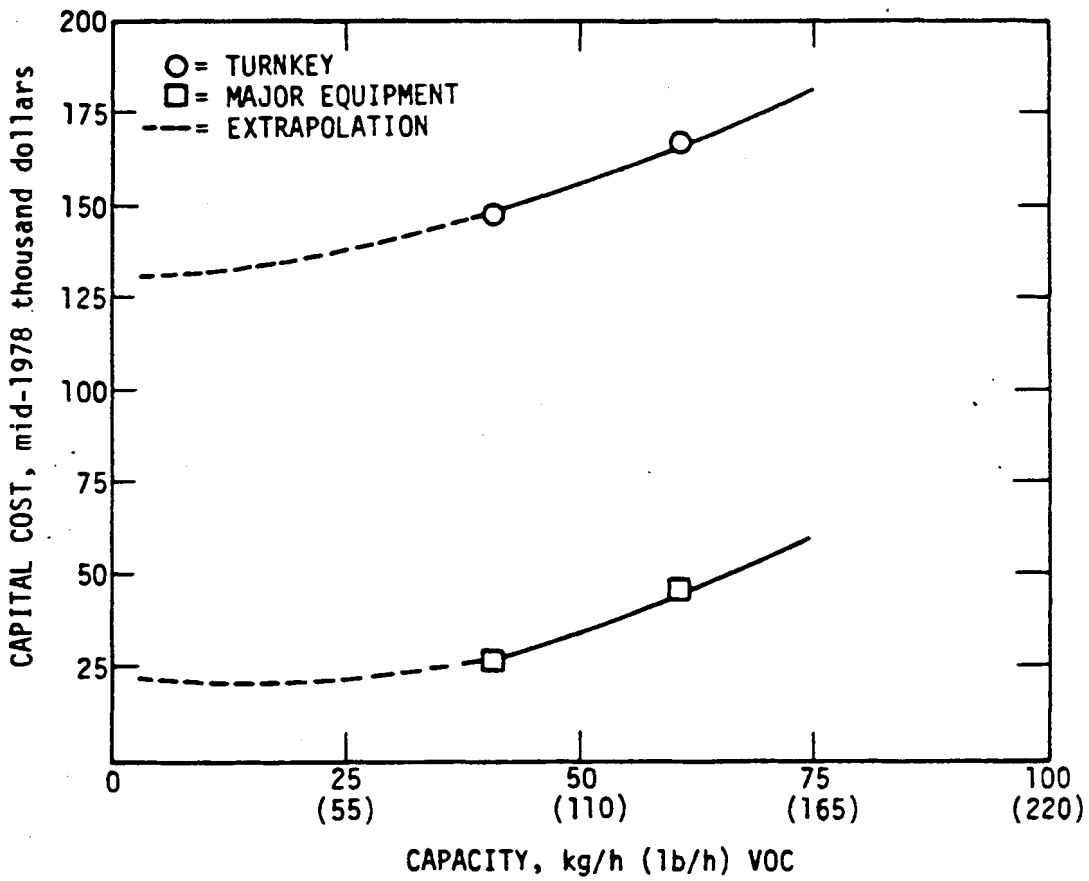


Figure 5-6. Annualized cost of pressure vessels.



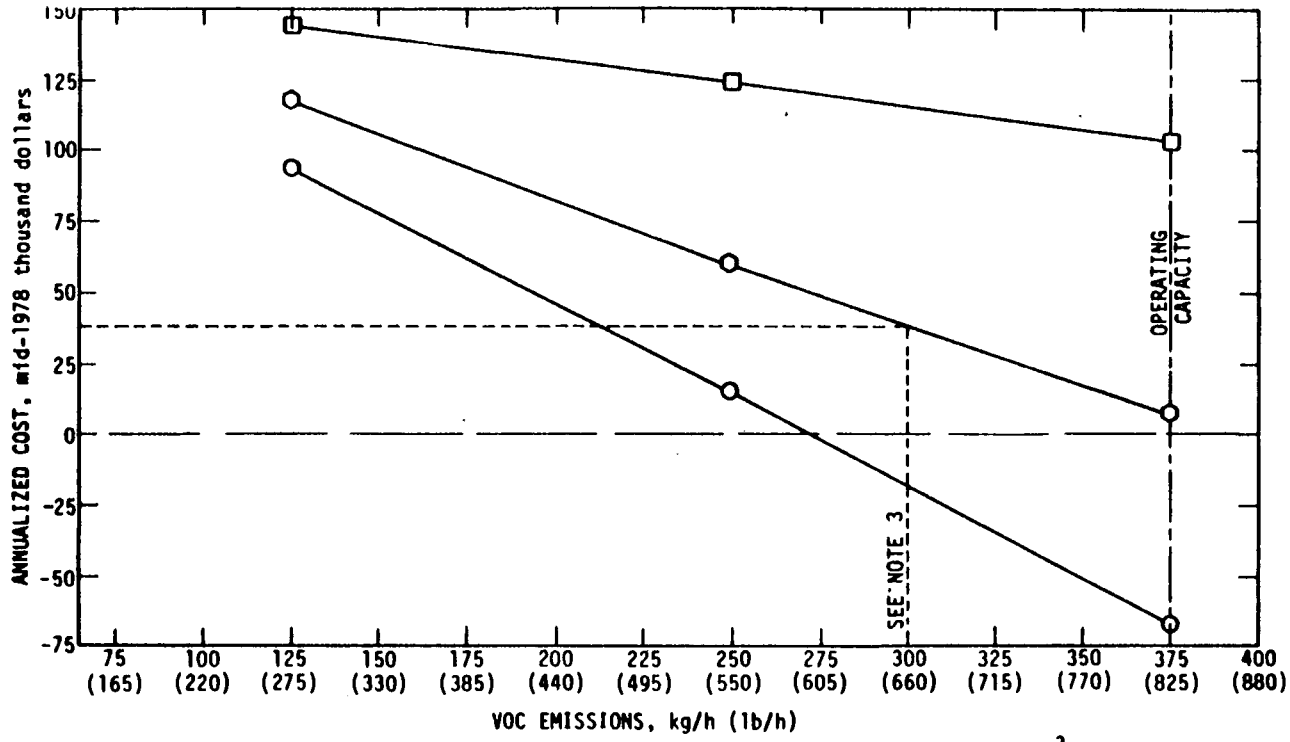
NOTE: 1. BASED ON GAS FLOW RATES OF 1.12 Nm^3/min per kg (18 scfm/lb).

Figure 5-7a. Capital cost of carbon adsorption systems (large, fully automatic system for continuous operation).



NOTE: 1. BASED ON GAS FLOW RATES OF 1.12 Nm^3/min per kg (18 scfm/lb).

Figure 5-7b. Capital cost of carbon adsorption systems (small, fully automatic system for continuous operation).



NOTES:

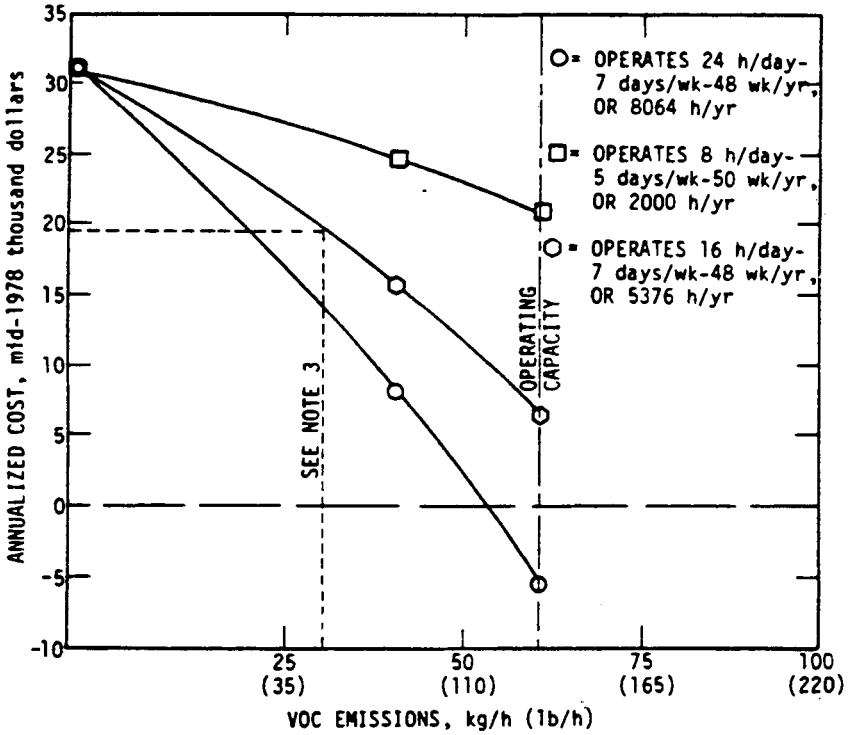
1. BASED ON 425 Nm^3/min (15,000 scfm) FOR ALL VOC CONCENTRATIONS.
2. COST INCLUDES VOC RECOVERY CREDIT. IF NOT RECLAIMED ADD $0.023/kg ($0.01/lb) VOC FOR LOST CREDIT AND $0.027/kg ($0.012/lb) VOC FOR WASTEWATER TREATMENT.
3. EXAMPLE: 300 kg/h x 5376 h/yr x $0.05/kg = $80,600 + $37,500 (FROM CHART).

○ = OPERATES 24 h/day-7 days/wk-48 wk/yr, OR 8064 h/yr

□ = OPERATES 8 h/day-5 days/wk- 50 wk/yr, OR 2000 h/yr

○ = OPERATES 16 h/day-7 days/wk-48 wk/yr, OR 5376 h/yr

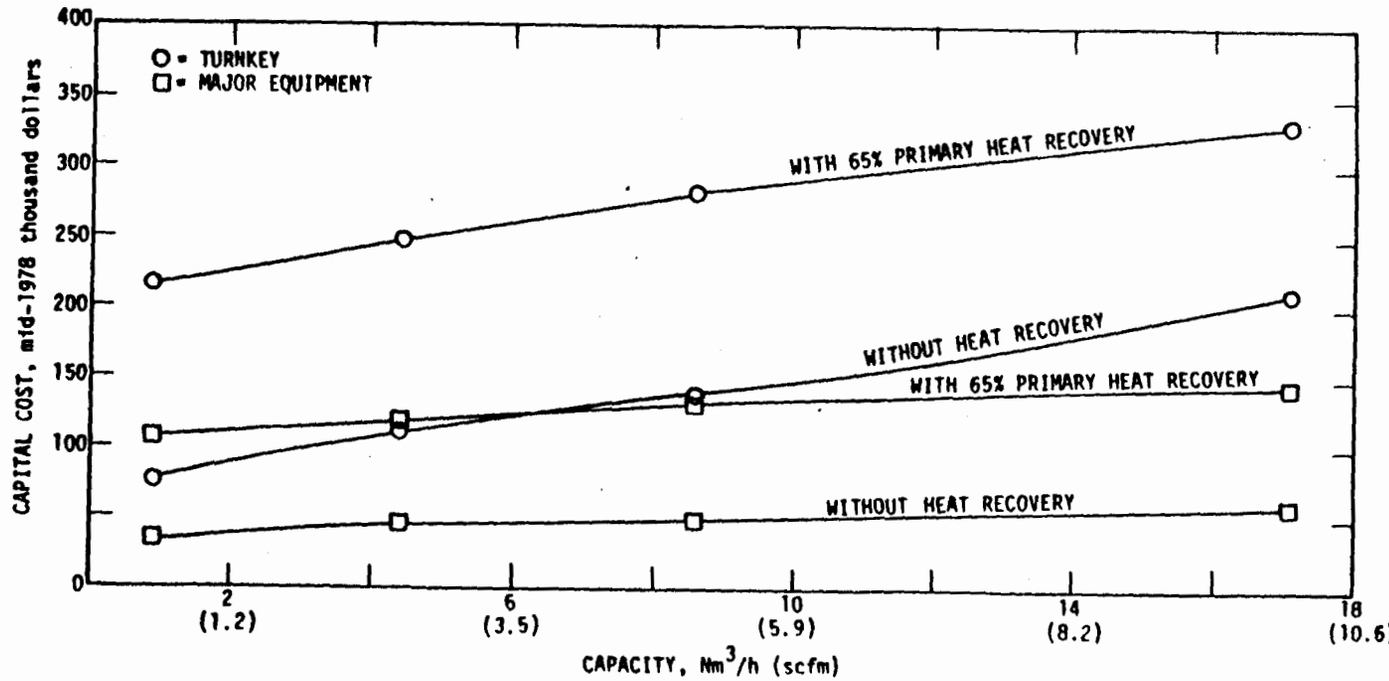
Figure 5-8a. Annualized cost of carbon adsorption systems (medium).



