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ENVIRONMENTAL STUDY OF THE PETROCHEMICALS INDUSTRY

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SECTORAL WORKING PAPERS

In the course of the work on major sectoral studies carried out by the UNIDO Division for Industrial Studies, several working papers are produced by the secretariat and by outside experts. Selected papers that are believed to be of interest to a wider audience are presented in the Sectoral Working Papers series. These papers are more exploratory and tentative than the sectoral studies. They are therefore subject to revision and modification before being incorporated into the sectoral studies.

This paper was prepared by Prof. E.J. Middlebrooks, UNIDO consultant, as a contribution to the Third Consultation on the Petrochemical Industry. The views expressed are those of the consultant and do not necessarily reflect the views of the UNIDO secretariat.

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EXECUTIVE SUMMARY

Petrochemicals include a wide variety of compounds which are listed in several international standard industrial classifications, and the following six industries were included in this study: synthetic rubbers, synthetic fibers, organic petrochemicals, plastics, carbon black and surfactants. Primary petrochemicals, produced from raw materials such as crude petroleum, natural gas, heavy fractions such as fuel oil, coal and biomass, include olefins, aromatics, syngas and carbon black. These first generation compounds are used as feedstocks in the synthesis of intermediate and third generation petrochemical products.

A wide variety of chemical reactions and unit processes may be included in petrochemical processes. Currently more than 500 different processing sequences are used in the petrochemical industry. This leads to a very complex waste problem.

Air Pollution Control

Air pollutants produced by petrochemical manufacturing practices include sulfur oxides, nitrogen oxides, carbon monoxide, particulate matter, odors and a wide variety of toxic organic compounds. Petrochemical plants discharge pollutants into the atmosphere that are either controlled or fugitive in nature. Controlled emissions are released through stacks and/or vents, and detailed information is available on emissions composition and rate of release. Emissions from points other than stacks and vents are considered fugitive emissions. Fugitive emissions may occur due to accidents, inadequate maintenance, poor planning, and from a range of process equipment such as valves, pumps, flanges, compressors and agitators.

Control of air pollutants emitted from controlled sources has been well studied. Many texts are available detailing the design of pollution control equipment for these sources.[1,2,3,4,5,6,7,8]

Valves, flanges and pump seals are the biggest contributors to fugitive emissions at petrochemical plants. Proper selection and maintenance of valves, flanges and pumps will reduce fugitive emissions and eliminate potential product losses which have been estimated to be over US $1800/day at a typical olefin plant. Techniques to measure fugitive emissions rates from petrochemical plants have been described by Hughes et al.[9] and Siversten.[10]

In a survey of petrochemical plants in the United States (US) the US Environmental Protection Agency determined that the manufacture of carbon black resulted in the emission of the largest mass of air pollutants with the manufacture of acrylonitrile a distant second. The mass of emissions is not the only criterion that must be considered in assessing the impact of petrochemical plant air pollutant emissions. The toxicity of emissions, odors and the persistence of the emitted compounds are some additional considerations.

The main difference between air emissions from petrochemical plants and other industrial processes is the emission of a wide variety of hydrocarbon compounds. Many of these hydrocarbons are considered toxic, and thus special precautions must be taken for their control. Hydrocarbon emission reduction systems at petrochemical plants are described by Pruessner and Broz,[11] Kenson[12] and Mashey and McGrath.[13]

Some techniques to reduce hydrocarbon emissions without emission control systems include: (1) appropriate specification, selection and maintenance of seals in valves, flanges and pumps, (2) installation of floating roof tanks to control evaporation of light hydrocarbons, (3) installation of vapor recovery lines to vents of vessels that are continually filled and emptied, (4) manifolding of purge lines used for start-ups and shutdowns to vapor recovery or flare systems, (5) venting of vacuum jet exhaust lines to vapor recovery systems, (6) shipment of products by pipeline, (7) covering waste separators, and (8) use of steam or air injection at flares.

Costs of air pollution control systems vary widely with the process and degree of control desired. The higher the removal rate required, the higher the removal cost per unit mass of pollutant removed. Many techniques which reduce air emissions produce economic benefits by reducing product loss and recovering usable compounds.

Wastewater Treatment and Disposal

Wastewater streams in the petrochemical production industry may be categorized into six source components:

(1) wastes discharged directly from production units during normal operation.

(2) utility operations such as blow down from energy production and cooling systems.

(3) sanitary sewage from administrative areas, locker rooms, shower and restroom facilities, and food handling areas.

(4) contaminated stormwater runoff from process areas.

(5) ballast water discharged from tankers during product handling.

(6) miscellaneous discharges from spills, turnarounds, etc.

The most commonly used method for predicting the quality and quantity of petrochemical production wastewaters is to study each individual unit process, and relate the quantity and quality of the wastestreams produced to the production units. For example, the isopropanol stripping still and intermediate flash column used in acetone production produces approximately 2.2 pounds of Chemical Oxygen Demand (COD) per ton of acetone produced. This is a difficult task because small changes in unit process operating conditions alter the characteristics of the wastestream produced.

Gloyna and Ford[14] conducted a survey designed to characterize petrochemical production wastes. As a part of this survey many petrochemical wastestreams were described in terms of conventional pollutional parameters such as acidity, alkalinity, color, turbidity, pH, Biochemical Oxygen Demand (BOD), COD, Total Organic Carbon (TOC), solids, surface activity, taste, odor, and temperaure. The characteristics of the wastestreams vary so widely it is impossible to make any generalizations. It is important to note, however, that petrochemical wastestreams may be very significant sources of many toxic substances.

The design of wastewater treatment facilities for petrochemical facilities will not be reliable unless wastewaters have been fully characterized and the performance characteristics of alternative treatment processes have been evaluated by treatability studies and pilot plant operations. Treatability studies should establish the effects of operational parameters such as hydraulic detention time, sludge age and temperature on organic removal rates, oxygen requirements, sludge production, sludge characteristics and process stability. Treatability studies can also identify wastestreams which should be treated separately to enhance process performance.

The unit processes capable of treating petrochemical manufacturing plant wastewaters are as varied as the unit processes used in the manufacturing plants themselves. Studies have shown that there are seldom cost effective alternatives to biological treatment used in conjunction with physical-chemical pretreatment and/or polishing where needed.[15,16] Biological treatment coupled with post-filtration has been defined by the US Environmental Protection Agency as the "best practicable technology" currently available for treating petrochemical processing wastewaters.

Special attention must be given to the removal of toxic substances from petrochemical processing wastewaters. These toxic substances frequently interfere with biological treatment and frequently are not removed during biological treatment. Removal of these toxics may require the use of other treatment processes such as activated carbon adsorption, chemical oxidation, steam stripping, solvent extraction, polymeric adsorption, chemical coagulation and sedimentation, wet air oxidation or pyrolysis.

The petrochemical industry lends itself to controlling pollution through process improvement rather than pollution abatement. Five alternative solutions may be developed for a pollution problem in the petrochemical industry. First, process modification to reduce the volume or mass of waste. Second, some wastes may be recovered as salable coproducts. Third, wastestreams can be recycled after some process modification for conversion to prime product or for reuse in the process as a reagent or intermediate. Fourth, the waste may be usable as a fuel. Fifth, and least desirable, wastes may be treated in waste treatment processes where they are converted to less harmful states and/or dispersed in quantities which may be assimilated by the environment. Many processes for wastewater treatment fitting into the first four categories are available in the petrochemical industry. Many techniques are also available for reducing the amount of water used at petrochemical plants, thus reducing the amount of wastewater to be treated.

As in air pollution control wastewater treatment costs vary significantly; however, as pointed out previously, the basic approach to pollution control will significantly affect pollution control costs. Many systems which have been designed to reduce pollution by eliminating the pollution at the source, recovering materials which have some economic benefit, or conserve water have resulted in an economic benefit rather than a cost. Burgess[17] reported that one US petrochemical company installed 450 pollution abatement projects with a total cost of US $20,000,000 in 1971. The net annual savings from these projects was estimated to be US $6,000,000, with an annual return on investment of 30 percent.

Solid Waste Management

Solid wastes in the petrochemical industry may occur as actual solids such as waste plastics, paper or metal; as semi-solids such as tars and resins, and as suspended and dissolved solids such as waste polymers and inorganic salts. These wastes include water treatment sludges, cafeteria and lunchroom wastes, plant trash, incinerator residues, plastics, metals, waste catalysts, organic chemicals, inorganic chemicals, and wastewater treatment solids. The materials may be characterized as combustible or non-combustible, organic or inorganic, inert or biodegradable, dry or mixed with either aqueous or nonaqueous liquids.

The solid wastes generated by the petrochemical process may be managed by many different methods which are dependent on existing condtions such as: (1) characteristics of the wastes (volume, weight, density, rate of production, toxicity, biodegradability, etc.), (2) potential value of salvaged materials, (3) adaptability of the disposal method to the waste of interest, and (4) availability of land and expected land use patterns. Almost every petrochemical plant has some form of solid waste handling and/or disposal facilities on the plant premises. A recent survey of the petrochemical industry disclosed that 90 percent of the solid wastes generated at petrochemical processing plants was disposed of on plant premises.[18]

Solid and semi-solid waste materials generated by the petrochemical industry may be disposed of by several techniques including: salvaging and reclamation, open dump burning, no-burning dump, landfill, land farming, lagooning, incineration, and ocean dumping.

Salvaging and reclamation operations are environmentally acceptable operations in which waste materials are collected and segregated for reclamation and reuse. Materials such as scrap metal, wood, spent catalyst, spent acids and caustics, contaminated oils and other hydrocarbons, plastics and polymers, rubbers and carbon black have been recovered and reused in salvage operations in the petrochemical industry.[19]

Open dump burning and no-burn dumping are normally considered unacceptable alternatives since they pose significant threats to public health and environmental quality.

Sanitary landfills provide the most economic environmentally acceptable method for the disposal of most non-toxic solid and semi-solid wastes generated at petrochemical processing plants.[19] In addition to the economic advantage, another advantage of sanitary landfills is that a low degree of technical expertise is required for operation. Soil and hydrogeological conditions must be favorable to prevent contamination of surface and groundwater supplies by water which may leach through the disposal site. Land-farming, lagooning, incineration and open-dumping may also prove to be acceptable alternatives under the proper conditions.

Hazardous Wastes Control

Many wastes generated by the petrochemical industry must be considered hazardous wastes. Hazardous wastes may be defined as any waste or combination of wastes which pose a substantial hazard or potential hazard to the health of humans or other living organisms because the wastes are lethal, nondegradable, persistent in nature, can be biologically magnified or otherwise cause detrimental cumulative effects.[20] The US EPA characterizes a waste as hazardous if it possesses any one of the following four characteristics: (1) ignitability, (2) corrosivity, (3) reactivity, or (4) toxicity. Hazardous wastes have been identified in petrochemical wastestreams by Hedley et al.,[21] Process Research, Inc.[22] and Wise and Fahrenthold.[23]

There are hundreds of documented cases of damage to life and the environment resulting from the improper management of hazardous wastes. These wastes are frequently bioaccumulated, very persistent in the environment and often toxic at very low concentrations. The source of the vast majority of these cases may be traced back to some part of the petrochemical industry.

Currently most of the process wastes from the petrochemical manufacturing industry are ultimately destined for land disposal or in some cases incineration. However, there are many alternative treatment processes available which may be classified as physical, chemical or biological and may be economically favorable to land disposal or incineration. These alternatives are evaluated in a report prepared by Process Research, Inc.[22] and are specific to the individual processes.

The desired options for managing hazardous wastes, listed in order of priority are:[24]

(1) minimizing the amount of waste generated by process modification.
(2) transfer the waste to another industry for use.
(3) reprocess the waste to recover materials and energy.
(4) separater the waste to another industry for use.
(3) reprocess the waste to recover materials and energy.
(4) separate hazardous and nonhazardous wastes.

(5) **subject the waste to some process which will render the waste nonhazardous.**

(6) **dispose of the waste in a secure (lined to prevent seepage into ground water) landfill.**

Hazardous waste management in the petrochemical industry is a very complex problem. In many cases it is impossible to assign monetary values to long-term damage to health and the environment that has resulted from improper management of hazardous wastes. The astronomical costs of cleaning up damage caused by poor disposal practices alone is reason enough to justify the cost of proper environmental controls. Several textbooks are currently available which discuss the problem of hazardous waste management.[24,25,26,27,28,29,30]

Energy Use

Energy use at pollution control facilities must be considered with respect to three different areas of growing concern, the direct cost of the energy used, the environmental effects of pollution generated directly and indirectly as a result of energy use, and depletion of important nonrenewable resources. Rapidly changing energy prices are forcing pollution control facilities operators to give serious consideration to the energy requirements of pollution control. Research has shown that energy costs will become the predominant factor in the selection of some pollution control facility alternatives.[31] For example, energy costs may be as much as 99 percent of the total annual operating cost of some air pollution control processes.

In addition to the cost of energy used for pollution control, consideration must be given to the environmental effects of pollution generated directly and indirectly as a result of energy use. The generation of power produces pollution. The processing of fuels used for energy production also results in the generation of environmental impacts. Since some pollution control alternatives may require large amounts of energy while other alternatives may result in a net energy savings, and since it is the goal of pollution control facilities to produce the least environmental impact within cost constraints, it is necessary to consider these costs of power generation when choosing between control alternatives.

Industry Growth

Many developing countries are rich in hydrocarbons and other raw materials necessary for petrochemical production. The availability of the necessary raw materials, an inexpensive labor force, and an increased demand for petrochemical products is expected to lead to the development of petrochemical production capabilities within these developing countries.

The information presented above has shown that petrochemical production will result in the generation of water and air pollutants, solid and hazardous wastes. An increase in petrochemical production could, therefore, have a significant impact on public health and environmental quality. The information contained in this report has also shown that the technology to control these potential pollutant emissions currently exists.

To avoid the adverse effects on public health and environmental quality of this increased petrochemical production, adequate pollution control regulations must be promulgated. Such regulations would require the evaluation of possible environmental impacts and public health effects of the construction and operation of petrochemical production facilities, and require measures to mitigate adverse effects.

To assess possible environmental impacts, a survey must be conducted of the existing environmental conditions at the proposed plant site. A survey of the wastes generated at a plant should also be conducted. The survey should include a characterization of the volume of wastes generated, the rate of flow of the wastes, and the physical, chemical, and biological characteristics of the generated wastes.

A review of the literature concerning the characteristics of waste products produced during the manufacture of petrochemical products has shown that petrochemical production can be a significant source of pollution. This same review has shown, however, that adequate, economic control technologies currently exist. To avoid the potential threat to environmental quality and public health that petrochemical production represents, governments must take an active role in regulating pollution control. If the proper steps are taken, the benefits that come from the introduction of a new industry may be realized while avoiding damage to environmental quality and public health.

Management Philosophy

It is advantageous to consider excess materials as an additional resource to be utilized either in the form discarded or after further processing. This approach to waste processing is economically and environmentally important. If **a government or ministry considers protection of the environment and maximum utilization of the base resource important, then the production management and the employees probably have an entirely different attitude toward performing this function and are more likely to take pride in producing high quality effluents and in recovering and utilizing as much of the material as possible.** The importance of protecting the quality of the environment and the impact that improper handling of waste materials has on the employees' life styles and the nation as a whole must be emphasized.

Environmental protection must be stressed when management is expected to meet production quotas. Under such production systems management tends to concentrate its talent on product output, if not reminded continually of the value placed on environmental protection by the ministry and the nation. Environmental protection must be considered as a valuable natural resource in the same manner as the labor, materials, and the capital investment required to produce the basic product.

The costs for environmental protection must be paid either now or in the future. The most effective method of handling excess products is to incorporate the facilities for protecting the environment and for further processing of the excess into useful products. It is much less expensive to install such equipment initially than to convert a production process and add pollution control equipment later; moreover, it has proved cheaper to spend today's currency than an inflated one of a later date. However, it is still less expensive to add to existing systems the facilities for processing excess materials than to allow excess to be wasted as environmental pollutants; to clean these up at a future time is costly and difficult. Indeed, the damage to the environment before installing equipment to correct a situation may be impossible to rectify. It is burdensome to assess the economic losses incurred by people and industry because of delayed pollution control; however, these are real economic factors which must be considered and emphasized. The losses of health, happiness, and productivity of people owing to environmental pollution are the greatest costs of all.

Long-term economic effects of industrial pollution must not be neglected. If an industry is allowed to develop in an area without pollution control facilities, eventually the area may deteriorate to a level unacceptable to many of the residents, and they move away. Relocation of the population depletes the tax base for public services and results in a further deterioration of the local living conditions. With an added tax burden the community is forced to extract more support from the industry, resulting in higher product costs. Environmental pollution also influences maintenance costs for homes, public buildings, and thoroughfares, as well as the industrial buildings and equipment themselves.

Pollution control is a good business practice which a nation cannot afford to neglect. Maintenance of the environment is much the same as maintenance of machinery, automobiles, and other devices. If a nation does not routinely care for the environment, eventually it deteriorates. Deterioration may occur to a level that is intolerable to flora and fauna and cost the people and the government more than the industry produces. A nation must not sacrifice its customs and desirable environment to short-term economic advantage.

Some form of industrial waste treatment must be practiced if degradation of environmental quality is to be prevented. Complete treatment at the industrial site may be necessary, pretreatment prior to discharge to a public sewer may be required, or discharge to a treatment facility serving an industrial complex may provide the effluent quality needed. The degree of treatment required varies with local and national standards and the economy of by-product recovery.

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CHAPTER 1

INTRODUCTION TO THE PETROCHEMICAL INDUSTRY

The Industry

In 1980 the world consumption of 23 major petrochemical products was well over 250 million metric tons per year. World consumption of these products is expected to grow, and the size of the petrochemical industry, coupled with the nature and complexity of the wastes produced in the industry have the potential for significant impact on public health and environmental quality.[1] The need for adequate waste management is obvious.

Petrochemicals, sometimes called petroleum-chemicals, are defined in this study as any chemicals which are derived from petroleum, natural gas or other sources. This definition includes a very wide variety of compounds from acetylene to vinyl chloride. Petrochemical compounds are included in several international standard industrial classifications, and the following six industries were included in this study: synthetic rubbers, synthetic fibers, organic petrochemicals, plastics, carbon black and surfactants.

Raw materials used in the production of petrochemicals include crude petroleum, natural gas, refinery gas, natural gas condensate, light tops or naphtha, heavy fractions such as fuel oil, coal and biomass. Primary or first generation petrochemicals are produced from these raw materials. Primary petrochemicals include: olefins such as ethylene, propylene, and butadiene; aromatics such as benzene, toluene, and xylene; syngas (mixture of hydrogen and carbon monoxide with or without nitrogen); and carbon black. These first generation compounds are used as feedstocks in the synthesis of intermediate and third generation petrochemical products.

Primary, intermediate, and third generation compounds are produced by exposure of feedstocks to specific process conditions, which dictate the chemistry of the transformation. A wide variety of chemical reactions may be induced in these processes including: polymerization, hydration, halogenation, epoxidation, alkylation, hydrocarboxylation, nitration, sulfonation, oxidation, dehydrogenation and cracking, isomerization and crystallization. Processes are designed to favor the formation of some desired product; however, undesired compounds, which become waste products, are often formed.

Processes and Waste Streams

More than 500 different processing sequences are used in the petrochemical industry. The wide variety of process sequences coupled with the wide variety of products produced by the petrochemical industry leads to a complex waste problem. A list of the principle petrochemical processes and the wastes which may be expected to result from their use is presented in Table 1.1.[2] Examination of the information presented in this table reveals that many air and water pollutants along with solid wastes are generated during the production of petrochemicals.

Petrochemical wastes may produce a variety of adverse effects on public health and the environment. Biodegradable organic matter discharged to receiving waters may produce anaerobic conditions in the receiving water. These conditions will kill or drive off any aerobic organisms including fish and other higher animals. Anaerobic decomposition may also produce odor and color problems.

