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CONTENTS

1	INTRODUCTION.	1
2	SUMMARY	3
	Pollution Abatement Legislation	3
	Pollution Abatement Expenditures.	5
	Capital Costs	5
	Operating Costs	5
	Waste Treatment Technology.	6
	Modular Waste Treatment Costs	8
	Fixed Capital Investment	8
	Operating Costs	9
	Examples of Module Cost Estimates	9
3	POLLUTION ABATEMENT LEGISLATION AND EXPENDITURES.	13
	Legislation in the United States.	13
	Air Pollution	13
	Water Pollution	16
	Land Pollution (Solids Disposal).	22
	Selected Reactions to U.S. Antipollution Legislation.	24
	Information Sources	25
	Legislation in Japan.	26
	Air Pollution	28
	Water Pollution	30
	Land Pollution.	32
	Chemical Substances Control Law	32
	Expenditures in the United States	33
	Capital Expenditures.	33
	Operating Costs	38
	Expenditures in Japan	41
4A	WASTEWATER TREATMENT TECHNOLOGY	43
	Pretreatment.	45
	Primary Treatment--Chemical	46
	Objective	46
	Ion Exchange.	54
	Electrodialysis	56
	Reverse Osmosis	58
	Neutralization.	58
	Oxidation and Reduction	60
	Chemical Addition	63
	Hydrolysis.	65
	Primary Treatment--Physical	67
	Sedimentation	67
	Hydrocycloning.	67

CONTENTS

4A	WASTEWATER TREATMENT TECHNOLOGY (continued)	
	Filtration and Centrifuging	70
	Flotation	72
	Solvent Extraction	76
	Crystallization	77
	Adsorption on Activated Carbon	77
	Secondary Treatment	80
	Air-Activated Sludge	80
	Oxygen-Activated Sludge	82
	Facultative Lagoons	85
	Trickle Filters	85
	Nitrification-Denitrification	87
	Sand Filters	89
	Tertiary Treatment	90
	Foam Fractionation	90
	Chlorination	91
	Ozonation	92
	Toxic Liquids Disposal	95
4B	GASEOUS WASTE TREATMENT AND DISPOSAL TECHNOLOGY	97
	Pretreatment	97
	Dry Systems	100
	Gas-Solid Separation	100
	Adsorption on Activated Carbon	101
	Liquid Systems	105
	Water and Solvent Scrubbing	105
	Acid or Ammonia Neutralization	105
	Limestone Desulfurization	105
	Waste Gas Disposal	106
	Steam Generation and Incineration	106
	Emergency Flaring	107
	Dispersion by a Stack	108
4C	SOLID WASTE TREATMENT AND DISPOSAL TECHNOLOGY	111
	Waste Solids Treatment	111
	Dewatering	111
	Drying	115
	Incineration	116
	Combustion	119
	Waste Solids Disposal	121
	Land Farming	121
	Stacking	122
	Sanitary Landfill	122
	Hazardous-Waste Landfill	124
	Other Disposal Methods	125

CONTENTS

5	COST CALCULATIONS FOR WASTE TREATMENT MODULES.	127
	Capital Cost Methods Used in This Study.	130
	Operating Costs.	133
	Module Cost Curves	134
6	WASTE TREATMENT COSTS FOR SELECTED CHEMICAL INDUSTRIES	189
	Methanol Plant Wastes.	190
	Treatment Methods.	190
	Treatment Costs.	190
	Discussion of Costs.	193
	Ethylene Plant Wastes.	195
	Treatment Methods.	195
	Treatment Costs.	195
	Discussion of Costs.	199
	Multipiant Wastes.	200
	Treatment Methods.	200
	Treatment Costs.	200
	Discussion of Costs.	204
	Phosphoric Acid Plant Wastes	205
	Treatment Methods.	205
	Treatment Costs.	207
	Discussion of Costs.	207
	Conclusion	208
	APPENDIX A Cost Basis.	211
	APPENDIX B Calculations for the Equalization of a Waste Stream Flow Variable	213
	APPENDIX C Design Steps for a Completely Mixed Activated Sludge System	217
	APPENDIX D Fixed Bed Active Carbon Adsorber Capacity	223
	CITED REFERENCES.	225

ILLUSTRATIONS

3.1	Annual Capital Expenditures by the U.S. Chemical Industry for Pollution Abatement.	34
3.2	Annual Operating Costs of the U.S. Chemical Industry for Pollution Abatement.	39
3.3	Annual Capital Expenditures by the Japanese Chemical Industry for Pollution Abatement as a Percentage of Total New Capital Investment	42
4.1	Wastewater Treatment Alternatives.	44
4.2	Multiple-Chamber Alternate-Membrane Electrodialysis Cell	57
4.3	Settling Curves at Various Suspended Solids Concentrations	68
4.4	Batch Suspended Solids Flux Curve for Design	69
4.5	Approximate Solid Size Range for Solid-Liquid Separation Equipment	71
4.6	Schematic Diagram of Dissolved-Air Flotation Tank with Recycle	75
4.7	Activated Sludge System.	81
4.8	Waste Gas Treatment Alternatives	98
4.9	Compressor Horsepower for Various Air Flow Rates	99
4.10	Pressure Drop for Air Flow Through Active Carbon at 70°F and 760 mm Hg.	104
4.11	Waste Solid Treatment Alternatives	112
4.12	Effect of Feed Size on Drying Centrifuge Capacity.	113
4.13	Effect of Feed Rate and Size on Drying Centrifuge Product Moisture	114
4.14	Stacking Procedure for Waste Gypsum.	123
5.1	Guthrie Method for Modular Cost Estimates.	129
5.2	Module Cost: Tanks	136
5.3	Module Cost: Thickener, Clarifier	137
5.4	Module Cost: Settling Lagoon	138
5.5	Module Cost: Oil Separators	139
5.6	Module Cost: Filters.	140
5.7	Module Cost: Centrifuges.	141
5.8	Module Cost: Hydraulic Cyclones	142

ILLUSTRATIONS

5.9	Module Cost: Distillation System.	143
5.10	Module Cost: Evaporators.	144
5.11	Module Cost: Stripper, Steam or Flue Gas.	145
5.12	Module Cost: Lime Neutralizer	146
5.13	Module Cost: System for Chemical Reaction or Precipitation	147
5.14	Module Cost: Ion Exchange System.	148
5.15	Module Cost: Electrodialysis and Reverse Osmosis Cells	149
5.16	Module Cost: Dissolved-Air Flotation Cell	150
5.17	Module Cost: Crystallization System	151
5.18	Module Cost: Active Carbon Adsorber for Liquid Stream . . .	152
5.19	Module Cost: Solvent Extraction System.	153
5.20	Module Cost: Biological Oxidation System Including Sludge Separation.	154
5.21	Module Cost: Faculative Lagoon.	155
5.22	Module Cost: Filters, Dual Media and Sand	156
5.23	Module Cost: Foam Fractionator.	157
5.24	Module Cost: Ozonation System	158
5.25	Module Cost: Denitrification System	159
5.26	Module Cost: Hydrolyzer	160
5.27	Module Cost: Chlorinator for Ammonia Removal.	161
5.28	Module Cost: Chlorinator for Disinfection and Equipment for Water Quality Control.	162
5.29	Module Cost: Pumping System and Deep-Welling System	163
5.30	Module Cost: Liquid Incinerator	164
5.31	Module Cost: Steam and Cooling Water Utilities.	165
5.32	Module Cost: Gas Combustor for Steam Generation	166
5.33	Module Cost: Gas Incinerator.	167
5.34	Module Cost: Flue Gas Desulfurization System.	168
5.35	Module Cost: Hydrocarbon Gas Flare.	169
5.36	Module Cost: Gas Dispersion Stack	170

ILLUSTRATIONS

5.37	Module Cost: Ammonia Neutralizer.	171
5.38	Module Cost: Acid Gas Neutralizer	172
5.39	Module Cost: Scrubbers, Hydrocarbon or Water.	173
5.40	Module Cost: Active Carbon Adsorber for Gaseous Stream. . .	174
5.41	Module Cost: Gas Compressor	175
5.42	Module Cost: Dust Separator	176
5.43	Module Cost: Gas Coolers	177
5.44	Module Cost: Gas Refrigeration System	178
5.45	Module Cost: Rotary Direct Dryer.	179
5.46	Module Cost: Dewatering Centrifuge.	180
5.47	Module Cost: Solids Incinerator	181
5.48	Module Cost: Solids Combustor	182
5.49	Disposal Cost: Land Farming	183
5.50	Disposal Cost: Gypsum Stacking.	184
5.51	Disposal Cost: Sanitary Landfill.	185
5.52	Disposal Cost: Hazardous-Waste Landfill	186
5.53	Transportation Cost	187
6.1	Treatment of Methanol Plant Wastes	191
6.2	Treatment of Ethylene Plant Wastes (Ethane/Propane Pyrolysis)	196
6.3	Treatment of Multiplant Wastes	201
6.4	Treatment of Process Phosphoric Acid Plant Wastes (Dihydrate Wet Process).	206
B.1	Probability Plot of BOD Value.	214
C.1	Determination of BOD Removal Rate Coefficient.	218
C.2	Determination of Oxygen Utilization Coefficient.	220
C.3	Determination of Sludge Production Coefficient	221
D.1	Breakthrough Curves for Three Columns in Series.	224
D.2	Service Time as a Function of Bed Depth.	224

TABLES

2.1	A Comparison of Modular Waste Treatment Estimates With Independently Estimated Values.	11
3.1	U.S. National Ambient Air Quality Standards.	15
3.2	Typical Effluent Limitations Promulgated by U.S. EPA According to the Federal Water Pollution Control Act Amendments of 1972	17
3.3	U.S. EPA List of Priority Toxic Pollutants as of December 1978.	19
3.4	U.S. EPA-Proposed Water (Micrograms/Liter) Quality Criteria for Selected Toxic Pollutants	21
3.5	Major Pollution Control Legislation by the U.S. Congress . . .	27
3.6	U.S. Pollution Abatement Expenditures for Air, Water, and Solids, by Chemical Industry Segment	36
3.7	U.S. Pollution Abatement Operating Costs for Air, Water, and Solids, by Chemical Industry Segment	40
3.8	Japanese Pollution Abatement Expenditures.	41
4.1	Typical Thickener and Clarifier Design Criteria.	46
4.2	Water Pollutant Treatment Methods	47
4.3	Toxic Inorganic and Organic Pollutants and Methods for Their Control.	48
4.4	Materials Rejected by Reverse Osmosis.	59
4.5	Commercial Oxidizing and Reducing Agents and Their Possible Applications to Waste Treatment	62
4.6	Typical Flocculants and Coagulants and Their Applications. . .	64
4.7	Some Typical Filter Applications	73
4.8	Typical Centrifuge Performance Characteristics	74
4.9	Activated Sludge Process Characteristics	83
4.10	Typical Compounds Susceptible to Ozonation	93
4.11	Applications of Gas-Solid Separation Equipment	101
4.12	Vapors Adsorbed by Activated Carbon.	103
4.13	U.S. EPA-Sponsored Waste Incineration Demonstration Plants	117

TABLES

5.1	SRI Module Investment Estimation Factors.	131
5.2	Comparison of Chemical Equipment Module Costs Estimated by Different Methods.	132
5.3	SRI Module Maintenance Cost Estimation Factors.	134
6.1	Treatment Costs for Methanol Plant Wastes	192
6.2	Treatment Costs for Ethylene Plant Wastes	197
6.3	Treatment Costs for Combined Multiplant Wastes.	202
6.4	Treatment Costs for Phosphoric Acid Plant Wastes (Dihydrate Wet Process)	209
B.1	Cumulative Normal Probability Distribution.	215

MCD 000016378

1 INTRODUCTION

For Process Economics Program reports, in the past, we have usually added a standard fixed percentage to the capital investment for control of water, air, and land pollution. In this study we have developed a convenient method to approximate the capital and operating costs for pollution control in specific chemical plants or complexes. We believe that this method will improve the accuracy of pollution control estimates in future PEP reports and at the same time provide a better understanding of the nature of these costs and how they might be minimized. Sufficient information is provided to enable PEP users to independently estimate or compare the pollution control costs of other plants or processes.

Sections 4A, 4B, and 4C briefly describe operations with present or potential application to the abatement of water, air, and land (solids) pollution. Their areas of utility are indicated and information is provided to enable one to roughly relate equipment size to pollutant stream flow rate. Previously published capital costs for these operations, where available, are also reported.

Section 5 details the procedures used in this study to derive module capital costs and operating requirements for the above pollution abatement operations. Module capital cost curves and tables of operating requirements, so obtained, are included. These cost data apply to a PEP Cost Index of 290 and a time base of January 1, 1979.

Section 6 illustrates the use of the above module cost curves and operation data to estimate the capital investment and operating costs of pollution control for a methanol plant, an ethylene plant, a wet process phosphoric acid plant, and a multipiant complex for making acrylonitrile, ethylene, propylene, hexamethylenediamine, and methanol. These estimates are compared with similar estimates derived independently elsewhere.

Section 3 first outlines the major pollution abatement legislation enacted in the United States and Japan over the past decade. It then summarizes the overall financial impact of the legislation on chemical and allied industries. With many pollution abatement deadlines now set for the mid-1980s, little or no near-term easing of this burden appears likely for the chemical industry in the United States.

Only fragmentary information on European pollution control legislation and on the costs of implementation was found in recently published literature. Thus, no European information is included in this report.

2 SUMMARY

Pollution Abatement Legislation

Much of the motivation for pollution abatement in the United States stems from legislation enacted by Congress over the past decade. The Clean Air Act Amendments of 1970 and 1977 define three area classifications:

Class I - Virtually no increase in air pollution is allowed
(national parks and wilderness areas)

Class II - Limited increases in air pollution are allowed (city, urban, and rural areas)

Class III - Higher air pollution in Class II areas is allowed on special request by the governor of the state.

The materials controlled are SO₂, NO₂, CO, ozone, hydrocarbons, lead, and particulates. A criticism of the Clean Air Act is that it allows pollution to increase in populated areas, where the most people are exposed to possible long-term effects.

The Occupational Safety and Health Act of 1970 regulates the concentration of hazardous vapors and gases in working environments.

The Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977 empower the Environmental Protection Agency (EPA)--which has the responsibility for administering most of the pollution control legislation--to establish purity standards for wastewater discharges from publicly owned treatment works (POTW) and industrial plants. These standards, to be established by mid-1980 and implemented by 1985, should prevent adverse effects on humans, fish, or wildlife.

EPA is developing a program requiring industrial plants to pretreat their wastes before discharging them to a POTW. Technical and financial assistance is available through EPA for implementation of the above legislation.

The volume of solid industrial waste generated in the United States is estimated at 336 million metric tons/yr, with about 9% of this being potentially hazardous waste. The Resource Conservation and Recovery Act of 1976 recognizes that, in the past, waste disposal precautions have been inadequate and provides for the identification and monitoring of hazardous wastes through generation, transportation, storage, and final disposal. A companion piece of legislation, the Toxic Substances Control Act of the 1976, requires extensive testing and record keeping before a new chemical material can be produced commercially.

The Marine Protection, Research, and Sanctuaries Act of 1972 has largely eliminated the ocean dumping of industrial wastes from the United States. Ocean dumping of sewage sludge (still several million tons annually) is to be eliminated by the end of 1981. Incinerator ships--currently in use in Europe--are being considered for the burning of U.S. industrial wastes at sea.

Legislation in Japan to control air and water pollution is similar to that in the United States but generally more restrictive. The Basic Law for Environmental Pollution Control was enacted in 1967 and was augmented by the Air Pollution Control Law in June, 1968 and the Water and Marine Pollution Control Law of 1970. These laws set national standards for air and water pollutant concentrations, and the Environmental Agency has responsibility for their implementation. However, local governments have the authority to set and enforce standards which are more severe than the national ones.

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Pollution Abatement Expenditures

Capital Costs

The capital investment in facilities for pollution abatement by the U.S. chemical and allied products industries has risen steeply from less than \$150 million in 1972 to almost one billion in 1977. Most of this cost pertains to water (60%) and air (35%). By 1985, capital expenditures for pollution control are expected to reach \$1.3 billion/yr, with most of this increase going for water pollution abatement.

Capital expenditures for pollution abatement since 1973 have been in the range of 10 to 13.5% of total new capital spending by the U.S. chemical industry. This is projected to continue until 1985. These are average figures and they differ appreciably for different segments of the chemical industry. For example, pollution abatement expenditures in 1976, as a percentage of new capital investments, was 22% for inorganic chemicals, 15% for organic chemicals, and 4% for drugs and pharmaceuticals. Moreover, expenditures within these segments vary widely.

Annual expenditures by the Japanese chemical industry reached a peak of 17% of new capital investment in 1975. They have since declined to about 4%. Water pollution represents about 50% of the 4.5×10^9 yen pollution abatement expenditure in 1979. Air pollution accounts for 30%, with solid waste disposal and noise pollution taking the balance. Incineration is the principal means for disposal of solid and hazardous wastes in Japan.