NOTES:

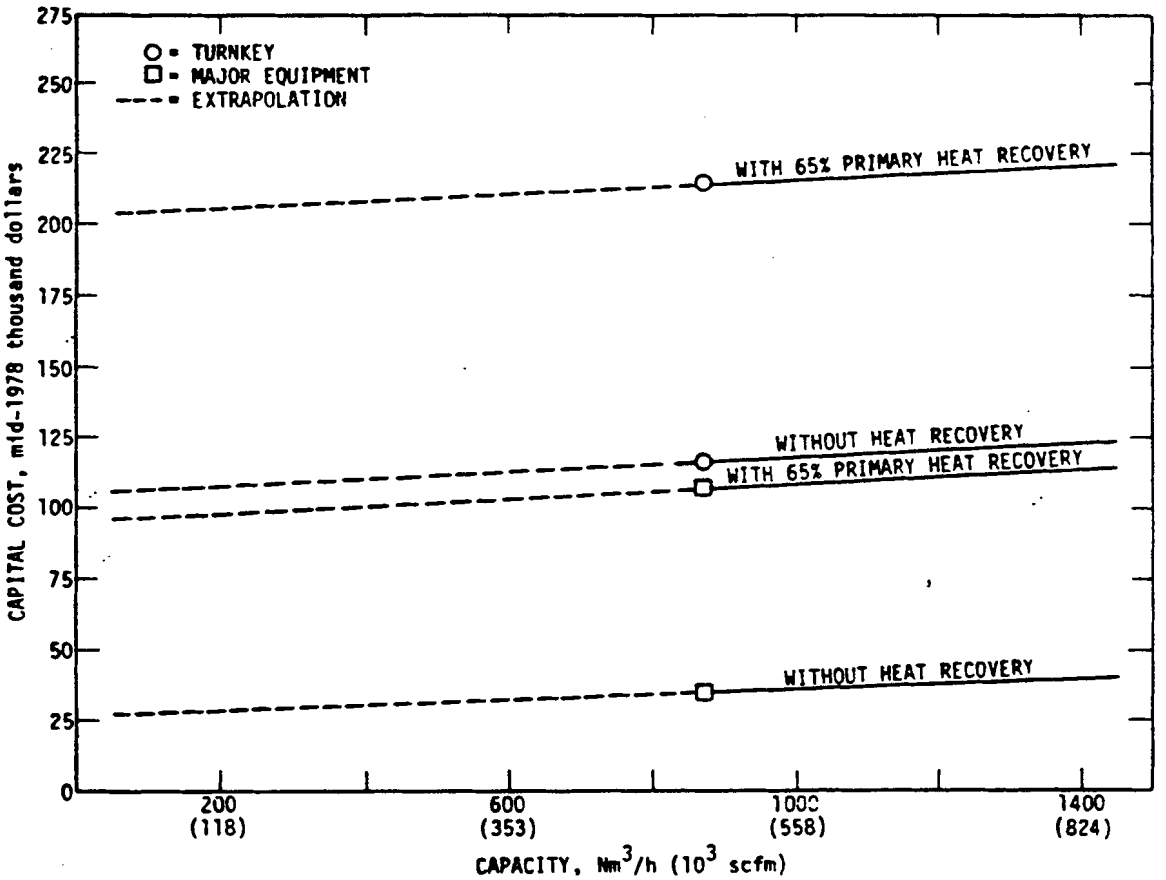
1. BASED ON 85 Nm^3/min (3000 scfm) FOR ALL VOC CONCENTRATIONS.
2. COST INCLUDES COST OF VOC RECLAIMED AT \$0.023/kg (\$0.01 lb) AND COST OF WASTEWATER TREATMENT AT \$0.027/kg (\$0.012/lb) OF VOC.
3. EXAMPLE: 30 kg/h x 5376 h/yr x \$0.05/kg = \$8060 + \$19,000 (FROM CHART).

Figure 5-8b. Annualized costs of carbon adsorption systems (small).



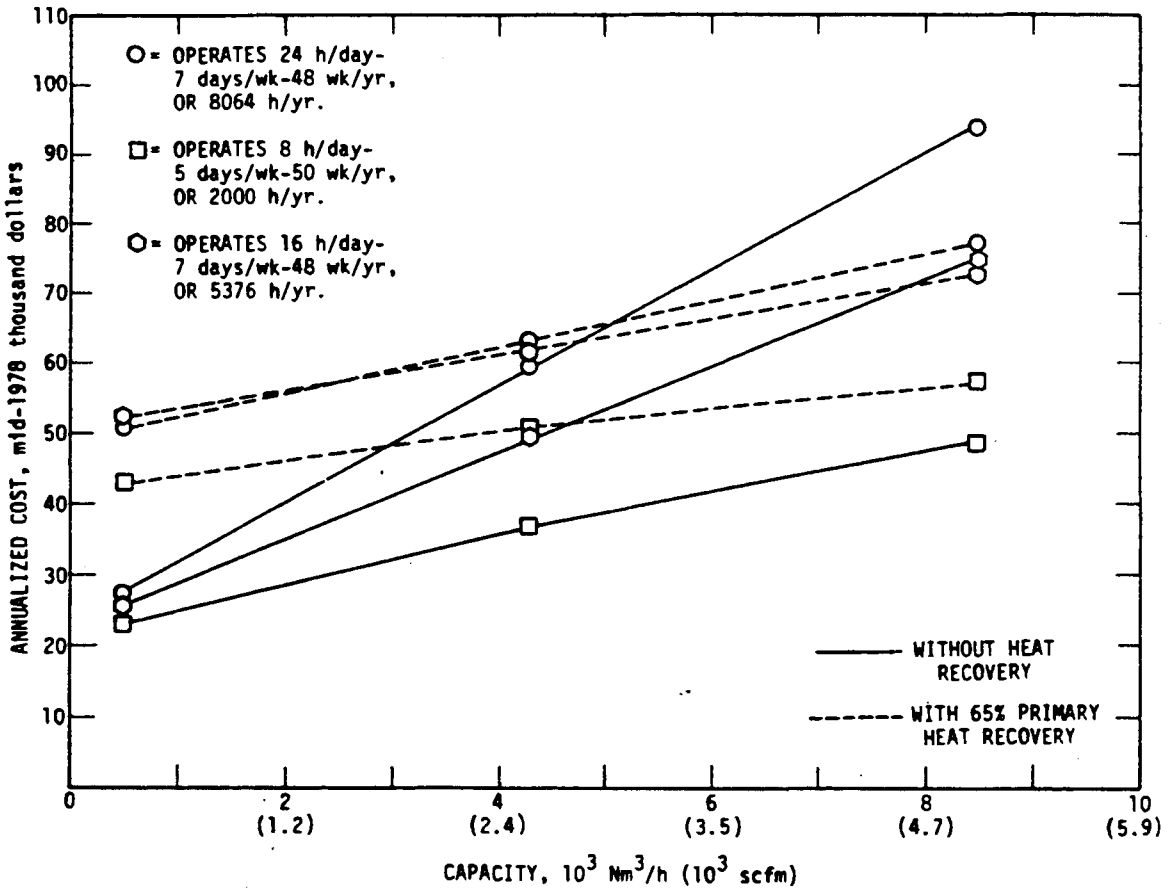
NOTE: 1. OIL-FIRED FOR OPERATION AT 25 % LEL.

Figure 5-9a. Capital cost of thermal incineration systems (large).



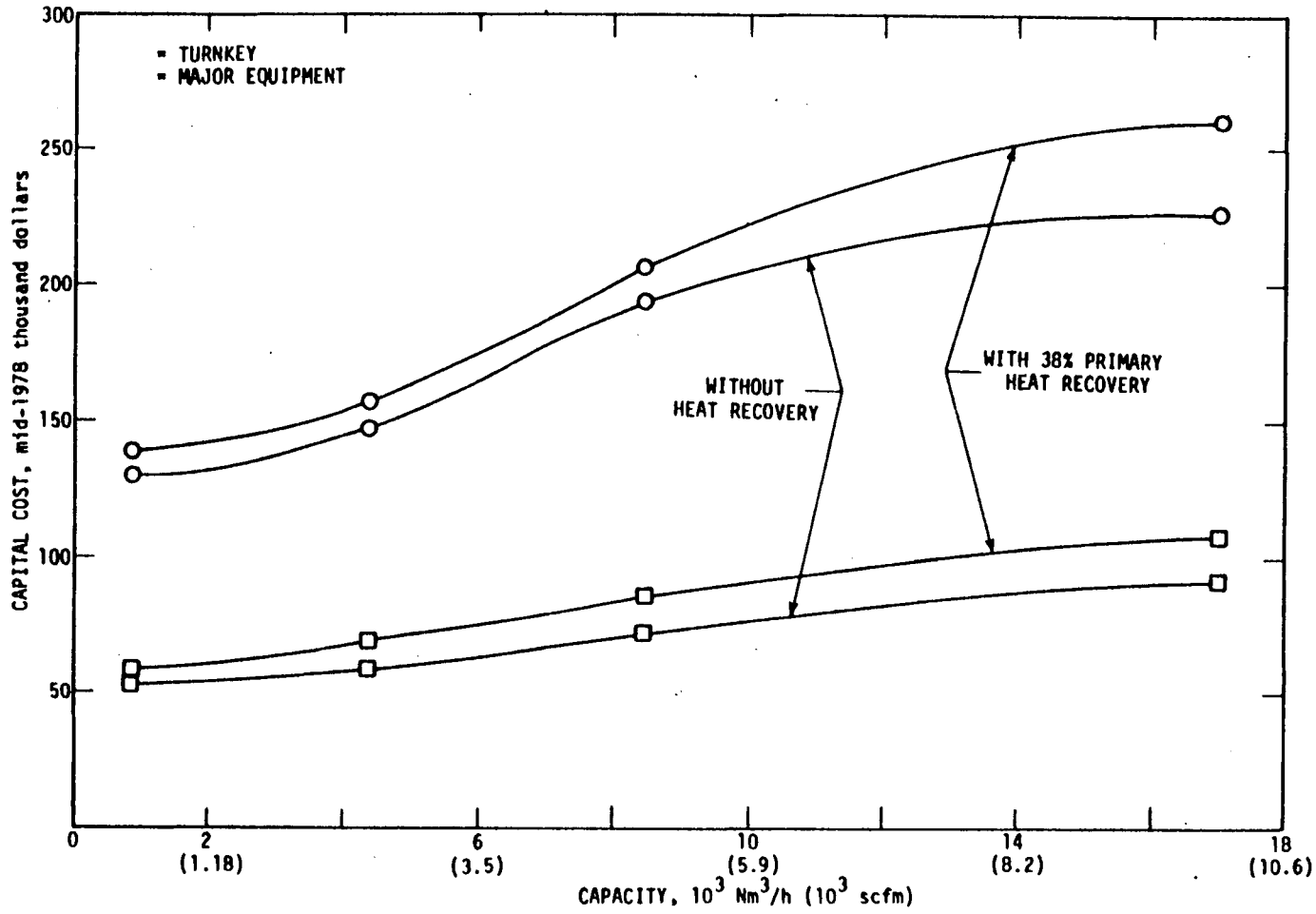
NOTES: 1. OIL-FIRED FOR OPERATION AT 25% LEL.

Figure 5-9b. Capital cost of thermal incineration systems (small).



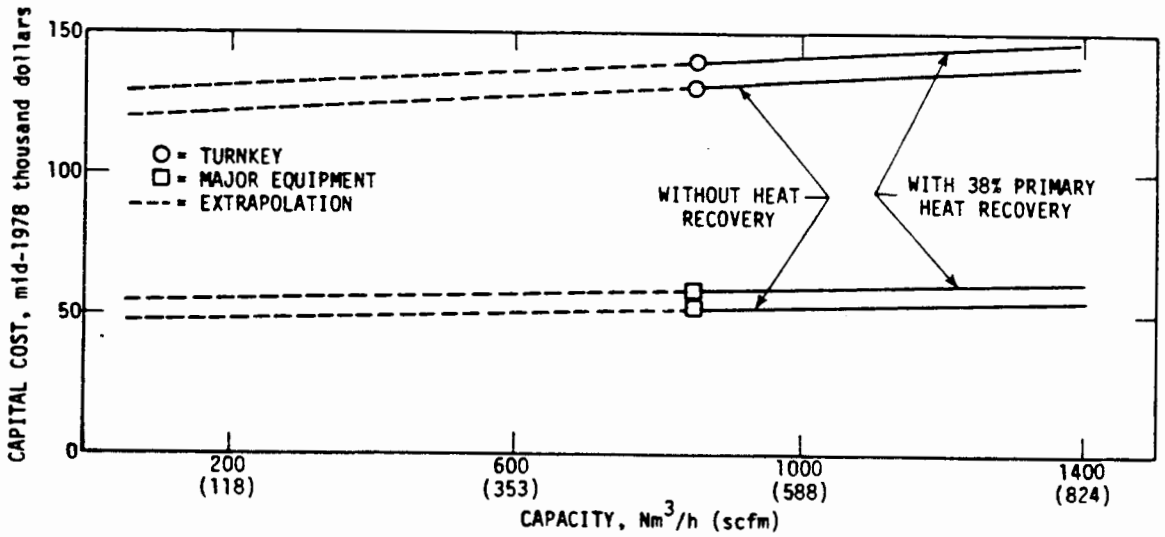
NOTES: 1. OIL-FIRED FOR OPERATION AT 25% LEL.

Figure 5-10. Annualized cost of thermal incineration systems.