Thermal pollution from petrochemical discharges will also affect receiving waters, including death or decreased productivity of many aquatic species. Increased water temperatures also decrease oxygen solubility,

TABLE 1.1

PETROCHEMICAL PROCESSES AS WASTE SOURCES[2]

Process	Source	Pollutants
Alkylation: Ethylbenzene		Tar, Hydrochloric Acid, Caustic Soda, Fuel Oil
Ammonia Production	Demineralization	Acids, Bases
	Regeneration, Process Condensates	Amonia
	Furnace Effluents	Carbon Dioxide, Carbon Monoxide
Aromatics Recovery	Extract Water	Aromatic Hydrocarbons
	Solvent Purification	Solvents - Sulfur Dioxide, Diethylene Glycol
Catalytic Cracking	Catalyst Regeneration	Spent Catalyst, Catalyst Fines (Silica, Alumina) Hydrocarbons, Carbon Monoxide, Nitrogen Oxides
	Reactor Effluents and Condensates	Acids, Phenolic Compounds, Hydrogen Sulfide Soluble Hydrocarbons, Sulfur Oxides, Cyanides
Catalytic Reforming	Condensates	Catalyst (particularly Platinum and Molybdenum), Aromatic Hydrocarbons, Hydrogen Sulfide, Ammonia
Crude Processing	Crude Washing	Inorganic Salts, Oils, Water Soluble Hydrocarbons
	Primary Distillation	Hydrocarbons, Tars, Ammonia, Acids, Hydrogen Sulfide
Cyanide Production	Water Slops	Hydrogen Cyanide, Unreacted Soluble Hydrocarbons

TABLE 1.1 (continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES[2]

Process	Source	Pollutants
Dehydrogenation		
Butadiene Prod. from n-Butane and Butylene	Quench Waters	Residue Gas, Tars, Oils, Soluble Hydrocarbons
Ketone Production	Distillation Slops	Hydrocarbon Polymers, Chlorinated Hydrocarbons, Glycerol, Sodium Chloride
Styrene from Ethyl-benzene	ysts	Spent Catalysts (Iron, Magnesium, Potasium, Copper, Chromium, and Zinc)
	Condensates from Spray Tower	Aromatic Hydrocarbons, including Styrene, Ethyl Benzene, and Toluene, Tars
Desulfurization		Hydrogen Sulfide, Mercaptans
Extraction and Purification		
Isobutylene	Acid and Caustic Wastes	Sulfuric Acid, C_4 Hydrocarbon, Caustic Soda
Butylene	Solvent and Caustic Wash	Acetone, Oils, C_4 Hydrocarbon, Caustic Soda, Sulfuric Acid
Styrene	Still Bottoms	Heavy Tars
Butadiene Absorption	Solvent	Cuprous Ammonium Acetate, C_4 Hydrocarbons, Oils
Extractive Distillation	Solvent	Furfural, C_4 Hydrocarbons

TABLE 1.1 (continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES[2]

Process	Source	Pollutants
Halogenation (Principally Chlorination)		
Addition to Olefins	Separator	Spent Caustic
Substitution	HCl Absorber, Scrubber	Chlorine, Hydrogen Chloride, Spent Caustic, Hydrocarbon Isomers and Chlorinated Products, Oils
	Dehydrohalogenation	Dilute Salt Solution
Hypochlorination	Hydrolysis	Calcium Chloride, Soluble Organics, Tars
Hydrochlorination	Surge Tank	Tars, Spent Catalyst, Alkyl Halides
Hydrocarboxylation (OXO Process)	Still Slops	Solule Hydrocarbons, Aldehydes
Hydrocyanation (for Acrylonitrile, Adipic Acid, etc.)	Process Effluents	Cyanides, Organic and Inorganic
Isomerization in General	Process Wastes	Hydrocarbons; Aliphatic, Aromatic, and Derivative Tars
Nitration		
Paraffins		By-Product Aldehydes, Ketones, Acids, Alcohols, Olefins, Carbon Dioxide
Aromatics		Sulfuric Acid, Nitric Acid, Aromatics

TABLE 1.1 (continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES[2]

Process	Source	Pollutants
Oxidation		
Ethylene Oxide and Glycol Manufacture	Process Slops	Calcium Chloride, Spent Lime, Hydrocarbon Polymers, Ethylene Oxide, Clycols, Dichloride
Aldehydes, Alcohols, and Acids from Hydrocarbons	Process Slops	Acetone, Formaldehyde, Acetaldehyde, Methanol, Higher Alcohols, Organic Acids
Acids and Anhydrides from Aromatic Oxidation	Condensates Still Slops	Anhydrides, Aromatics, Acids Pitch
Phenol and Acetone from Aromatic Oxidation	Decanter	Formic Acid, Hydrocarbons
Carbon Black Manufacture	Cooling, Quenching	Carbon Black, Particulates, Dissolved Solids
Polymerization, Alkylation	Catalysts	Spent Acid Catalysts (Phosphoric Acid), Aluminum Chloride
Polymerization (Polyethylene)	Catalysts	Chromium, Nickel, Cobalt, Molyhdenum
Butyl Rubber	Process Wastes	Scrap Butyl, Oil, Light Hydrocarbons
Copolymer Rubber	Process Wastes	Butadiene, Styrene Serum, Softener Sludge
Nylon 66	Process Wastes	Cyclohexane Oxidation Products, Succinic Acid, Adipic Acid, Glutaric Acid, Hexamethylene, Diamine, Adiponitrile, Acetone, Methyl Ethyl Ketone

TABLE 1.1 (continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES[2]

Process	Source	Pollutants
Sulfation of Olefins		Alcohols, Polymerized Hydrocarbons, Sodium Sulfate, Ethers
Sulfonation of Aromatics	Caustic Wash	Spent Caustic
Thermal Cracking for Olefin Production (including Fractionation and Purification)	Furnace Effluent and Caustic Treating	Acids, Hydrogen Sulfide, Mercaptans, Soluble Hydrocarbons, Polymerization Products, Spent Caustic, Phenolic Compounds, Residue Gases, Tars and Heavy Oils
Utilities	Boiler Blow-down	Phosphates, Lignins, Heat, Total Dissolved Solids, Tannins
	Cooling System Blow-down	Chromates, Phosphates, Algicides, Heat
	Water Treatment	Calcium and Magnesium Chlorides, Sulfates, Carbonates

enhance atmospheric oxygen transfer, and may produce an increased biological activity. The net result will be a higher oxygen demand on the system.

Petrochemical plant discharges to receiving waters may also produce aesthetic effects such as objectionable odors, unsightly floating material, colored or turbid water, and foaming. These conditions may make a water unsuitable for recreational and other beneficial uses.

Wastestreams from petrochemical unit operations have also been found to contain toxic substances in many cases.[3] Several characteristics of these substances make them of particular concern. First, many of these substances are toxic at very low levels, sometimes in the ug/L range. Second, many of these compounds are biomagnified. This means high levels of these substances may be accumulated in organisms at high trophic levels. Third, many of these substances are refractory in nature. In other words, they are not easily degraded in the environment.

Petrochemical processing plants can also be significant sources of air pollution. A list of the air pollutants emitted from petrochemical processing plants and the major sources of these emissions is found in Table 1.2.[4] Air pollution from petrochemical plants is produced by the combustion of fuel and by various losses from processing equipment.

Particulate matter, carbon monoxide, sulfur oxides and nitrogen oxides emissions are mainly a result of the combustion of fuels; however, other processes in the plant may cause these substances to be emitted. Hydrocarbon emissions may occur due to fuel combustion or various process losses, including leaking valves, flanges, pumps and compressors, evaporation from process drains, wastewater treatment processes, cooling water and blowdown systems, and losses from relief valves on operating and storage vessels. Research has shown that hydrocarbon emissions may be as great as 0.6%, by weight of total plant

TABLE 1.2

AIR POLLUTANTS EMITTED FROM PETROCHEMICAL PROCESSING PLANTS[4]

Pollutant	Source of pollutant
sulfur oxides	cracking units, treating units, flares, decoking operations, and all combustion operations
nitrogen oxides	combustion operations, compressor engines, catalyst regeneration
particulates	evaporation from storage tanks, loading facilities, sampling, spillage, processing equipment leakage, barometric condensors, cooling towers
carbon monoxide	combustion operations, decoking, catalyst regeneration
odors	hydrogen sulfide, mercaptans, wastewater treating units, barometric condensors

production. Hydrogen sulfide and mercaptans, produced during some production processes and emitted by various process losses, may create significant odor problems.

These air pollutants have been shown to have significant health effects. Air pollutants may adversely affect plant life, reducing crop yields, and plant growth rate and in some cases causing the death of susceptible plants. Air pollution may also have corrosive effects on metals, building materials and textiles.

Management Philosophy

It is advantageous to consider excess materials as an additional resource to be utilized either in the form discarded or after further processing. This approach to waste processing is economically and environmentally important. If a government or ministry considers protection of the environment and maximum utilization of the base resource important, then the production management and the employees probably have an entirely different attitude toward performing this function and are more likely to take pride in producing high quality effluents and in recovering and utilizing as much of the material as possible. The importance of protecting the quality of the environment and the impact that improper handling of waste materials has on the employees' life styles and the nation as a whole must be emphasized.

Environmental protection must be stressed when management is expected to meet production quotas. Under such production systems management tends to concentrate its talent on product output, if not reminded continually of the value placed on environmental protection by the ministry and the nation. Environmental protection must be considered as a valuable natural resource in the same manner as the labor, materials, and the capital investment required to produce the basic product.

The costs for environmental protection must be paid either now or in the future. The most effective method of handling excess products is to incorporate the facilities for protecting the environment and for further processing of the excess into useful products. It is much less expensive to install such equipment initially than to convert a production process and add pollution control equipment later; moreover, it has proved cheaper to spend today's currency than an inflated one of a later date. However, it is still less expensive to add to existing systems the facilities for processing excess materials than to allow excess to be wasted as environmental pollutants; to clean these up at a future time is costly and difficult. Indeed, the damage to the environment before installing equipment to correct a situation may be impossible to rectify. It is burdensome to assess the economic losses incurred by people and industry because of delayed pollution control; however, these are real economic factors which must be considered and emphasized. The losses of health, happiness, and productivity of people owing to environmental pollution are the greatest costs of all.

Long-term economic effects of industrial pollution must not be neglected. If an industry is allowed to develop in an area without pollution control facilities, eventually the area may deteriorate to a level unacceptable to many of the residents, and they move away. Relocation of the population depletes the tax base for public services and results in a further deterioration of the local living conditions. With an added tax burden the community is forced to extract more support from the industry, resulting in higher product costs. Environmental pollution also influences maintenance costs for homes, public buildings, and thoroughfares, as well as the industrial buildings and equipment themselves.

Pollution control is a good business practice which a nation cannot afford to neglect. Maintenance of the environment is much the same as maintenance of machinery, automobiles, and other devices: if a nation does not routinely care for the environment, eventually it deteriorates. In this case, deterioration may occur to a level that is intolerable to flora and fauna and cost the people and the government more than the industry produces. A nation must not sacrifice its customs and desirable environment to short-term economic advantage.

Summary

Some form of industrial waste treatment must be practiced if degradation of environmental quality is to be prevented. Complete treatment at the industrial site may be necessary, pretreatment prior to discharge to a public sewer may be required, or discharge to a treatment facility serving an industrial complex may provide the effluent quality needed. The degree of treatment required varies with local and national standards and the economy of by-product recovery.

CHAPTER 2

AIR POLLUTION

Air pollutants produced by petrochemical manufacturing practices include sulfur oxides, nitrogen oxides, carbon monoxide, particulates, odors, and a wide variety of hydrocarbons. These pollutants may be emitted from combustion operations (for energy and/or product production); cracking units, decoking operations and other unit processes; catalyst regeneration; flares; evaporation from storage tanks; spillage; leakage; cooling towers and condensers. The diversity and complexity of processes used in the petrochemical industry make it difficult to make sweeping generalizations about air pollutants emitted during petrochemical processing.

The U.S. EPA in an attempt to determine the significance of air pollution from the petrochemical industry conducted a study to determine industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions, and descriptions of emission control devices used. As a part of this survey, a method for rating the significance of air emissions was established and used to rank the processes studied and to select several processes for in-depth study.

The U.S. EPA studied a total of 33 distinctly different processes used to produce 27 petrochemicals, and these processes are listed in Table 2.1. The results obtained from this study are contained in a four volume series.[5,6,7,8] A summary of the estimated air emissions that would be emitted in 1980 from all of the plants utilizing these processes in the United States is shown in Table 2.2. The results shown in Table 2.2 are based on assorted sources of data and should be used as a guide as to what might be expected but not as a rigorous

TABLE 2.1

PETROCHEMICAL PROCESSES SURVEYED[5,6,7,8]

Acetaldehyde via Ethylene
Acetaldehyde via Ethanol
Acetic Acid via Methanol
Acetic Acid via Butane
Acetic Acid via Acetaldehyde
Acetic Anhydride
Adipic Acid
Adiponitrile via Butadiene
Adiponitrile via Adipic Acid
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene-Butadiene Rubber
Vinyl Acetate via Acetylene
Vinyl Acetate via Ethylene
Vinyl Chloride via EDC Pyrolysis
Maleic Anhydride
Nylon 6
Nylon 6, 6
Oxo Process[a]
Phenol
High Density Polyethylene
Low Density Polyethylene
Carbon Disulfide
Cyclohexanone
Dimethyl Terephthalate (and Terephthalic Acid)
Ethylene
Ethylene Dichloride (Direct)
Formaldehyde (Silver Catalyst)
Glycerol (Allyl Chloride)
Hydrogen Cyanide (Andrussow)
Isocyanates via Amine Phosgenation

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[a] Oxonation, or more properly, hydroformylation for the production of aldehydes and alcohols from olefins and synthesis gas.

TABLE 2.2

ESTIMATED AIR EMISSIONS FROM UNITED STATES PETROCHEMICAL PLANTS[5,6,7,8]

	ESTIMATED ADDITIONAL[a] AIR EMISSIONS IN 1980, MILLION LBS/YEAR					
	Hydrocarbons[b]	Particulates	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2
via Ethanol	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04
via Butane	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15
Acrylonitrile	284	0	8.5	0	304	596
Adipic Acid	0	0.14	19.3	0	0.09	19.5
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4
Via Adipic Acid	0	0.5	0.04	0	0	0.54
Carbon Black	64	3.3	2.8	8.9	1,590	1,670
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24
Cyclohexanone	77.2	0	0	0	85.1	162
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7
Ethylene	14.8	0.2	0.2	61.5	0.2	77
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136
via Direct Chlorination	34.2	0	0	0	0	34.2
Ethylene Oxide	32.8	0	0.15	0.05	0	33
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9
Hydrogen Cyanide Direct Process	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87
Maleic Anhydride	31	0	0	0	241	272
Nylon 6	0	3.2	0	0	0	3.2
Nylon 6, 6	0	5.3	0	0	0	5.3

TABLE 2.2 (continued)

ESTIMATEDAIREMISSIONS FROMUNITED STATES PETROCHEMICAL PLANTS[5,6,7,8]

	ESTIMATED ADDITIONAL[a] AIR EMISSIONS IN 1980, MILLION LBS/YEAR					
	Hydrocarbons[b]	Particulates	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total
Oxo Process	3.86	0.01	0.05	0	14.3	18.2
Phenol	21.3	0	0	0	0	21.3
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134
via Naphthalene	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216
Low Density Polyethylene	262	5	0	0	0	267
Polypropylene	152	0.5	0	0	0	152.5
Polystyrene	20	0.34	0	1.13	0	21.47
Polyvinyl Chloride	53	10	0	0	0	63
Styrene	3.1	0.05	0.1	0	0	3.25
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5
via Ethylene	0	0	TR	0	0	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9

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[a] Assumes future plants will employ best current control techniques.

[b] Excludes methane, includes H_2S and all volatile organics.

c Includes non-volatile organics and inorganics.

comparison of process emissions. Some of the results are based on a 100 percent survey of the industry, while others are based on a limited data base or on engineering judgement.

In terms of mass of material emitted, the manufacture of carbon black leads by a large margin with the manufacture of acrylonitrile a distant second, emitting approximately one-third the mass of material discharged by carbon black. The mass of emissions per year is not the only criterion that must be considered in assessing the impact of an industry. The toxicity of emissions, odors and the persistence of the emitted compounds are some of the additional considerations. It can be seen from Table 2.2 that the petrochemical processing industry has the potential to be a significant source of air pollution.

Information about specific pollutants emitted from petrochemical processing plants may be found in Hedley et al.[9] One hundred and ninety petrochemical processes were identified, pollutant emissions from each process were identified, and emission stream compositions were tabulated (see Table 3.3 for a list of the 190 processes). Many of the individual hydrocarbons emitted from each of the processes are specifically named, and it is important to know specifics about discharges because of the wide range of toxicological properties of the substances.

Petrochemical plants discharge emissions into the atmosphere that are either controlled or fugitive in nature. Controlled emissions are released through stacks and/or vents, and detailed information is usually available on emissions composition and rate of release. Emissions from points other than stacks and vents are considered fugitive emissions. Fugitive emissions may occur due to accidents, inadequate maintenance, poor planning, and from a range of process equipment such as valves, pumps, flanges, compressors, and agitators.

Control of air pollutants emitted from controlled sources has been well studied. Many texts are available detailing the design of pollution control equipment for these sources.[10,11,12,13,14,15,16,17,18,19] Due to the complexity of the processes used in petrochemical processing, it is difficult to make generalizations about the methods used to control air pollutant emissions at petrochemical plants; however, a few brief observations can be made.

The emission of carbon monoxide and particulate matter can be controlled with modern techniques of furnace design, proper fuel atomization and burner design. In other words, proper combustion process design will lead to lower pollutant emissions, while in most instances increasing the efficiency of the combustion process.

Oxides of nitrogen result from the high temperature combustion of fuels such as gas and oil. These nitrogen oxides, in the presence of hydrocarbons, and in sunlight, will produce photochemical smog with the conversion of nitric oxide to nitrogen dioxide (the more toxic nitrogen oxide) being accelerated. The amounts of nitrogen oxides emitted may be reduced by lowering the peak-flame temperatures of combustion processes, where the required reaction temperatures of the petrochemical processes will allow this temperature reduction.

Emissions of oxides of sulfur may be reduced in several ways. First, reduction of the sulfur content of the fuels used in the combustion process will result in lower sulfur oxides production. Desulfurization processes are available for coal, gas and liquid fuels.[20] Combustion processes may also be modified to produce lower sulfur emissions. Several processes are also available for the removal of sulfur compounds from combustion gases, including processes designed for recovery of sulfur compounds (lime/limestone process, sodium alkali process, dual alkali process and dilute sulfuric acid process), non-recovery processes (magnesium oxide process, sodium sulfite process, and aqueous carbonate process), dry removal processes, and combined removal of sulfur dioxide and oxides of nitrogen.[20]

Emissions of the fugitive type can occur from a range of circumstances and process equipment. Valves and flanges are the biggest contributors to fugitive losses at petrochemical plants. The large number of valves and flanges in a petrochemical processing plant means that even an average valve leak rate of 5 g/h will give a loss of 75 kg/h from valves alone at a typical olefin plant which may contain 15,000 valves. In fact, the U.S. EPA has determined that the average emission factor for valves at an olefin plant is 8.8 g/h.[21] Based on this information it is not hard to justify efforts to reduce fugitive emissions from valves, flanges, and pumps since potential losses have been estimated to be over US $1800/day at a typical olefin plant.

Techniques used to measure fugitive emissions rates from petrochemical plants have been described by Hughes et al.[22] and Siversten.[23] Hughes et al.[22] measured fugitive hydrocarbon emission rates at petrochemical plants manufacturing monochlorobenzene, butadiene, ethylene oxide/glycol and dimethyl terephthalate. Emission rates of the various sources measured at these plants are listed in Table 2.3.

Siversten[23] conducted tracer experiments to quantify fugitive hydro-carbon emission rates at two petrochemical complexes. A simple proportionality model was applied to estimate leakage rates of ethylene, propylene, ethane, propane

TABLE 2.3

HYDROCARBON EMISSION RATES FOR FUGITIVE SOURCES BY PROCESS, G/HOUR[22]

	Average Emission Rate for Significant Fugitive Sources[a] (g/hr)			
Source Type	Monochlorobenzene	Butadiene	Dimethylterephthalate	Ethylene Oxide/Glycol
Pump Seals	23	160	20	82
Compressor Seals	--	59	--	11
Valves	1.5	120	32	1.6
Flanges	82	0	110	1.0
Relief Devices	--	14	0	0
Process Drains	--	--	--	68
Agitator	200	--	218	--
Sample Valves	--	--	91	--
	Average Emission Rate for all Potential Sources[b]			
Pump Seals	7.7	63	3.3	13
Compressor Seals	--	54	--	5.9
Valves	0.05	17	1.5	0.07
Flanges	2.2	0	3.4	0.03
Relief Devices	--	5	0	0
Process Drains	--	--	--	40
Agitator	200	--	145	--
Sample Valves	--	--	40	--

Note: Dashes indicate source type nonexistent in process.

[a] Significant fugitive sources are those having an emission rate greater than or equal to 0.5 g/hr as determined by sampling and analysis.

[b] Emission rates were determined by calculating the mass of fugitive emissions from the emission rates for significant sources. The mass of emission was divided by the total number of sources screened to arrive at an average fugitive emission rate for all sources.

and isobutane from different parts of the complex. A dispersion model was then applied to verify concentration profiles and identify leakage areas.

Hydrocarbon emission reduction systems at petrochemical plants are described by Pruessner and Broz,[24] Kenson,[25] and Mashey and McGrath.[26] Pruessner and Broz[24] described the design and operation of three incinerators, five condensation systems and two absorption systems for controlling hydrocarbon emissions. Tables 2.4 through 2.6 contain summaries of the operating conditions and costs of these systems. Treatment of waste air from three air oxidation processes by incineration achieved high removals (92-93%) of hydrocarbon contamination. Contaminant concentrations ranged from 150 ppm in a 1 million lb/hr gas flow rate to 4,000 ppm in a 235,000 lb/hr gas flow rate. Large volumes of natural gas are required to treat these large flows at high temperatures; therefore, energy recovery is an important part of these systems (Table 2.4). Condensation was used to remove up to 98 percent of a high hydrocarbon concentration from small noncondensable waste gas flows. The main advantages of condensation are product recovery and a relatively low energy requirement to remove the pollutants (Table 2.5). The two absorption systems utilized oil to absorb hydrocarbon from nitrogen waste gas streams. The oil is a mixture of parafinnic and aromatic oils which reduces the tendency for polymerization of the hydrocarbons contained within the tower. Fresh oil starts at the top of a five-stage tower and progresses through each stage, and at the bottom the oil contains about 3% hydrocarbon. Overall removal efficiency for hydrocarbons exceeds 98 percent for a gas flow rate of 275 lb/hr containing 125 lb/hr hydrocarbon contamination. The recovered hydrocarbon is stripped from the oil and used in the process (Table 2.6).

TABLE 2.4

OPERATING CONDITIONS AND COSTS OF INCINERATOR SYSTEMS USED FOR HYDROCARBON EMISSIONS REDUCTION[24]

	Maleic Incinerator	Oxo Incinerator	Houdry[a] "Puff" Reactor
Waste Gas Flow, lb/hr	220,000	235,000	900,000 (total) 13,000 (Puff reactor[b])
Contaminants, wt %			
Hydrocarbon	0.25	0.4	0.5
Carbon Monoxide	1.8	0.7	—
Removal Efficiency, %			
Hydrocarbon	93	93	92
Carbon Monoxide	95	95	—
Construction:			
Year	1975	1976	1975
Cost, US $	1,750,000	2,500,000	725,000
Heat Efficiency, %	85	82	80
Natural Gas Added, Std. cu ft/hr	80,000	130,000	0
Retention Time, Sec	0.7	0.5	0.3

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[a] Modification of Houdry butane dehydrogenation process where hydrocarbon pollutants are concentrated in about 1% of the reheat air flow, thereby significantly reducing the discharge of pollutants.

[b] Waste gas flow diverted through the "Puff" reactor. This waste stream contains most of the hydrocarbon pollutants.

TABLE 2.5

OPERATING CONDITIONS AND COSTS OF CONDENSATION SYSTEMS USED FOR HYDROCARBON EMISSIONS REDUCTION[24]

	Neoprene Monomer Isomerization Tower	Neoprene Monomer[a] Topping Column	Neoprene Polymer[a] Vessel Vents	Neoprene Latex Stripper Vent	Neoprene Polymer Emergency Dump System
Type of Heat Exchanger	S&T[b]	S&T	DC[c]	S&T	DC
Waste Gas Flow, lbs/hr Hydrocarbon	159	---	126	1,140	15,200
Waste Gas Flow, lb/hr Total	331	542	275	2,875	32,000
Hydrocarbon Removal Efficiency, %	81	99	43	99.8	99.995
Heat Load, Btu/hr	22,000	93,000	110,000	1.2Mill	10,000 Steady State 3 Million Heat Sink/Dump
Operating Temperature, °F	-2	-2	.36	-2	40 to 75
Construction:					
Year	1973	1973	1974	1969	1974
Cost US $	20,000	30,000	40,000	120,000	250,000

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[a] Waste gas exiting this system is further treated in absorption system.

[b] Shell-and-Tube.