Operating Costs

Operating costs for air, water, and land pollution abatement have also been rising steadily in the United States since 1973, at an average annual rate of 24%. They currently amount to \$1.7 billion/yr, or about 2.2% of the value added by the chemical and allied industries. By 1985, annual operating costs may reach \$1.7 billion, or 2.7% of the value added.

The operating costs vary appreciably among industry segments. In 1976, pollution abatement operating costs as a percentage of the value added averaged 3.5% for industrial organic chemicals, 2.7% for inorganic chemicals, and 0.4% for drugs and pharmaceuticals. Within a given segment, however, the costs may vary widely. A sulfate process titanium dioxide pigment plant, for example, may have a pollution abatement cost equal to 10% of value added.

Waste Treatment Technology

The technology for pollution abatement consists mainly of the same physical and chemical separations and reaction technologies used in chemical manufacture.

For wastewater, pretreatment by screening, settling, or steam stripping, may be used to remove suspended solids or immiscible liquids. This can be followed by a primary treatment consisting of physical operations such as centrifuging, flotation, reverse osmosis, and evaporation, or chemical reactions such as neutralization, precipitation, and ion exchange to separate dissolved or finely suspended impurities. Secondary treatment consists of biological oxidation (this is the only technology pertaining primarily to wastewater treatment). The oxidation can be performed in tanks, deep shafts, lagoons, or trickle filters, with air or oxygen being used to convert nontoxic organic impurities to an insoluble sludge. This sludge can then be separated by thickening, filtration, or centrifuging and sent to solids disposal.

When the wastewater is to be recycled or used by animals or humans, tertiary treatment may be necessary. This consists of ozonation, distillation, or absorption by activated carbon to remove traces of organic colors, tastes, and odors, or of ion exchange, electrodialysis, and precipitation to eliminate residual dissolved solids. Finally, the water is chlorinated or ozonated to destroy bacteria and other microorganisms.

The choice of operations for treating a given aqueous waste is determined by:

- Quantity and composition of waste stream
- Existing or impending pollution abatement laws and regulations
- Nature of surrounding facilities and environment.

In some cases, it may be more economic to eliminate a waste stream by modifying the process or raw materials from which it is generated.

Gaseous wastes may need to be precooled or compressed to facilitate subsequent treatment. Suspended solids are separated by cyclone, bag filter, or electrostatic precipitator. Harmful gaseous impurities are removed by adsorption on active charcoal or by scrubbing with water, solvent, or aqueous acid or alkaline solution. Combustible impurities in the waste gases can be burned or flared. Residual inert, or largely inert, gases are released to the atmosphere.

The treatments and disposal alternatives available for solid wastes are few. Moisture or adsorbed liquids can be separated in a dewatering centrifuge or a drier. Incineration can be used to convert toxic wastes to gaseous and solid wastes more easily disposed of. A combustible solid waste can be used as a fuel in the plant.

The disposal of waste solids, as previously indicated, is coming under increasing regulations and record keeping. Ocean dumping is no longer permitted from the United States. Deep-welling of slurried solids is feasible only for some areas and with extensive precautions, monitoring, and record keeping. The same is true for hazardous-waste landfill. Nonhazardous waste solids can be stored in sanitary landfills, stacked or, in the case of biologically decomposable solids, destroyed by land farming. These methods can require sizable land areas.

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Modular Waste Treatment Costs

Fixed Capital Investment

The several methods normally used for estimating the capital cost of waste treatment facilities are cumbersome, expensive, and/or requiring of detail more akin to a final engineering design than to a preliminary cost estimate. In this study, we developed a quick and simple procedure to estimate both capital investments and operating costs.

Typical installed costs for chemical equipment ranges from about 1.8 to 5.0 times the equipment f.o.b. price, depending on the extent of foundations, supports, field labor, piping, insulation, electrical wiring, instrumentation, and building enclosure that is required. Thus, by placing each of these installation requirements at "little," "some," or "extensive," as shown below, we obtain installation factors varying between 1.8 and 5.0:

	<u>Little</u>	<u>Some</u>	<u>Extensive</u>
Base factor	1.0	1.0	1.0
(A) Foundations, steel supports, field labor	0.2	0.6	1.0
(B) Connecting piping	0.2	0.6	1.0
(C) Insulation, electrical connections, instrumentation	0.2	0.6	1.0
(D) Building or enclosure	<u>0.2</u>	<u>0.6</u>	<u>1.0</u>
Totals (module factor = f_M)	1.8	3.4	5.0

A centrifuge with "some" foundations and supports; "some" connecting piping; "little" electrical, insulation, or instrumentation; and complete enclosure in a building would have a module factor (f_M) = $1.0 + 0.6 + 0.6 + 0.2 + 1.0 = 3.4$. The module cost is then the equipment price of \$25,000 $\times$ 3.4, or \$85,000. A comparison of equipment module costs so obtained with those by Icarus Corporation and Guthrie showed individual variations of $\pm 30\%$ but, when nine modules were totalled, the differences were less than 5%.

The total fixed capital investment is the sum of the modular costs plus 30% to allow for indirect costs--construction, overhead, engineering, freight, equipment rental, etc.--and general facilities such as stores, maintenance shops, change rooms, roads, and fencing.

Operating Costs

The operating costs for each equipment module are functions of capital cost, feed rate, and process complexity. Capital-related costs--i.e., taxes, and insurance, depreciation, return on investment, and maintenance--are, with the exception of maintenance, defined in PEP estimates as given percentages of the capital investment. Factors influencing maintenance costs are:

- Corrosivity and special construction materials
- Operating temperatures above ambient
- Power usage and numerous moving parts
- Connecting equipment
- Abrasive solids handling.

If each of these five factors is given a value of zero, one, or two--depending on whether it has no influence, some influence, or appreciable influence--the annual maintenance cost can readily be estimated as a percentage of the process module cost.

Process materials and utilities usages are normally specific to a particular waste treatment operation and feed flow rate, and labor is related to the type of processing, with only minor sensitivity to feed rate. These relationships are given in tables on the graphs of module costs. Thus, using the table and the graph, one can derive the approximate capital and operating costs for each equipment module.

Examples of Module Cost Estimates

Modular capital and operating cost curves and data were employed to estimate waste treatment costs for the following chemical plants or complexes:

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- A 660 million lb/yr methanol plant
- A 1.0 billion lb/yr ethylene plant
- A multiplant complex of adiponitrile, ethylene/propylene, hexamethylenediamine, and methanol with capacities of 210, 900, 200, and 750 million lb/yr respectively.
- A 50 million lb P_2O_5 /yr wet process phosphoric acid plant.

These costs, together with comparative figures obtained from independent sources, are shown in Table 2.1. Modularly estimated fixed capital investments for each of the three single-process plants and for the multiplant complex are well within $\pm 20\%$ of the comparison estimates. Similarly, annual operating costs--except those for the methanol plant--are generally within the same range. In all cases, the investment in waste treatment is less than 5% of the plant investment, and operating costs represent 0.4¢/lb or less of the product value.

Minimizing the waste treatment cost of any new chemical plant necessitates judicious selection of process, location, and raw materials.

Table 2.1
A COMPARISON OF MODULAR WASTE TREATMENT ESTIMATES WITH INDEPENDENTLY ESTIMATED VALUES*

PeP Cost Index: 290

	Waste Treatment Module Estimates				Independent Waste Treatment Estimates			
	Fixed Capital	% of Plant	Operating Cost	c/lb of	Fixed Capital	% Deviation	Operating Cost	% Deviation
Chemical plants (Capacity, 1,000 t/yr)	\$1,000	Investment	\$1,000/yr	Product	\$1,000	from Module	\$1,000/yr	from Module
Methanol [†] (330)	858	1.7	162	0.16	712	-17.0	116	-26
Ethylene [‡] (500)	1,370	0.7	735	0.07	1,400	+2.2	620	-10.6
Multiplant complex								
adiponitrile (105)	12,400	3.2	3,210	0.15	9,100 or 14,100	-6.5**	1,600 or 3,100	-26.8
Ethylene/propylene (450)								-26.8**
Hexamethylenediamine (100)								
Methanol (375)								
Wet process phosphoric acid (50) ^{††}	430	4.3	394	0.40	368	-14.4	400	+1.5

*Independent values have been adjusted where necessary to a PEP Cost Index of 290, corresponding to a time basis of January, 1979.

[†]These figures include only the biological air oxidation of methanol aqueous wastes. Natural gas raw material is assumed to be delivered with a low sulfur content. Other wastes are negligible or are returned to supplier for recovery of metals.

[‡]Waste treatment costs have been adjusted to a small plant capacity for the independent estimates to correspond to waste stream quantities used for the module estimates.

**The independent waste treatment estimate includes two systems—one according to the best available demonstrated technology (BADO) and also according to the best available technology (BAT). The average of these is used for comparison.

^{††}Capital and operating cost to pump slurry wastes to the disposal area are not included in either set of figures.

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3 POLLUTION ABATEMENT LEGISLATION AND EXPENDITURES

Legislation in the United States

Air Pollution

The first legislation in the United States directed to the control of air pollution was the Air Quality Act of 1963. This act provided for research, technical assistance, matching grants to state and local agencies, and enforcement authority for the abatement of air pollution (B-13932). This was followed by the Air Quality Act of 1967, which initiated a two year study of air pollution, the issuance of air quality criteria, and the development of methods for their control. Primary enforcement was placed at the state level with federal fallback authority when needed.

The Clean Air Act Amendments of 1970 was next, with the following provisions:

- Inclusion of all areas of the United States in air quality control regions.
- Promulgation of performance standards for new sources.
- Development of national standards for deleterious pollutants.
- Monitoring and record keeping of emission sources.
- Imposition of fines and criminal penalties for violation of air quality standards.

Administrative responsibility for overseeing the implementation of these provisions was given to the Environmental Protection Agency.

The most recent and comprehensive legislation is the Clean Air Act Amendments of 1977 (447094). This legislation set up three area classifications: Class I, which permits virtually no pollution increase; Class II, which allows for a moderate increase; and Class III, which provides for a more extensive increase. Class I includes national

parks and wilderness preserves. All other areas are Class II, except where a Class III designation has been requested by the state governor. The act also sets national air quality standards (see Table 3.1), with a January 1979 deadline for meeting these standards--now extended to December 1982 (B-13938).

The major sources of pollution (each capable of emitting more than 100 tons of pollutant per year) have been identified in the United States (B-13938). Out of approximately 23,000 major sources, 87% were in compliance as of October 1977. However, prior enforcement actions initiated by EPA and the states exceeded 16,000. Pollution increments--intended for the prevention of significant deterioration (PSD)--have been established for new sources, and a complicated procedure is required to obtain a permit for a new source. The time interval for completion of this procedure ranges from 18 to 43 months (447002).

Local concentrations of toxic gases resulting from various manufacturing and chemical processing operations are covered by the Occupational Safety and Health Act of 1970 (OSHA) (447095). This act, administered by the U.S. Dept. of Labor, provides for a network of inspectors to investigate working areas. OSHA can issue citations when the concentration of a hazardous material--such as vinyl chloride vapor--is above a specified safe concentration. Fines and/or imprisonment can be imposed for noncompliance with OSHA safety standards. Some of the problems arising from OSHA inspections of a working environment have been discussed by Moran (447096).

The above act also sets up a National Institute for Occupational Safety and Health (NIOSH), which operates within the Dept. of Health, and Human Services to measure and report the safe exposure limits for hazardous materials. Over 16,000 toxic substances have been identified and threshold concentrations for their toxicity to marine and animal life have been established (B-13937). Safe concentration limits for over 300 gases have also been published (447006).

Table 3.1

U.S. NATIONAL AMBIENT AIR QUALITY STANDARDS

Pollutant	Time Period	Units	Primary* Standard	Secondary† Standard
Sulfur dioxide	3 hr [§]	μg/m ³	—	1,300
	24 hr [§]	μg/m ³	365	—
	Annual	μg/m ³	80	—
Nitrogen dioxide	Annual	μg/m ³	100	100
Total suspended particulates	24 hr [§]	μg/m ³	260	150
	Annual	μg/m ³	75	60
Carbon monoxide	1 hr [§]	mg/m ³	40	40
	8 hr [§]	mg/m ³	10	10
Lead	3 month avg.	μg/m ³	1.5	1.5
Hydrocarbons (other than methane) [#]	3 hr [§]	μg/m ³	160	160
Ozone	1 hr [§]	ppm	0.12	0.12

Prevention of Significant Deterioration,
Maximum Allowable Increment (μg/m³)

Pollutant	Class I	Class II	Class III
Particulate matter			
Annual mean	5	19	37
24 hr maximum	10	37	75
Sulfur dioxide			
Annual mean	2	20	40
24 hr maximum	5	91	182
3 hr maximum	25	512	700

*Threshold level for effects on human health.

†Threshold level for environmental effects, foliage, visibility, etc.

§Levels not to be exceeded more than once per year.

[#]Suggested maximum if ozone limits are to be realized.

Source: 447094

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Water Pollution

The Federal Water Pollution Control Act Amendments of 1972, which replaced all previous federal water laws, was the most comprehensive water control legislation to come out of the Congress of the United States. It empowered EPA to set standards for wastewater discharges from existing industries to be achieved by July 1, 1977, by the "best practicable control technology currently available" (BPCTCA or BPT). New plants were required to file for a National Pollution Discharge Elimination System (NPDES) permit 24 months before beginning the discharge and to meet an effluent concentration according to the "best available demonstrated control technology" (BADCT or BADT). Industry was directed to attain, by July 1, 1983, aqueous pollutant discharge levels consistent with the "best available control technology economically achievable" (BATEA or BAT) and 1985 was set as the year for achieving zero pollutant discharge. Monitoring and reporting could be required and fines up to \$25,000 and/or 1 year imprisonment could be imposed for the first conviction of false reporting, negligence, carelessness, or willful violation. Discharges to publicly owned treatment works did not require a permit provided they did not contain pollutants which interfere with normal operation and provided the discharger bore a proportionate share of the POTW capital and operating costs.

EPA implementation of this law separated the chemical and related industries into subcategories ranging from A₁ through C₁₁. Each category was allowed a maximum one day and a maximum 30 day discharge of chemical oxygen demand (COD), biological oxygen demand measured over 5 days at a constant temperature (BOD₅), total suspended solids (TSS), and pH, as shown in Table 3.2, for the three control levels BPT, BDT, and BADT.

The above law was not sufficiently specific--small quantities of chlorinated organics or heavy metal salts, which can be very damaging to the environment, were not covered by effluent specifications.

Table 3.2
TYPICAL EFFLUENT LIMITATIONS PROMULGATED BY U.S. EPA
ACCORDING TO THE FEDERAL WATER POLLUTION CONTROL ACT AMENDMENTS OF 1972

Subcategory	Product and Processes	Effluent Characteristics	lb/1,000 lb of Product or kg/1,000 kg of Product					
			SPT		3ADT		3AT	
			Maximum for 1 Day	Average of 30 Consecutive Days Shall Not Exceed	Maximum for 1 Day	Average of 30 Consecutive Days Shall Not Exceed	Maximum for 1 Day	Average of 30 Consecutive Days Shall Not Exceed
A	BTX aromatics by hydration of pyrolysis gasoline; BTX aromatics by solvent extraction of reformate; cyclohexane by hydrogenation of benzene; and vinyl chloride by HCl addition to acetylene.	COD	—	—	—	—	0.062	0.015
		BOD ₅	0.045	0.02	0.037	0.017	0.015	0.0085
		TSS	0.067	0.03	0.034	0.015	0.022	0.013
		pH	6.0 to 9.0		6.0 to 9.0		6.0 to 9.0	
B ₁	Acetone by dehydrogenation of isopropanol; butadiene by-product of ethylene; ethylbenzene by alkylation of benzene; ethylene and propylene by hydrocarbon pyrolysis; ethylene dichloride by chlorination of ethylene; ethylene oxide by catalytic oxidation of ethylene; formaldehyde by oxidation of methanol; methanol by steam reforming of natural gas; methyl amines by addition of ammonia to methane; vinyl acetate from ethylene and acetic acid; vinyl chloride by cracking of ethylene dichloride.	COD	—	—	—	—	0.80	0.58
		BOD ₅	0.13	0.58	0.11	0.048	0.044	0.025
		TSS	0.20	0.088	0.10	0.044	0.066	0.040
		pH	6.0 to 9.0		6.0 to 9.0		6.0 to 9.0	
E ₃	Adiponitrile by chlorination of benadiene; benzoic acid by catalytic oxidation of toluene; and methyl chloride by HCl reaction with methanol.	COD	—	—	—	—	16.6	11.9
		BOD ₅	0.94	0.42	0.78	0.35	0.25	0.14
		TSS	1.11	0.49	0.56	0.25	0.37	0.21
		pH	Between 6 and 9		Between 6 and 8		Between 6 and 8	

Source: Federal Register, Vol. 39, No. 81, pp. 14676-14685, April 25, 1974. (Also B-13934.)