NOTE: 1. OIL-FIRED

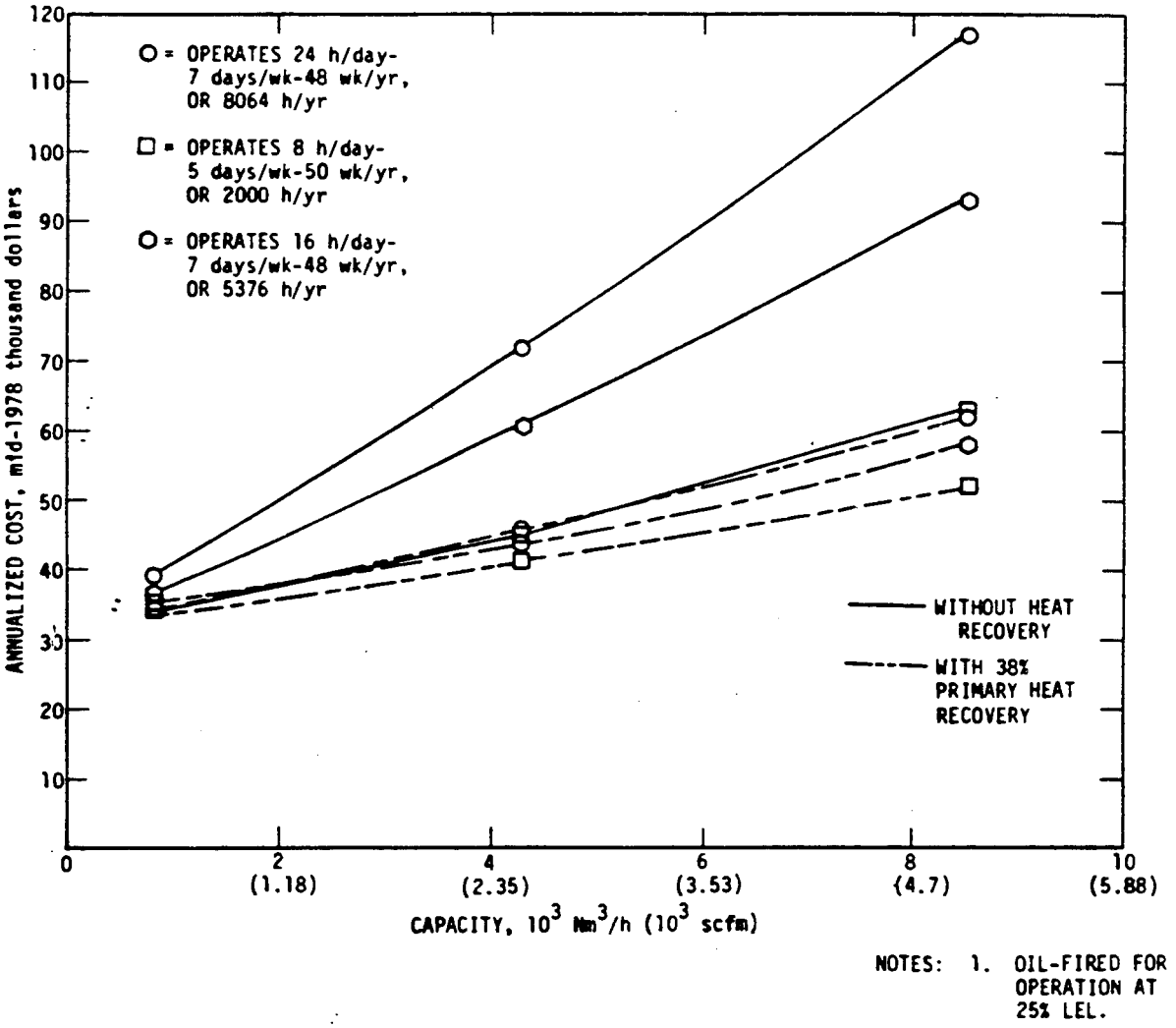
Figure 5-11a. Capital cost of catalytic incineration systems (large).



NOTE: 1. SEE FIGURE 5-11a FOR LARGER SIZES.

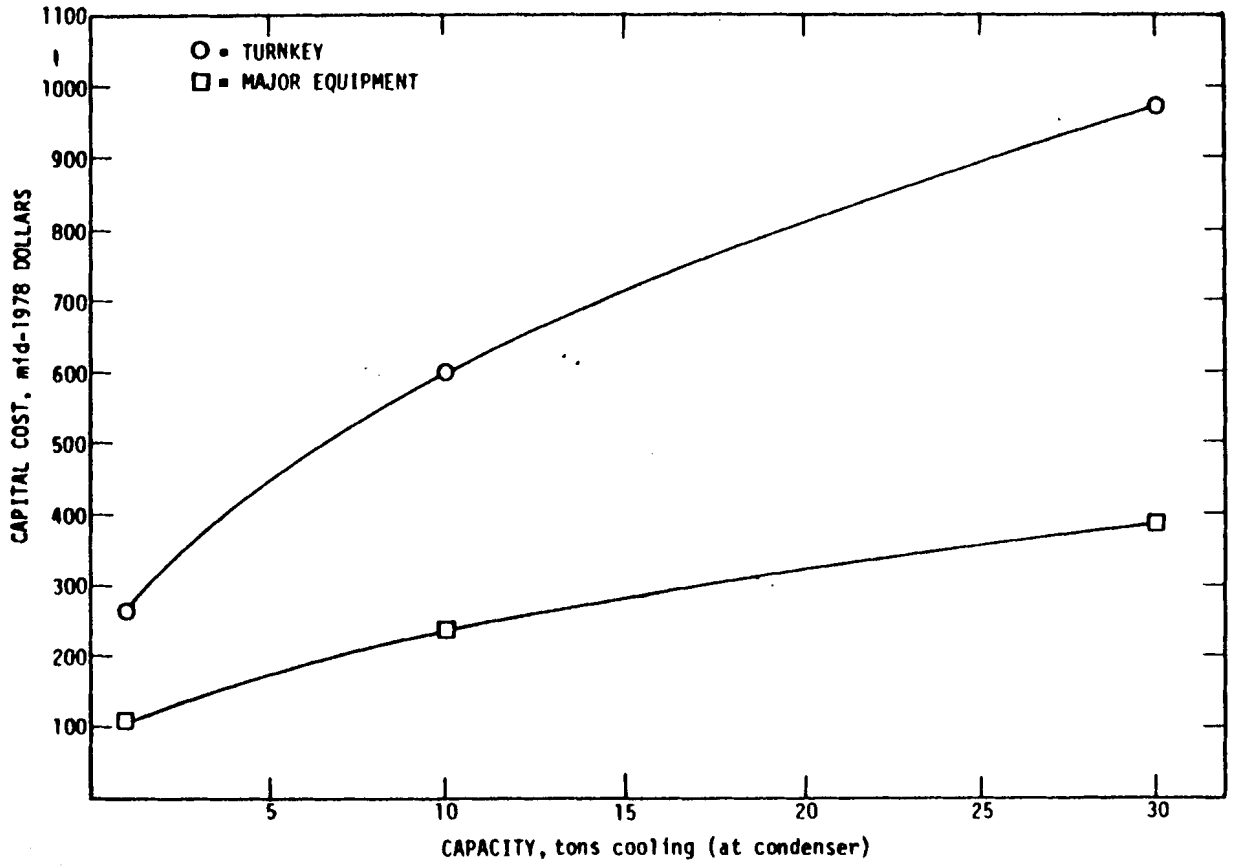
2. OIL-FIRED.

Figure 5-11b. Capital cost of catalytic incineration systems (small).



NOTES: 1. OIL-FIRED FOR OPERATION AT 25% LEL.

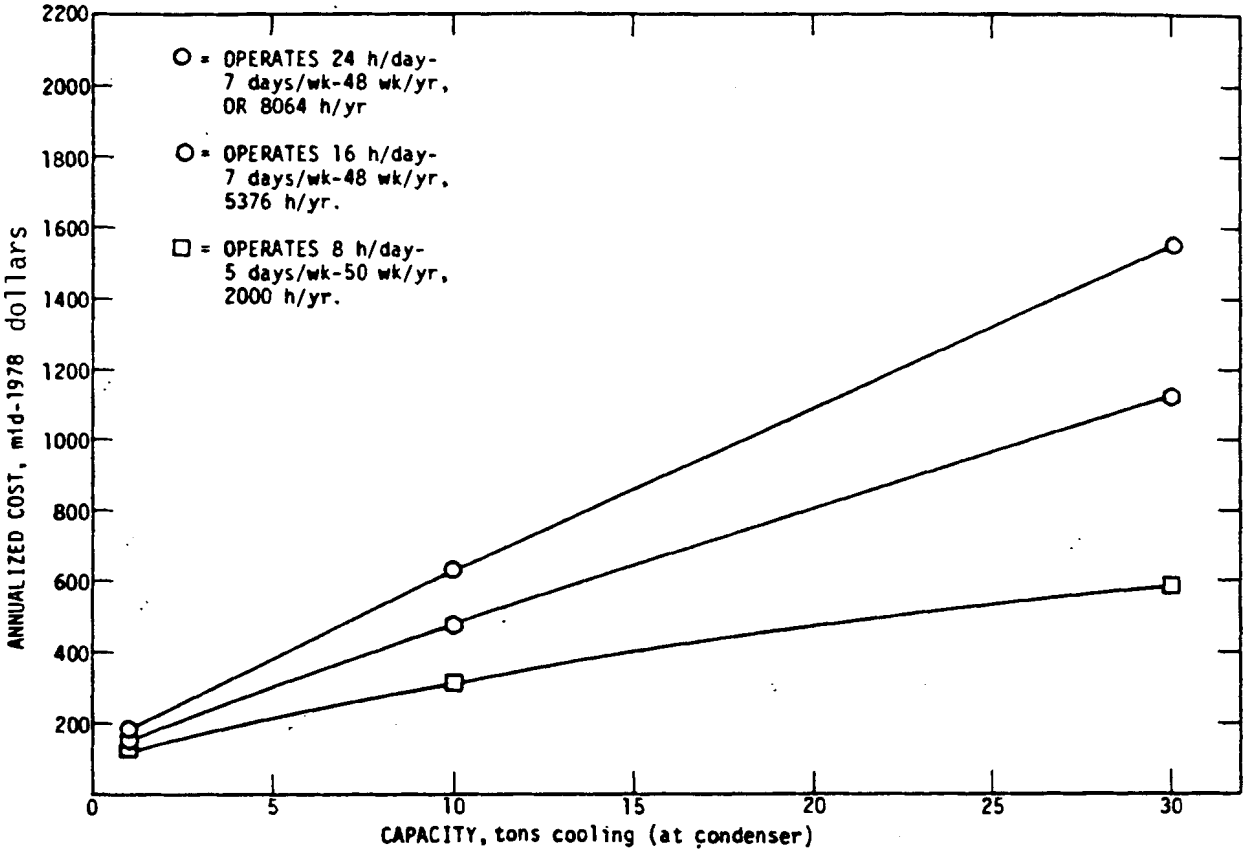
Figure 5-12. Annualized cost of catalytic incineration systems.



NOTES: 1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.

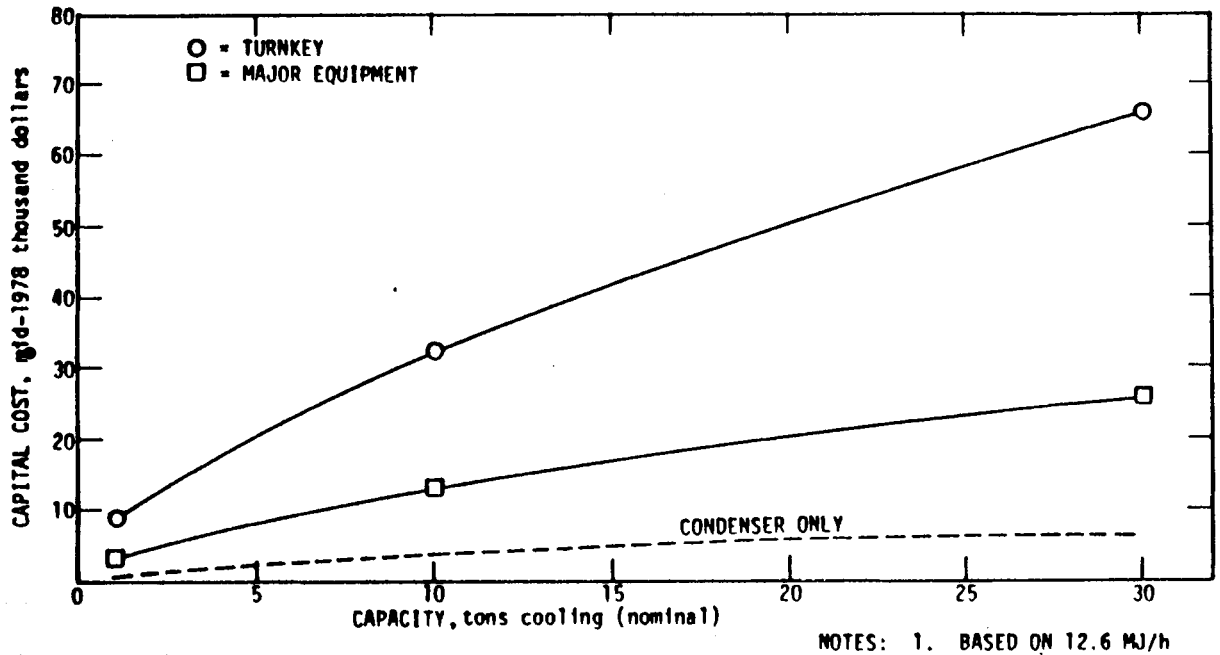
2. BASED ON CONDENSING ETHANOL VAPOR AT 78°C (172°F), WITH 24°C (75°F) WATER FROM A COOLING TOWER.

Figure 5-13. Capital cost of water-cooled condensers



NOTES:
1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.
2. BASED ON CONDENSING ETHANOL VAPOR AT 78°C (172°F), WITH 24°C (75°F) WATER FROM A COOLING TOWER.
3. SEE FIGURE 5-25 FOR VOC RECOVERY CREDITS.