[c] Direct contact with water

TABLE 2.6

OPERATING CONDITIONS AND COSTS OF ABSORPTION SYSTEMS USED FOR HYDROCARBON EMISSIONS REDUCTION[24]

	Neoprene Monomer Absorber	Neoprene Polymer Vent Absorber
Spray Tower Stages	2	5
Waste Gas Flow to ABS[a]		
Hydrocarbon, lbs/hr	31	72
Waste Gas Flow, Total, lb/hr	36	187
Absorber Efficiency, %	90	97
Heat Load, Btu/hr	13,000	330,000[a]
Operating Temperature, °F	65	45
System Efficiency Including Condensation, %	99.5	98.4
Construction		
Year	1975	1974
Cost US $	60,000	300,000

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[a] Includes heat load for recovery of hydrocarbons

Operating costs were not discussed for these systems. In the case of the condensation and absorption systems, hydrocarbons removed from the waste gas flow were returned to the process for further utilization. This would lower the net operating costs of the processes significantly, possibly resulting in a benefit rather than a cost.

Kenson[25] reported on the engineered design of systems for organic emissions control at petrochemical plants. Two examples of toxic emission control were discussed, vinyl chloride monomer emission control at a polyvinyl chloride plant and benzene emission control. Multiple radial carbon beds in a single tank with regeneration by vacuum and indirect steam heating removed greater than 99 percent of the vinyl chloride monomer (VCM) emissions. By using vacuum and indirect carbon bed heating, the steam condensate was not contaminated with VCM. The carbon beds are capable of producing an effluent containing less than 5 ppm of VCM, and large quantities of VCM can be recovered for reuse in the PVC manufacturing process. An economic analysis showed that the value of the VCM recovered can pay for the VCM control system in three years. An economic analysis of a carbon adsorption system designed to control benzene emissions showed a credit of US $43,000 per year as a result of solvent recovery.[25] The following five concepts were presented for the design of an organic chemical emission control system:

1. The problem to be solved must be defined as thoroughly as possible. This requires a careful analvsis of the temperature composition and volume flow rate of the exhaust stream, including the maximum and minimum values. Particulate concentration/size data may also be required.

2. The degree of control required must be well defined. This will allow the proper evaluation and selection of all the alternative control systems which might achieve this control efficiency.
3. The technical advantages and disadvantages of all the alternate control systems capable of achieving the desired degree of control must be weighed before final selection. If this is done, before system choice is made, the best control concept for that particular application may be passed up.
4. The total cost (capital and operating) of the alternative control system, including energy consumption and energy price sensitivity, must be evaluated to find which is most cost-effective for that application. Otherwise, the choice may be for the lowest capital cost system, which may be exceeded in 1-2 years by the cost of energy consumption in that system.
5. The final system choice must be designed to optimally control that particular exhaust stream. If a standard off-the-shelf system is used, it may give less than the desired degree of control and may have excessive operating costs. An engineered system may cost no more than an off-the-shelf solution.

Mashey and McGrath[26] described another approach to the engineered design of organics emission control systems in which a detailed explanation is given of the design of the vapor collection systems necessary to transport emissions to control devices. Various types of control systems were discussed including thermal oxidation systems, catalytic oxidation systems, carbon adsorption, and gas compression/condensation systems. Cantrell[27] also described techniques of organic vapor recovery at petrochemical plants.

Some other techniques used to reduce hydrocarbon emissions include: 1) appropriate specification, selection , and maintenance of seals in valves, pumps, and flanges,[21] 2) installation of floating roof tanks to control evaporation of light hydrocarbons, 3) installation of vapor recovery lines to vents of vessels that are continually filled and emptied, 4) manifolding of purge lines used for start-ups and shutdowns to vapor recovery or flare systems, 5) venting of vacuum jet exhaust lines to vapor recovery systems, 6) shipment of products by pipeline rather than car or truck, 7) covering of wastewater separators, and 8) the use of steam or air injection at flares.[4]

Excellent case studies which include data on plant emissions, control devices, and cost effectiveness may be found in a report prepared by Air Products and Chemicals, Inc.[28,29,30,31,32,33,34,35,36] These reports contained detailed information about nine of the industries surveyed by Pervier et al.,[5,6,7,8] mentioned previously. Because of the diversity of the unit operations involved in this industry and the complexity of the air emissions control problem, space does not permit a detailed case history of the plants. Summaries of efficiencies and economics of control devices which may be used to control pollution produced in the production of polyvinyl chloride and vinyl chloride monomer are presented in Tables 2.7 and 2.8. Anaylsis of the data contained in these tables illustrates the relationship between relative pollution control effectiveness and cost. In Table 2.7, the data show that 54 percent of the pollutants were removed at a capital investment of US $1,005,000. The removal of an additional 26 percent of the hydrocarbons cost approximately 2.3 times as much, or US $2,310,000, and the operating costs increased significantly. This same trend is seen in Table 2.8 where a 55 percent pollutant removal is accomplished with a capital investment of US

TABLE 2.7

COST EFFECTIVENESS OF ALTERNATIVE EMISSION CONTROL DEVICES IN POLYVINYL CHLORIDE MANUFACTURE[36]

(Based on 200 million lbs/yr PVC Plant)

	Plant W/O Control	Model Plant I	Model Plant II
Vinyl chloride monomer (VCM) Emissions, kg/kg of product			
Source			
A. Solution Storage	0.0030	0.0015	0.0005
B. Precipitation Tank	0.0030	0.0020	0.0005
C. Slurry Tank	0.0032	0.0010	0.0010
D. Crude Solvent Storage	0.0048	0.0015	0.0003
E. Blend Tank	0.0042	0.0015	0.0005
F. Centrifuge	0.0013	0.0002	0.0002
G. Bin Storage	0.0070	0.0030	0.0010
H. Fugitive	0.0080	0.0050	0.0030
Total	0.0345	0.0157	0.0070
Capital Cost of Control Devices			
High vacuum and compressor for maximum stripping		750,000	750,000
Refrigeration on condenser		70,000	
Substitute canned pumps		10,000	10,000
Monitoring equipment		175,000	175,000
Scrubber for VCM Recovery Vent System			125,000
Gas Holder			950,000
Solvent Cleaning of Reactors			300,000
		$ 1,005,000	$ 2,310,000
Operating Cost			
Cooling Water required, gpm		35	115
Electric power required, kwh/hr		95	126
Labor, men/shift		2.5	3
Steam, lbs/hr			1,000
Chemicals, US $/yr			62,100

TABLE 2.8

COST EFFECTIVENESS OF ALTERNATIVE EMISSION CONTROL DEVICES IN VINYL CHLORIDE MONOMER MANUFACTURE BY THE BALANCED PROCESS[35]
(Based on 200 million lbs/yr PVC Plant)

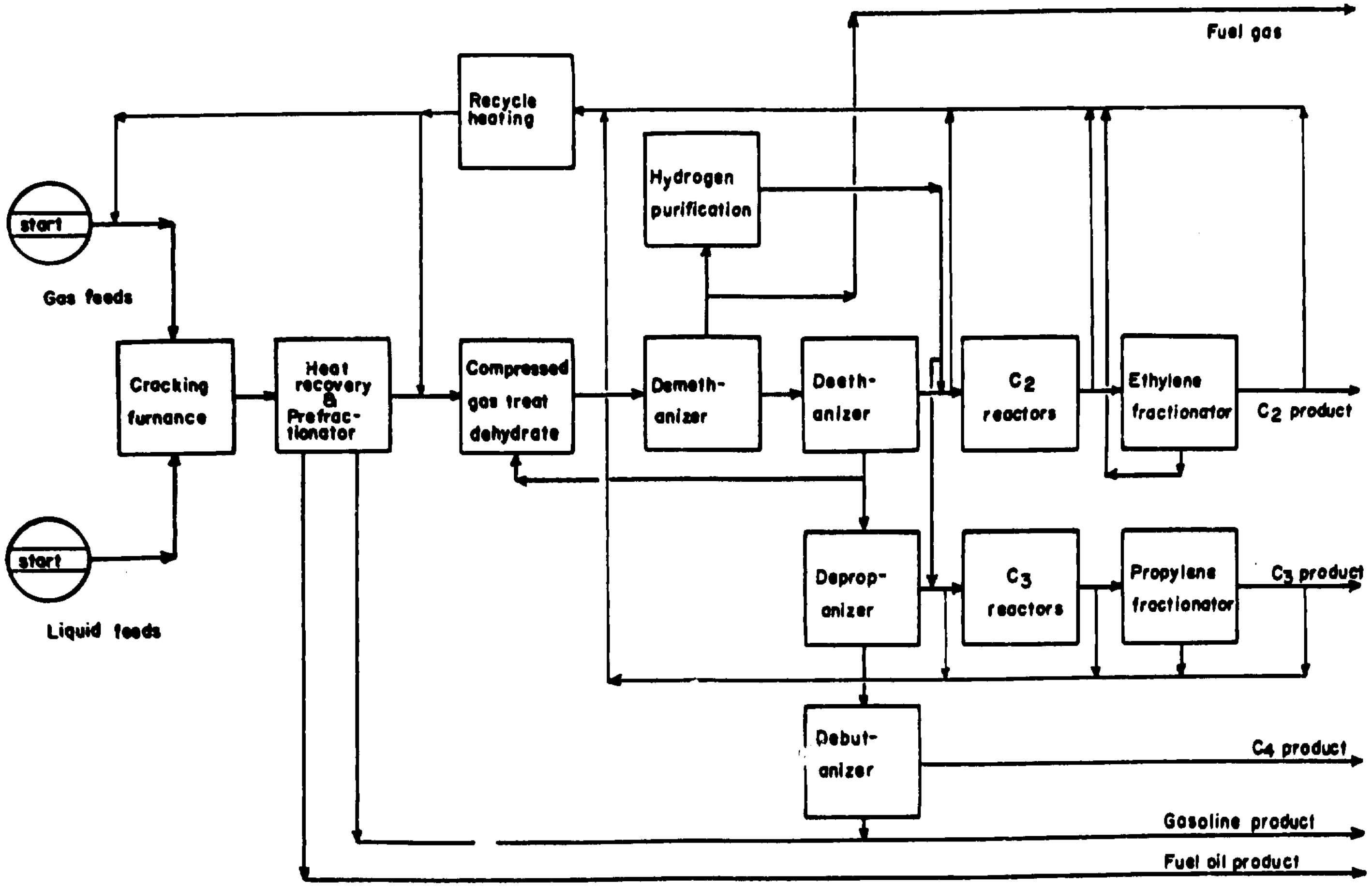
	Existing Plant	Model Plant I	Model Plant II
Vinyl chloride monomer (VCM) Emissions, kg/kg of product			
Ethylene dichloride (EDC) Distillation Column	0.000500	0.000100	0.000100
Scrubber Vent Stack	0.002400	0.000600	0.000048
Loading Losses	0.000796	0.000119	0.000119
Sampling	0.000038	0.000009	0.000009
Neutralizers and Filters	0.000003	0.000003	0.000003
Process Vessels	0.000078	0.000078	0.000078
Oxychlorination Vent	0.001320	0.001320	0.000026
Fugitive	0.000300	0.000225	0.000150
Total	0.005435	0.002454	0.000533
Capital Cost of Control Devices (US $)			
Refrigeration		200,000	--
Waste Heat Boiler		--	300,000
Incineration & Water Heat Boiler		--	1,140,000
Compressor and Refrigeration		200,000	200,000
Continuous Loop Sampler		50,000	50,000
Canned Pumps		--	200,000
Monitoring VCM Leaks		200,000	200,000
Total		$ 650,000	$ 2,090,000
Operating Costs			
Electricity, kwh/hr		80	185
Cooling water, gpm		60	30
Process water, gpm			90
Boiler feed water, gpm			82
Caustic lb/hr			1,350
Fuel million BTU/hr			16-30
Steam generated lbs/hr			38,800

$650,000. An additional 35 percent of the pollution is removed at 3.2 times the cost, or US $2,090,000. Again, the operating costs increased significantly. These data show that the higher the removal rate, the higher the removal cost. For this reason, the selection of emission standards which must be met is very important.

As noted previously, many techniques which reduce air emissions produce economic benefits by reducing product loss and recovering usable compounds. Max and Jones[37] reported on an operation technique that not only reduced air emissions but reduced production costs at an ethylene plant. Off specification products produced during start-up, shutdown, and upsets are recycled through the process train. The authors reported that as much as US $250,000 can be saved per start-up including product and feedstock losses. Figure 2.1 is a simplified flow scheme for this technique.

FIGURE 2.1

SIMPLIFIED FLOW SCHEME FOR ETHYLENE PLANT SHOWING RECYCLE OF OFF-SPEC PRODUCTS TO REDUCE AIR EMISSIONS AND PRODUCE ECONOMIC SAVINGS[37]



CHAPTER 3

WATER POLLUTION

Wastewater Streams

Wastewater streams in the petrochemical production industry may be categorized into six logical source components:[38]

1) wastes discharged directly from production units during normal operation;
2) utility operations such as blowdown from energy production and cooling systems;
3) sanitary sewage from administrative areas, locker rooms, shower and restroom facilities, and food handling areas;
4) contaminated storm runoff from process areas;
5) ballast water discharged from tankers during product handling;
6) miscellaneous discharges from spills, turnarounds, etc.

The many combinations of production processes make it difficult to make generalizations about petrochemical wastewaters; however, petrochemical wastes may include various chemicals derived from petroleum derivatives and natural gas, toxic substances, lubricants, gas oil, fuel oil, wax, asphalt and petroleum coke. The hydrocarbons found in these wastestream generally originate from leaks, spills, and product dumps. Steam condensate from reflux systems may contain hydrogen sulfide and mercaptans. Caustics, when used to purify hydrocarbon streams, produce alkaline wastestreams which are potentially toxic.

Ammonia may be introduced into petrochemical wastestreams from two sources: it may be added to product streams for corrosion control, and by the breakdown of nitrogenous compounds present in the feedstock. Other components of petrochemical wastestreams which may be of concern are corrosion inhibitors, particularly heavy metals.

Wastewater Characteristics

Gloyna and Ford[2] conducted a survey designed to characterize petrochemical production wastes and to define the pollution problems associated with these wastes. Effects were described of petrochemical wastewater streams on receiving waters, on water used for other beneficial uses, and in-plant reuse. Several petrochemical wastewaters were also described in terms of conventional pollutional parameters such as acidity, alkalinity, color and turbidity, pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), solids, surface activity, taste and odor and temperature. The results of effluent analyses from several typical petrochemical plants are presented in Table 3.1.[2]

The data shown in Table 3.1 illustrate the variability of waste characteristics in the petrochemical industry. The pH values of petrochemical wastewaters are generally greater than 7, and the wastestreams typically contain large amounts of total solids and low concentrations of suspended solids, indicating that most solids in these wastewaters are in the dissolved form. The variability in the data found in Table 3.1 suggests that each petrochemical wastestream must be analyzed separately to predict its characteristics. The variability can be attributed to the large number of choices of processes that may be selected to form a petrochemical plant.

The most commonly used method for predicting the quality and quantity of petrochemical production wastewaters is to study each individual unit process and relate the quantity and quality of the wastestreams produced to production

TABLE 3.1

TOTAL PLANT EFFLUENT ANALYSES TYPICAL PETROCHEMICAL PLANTS[2]
(Process Waste Before Treatment)

Plant Products	Mixed Chemicals incl. ethylene oxide, propylene oxide, glycols, amines, and ethers	Refinery, Detergent Alkylate	Refinery Butadiene, Butyl Rubber
Alkalinity (mg/L)	4,060	365	164
BOD (mg/L)	1,950	345	225
Chlorides (mg/L)	430-800	1,980	825
COD (mg/L)	7,970-8,540	855	610
Oils (mg/L)	547	73	-
pH	9.4-9.8	9.2	7.5
Phenols (mg/L)	-	160	17
Sulfates (mg/L)	655	280	-
Suspended Solids (mg/L)	27-60	121	110
TOC (mg/L)	-	-	160**
Total Nitrogen (mg/L)	1,160-1,253	89	48
Total Solids (mg/L)	2,191-3,029	3,770	2,810
Misc. as Indicated		Sulfide= 150 ppm*	PO_4=trace

* Cooling Water Excluded

** Filtered

TABLE 3.1 (continued)

TOTAL PLANT EFFLUENT ANALYSES
TYPICAL PETROCHEMICAL PLANTS[2]
(Process Waste Before Treatment)

Plant Products	Mixed Organics	2,4,5-Tri chloro-phenol	2,4-Dichloro-phenol	Nylon
BOD_5 (mg/L)	1,950	16,800	16,700	170
Chlorides (mg/L)	800	96,300	144,000	800
COD (mg/L)	1,972	21,700	27,500	2,000
Oils (mg/L)	547	---	---	45
Phenols (mg/L)	10-50	---	---	400
Suspended Solids (mg/L)	60	700	348	neg.
Total Nitrogen (mg/L)	1,253	40	45	100
Total Solids (mg/L)	3,029	172,467	167,221	3,000
Misc. as Indicated	SO_4=655 mg/L	%Vol.TS= 10.5	%Vol.TS=13.2	H_2S=12 mg/L

TABLE 3.1 (continued)

TOTAL PLANT EFFLUENT ANALYSES
TYPICAL PETROCHEMICAL PLANTS[2]
(Process Waste Before Treatment)

Plant Products	Phenols, Cresols
Alkalinity (mg/L)	192
BOD_5 (mg/L)	550-850
Chlorides (mg/L)	230
COD (mg/L)	990-1,940
Color (Color Units)	50
Hardness (mg/L)	250
IOD (mg/L)	17
Kjeldahl-N (mg/L)	trace
NH_3-N (mg/L)	trace
Oil (mg/L)	trace
pH	4.6-7.2
Phenols (mg/L)	280-550
PO_4 (mg/L)	3
Sulfides (mg/L)	trace-1
Suspended Solids (mg/L)	12-88
Temperature °C	24.5
TOC (mg/L)	320-580
Total Solids (mg/L)	1,870-2,315

units. For example, the isopropanol stripping still and intermediate flash column used in acetone production produces approximately 2.2 pounds of COD per ton of acetone produced.[9] The nature of production and processing can make this a difficult task. Small changes in unit process operating conditions such as temperature, pressure, flowrate, and variations in feedstock quality may significantly alter the characteristics of the wastestreams produced. A knowledge of the chemistry involved in the process, process operating conditions, feedstock used, and quantity of product produced by the unit operation can lead to the estimation of pollutant characterization and quantification.

The BOD and COD of many organic compounds that may be produced during the production of petrochemical products is available from several sources. Bridie et al.[39] has presented the COD, BOD and theoretical oxygen demand for 118 petrochemical compounds. Other BOD and COD data may be found in Pritter,[40] Price et al.,[41] Meinck et al.,[42] and Heukelekian and Rand.[43]

Many toxic substances may be produced during the production of petrochemical products. The U.S. Environmental Protection Agency (USEPA) has identified 129 toxic organic chemicals which have been found in the waters of the nation, and these chemicals have become known as "priority pollutants." Wise and Fahrenthold[3] presented a method which can be used to predict the occurrence of these 129 "priority pollutants" in petrochemical processing wastewaters. Critical precursor and generic process combinations that generate "priority pollutants" in 172 petrochemical manufacturing effluents are reported in Table 3.2.[3]

Hedley et al.[9] conducted a survey of the processes associated with petrochemical production designed to characterize the wastes produced. The

TABLE 3.2

CRITICAL PRECURSOR/GENERIC PROCESS COMBINATIONS THAT GENERATE PRIORITY POLLUTANTS[3]

			Generic Processes		
Precursor	Oxidation products	Chlorination products	Nitration products	Diazotization products	Reduction products
Benzene	Phenol	Chloroaromatics Chlorophenols	Nitroaromatics Nitrophenols		
Toluene	o,m-Cresol		Nitroaromatics		
Xylene	2,4-Dimethylphenol		2,4-Dimethylphenol		
Naphthalene		2-Chloronaphthalene			
Phenol		Chlorophenols	Nitrophenols		
Cresols		4-Chloro-m-cresol	4,6-Dinitro-o-cresol		
Chloroanilines				Chlorophenols Chloroaromatics Aromatics	

TABLE 3.2 (continued)

CRITICAL PRECURSOR/GENERIC PROCESS COMBINATIONS THAT GENERATE PRIORITY POLLUTANTS[3]

	Generic Processes				
Precursor	Oxidation products	Chlorination products	Nitration products	Diazotization products	Reduction products
Nitroanilines				Nitrophenols Nitroaromatics Aromatics	
Nitrobenzene m-Chloronitrobenzene				N-Nitrosodiphenylamine[a] Benzidines[b]	Aniline (diphenylamine[a]) 1,2-Diphenylhydrazines[b]
Ethylene		Chlorinated C2's Chlorinated C4 Chloroaromatics			
Propylene	Acrolein	Chlorinated C3's			
Methane		Chlorinated methanes			

[a] Derived directly from aniline, or indirectly via phenylhydrazine, diphenylamine is one of three secondary amines that are precursors for nitrosamines when exposed to nitrites (as in diazotization) or NO_x.

[b] Diphenylhydrazines rearrange to benzidines under acid conditions (as in diazotization).

major potential sources of pollutants from the production of petrochemicals were identified. Published and unpublished data were used to describe emission sources and the composition of the emission streams from the 190 petrochemical production processes studied. Hedley et al.[9] presented process characterization sheets for each of these 190 processes which included a brief description of the process, utility requirements, feed materials, emissions sources, and potential pollutants. If details are needed for a specific process the report should be consulted.

Treatment Methods

The design of wastewater treatment facilities for petrochemical production facilities will not be reliable unless wastewaters have been fully characterized and the performance characteristics of alternative treatment processes have been evaluated by treatability studies and pilot plant operations. Treatability studies should establish the effects of operational parameters such as hydraulic detention time, sludge age and temperature on organic removal rates, oxygen requirements, sludge production, sludge characteristics, and process stability.

Treatability studies can identify wastestreams which should be treated separately to enhance process performance.[44] Engineering-Science, Inc.[45] outlined the components of a preliminary wastewater survey and treatability study in the petrochemical industry (Table 3.3).

Clements and Cheng[46] described techniques which provide both qualitative and quantitative identification of major components of a process wastestream. The techniques and instrumentation used in this process were chosen to be within the technical and financial reach of even small company laboratories. Component identification was accomplished by using infrared spectroscopy,

TABLE 3.3

COMPONENTS OF A WASTEWATER SURVEY AND TREATABILITY STUDY PROGRAM[45]

I. Wastewater Survey
    A. Identify all significant waste sources
    B. Obtain detailed information on waste flowrates
II. Wastewater Characterization
    A. Characterize organic content of wastestream
    B. Characterize inorganic content of wastestream
    C. Identify toxic wastestreams
    D. Identify wastestreams with reuse or product recovery potential
III. In-plant Considerations
    A. Implement educational programs for plant personnel designed to reduce wastewater generation
    B. Eliminate waste by process research and development
    C. Install waste segregation devices at source
IV. Treatability Study
    A. Select appropriate process alternatives based on wastewater survey and characterization data
    B. Define process operating parameter by bench or pilot scale process simulations
    C. Evaluate process alternatives based on treatment costs and treatment requirements
V. Incorporation of Results

ultraviolet spectroscopy, gas chromatography, and thin-layer chromatography techniques. The sample preparation steps consist of an initial series of extractions which isolated compounds into organic acid, base and neutral compounds and a totally water soluble phase. Each fraction was then concentrated and subjected to the appropriate analytical technique. This procedure was found to be the most economical for wastestreams with contaminant concentrations in excess of 1000 mg/L, as is often found in petrochemical wastewaters.