Moreover, some of the deadlines for compliance were impractical and the BAT, BADT, and BPT classifications of pollution control technology were confusing.

The Clean Water Act of 1977 was designed primarily to overcome the deficiencies of the 1972 law. It includes the following provisions (B-13938):

- EPA was permitted to issue individual extensions up to April 1979 to the 1977 deadline, if there was a genuine commitment to compliance.
- A list of toxic pollutants which must be controlled by July 1, 1984 and to which EPA could add or subtract was issued. (This list as of December 1978, is shown in Table 3.3.)
- EPA was directed to publish a list of conventional pollutants--BOD, suspended solids, fecal coliform, and pH--which industry must control by July 1, 1984, using best available current pollution control technology (BACT or BCT). This new standard of control was to be specified by EPA through effluent limitation guidelines.
- Discharger of nonconventional pollutants--neither toxic nor conventional--must install best available control technology by July 1, 1984 or, within 3 years after EPA issues effluent limitation guidelines, whichever is later, but not later than July 1, 1987. Variances from this requirement are possible if it can be shown that this variance will not adversely effect water supplies, shellfish, fish, wildlife, or recreational use of the water.
- Provisions in the 1972 law which allowed EPA to grant economic variances from toxic pollution standards were eliminated.

A partial listing of water quality criteria proposed by EPA, is shown in Table 3.4. Additional criteria and revised effluent standards for the organic and inorganic chemical industries, as well as for petroleum refining, were scheduled for publication before mid-1980.

To achieve the goals of the Clean Water Act, EPA is developing a national program to pretreat nondomestic wastes before their discharge to municipal plants (Federal Register, 27736, June 26, 1978). Each publicly owned treatment works (POTW) with a design flow above 5 million gallons per day is required to develop and enforce pretreatment

Table 3.3

U.S. EPA LIST OF PRIORITY TOXIC POLLUTANTS AS OF DECEMBER 1978*

Volatile Halogenated Organics (VHO)

6. Carbon tetrachloride
7. Chlorobenzene
8. 1,2,4-Trichlorobenzene
10. 1,2-Dichloroethane
11. 1,1,1-Trichloroethane
12. Hexachloroethane
13. 1,1-Dichloroethane
14. 1,1,2-Trichloroethane
15. 1,1,2,2-Tetrachloroethane
16. Chloroethane
23. Chloroform
25. 1,2-Dichlorobenzene
26. 1,3-Dichlorobenzene
27. 1,4-Dichlorobenzene
29. 1,1-Dichloroethylene
30. 1,2-Dichloroethylene
32. 1,2-Dichloropropane
33. 1,3-Dichloropropylene
44. Methylene chloride
45. Methyl chloride
46. Methyl bromide
47. Bromoform
48. Dichlorobromomethane
49. Trichlorofluoromethane
50. Dichlorodifluoromethane
51. Chlorodibromomethane
52. Hexachlorobutadiene
53. Hexachlorocyclopentadiene
85. Tetrachloroethylene
87. Trichloroethylene
88. Vinyl chloride

Aromatic Hydrocarbons

1. Acenaphthene
4. Benzene
38. Ethylbenzene
39. Fluoranthene
55. Naphthalene
72. 1,2-Benzanthracene
73. Benzo[a]pyrene
74. 3,4-Benzofluoranthene
75. 11,12-Benzofluoranthene
76. Chrysene
77. Acenaphthylene
78. Anthracene
79. 1,12-Benzoperylene
80. Fluorene
81. Phenanthrene
82. 1,2:5,6-Dibenzanthracene
83. Indeno[1,2,3-C,D]pyrene
84. Pyrene
86. Toluene

Phthalate Esters

66. Bis(2-ethylhexyl)phthalate
67. Butyl benzyl phthalate
68. Di-n-butyl phthalate
69. Di-n-octyl phthalate
70. Diethyl phthalate
71. Dimethyl phthalate

Amines

5. Benzidine
28. 3,3'-Dichlorobenzidine
37. 1,2-Diphenylhydrazine

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Table 3.3 (Concluded)

U.S. EPA LIST OF PRIORITY TOXIC POLLUTANTS AS OF DECEMBER 1978*

Chlorinated Esters

17. Bis(chloromethyl)ether
18. Bis(2-chloroethyl)ether
19. 2-Chloroethyl vinyl ether (mixed)
40. 4-Chlorophenyl phenyl ether
41. 4-Bromophenyl phenyl ether
42. Bis(2-chloroisopropyl)ether
43. Bis(2-chloroethoxy)methane

Other Aromatic Compounds

9. Hexachlorobenzene
20. 2-Chloronaphthalene
35. 2,4-Dinitrotoluene
36. 2,6-Dinitrotoluene
56. Nitrobenzene
106. PCB-1242 (Aroclor[®] 1242)
107. PCB-1254 (Aroclor[®] 1254)
108. PCB-1221 (Aroclor[®] 1221)
109. PCB-1232 (Aroclor[®] 1232)
110. PCB-1248 (Aroclor[®] 1248)
111. PCB-1260 (Aroclor[®] 1260)
112. PCB-1016 (Aroclor[®] 1016)
129. 2,3,7,8-Tetrachlorodibenzo-p-dioxin

Pesticides and Metabolites

89. Aldrin
90. Dieldrin
91. Chlordane (technical mixture & metabolites)
92. 4,4'-DDT
93. 4,4'-DDE (p,p'-DDX)
94. 4,4'-DDD (p,p'-TDE)
95. Alpha-Endosulfan
96. Beta-Endosulfan
97. Endosulfan sulfate
98. Endrin
99. Endrin aldehyde
100. Heptachlor
101. Heptachlor epoxide
102. Alpha-BHC
103. Beta-BHC
104. Gamma-BHC (lindane)
105. Delta-BHC
113. Toxaphene

Nitrosamines

61. N-Nitrosodimethylamine
62. N-Nitrosodiphenylamine
63. N-Nitrosodi-n-propylamine

Phenols

21. 2,4,6-Trichlorophenol
22. p-Chloro-m-cresol
24. 2-Chlorophenol
31. 2,4-Dichlorophenol
34. 2,4-Dimethyl phenol
57. 2-Nitrophenol
58. 4-Nitrophenol
59. 2,4-Dinitrophenol
60. 4,6-Dinitro-o-cresol
64. Pentachlorophenol
65. Phenol

Miscellaneous Compounds

2. Acrolein
3. Acrylonitrile
54. Isophorone
116. Asbestos (fibrous)
121. Cyanide (total)

Elements (total)

114. Antimony
115. Arsenic
117. Beryllium
118. Cadmium
119. Chromium
120. Copper
122. Lead
123. Nickel
124. Mercury
125. Selenium
126. Silver
127. Thallium
128. Zinc

*The categorization of impurities has been done by SRI.

Source: B-13938.

Table 3.4

U.S. EPA-PROPOSED WATER (MICROGRAMS/LITER) QUALITY CRITERIA FOR SELECTED TOXIC POLLUTANTS

	Freshwater Aquatic Life		Saltwater Aquatic Life		Human Health Effects
	24 hr Average	Ceiling	24 hr Average	Ceiling	
Acenaphthene	110	240	7.5	17	(0.02 mg/l)
Acrolein	1.2	2.7	0.88	2.0	6.5
Antimony	120	1,000	—	—	1.5
Chlorinated phenols					
4-Chlorophenol	45	180	—	—	30
2,4,6-Trichlorophenol	52	150	—	—	100 ^b
3-Chlorophenol	—	—	—	—	50
2,5-Dichlorophenol	—	—	—	—	3.0
2,6-Dichlorophenol	—	—	—	—	3.0
2,4,5-Trichlorophenol	—	—	—	—	10 ^b
2,3,4,6-Tetrachlorophenol	—	—	—	—	263 ^b
Copper	$e(0.65 \ln(\text{hardness})-1.03)$	$e(0.88 \ln(\text{hardness})-1.03)$	0.79	18	(1 mg/l)
Cyanide	1.4	38	—	—	(0.2 mg/l)
3,3'-Dichlorobenzidine	—	—	—	—	0 ^a
Dichloropropenes(enes)					
1,1-Dichloropropene	410	930	—	—	203
1,2-Dichloropropene	920	2,100	400	930	233
1,3-Dichloropropene	4,800	11,000	79	180	203
1,1-Dichloropropene	18	250	5.5	14	0.63
Dinitrotoluene					
2,3-Dinitrotoluene	12	27	4.4	10	0 ^a
2,4-Dinitrotoluene	620	1,400	—	—	0 ^a
Diphenylhydrazine	17	38	—	—	0 ^a
Endosulfan	0.042	0.49	—	—	(0.1 mg/l)
Endrin	0.0020	0.10	0.0047	0.031	1
Ethylbenzene	—	—	—	—	(1.1 mg/l)
Halocethers					
4-Bromophenylphenyl	6.2	14	—	—	—
Halomethanes					
Methyl chloride	7,000	16,000	3,700	8,400	2
Methyl bromide	140	320	170	380	2
Methylene chloride	4,000	9,000	1,900	4,400	2
Bromotoluene	840	1,900	180	420	2
Bromochloroethane	—	—	—	—	2
Dichlorodifluoromethane	—	—	—	—	3,000
Trichlorofluoromethane	—	—	—	—	3,100
Isophorone	2,100	4,700	97	220	460
Naphthalene	—	—	—	—	143
Nickel	$e(1.02 \ln(\text{hardness})-1.02)$	$e(0.47 \ln(\text{hardness})+4.19)$	—	—	133
Nitrobenzene	480	1,100	53	120	30
Nitrophenols					
2-Nitrophenol	2,700	6,200	—	—	—
4-Nitrophenol	240	550	53	120	—
2,4-Dinitrophenol	79	180	37	84	68.6
2,4-Dinitroresol	57	130	—	—	12.8
2,4,6-Trinitrophenol	1,500	3,400	150	340	10
Phenol	600	1,400	—	—	(3.4 mg/l)
Phthalate esters					
Dimethyl phthalate	—	—	—	—	(160 mg/l)
Diethyl phthalate	—	—	—	—	(60 mg/l)
Dibutyl phthalate	—	—	—	—	(5 mg/l)
Di-2-ethylhexyl phthalate	—	—	—	—	(10 mg/l)
PCB	0.0015	6.2	0.024	20	0 ^a
Toluene	2,300	5,200	100	230	(12.4 mg/l)
Toxaphene	0.007	0.47	0.19	0.12	0 ^a
Zinc	$e(0.67 \ln(\text{hardness})+0.67)$	$e(0.64 \ln(\text{hardness})+2.46)$	—	—	(5 mg/l)

^aProposed levels not yet established.

^bData are insufficient to set criterion, but EPA recommends minimizing exposures.

^cOrganoleptic effects.

Source: Toxic Material News, Weekly Business letter, July 25, 1978, Business Publishers Inc., P. O. Box 1067, Silver Springs, MD, 20910.

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programs in accordance with the standards issued by EPA. By 1983, this could affect as many as 38,000 to 55,000 dischargers in the United States (B-13938).

Technical and financial assistance is available through EPA to industries and to POTW's for the implementation of this program (B-13939). User charges are designed to fairly apportion POTW capital, and operating and maintenance costs between public and private sources (Federal Register, 17690, April 25, 1978).

Land Pollution (Solids Disposal)

The secure disposal of solid wastes presents an enormous environmental problem in the United States. EPA estimates the output of solid industrial wastes at 336 million metric tons/yr (wet basis)--enough to fill the New Orleans Superdome, from floor to ceiling, four times every day of the year (B-13938). The proportion of potentially hazardous wastes is believed to be about 29 million metric tons/yr (8.6%) and growing at the annual rate of 3 to 4%, mostly generated by the chemical and refining industries. Some of this has been handled by inadequate disposal practices as evidenced by the problems at Love Canal, near Buffalo, New York, and the "Valley of the Drums," near West Point, Kentucky, from wastes discarded as much as 10 years ago. Companies generating these wastes in the United States do not escape legal responsibility for their safe disposal by turning them over to an independently operated for-fee disposal facility.

The Solid Waste Disposal Act of 1965 was the first federal legislation addressing the solid waste problem. It provided mainly for research and development for waste treatment and resource recovery. The first comprehensive legislation concerning solid waste was the Resource Conservation and Recovery Act of 1976 (RCRA). This act includes the following provisions (B-13938, 447085):

- Federal financial and technical assistance for the development of waste management programs.
- Identification and regulation of hazardous wastes from point of generation through disposal.
- Research, demonstration, studies, and information activities relating to solid waste problems.
- Standards of performance for those who transport, store, treat, or dispose of such wastes, including up to \$5 million in liability insurance.
- Regulatory control of hazardous wastes by EPA, where state or local programs do not meet federal standards.
- Civil and criminal penalties (up to \$25,000 fine and 1 year in jail for the first conviction) for false statements or noncompliance with enforcement orders.

An augmenting piece of legislation is the Toxic Substances Control Act of 1976 (TSCA) (B-13938). This regulates the manufacture and use of toxic substances. It provides for a review of materials which may be hazardous to health or environment before they may be manufactured for commercial purposes. This law alone requires a monumental amount of testing and record keeping, since there are over 70,000 chemicals in commerce and over 1,000 new ones are introduced each year. In three years, the budget for EPA implementation of TSCA has grown to \$58 million. Violators of this act can be subjected to civil and criminal penalties similar to those of RCRA.

A third act of Congress with profound effects on the costs of solid (and liquid) wastes disposal is the Marine Protection, Research, and Sanctuaries Act of 1972, which proposes to phase out all dumping of sewage sludge and industrial wastes by December 31, 1981 (B-13938). During 1977, ocean dumping of industrial wastes from the United States dropped from 2.7 to 1.8 million tons/yr and sewage sludge dumping declined 12% to 7.4 million tons/yr. The dumping of industrial wastes has now been largely eliminated but sewage sludge still amounts to about 4 to 5 million tons annually.

The new restriction on ocean dumping has generated interest in sludge evaporation to yield animal feed, fuel, and fertilizer (447082), and in incineration aboard ocean vessels (447083). EPA has also

investigated the economics of land-based waste management facilities for hazardous waste disposal (447077) and has published a list of such facilities operating as of January 1977 (447092).

Selected Reactions to U.S. Antipollution Legislation

The enactment of comprehensive legislation requiring vast expenditures for reduction of air, water, and land pollution has understandably given rise to protest from those concerned with meeting and financing compliance standards. Hooker Chemicals for example, estimates a 10 to 12% loss of existing vinyl chloride plant capacity in meeting EPA standards of 10 ppm for vinyl chloride concentration in air (447097). For vinyl chloride dispersion resins, the limitation of 400 ppm vinyl chloride weighted average on the resins, could reduce plant capacities by as much as 20%.

The difficulties in measuring EPA toxic compound concentrations (e.g., those for arsenic) as low as 0.0002 microgram per liter (0.2 ppb), let alone controlling them, is dismaying to some segments of the chemical industry (447080). In many cases, it may be less expensive to meet effluent standards by process modifications rather than by end-of-pipe treatments.

A study of the economic impact of the Federal Water Pollution Control Act of 1972, prepared by 10 major chemical companies (447100), indicated that 80 to 90% of the BAT water pollution levels could be realized with 40 to 50% of the total capital expenditure for water cleanup, and that achieving the last 10 to 20% of the required improvements (zero pollutant discharge) would take the other 50 to 60% capital investment. Thus, a major portion of the cost is required to meet the last increment of improvement. In this respect, Reference 447099 cites a General Accounting Office opinion that zero pollutant discharge is unnecessary because there is an inherent degree of self-cleansing capability in the nation's waterways.

The Manufacturing Chemists Association in the United States claims that the economic burden placed on the chemical industry by the Toxic Substances Control Act, for extensive testing and reporting of new products will impact on innovation. MCA has suggested an alternative simplified report form and a three-year status report (447081). MCA also proposes that less hazardous materials, e.g., ignitable wastes, should be given a different classification and standards than severely toxic materials (447084). The hazardous classification is said by others to be too narrow because it does not include known carcinogens, teratogens, and neurotoxins.

The Clean Air Act Amendments of 1970, which established uniform air quality standards across the United States, was controversial because it permitted deterioration of air quality in pristine areas to the same level as that in industrial regions (447098). As a consequence, the Clean Air Act Amendments of 1977 were passed for the prevention of significant deterioration (PSD) of air quality. The pure air of park lands and wilderness reserves would be maintained while pollution in urban areas would be allowed to increase to levels believed acceptable. This legislation is also controversial, because it permits increased air pollution in areas where the most people are exposed. Moreover, currently acceptable pollution levels may prove unacceptable for continuous long term exposure. A second point of contention concerns the accuracy of atmospheric dispersion models (447098). Air quality standards are generally applied at ground level, whereas the concentration issuing from an elevated stack is generally much higher. Under some circumstances--atmospheric or topographical--this dispersion model may be inaccurate.