Figure 5-14. Annualized cost of water-cooled condensers

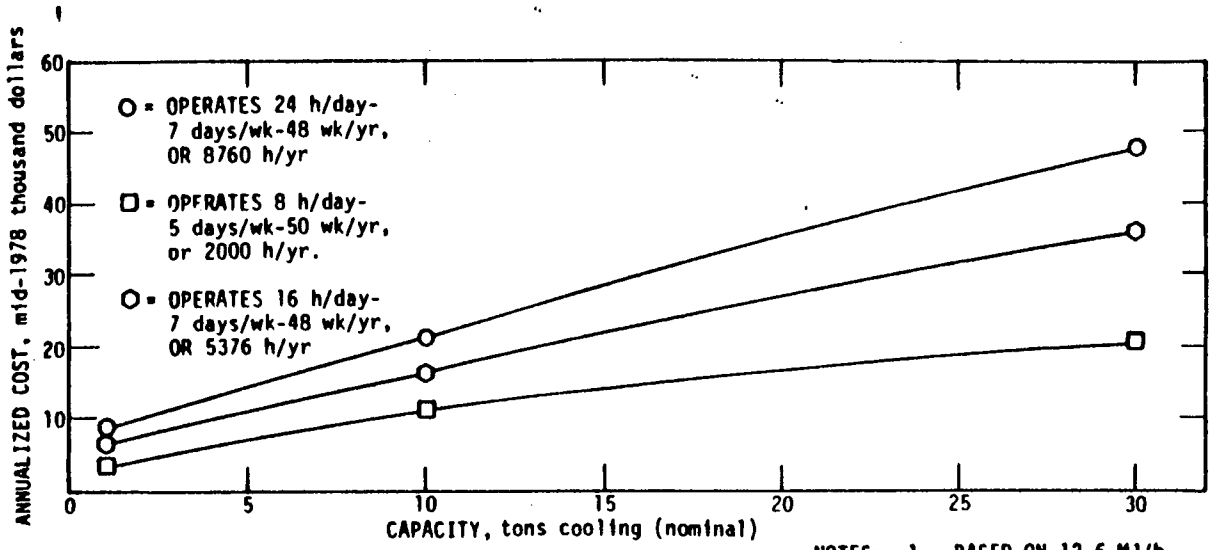


Ratio of net tons available for cooling/nominal tons refrigeration for 27°C (80°F) air to refrigerant condenser and various brine (or chilled water) temperatures from the VOC condenser.

Ratio Tons Cooling Net/Nominal	Temperature from VOC condenser °F	°C
1.00	50	10
0.80	40	4.4
0.50	10	-12.2
0.25	-10	-23

NOTES:
1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.
2. Nominal tons of cooling is machine rating for 10°C (50°F) water leaving the VOC condenser and 27°C (80°F) air into the refrigerant condenser.

Figure 5-15. Capital cost of chilled-water-cooled VOC condensers and water chiller



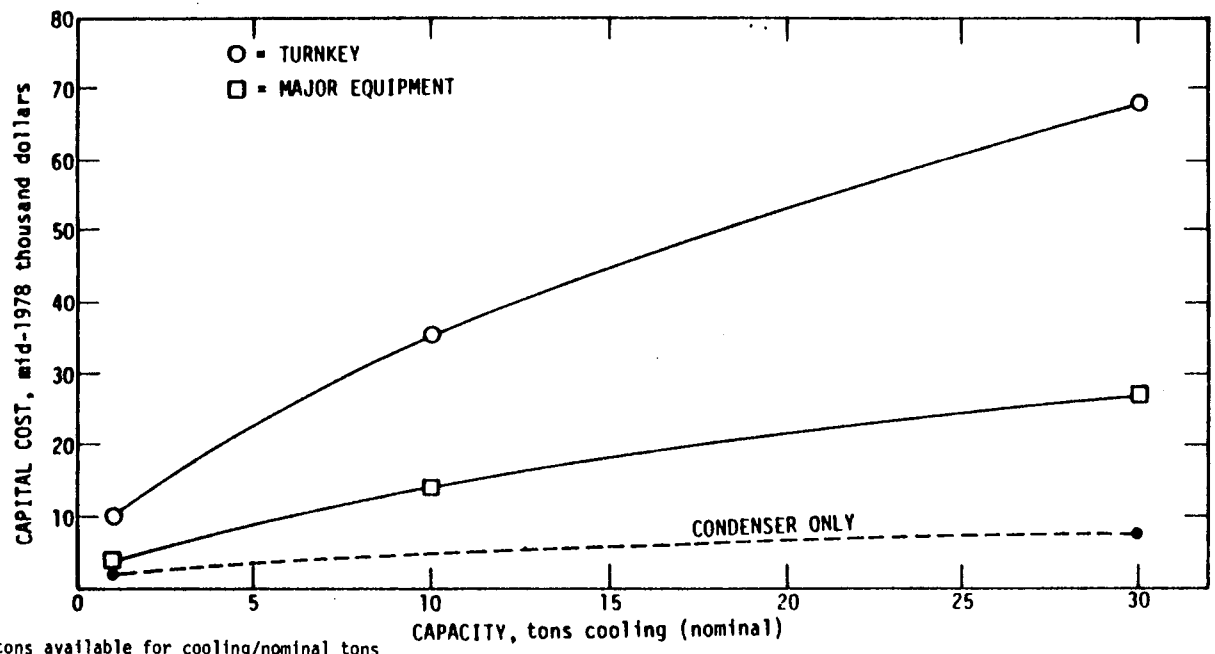
Ratio of net tons available for cooling/nominal tons refrigeration for 27°C (80°F) air to refrigerant condenser and various brine (or chilled water) temperatures from the VOC condenser.

NOTES: 1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.

2. See Figure 5-25 for VOC recovery credits.

Ratio Tons Cooling Net/Nominal	Temperature from VOC condenser °F	°C
1.00	50	10
0.80	40	4.4
0.50	10	-12.2
0.25	-10	-23

Figure 5-16. Annualized cost of chilled-water-cooled VOC condensers and water chiller



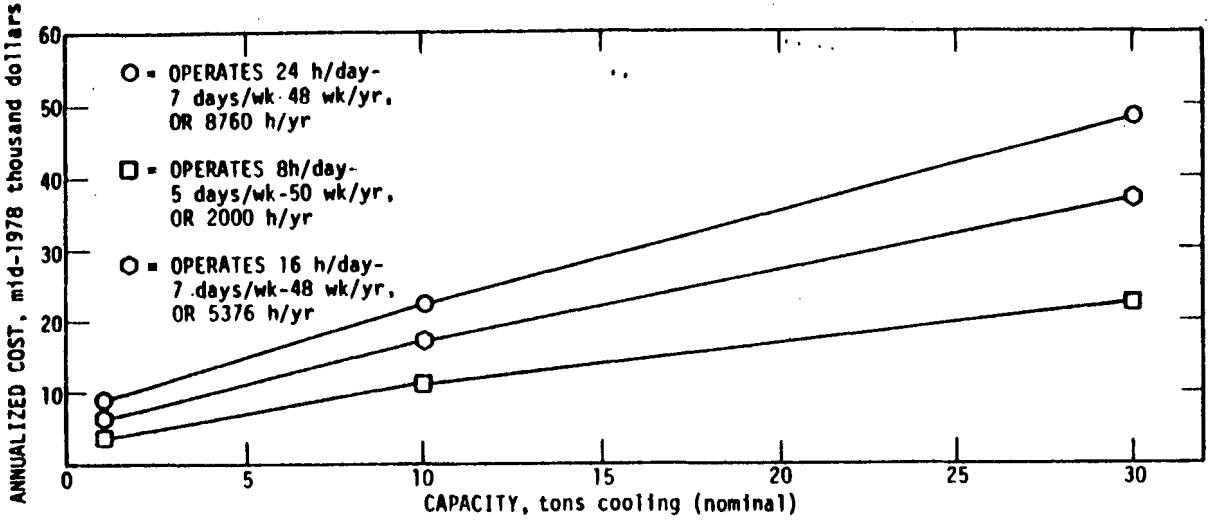
Ratio of net tons available for cooling/nominal tons refrigeration for 27°C (80°F) air to refrigerant condenser and various brine (or chilled water) temperatures from the VOC condenser.

Ratio Tons Cooling Net/Nominal	Temperature from VOC condenser °F	°C
1.00	50	10
0.80	40	4.4
0.50	10	-12.2
0.25	-10	-23

NOTES: 1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.

2. Nominal tons of cooling is machine rating for 10°C (50°F) water leaving the VOC condenser and 27°C (80°F) air into the refrigerant condenser.

Figure 5-17. Capital cost of chilled-brine-cooled VOC condenser and brine chiller



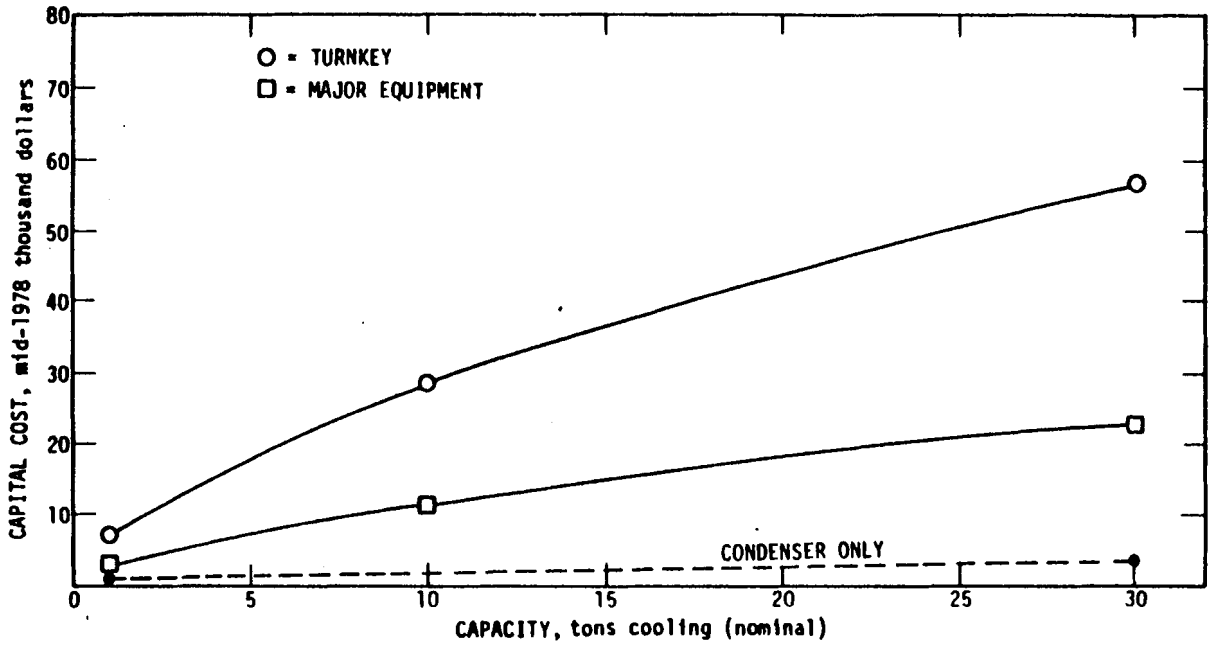
NOTES: 1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.

2. See Figure 5-25 for VOC recovery credits.

Figure 5-18. Annualized cost of chilled brine-cooled VOC condenser and brine chiller

Ratio of net tons available for cooling/nominal tor refrigeration for 27°C (80°F) air to refrigerant condenser and various brine (or chilled water) temperatures from the VOC condenser.

Ratio Tons Cooling Net/Nominal	Temperature from VOC condenser °F	°C
1.00	50	10
0.80	40	4.4
0.50	10	-12.2
0.25	-10	-23

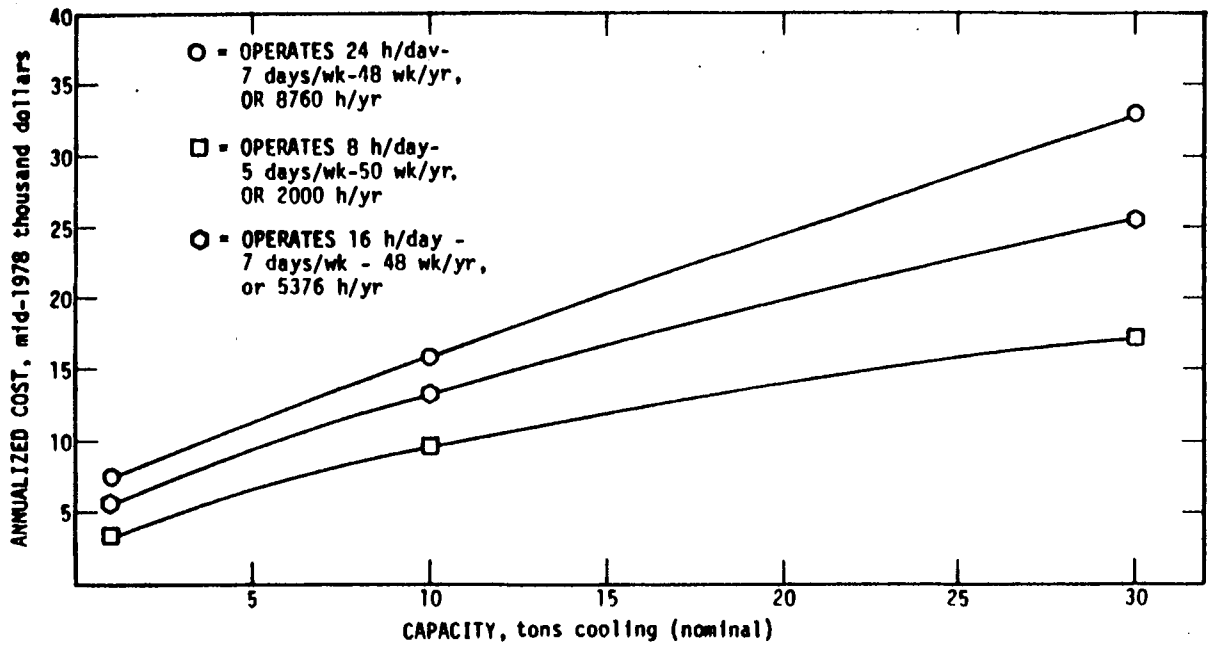


Ratio of net tons available for cooling/nominal tons refrigeration for 27°C (80°F) air to refrigerant condenser and various Freon temperatures to VOC condenser.