The unit processes which can provide treatment of petrochemical manufacturing plant wastewaters are as varied as the unit processes used in the manufacturing plants themselves. Studies have shown, however, that there are seldom cost effective alternatives to biological treatment coupled with physical-chemical pretreatment and/or polishing where needed.[38,44,47] Biological treatment coupled with post-filtration has been defined by the US EPA as the "best practicable technology" currently available for treating petrochemical processing wastewaters.

In order to produce a high quality effluent, it is probable that most petrochemical wastewater systems will include all or some of the processes listed in Table 3.4.[38]

Nijst[47] of the Petrochemicals/Ecology group of the European Council of Chemical Manufacturers Federation reports that a central biological treatment plant is the preferred method of treating the aqueous effluents of the petrochemical industry. Biological treatment processes were chosen because: 1) they are geared to BOD removal, which was generally required by the responsible authorities, 2) biological process costs to achieve BOD removal are low compared to other treatment processes, and 3) when effluent limitations are in

TABLE 3.4

PETROCHEMICAL WASTEWATER TREATMENT SYSTEMS[38]

Pretreatment:

- API separators
- Tilted plate separators
- Filtration for oil removal
- pH control
- Stripping processes
- Primary sedimentation
- Monitoring system to detect break down and spills

Intermediate treatment:

- Dissolved air flotation
- Coagulation-precipitation
- Equalization
- Detoxification for biological treatment

Secondary/Tertiary treatment:

- Biological oxidation
- Chemical oxidation
- Filtration
- Adsorption

terms of COD, biological processes will remove a significant amount of COD with less expense than a nonbiological process designed to remove the same amount of COD. This report further states that effluents from biological treatment systems may still contain dissolved organics and suspended solids which may be removed by further treatment such as aerated lagoons and polishing ponds, sand or multimedia filtration or other physical-chemical processes such as reverse osmosis, ultrafiltration, extration and chemical oxidation. Activated carbon adsorption preceded by filtration for solids removal was generally found to be the best economically available technology for reducing the residual COD of biologically treated effluents.[47]

Kulperger[48] used a high purity oxygen activated sludge system for treating petrochemical wastes. The system consisted of a four stage biological reactor and a center feed clarifier. Pilot plant studies showed that the system could provide a BOD removal of 90% in a wastestream which contained 2,700 to 4,000 mg/L BOD. The plant was operated at biomass loadings of 0.49 to 0.82 pounds of BOD_5 per pound of MLVSS and required 1.6 pounds of oxygen to remove one pound of BOD at a loading rate of 0.6 pounds of BOD per pound of MLVSS-day.

The utility of anaerobic lagoon pretreatment of petrochemical waste was investigated by Hovious et al.[49] A design procedure for the selection of lagoon volume based on organic loading and temperature was presented. Using this design procedure it was estimated that a lagoon with a hydraulic detention time of about 10 days and a temperature of 20°C would achieve a 40 percent COD removal and a 50 percent BOD removal when the influent contained 3,000 mg/L of COD. Examination of chromatographically identifiable organic compounds in the waste used during this research indicated that all compounds, except metabolic intermediates, were removed to a significant degree in the anaerobic lagoon (Table 3.5).

Britz et al.[50] reported the successful use of downflow fixed bed anaerobic reactors for the treatment of a petrochemical effluent. COD reductions of 93-95% were found at an optimum retention time of 2.3 days and a loading rate of 4.7 kg COD/m^3/d. Approximately 0.88 m^3/m^3/d (at standard temperature and pressure) of biogas was produced with a methane content of 90-96%.

Fisher et al.[51] also investigated the use of anaerobic processes for petrochemical waste treatment. Packed bed, mixed digester and anaerobic lagoon processes were evaluated. The anaerobic lagoon was found to be the process of choice. Investment and operating costs were the lowest of the studied systems, and a microbiological sulfur reduction-oxidation cycle occurred in the lagoon in which sulfates were used and organics removed. The anaerobic system produced smaller amounts of biomass and required less energy for operation. Some compounds were degraded in the anaerobic system which could not be aerobically degraded.

Temperature effects on the biological treatment of petrochemical wastewaters were investigated by del Pino and Zirk.[52] Empirical models were developed to fit the relationship between effluent BOD and COD and hydraulic retention time, mixed liquor volatile suspended solids, temperature and influent substrate concentration. The effects of temperature on the biological treatment of petrochemical wastewaters were observed to be more drastic than temperature effects on municipal wastewater treatment systems. Tests to measure the effects of temperature on sludge characteristics were inconclusive.

TABLE 3.5

REMOVAL OF SPECIFIC ORGANICS IN ANAEROBIC LAGOONS[49]

Compound	Dilute Wastes[a]		Concentrated Wastes[a]		
	Loading Rate 13 lb COD/day/ 1,000 cu ft			Loading Rate 22 lb.COD/day/ 1,000 cu ft	Loading Rate 48 lb.COD/day/ 1,000 cu ft
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Effluent (mg/L)
Methanol	80	35	380	135	145
Ethanol	80	15	270	120	130
n-Propanol	--	--	170	35	40
Isopropanol	60	30	175	45	55
n-Butanol	--	--	170	75	80
Isobutanol	--	--	250	80	85
n-Pentanol	--	--	315	70	100
Isopentanol					
Hexanol	--	--	140	20	30
Acetaldehyde	30	10	80	35	40
n-Butyraldehyde	--	--	190	50	35
Isobutyraldehyde	--	--	210	50	50
Acetone	90	60	150	80	70
Methylethyl ketone	10	5	---	---	---
Benzene	10	5	---	---	---
Ethylene glycol	135	30	755	155	190
Acetic acid	215	220	2,120	2,280	2,620
Propionic acid	—	—	0	505	470
Butyric acid	—	—	0	330	300

[a] Data are averaged from 5 to 12 occurrences in grab or composite samples.
Note: Lb/day/1,000 cu ft x 16 = g/day/cu m.

The biological treatment of a complex petrochemical wastestream using a sequence of anaerobic digestion and activated sludge was studied by Humphrey et al.[53] Bench scale and pilot plant studies using various composite samples and process wastewater blends indicated the need for stream segregation and waste reduction. The system was effective in removing the biodegradable portion of the pretreated wastewater stream. The average influent composition of approximately 6000 mg BOD/L, 8000 mg COD/L and 1000 mg nitrates/L was reduced to an effluent with approximately 50 mg BOD/L, 1200 mg COD/L, 200 mg suspended solids/L and essentially no nitrates. These data show that a significant amount of COD could not be removed by conventional biological treatment processes.

Studies conducted by Medley and Stover[54] and Stover et al.[55] have shown that pretreatment with ozone can increase the biodegradation of some organic compounds found in petrochemical wastewaters. Ozone addition was found to be beneficial; however, it is not a "cure-all" and studies should be conducted on each compound to determine if it is effective and economical. The addition of powdered activated carbon (PAC) to biological oxidation processes may also significantly enhance the efficiency of biological treatment processes.[56]

Recent advances in the field of bioengineering have lead to the development of microbial cultures which have the ability to break down molecules resistant to biological degradation. Thibault and Zitrides[57] have reported that a specially adapted strain of bacterial inoculum applied to the biological treatment process at a petrochemical processing plant significantly improved effluent quality. The addition of these selectively adapted microbes reduced effluent total oxygen demand, and biochemical oxygen demand, improved system stability, eliminated an existing foam problem, and resulted in the elimination of at least one compound (tertiary butyl alcohol) from the effluent not previously degraded. These results, combined with recent advances and interest in genetic engineering, suggest that biological treatment processes may be improved by these techniques; however, further research is required.

Physical-chemical processes play an important role in petrochemical wastewater treatment. Many physical-chemical treatment processes are used to pretreat petrochemical wastewater in preparation for biological treatment. API separators are used to remove materials less dense than water, such as free oil, and suspended matter that is more dense than water. Tilted plate separators are also used to remove materials less dense than water. Several types of filtration devices are also used to remove free oil and solids from wastestreams prior to biological treatment.

Neutralization is commonly required in the treatment of petrochemical wastewaters. Acid streams may be neutralized by fluidized mixing with lime slurries, dolomitic lime slurries, caustic or soda ash. Alkaline streams may be neutralized with sulfuric or hydrochloric acid or with boiler flue gas (carbon dioxide). Neutralization can often be accomplished by mixing internal wastewater streams.[38] Volatile organic compounds, hydrogen sulfide and ammonia are often removed from wastewater streams by stripping processes.

Dissolved Air Flotation (DAF) is commonly used in petrochemical waste treatment plants to enhance oil and suspended solids removal. DAF units, while not as economical as API separators and tilted plate separators, produce a better quality effluent which is often required to meet effluent oil limitations. If a significant portion of the oil is emulsified, chemical addition with flocculation chambers may be a part of the flotation unit.

Coagulation-flocculation processes are effective in removing suspended solids, some nutrients and heavy metals from petrochemical wastestreams.[38]

Activated carbon adsorption systems may be used to remove residual organic compounds from petrochemical wastewaters. A review of the literature on activated carbon adsorption as a treatment concept for petrochemical wastewaters was presented by Matthews.[58] Compounds in the alcohol, aldehyde, amine, pyridine and morpholine, aromatic, ester, ether, glycol and glycol ether, ketone, organic acid, oxide, and halogenated organic groups were found to be amenable to carbon adsorption.[59]

Petrochemical wastewater was treated in a treatment system consisting of oil removal, biological oxidation, chemical treatment, filtration and activated carbon adsorption. The COD was reduced from 3,200 mg/L to 30 mg/L. The activated carbon columns were found to remove dissolved organics not amenable to biological treatment along with color.[60]

Four physical-chemical unit operations were studied by Coco et al.[61] to determine their feasibility for removing biorefractory organics found in petrochemical wastestreams. Steam stripping was evaluated using petrochemical process effluents containing chlorinated hydrocarbons and aromatic hydrocarbons. This unit operation removed up to 75 percent of the total organic carbon (TOC) in the process effluent. The cost of this treatment process was significantly reduced by the recovery of lost product.

Solvent extraction was evaluated using process effluents containing chlorinated hydrocarbons and aromatic hydrocarbons. Straight chain paraffin hydrocarbons in the C_{10} to C_{12} range were found to give maximum TOC removal with minimum TOC residual. Organic removals in the 90 percent range were frequently obtained during pilot plant operation.[61] Product present in the wastestream was also recovered in this process, and thus contributes to reduced treatment costs.

Ozonation was an effective method of pretreating wastewaters from the manufacture of toluene di-isocyanate, ethylene glycol, styrene monomer, and ethylene dichloride. Batch oxidation studies showed that ozonation improved biotreatability of these wastewaters. Complete oxidation with ozone was found to be uneconomical.[61] Carbon adsorbtion removed C_1 and C_2 chlorinated hydrocarbons from the wastestreams studied. Adsorption characteristics of different commercially available activated carbons were evaluated. In addition, an activated carbon was developed from a by-product soot produced in the acetylene process. This carbon was found to have about 80 percent of the absorptive capacity of commercial products.[61]

Other processes which have been used for the treatment of petrochemical wastewaters include: polymeric adsorption,[62,63] wet air oxidation,[64] pyrolysis,[65] and free radical oxidation.[66]

Process Modification, Conservation and Treatment

The petrochemical industry lends itself to controlling pollution through process improvement rather than pollution abatement. Four alternative possible solutions may be developed for a pollution problem in the petrochemical industry depending on the waste produced. First, some wastes may be recovered as salable coproducts. Second, wastestreams can be recycled after some process modification for conversion to prime product or for reuse in the process as a reagent or intermediate. Third, the waste may be usable as a fuel. Fourth, and least desirable, wastes may be treated in waste treatment processes where they are converted to less harmful states and/or dispersed in quantities which may be assimilated by the environment.

Summaries of some process improvements which have aided in the reduction of pollutants in the petrochemical industry may be found in Burroughs,[67] Mencher,[4] the Oil and Gas Journal,[68] and Rickles.[69]

Process technology in the petrochemical production industry is constantly changing. Some unit processes will produce desired products with a reduction in the quantity of pollutants generated when compared to other technologies. Tavlarides[70] developed a matrix of significant pollution problems and process modifications which will reduce or, in some cases, eliminate the production of these pollutants for the explosives industry. Matrices for nitric acid, TNT, and nitrocellulose production were presented. The matrices describe individual processes, the pollutants and their sources in the process, the nature of the pollutant and the process modification for mitigation or reduction of the pollutant. Analysis of production unit processes may, therefore, lead to the production of smaller amounts of water-borne pollutants.

Several schemes were suggested by Quartulli[71] to reduce water consumption and increase the use of waste streams as process raw materials in steam-hydrocarbon reforming plants. The processes proposed recycling essentially all of the process condensate to the process system, (with minimum offsite treatment), and bypassing feedwater, boiler and steam turbine systems.

Petrochemical wastewaters containing high concentrations of salt and refractory organic contaminants were treated by activated carbon adsorption for the removal of organic constituents.[72] The remaining salt solution was treated with a hybrid electrodialysis-reverse osmosis process to produce fresh water and a concentrated brine solution. Organics recovered by the system were recycled and the processed water was suitable for reuse.

Conserving and reusing water have become key concerns in chemical processing industry plants as the availability and quality of water supplies diminish and wastewater discharge regulations become more stringent. Holiday[73] has discussed the use of eight technologies which may be applied to reduce water usage by either cutting usage at some point in the plant or by recycling and reusing a waste stream. The technologies described include vapor-compression evaporation, waste-heat evaporation, reverse osmosis and ultrafiltration, electrodialysis, steam stripping, combination wet/dry cooling towers, air-fin cooling and cooling water sidestream softening. A list of the characteristics of these processes is contained in Table 3.6.[73] The use of reverse osmosis as a water purification process in the petrochemical industry was reported by Kosarek.[74]

Willenbrink[75] reported the use of several techniques to reduce or concentrate wastestreams containing phenol, ammonia and hydrogen sulfide. In one process, the use of a dilute caustic in product purification washes drastically reduced the amount of phenol in the wash water wastestream. This system not only reduced the amount of phenol to be treated, but also reduced the consumption of caustic with no noticeable product deterioration. Steam stripping regenerated cataylst was used to minimize the introduction of oxygen into a fluid catalytic cracking operation to reduce the production of phenolic compounds. Wash waters and steam condensates which have been in contact with hydrocarbons were collected from various unit operations for use as wash water to prevent corrosion and salt build up. A fraction of the phenol present in this washwater is absorbed by the hydrocarbons being washed. Reductions of approximately 50% of the phenol present have been observed.

TABLE 3.6

CONSERVING AND REUSING WATER
WATER CONSERVATION AND REUSE TECHNOLOGIES THAT ARE SEEING WIDER APPLICATION[73]

Technique	Application	Limitations	Relative costs		Comments
			Capital	Operating	
Vapor-compression evaporation	Concentration of wastewater or cooling-tower blowdown Concurrent production of high-purity water	Not for organics that form azeotropes or steam-distill Fouling must be controllable	High	High	Rapid growth High-quality distillate Handles broad range of contaminants in water
Waste heat evaporation	Concentration of wastewater Condensate recovery	Not for organics that form azeotropes or steam-distill	Medium	Medium	Not widely used now Future potential good
Reverse osmosis, ultrafiltration	Removal of ionized salts, plus many organics Recovery of heavy metals, colloidal material Production of ultrapure water	Fouling-sensitive Stream must not degrade membranes Reject stream may be high-volume	Medium	Medium	Future potential strong Intense application development underway
Electrodialysis	Potable water from saline or brackish source	Limited to ionizable salts	Medium-high	Medium	Modest future potential

TABLE 3.6 (continued)

CONSERVING AND REUSING WATER
WATER CONSERVATION AND REUSE TECHNOLOGIES THAT ARE SEEING WIDER APPLICATION[73]

Technique	Application	Limitations	Relative costs		Comments
			Capital	Operating	
Steam stripping	Recovery of process condensates and other contaminated waters Removal of H_2S, NH_3, plus some light organics	Stripped condensates may need further processing	Medium	Medium-high	Well-established as part of some processes
Combination wet/dry cooling towers	Puts part of tower load on air fins Can cut fogging	Costly compared with wet cooling tower	Medium	Medium	Growth expected in arid areas
Air-fin cooling	Numerous process applications	For higher-level heat transfer Can be prone to freeze-up, waxing	Medium	Medium	Well-established Good for higher-temperature heat rejection
Sidestream softening	Reduce cooling-tower blowdown	Dissolved solids must be removable Control can be difficult	Low-medium	Low-medium	Not widely used Future potential good

Several water reuse and recycling systems currently used in the petrochemical industry were described by Dennis.[76] The processes include separation of potable and process water, recycled non-contact cooling water systems, process water recycle, and spray irrigation of process wastewater. A computer monitored and controlled system designed to manage water and energy at petrochemical plants was developed by Kempen.[77] This system helped reduce water use, wastewater treatment costs and energy use.

Case Histories

Wastewater from a petrochemical plant which produces raw materials for the polyester fiber and film and polystyrene industries are treated by an activated sludge plant consisting of equalization basins, biological oxidation basins, clarification, dissolved air flotation, polishing ponds and filtration (Figure 3.1). The waste treatment facilities are described in Table 3.7.[78] This facility produced an effluent which contained 8 mg/L BOD and 11 mg/L suspended solids while removing 98% of the TOC present. A unique management strategy was employed at the facility. Each production unit is held accountable for the wastes they generate. Waste treatment costs are charged back to the individual production units based on the amount of organics discharged to the treatment plant. This system creates incentives for personnel at each unit to reduce waste loads and product losses.

Ford et al.[79] described the development of a water pollution control system for the Zulia El Tablazo Petrochemical Complex in Venezuela. The first task in designing the treatment system was to define each of the production processes and predict the qualitative and quantitative characteristics of the wastewaters. Treatability studies were then performed to evaluate treatment

FIGURE 3.1

WASTE TREATMENT FLOW DIAGRAM[78]

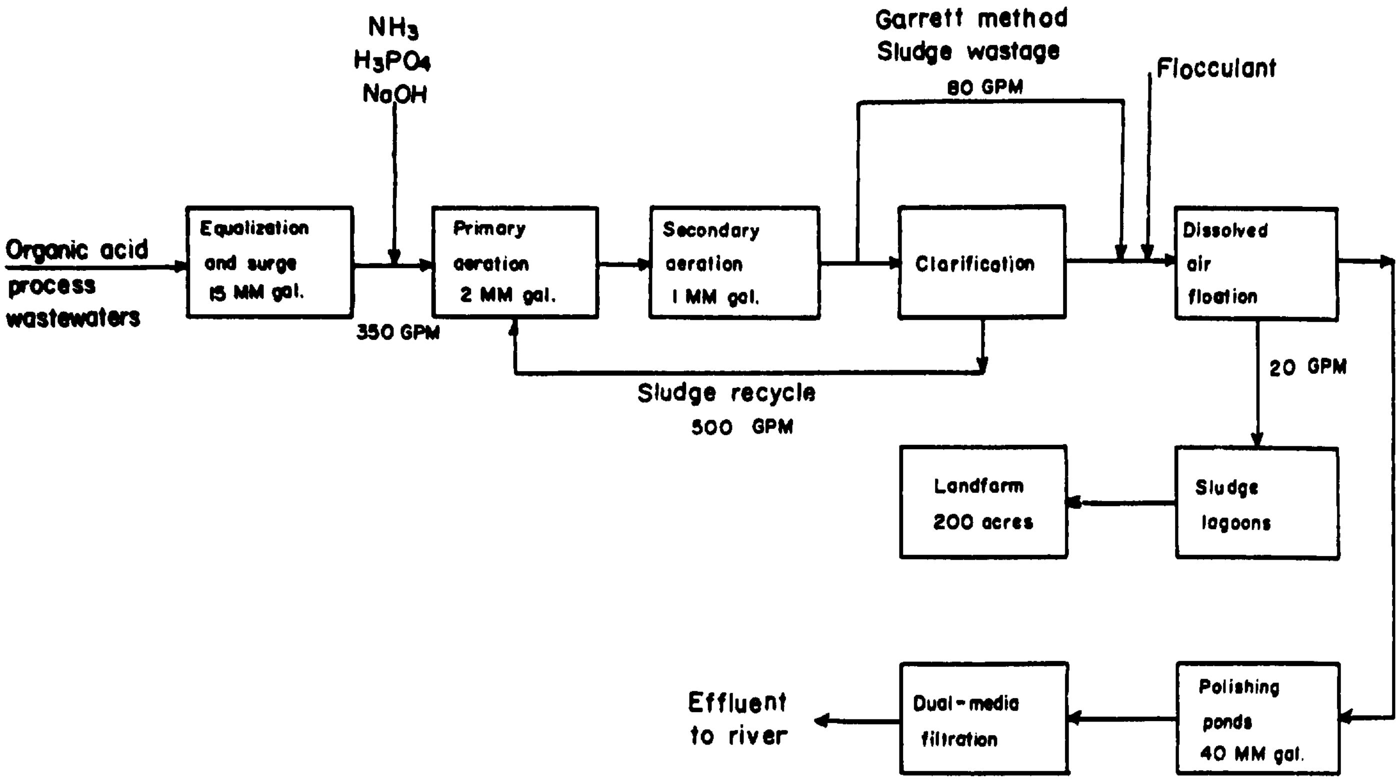


TABLE 3.7

WASTEWATER TREATMENT PLANT - DATA SHEET[78]

Utilizes activated sludge process for treating high strength organic acid wastewaters before final discharge to the Des Plaines River.

Facilities

	Capacity	Detention time
Feed Equalization & Surge	15 million gallons	30 days
6 Aeration Basins	3 million gallons	6 days
2 Secondary Clarifiers	188,000 gallons	
Dissolved Air Flotation Unit	59,000 gallons	
Polishing Lagoon	40 million gallons	60 days
Dual Media Filter	1,000 gpm	
Sludge Storage	3.5 million gallons	4 months
Sludge Landfarm	200 acres	

Manpower

Operators	1 per shift
Sludge hauling operator	1 per day shift
Foreman	1 per shift
Supervisor	1
Engineer	1
Lab technician	1
Maintenance	3 per day shift

Raw wastewater

	Average	Capacity
Flow, gal/day	500,000	700,000
Concentration, mg/L TOC	3,000-4,000	
TOC Load, lbs/day	14,000	24,000
COD Load, lbs/day	35,000	60,000
BOD_5 Load, lbs/day	25,000	43,000
Population Equivalent	150,000	250,000

Effluent quality

BOD_5, mg/L	8
Suspended Solids, mg/L	11
TOC Reduction, %	98

Costs

Total capital expenditure to date	US $9 million (1982 US dollars)
Annual operating, maintenance, and fixed costs	US $2.5 million
Treatment cost, per pound of TOC	US $0.50

alternatives. Design criteria were developed from the results of treatability tests and conceptual flowsheets were developed.