Information Sources

The complex and growing array of environmental regulations not including state and local actions, which now pours out of Washington in the form of legislation, implementing standards and requirements, consent decrees, and informational literature is staggering. There are,

however, a number of publications which are helpful in keeping abreast of this paper torrent.

Table 3.5 lists the major legislation dealing with air, water, and solids pollution passed by the U.S. Congress in the past two decades. Actions taken by EPA to implement and enforce this legislation are published daily in the Federal Register. However, since the Federal Register also includes the administrative actions of most other government agencies, it is a very voluminous publication. Fortunately, two weekly reports--one on air/water pollution and one on toxic materials--review current Washington developments in these areas. Both are published by Business Publishers Inc., P.O. Box 1067, Silver Springs, Maryland, 20910. "Environmental Quality" is an annual publication of the Govt. Printing Office which reviews the developments in pollution abatement. In addition, Pollution Engineering Journal (1301 S. Grove Ave., Barrington, Illinois, 60010), in years past, has published a December status report of EPA actions and regulations.

Some recent journal articles dealing with pollution control rules and regulations are listed as References 447002, 447085, 447094, 447102, and 447103. Several of the books dealing with pollution control legislation are listed as References B-13941, B-13942, and B-13943.

Legislation in Japan

Pollution abatement legislation in Japan is somewhat similar to that in the United States but with generally stricter limits on the allowable concentrations and quantities of pollutants. Basic pollution laws are enacted by the Diet, with implementation and enforcement being handled by the Environmental Agency (B-13940). Local governments--industrial districts and cities--have the authority to require more stringent pollutant limitations and controls than those adopted nationally. Thus, as in the United States, the acceptable levels of pollutants can vary appreciably in different parts of the country.

Table 3.5

MAJOR POLLUTION CONTROL LEGISLATION BY THE U.S. CONGRESS

<u>Congressional Act</u>	<u>Public Law Number</u>	<u>Congress</u>	<u>Statute</u>	<u>Date</u>
<u>Air Pollution</u>				
Air Quality Act of 1963	88-206	77th	392	Dec. 17, 1963
Air Quality Act of 1967	90-148	81st	485	Nov. 21, 1967
Occupational Safety and Health Act of 1970	91-596	84th	596	Dec. 31, 1970
Clean Air Act Amendments of 1970	91-604	84th	1676	Dec. 31, 1970
Clean Air Act Amendments of 1977	95-95	91st	685	Aug. 7, 1977
<u>Water Pollution</u>				
Federal Water Pollution Control Act Amendments of 1972	92-500	86th	816	Oct. 18, 1972
Marine Protection, Research, and Sanctuaries Act of 1972	92-532	86th	1052	Oct. 23, 1972
Clean Water Act of 1977	95-217	91st	1566	Dec. 20, 1977
<u>Solids Pollution</u>				
Solid Waste Disposal Act of 1965	89-272	79th	997	Oct. 20, 1965
Toxic Substances Control Act of 1976	94-469	90th	2003	Oct. 11, 1976
Resource Conservation and Recovery Act of 1976	94-580	90th	2795	Oct. 21, 1976

Source: Reports of the U.S. Congress House of Representatives and Senate, issued by
Superintendent of Documents, Government Printing Office, Washington, D.C., 20402.

The Basic Law for Environmental Pollution Control, enacted in August 1967, in Japan, set the stage for regulation and abatement of air, water, and noise pollution and, indirectly, of land pollution by solids (B-13940).

Air Pollution

The subsequent and comprehensive Air Pollution Control Law of June 1968, established national ambient air quality standards in Japan as follows:

	<u>Daily Average Hourly Value, Max.</u>	<u>Hourly Value, Max.</u>
Sulfur dioxide	< 0.04 ppm	< 0.1 ppm
Carbon monoxide	< 10 ppm	< 20 ppm for 8 consec. hours
Suspended particulate matter	< 0.10 mg/m ³	< 0.20 mg/m ³
Nitrogen dioxide	< 0.04-0.06 ppm	--
Photochemical oxidants	< 0.06 ppm	--

A 1978 amendment to the sulfur dioxide emission standards made the following revisions:

- The hourly volume of SO_x (Nm^3/hr) from a stack should not exceed:

$$K \times 10^{-3} \times \text{He}^2$$
 where K = a constant
 He = effective stack height, meters
- The total emissions of SO_x (Nm^3/hr) from a plant should not exceed:

$$a \times F^b$$
 where a and b = constants
 F = fuel oil usage, kl/hr.
- Small plants, using less than 1 kl/hr, are exempt from the above two rules but they are required to burn fuel oil with less than a designated sulfur content.

The values of the constants (K, a, and b) and of the sulfur content of fuel oil are set by local governments. In Kawasaki, which has the most restrictive limits of any area in Japan, the values for K, a, and b are 1.17, 1.5, and 0.865 respectively. The maximum allowable sulfur content in fuel oil burned by small industries is 0.30 wt%.

A June 22, 1971 amendment to the Basic Pollution Law in Japan sets standards for soot and dust particulate emissions depending on the type and size of an industrial operation. For example, a small boiler burning liquid or gas has a limit of 0.30 g/Nm³, whereas, for a large scale boiler, this limit is 0.10 g/Nm³ and, for a boiler operating on lower grade coal, it is 0.80 g/Nm³ (B-13940). Continuous incinerators have ordinary solid emission standards of 0.20 and 0.70 g/Nm³ for large and small scales.

The most recent amendment for control of NO_x pollutants in air sets upper emission limits for various facilities in Japan:

Facility	Effluent Flow Rate (10 ³ Nm ³ /hr)	Upper Limit for NO _x Conc. (ppm)
Boilers		
Gas burning	>500	60
	40 to 500	100
	10 to 40	130
	<10	150
Coal burning	--	400
Oil burning	>500	130
	10 to 500	150
Petroleum fired heaters		
	>40	100
	10 to 40	130
	5 to 10	150
	<5	180
Cement kilns	>100	250
	<100	350
Nitric acid plants	--	200

These limits apply to new operations installed later than June 1977. Somewhat higher limits are permitted in older facilities.

The air pollution amendment of June 1971, also specified emission limits for five types of toxic substances:

<u>Substance</u>	<u>Upper Limit (mg/Nm³)</u>
Cadmium and its compounds	1.0
Chlorine	30
Hydrogen chloride	80
Fluorine, hydrogen fluoride, and silicon fluoride	1 to 20
Lead and its compounds	1 to 20

Hydrogen chloride emission rates as high as 700 mg/Nm³ are possible for incinerators of waste chlorides. The fluorine and lead range between 1 and 20 mg/Nm³, depending on the nature of the manufacturing operation.

Water Pollution

The Law for the Preservation of Water Quality in Public Water Bodies was enacted in December 1958 in Japan. This was augmented in December 1970, by the Water and Marine Pollution Control Law and by the Revised Sewage System Law.

National limits have been set for the following conventional water characteristics or impurities:

	<u>Allowable Quantity</u>
pH - effluent discharged to public waters	5.8 to 8.6
- effluent discharged to coastal waters	5.0 to 9.0
BOD, COD - maximum	160 mg/liter
- daily average	120 mg/liter
Suspended solids - maximum	200 mg/liter
- daily average	150 mg/liter
n-Hexane extract-mineral oil	5 mg/liter
-animal and vegetable fat	30 mg/liter
Coliform groups/cc - daily average	3,000

Limits have also been established in Japan for a number of metals and toxic materials:

	<u>Allowable Quantity</u> <u>(mg/liter)</u>
Phenols	5
Copper	3
Zinc	5
Dissolved iron	10
Dissolved manganese	10
Chrome	2
Fluorine	15
Cadmium and its compounds	0.1
Cyanide compounds	1.0
Organic phosphorus compounds	1.0
Lead and its compounds	1.0
Sexivalent chrome compounds	0.5
Arsenic and its compounds	0.5
Total mercury	0.005
Alkyl mercury compounds	Not detectable
PCB	0.003

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As in the case of air pollution, local governments have the authority to set and enforce lower limits for these and other pollutants in water effluents. Such areas include the Seto Inland Sea, Tokyo Bay, and Ise Bay (B-13940).

In Japan, it is customary for chemical producers to conclude a pollution prevention agreement with the local authorities or public waste treatment facility. Over 1,250 such agreements had been signed by October 1978. Prospective new chemical producers must have the approval of both the Environmental Agency and the local government before plant construction can be started.

Land Pollution

The high value and limited availability of land in Japan effectively limits the use of land for solid waste disposal. The incineration of solid and liquid wastes is common in Japan, with any ashes going to landfill. In these instances, regulations relating to air pollution and to ground water contamination will apply. A small number of solid waste disposal sites are closely regulated by national and regional government.

In some areas of Japan appreciable areas of agriculture land have been contaminated by cadmium, copper, or arsenic resulting from air and water pollution. The total land area affected is about 3,850 ha (9,500 acres). Remedial measures include replacement of top soil, and diversion of water sources.

Chemical Substances Control Law

The Chemical Substances Control Law, enacted in 1973 in Japan, is designed to cover those areas of chemical production and use not previously subject to pollution controls. It requires a thorough screening and testing of any new chemical before a permit for its importation or manufacture is issued.

Existing chemicals are being catalogued and checked for biodegradability and for hazards to humans or to the environment by the Ministries of International Trade and Industry and of Health and Welfare. If a substance is found to be environmentally harmful, such as in the case of a polychlorinated biphenyl (PCB), the government can halt its importation or manufacture.

The checking and control of potentially hazardous materials in working environments is covered by the July 1977, revision of the Labor Safety and Sanitation Law, with implementation by the Ministry of Labor.

Expenditures in the United States

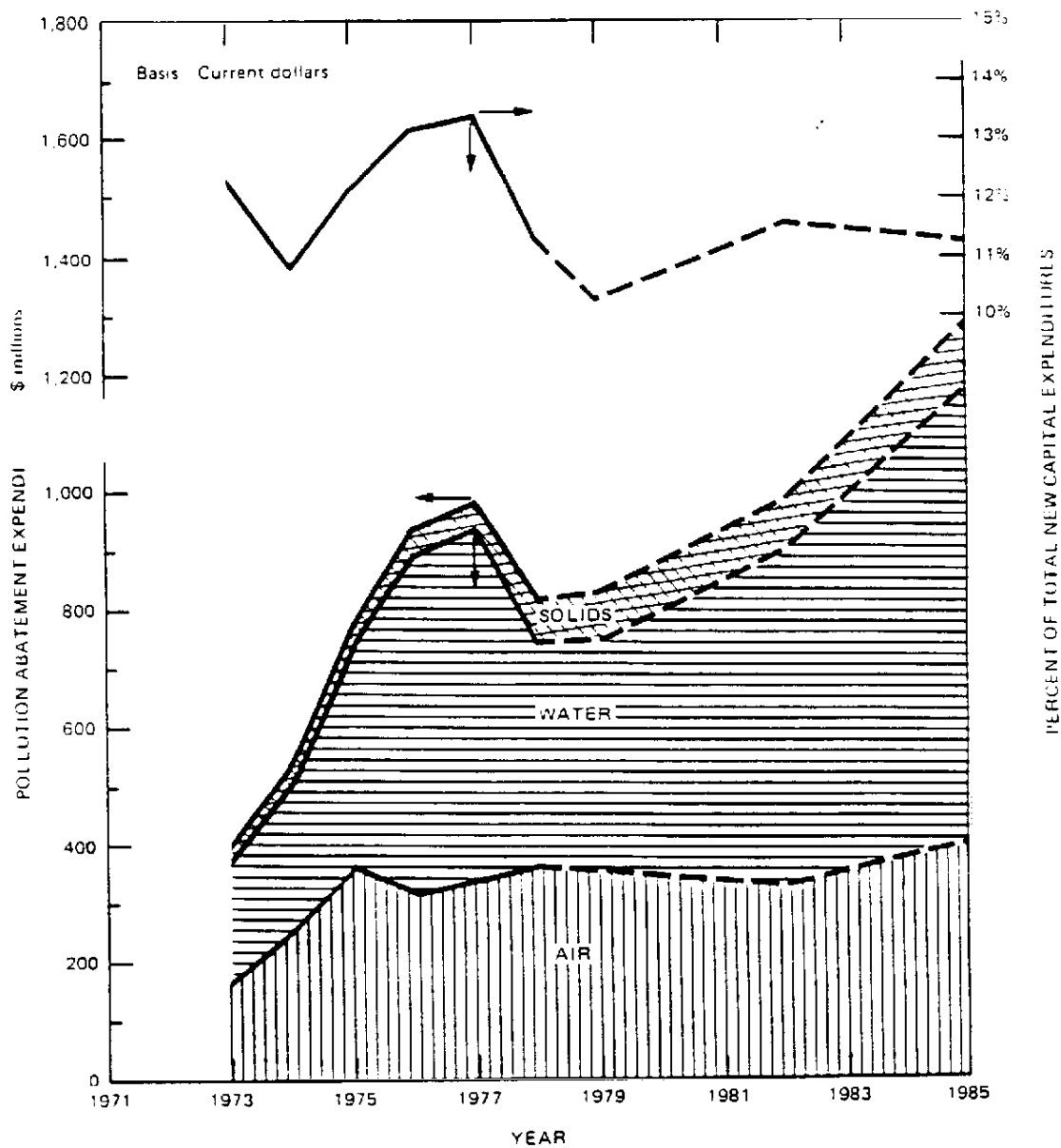
Expenditures for pollution abatement in the United States have been recorded since 1973 by the Bureau of the Census and the Bureau of Economics Analysis--both divisions within the U.S. Dept. of Commerce. These are the sources for most of the U.S. information on pollution expenditures and performance. The census figures, which cover manufacturing industries, are believed to give the more detailed classification by industry type, nature of pollutant, and state and urban locations. BEA figures include manufacturing pollution sources as well as nonmanufacturing pollution sources such as utilities and transportation.

Capital Expenditures

Capital spending in the United States, since 1973, for the alleviation of air, water, and land pollution is shown graphically in Figure 3.1. Also shown are the projected estimates for 1982 and 1985, together with the pollution abatement capital expenditure (PACE) as a percentage of total new capital spending by the chemical industry. Capital investment for pollution abatement in 1977 was almost \$1,000 million, or about 13.5% of total new capital spending. Water treatment accounted for 60% of this cost, air cleaning for 35%, and solids

Figure 3.1

ANNUAL CAPITAL EXPENDITURES BY THE U.S. CHEMICAL INDUSTRY
FOR POLLUTION ABATEMENT



Source: *Pollution Abatement Costs and Expenditures*
Current Industrial Reports, MA-200, 1973 thru 1977,
Bureau of Census, U.S. Dept. of Commerce, Washington, D.C.
and Reference 447003.

disposal for the remaining 5%. Most of the air and water expenditure (88%) was for end-of-line treatment, and only 12% was for in-process changes.

Between 1979 and 1985, PACE is expected to rise from \$830 million/yr to about \$1,300 million/yr, with practically all of this increase going for water treatment facilities. This represents an average increase of about 8%/yr in current dollars or 16% per year, if 8.0% inflation is assumed. As a percent of total new capital expenditures, PACE is expected to remain in the range of 10 to 12%. Presumably, if the goals of the 1977 Clean Water Act are met by 1985, this percentage will then drop to some lower figure corresponding only to new plant pollution control requirements.

The distribution of pollution abatement expenditures among air, water, and land for the eight sections of the chemical industry as reported by the U.S. Census Bureau is shown in Table 3.6. The major abatement expenditures, in column one of this table, are made by inorganic chemicals (16% of total expenditures), plastic materials (15%), industrial organic chemicals (45%), and agricultural chemicals (15%). Drugs, soaps, paints, and miscellaneous chemical products make up the remaining 9%. While PACE for the overall industry is 13.2%, for the organic and inorganic segments, the expenditures are 15.4 and 21.8% respectively.