Ratio Tons Cooling Net/Nominal	Temperature to VOC condenser °F	°C
.40	-10	-23
.25	-22	-30

NOTES:
1. BASED ON 12.6 MJ/h (12,000 Btu/h) per ton.
2. Nominal tons of cooling is machine rating for chiller service with 10°C (50°F) water leaving the VOC condenser and 29°C (80°F) air into refrigerant condenser.

Figure 5-19. Capital cost of VOC condenser chilled with Freon and Freon refrigeration system



NOTES: 1. BASED ON 12.6 MJ/h (12,000 Btu/lb) per ton.

2. SEE FIGURE 5-25 FOR VOC RECOVERY CREDITS.

Ratio of net tons available for cooling/nominal tons refrigeration for 27°C (80°F) air to refrigerant condenser and various Freon temperatures to VOC condenser.

Ratio Tons Cooling Net/Nominal	Temperature to VOC condenser °F	°C
.40	-10	-23
.25	-22	-30

Figure 5-20. Annualized cost of VOC condenser cooled with Freon and Freon refrigeration system

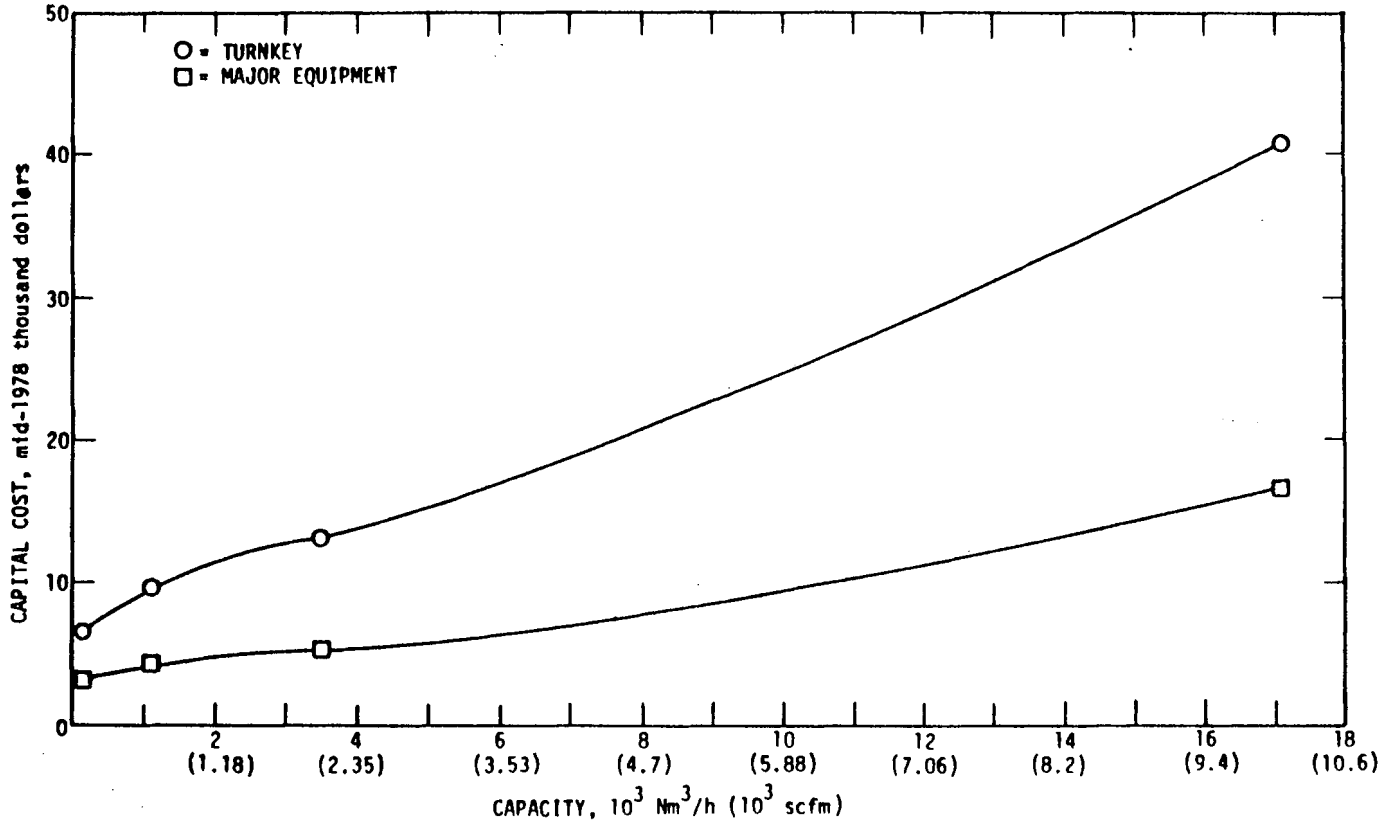
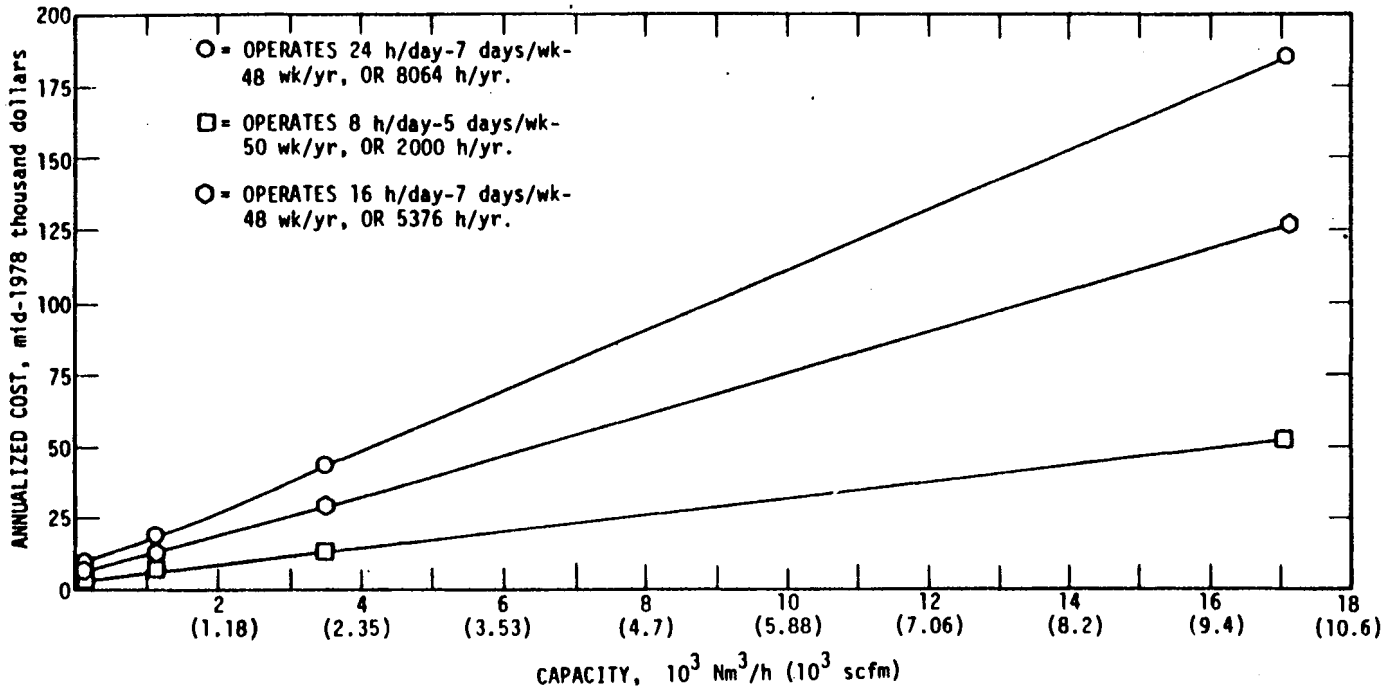


Figure 5-21. Capital cost of packed bed scrubbers.



NOTES:
1. BASED UPON GAS STREAM EMISSIONS AT 21°C (70°F) AND SATURATED WITH VOC (ETHANOL).
2. ANNUALIZED COSTS INCLUDE WASTEWATER TREATMENT OF BOD'S AT $0.027/kg ($0.06/lb) VOC.

Figure 5-22. Annualized costs of packed bed scrubbers.

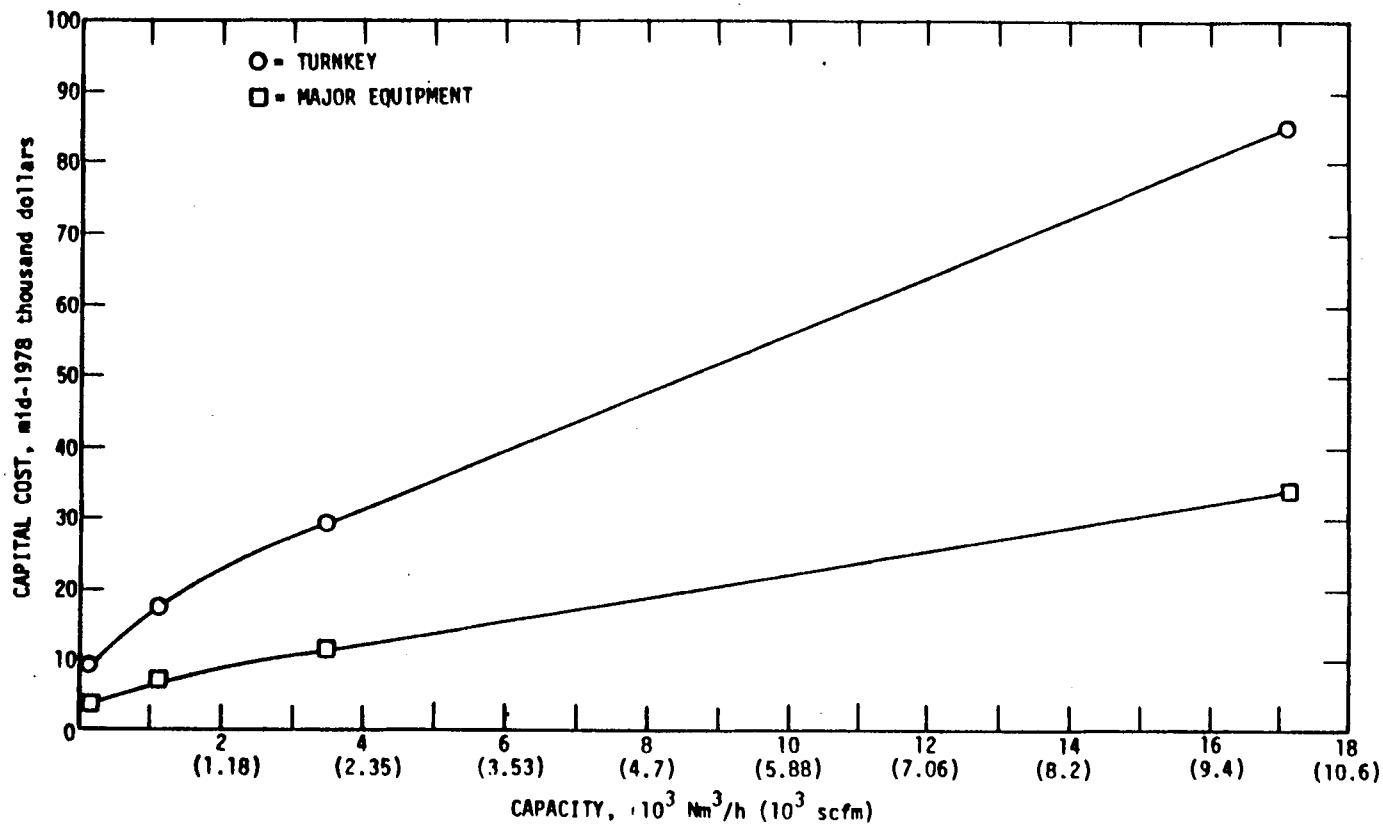


Figure 5-23. Capital cost of venturi scrubbers.