An activated sludge system was deemed to be the most practical, reliable and economical method of treating the El Tablazo wastewaters to the desired level. This decision was made based on treatability study data and the experience of a consultant in previous investigation, design, and operation of petrochemical plant wastewater treatment systems.[79]

A simplified schematic of the treatment system is shown in Figure 3.2. The system was devised so that all dry weather organic sewer flow is treated. An impoundment basin was constructed for temporary storage and controlled release of specific wastewaters to the treatment process. The system also includes an equalization basin to minimize hydraulic and waste load variations. The equalized flow enters parallel activated sludge basins. Additional parallel units may be added as more treatment capacity is required. Excess biological sludges are aerobically digested, thickened, dewatered by basket centrifugation and hauled to land disposal sites.[79]

A primary and secondary biological wastewater treatment plant was installed at a petrochemical plant in Puerto Rico. The petrochemical complex produces 352 million kilograms (775 million pounds) of ethylene per year and derivative products including butadrene, ethylene oxide, phenol, cumene, polyethylene, bisphenol-A, and plasticizers.[80] The total waste load to the plant was based on flow measurements and laboratory analyses of waste streams from existing plants plus estimates of aqueous waste loads from new process units based on an understanding of process chemistry and engineering principles. The major components of the waste treatment facility are shown in Figure 3.3. The facility includes waste collection equipment, primary

FIGURE 3.2

EL TABLAZO TREATMENT COMPLEX[79]

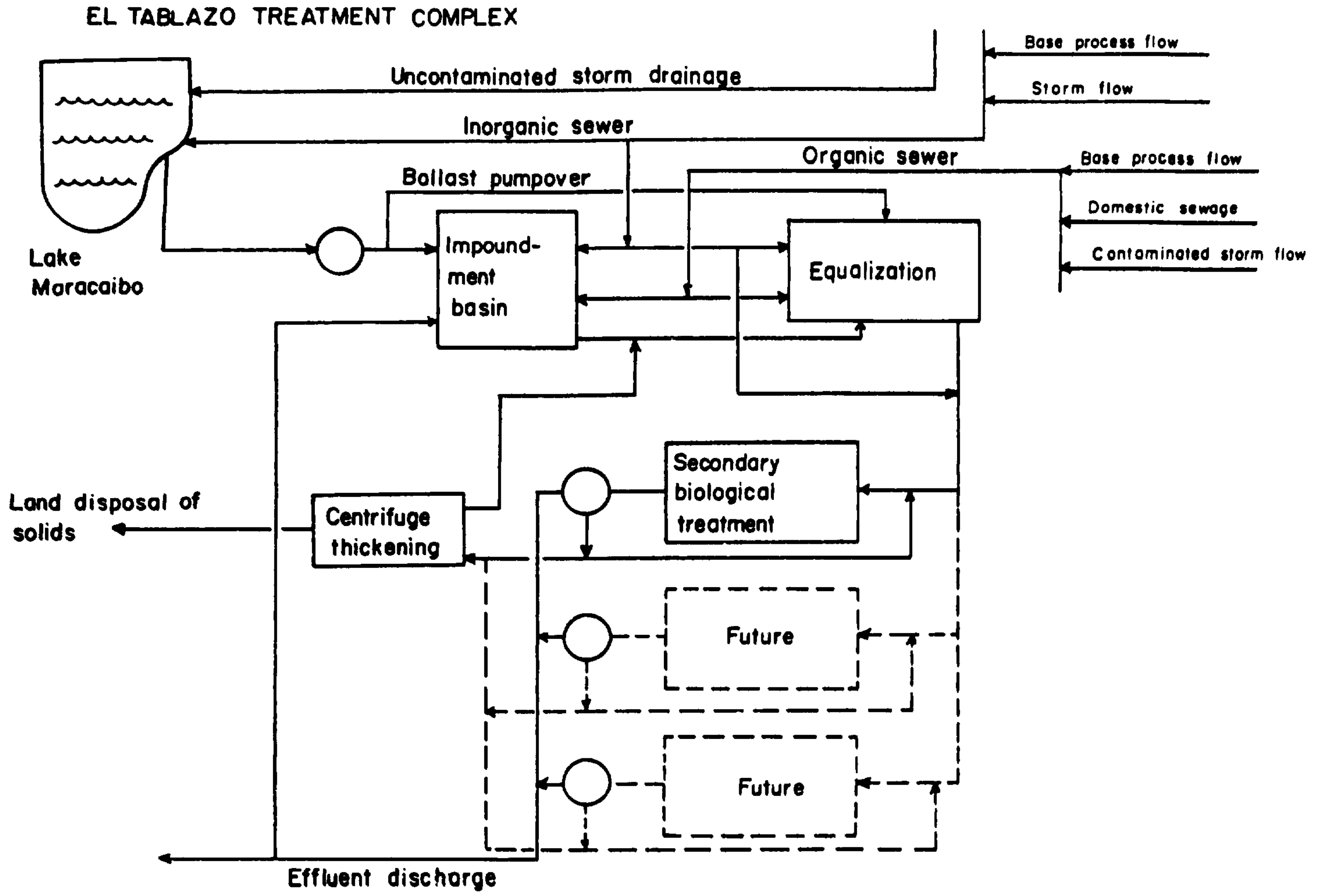
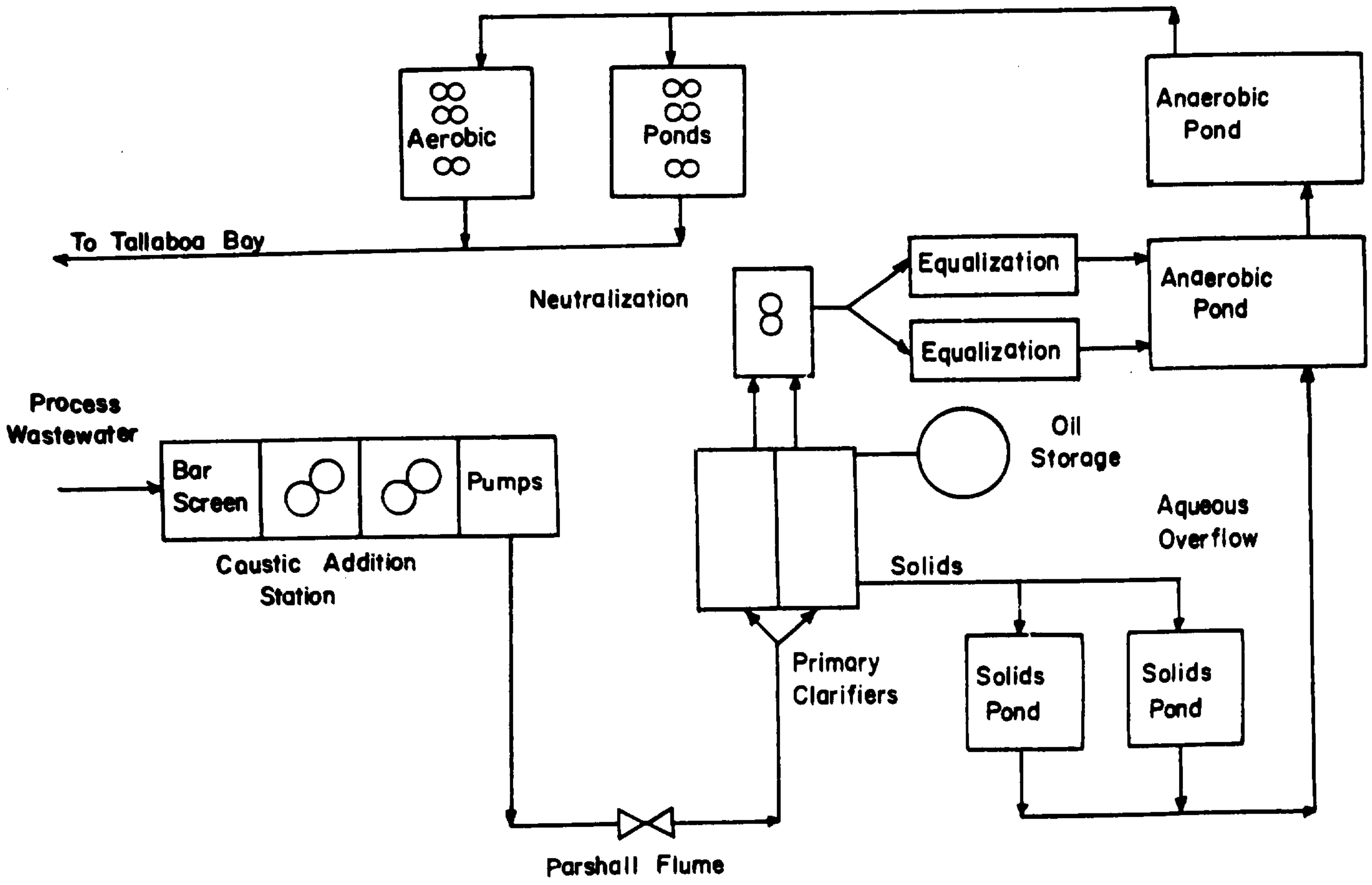


FIGURE 3.3

FLOW DIAGRAM OF WASTEWATER TREATMENT FACILITY AT PONCE, PUERTO RICO[80]



treatment, neutralization, equalization and biological treatment using an anaerobic pond-mechanically mixed aerobic pond stabilization system. Storm and/or fire protection waters are separated from process waste streams and treated separately.

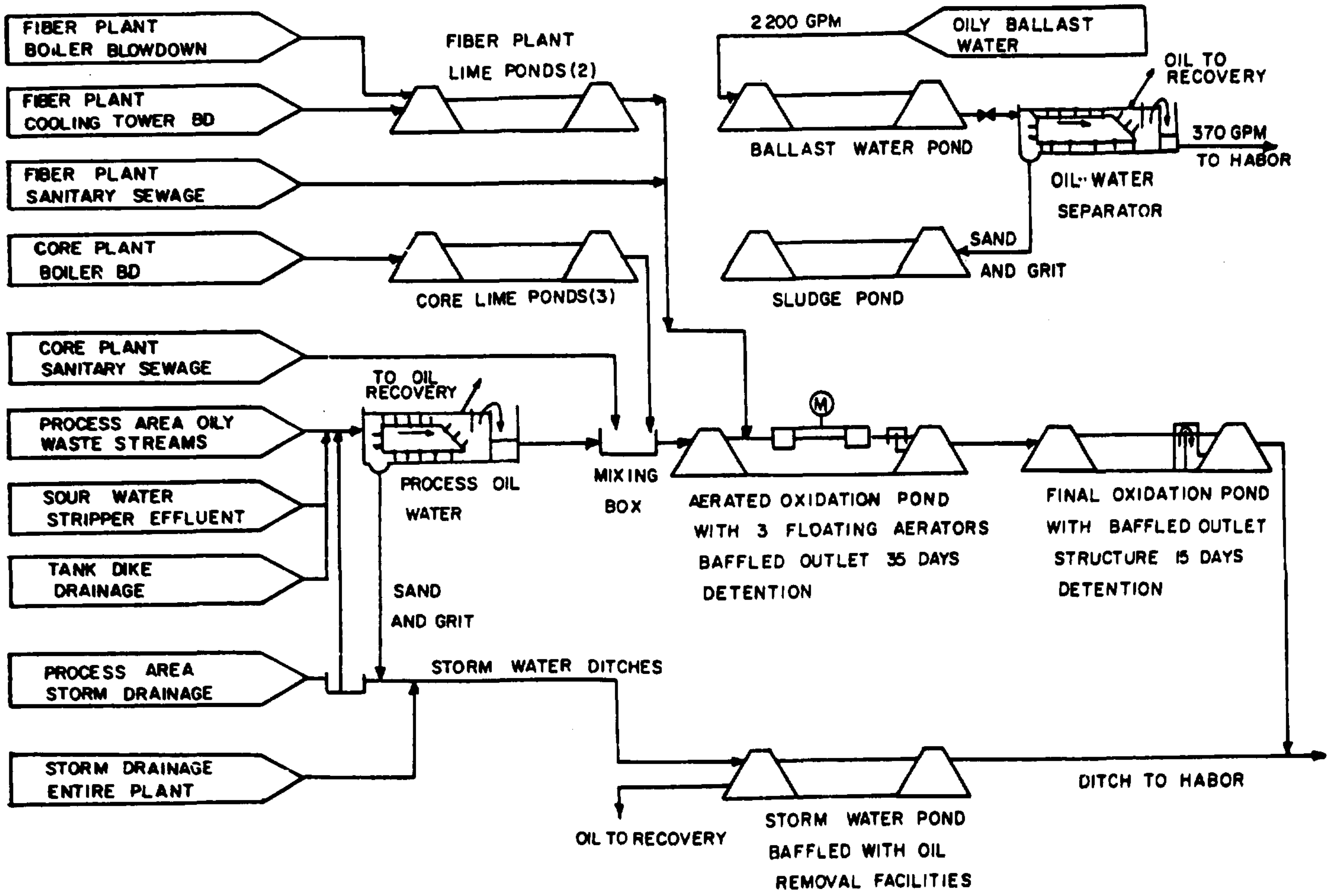
The wastewater treatment facilities at another Puerto Rican petrochemical plant were described by Figueroa.[81] This petrochemical plant uses 5,962 m^3/d (50,000 barrels/d) of naphtha to produce various products including paraxylene, orthoxylene, cyclohexane, benzene, toluene, mixed xylenes, parraffinic naphtha, and high octane motor fuel. Wastewaters are segregated into six separate sewers which have been designated as the oily water sewer, the boilers blowdown sewer, the cooling water sewer, the sanitary sewer, the storm water sewer and the combined sewer. The basic pattern of wastewater segregation and treatment are shown in Figure 3.4. The process basically consists of pretreatment (neutralization, oil-water separation), followed by biological oxidation in aerated ponds. The facilities proved to provide adequate water pollution control while permitting future expansion.[81] The treatment plant effluent was found to contain an average of 25 mg/L of total suspended solids and have an average COD of 150 mg/L.

Economics

The cost of constructing a new petrochemical processing plant usually will require that approximately 5 to 10 percent of the capital investment be in pollution control facilities; however, in existing facilities it's frequently possible to make modifications in the processes or install pollution control equipment that will recover the cost in a relatively short period of time. Examples of savings from the installation of modifications and pollution control equipment are presented below.

FIGURE 3.4

SIMPLIFIED FLOW SHEET, WASTEWATER TREATMENT, GUAYAMA PETROCHEMICAL COMPLEX[81]



The economic aspects of various pollution control projects has been documented by Burgess.[82] One petrochemical company installed 450 pollution abatement projects with a total cost of US $20,000,000 during 1971. The annual net savings from these projects was estimated to be US $6,000,000, with an average return on investment of 30%. As an example of these projects, three organic chemical plants installed mixers and subcoolers to increase yield by 3%. This process change reduced the COD in the wastewater by 30 pounds per minute. It cost US $200,000 to install the equipment and US $42,000 per year to operate it, but US $709,000 worth of raw materials are saved per year, producing a net savings of US $667,000 per year while reducing the pollutional load. Emphasizing waste prevention rather than waste treatment was shown to be a cost effective pollution control strategy.

Pollution control efforts of one division of the above mentioned petrochemical company reduced BOD discharges by 25%, COD discharges by 26% and soluble solids discharges by 72%. Ninety pollution control projects were conducted to produce this reduction. Fifty-five of these projects had a negative return and 35 had a positive return. Economic analysis showed an annual savings of US $2,960,000 on a US $6,100,000 investment (1971 dollars). An US $8,300,000 capital investment produced a net annual savings of more than US $1,000,000 in another division of this company, while an investment of US$2,100,000 produced a US $1,300,000 yearly savings in still another division.[82]

A flow measurement system coupled with computer control reduced the cost of water, steam generation, and steam distribution and produced less waste at a Belgian petrochemical plant.[77] The computer control system provided water and energy management practices which reduced energy requirements and water and wastewater treatment costs at the plant. The total project cost was approximately US $435,000 (1982) and was projected to produce a return on investment of better than 64 percent.

A polymeric adsorption system efficiently removed and recovered phenol and was also found to produce a net savings while eliminating a waste treatment problem.[62] In this process phenolic compounds may be removed from a wastestream by adsorption onto a polymeric resin. During resin bed regeneration, the phenolic compounds may be recovered. In one application, it was estimated this system would produce a net savings of US $235,000 per year, while producing an effluent with less than 1 mg/L of phenol.

Chlorinated and aromatic hydrocarbons were removed from petrochemical process effluent by steam stripping at a cost of US $0.00041 per liter of treated wastewater including product recovery credit. Solvent extraction was also used and the cost of treatment, including product recovery credit, was estimated to be US $0.0007 per liter of treated wastewater. Ozonation was an effective treatment method, but costs were much higher than those observed for steam stripping and solvent extraction. The operating costs for a carbon adsorption system removing organics from an ethylene dichloride plant effluent were estimated to be US $3.50 to 4.50 per kilogram of organics removed or US $0.045 to 0.07 per kilogram of product.[61]

CHAPTER 4

SOLID WASTES MANAGEMENT

Introduction

Solid wastes in the petrochemical industry may occur as actual solids such as waste plastics, paper or metal; as semi-solids such as tars and resins and as suspended and dissolved solids such as waste polymers and inorganic salts. These materials may be characterized as combustible or non-combustible, organic or inorganic, inert or biodegradable, dry or mixed with either aqueous or non-aqueous liquids.

The solid wastes generated by the petrochemical industry may be stored, handled and disposed of by many different methods and combination of methods. The method or combination of methods used is dependent on existing conditions. Factors which are considered when designing solid waste processing facilities include: 1) characteristics of the wastes (volume, weight, density, ease of handling, rate of production, toxicity, biodegradability, combustibility, etc., 2) potential value of salvaged material for recycle into the same process or into new or different processes at the plant or at other plant facilities, 3) adaptability of the disposal method to the waste in question, and 4) availability of land and expected future land use patterns. Several types of solid wastes and disposal methods which have been used in the petrochemical industry are presented in Table 4.1.[83]

Almost every existing petrochemical manufacturing plant has some form of solid waste handling or disposal facilities on the plant premises. In a recent survey of the petrochemical industry it was observed that 90% of the solid wastes generated at petrochemical processing plants was disposed of on the

TABLE 4.1

PETROCHEMICAL SOLID WASTE SURVEY[83]

Disposal Methods Used	Water Treatment Sludges	Cafeteria and Lunchroom	Plant Trash	Ashes, Flyash, Incinerator Residue	Plastic	Ferrous and Non-Ferrous Metals	Catalysts	Organic Chemicals	Inorganic Chemicals	Wastewater Treatment Sludges, Filter Cakes, and Viscous Solids
	TYPE OF WASTE									
Land Disposal										
Lagoon	x						x	x	x	x
Spread on Land	x			x			x	x	x	x
Sanitary Landfill	x	x	x	x	x	x	x			x
Dumps	x	x	x	x	x	x	x		x	x
Incineration										
Stationary Hearth Furnace		x	x		x					
Multiple Hearth Furnace		x	x		x					x
Rotary Kiln		x	x		x			x	x	x
Open Pit			x		x					
Liquid Burner								x	x	
Fluidized Bed Reactor								x	x	x
Salvage and Recycle				x	x	x	x		x	
Chemical Treatment								x	x	
Biological Treatment								x		
Ocean Disposal										
Bulk Dumping								x	x	
Sealed Container Dumping								x	x	

plant premises.[84] This means approximately 10% of these wastes are disposed of by the use of offsite or commercial disposal facilities.

Types of Solid Wastes

Solid wastes generated during the petrochemical manufacturing process include water treatment sludges, cafeteria and lunchroom wastes, plant trash, incinerator residues, plastics, metals, waste catalysts, organic chemicals, inorganic chemicals, and wastewater treatment solids. A brief discussion of each type of waste is necessary to understand the problems associated with petrochemical solid waste disposal.

Water treatment facilities may be found at many petrochemical processing plants. Solids composed of silt, sand and lime, or alum based flocculant material are produced during the water treatment process and require treatment and/or disposal. Cafeteria and lunch room wastes consist of food waste and paper and plastic products used in the cafeteria operation as packaging material.

Plant trash is the general term used to describe all the miscellaneous wastes which may be found at the manufacturing facility. Trash is often classified as combustible or non-combustible. Combustible material would include paper, fiberboard containers, packaging material, miscellaneous plastic and rubber products, and waste wood. Non-combustible material would include metal scraps, glass, pottery, floor sweepings, solids from storm sewers, and construction and demolition debris.

Ashes and incineration residue wastes include residues from the incineration of trash, sludges and other wastes, and residues from plant heating, steam production, water heating, and power generation facilities. The majority of the metal scraps generated in the petrochemical industry are produced during the demolition and/or construction of process equipment. Most scrap metal that is generated is bulky and of ferrous composition. This material may be contaminated by exposure to toxic substances generated during the production process.

The plastics encountered in the petrochemical industry are primarily polyethylene, polypropylene, polystyrene, and polyvinvylchloride. The reported physical form of polymer wastes encountered in the plastics industry are presented in Table 4.2.[85] Plastic particles may range in size from powders and pellets to chunks weighing more than 100 pounds. Waste plastics are generated by off-specification production, spills, product contamination, cleanout, emergency dumps,and miscellaneous other sources during plastics manufacturing.[85] Plastics are generally biologically inert substances.

Spent catalysts may be liquid, semi-solid, or solid. Catalysts possess a wide range of chemical characteristics. These catalysts may possess toxic qualities and thus would require special handling. A wide variety of other organic and inorganic chemicals may enter the wastestream as a result of production processes. A large portion of these substances become part of wastewater flow streams and must be separated from these liquid wastestreams prior to treatment and/or disposal. Gloyna and Ford[2] report that the majority of all solids found in petrochemical wastes are present as dissolved solids in liquid waste streams.

During wastewater treatment processes, suspended and/or dissolved solids are separated from wastestreams by physical chemical unit processes producing sludges which must be disposed. Biological unit operations used in wastewater treatment processes such as activated sludge, trickling filters, extended aeration, wastewater stabilization ponds, and anaerobic digestion also produce

TABLE 4.2

FORMS OF POLYMER WASTES[85]

	Average Percent of Each Form	
	Primary Resin Producers	Processors and Fabricators
Pellets	18	14
Chopped or shredded	0	3
Dust or powder	23	3
Random large (>100 lb)	10	28
Random small (<100 lb)	14	17
Other, off-specification product and contaminated product	35	35
	100	100

sludges which require disposal. Wastewater treatment sludges may contain a wide variety of organic and inorganic components depending on the production process which produces the wastestream being treated.