The distribution of capital expenditures in 1977 for the composite chemical industry is 35, 60, and 5% respectively between air, water, and land pollutants. For air purification, particulate removal represents the major portion (43%) of its capital investment; NO_x is next at 32%; heavy metals, radioactive materials, toxics, and others represent 19%; and sulfur oxides are last at 6%. In 1977, the estimated amounts of pollutants removed from air by the U.S. chemical industry were as follows:

Table 3.6

U.S. POLLUTION ABATEMENT EXPENDITURES FOR AIR, WATER, AND SOLIDS, BY CHEMICAL INDUSTRY SEGMENT
(Millions of Current Dollars)

Industry Segment	Pollution Abatement Capital Expenditure (PAEC)	PACE as % of Total New Capital Expenditure*	Distribution of Air Pollution Abatement Expenditure							
			Total	%	End of Line	Process	Partic- ulates	SO ₂	NO _x	Other
Inorganic chemicals, alkalies, chlorine, gases, pigments, misc.	156.0	21.3%	56.0	35.9	51.5	4.5	30.2	3.4	5.9	16.5
Plastic materials resins, rubber, cellulose and organic fibers	154.4	9.6	88.6	57.4	77.9	10.7	48.7	0.3	27.6	12.0
Drugs and pharmaceuticals	14.4	4.0	3.3	22.9	3.1	0.2	1.8	0.3	0.5	0.7
Soaps, detergents, polishes, toilet preparations, etc.	22.1	4.4	8.9	40.2	8.5	0.4	2.5	1.5	1.0	3.9
Paints and allied products	3.4	4.5	1.1	32.4	1.0	0.1	0.8	—	0.2	0.1
Industrial organic chemicals, inter- mediates, wood chemicals, gums and cyclic organics	437.6	15.4	111.2	25.4	91.6	17.6	22.3	11.0	59.4	18.4
Agricultural chemicals and fertilizers	149.8	14.1	52.3	34.9	45.3	7.0	26.7	2.4	9.4	14.1
Miscellaneous chemi- cal products, adhe- sives, explosives, carbon black, etc.	44.7	10.8	18.6	41.6	16.0	2.6	12.0	1.2	5.1	0.2
Industry total	982.4	13.2%	340	34.6	296.9	43.1	145	20.1	109.1	65.8

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Table 3.6 (Concluded)

U.S. POLLUTION ABATEMENT EXPENDITURES FOR AIR, WATER, AND SOLIDS, BY CHEMICAL INDUSTRY SEGMENT
(Millions of Current Dollars)

Industry Segment	Distribution of Pollution Abatement Expenditure					
	Total	%	End of		Total	
			Line	Process	Water	Solids
Inorganic chemicals, alkalis, chlorine, gases, pigments, misc.	86.4	55.4	81.2	5.2	13.6	8.6
Plastic materials resins, rubber, cellulose and organic fibers	62.9	40.7	55.2	7.7	2.9	1.9
Drugs and pharmaceuticals	8.9	61.8	8.7	0.2	2.2	15.3
Soaps, detergents, polishes, toilet preparations, etc.	12.4	56.1	12.3	0.1	0.8	3.7
Paints and allied products	1.7	50.0	1.5	0.2	0.7	17.6
Industrial organic chemicals, intermediates, wood chemicals, gums, and cyclic organics	302.3	69.1	276.0	26.3	24.2	5.5
Agricultural chemicals and fertilizers	93.1	62.1	77.6	15.5	4.4	1.0
Miscellaneous chemical products, adhesives, explosives, carbon black, etc.	25.3	56.6	17.5	7.8	0.8	1.8
Industry total	593	60.4	530	63.0	49.4	5.0

*All figures are for the calendar year 1977, except the pollution abatement expenditures (PACE) as a % of total new capital expenditures, which are for 1976.

Source: Current Industrial Reports, "Pollution Abatement Costs and Expenditures", 1976 and 1977, MA-200(76)-2 and MA-200(77)-2, U.S. Dept. of Commerce, Bureau of the Census, U.S. Govt. Printing Office, Washington, D.C.

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	<u>Thousands of Short Tons</u>
Particulates	3,447
Nitrogen oxides, hydrocarbons, and CO	1,815
Heavy metals, radioactive materials, toxics, others	700
Sulfur oxides	<u>1,033</u>
Total	7,024

Operating Costs

The growth of operating costs for pollution abatement by the U.S. chemical industry between 1973 and 1978 was approximately 3-fold as shown in Figure 3.2. This corresponds to average annual growth rates--in current dollars--of 18%, 26%, and 29% for air, water, and land. (Constant dollar percentages are 6, 14, and 17%). The combined annual operating costs for pollution abatement were equal to 2.0% of the value added by the chemical industry in 1977. By 1985, this percentage could reach 2.7 to 3.0% of value added.

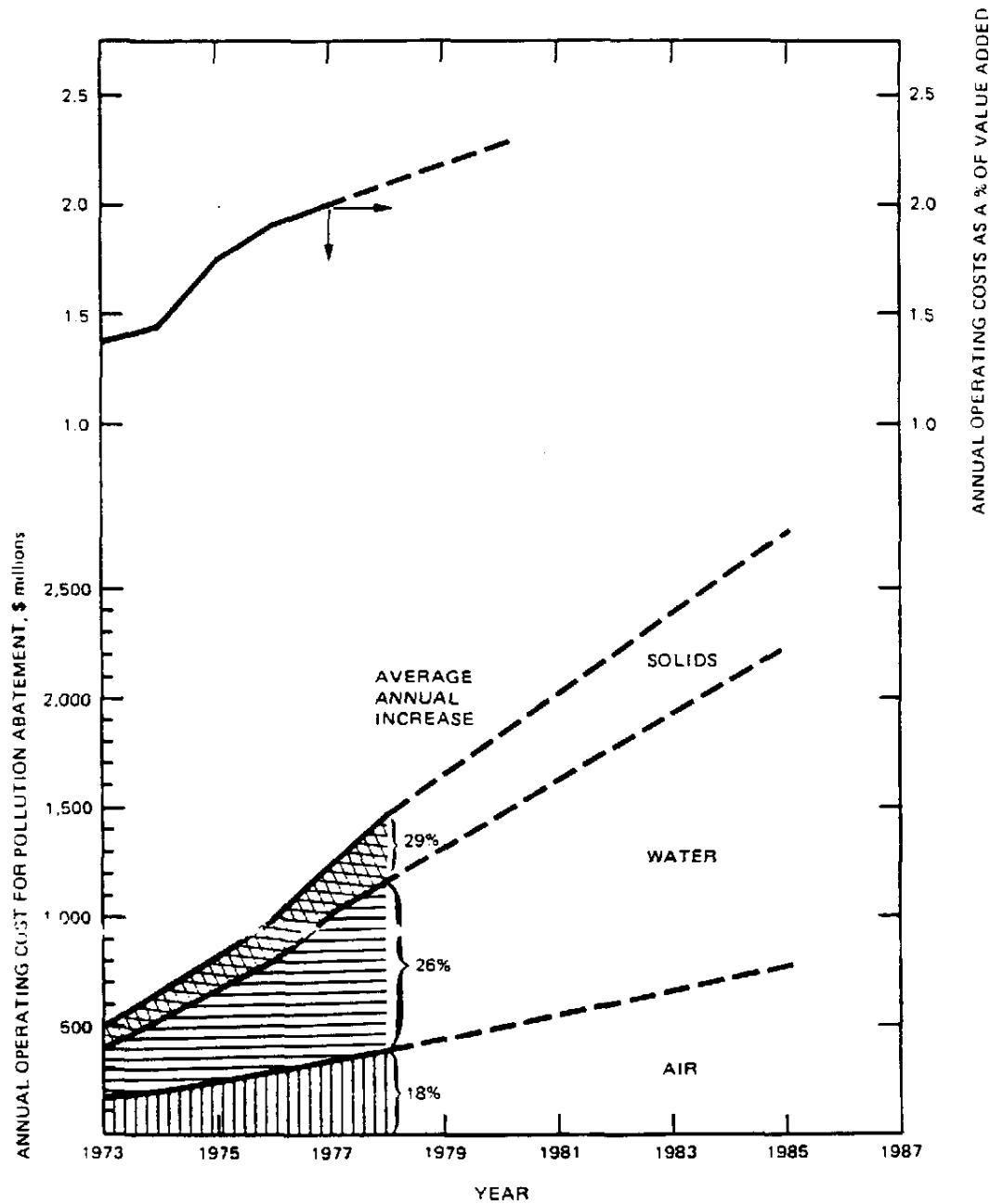
Pollution abatement operating costs by chemical industry segment are reported in Table 3.7. Also shown is the distribution among air, water, and land, and the nature of the costs. Pollution abatement operating costs for drugs, soaps, and paints are 0.6% or less of their value added. However, for inorganic chemicals, they are 2.7%, and for industrial organic chemicals and agricultural chemicals, they are 3.5 and 3.7%.

Sizable variations in operating costs also occur within the chemical industry sections. Within the industrial inorganic chemical section, for example, which includes pigments and industrial gases, pollution abatement costs for a sulfate process titanium dioxide pigment plant can equal 10% of value added, whereas those for an air separation plant are less than 0.20%.

Reported research and development expenditures by the U.S. chemical industry for pollution control has grown from \$55 million in 1973 to \$84 million in 1977. However, this latter figure is exceeded

Figure 3.2

ANNUAL OPERATING COSTS OF THE U.S. CHEMICAL INDUSTRY
FOR POLLUTION ABATEMENT



Sources: See Figure 3.1.

Table 3.7
U.S. POLLUTION ABATEMENT OPERATING COSTS FOR AIR, WATER, AND SOLIDS, BY CHEMICAL INDUSTRY SECTOR
(Millions of Current Dollars)

Industry Sector	Total Operating Cost		Distribution of Operating Costs (\$ Millions)								
	(\$ Millions)	% of Value Added*	By Form of Abatement			Depreciation	Labor	Equip. Leasing	By Kind of Cost		Costs Recovered
			Air	Water	Solids				Material Supplies, Services, Other	Payments to Government	
Inorganic chemicals, alkalis, chlorine, gases, pigments, misc.	224.3	2.7	76.2	112.7	15.4	27.1	46.3	3.5	141.4	3.3	13.1
Plastic materials, resins, rubber, cellulose and organic fibers	155.2	2.2	38.3	88.7	28.2	27.0	15.0	1.3	86.3	4.6	27.1
Drugs and pharmaceuticals	45.7	0.4	8.7	26.6	10.4	5.5	7.2	0.7	25.2	6.1	1.3
Soaps, detergents, polishes, toilet preparations, etc.	26.6	0.3	7.2	12.4	7.0	3.5	3.7	0.3	14.4	4.7	4.6
Paints and allied products	14.4	1.6	1.1	5.3	7.3	1.1	2.3	0.2	9.0	1.8	1.3
Industrial organic chemicals, intermediates, wood chemicals, gums and cyclic organics	550.0	3.5	133.4	331.1	35.5	94.6	99.7	3.5	334.8	15.4	76.4
Agricultural chemicals and fertilizers	158.8	3.7	46.9	87.1	24.8	38.9	25.8	1.2	91.1	1.3	31.8
Miscellaneous chemical products, adhesives, explosives, carbon black, etc.	53.2	1.6	22.7	21.7	8.9	8.8	18.7	0.3	33.2	2.3	14.3
Industry Total	1,238.3	1.9	335.5	685.3	217.5	219.5	238.9	13.0	725.4	41.5	206.6

*All figures are for the calendar year 1977, except the total operating costs as a percent of value added, which is for 1976. Value added includes all manufacturing costs other than raw materials.

†Recovered costs are the value of salable wastes such as scrap and fertilizer or of recyclable material.

Sources: Current Industrial Reports, "Pollution Abatement Costs and Expenditures", 1977, MA-200(76)-2, also Annual Survey of Manufactures, General Statistics for Industry Groups-1975 and 1976. Both U.S. Dept. of Commerce, Bureau of the Census, U.S. Govt. Printing Office, Washington, D.C.

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by the petroleum refining industry, with \$88 million, and vastly so by motor vehicles and equipment, with \$485 million.

Expenditures in Japan

Expenditures by the Japanese chemical industry for pollution abatement have grown from 7.5% of new capital investment in 1971 to 17.7% in 1975, as shown in Figure 3.3. However, since 1975, this percentage has declined steadily to 3.7% in 1979. The yearly expenditure for pollution abatement in 1979, was 4.5×10^9 yen (= \$18 million).

The distribution of pollution abatement expenditures in Japan, by type of pollutant, for the years 1977 through 79 are given in Table 3.8.

Table 3.8

JAPANESE POLLUTION ABATEMENT EXPENDITURES

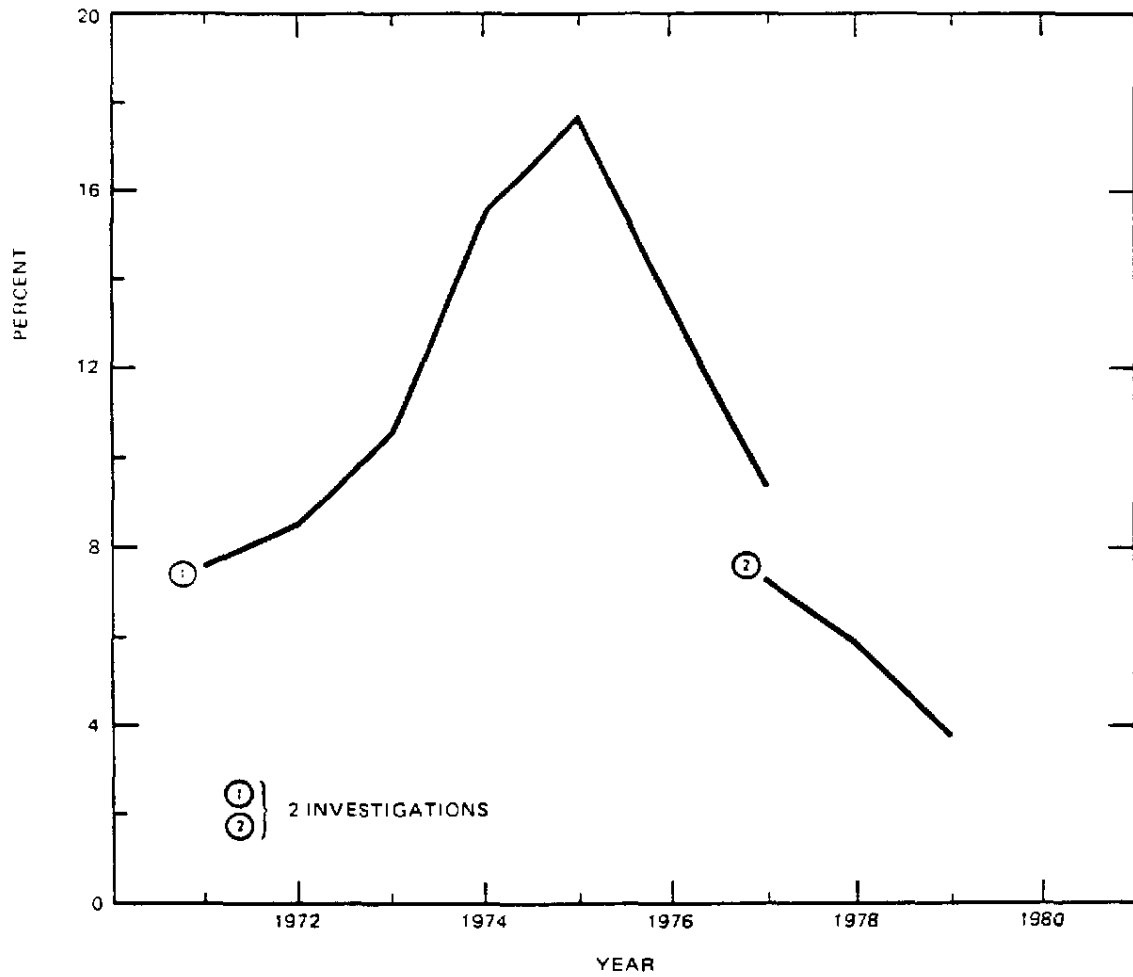
	<u>1977</u>	<u>1978</u>	<u>1979</u>
Pollution abatement expenditure (10^9 yen)	14.2	6.2	4.5
Distribution of expenditure (%)			
Air pollution abatement	36.6	33.9	29.3
Water pollution abatement	33.8	33.9	47.3
Noise reduction	4.9	1.6	0.9
Waste disposal (mainly incineration)	9.9	22.5	13.5
Other related activities	<u>14.8</u>	<u>8.1</u>	<u>9.0</u>
Total %	100.0	100.0	100.0

Source: Ministry of International Trade and Industry.

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Figure 3.3

ANNUAL CAPITAL EXPENDITURES BY THE JAPANESE CHEMICAL INDUSTRY
FOR POLLUTION ABATEMENT AS A PERCENTAGE OF TOTAL
NEW CAPITAL INVESTMENT



Source: Ministry of International Trade and Industry

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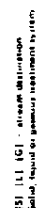
4A WASTEWATER TREATMENT TECHNOLOGY

The various levels of wastewater treatment may be defined as follows (447041):

- (1) Pretreatment: To equalize flows and separate immiscible oils or quick settling solids.
- (2) Primary Treatment: To eliminate dissolved or finely suspended solids and liquids by chemical or physical means.
- (3) Secondary Treatment: To make a biomass sludge from organic materials by biological oxidation.
- (4) Tertiary Treatment: To remove residual impurities or make the water sufficiently pure for human use.