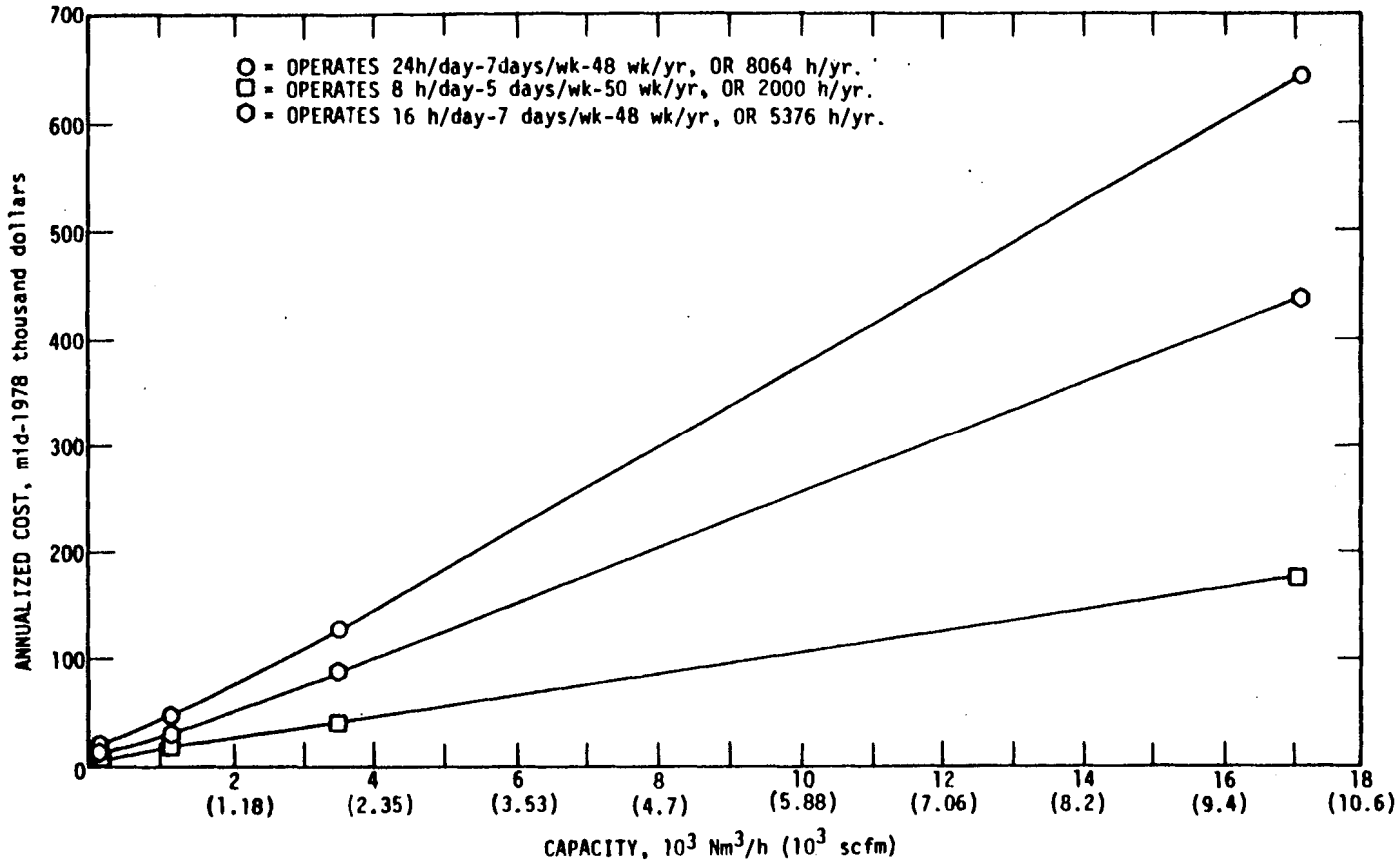
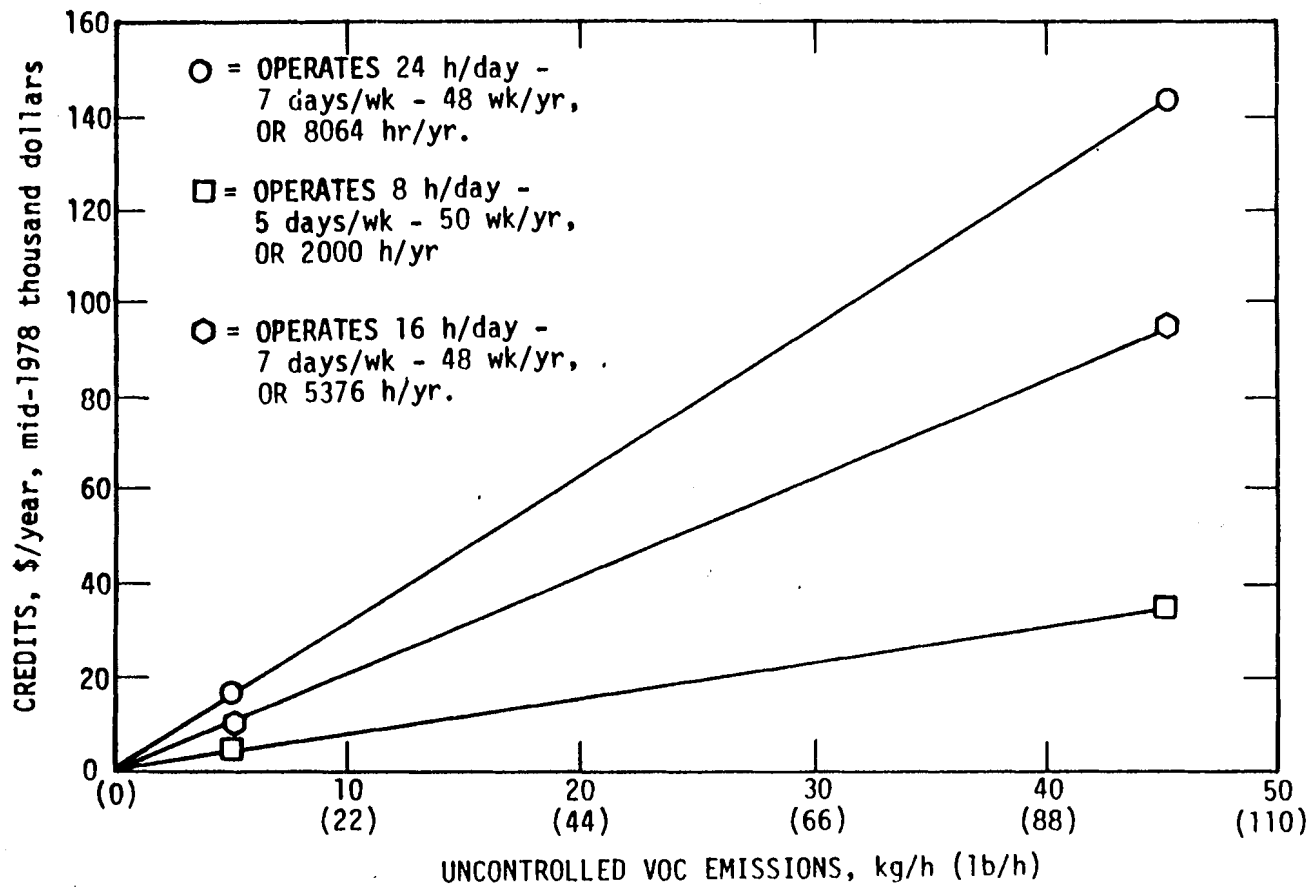


Figure 5-24. Annualized cost of venturi scrubbers.



NOTE: CHART BASED ON 95% RECOVERY OF $0.37/kg ($0.17/lb) ETHANOL VOC.

Figure 5-25. Credits to annualized cost from condensation and pressure control systems.

Table 5-4. Capital Cost Factors*

Cost Items	Conservation Vents	Pressure Tanks	Floating Roofs	Carbon Adsorbers	Incinerators	Condensers	Scrubbers
Direct Costs							
Equipment	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Instrumentation		0.10		0.05	0.05	0.05	0.05
Piping	0.39	0.30		0.16	0.05	0.10	0.15
Electrical		0.04		0.05	0.05	0.05	0.05
Foundations		0.20		0.07	0.02	0.05	0.05
Structural		0.10	1.10	0.07	0.10	0.05	0.05
Sitework		0.04		0.04	0.01	0.01	0.01
Insulation				0.03		0.05	
Painting		0.03	0.09	0.01	0.01	0.01	0.01
Ducts				0.10	0.20	0.10	
Offsite Oil Storage					0.18		
DIRECT COST SUBTOTAL	1.39	1.81	2.19	1.58	1.67	1.47	1.47
Indirect Costs							
For all control systems, indirect costs include the following items (listed as a percentage of Direct Cost Subtotal):	0.97	1.27	1.53	1.11	1.17	1.03	1.03
Field Overhead 15 percent							
Contractor's Fee 10 percent							
Engineering 10 percent							
Freight 2 percent							
Taxes 3.5 percent							
Allowance for shake-down 2 percent							
Spares 2.5 percent							
Testing 2.5 percent							
Contingency 20 percent							
Interest during construction 2.5 percent							
Installed Cost Factor	2.36	3.08	3.72	2.69	2.84	2.50	2.50

*As a fraction of equipment costs

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4. Control of Hydrocarbons from Miscellaneous Refinery Sources. Draft Document. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 27, 1977.

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13. Personal Communication between K.A. Napier, Oxy-Catalyst, Inc., Research-Cottrell, Inc., West Chester, Pennsylvania, and A.C. Knox, PEDCo Environmental, Inc., Cincinnati. February 1978.

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6.C ADVERSE EFFECTS OF APPLYING THE CONTROL TECHNOLOGY

This chapter addresses energy and environmental effects resulting from application of four major control techniques discussed in chapters 3 and 4.

6.1 CONDENSATION

The amount and type of energy required for a condenser will depend primarily on the type of system employed. In general, energy is required for powering the coolant refrigeration system, for transporting the gas stream, and for circulating the coolant. Energy for refrigeration depends on the type and operating temperature of coolant used which in turn is determined by the characteristics of waste gases condensed. Chapter 5 contains more information on energy use and costs for condensers.

A condenser will create few secondary environmental problems. Since the condensers use energy, there will be air pollutants emitted during energy generation. Use of contact condensers will increase plant water requirements and create an additional load on a wastewater treatment plant. Most condensers installed as retrofit control will be surface type rather than contact type.

6.2 SCRUBBING

Energy is needed to power scrubber pumps, cooling water system, and blower. Amounts of energy needed vary widely and depend on the following variables: waste gas VOC concentration, absorbent flow rate, gas flow rate, and type of scrubber used. Venturi scrubbers normally use more energy than tray tower or

packed bed scrubbers of comparable size.

Adverse environmental effects from operation of scrubbers include secondary air pollutants from electricity generation, increased water usage and increased VOC laden wastewater load to sewer or treatment plant.

6.3 ADSORPTION

The energy required for an adsorption system includes a supply of steam, air, or inert gas and sometimes a vacuum pump for carbon regeneration and electricity to pump cooling water and to power a gas blower. Adsorber energy requirements are dependent on waste gas flow rate, temperature of the waste gas to the adsorber, the type of VOC(s) treated, and VOC concentration. Figure 6-1 shows a plot of adsorber energy use versus waste gas flow rate.[1] The graph represents systems with the following characteristics:

1. dual fixed bed adsorber operating at 38°C,
2. steam regeneration and solvent recovery with condenser and decanter,
3. and VOC concentration at 25 percent LEL (lower explosive limit) or 15 percent LEL (for a 50/50 benzene-hexane mixture) and 77°C.

When steam is used to desorb the organic vapors from the adsorption bed, the majority of the total energy required is for the production of this steam. The amount of steam needed is approximately 3-6 lb steam/lb (3-6 kg/kg) organic vapor adsorbed. Steam regeneration has the advantage of leaving the bed wet, providing a heat sink for the heat of adsorption on the next cycle. Alternatives to steam regeneration are non-condensable gas regeneration and vacuum stripping. Energy requirements for this system are for heating and transporting the non-condensable gas, usually air.

Waste gases exiting the process are usually hotter than the optimum adsorption temperature. Energy in the form of a cooling water system is needed to cool this waste gas stream. For Figure 6-1 cooling water requirements were approximately 3 gallons per hour/SCFM (400 liters per hour/Nm^3 per minute).[2]

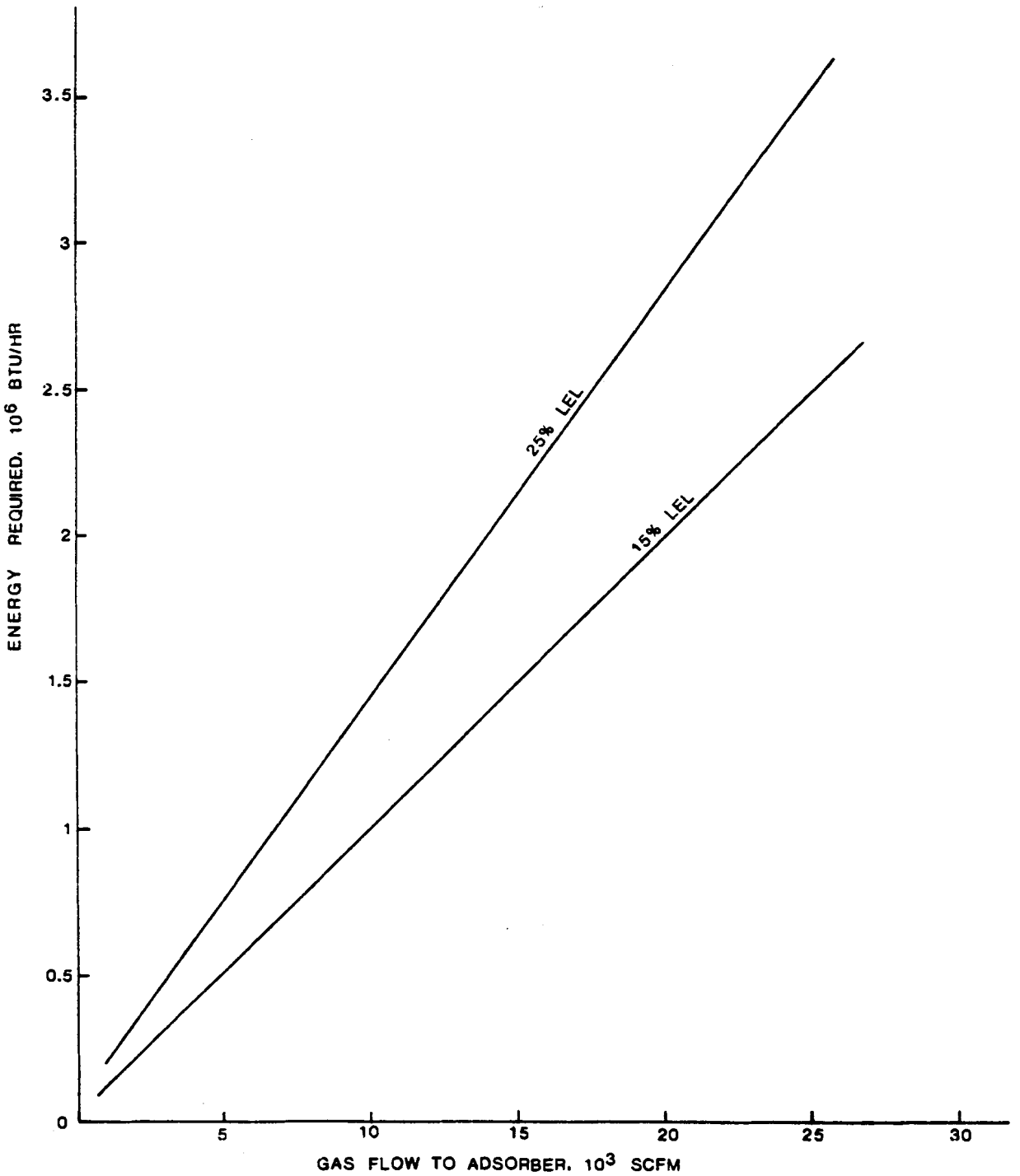

Figure 6-1. Energy Requirements for Adsorption-Solvent Recovery System

A blower is used to overcome the pressure drop encountered by the gas moving through the adsorption bed. The only requirement for the blower is electrical power. The amount of electricity consumed depends upon the type and configuration of the packing.