Disposal Techniques

Solid and semi-solid waste materials generated in the petrochemical industry may be disposed of by several techniques including: salvaging and reclamation, open dump burning, no-burning dump, landfill, land farming, lagooning, incineration, and ocean dumping.

In salvaging and reclamation operations, waste materials are collected and segregated for reclamation and reuse. Salvaged materials may be reused for the original purpose or an entirely different purpose, within the same plant or outside the plant. Materials such as scrap metal, wood, spent catalyst, spent acids and caustics, contaminated oils and other hydrocarbons, plastics and polymers, rubbers and carbon black have been recovered and reused in salvage operations in the petrochemical industry.[83]

Open dump burning is normally an unacceptable disposal alternative and may be illegal in many areas. Combustible materials are transported to an isolated location and burned in this disposal technique. The residue may or may not receive further treatment. This technique is simple, has low time and labor requirements, and has low capital and operating costs; however, this technique produces undesirable health and safety hazards and results in the production of air pollutants.

No-burn dumping involves the dumping of waste material on the ground or into pits. This technique is primarily used for non-combustible materials. This method requires large areas of land which may be rendered unsaleable for future development. Disposal by this technique also produces the potential for groundwater and surface water contamination.

Sanitary landfills are areas where wastes are buried in a controlled manner to minimize the deleterious effects on public health and environmental quality. In a sanitary landfill, refuse is confined to a small area and covered with a layer of earth each day, or more frequently, if necessary. Sanitary landfills provide the most economic environmentally acceptable method for the disposal of most non-toxic solid and semi-solid wastes generated at petrochemical processing plants.[83]

In addition to providing the most economic environmentally acceptable disposal method for most solid wastes generated in a petrochemical manufacturing plant, sanitary landfills provide other advantages. First, a low degree of technical expertise is required to operate a landfill. Another advantage is the ease and simplicity of the operation. Disadvantages include the land requirements. Sanitary landfills require more land than other land disposal techniques. Soil and hydrogeological conditions must also be favorable.

Sanitary landfills must be constructed in areas where water will not leach through the disposal site and contaminate surface or groundwater supplies. To insure protection of water supplies, a monitoring system is desirable. This monitoring system may include drain systems around the landfill area and groundwater monitoring wells. Pritchard et al.[86] described a three component monitoring system designed to protect water quality at an ethylene glycol plant. Landfilling practices are described in detail by Tchobanoglous et al.[87]

Another solid waste disposal technique which has been used in the petrochemical industry is "land-farming". In land-farming waste materials are spread in a thin layer over a relatively large area of land. The wastes may then be worked into the soil or left with no further treatment. This method is usually used for semi-solid materials or solids which have been mixed with liquids. The liquid portion of the waste is allowed to evaporate or percolate into the soil. The remaining solids are degraded by soil microorganisms. Land-farming has been shown to be an adequate disposal technique for petrochemical wastes of a predominately paraffinic nature.[88,89] Cihonski et al.[90] report that land-farming may also be an adequate method for disposing of sludges containing aromatic species.

Ganze and Teller[91] describe the operation of a land-farming, or land-spreading facility which was developed to dispose of sludge from a petrochemical processing complex wastewater treatment plant which treats 87,000 m^3/day (23 mgd). Both primary and digested waste biological sludges are disposed of on 20,000 m^2 (approximately 5 acre) plots in a 610,000 m^2 (150-acre) land-spreading area. The primary sludges disposed in this area included oily silts from API separators, chemical precipitates which are produced by pH adjustment prior to biological wastewater treatment, and solids transported from the petrochemical complex by rainfall and runoff. Sludge was pumped onto each plot to a total depth of 300-460 mm (12-18 in). The sludge is allowed to settle. Carriage water is then decanted and pumped back to the wastewater treatment plant for treatment. The sludge layer is allowed to air dry after which it is tilled into the soil.

Soil TOC and COD showed significant increases after the first sludge application. On the same plot, after subsequent applications, little change in these parameters was noted. Heavy metals concentrations appeared to be the limiting factor for determining the useful life of this land-spreading operation. Lead, nickel, manganese, copper, chromium, and arsenic concentrations increased with each sludge application. Sufficient data to estimate plot life was not obtained. Operating and maintenance costs were calculated to be US $7.75 per ton of solids disposed (1977 dollars). It was concluded that landspreading could be an effective low cost sludge disposal alternative when: 1) reasonably priced land was available, 2) climatic conditions permit, i.e., annual evaporation rate is equal to or greater than rainfall; and 3) soil types and geology preclude groundwater contamination.[91]

Lagooning is another technique used in the petrochemical industry. In lagooning, solid, semi-solid and liquid wastes are dumped into ponds or pits. Liquid may be discharged and possibly receive further treatment or the liquid may be retained and allowed to evaporate. Organic solids and liquids retained in the pond may be degraded biologically depending on their nature. Low construction and maintenance costs and negligible operation costs are associated with lagooning; however, lagoons used for the disposal of solid wastes generated in petrochemical production are often highly odoriferous and unsightly and have a high potential for ground and surface water pollution. Also, many of the solid and semi-solid wastes generated in petrochemical production will not degrade significantly in lagoons and will require some other method of ultimate disposal.

Incineration is a controlled combustion process for burning solid, liquid or gaseous combustible waste to gases and a residue containing little or no combustible material. Several incineration processes are used in the petrochemical industry including stationary hearth incinerators, multiple hearth furnaces, dual chamber incinerators, rotary kilns, fluidized bed reactors, open pit incinerators, and the liquid burner. The type of incinerator used in a particular application is dependent on the characteristics of the waste. Important physical and chemical characteristics which should be considered when selecting an incinerator type include material state (solid, semi-solid, liquid, gas), ease of handling, moisture content, energy value, combustion temperature, reactivity, combustion products, and ash content.[92]

Chemical Engineering[93] describes the operation of a dual chamber incinerator which was designed to combust the wastes generated at a petrochemical plant. The incinerator received approximately 5,670 kg/day (12,500 lb/day) of solid wastes from the petrochemical operation, a highly acidic and cokelike material with a high carbon content and low-ash content, and 1,130 kg/day (2,500 lb/day) of miscellaneous plant trash which was treated in an 8 hour work shift. The incinerator was made of two chambers, one for vaporization, the other for vapor combustion. The temperature of the first chamber was between 200 and 400°C (400 and 800°F) while the temperature of the second (combustion) chamber was approximately 1,200°C (2,200°F). Combustion of the waste left less than 5% of the original material as ash which was removed and landfilled every two to three weeks.

The dual chamber unit and the necessary waste collection facilities described in Chemical Engineering[93] cost over US $100,000. The cost of fuel-gas to operate the incinerator was estimated to be US $5,000/year, electricity costs were estimated to be approximately US $1,000/year. One man working 40 hours/week was required to operate the facility.

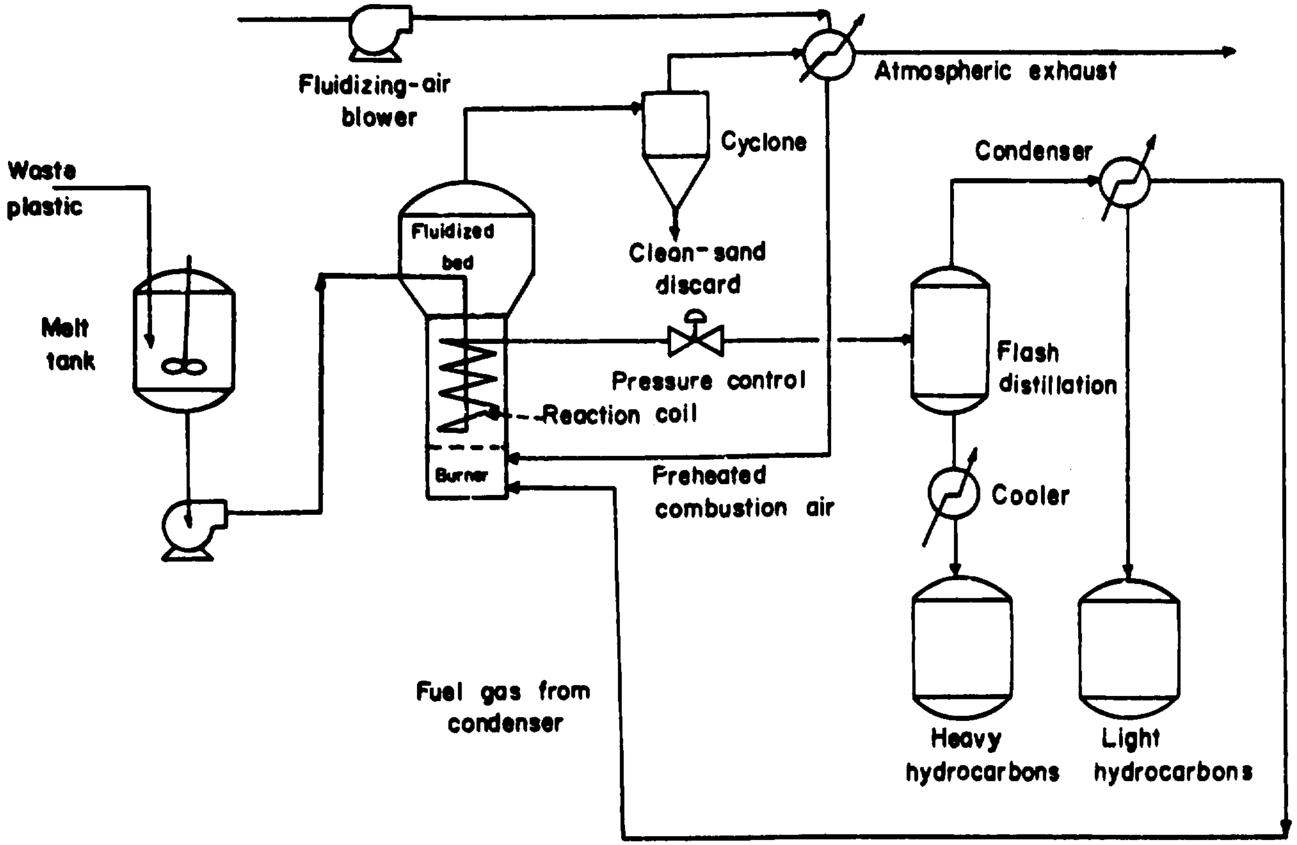
Ocean dumping of solid wastes may consist of piping to in-shore waters, bulk dumping in off-shore waters, and deep sea dumping of containerized wastes. If a processing plant is located close to the sea, aqueous slurries with low organic concentrations can be pumped to in-shore waters. A tide or current which will disperse the waste material is essential. Bulk wastes such as filter cakes, sludges, and slurries may be barged to off-shore waters where they are dumped. These wastes are normally dumped 30 to 500 km (20 to 300 miles) off-shore in 300 to 500 fathoms of water by discharging the wastes through a pipe at depths of 3 to 6 m (10 to 20 ft).[83] Toxic liquids and sludges have been placed in containers and dumped at sea.

Smith and Brown[94] reported that approximately 730,000 metric tons (800,000 tons) of refinery and petrochemical wastes are barged to sea and disposed each year in the United States at an average cost of US $1.90/metric ton (US $1.70/ton) (1970 dollars), and that approximately 7,300 metric tons (8,000 tons) of containerized wastes are disposed at sea with an average cost of US $26/metric ton ($24/ton). Little information is available regarding the environmental impact of ocean dumping; however, the small amount of information available suggests the impact may be quite severe.

Bhatia and Rossi[95] report on a pyrolysis process used to convert waste polymers to fuel oils. This noncatalytic cracking process was used to recover almost 94% of the available fuel value from a waste plastic stream of atactic polypropylene. In the process a tubular, plug-flow pyrolysis reactor, immersed in a gas-heated fluidized bed of sand, is used to thermally crack molten atactic polymer to gaseous and liquid components (Figure 4.1). The plant capacity was 8 billion kg/year (17 billion pound/year). The atactic polymer is converted to No. 6 and No. 2 fuel oils and gaseous fuels. Research has shown that under the proper operating conditions other petrochemical wastes may be converted to gasoline additives, lighter fluid, spot remover, solvents, and

FIGURE 4.1

PYROLYSIS PROCESS[95]



petrochemical feedstocks. An estimate of the costs associated with building a conversion plant for atactic polypropylene is presented in Table 4.3.[95]

TABLE 4.3

PYROLYSIS PROCESS ECONOMIC ESTIMATES[95]

Atactic-Polypropylene Conversion Plant Economics	
Basis: 25 million lb/yr of atactic polymer (800 h/yr of operation)	
Products	
No. 6 fuel oil	6.9 million lb/yr
No. 2 fuel oil	15.1 million lb/yr
Gaseous fuels (net)	1.0 million lb/yr
Capital Investment (est.)	US $3.06 million
Operating Costs	
Utilities	
Electricity, 100 hp	US $33,600
Cooling water, 60 gpm	3,000
Direct labor (1/3 of a person per shift)	26,000
Maintenance,	
Overhead and G & A	286,050
Other	147,000
	US $496,250
Payback	2.4 yr

CHAPTER 5

DISPOSAL OF HAZARDOUS WASTES

Hazardous wastes pose a potential hazard to the health of humans or other living organisms because the wastes are lethal, nondegradable, persistent in nature, can be biologically magnified or otherwise cause detrimental cumulative effects.[96] The U.S. Environmental Protection Agency characterizes a waste as hazardous if it possesses any one of the following four characteristics: (1) ignitability, (2) corrosivity, (3) reactivity, or (4) toxicity (Section 4, U.S. Code of Federal Regulations, Part 261).

An ignitable waste is any waste which will present a fire hazard during routine management. A corrosive waste is any waste which is able to deteriorate standard containers or to dissolve toxic components of other wastes. A reactive waste is any waste which has a tendency to become chemically unstable under normal management conditions, which will react violently when mixed with water, or which will generate toxic gases. A toxic waste is any waste which will pose a substantial hazard or potential hazard to human health. Based on these definitions and the previous discussions of air and water pollution and solid wastes generated during petrochemical manufacturing many of these wastestreams may be characterized as hazardous.

There are hundreds of documented cases of damage to life and the environment which have resulted from the improper management of hazardous wastes. Hazardous wastes have been found to contaminate ground water supplies, rivers, lakes and other surface waters, polluted the air, caused fires and explosions, caused serious illness by contaminating foodstuffs and by direct contact.[97] These wastes are frequently bioaccumulated, very persistent in the environment and often toxic at very low concentrations. The source of the vast majority of these cases may be traced back to some part of the petrochemical industry.

Harm to human health and the environment which was caused by past mismanagement of hazardous waste has led to increased public concern about hazardous waste management. Proper management means more than just careful disposal. A range of management options must be considered. In order of priority the desired options for managing hazardous wastes are:[97]

(1) minimizing the amount of waste generated by modifying the industrial process involved,

(2) transfer the waste to another industry which may use the waste,

(3) reprocess the waste to recover materials and energy,

(4) separate hazardous and nonhazardous materials,

(5) subject the waste to some process which will render the waste nonhazardous, and

(6) dispose of the waste in a secure landfill.

There are an estimated two million recognized chemical compounds with more than 60,000 chemical substances in past or present commercial use. Approximately 600 to 700 new chemicals, mostly synthetic organics produced from petrochemicals, are introduced each year; but published reports of animal testing have been issued for only about 15,000. Some of these substances may possess carcinogenic, mutagenic, and teratogenic effects which may be extended in time, perhaps for 10, 20 , or 30 years, to the point where direct relationships with morbidity and mortality are difficult to conclusively prove.[98] For these reasons the proper management of hazardous wastes in the petrochemical industry is very important.

The survey conducted by Hedley et al.[9] of 190 petrochemical production processes (listed in Table 3.1) is very useful in identifying hazardous wastestreams that originate from these processes. A survey of the hazardous wastestreams from 24 organic chemical, pesticide, and explosives manufacturing plants was conducted by Process Research, Inc.[99] In this survey 16 organic chemical manufacturing, 5 pesticide manufacturing, and 3 explosives manufacturing industries (all of which use petrochemicals as feedstocks) were surveyed and the major hazardous wastestreams from each industry were identified. Table 5.1 contains a list of these industries and the identified hazardous wastestreams.

The U.S. Environmental Protection Agency has identified 129 toxic hazardous wastes which have become known as "priority pollutants". Wise and Fahrenthold[3] in a study of petrochemical processes identified these hazardous "priority pollutants" in many petrochemical process wastewaters. A list of plastics/synthetic fibers manufacturing processes which contain these "priority pollutants" may be found in Table 5.2. Currently, most of the process wastes from the petrochemical manufacturing industry are ultimately destined for land disposal or in some cases incineration.

Transferring a hazardous waste to another industry has received increasing attention. This process may take place in a materials exchange to handle, treat and physically exchange wastes or an information exchange. Such a clearinghouse leaves generators and purchasers to negotiate directly. The first information exchange was established in the Netherlands in 1972. Since then the idea has spread through Europe and is growing in the United States.[97]

TABLE 5.1

HAZARDOUS WASTESTREAMS IDENTIFIED IN SOME PETROCHEMICAL MANUFACTURING PROCESSES[99]

Product and Typical Plant Size	Hazardous Wastestream Components	Waste Generation KKg*/yr
Perchloroethylene 39,000 KKg/yr	Hexachlorobutadiene Chlorobenzenes Chloroethanes Chlorobutadiene Tars	12,000
Nitrobenezene 20,000 KKg/yr	Crude Nitrated Aromatics	50
Chloromethane 50,000 KKg/yr	Hexachlorobenzene Hexachlorobutadiene Tars	300
Epichlorohydrin 75,000 KKg/yr	Epichlorohydrin Dichlorohydrin Chloroethers Trichloropropane Tars	4,000
Toluene Diisocyanate 27,500 KKg/yr	Polyurethane Ferric Chloride Isocyanates Tars	358
Vinyl Chloride Monomer 136,000 KKg/yr	1, 2 Dichloroethane 1, 1, 2 Trichloroethane 1, 1, 1, 2 Tetrachloroethane Tars	1,400
Methyl Methacrylate 55,000 KKg/yr	Hydroquinone Polymeric Residues	4,730
Acrylonitrile 80,000 KKg/yr	Acrylonitrile Higher Nitriles	160
Maleic Anhydride 11,000 KKg/yr	Maleic Anhydride Fumaric Acid Chromogenic Compounds Tars	333
Lead Alkyls 60,000 KKg/yr	Lead	30,000

TABLE 5.1 (continued)

HAZARDOUS WASTESTREAMS IDENTIFIED IN SOME PETROCHEMICAL MANUFACTURING PROCESSES[59]

Product and Typical Plant Size	Hazardous Wastestream Components	Waste Generation KKg*/yr
Ethanolamines 14,000 KKg/yr	Triethanolamine Tars	1,120
Furfural 35,000 KKg/yr	Sulfuric Acid Tars & Polymers	19,600
Furfural 35,000 KKg/yr	Fines & Particulates From Stripped Hulls	350
Fluorocarbon 80,000 KKg/yr	Antimony Pantachloride Carbon Tetrachloride Trichlorofluoromethane Organics	18
Chlorotoluene 15,000 KKg/yr	Benzylchloride Benzotrichloride	15
Chlorobenzene 32,000 KKg/yr	Polychlorinated Aromatic Resinous Material	1,400
Atrazines 20,000 KKg/yr	Water Sodium Chloride Insoluble Residues Caustic Cyanuric Acid	224,600
Trifluralin 10,000 KKg/yr	Spent Carbon Fluoroaromatics Intermediates and Solvents	1,150
Malathion 14,000 KKg/yr	Filter Aid Toluene Insoluble Residues Dimethyl Dithiophosphoric Acid	1,816
Malathion 14,000 KKg/yr	Malathion Toluene Impurities Sodium Hydroxide	14,350 (W) 350 (D)

TABLE 5.1 (continued)

HAZARDOUS WASTESTREAMS IDENTIFIED IN SOME PETROCHEMICAL MANUFACTURING PROCESSES[99]

Product and Typical Plant Size	Hazardous Wastestream Components	Waste Generation KKg*/yr
Parathion 20,000 KKg/yr	Diethylthiophosphoric Acid	2,300
Explosives 93,000 KKg/yr	Activated Carbon Nitrobodies (Any organic nitrated byproduct)	330 (W) 200 (D)
Explosives 30,000 KKg/yr	Redwater (Waste from purification of crude TNT)	15,000
Explosives 125,000 KKg/yr	Waste Explosives	250

*1 KKg = 1 Metric Ton (MT)
(W) Wet Basis
(D) Dry Basis

TABLE 5.2

PLASTICS/SYNTHETIC FIBERS EFFLUENTS WITH CONCENTRATIONS GREATER THAN 0.5 ppm OF PRIORITY POLLUTANTS[3]

Product	Monomer(s)	Associated priority pollutants
ABS resins	Acrylonitrile Styrene Polybutadiene	Acrylonitrile Aromatics
Acrylic Fibers	Acrylonitrile Comonomer (variable): Vinyl Chloride	Acrylonitrile Chlorinated C2's
Acrylic resins (Latex)	Acrylonitrile Acrylate ester Methylmethacrylate	Acrylonitrile Acrolein
Acrylic resins	Methylmethacrylate	Cyanide
Alkyd resins	Glycerin Isophthalic acid Phthalic anhydride	Acrolein Aromatics Polyaromatics
Cellulose acetate	Diketene (acetylating agent)	Isophorone
Epoxy resins	Bisphenol A Epichlorohydrin	Phenol Chlorinated C3's Aromatics
Petroleum hydrocarbon resins	Dicyclopentadiene	Aromatics
Phenolic resins	Phenol Formaldehyde	Phenol Aromatics
Polycarbonates	Bisphenol A Phosgene	(Not investigated) Predicted: phenol Chloroaromatics Halomethanes
Polyester	Terephthalic acid/dimethylterephthalate Ethylene glycol	Phenol Aromatics

TABLE 5.2 (continued)

PLASTICS/SYNTHETIC FIBERS EFFLUENTS WITH CONCENTRATIONS GREATER THAN 0.5 ppm OF PRIORITY POLLUTANTS[3]

Product	Monomer(s)	Associated priority pollutants
HD polyethylene resin	Ethylene	Aromatics
Polypropylene resin	Propylene	Aromatics
Polystyrene	Styrene	Aromatics
Polyvinvy chloride resin	Vinyl chloride	Chlorinated C2's
SAN resin	Styrene Acrylonitrile	Aromatics Acrylonitrile
Styrene-Butadiene resin (Latex)	Styrene (50%) polybutadiene	Aromatics
Unsaturated polyester resin	Maleic anhydride Phthalic anhydride Propylene glycol (Styrene-added lated)	Phenol Aromatics

With shortages of raw materials and more restrictive disposal regulations, recovery has become a more attractive alternative. Many wastes contain valuable substances which can be extracted from concentrated wastestreams more economically than processing from virgin materials.