Each of these stages may consist of one or several operations, depending on the impurities in the wastewater and on the degree of purification desired. Figure 4.1 illustrates most of the operations which are currently available commercially for the treatment of aqueous wastes (B-1393, B-1394). Wastewater streams such as process water, boiler blow-down, and runoff water may be treated separately or collectively through the appropriate operations in one or more of the treatment stages shown. Streams requiring different methods are kept separate and then combined at that point where subsequent treatment becomes similar. For example, runoff waters might be settled in a thickener; process water might be neutralized and filtered; and the sanitary sewer flow might be treated by secondary activated sludge and vacuum filtration. All three streams might then be combined for a water quality check, flow equalization, and discharge to a municipal sewer or an adjacent water body. Where an additional liquid waste stream is generated, such as by thickening or ion exchange, a treatment flow path is developed for it in the same manner as for the original waste stream.

Figure 4.1



Pretreatment

The equalization of flow to a waste treatment plant serves several purposes:

- Easier control of subsequent operations and a more uniform composition.
- Saving in capital investment since the plant can be designed for smaller flows.
- Surge capacity (in the equalization reservoir) for short downstream stoppages or for an orderly shutdown of industrial waste flows.

Appendix B gives an example of a typical equalization calculation to minimize the BOD variation in a waste treatment plant. BOD values range from 200 to 1,100 mg/liter over a 12 hour cycle in a waste flow of 1 mgd (million gallons per day). To control the BOD in the feed at 680 mg/liter (± 13 mg/liter) would require an equalization reservoir of 1.3 million gallons.

The flow equalization function can be combined with that of a thickener so that settleable solids are simultaneously removed. Table 4.1 gives typical settling areas for a variety of solids in aqueous suspension. These vary from 0.4 sq ft/ton solids/day for -325 mesh iron ore to 600 sq ft/ton solids/day for a manganese sulfide precipitate. Thickener design requires laboratory data on the settling rate of the suspended solids at various concentrations, and on the thickness of clear water, feed, settling and solids contact zones. From this, the thickener area, depth and underflow solids concentration are calculated (B-1, B-1395).

Floating solids or oils can be removed by a skimmer on top of the thickener (447043). Emulsified volatile liquids can be separated after equalization by stripping with steam or flue gas.

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Table 4.1

TYPICAL THICKENER AND CLARIFIER DESIGN CRITERIA

Suspended Solids	Percent Solids		Settling Area* (sq ft/ton solids/day)	Equivalent Solids Flux (lb/sq ft/day)
	Feed	Underflow		
Asbestos	9-12	20-27	7-15	133-285
Cement kiln dust	9-10	45-55	3-18	111-666
Cyanide slimes	16-33	40-55	5-13	154-400
Iron ore, -325 mesh	20-35	60-70	0.4-0.8	2,500-5,000
Lime slurry (acetylene)	12-15	30-40	15-33	60-133
Manganese sulfide precipitate	0.5	5-8	400-600	3.3-5
Power plant flue dust	1-5	50-60	2-10	200-1,000

*Depths normally range from 8 to 15 feet for diameters from 10 to 150 feet.

Source: B-1, page 19-55.

Primary Treatment--Chemical

Objective

The purpose of primary treatment is to prepare the waste stream for biological oxidation by removing those materials which are not amenable to, or which interfere with, bacterial oxidation. It also removes those suspended liquids or solids which are not removed in the pretreatment reaction by simple sedimentation or skimming methods. The chemical and physical methods employed here are well established industrial practices. This report will deal with these technologies only as they relate to waste treatment.

Pre- or primary treatment is generally necessary when the pollutant levels in Table 4.2 are exceeded.

Table 4.2
WATER POLLUTANT TREATMENT METHODS

<u>Pollutant</u>	<u>Limiting Concentration</u>	<u>Treatment</u>
Suspended solids	125 mg/liter	Lagooning, sedimentation, filtration, centrifuging, flotation.
Oil or grease	50 mg/liter	Skimming, centrifuging, separation.
Heavy metals	See Table 4.3	Precipitation, ion exchange, active carbon adsorption, reverse osmosis.
Alkalinity	0.5 mg as CaCO ₃ per mg BOD	Neutralization.
Acidity	Free mineral acid	Neutralization.
Toxic organics	See Table 4.3	Active carbon adsorption, ion exchange, evaporation.
Sulfides	100 mg/liter	Precipitation, stripping.
Phenols	70-160 mg/liter	Active carbon adsorption, solvent extraction.
Ammonia	1,600 mg/liter	Dilution, neutralization, stripping
Dissolved salts	16,000 mg/liter	Dilution, ion exchange.

Sources: B-1394 and B-13913.

Table 4.3 lists certain inorganic and organic chemical pollutants which are toxic to humans and animals and which, at sufficient concentrations, inhibit biological oxidation systems. It includes 129 elements and compounds--a large portion of which consists of halogenated organics--selected by the U.S. Environmental Protection Agency (EPA) as priority pollutants (i.e., those waste materials in need of immediate attention). Suggested maximum concentrations in aquatic freshwater for many of the insecticides and herbicides included above are in the range of 0.001 to 0.1 mg/liter (1 to 100 ppb). Control

Table 4.1
TOXIC INORGANIC AND ORGANIC POLLUTANTS AND METHODS FOR THEIR CONTROL

Pollutant	Ionic State	Toxicity or Hazard (Humans)			Threshold Conc. Inhibitory to Biological Processes (mg/liter)		
		PCV*	Solution	Salts	Activated Sludge	Anaerobic Digestion	Nitrification
<u>Inorganic</u>							
Ammonia	NH ₄ ⁺	25 ppm	Skin burns	Some explosive	480	1,500	—
Antimony [†]	Sb ⁺	0.5 mg/m ³	Skin irritation	Poisonous (sol. salts)	—	—	—
Arsenic [†]	As ⁺	0.5 mg/m ³	Skin irritation	Poisonous	0.1	1.6	—
Asbestos (fibrous) [†]	—	2 fibers/cm ³ (carcinogenic)	—	—	none	none	none
Boron (halides)	BO ₃ ⁻³	(1 ppm)	Skin burns (halides)	Very toxic	—	—	—
Beryllium [†]	B ⁺	0.002 mg/m ³	—	Poisonous	—	—	—
Cadmium [†]	Cd ⁺	0.05 mg/m ³	—	Toxic (some explosive)	10-100	0.02	—
Calcium	Ca ⁺	—	Skin irritant (alkali)	—	2,500	—	—
Chromium-hexavalent [†]	Cr ⁺	0.1 mg/m ³ (CrO ₃)	Skin irritant	Toxic (chromates)	1-10	5-50	0.25
Trivalent [†]	Cr ⁺	—	—	—	50	50-500	—
Copper [†]	Cu ⁺	Toxic (dust)	Toxic	Toxic	1.0	1.0	0.005-0.5
Cyanide [†]	CN ⁻	10 ppm (HCN)	Poisonous	Poisonous	0.1-5.0	4	0.34
Iron	Fe ⁺	—	Decomp to HCl	Toxic, skin burns (FeCl ₃)	1,000	5	—
Lead [†]	Pb ⁺	15 mg/m ³	Toxic	Poisonous	0.1	—	0.5
Manganese	Mn ⁺	—	(MnF ₃ very reactive)	—	10	—	—
Magnesium	Mg ⁺	—	—	—	—	1,000	50
Mercury [†]	Hg ⁺	0.01 mg/m ³ (metal)	Toxic	Toxic	0.1-5	1,365	—
Nickel [†]	Ni ⁺ , Ni ⁺	0.1 mg/m ³	Irritating	Toxic	1.0-2.5	2.0	0.53
Selenium [†]	SeO ₄ ⁺	0.2 mg/m ³	Toxic	Poisonous	—	—	—
Silver [†]	Ag ⁺	0.01 mg/m ³	Toxic	Toxic	5	—	—
Sodium	Na ⁺	2 mg/m ³ (NaOH)	Skin burns (NaOH)	—	1,500	—	—
Sulfate	SO ₄ ⁺	1 mg/m ³ (H ₂ SO ₄)	Burns (H ₂ SO ₄)	—	—	—	500
Sulfide	S ⁻	15 mg/m ³ (H ₂ S)	—	Toxic (H ₂ S)	—	50	—
Thallium [†]	Tl ⁺	0.1 mg/m ³	Poisonous	Poisonous	—	—	—
Zinc [†]	Zn ⁺	—	—	—	0.3	—	0.08-0.5

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Table 4.3 (Continued)

TOXIC INORGANIC AND ORGANIC POLLUTANTS AND METHODS FOR THEIR CONTROL

Pollutant	Control Methods				
	Carbon Adsorption	Precipitation with Ca(OH) ₂	NaS	Ion Exchange	Reverse Osmosis [§]
<u>Inorganic</u>					
Ammonia	X				X
Antimony [†]				X	X
Arsenic [†]	X		X		
Asbestos (fibrous) [†]					
Boron (halides)				X	X
Beryllium [†]				X	X
Cadmium [†]		X		X	X
Calcium					X
Chromium-Hexavalent [†]				X	X
Trivalent [†]		X	X	X	
Copper [†]		X		X	X
Cyanide [†]				X	X
Iron		X	X		X
Lead [†]			X		X
Manganese			X	X	X
Magnesium				X	X
Mercury [†]			X		
Nickel [†]		X	X		X
Selenium [†]					
Silver [†]					X
Sodium					X
Sulfate					X
Sulfide					
Thallium [†]				X	
Zinc [†]			X	X	

[†]Threshold limit values for repeated 8 hour day exposures without adverse effect.

[‡]Source: U.S. EPA, Guidelines of the Environmental Protection Agency.

[§]Reverse osmosis gives a 94 to 99% rejection of most metal ions from feed solutions of up to 12 wt% concentration. Electrodialysis concentrates most aqueous inorganic salts from 1,000 to 5,000 ppm to about 10,000 ppm but with 100 to 300 ppm left in the purified stream.

Sources: 8-1394, 8-1397, 8-1398, 447028.

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Table 4.3 (Continued)
TOXIC INORGANIC AND ORGANIC POLLUTANTS AND METHODS FOR THEIR CONTROL

Pollutant	Normal State Liquid, Solid, Gas	Boiling Point (°C)	BOD ₅	Theoretical Oxygen Demand, ThOD	Toxicity to Goldfish, Concentration and Time for 50% Fatality
<u>Organic</u>					
Acenaphthene [†]	S	177	—	—	—
Acrolein [†]	L	52.5	0.0	1.72 (COD)	0.08 mg/l, 24 hr
Acrylonitrile [†]	L	77.4	0.72	1.17	11.8 mg/l, 96 hr (Bluegill)
Allyl alcohol	L	96.9	0.2	2.2	1.0 mg/l, 24 hr
Allyl chloride	L	45.5	0.23 [†]	1.64	20.9 mg/l, 96 hr
Benzene [†]	L	80.1	2.18	3.10	7.46 mg/l, 24 hr
Benzidine [†]	S	302	—	—	—
Carbon tetrachloride [†]	L	76.7	0.0	0.21	—
Chloroform [†]	L	62	0.02	1.346	—
Cresol	L	191	1.8	2.52	49 mg/l, 96 hour
Crotonyl alcohol	L	121	—	—	—
Chrysene [†]	S	348	—	—	—
1,4-Dimethoxyphenol [†]	S	211.5	—	—	18 mg/l, 96 hour
1,4-Dinitrochlorene [†]	S	300	—	—	10 mg/l
Di-(2-ethylhexyl)phthalate [†]	L	385	—	—	—
Di-n-butyl phthalate [†]	L	340	0.43	2.24	—
Ethylbenzene [†]	L	136.2	—	—	94.4, 96 hr
n-Heptyl alcohol	L	176	30% of ThOD	—	—
n-Hexyl alcohol	L	158	28% of ThOD	—	—
Isophorone [†]	L	215	—	—	—
Methylene chloride [†]	L	42	—	—	—
Naphthalene [†]	S	218	0	2.99	—
Nitrobenzene [†]	L	211	0	1.95	—
o-Nitrophenol [†]	S	214-217	—	—	—
p-Nitrophenol [†]	S	279	—	—	—
n-Octanol	L	195	38% ThOD	2.95	—
Phenol [†]	L	182	1.4	2.4	57 mg/l, 96 hr

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Table 4.3 (Continued)
TOXIC INORGANIC AND ORGANIC POLLUTANTS AND METHODS FOR THEIR CONTROL

Pollutant	Threshold Conc. Inhibitory to Biological Process (mg/liter)			Control Methods
	Activated Sludge ^a	Anaerobic Digestion	Nitrification	
Organic				
Acenaphthene ^b	--	--	--	--
Acrolein ^b	0.21	--	--	15 wt% retention on active carbon, water scrubbing, $KMnO_4$
Acrylonitrile ^b	53	--	--	Biodegradation by mutant microorganisms
Allyl alcohol	--	100	19.5	Activated carbon (retention = 0.024 g/g)
Allyl chloride	--	--	180	Evaporation @ 25°C (90% of 1 ppm after 89 min)
Benzene ^b	92	--	--	Active carbon (0.08 g/g), air stripping, anaerobic lagoon (13 lb/day/1,000 sq ft; 10 mg/l in, 5 mg/l out)
Benzidene ^b	--	--	--	--
Carbon tetrachloride ^b	10	10-20	--	Evaporation @ 25°C (90% of 1 ppm after 97 min)
Chloroform ^b	125	10-16	--	Evaporation @ 25°C (90% of 1 ppm after 63 min)
Cresol	33	--	4-16	Ion exchange (100% retention on Amberlite [®] XAD-2)
Crotonyl alcohol	--	500	--	--
Chrysene ^b	--	--	--	--
2,4-Dimethylphenol ^b	500 (E. Coli)	--	--	Ion exchange (100% retention on Amberlite [®] XAD-2)
2,4-Dinitrochloroene ^b	57	--	--	--
Di-(2-ethylhexyl)phthalate ^b	--	--	--	Biodegradation in freshwater hydrosol
Di-N-butyl phthalate ^b	--	--	--	Active carbon (85% retention at 100 g/l)
Ethylbenzene ^b	12	--	--	Activated sludge (27% oxidation at 500 ppm after 12 hr)
n-Heptyl alcohol	67	500	--	Activated sludge (29% of ThOD after 24 hr)
n-Hexyl alcohol	--	1,000	--	Active carbon (adsorbability = 0.19 g/g); reverse osmosis (47% rejection from 0.01 M solution); ion exchange on Amberlite [®] XAD-2 (85% retention at 200 ppm). Anaerobic lagoon (48 lb COD/day @ 140 mg/l in and 30 mg/l out)
Isophorone ^b	--	--	--	Active carbon (0.193 g/g, 97% retention from 1,000 mg/l inflow)
Methylene chloride ^b	1	100-500	--	Evaporation from water at 25°C (90% of 1 ppm after 80 min)
Naphthalene ^b	--	--	--	Ion exchange, 100% absorption on Amberlite [®] XAD-2
Nitrobenzene ^b	7	--	--	Active carbon @ .196 g/gC (96% adsorbance @ 1,000 mg/l)
o-Nitrophenol ^b	0.9	--	--	Biodegradation by soil microflora
p-Nitrophenol ^b	4	--	--	Ion exchange (100% retention on Amberlite [®] XAD-2 at 0.2 ppm)
n-Octanol	50	200	--	Reverse osmosis (68% rejection from 0.01 M Soln)
Phenol ^b	200	--	4-10	(1) Active carbon 0.161g/g C (81% adsorption from 1,000 mg/l) (2) Adsorption on Amberlite [®] XAD-7 (86% effec at 0.4 ppm) (3) Solvent extraction with light oil (95%) (4) Trickling filter (100% removal at 10 ppm)

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Table 4.3 (Continued)
TOXIC INORGANIC AND ORGANIC POLLUTANTS AND METHODS FOR THEIR CONTROL

Pollutant	Normal State Liquid, Solid, Gas	Boiling Point (°C)	BOD ₅	THOD	Toxicity to Goldfish, Concentration and Time for 50% Fatality
Propargyl alcohol	L	115	25 THOD	—	—
Tetrachloroethylene ¹	L	121.4	0.06	0.39	—
Trichloroethylene ¹	L	86.7	—	—	—
Toluene ¹	L	110.8	2.15	3.13	58 mg/l, 96 hr
Vinyl chloride ¹	G	-13.9	—	—	—

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Table 4.3 (Concluded)
TOXIC INORGANIC AND ORGANIC POLLUTANTS AND METHODS FOR THEIR CONTROL

Pollutant	Threshold Conc. Inhibitory to Biological Process (mg/liter)			Control Methods
	Activated Sludge*	Anaerobic Digestion	Nitrification	
Propargyl alcohol	--	500	--	--
Tetrachloroethylene†	--	500	--	Evaporation from water at 25°C (90% of 1 ppm after 90 min)
Trichloroethylene†	55 mg/l	--	--	Evaporate from water at 25°C (90% of 1 ppm after 80 min)
Toluene†	19	--	--	Active carbon 0.05g/gC (79% adsorption from 317 mg/l). Active sludge digestion 3440 mg/l.
Vinyl chloride†	--	--	--	Evaporation from water at 25°C (90% of 1 ppm after 96 min)

*Threshold inhibitory concentrations here were determined with bacteria "Pseudomonas putida" and biological decomposition is possible in some cases at higher concentrations.