There will be some secondary impacts from use of an adsorption unit. If a steam desorption cycle is used and the recoverable VOC are soluble in water, then the condensate from desorption will contain VOC. This is an additional wastewater stream that increases treatment plant or sewer load.

Secondary air pollutants will result from generation of electricity and steam used to power an adsorber. The amount of air pollutants created depends on the type of fuel used in the power plant.

If carbon is not regenerated, spent carbon must be disposed of and will add to the amount of solid waste produced by the plant.

6.4 INCINERATION

Energy requirements for a typical incinerator system includes supplemental fuel and a gas blower to convey the waste gases. The amount of supplemental fuel needed depends on waste gas temperature, VOC concentration in the gas, incineration temperature, and type of heat recovery employed. Table 6-1 lists fuel requirements for several different incineration situations.[3]

Possible adverse environmental effects from incineration include generation of sulfur oxides, nitrogen oxides, and carbon monoxide during combustion of the waste gas. In catalytic systems, the catalyst must be replaced periodically as performance decreases over a period of time. This creates an additional solid waste problem for the plant.

Table 6-1. BURNER REQUIREMENTS FOR INCINERATORS IN 10^6 BTU/HR[a]

THERMAL INCINERATORS	0 percent LEL	5 percent LEL	15 percent LEL	25 percent LEL
No Heat Recovery				
5,000 scfm	8.00	7.10	5.32	3.56
15,000 scfm	24.00	21.31	15.98	10.66
Primary Heat Recovery (35 percent efficient)				
5,000 scfm	5.07	4.19	2.42	0.68
15,000 scfm	15.40	12.71	7.34	1.96
CATALYTIC INCINERATORS				
No Heat Recovery				
5,000 scfm	2.95	2.95	2.95	2.53
15,000 scfm	8.85	8.85	8.85	7.12
Primary Heat Recovery (35 percent efficient)				
5,000 scfm	1.91	1.63	1.11	0.19
15,000 scfm	5.73	4.89	3.32	0.57

[a]Based on 70°F waste gas temperature; 1400°F outlet temperature for thermal incinerator; 1200°F outlet temperature for catalytic incinerator. Waste gas is toluene.

6.5 REFERENCES

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2. Reference 1.
3. CE Air Preheater, Industrial Gas Cleaning Institute, Report of Fuel Requirements, Capital Cost and Operating Expense for Catalytic and Thermal Afterburners, EPA-450/3-76-031, September, 1976.

7.0 COMPLIANCE TESTING METHODS AND MONITORING TECHNIQUES

A realistic regulatory approach is a combination of operating and equipment standards for significant VOC sources within this industry. Compliance methods and monitoring techniques then, will simply assure that the operating and equipment standards are being maintained.

7.1 OBSERVATION OF CONTROL EQUIPMENT AND OPERATING PRACTICES

Regulations expressed as equipment and operating standards can be enforced by verifying that the equipment has been designed and installed properly and that it is being operated properly.

7.1.1 Adsorption

Most carbon adsorption instrumentation has been used to program the regeneration cycles. The cycle is usually adjusted so that regeneration is started before breakthrough occurs in the carbon bed. A sensing device should be used, to assure that breakthrough does not go undetected. The monitor should be connected to an alarm bell, light, or device to alert operating personnel immediately that breakthrough has occurred.

7.1.2 Condensation

Temperature sensors can be placed in the exit gas stream from a condenser as an indicator of how well the condenser is operating. Indicated temperature can be checked against design temperature and conditions observed during tests.

7.1.3 Incineration

All incinerators should be equipped with temperature indicators. Records may be required in the range of 490°-820°C (1200-1800°F) for thermal incinerators, 204°-426°C (400-800°F) for catalytic units. Residence time and turbulence are fixed by incinerator design and should be checked before a unit is built. Aging, masking, or poisoning of catalyst in catalytic units would be reflected in a decreased temperature downstream of the bed.

7.1.4 Scrubbing

Scrubbers should be equipped with flow meters to measure the flow rate of the scrubbing medium. The pressure drop across the scrubber may also be a useful parameter to measure, especially for venturi scrubbers. Pressure drops deviating from design conditions can indicate plugging problems, channeling of packing, and other abnormal situations that may reduce VOC removal efficiency. As an alternate to using flow meters on systems recirculating the scrubbing medium, the back pressure may be measured. This coupled with the pressure drop across the scrubber will provide suitable indication of flow.

7.2 EMISSION TESTS

Emission measurement tests of off-gas streams from carbon adsorbers, scrubbers, or condensers may occasionally be necessary to evaluate the control efficiency of a system. Measurements of velocity and flow rates may be determined for larger stacks using EPA Tests Methods 1 and 2. For stacks less than 0.3 meter (12 inches) diameter, other flow determining methods may have to be used to provide reasonable accuracy. Gas chromatographic techniques for organic solvents are discussed in EPA 450/2-76-028, "Control of Volatile Organic Emissions from Existing Stationary Sources, Volume I: Control Methods for Surface Coating Operations," November, 1976.

APPENDIX A

TABULAR PRESENTATION OF SOLVENT DISPOSITION DATA SUBMITTED BY THE PHARMACEUTICAL MANUFACTURERS ASSOCIATION

TABLE A-1. COMPILATION OF DATA SUBMITTED BY THE PMA FROM 26 MANUFACTURERS OF ETHICAL DRUGS[1]
(metric tons)

Type of Volatile Organic Compound	Annual Purchase	Disposition						Total	Solvent Recovery
		Air Emissions	Sewer	Incineration	Contract Haul	Disposal*	Product		
Methylene Chloride	10,000	5,310	455	2,060	2,180	-	5	82,320	73,400
Skelly Solvent B (hexanes)	1,410	410	23	980	-	-	-	1,500	90
Methanol	7,960	2,480	3,550	1,120	410	30	340	1,117,600	-
Toluene†	6,010	1,910	885	1,590	1,800	-	-	30,040	23,850
Acetone†	12,040	1,560	2,580	4,300	770	-	2,210	52,100	40,760
Dimethyl Formamide†	1,630	1,350	60	380	120	-	-	7,000	5,100
Ethanol	13,230	1,250	785	915	200	-	10,000	20,740	7,570
Isopropanol†	3,850	1,000	1,130	1,150	470	25	3,090	10,770	3,880
Amyl Alcohol†	1,430	775	-	-	0	-	9	77,700	76,900
Ethyl Acetate	2,380	710	1,110	480	80	-	-	3,110	715
Chloroform	500	280	23	-	175	17	-	1,710	1,210
Benzene†	1,010	270	350	150	80	-	90	21,440	20,500
Ethyl Ether	280	240	12	-	30	-	-	111,100	110,800
Methyl Isobutyl† Ketone	260	260	-	-	-	-	65	6,470	6,160
Carbon Tetrachloride	1,850	210	120	1,510	-	-	-	1,850	-
Xylene†	3,090	170	510	1,910	140	-	3	12,140	9,400

TABLE A-1. COMPILATION OF DATA SUBMITTED BY THE PMA FROM 26 MANUFACTURERS OF ETHICAL DRUGS (metric tons)

Type of Volatile Organic Compound	Annual Purchase	Disposition						Total	Solvent Recovery
		Air Emissions	Sewer	Incineration	Contract Haul	Disposal*	Product		
Methyl Ethyl Ketone	260	170	30	60	-	-	-	6,720	6,460
Trichloroethane	135	135	-	-	-	-	-	135	-
Hexane†	530	120	-	100	475	-	-	26,370	25,670
Amyl Acetate	285	120	165	-	-	-	-	3,800	3,510
Isopropyl Acetate	480	105	45	230	-	-	-	2,230	1,840
Methyl Cellosolve	195	90	100	-	-	-	-	550	360
Butanol†	320	85	30	5	130	-	110	1,390	1,040
Isobutyraldehyde	85	40	40	-	-	-	-	225	145
Acetonitrile	35	30	6	-	-	-	-	165	125
Tetrahydrofuran	4	-	-	4	-	-	-	4	-
Isopropyl Ether	25	12	12	-	-	-	-	37	12
Acetic Acid	930	12	770	-	-	-	160	1,980	1,040
Acetic Anhydride	1,265	8	550	-	-	-	410	1,265	300
Dimethylacetamide	95	7	-	-	90	-	-	95	-
Formaldehyde	30	5	20	-	-	-	1	25	-
Dimethylsulfoxide	750	4	210	535	-	-	-	5,510	4,760
1, 4-Dioxane	43	2	-	-	41	-	-	43	-

TABLE A-1. COMPILATION OF DATA SUBMITTED BY THE PMA FROM FROM 26 MANUFACTURERS OF ETHICAL DRUGS
(metric tons)

Type of Volatile Organic Compound	Annual Purchase	Disposition						Total	Solvent Recovery
		Air Emissions	Sewer	Incineration	Contract Haul	Disposal*	Product		
o-Dichlorobenzene	60	1	60	-	-	-	-	7,120	7,060
Diethyl Carbonate	30	1	20	-	-	-	7	30	-
Blendan (Amoco)	530	-	-	-	-	-	530	530	-
Ethyl Bromide	45	-	45	-	-	-	-	7,215	7,170
Cyclohexylamine	3,930	-	-	-	-	-	3,930	3,930	-
Methyl Formate	415	-	310	-	50	-	60	1,550	1,130
Formamide	440	-	290	-	110	-	30	440	-
Ethylene Glycol	60	-	60	-	-	-	-	120	60
Diethylamine	50	50	3	-	-	-	-	350	300
Freons	7,150	6	-	-	-	-	7,145	7,150	-
Diethyl-ortho Formate	54	-	21	-	-	-	33	54	-
Pyridine	3	-	3	-	-	-	-	3	-
Polyethylene Glycol 600	3	-	-	-	-	-	3	3	-
TOTALS	85,170	19,190	14,380	17,480	7,350	72	27,700	1,636,100	441,320

[1]Source - 26 member companies of the Pharmaceutical Manufacturers Association (PMA) reported these data which they feel represent 85 percent of the volatile organic compounds used in their operations; these reporting companies account for approximately 53 percent of the 1975 domestic sales of ethical pharmaceuticals.

*Deepwell or landfill.

†Annual disposition does not closely approximate annual purchase.

APPENDIX B

EQUATIONS FOR ESTIMATING EMISSION RATES FROM PROCESS EQUIPMENT

APPENDIX B

VOC EMISSION CALCULATIONS

B.1 INTRODUCTION

The following methods have been developed to calculate the uncontrolled emissions from the following pharmaceutical process operations. These process operations are:

I. Charging

II. Evacuation (Depressuring)

III. Nitrogen or Air Sweep

IV. Heating

V. Gas Evolution

VI. Vacuum Distillation

VII. Drying

Some simplifying assumptions have been made; the general assumption for most of the following calculations is that the Ideal Gas Law applies. In applying these equations, it is important to use the correct number of operating hours for calculating daily or annual emission estimates.

Equation No. 1: $$n = \frac{PV}{RT}$$

where:
n = # of pound moles;
P = absolute pressure, in mm Hg;
V = volume, in $ft.^3$;
T = temperature, in ^oK; ($^oK = {}^oC + 273$)
R = gas law constant, 999 $\left(\frac{ft^3\ mm\ Hg}{^oK\ lb\ moles}\right)$

The Ideal Gas Law is used to calculate the lbs/hr of VOC emitted, as follows:

Equation No. 2: $$Se = \frac{Pi\ (Xi)\ Vr\ (MWi)}{RT}$$

where:
Se = lbs/hr of VOC emitted;
Pi = vapor pressure of VOC at T, in mm Hg;
Xi = mole fraction of VOC in liquid mix;
Vr = rate of displacement, in ft^3/hr;

$$R = 999 \frac{\text{mm Hg ft}^3}{\text{lb mole } ^oK}$$
$$T = \text{temperature in } ^oK;$$
$$MWi = \text{molecular weight of VOC, in lbs/lb mole.}$$

The mole fraction, Xi, above must be included in the case of a liquid mix.