Incineration has proven to be a viable method of destroying organic wastes without posing a threat to the environment. Chlorine- or bromine-containing compounds have been destroyed successfully in cement kilns and special incinerators aboard ships at sea.[97]

For further study on hazardous waste management in the petrochemical manufacturing industry several textbooks are currently available.[97,100,101,102,103,104,105]

Tragedies such as those that have occured in Love Canal, New York and Kentucky's "Valley of the Drums" have focused attention on what can happen when hazardous wastes are improperly managed. Technologies exist for environmentally sound management, but these have not been widely used because they appear to be costly and because often there is no legal requirement for their use. In many cases it is impossible to assign monetary values to the long-term damage to health and the environment that has resulted from improper management of hazardous wastes. But the astronomical costs of cleaning up damage caused by poor disposal practices alone is reason enough to justify the cost of proper environmental controls. In this case an ounce of prevention is a sound investment.

CHAPTER 6

PETROCHEMICALS INDUSTRY IN DEVELOPING COUNTRIES

Many developing countries are rich in hydrocarbons and other raw materials necessary for petrochemical production.[1,106] The availability of the necessary raw materials, an inexpensive labor force, and an increased demand for petrochemical products is expected to lead to the development of petrochemical production capabilities within these developing countries.

The information presented in previous chapters of this report has shown that petrochemical production will result in the generation of water and air pollutants, solid and hazardous wastes. An increase in petrochemical production could, therefore, have a significant impact on public health and environmental quality. The information contained in this report has also shown that the technology to control these potential pollutant emissions currently exists.

To avoid the adverse effects on public health and environmental quality of this increased petrochemical production, adequate pollution control regulations must be promulgated. Such regulations would require the evaluation of possible environmental impacts and public health effects of the construction and operation of petrochemical production facilities, and require measures to mitigate adverse effects.

To assess possible environmental impacts, a survey must be conducted of the existing environmental conditions at the proposed plant site. A survey of the wastes generated at a plant should also be conducted. The survey should include a characterization of the volume of wastes generated, the rate of flow of the wastes, and the physical, chemical, and biological characteristics of the generated wastes.

The need for environmental regulation of petrochemical production has been recognized in some developing countries. Tewari et al.[107] described pollution control efforts in the petrochemical industry in India. Industry in India is concentrated in a few limited areas such as Baroda, Bombay, Calcutta, and Kanpur. The Water/Air Pollution (Prevention and Control) Act, 1974/78 and the constitution of central and state boards for water pollution control contain regulations designed to protect the environment from industrial pollutants in India. Tewari et al.[107] noted that proper waste management in India has not only helped abate pollution problems but has also improved economic viability of various industries when the most efficient and economical pollution control facilities were used.

The government of the Taiwan Province of China has developed a special industrial estate in southern Taiwan Province in which wastewater treatment is one of the most important considerations.[108] The Linyuan Industrial Estate is a 380 hectare industrial estate designed for petrochemical industries. The Estate is located on the banks of the Kaoping River and will contain more than 30 industries. Primary and intermediate petrochemical products were expected to be produced at this complex. A list of some of the water pollution standards in the Taiwan Province, which had to be met by this project, are found in Table 6.1.[108] Several alternative treatment processes were evaluated including primary treatment with an ocean outfall, secondary treatment with a short-distance marine outfall, and tertiary treatment with river discharge. Secondary treatment with the improved Kraus Process of air aeration activated sludge followed by a marine outfall was selected (Figure 6.1)

TABLE 6.1

WATER STANDARDS FOR VARIOUS USES IN TAIWAN PROVINCE[108]

I. Fresh Water - Rivers, Lakes and Ponds
Conventional Constituents

Class	Best Usage	Standard of Water pH	Biological Oxygen Demand (5 day, 20°C) mg/L	Dissolved Oxygen mg/L	Coliform Bacteria Median No/100 mL (MPN)	Suspended Solids mg/L
AA	Public water supply (I) bathing, or any lesser use	6.5-8.5	1	6.5	50	
A	Public water supply (II), fishing (I), or any lesser use	6.0-9.0	2	5.5	5,000	25
B	Public water supply (III), fishing (II), industrial water supply (I), or any lesser use	6.0-9.0	4	4.5	10,000	40
C	Irrigation and Industrial water supply (II) or any lesser use	6.0-9.0		2		100
D	Environmental protection	6.0-9.0		2		No floating

Organics and Metals

Cyanide mg/L	Organic Phosphate mg/L	Cd mg/L	Pb mg/L	Cr + 6 mg/L	As mg/L	Total Hg mg/L	Se mg/L	Phenol mg/L
0.01	None detectable	0.01	0.1	0.05	0.1	0.005	0.05	0.001

*The Above Water Standards are Based on the River Flow of Yearly Duration at 75%.

Water Supply (I) : Source of drinking water after disinfection.
Water Supply (II) : Source of drinking water after conventional water treatment process.
Water Supply (III): Source of drinking water after additional treatment other than conventional process.

TABLE 6.1 (continued)

WATER STANDARDS FOR VARIOUS USES IN TAIWAN PROVINCE[108]

II. Marine Waters
Conventional Constituents

		Standard of Water				
Class	Best Usage	pH	Biological Oxygen Demand (5 day, 20°C) mg/L	Dissolved Oxygen mg/L	Coliform Bacteria Median No/100 mL (MPN)	Suspended Solids mg/L
A	Fishing (I), bathing, or any lesser use	7.5-8.5	2	6	1,000	2
B	Fishing (II), industrial water supply (II), or any lesser use	7.5-8.5	3	5		3
C	Environmental protection	7.0-8.5	8	2		8

Fishing (I) : Fresh water for silver carp & grass carp, marine water for striped mullet & sea weeds.
Fishing (II) : Fresh water for carps & shellfish, marine water for milk fish.

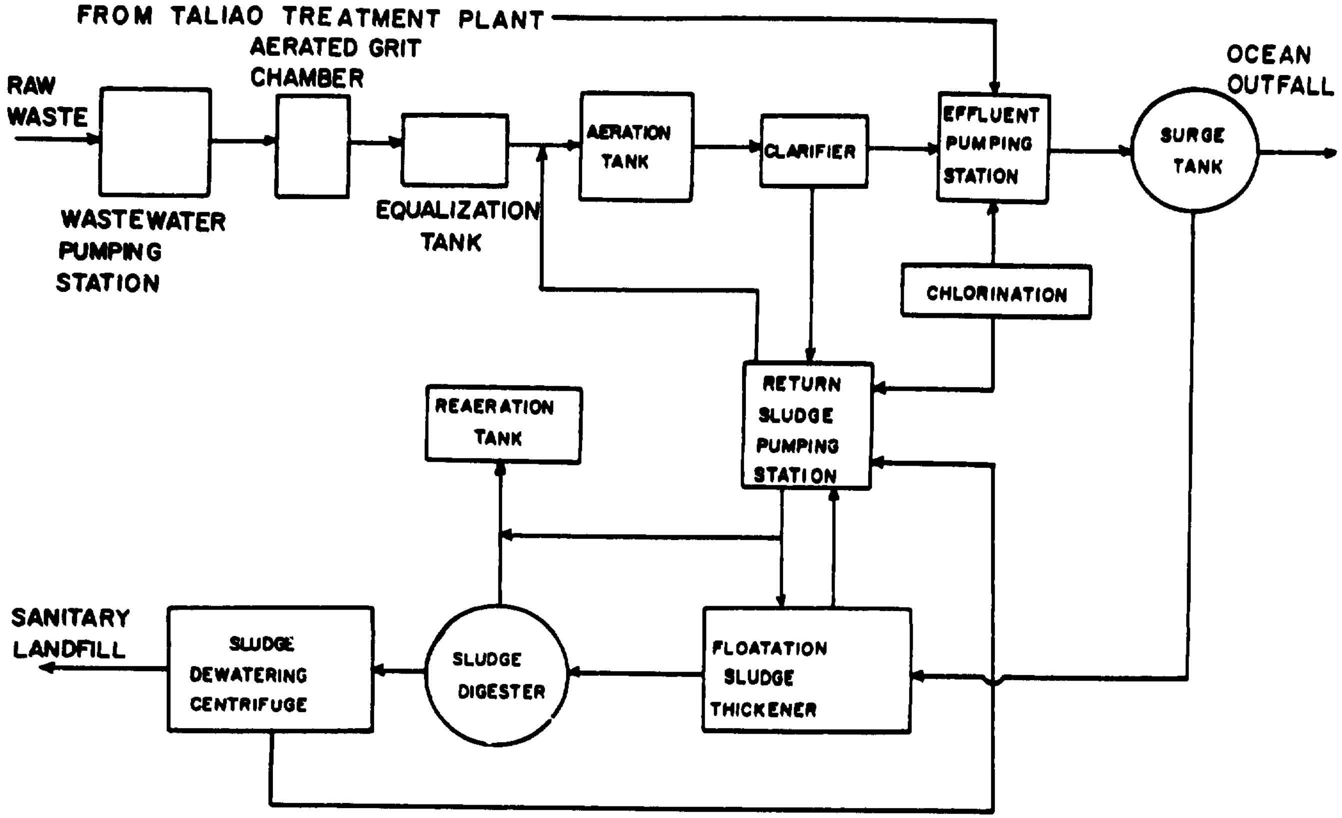
Industrial Water Supply (I) : Industrial water for processing use.
Industrial Water Supply (II) : Industrial water for cooling use.

Organics and Metals

The Restrictions Over the Content of Cyanide, Organic Phosphate, and Heavy Metals are the Same as Those Over Fresh Water.

FIGURE 6.1

SCHEMATIC FLOW DIAGRAM OF LINYUAN INDUSTRIAL WASTEWATER TREATMENT PLANT[108]



Pollution control was also a concern at the Zulia El Tablazo Petrochemical Complex in Venezuela.[79] The construction of the giant Zulia El Tablazo Petrochemical Complex on the shore of Lake Maracaibo at El Tablazo in the State of Zulia represented a joint venture between the Venezuelan government and private corporations. The capital investment exceeded $1.2 billion in 1979. It was recognized by the government that this facility represented a potential source of pollution to an ecologically sensitive body of water that was already receiving various levels of pollutional input. To avoid further damage to Lake Maracaibo, the government initiated a pollution control program through the Instituto Venezolano de Petroquimica (IVP). The program was designed to contain and treat wastewaters discharged from the petrochemical production facilities to a level that would not damage the estuary.

The project was planned and implemented under the manifestation of the Venezuelan governmental policy for industrial development with environmental control. At the time of initiating the project, there were no specific discharge standards established by the government. It was the responsibility of IVP to establish acceptable effluent standards and to predict the impact of the discharge of the treated wastewater. Guidelines prepared for similar situations in the United States of America were selected as guides and used to develop the treatment program. The environmental impact assessment (EIA) was limited to the wastewater treatment associated with the petrochemical complex. Air pollution and solid wastes disposal, excluding sludge disposal for the wastewater treatment process, were not considered in the assessment.

The economic and social impacts were assessed by the Venezuelian government, and a decision to proceed with construction was made. Therefore, economic and social factors, other than the protection of the uses of the estuary, were not a factor in assessing the need for the wastewater treatment facility.

The first step in the assessment of wastewater treatment needs was to conduct a base line survey to determine the quality of the water in the estuary before constructing the plant. Water samples were collected at various locations and depths during the various seasons of the year and analyzed for chemical and biological content. Results of dispersion studies were used to develop a one dimensional model to predict the movement of water in the estuary.

Various types of wastewater treatment processes were evaluated on a laboratory scale, and the results of these tests were used to select a treatment process capable of producing an effluent quality acceptable for discharge to the estuary.

Samples of wastewaters from similar petrochemical processes were collected for analysis and composited in proportion to the volume of wastewater expected from the El Tablazo Complex. This composited wastewater was used in the treatability studies and served as a basis for design of the wastewater treatment facility.

A detailed monitoring scheme was prepared and incorporated into the operating plan for the wastewater treatment facility. Sampling schedules were devised to determine the characteristics of the raw wastewater entering the treatment facility as well as the treatment plant effluent. Periodic sampling of the estuary was included in the monitoring scheme. All processes at the complex discharging wastewater were required to prove that the wastewater was not toxic by using fish bioassays. Dispersion models were used to predict the impact of the discharges to Lake Maracaibo. Adherence to the monitoring plan will assure the protection of Lake Maracaibo.

Experience from this project has shown that answers to potential environmental problems can be resolved only by properly combining governmental initiative and support with sound planning and engineering. Governmental commitment to environmental protection and control has produced a thorough investigation, a comprehensive plan, and proficient engineering.[79]

A review of the literature concerning the characteristics of waste products produced during the manufacture of petrochemical products has shown that petrochemical production can be a significant source of pollution. This same review has shown, however, that adequate, economic control technologies currently exist. To avoid the potential threat to environmental quality and public health that petrochemical production represents, governments must take an active role in regulating pollution control. If the proper steps are taken, the benefits that come from the introduction of a new industry may be realized while avoiding damage to environmental quality and public health.

CHAPTER 7

ENERGY CONSIDERATION IN POLLUTION CONTROL

The selection of processes used in pollution control facilities must be considered with respect to three energy areas of growing concern: the direct cost of the energy used, the environmental effects of pollution generated directly and indirectly as a result of energy use, and depletion of important nonrenewable resources. Rapidly changing energy prices are forcing pollution control facilities operators to give serious consideration to the energy requirements of pollution control. Research has shown that energy costs will become the predominant factor in the selection of some pollution control alternatives.[109] Table 7.1 is an example of information available for many processes used in the petrochemical industry.[28-36] These tables contain information about air pollution control alternatives for several different petrochemical manufacturing processes and the energy cost for each air pollution control alternative. Knowing the basis of these cost estimates (electricity costs were assumed to be US $0.01/kw-hr), power requirements may also be computed for each alternative process.

An analysis of the data contained in Table 7.1 and similar tables in the Air Products and Chemicals, Inc.[28-36] reports showed that energy costs may be as much as 99 percent of the total annual operating cost (minus depreciation and interest on capital) of an air pollution control process. Some air pollution control alternatives may result in a net energy production, as in the use of a boiler house vent gas burner on absorber vent gas in the manufacture of formaldehyde with the silver catalyst process.

Very little information is available concerning energy requirements of wastewater treatment processes when used in the petrochemical manufacturing

TABLE 7.1

COST EFFECTIVENESS OF ALTERNATIVE EMISSION CONTROL DEVICES USED IN THE MANUFACTURE OF PHTHALIC ANHYDRIDE FROM ORTHO-XYLENE[28-36]

(BASED ON 130 MILLION LBS/YR PHTHALIC ANHYDRIDE PRODUCTION)

Stream	Main Process Vent Gas					Waste Products
Type of Emission Control Device	Water Scrubber	+ Incineration	Direct Incineration$^{(g)}$	Incineration	+ Waste Heat Boiler	Direct Incineration
Number of Units	2	1	2	2	2	1
Capacity of each Unit - %	50	100	50	50	50	100
Feed Gas						
Total Flow - Lbs/Hr	536,962	10,460 (b)	536,962	536,962		5,792
SCFM	119,300		119,300	119,300		
Composition - Ton/Ton PAN						
Hydrocarbons						
Particulates (inc PAN,MAN & Org Acids)	0.0756(a)	0.1221	0.0692	0.0692		0.0557
NO_x						
SO_x	0.0047		0.0047	0.0047		
Carbon Monoxide	0.1507		0.1507	0.1507		
Gaseous Effluent						
Total Flow - Lbs/Hr	544,005	39,235	540,052	545,767		19,497
SCFM	122,100	9,700	120,200	122,350		4,900
Composition - Ton/Ton PAN						
Hydrocarbons						
Particulates (inc PAN,MAN & Org Acids)	0.0036	0.0009	0.0036	0.0036		0.0004
NO_x		0.0002	0.0006	0.0012		0.0001
SO_x	0.0047		0.0047	0.0047		
Carbon Monoxide	0.1507	0.0026	0.0076	0.0076		0.0025
Emissions Control Efficiency (d)						
CCR-definition on Pg.2 of Table 7.1		98	95	95		97
SERR-definition on Pg.2 of Table 7.1	86	99	92	92		99
SE-definition on Pg.2 of Table 7.1	96 (organics)					

PAN = Phthalic Anhydride

MAN = Maleic Anhydride

SCFM = Standard cubic feet per minute

TABLE 7.1 (continued)

COST EFFECTIVENESS OF ALTERNATIVE EMISSION CONTROL DEVICES USED IN THE MANUFACTURE OF PHTHALIC ANHYDRIDE FROM ORTHO-XYLENE[28-36]

(BASED ON 130 MILLION LBS/YR PHTHALIC ANHYDRIDE PRODUCTION)

Stream	Main Process Vent Gas					Waste Products
Type of Emission Control Device	Water Scrubber	+	Incineration	Direct Incineration[(g)]	Incineration + Waste Heat Boiler	Direct Incineration
Investment - US $						
Purchased Cost	275,000		120,000	576,000	625,000	85,000
Installation	825,000		730,000	285,000	625,000	65,000
Total Capital (c)	1,100,000		850,000	860,000	1,250,000	150,000
Operating Cost - US $/Yr						
Depreciation (10 years)	110,000		35,000	86,000	125,000	15,000
Interest on Capital (6%)	66,000		21,000	51,600	75,000	9,000
Maintenance	55,000 (5%)		35,000 (10%)	34,400 (4%)	50,000 (4%)	7,500 (5%)
Labor - US $4.85/Hr	6,500		5,000	5,000	20,000	3,000
Utilities and Chemicals						
Power - US $0.01/KWH	25,000		5,000	19,800		1,000
Fuel - US $0.40/million BTU			55,500	198,300	562,300	12,800
Process Water - US $0.10/mil gal	1,100					
Boiler Feed Water - US $0.30/mil gal					34,200	
Total Utilities and Chemicals	26,100		60,500	218,100	596,500	13,800
Total Operating Cost:	263,600		156,500	395,100	866,500	48,300
Steam Production-US $0.59/LBs (450 PSIG, 750°F)					(465,000)[(f)]	
Net Annual Cost - US $/Yr		420,100		395,100	401,500	48,300

(a) Includes 0.0064 T/T of organic material contained in separate liquid reject stream from product fractionation system ejector.

(b) Liquid rejected from scrubber system plus light and heavy ends removed in product fractionation.

(c) It is possible that future fuel cost will be considerably higher than figure used in this comparison.

(d) Emission control efficiencies are defined by the equations given below.

$$CCR = \frac{\text{pounds of } O_2 \text{ that react with pollutants to feed device}}{\text{pounds of } O_2 \text{ that theoretically could react with these pollutants}} \times 100$$

$$SERR = \frac{\text{weighted pollutants in} - \text{weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(e) Developed from 1970-1971 cost figures provided by PAN manufacturer with 10-15 percent added for escalation to 1973 costs.

(f) Shown at fuel plus BFW cost since this steam only replaces operating cost of stand-by boilers.

(g) With feed preheat.

industry; however, many of the processes used for wastewater treatment in the petrochemical industry are similar or identical to the processes used in municipal wastewater treatment. Therefore, the energy data compiled for municipal treatment facilities may be used to estimate the energy requirements of similar processes in the petrochemical industry, taking into account the differences in wastewater characteristics and economies of scale.

Wesner et al.[110] presented a detailed analysis of energy requirements by unit operations and unit processes employed in municipal wastewater treatment. The results of the Wesner et al.[110] study were presented in graphical form, with accompanying tables outlining the design considerations employed in developing the graphs. Energy requirements were presented in terms of the design flow rate of the treatment system in most cases, but when a wide choice of loading rates was applicable, the graphs were presented in terms of surface area or of flow rate applied to the component of the system. Using these more detailed energy usage data will be helpful in estimating the energy requirements of petrochemical wastewater treatment facilities.

Middlebrooks et al.[109] presented analyses of the energy requirements of small wastewater treatment systems, including advanced physical-chemical treatment processes which may be necessary when treating petrochemical wastestreams which contain complex synthetic organics. It was concluded that increasing energy costs were a[illegible]ng a greater proportion of the annual operating costs of wastewater treatment facilities of all sizes, and could become the predominant factor in selecting cost-effective treatment alternatives. It was observed that low energy consuming treatment systems were generally easier to operate and maintain than energy-intensive systems, making low energy consuming systems even more attractive. When applicable, simple biological processes were also found to require much less energy than mechanical and physical-chemical systems.[109]

Culp[111] presented an analysis of alternatives for future wastewater treatment at an advanced treatment facility that illustrates the sensitivity of energy costs. Energy use was not considered in the original design of the advanced wastewater treatment facility in the late 1960's. The energy required for alternative processes is compared to the energy required by the original design in Table 7.2.[111,112] It was anticipated that the final effluent from the flood irrigation alternative would be at least equal in quality to the effluent from the original physical chemical process.

In addition to the cost for pollution control energy use, consideration also must be given to the environmental effects of pollution generated directly and indirectly as a result of energy use. The generation of power produces pollution. The amount of pollution produced as a direct result of energy production is a function of the power generation process used, the fuel used, the amount of power produced and the pollution control facilities at the point of generation. Because power generation produces pollution, the use of energy indirectly results in the production of pollution. The processing of the fuels used in energy production also produces significant impacts on environmental quality, and this impact can be considered to be pollution generated indirectly from the use of energy. Since it is the goal of pollution control facilities to produce the least environmental impact within cost constraints, it is necessary to consider this "indirect" generation of pollution when choosing between pollution control alternatives. An example of how to avoid "indirect" pollution would be the selection of an applicable low energy consuming and simply constructed process such as land application of wastes instead of a

TABLE 7.2
ENERGY REQUIREMENT OF A 2.8 x 10^4 m^3/d (7.5 mgd), ADVANCED WASTEWATER TREATMENT SYSTEM[111,112]

Alternative	Total energy[a] (electricity and fuel expressed as equivalent M kWh/yr)[b]
Original system complete secondary treatment, AWT system, effluent export to Indian Creek Reservoir (storage reservoir)	64,500
1978 alternatives	
Continue secondary, nitrification, effluent export to Indian Creek Reservoir	39,400
Continue secondary, nitrogen removal (ion exchange) effluent export to Indian Creek Reservoir	40,244
Continue secondary on-site, flood irrigation land treatment in Carson River Basin	25,000

[a] Does not include secondary energy requirements for chemical manufacture

[b] 1 kWh = $3.6 \cdot 10^6$J

complex physical-chemical process. This would result in less pollution discharged to the environment, because less energy would be consumed in the treatment process and energy would be saved by reducing the consumption of chemicals and construction materials.

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GLOSSARY

ABSORPTION: The process by which one substance is taken into and included within another substance, as the absorption of water by soil or nutrients by plants.

ACIDITY: Quantitative capacity of aqueous solutions to react with hydroxylions. Measured by titration, with a standard solution of a base to a specified end point. Usually expressed as milligrams per liter of calcium carbonate.