†Listed as priority pollutants by the Environmental Protection Agency. Other priority pollutants not listed above are as follows:

Halogen Containing Compounds

Chlorobenzene, 1,2,-trichlorobenzene, hexachlorobenzene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, chloroethane, bis(chloromethyl) ether, bis(chloroethyl) ether, 2-chloroethyl vinyl ether (mixed), 2-chlorophenanthrene, 1,1,1-trichloroethene, parachlorometacresol, 2-chlorophenol, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,3-dichlorobenzidine, 1,1-dichloroethylene, 1,2-trans-dichloroethylene, 1,2-dichlorophenol, 1,3-dichloropropane, 1,3-dichloropropylene, fluoranthene, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, bis(2-chloroethoxy) methane, methyl chloride, methyl bromide, propofom, dichlorobromomethane, trichlorofluoromethane, dichlorodifluoromethane, chlorodibromomethane, hexachlorobutadiene, hexachlorocyclopentadiene, pentachlorophenol, 3,4-benzofluoranthene, fluorene Aldrin, dieldrin, chlordane, DDT, DDE, DDD, heptachlor, heptachlor/epoxide, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, Aroclor® 1216, 1221, 1231, 1242, 1248, 1254, and 1260, and toxaphene

Others

1,6-Dinitrocoluene, 1,2-diphenylhydrazine, 2,4-dinitrophenol, 4,6-dinitroresol, N-nitrosodimethylamine, N-nitrosodiphenylamine, N-nitrosodi-n-propylamine, butyl benzyl phthalate, di-n-octyl phthalate, diethyl phthalate, dimethyl phthalate, 1,2-benzanthracene, 3,4-benzopyrene, anthracene, 1,12-benzoperylene, phenanthrene, dibenzo (a, h) anthracene, indol(1,2,3-cd) pyrene, pyrene, alpha-endosulfan, beta-endosulfur, and endosulfan sulfate.

Sources: B-1396, B-1397.

MCD 000016431

methods include adsorption on resins or active carbon, reverse osmosis, and ozone oxidation. Dissolved metal salts such as copper sulfate and lead chloride can be precipitated with calcium hydroxide or hydrogen sulfide, or adsorbed on ion exchange resins (B-1394).

The above control methods, in most cases, serve to concentrate the pollutants. It is still necessary to dispose of or destroy the concentrated wastes by containment, incineration, or chemical degradation (see Section 4C on solid wastes).

Ion Exchange

Ion exchange can be used to remove or concentrate the following substances (B-1394):

- Metallic elements present in solution as either cationic or anionic species.
- Inorganic anions such as halides, sulfate, nitrate, and cyanide.
- Organic acids such as carboxylics, sulfonics, and some phenols, at a pH sufficiently alkaline to give the ions.
- Amines, when the solution acidity is sufficient to form the corresponding acid salts.
- Anionic and cationic surfactants such as quaternary amines or alkylsulfates.

Generally, the upper concentration of exchangeable ions for economic operation is about 2,500 mg/liter (0.05 equivalents/liter expressed as CaCO_3). At higher concentrations, the resin inventory and the regnerant consumption are sufficiently large, that other separation methods, such as solvent extraction or precipitation, are more attractive.

Ion exchange resins are divided into three classes (B-1399):

- (1) Sodium cation--where the sodium ion is exchanged for a calcium or magnesium ion such as in water softening. Sodium chloride is the regnerant.
- (2) Hydrogen cation--where the hydrogen ion is exchanged for all cations, and regeneration is usually with sulfuric acid.

- (3) Anion exchangers--may use two resin types--highly basic or weakly basic. Both types remove strong acids such as sulfuric, hydrochloric, or nitric but only the highly basic exchange resin will remove weakly ionized acids such as silicic and carbonic.

Highly basic exchangers are regenerated with caustic soda, and weakly basic exchangers, with caustic soda, soda ash, or ammonium hydroxide. Capacities for anion exchangers average about 5 milli-equivalents per gram and 3 m.e./g for cation exchangers (B-13910).

Most ion exchange operations are fixed bed, requiring only cylindrical ion exchange beds, tanks for regenerant storage, and pumps. Continuous ion exchangers are much more complex and have limited applications (B-1394).

The capital investment to treat 80,000 gal/day of metal finishing wastes (Zn:Cu:CN:Cr: = 15:5:19:22 mg/liter) at pH = 10, estimated by A. D. Little (B-1394) and extrapolated to January 1979 is \$430,000. Operating costs, consisting principally of labor (36%) and regenerant (38%), are \$73,000/year. Modular capital costs for ion exchange systems, estimated by Icarus Corporation (B-13919) and adjusted to a 1979 PEP Cost Index by SRI, are as follows, in thousands of dollars for various resin volumes:

	<u>40 ft³</u>	<u>100 ft³</u>	<u>400 ft³</u>
Sodium cation	40	64	154
Hydrogen cation	71	112	278
Anion	91	144	353

The use of a stratified bed of weak- and strong-acid cation exchange resin is said to reduce regenerant costs since the resin is regenerated by a lower acid concentration without sacrificing recovery. A natural zeolite (clinoptilolite) has been employed for the selective separation of ammonium ions from sodium, magnesium, and calcium (B-13911). The regenerant is recycled so that no liquid wastes are produced; activated alumina is suggested as a selective exchange material for removal of phosphate ions (B-13911).

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Electrodialysis

An electrodialysis cell consists of multiple compartments separated by alternate cation- and anion-permeable membranes, as illustrated in Figure 4.2. Cations diffuse toward the cathode end of the cell until they are contained by an anion-permeable membrane. Similarly, anions diffuse toward the anode and are halted by a cation-permeable membrane. In this manner, water is depleted in ions in some chambers and concentrated in adjacent chambers. The ion-permeable membranes can be made of plastic film with the ion exchange resin imbedded in the film, or the ion exchange group may be part of the chemical structure of the membranes. Liquid flow through the cells is continuous and the ions reacting at the end electrodes are a small fraction of the total ions.

Electrodialysis performs most efficiently with salt feed concentrations in the range of 200 to 5,000 ppm. At higher concentrations, operating costs become unattractive, and at lower values, reduced electrolytic conductivity reduces cell efficiency (B-1394). In some instances electrodialysis may be followed by reverse osmosis to obtain low salt concentrations in the treated water.

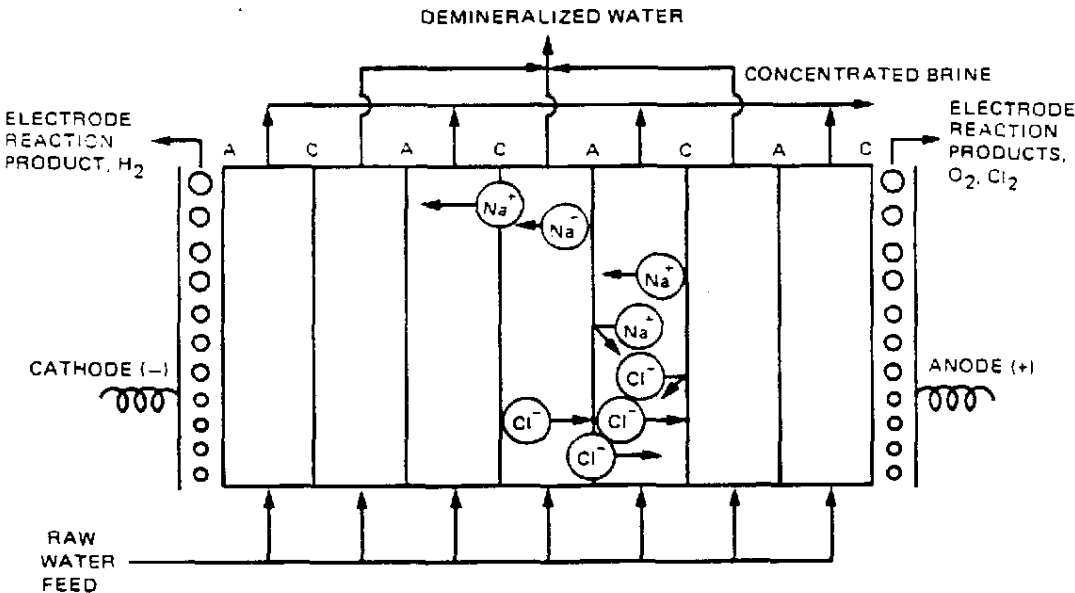
Typical applications of electrodialysis to date include the desalination of brackish water, the demineralization of water from cheese production, the treatment of metal plating and rinse solutions, and wood pulp wash water (B-13912).

Estimated capital investment for an electrodialysis plant to treat 1.0 mgd and reduce the dissolved salts from 2,000-5,000 mg/liter to 500 mg/liter is \$1 million and 90¢/k gal. At 10 mgd, this figure becomes \$8.0 million and 78¢/k gal (443053, adjusted to January 1979). Energy requirements are 0.5 and 7 kwh per 1,000 gallons of salt water, with 1,000 ppm removal of dissolved solids. Annual maintenance costs are 4 to 6% of investment.

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Figure 4.2

MULTIPLE-CHAMBER ALTERNATE-MEMBRANE ELECTRODIALYSIS CELL:
A, THE ANION-SELECTIVE MEMBRANE;
C, THE CATION-SELECTIVE MEMBRANE



Source: B-13910.

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Reverse Osmosis

Reverse osmosis depends on the ability of some membranes and fibers to allow passage of small molecules but not large ones. Thus, for a solution of sodium chloride, water molecules can pass through the membrane but the sodium chloride cannot. Unlike electrodialysis, the solvent and not the solute, is the diffusing component and it is independent of ionic charges. Diffusion is facilitated by applying a pressure drop (usually 400 to 600 psi) across the fiber or supported membrane. The membrane can become blocked by film-forming organics or by insoluble salts. Cellulose acetate; polysulfones, polyurethane, polyamide, and nylon are suitable membrane or fiber materials. Reverse osmosis equipment developed by Du Pont uses hollow fibers 50 μ o.d. and 25 μ i.d. packed in bundles of 4 to 8 foot lengths (Permassep[®]). Solution under pressure is introduced around the outside of the fibers, and purified water is removed from the ends of the fibers cemented into plastic headers. One permeator, 4 inch i.d. by 4 feet long with 1,900 sq ft of fiber surface can treat 2,000 gpd at a pressure difference of 400 psi. (Chemical Engineer, Feb. 8, 1971 and Nov. 29, 1971). Water recovery averages about 75% for feed solids concentrations of 800 ppm (B-13912). Table 4.4 shows the rejections of dissolved salts and organic solids by a cellulose acetate membrane.

Capital and operating costs for a reverse osmosis plant to purify 1.0 mgd of brackish water are estimated at \$850,000 and 108c/1,000 gal respectively. At 10 mgd these figures are \$5.3 million and 84c/1,000 gal (443053, adjusted to January 1979).

Neutralization

Bacteria and aquatic life are sensitive to rapid pH variations and to pH levels outside the range of 6.5 to 8.5. Consequently, excessively acid or basic wastewater must be neutralized before discharge. The neutralization system consists essentially of:

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Table 4.4
MATERIALS REJECTED BY REVERSE OSMOSIS

	<u>Percent Rejection</u>	<u>Max. Feed Concentration (%)</u>
<u>Cations</u>		
Ca ²⁺ , Mg ²⁺ , Fe ²⁺ , Mn ²⁺	96-98	*
Na ¹⁺ , K ¹⁺	94-98	3-4
Al ³⁺	99	5-10
NH ₄ ¹⁺	88-95	3-4
Cu ²⁺ , Ni ²⁺ , Cd ²⁺	95-99	8-12
Ag ¹⁺	94-96	*
<u>Anions</u>		
Cl ¹⁻ , NO ₃ ¹⁺ , F ¹⁻ , Br ¹⁻	93-96	3-4
SO ₃ ²⁻ , SO ₄ ²⁻ ,	98-96	8-12
HCO ₃ ¹⁻	95-96	5-8
PO ₄ ³⁻ , S ₂ O ₃ ²⁻ , Fe(CN) ₆ ³⁻	99	8-12
CN ¹⁻	90-95	4-12
<u>Organics</u>		
Sucrose, lactose	100	25
Protein (+10,000 mol wt)	100	10-20
Dyes (400 to 900 mol wt)	100	—
BOD	90-99	--
Bacteria and virus (5,000 to 100,000 mol wt)	100%	

* Precipitation possible, depending on presence of other ions.

Source: B-1394.

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- (1) Storage and handling of neutralizing liquid or solid
- (2) Mixing of waste stream with the neutralizing agent
- (3) Provision for residence time sufficient to attain the desired uniform pH.

Suitable metering and pH controls are usually required and when precipitation occurs--such as alkaline precipitation of heavy metals or sulfuric acid precipitation of calcium salts--subsequent separation of solids by filtration, centrifuging, or other means is required.

A typical neutralizer for basic wastes is sulfuric or hydrochloric acid, and that for acid wastes is quicklime or calcium hydrate. The relative costs of acid and base neutralizing agents are as follows:

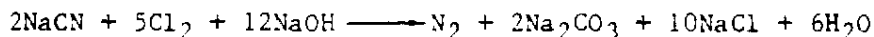
<u>Agent</u>	<u>Price (\$/ton f.o.b. works)</u>	<u>pH Factor</u>	<u>\$/ton Acidity or Basicity</u>	<u>Relative Cost</u>
H ₂ SO ₄ (100%)	58.00 (tanks)	1.00	58.00	1.0
HCl (28%)	45.00 (tanks)	0.14	322.00	5.6
CaO	32.00 (bulk)	0.941	34.00	1.0
Ca(OH) ₂	33.50 (bulk)	0.710	47.20	1.4
Limestone	32.00 (bulk)	0.489	65.20	1.9
Soda ash	61.00 (bulk)	0.507	120.40	3.5
NaOH (50%)	157.50 (tanks)	0.450	350.00	10.3

The design of neutralization systems is discussed by Adams (E-1395). The estimated investment for a lime slurry neutralization of a 1 mgd waste stream (1% H₂SO₄ by vol) is \$1.15 million (B-1394, adjusted to January 1979). Operating costs are \$2.72/1,000 gal, with material, operating, and fixed charges accounting for 58%, 20%, and 22% respectively.

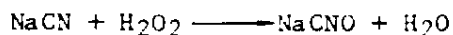
Oxidation and Reduction

Oxidation and reduction reactions are used to convert toxic or difficult-to-treat wastes into materials which are nonobjectionable or which are more easily treated or removed. A disadvantage is the addition of other, possibly undesirable, chemicals into the waste stream.

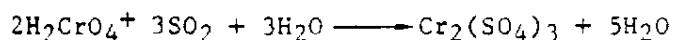
A typical oxidation reaction is the destruction of sodium cyanide by reaction with chlorine and sodium hydroxide (B-1394):



Oxidation with hydrogen peroxide converts the cyanide to the less toxic cyanate:



The reduction of chromic acid (Cr^{6+}) by sulfur dioxide gives chromic (Cr^{3+}) sulfate, which precipitates readily in alkaline solution:



Commercially available oxidizing and reducing agents together with their January 1979 list price and potential applications to waste treatment are shown in Table 4.5. In most cases, the waste component is merely converted to a different form and it still must be removed by precipitation, filtration, adsorption, or biological treatment.

Equipment for oxidation and reduction reactions is relatively simple. It consists of an agitated vessel to provide contact of agent and wastes and sufficient residence time for the reaction to occur. Reagent storage and metering is also required along with instrumentation to monitor the reaction completion. The estimated investment (adjusted to 1979 dollars) required to treat 1,000 gpd of cyanide plating solution containing 7,000 ppm $\text{Cu}(\text{CN})_2$ and 1,000 ppm NaCN is \$110,000. Production costs are 25¢/gallon, with labor and maintenance accounting for 50% of this; chemicals, 14%; utilities, 1%; and taxes, insurance, and 10%/yr amortization, the remaining 35%.

The investment needed to treat 2,000 gpd of chrome plating wastes (e.g., 100,000 ppm CrO_3 in 20% H_2SO_4) is estimated at \$110,000. The production cost is 24¢/gallon of wastes treated (E-1394, adjusted to January 1979).

Table 4.5

COMMERCIAL OXIDIZING AND REDUCING AGENTS
AND THEIR POSSIBLE APPLICATIONS TO WASTE TREATMENT

Agent	List Price* (\$/lb)	Possible Waste Materials for Treatment
Oxidizing		
Chlorine gas	7.5	Sulfides, mercaptans, cyanide
Calcium hypochlorite	47	Cyanide
Chromic acid	71	Organic compounds
Hydrogen peroxide	15.5 (35% soln)	Phenol, sulfur compounds, lead, cyanide
Potassium permanganate	68	Trace amounts only of phenol, diquat [†] , paraquat [†] , organic sulfur compounds, rotenone, formaldehyde, manganese, cyanide
Sodium hypochlorite	68 (est)	Lead, cyanide
Air	--	Sulfites, sulfides, ferrous iron
Reducing		
Ferrous sulfate	2.6	Chromium ⁶⁺
Sodium bisulfate	16	Chromium ⁶⁺
Sulfur dioxide	10	Chromium ⁶⁺
Sodium borohydride	15	Mercury, tetraalkyl lead, silver
Scrap iron	--	Ferric iron

*January 1979.