Mole fraction is calculated as follows:

Equation No. 3:

$$Xi = \frac{\text{moles of i in liquid mix}}{\text{total moles of liquid mix}}$$

where: Xi = mole fraction of i;
i = denotes the VOC in question

For one component systems, Xi = 1.

The vapor pressure, Pi, is calculated using Antoine's equation or taken from tables of vapor pressure.

Equation No. 4:

$$\text{Log}_{10}Pi = a - \left(\frac{b}{c+Ti}\right)$$

where: Pi = vapor pressure of the VOC (mm Hg);
Ti = temperature of the air containing the VOC vapor (^oC);
a,b,c = Antoine's equation constants. See Lange's Handbook of Chemistry[1]

Vapor Pressure Tables

Vapor pressures from Perry's[2] are interpolated or extrapolated using a Cox chart. An example is included as Figure 4-1.

B.2 METHODS AND CALCULATIONS

I. Charging

This method can be used to calculate emissions from a vessel containing a liquid VOC when a liquid is charged into the vessel.

Assumptions - The volume of gas displaced from the vessel is equal to the volume of liquid charged into the vessel. The air displaced from the vessel is saturated with the VOC vapor at the exit temperature. (Note: if data are available to calculate concentration, then this can be used in place of saturation.)

Calculations -

1. Calculate the rate of air displacement in ft^3/hr:

Equation No. 5: $Vr = Lr\ (0.134\ ft^3/gal)\ (60\ \frac{min}{hr})$

where: Vr = the rate of air displacement, in ft^3/hr;
Lr = liquid pumping rate, in gpm.

2. Determine the mole fraction of each VOC in the vessel during the pumping, Xi, using Equation No. 3.
3. Calculate the vapor pressure of each pure VOC, Pi, using Equation No. 4.
4. Calculate the lbs/hr of each VOC emitted, Se, using Equation No. 2.

II. Evacuation (Depressuring)

This method is used to calculate emissions from the evacuation (or depressuring) of any vessel containing a VOC and a "noncondensable." Usually the vessel will be a still and the "noncondensable" will be air or nitrogen.

Assumptions - The absolute pressure in the vessel decreases linearly with time. There is no air leakage into the vessel. The composition of the VOC mix does not change during the evacuation (or depressuring) and there is no temperature change. The air displaced is saturated with the VOC vapor at the vessel temperature.

Calculations -

1. Calculate the mole fraction, Xi, for each VOC in solution using Equation No. 3.
2. Calculate the vapor pressure, Pi, of each VOC at the vessel temperature using Equation No. 4.
3. Calculate the initial volume of the air in the vessel:

$$Vi = \left[\frac{Pa_1 - \Sigma(PiXi)}{760}\right] F_s$$

where: Vi = the initial air volume in the vessel, ft^3 (standard);

$\Sigma (PiXi)$ = the sum of the products of the vapor pressures and the mole fractions of each VOC in the solution;

Pa_1 = initial pressure, in mmHg,

760 = atmospheric pressure, in mmHg.

F_s = free space in the still, in $ft.^3$

4. Calculate the final air volume in the vessel:

$$V_f = \left[\frac{Pa_2 - \Sigma (PiXi)}{760}\right] F_s$$

V_f = the final air volume in vessel, in ft^3 (standard);

where: Pa_2 = final air pressure in the vessel, mmHg.

5. Calculate the rate of air removal from the vessel:

$$Vr = \frac{Vi - Vf}{t}$$

where: Vr = the rate of air removal from the vessel, in ft^3/hr;

t = time of evacuation of vessel, in hrs.

6. Calculate initial ratio of air to total VOC vapor:

$$Ri = \frac{760 - \Sigma (PiXi)}{\Sigma (PiXi)}$$

where: $Ri = \frac{\text{moles air}}{\text{moles VOC}}$

7. Calculate final ratio of moles air to moles total VOC vapor:

$$R_f = \frac{Pa_2 - \Sigma (PiXi)}{\Sigma (PiXi)}$$

where: $R_f = \frac{\text{moles air}}{\text{moles VOC}}$

8. Calculate the average ratio of moles air to moles total VOC vapor:

$$Ra = \frac{Ri + Rf}{2}$$

9. Calculate volume of total VOC vapor discharged, ft^3/hr:

$$VRS = \frac{Vr}{Ra}$$

where: VRS = VOC emission from the system, ft^3/hr.

10. Calculate the emission rate, Se, for each VOC in lbs/hr using Equation No. 2 substituting VRS for Vr and use pressure of one atmosphere.

III. Nitrogen or Air Sweep

This method is used to calculate emissions when nitrogen, air, or other "noncondensable" is used to purge or sweep a vessel or other device.

Assumptions - The nitrogen gas exiting the vessel is saturated with VOC vapor at the exit temperature.

Calculations -

1. Calculate the rate of nitrogen sweep in ft^3/hr:

Equation No. 6: $Vr_1 = Ns \times 60$ min/hr

where: Vr_1 = the rate of nitrogen sweep in ft^3/hr, standard;

Ns = the rate of nitrogen sweep in ft^3/min, standard.

2. Calculate the mole fraction, Xi, for each VOC using Equation No. 3.

3. Calculate the vapor pressure, Pi, for each VOC at the exit temperature using Equation No. 4.

4. Calculate the rate of total gas displaced from the vessel, ft^3/hr.

Equation No. 7:

$$Vr_2 = Vr_1 \left[\frac{760}{760 - \Sigma(PiXi)}\right]$$

where: Vr_2 = rate of gas displaced from vessel, in ft^3/hr, standard;

Vr_1 = rate of nitrogen sweep, in ft^3/hr;

$\Sigma(PiXi)$ = the sum of the products of the vapor pressures and mole fractions for each VOC;

760 = vapor pressure of nitrogen sweep , in mmHg.

5. Calculate the rate of VOC emission in lbs/hr, Se, for each VOC using Equation No. 2 substituting Vr_2 for Vr.

IV. Heating

This method is used to calculate the emissions from the heating of a still containing a VOC and a "noncondensable," usually air.

Assumptions - The moles of air displaced from the still are a result of (1) the expansion of air upon heating and (2) an increase in VOC vapor pressure. The moles of air displaced from the receiver are equal to the moles of air displaced from the still. The air displaced from the receiver is saturated with VOC vapor in equilibrium with the VOC mixture in the receiver at the temperature of the receiver.

Calculations -

1. Calculate the mole fraction, Xi, for each VOC in the still using Equation No. 3.
2. Calculate the vapor pressure, Pi, of each pure VOC at the initial temperature (T_1) using Equation No. 4.
3. Calculate the initial pressure of the air in the still:

Equation No. 8: $$Pa_1 = 760 - \Sigma(PiXi)_{T_1}$$

where: Pa_1 = the initial air pressure in the still in mmHg ;

$\Sigma(PiXi)_{T_1}$ = the sum of the products of the vapor pressures and the mole fractions of each VOC at the initial temperature;

760 = atmospheric pressure, in mmHg.

4. Calculate the vapor pressure, Pi, of each pure VOC at the final temperature (T_2) using Equation No. 4.
5. Calculate the final pressure of air in the still:

Equation No. 9: $$Pa_2 = 760 - \Sigma(PiXi)_{T_2}$$

where: Pa_2 = final air pressure in the still, in mmHg;

$\Sigma(PiXi)_{T_2}$ = sum of the products of the vapor pressures and the mole fractions for each VOC at the final temperature;

760 = atmospheric pressure, in mmHg.

VI. Vacuum Operations

This method is used to calculate emissions from vacuum operations. Air leaks into the system and becomes saturated with the VOC vapor at the receiver temperature and is subsequently discharged by the jet to the atmosphere.

The air leak rate is best determined by closing off the jet from the still, condenser, and receiver and noting the rise in absolute pressure over a short period of time. The air leak rate can then be calculated using Equation No. 14 below. Maximum air leakage has also been estimated for "commercially tight systems" for various system volumes and pressures.[3]

Assumptions - The air that leaves the system is saturated with solvent vapor at the receiver temperature.

Calculations -

1. Calculate the air leak rate into the system:

Equation No. 14:

$$Vr_1 = \frac{273\ Fs}{Tt}\left(\frac{P_2 - P_1}{760}\right)$$

where:

Vr_1 = air leak rate, in ft^3/hr (standard);

Fs = total free space under vacuum, in $ft.^3$;

P_1 = absolute pressure at start of test, in mmHg;

P_2 = absolute pressure at end of test, in mmHg;

t = time of test, in hrs;

T = temperature of still, in °K;

273 = temperature at standard conditions, in °K.

2. Calculate the rate of VOC emissions, lbs/hr:

Equation No. 15:

$$Se = MWs\ \frac{Vr_1}{359}\left(\frac{P\ system}{P\ system - Ps} - 1\right)$$

where:

Se = rate of VOC emission, in lbs/hr;

P system = absolute pressure of receiver, in mmHg;

Ps = vapor pressure of the VOC at the receiver temperature, in mmHg;

MWs = molecular weight of VOC, in lb/lb mole;

359 = the volume that 1 lb mole of gas occupies at standard conditions, in $ft.^3$.

3. If leak rate is obtained in lbs/hr from reference 3, calculate VOC emission lbs/hr:

Equation No. 16:

$$Se = \frac{La\ MWs}{29}\left(\frac{P\ system}{P\ system - Ps} - 1\right)$$

where: La = leak of air into the systems, in lb/hr;
29 = molecular weight of air, in lb/lb mole.

VII. Drying

This method is used to calculate VOC emissions from either batch or continuous drying operations. Although it is possible to determine emissions from an analysis of the dryer off-gas, it is usually simpler and more accurate to use a material balance.

Assumptions - Samples of the product before and after the dryer are analyzed for VOC content.

Calculations -

1. Calculate the rate of VOC emissions, lbs/hr:

Equation No. 17:

$$Se = \frac{B}{t}\left(\frac{PS_1}{100 - PS_1} - \frac{PS_2}{100 - PS_2}\right)$$

where: Se = rate of VOC emission, lbs/hr;
B = weight of batch (dry), lbs;
t = time of drying operation, hrs;
PS_1 = percent of VOC in wet material into dryer;
PS_2 = percent of VOC in less wet material from dryer.

B.3 REFERENCES

1. Lange's Handbook of Chemistry, John A. Dean, Editor, 11th Edition, 1973, McGraw-Hill Book Company, New York, New York, pp. 10-31 to 10-45.

2. Chemical Engineers Handbook, Perry and Chilton, Editors, Fifth Edition, 1973, McGraw-Hill Book Company, New York, New York, p. 3-54.

3. Power, R. B., "Steam-Jet Air Ejector," Hydrocarbon Processing and Petroleum Refiner, March, 1964, Vol. 43, No. 3., p. 59.

APPENDIX C

Aids to Calculating Storage Tank Emissions

APPENDIX C

Below are graphs depicting variation in adjustment factor (C) and turnover factor (K_N) for a range of situations. These graphs are presented to aid the reader in making emission calculations for various storage situations.

The graphs are taken from the EPA publication entitled "Supplement No. 7 for Compilation of Air Pollutant Emission Factors, Second Edition" printed in April 1977.

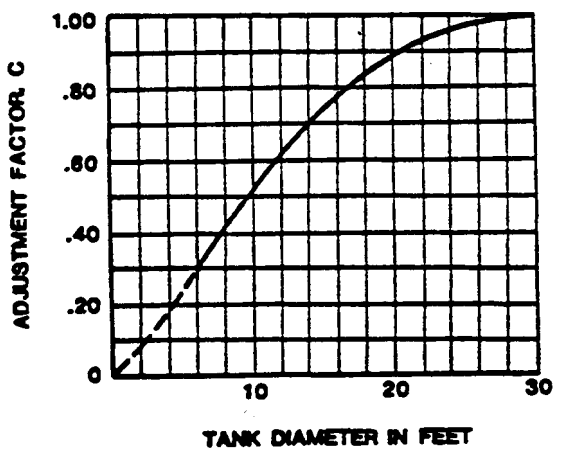
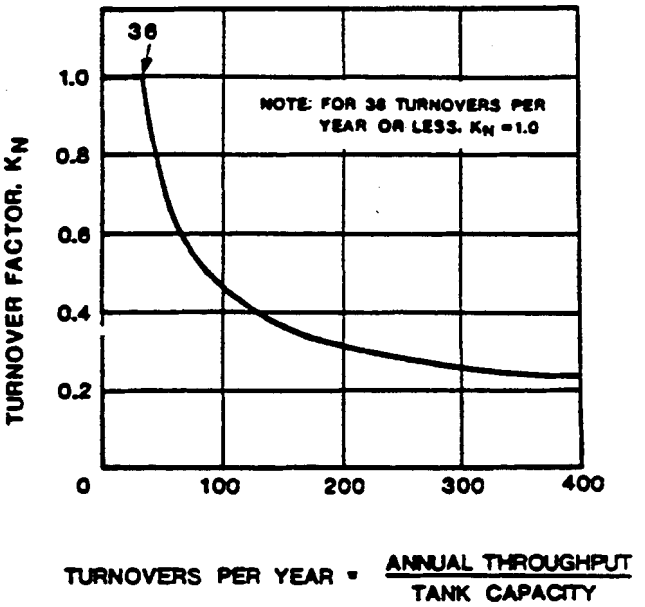


Figure 4.3-10. Adjustment factor (C) for small diameter tanks.



Turnover factor (K_N) for fixed roof tanks.