ACTIVATED CARBON: Carbon "activated" by high-temperature heating with steam or carbon dioxide, producing an internal porous particle structure. Total surface area of granular activated carbon is estimated to be 1,000 m^2/gm.

ACTIVATED SLUDGE PROCESS: A biological wastewater treatment process in which a mixture of wastewater and activated sludge is agitated and aerated. The activated sludge is subsequently separated from the treated wastewater (mixed liquor) by sedimentation and wasted or returned to the process as needed.

ADSORPTION: Adhesion of an extremely thin layer of molecules (gas or liquid) to the surfaces of solids (e.g., granular activated carbons) or liquids with which they are in contact.

AERATE: To permeate or saturate a liquid with air.

AEROBIC: (a) Having molecular oxygen as a part of the environment. (b) Growing or occurring only in the presence of molecular oxygen, such as aerobic organisms.

AGGLOMERATION: A phenomenon where particles mass together.

ALKALINE: Presence of the hydroxides, carbonates, and bicarbonate of elements, such as calcium, magnesium, sodium, potassium; or of ammonia. Alkaline pH values ranges from 7.1 to 14.

ALKALINITY: Capacity of water to neutralize acids, imparted by the water's content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates. Expressed in milligrams per liter of equivalent calcium carbonate.

AMORTIZATION: The serial repayment of principal.

ANAEROBIC: (a) The absence of molecular oxygen. (b) Growing in the absence of molecular oxygen (such as anaerobic bacteria).

ANAEROBIC CONTACT PROCESS: An anaerobic waste treatment process in which the microorganisms responsible for waste stabilization are removed from the treated effluent stream by sedimentation or other means, and held in or returned to the process to enhance the rate of treatment.

ANAEROBIC WASTE TREATMENT: Waste stabilization brought about by the action of microorganisms in the absence of air or elemental oxygen. Usually refers to waste treatment by methane fermentation.

AQUACULTURE: The culture of fish or other aquatic life in water.

ASSIMILATIVE CAPACITY: Capacity of a natural body of water to receive (a) wastewaters, without deleterious effects; (b) toxic materials, without damage to aquatic life or humans consuming the water; and (c) BOD, within prescribed dissolved oxygen limits.

AUTOTROPHIC: Self-nourishing: denoting the green plants and those forms of bacteria that do not require organic carbon or nitrogen, but can form their own food out of inorganic salts and carbon dioxide.

BIOASSAY: Assay method using a change in biological activity as a qualitative or quantitative means of analyzing the response of biota to industrial wastes and other wastewaers. Viable organisms, such as live fish or daphnia, are used as text organisms.

BIOCHEMICAL OXYGEN DEMAND (BOD_5): The 5-day, 20°C, BOD_5 test is widely used to determine the pollutional strength of wastewater in terms of oxygen required to oxidize or convert the organic matter to a nonputrescible end product. The BOD_5 test is a bioassay procedure that measures the oxygen consumed by living organisms while utilizing the organic matter present in the wastewater under conditions as similar as possible to those that occur in nature. To make results comparable, the test has been standardized. The BOD_5 test is one of the most important in stream pollution control.

BIOLOGICAL OXIDATION: Process in which living organisms in the presence of oxygen convert the organic matter contained in wastewater into a more stable or mineral form.

BLOWDOWN: Periodic or continuous draw-off of a mixture from a system to prevent buildup of contaminants.

BOD: Biochemical Oxygen Demand

CAPITAL COSTS: The costs of the project from its beginning to the time the works are placed in operation. Included are (a) the purchase of property and rights-of-way; (b) payments for equipment and construction and for engineering and legal services; and (c) interest charges during construction.

CATALYTIC INCINERATORS: Incinerators for gaseous materials which utilize a catalyst to reduce the operation temperature.

CATION EXCHANGE: The interchange between a cation in solution and another cation on the surface of any surface-active matrial, such as clay or organic colloids.

CHEMICAL COAGULANT: Destabilization and initial aggregation of colloidal and finely divided suspended matter by the addition of floc-forming chemical.

CHEMICAL OXYGEN DEMAND (COD): The COD test is an alternative to the BOD_5 test. It is widely used and measures the quantity of oxygen required to oxidize the materials in wastewater under severe chemical and physical conditions. The major advantage of the COD test is that only a short period (3 hours) is required to conduct the test. The major disadvantage is that the test does not indicate how rapidly the biologically active material would be stabilized in natural conditions.

CHEMICAL PRECIPITATION: Separating a substance from a solution, resulting in the formation of relatively insoluble matter.

CHLORINATION: Application of chlorine to water or wastewater, generally for the purpose of disinfection, but frequently for accomplishing other biological or chemical results.

CHLORINE RESIDUAL: The total amount of chlorine (combined and free available chlorine) remaining in water, sewage, or industrial wastes at the end of a specified contact period following chlorination.

CLARIFICATION: Any process or combination of processes to reduce the concentration of suspended matter in a liquid.

CLARIFIERS: Settling tanks. The purpose of a clarifier is to remove settleable solids by gravity, or colloidal solids by coagulation.

COAGULATION: Process by which chemicals (coagulants) are added to an aqueous system, to render finely divided, dispersed matter with slow or negligible settling velocities into more rapidly settling aggregates. Forces that cause dispersed particles to repel each other are neutralized by the coagulants.

COD: Chemical Oxygen Demand

COLIFORM-GROUP BACTERIA: A group of bacteria predominantly inhabiting the intestines of man or animal, but also occasionally found elsewhere. Used as an indicator of human fecal contamination.

COLLOIDS: The finely divided suspended matter which will not settle, and the apparently dissolved matter which may be transformed into suspended matter by contact with solid surfaces or precipitated by chemical treatment. Substances which are soluble as judged by ordinary physical tests, but will not pass through a parchment membrane.

COMPOSTING: Controlled decomposition of organic matter under aerobic conditions by which material is transformed into humus. The process is normally exothermic resulting in a rise in temperature.

DENITRIFICATION: The reduction of nitrate to nitrogen gas by denitrifying organisms.

DETENTION TIME: Average period of time a fluid element is retained in a basin or tank before discharge.

DIALYSIS: Separation of a colloid from a substance in true solution, by allowing the solution to diffuse through a semi-permeable membrane.

DIGESTION: The controlled decomposition of organic substances, normally under anaerobic conditions.

DIGESTER: The unit in which anaerobic digestion takes place, and the unit often has the capability of retaining the biogas produced by anaerobic digestion.

DISINFECTION: Killing pathogenic microbes on or in a material without necessarily sterilizing it.

DISSOLVED OXYGEN (DO): The oxygen dissolved in water, wastewater, or other liquid, usually expressed in milligrams per liter (mg/L), parts per million (ppm), or percent of saturation.

DISSOLVED SOLIDS: Theoretically, the anhydrous residues of the dissolved constituents in water. Actually, the term is defined by the method used in determination.

DO: Dissolved Oxygen

DUAL MEDIA FILTRATION: Filtration process that uses a bed composed of two distinctly different granular substances (such as anthracite coal and sand), as opposed to conventional filtration through sand only.

ECOLOGY: The branch of biology that deals with the mutual relations of living organisms and their environments, and the relations of organisms to each other.

ECOSYSTEM: The functioning together of the biological community and the non-living environment.

ELECTRICAL CONDUCTIVITY: Reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature. Expressed as microhms per centimeter in degrees Celsius.

EFFLUENT: Sewage, water, or other liquid, partially or completely treated or in its natural state, flowing out of a reservoir, basin, or treatment plant.

ELECTROSTATIC PRECIPITATION: A process in which particles are collected by means of electric charge.

EMISSION: In environmental work, a reference to gaseous discharges to the atmosphere as opposed to effluent which refers to liquid and solid discharges.

EUTROPHIC WATERS: Waters with a good supply of nutrients; they may support rich organic production, such as algal blooms.

EUTROPHICATION: Process whereby lakes or streams become enriched with biological nutrients, usually nitrogen and phosphorus.

EXTENDED AERATION: A modification of the activated sludge process which provides for aerobic sludge digestion within the aeration system.

FATS: Triglyceride esters of fatty acids. Erroneously used as synonym for grease.

FECAL COLIFORM: An indicator organism for evaluating the microbiological suitability of the water.

FLOC: An agglomeration of finely divided or colloidal particles.

GREASE: In wastewater, a group of substances, including fats, waxes, free fatty acids, calcium and magnesium soaps, mineral oils, and certain other nonfatty materials. The type of solvent and method used for extraction should be stated for quantification.

HARDNESS: Characteristic of water imparted by salts of calcium, magnesium, and iron (such as bicarbonates, carbonates, sulfates, chlorides, and nitrates), which causes curdling of soap, deposition of scale in boilers, damage in some industrial processes, and sometimes objectionable taste. It may be determined by a standard laboratory procedure or computed from the amounts of calcium, magnesium, iron, aluminum, manganese, barium, strontium, and zinc, and is expressed as equivalent calcium carbonate.

HYDRAULIC LOADING: Quantity of flow passing through a column or packed bed, expressed in the units of volume per unit time per unit area; e.g., $m^3/m^2 \cdot s$ ($gal/min/ft^2$)

IMMEDIATE OXYGEN DEMAND: Oxygen consumed by a wastewater sample within a brief period (1 to 2 minutes) after aeration commences.

INCINERATION: With reference to gaseous materials, an abatement technique where the streams are heated to a specified temperature for a significant length of time to enable combustion of the products.

INFLUENT: Water, wastewater, or other liquid flowing into a reservoir, basin, or treatment plant.

INTEREST: The cost of borrowing money. It is a function of the unrepaid principal and is expressed as a per cent per year.

IOD: Immediate Oxygen Demand

LIMNOLOGY: The study of the physical, chemical, and biological aspects of inland waters.

MIXED LIQUOR: Mixture of activated sludge and wastewater undergoing activated sludge treatment in the aeration tank.

MIXED LIQUOR SUSPENDED SOLIDS (MLSS): Concentration of suspended solids carried in the aeration basin of an activated sludge process.

MLSS: Mixed Liquor Suspended Solids.

MPN: Most probable number. Expressed as density of organisms per 100 mL.

NITRIFICATION: The bacterial oxidation of nitrogenous compounds, such as the production of nitrite and nitrate from ammonia and proteinaceous substances.

NONSETTLEABLE SOLIDS: Suspended matter that does not settle or float to the surface of water in a period of 1 hour.

NUTRIENT: Any substance assimilated by an organism which promotes growth and replacement of cellular constituents.

OIL AND GREASES: Oils and greases are determined by multiple solvent extractions of the filterable portion of a sample of waste water; therefore, floating oils and greases are not included in the analysis. Several solvents are commonly used and each gives a different result with the same sample. Standardized tests are recommended, but there is much disagreement as to what constitutes the best method. Solvents such as hexane, ether, Freon, and carbon tetrachloride are used, and it is important that the solvent be specified. Oil and grease exert an oxygen demand, cause unsightly conditions, and can interfere with anaerobic biological treatment systems.

OLIGOTROPHIC WATERS: Waters with a small supply of nutrients; hence, they support little organic production.

ORGANIC MATTER: Chemical substances of animal or vegetable origin of basically carbon structure, comprising compounds consisting of hydrocarbons and their derivatives.

ORGANIC NITROGEN: Nitrogen combined in organic molecules, such as protein, amines, and amino acids.

OVERFLOW RATE: One of the criteria for the design of settling tanks in treatment plants, expressed in cubic meters per day per square meter (gallons per day per square foot) of surface area in the settling tank.

OXIDATION: Addition of oxygen to a compound. More generally, any reaction involving the loss of electrons from an atom.

OXIDATION POND OR LAGOON: Basin used for retention of wastewater before final disposal, in which biological oxidation of organic material is effected by natural or artificially accelerated transfer of oxygen to the water from air.

OXIDIZING AGENTS: Any substance which can receive electrons and thereby cause some other chemical to increase in positive charge.

PARTICULATE MATTER: Any material except uncombined water which exists in a finely divided form as a liquid or solid.

pH: Unit used to describe acidity or alkalinity. A pH value of 7 is neutral; above 7 is alkaline and below 7 is acidic.

POPULATION EQUIVALENT: The total mass BOD in an industrial wastewater divided by the mass of BOD contributed per person per day to a domestic wastewater, i.e. 1000 kg of BOD in an industrial wastewater/0.114 kg per capita = 8,772 people.

PRIMARY TREATMENT: (a) First (sometimes only) major treatment in a wastewater treatment works, usually sedimentation; or (b) removal of a substantial amount of suspended matter, but little or no colloidal and dissolved matter.

PRIORITY POLLUTANT: One of 129 pollutants identified by the U.S. Environmental Protection Agency as being particularly toxic. This list of 129 pollutants includes 116 organic and 13 inorganic chemicals.

RECEIVING WATER: Surface waters which assimilate effluent discharge.

SANITARY LANDFILL: A controlled method of refuse disposal in which refuse is dumped on land in accordance to a preconceived plan, compacted and covered during and at the end of each day.

SANITARY SEWER: Sewer that carries liquid and water-carried human wastes from residences, commercial buildings, industrial plants, and institutions, together with minor quantities of storm, surface, and groundwater(s) that are not admitted intentionally. Significant quantities of industrial wastewater are not carried in sanitary sewers.

SCFM: Standard cubic feet per minute. Air flow corrected to predefined standard conditions of temperature and pressure, generally 32°F and one atmosphere in air pollution work.

SCRUBBER: In air pollution, a device in which a contaminated stream is contacted with a liquid to reduce contaminant emission.

SECONDARY WASTEWATER TREATMENT: Treatment of wastewater by biological methods after primary treatment by sedimentation.

SEDIMENTATION: Process of subsidence and deposition of suspended matter carried by water, wastewater, or other liquids, by gravity. Usually accomplished by reducing the velocity of the liquid to below the point at which it can transport the suspended material. Also called settling.

SEPTIC: Causing anaerobic biological activities due to insufficient oxygen present in wastewaters.

SELF-PURIFICATION: Natural processes occurring in a stream or other body of water resulting in the reduction of bacteria, satisfaction of the BOD, stabilization of organic constituents, replacement of depleted dissolved oxygen, and the return of the stream biota to normal. Also called natural purification.

SETTLEABLE SOLIDS: That matter in wastewater which will not stay in suspension during a preselected settling period, such as one hour, but either settles to the bottom or floats to the top.

SLUDGE: The slurry of settled particles resulting from the process of sedimentation.

SLUDGE VOLUME INDEX (SVI): Numerical expression of the settling characteristics of activated sludge. The ratio of the volume in milliliters of sludge settled from a 1,000-mL sample in 30 minutes to the concentration of mixed liquor in milligrams per liter multiplied by 1,000.

SOLIDS: Material in the solid state.

Total: The solids in water, sewage, or other liquids; includes suspended and dissolved solids; all material remaining as residue after water has been evaporated.

Dissolved: Solids present in solution.

Suspended: Solids physically suspended in water, sewage, or other liquids. The quantity of material deposited when a quantity of water, sewage, or liquid is filtered through an asbestos mat or glass fiber filter.

Volatile: The quantity of solids in water, sewage, or other liquid lost on ignition of total solids.

SOLIDS RETENTION TIME (SRT): The average residence time of suspended solids in a biological waste treatment system, equal to the total weight of suspended solids in the system divided by the total weight of suspended solids leaving the system per unit time (usually per day).

SS: Suspended solids.

STABILIZATION PONDS: Ponds or lagoons used in treatment of sewage, also called oxidation ponds or stabilization lagoons. These may be either anaerobic (due to high sewage loads and lack of oxygen), aerobic (with oxygen provided by algae), or more commonly facultative (being aerobic in the surface layers and anaerobic toward the bottom).

SUSPENDED SOLIDS (SS): Suspended solids are the suspended material that can be removed from wastewaters by laboratory filtration excluding coarse or floating solids that can be screened or settled out readily. Suspended solids are a vital and easily determined measure of pollution and also a measure of the material that may settle out in slow-moving streams. Both organic and inorganic materials are measured by the SS test.

SVI: Sludge Volume Index.

TOC: Total Organic Carbon.

TOTAL ORGANIC CARBON (TOC): Measure of the amount of organic material in a water sample, expressed in milligrams per liter of carbon. Measured by carbonaceous analyzer in which the organic compounds are catalytically oxidized to CO_2 and measured by an infrared detector. Frequently applied to wastewaters.

TOTAL SOLIDS: Sum of dissolved and undissolved constituents in water or wastewater, usually expressed in milligrams per liter.

TSS: Total suspended solids. Amount of solids separated by filtration of a sample of wastewater.

TURBIDITY: Condition in water or wastewater caused by the presence of suspended matter, resulting in the scattering and absorption of light rays. Measure of fine suspended matter in liquids. Analytical quantity, usually expressed in Jackson turbidity units (Jtu), determined by measurements of light diffraction.

ULTIMATE BIOCHEMICAL OXYGEN DEMAND (UBOD): Quantity of oxygen required to satisfy completely biochemical oxygen demands.

VAPOR PRESSURE: (a) The pressure exerted by a vapor in a confined space. It is a function of the temperature. (b) The partial pressure of water vapor in the atmosphere. (c) Partial pressure of any liquid.

VENTURI SCRUBBER: A scrubber in which gas velocity is increased in the presence of a liquid due to a decrease in cross sectioned area of the duct causing particulate matter to be captured by impaction into the liquid.

VOLATILE SOLIDS: Quantity of solids in water, wastewater, or other liquids lost on ignition of the dry solids at 600° C.

VSS: Volatile suspended solids.

APPENDIX A

CONVERSION FACTORS

TABLE A.1

CONVERSION FACTORS

INSTRUCTIONS ON USE: TO CONVERT, MULTIPLY IN DIRECTION SHOWN BY ARROWS

	SI UNITS	-->	<--	U.S. UNITS
Length	centimeter	0.3937	2.5400	inch
	centimeter	0.032808	30.480	foot
	meter	39.3701	2.540×10^{-2}	inch
	meter	3.2808	0.30480	foot
	meter	1.0936	0.91441	yard
	kilometer	3,280.833	3.0480×10^{-4}	foot
	kilometer	0.6214	1.6093	mile
Area	centimeter^2	0.1550	6.4516	inch^2
	meter^2	10.7639	9.2903×10^{-2}	foot^2
	meter^2	1.1960	0.83612	yard^2
	meter^2	2.4711×10^{-4}	4046.78	acre
	meter^2	3.8610×10^{-7}	2.5900×10^{6}	mile^2
	kilometer^2	1.0764×10^{7}	9.29023×10^{-8}	foot^2
	kilometer^2	247.1044	4.0469×10^{-3}	acre
	kilometer^2	0.3861006	2.59000	mile^2
	hectare	107,638.7	9.290339×10^{-6}	foot^2
	hectare	2.47104	0.40468	acre

TABLE A.1 (continued)

CONVERSION FACTORS

INSTRUCTIONS ON USE: TO CONVERT, MULTIPLY IN DIRECTION SHOWN BY ARROWS

	SI UNITS	-->	<--	U.S. UNITS
Volume	centimeter^3	0.06102	16.3934	inch^3
	centimeter^3	3.5314×10^{-5}	2.8317×10^{4}	foot^3
	centimeter^3	2.6417×10^{-4}	3.7854×10^{3}	gallon
	meter^3	61,023.38	1.638716×10^{-5}	inch^3
	meter^3	35.3147	2.83168×10^{-2}	foot^3
	meter^3	1.3079	0.76458	yard^3
	meter^3	264.1720	3.7854×10^{-3}	gallon
	meter^3	8.3865	0.11924	barrel
	meter^3	8.1071×10^{-4}	1,233.487	acre-foot
	liter	33.8143	0.0295733	ounce
	liter	1.05668	0.946360	quart
	liter	0.2642	3.7853	gallon
	liter	61.025	0.016387	inch^3
	liter	0.0353	28.329	foot^3
Mass	milligram	0.015432	64.8004	grain
	milligram	3.5274×10^{-5}	28,349.49	ounce
	milligram	2.2046×10^{-6}	4.536×10^{5}	pound
	gram	0.035274	28.34949	ounce
	gram	0.002205	453.6	pound
	kilogram	2.2046	0.4536	pound
	kilogram	0.0011023	907.194	ton

TABLE A.1 (continued)

CONVERSION FACTORS

INSTRUCTIONS ON USE: TO CONVERT, MULTIPLY IN DIRECTION SHOWN BY ARROWS

	SI UNITS	-->	<--	U.S. UNITS
Velocity	meters/second	3.2808	0.304804	feet/second
	kilometers/sec	2.2369	0.44705	miles/hour
Acceleration	meters/second^2	3.2808	0.30480	feet/second^2
	meters/second^2	39.3701	2.5400×10^{-2}	inches/second^2
Temperature	Celsius ($^\circ$C)	$1.8(^\circ C) + 32$	$\frac{(^\circ F) - 32}{1.8}$	Fahrenheit ($^\circ$F)
	Kelvin ($^\circ$K)	$1.8(^\circ K) - 459.67$	$\frac{(^\circ F) + 459.67}{1.8}$	Fahrenheit ($^\circ$F)
Flow Rate	liters/second	15.8508	0.063088	gallons/minute
	liters/second	22,824.5	4.38126×10^{-5}	gallons/day
	liters/second	0.0228245	43.8126	million gallons/day
	liters/second	0.035316	28.3158	feet^3/second
	meters^3/second	15,850.3	6.3088×10^{-5}	gallons/minute
	meters^3/second	2.28245×10^7	4.38126×10^{-8}	gallons/day
	meters^3/second	22.8245	4.38126×10^{-2}	million gallons/day
	meters^3/second	35.316	0.028316	feet^3/second
Energy	joule	0.9478	1.0551	British thermal unit
	joule	2.778×10^{-7}	3.600×10^6	kilowatt-hour
	joule	0.7376	1.3557	foot-pound (force)
	joule	1.000	1.0000	watt-second
	joule	0.2388	4.1876	calorie
	joule	2.778×10^{-4}	3,599.71	watt-hour

TABLE A.1 (continued)

CONVERSION FACTORS

INSTRUCTIONS ON USE: TO CONVERT, MULTIPLY IN DIRECTION SHOWN BY ARROWS

	SI UNITS	-->	<--	U.S. UNITS
Power	watt	0.7376	1.35575	foot-pounds(force)/second
	watt	0.001341	745.7	horsepower
	watt	9.478×10^{-4}	1,055.1	British thermal units/second
	watt	0.014333	69.7691	calories/minute
Pressure	pascal	1.4504×10^{-4}	6,894.65	pounds(force)/inch^2
	pascal	2.0885×10^{-2}	47.88125	pounds(force)/foot^2
	pascal	2.9613×10^{-4}	3,376.895	inches of mercury (60°F)
	pascal	4.0187×10^{-3}	248.8367	inches of water (60°F)
	pascal	9.8687×10^{-6}	101,330	atmosphere

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