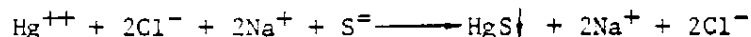
[†]Insecticides.

Source: B-1394.

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Chemical Addition

A variety of chemicals can be used to precipitate dissolved salts. Typical precipitants are ionizable compounds which form an insoluble product with one ion of the dissolved salt. An example is the addition of sodium sulfide to mercury chloride solution at a pH of 6.5 (447028):



This addition is relatively straightforward, requiring only a mixing vessel and means for handling and controlling the reagent addition. The flocculation of the precipitate or other finely suspended solids may, however, require additional reagents and considerably longer residence time. This flocculation can be encouraged by one of two means (B-13914):

- Physical enmeshing of the particles in a gelatinous inorganic precipitate such as alum, lime, or ferric salts in alkaline solution (coagulation).
- Destabilization of the repulsive charges on particle surfaces by the addition of surfactants or polyelectrolytes, thus allowing the particles to adhere to each other (flocculation).

In some instances, a flocculant may also act as a coagulant but not vice versa (B-13915). A few typical flocculants and coagulants are listed in Table 4.6.

Mixing during flocculation or coagulation should be slow and gentle so as to maintain the agglomerates. Also sufficient residence time is required for the agglomerates to settle. Some suggested loadings for clarifiers up to 125 ft in diameter are as follows:

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Table 4.6

TYPICAL FLOCCULANTS AND COAGULANTS AND THEIR APPLICATIONS

Flocculant or Coagulant	Composition	Type	Typical Application	Effective Range		Approx. Price* (c/lb)
				pH	Concentration	
Alum	$Al_2(SO_4)_3 \cdot xH_2O$	Coagulant	Water treatment	5-10	15 ppm	8.0
Ferric sulfate	$Fe_2(SO_4)_3 \cdot xH_2O$	Coagulant	Phosphate precipitation	Maximum at 4-6	Above 1 mg/l	3.7
Sodium CMC	Sodium carboxy methylcellulose	Flocculant & coagulant	Mineral separation	3-9	0.03 to 0.05 lb/ton	76
Separan ^o	Acrylamide powder	Flocculant	Chemical processing	2-10	0.2 to 10 ppm	60
Fibrefloc ^o	Animal glue	Flocculant	Waste Treatment	1-9	5 to 30 ppm	55
Silica sol	Activated silica sol	Coagulant	Waste treatment	4-6	1 to 20 ppm	10 (as sodium silicate)
Sodium aluminate	$NaAlO_2$	Coagulant	Water treatment	3-12	2 to 10 ppm	27
Guar gum	--	Flocculant	Mineral processing	2-12	0.02 to 0.03 lb/ton	55

*Chemical Marketing Reporter, April 16, 1979, Schnell Publishing Co., 100 Church Street, New York, NY 10007.

Source: S-13915, except for the prices.

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<u>Settling Application</u>	<u>Loading (gph/ft²)</u>
Lime coagulation	50
Alum/iron coagulation	40
Flue dust	30-50
Secondary biodegradable solids	
MLSS* = 2,000-5,000 mg/liter	
SVI [†] = 50-100	30-40
SVI = 200-300	20-30
SVI = 350-400	20

*MLSS--mixed liquor suspended solids.

[†]SVI--sludge volume index.

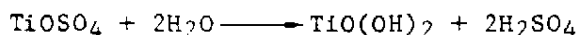
For clarifiers larger than 125 ft diameter, the suggested loading rates are 15 to 25% lower and, for MLSS values above 10,000 mg/liter, further reductions are applicable (B-13914). In most wastewater treatment applications, the overflow rate varies within the range of 100 gpd/sq ft to 1,500 gpd/sq ft. Where agglomeration takes place as part of primary treatment, the clarifier may serve the additional functions of a pretreatment clarifier and/or a flow equalizer.

The capital cost to precipitate and coagulate 410,000 gal of automotive plating wastes containing 113 mg/liter of zinc is estimated at \$360,000 (B-1394, adjusted to January 1979). Operating costs, including 10 year depreciation, are \$1.10/1,000 gal. Lime and a poly-electrolyte coagulant (2 mg/liter) are added to the wastewater stream and a sludge (4% solids by wt) is drawn off the bottom of the clarifier. If the scale of operation is reduced by a factor of 5, the capital investment becomes \$106,000 and the operating cost is \$2.43/1,000 gal. If the scale is raised fivefold, these figures become \$1,000,000 and \$0.54/1,000 gal.

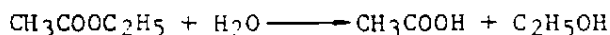
Hydrolysis

Hydrolysis is the reaction of a salt or an ester with water, alkali, or acid to decompose the salt or ester. Typical examples are

the hydrolysis of titanyl sulfate to yield titanyl hydroxide and sulfuric acid:



and the hydrolysis of ethyl acetate to ethyl alcohol and acetic acid:



If sodium hydroxide is the hydrolyzing agent, sodium acetate replaces acetic acid.

While hydrolysis is a frequently used reaction in commercial chemical production (B-13910), its application to waste disposal systems is still very limited. Hydrolysis can, in some instances, convert a waste material to more easily recoverable or usable components. The hydrolysis of waste cellulose to glucose, which can be fermented to ethanol, has been investigated by Fagan (447038). The cellulose is ground, heated to 400° to 450°F in dilute acid solution to yield 30 lb of glucose per 100 lb of cellulose. Fagan predicts an optimum yield of 52% glucose sugar at 445°F with 1.0% sulfuric acid catalyst.

The hydrolysis of waste polyurethane foam to recover toluene diamines (intermediates in toluene diisocyanate production) has been proposed by Mahoney (449593). The reaction is carried out in water at 400°F for 30 to 60 minutes to give 65 to 80% theoretical recovery of 2, 4- and 2,6-toluenediamine.

Hydrolysis reactions can be performed batchwise in agitated, jacketed reactors, or continuously in heat columns. However, residence times and construction materials differ sufficiently so that each design is usually specific to a particular application (B-13916).

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Primary Treatment--Physical

Sedimentation

Settleable solids are defined as those larger than 0.45 and which are separable by a 2 hour quiescent settling period (B-13914). The rate of settling is affected by particle size, shape, and specific gravity as well as by the water temperature. The settling velocity for a given solids-liquid slurry can be determined by timing the subsidence of a slurry-liquid interface in a graduated cylinder for various suspended solids concentrations (Figure 4.3). The initial slope of each curve is the zone settling velocity (ZSV) for that percentage of suspended solids. From this can be calculated the settling velocity (ft/min) and hence the solids flux (lb/sq ft/day) for the various suspended solids concentrations (B-1395). This flux is plotted against suspended solids concentrations, as shown in Figure 4.4. A line is drawn through the desired 2.5% underflow suspended solids concentration, tangential to the curve and the intersection of this line with the "y" axis is the required solids flux (16.5 lb/sq ft/day). The thickener area is the solids inflow (lb/day) divided by the flux. If the loading is increased to 26.1 lb/sq ft/day, the effluent suspended solids concentration will drop to 2.0%. Because settling velocity decreases with increased suspended solids loadings, as indicated in Figure 4.3, the effluent solids concentration is also reduced.

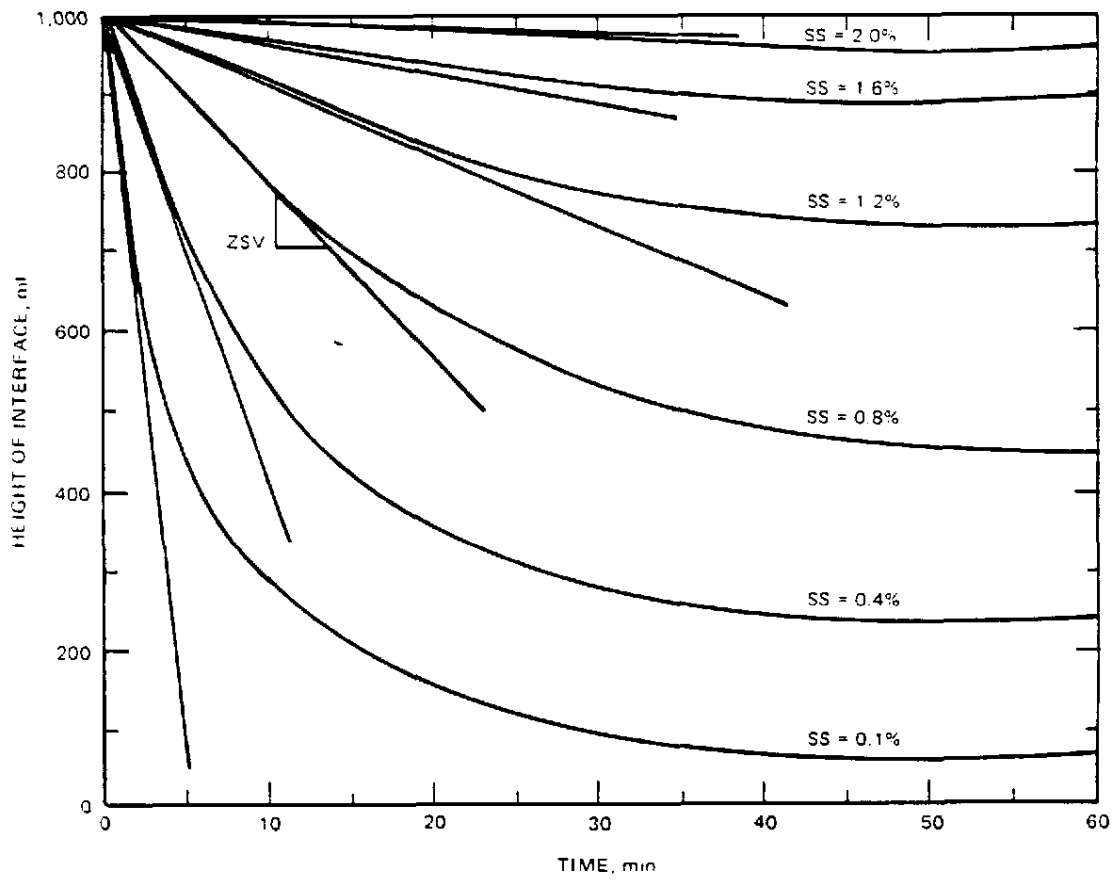
Some typical settling rates for a number of aqueous slurries are shown in Table 4.1. Purchas (B-1395) describes a method for calculating settling velocities on the basis of physical properties of the solid and liquid. The accuracy is said to vary by a factor of 2 to 5 for diameters between 20 and 100 feet.

Hydrocycloning

Hydrocyclones employ stronger centrifugal forces, rather than gravity, to separate liquids and solids of differing densities and thus are able to achieve higher separation efficiencies and rates with smaller equipment sizes.

Figure 4.3

SETTLING CURVES AT VARIOUS SUSPENDED SOLIDS CONCENTRATIONS*



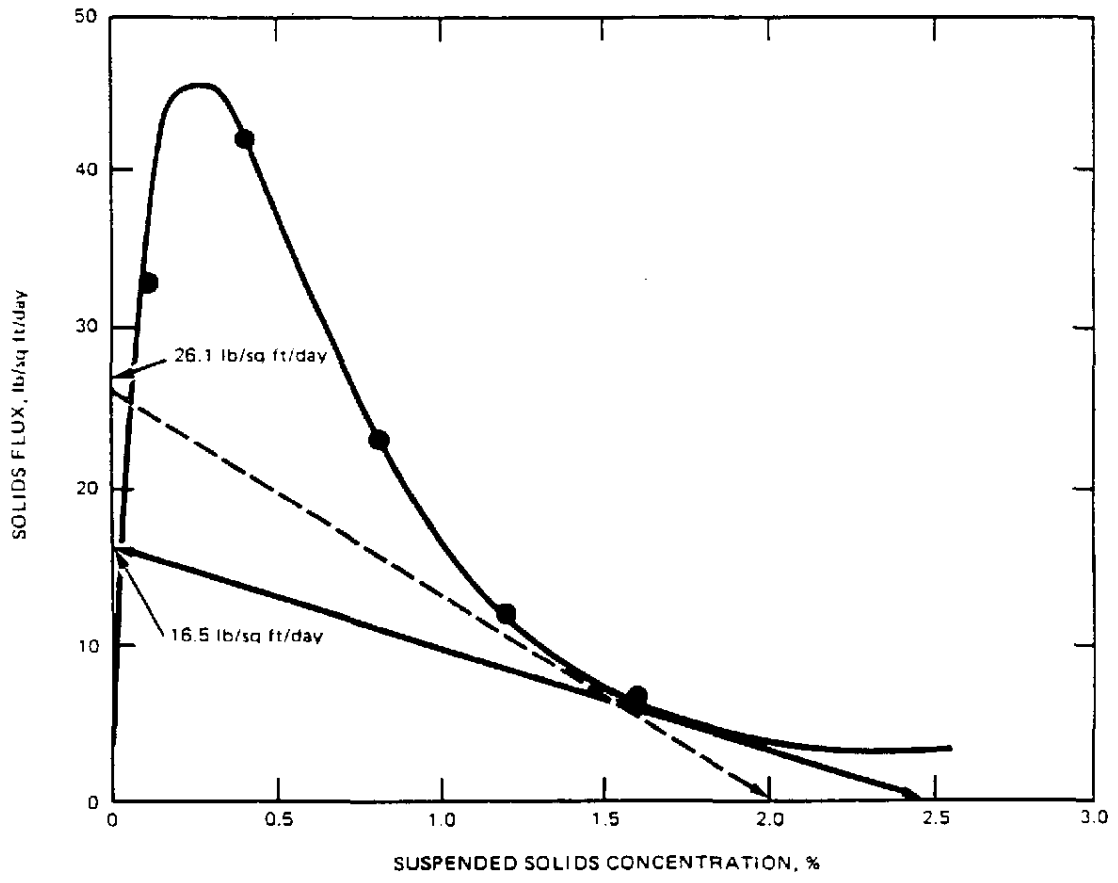
* Measured in a 1,000 ml graduate.

Source: B-1395.

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Figure 4.4

BATCH SUSPENDED SOLIDS FLUX CURVE FOR DESIGN



Source: B-1395.

MCD 000016447

Hydrocyclone efficiency is sometimes expressed as the particle diameter which has a 50% separation. This is related to physical properties of the systems by the following equation (B-13915):

$$d_{50} = 56.3 \left(\frac{D_c^3 \eta}{Q(e_s - e_l)} \right)^{0.5}$$

where: d_{50} = particle diameter with 50% separation efficiency, μ
 D_c = hydrocyclone diameter, inches
 η = liquid viscosity, centipoises
 Q = liquid feed rate, U.S. gal/min
 e_l and e_s = density of liquid and solid, lb/ft³

Separation efficiency varies from about 0% at 0.25 d_{50} to 100% at 2 d_{50} . Cyclone size also affects separations efficiency. A 24 inch cyclone may handle 1,500 gpm but might not separate particles smaller than 50 μ . A 10 mm cyclone would separate particles down to 5 μ but would handle only 1 gpm. Adequate capacity is obtained for the smaller sizes by connecting numerous cyclones in parallel. Pressure drop through a hydrocyclone is typically 40 to 50 psig. Hydrocyclones occupy much less space than gravity settlers and have a lower capital investment (<50%). Disadvantages are higher abrasion, higher pumping costs, and the inability to separate concentrated slurries.

Filtration and Centrifuging

The choice of a means to separate solids from liquid is often determined by particle size and concentration, as shown in Figure 4.5. Filters generally are used for solids consisting of particles in the range of 0.001 to 5 mm at concentrations up to 20 wt%. The centrifuge is applicable to sizes from 0.001 to 0.01 mm, at lower concentrations. The factors affecting the selection of particular types of filter or centrifuge are covered in Perry (B-1), Ballew (447036), and Cleasby

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Figure 4.5

**APPROXIMATE SOLID SIZE RANGE FOR SOLID-LIQUID
SEPARATION EQUIPMENT**

inches		12	8	4	2	1	1/2	1/4	Tyler mesh																					
mm		400	200	100	80	60	40	20	10	8	6	4	2	1	0.8	0.6	0.4	0.2	0.1	0.08	0.06	0.04	0.02	0.01	0.008	0.006	0.004	0.002	0.001	
PRESEPARATION																														
Flow Rate		Bar racks																												
< 200 gpm																														
35-50 gpm/ft ²		Drum screens																												
30-40 gpm/ft ²		Belt screens, hydrosieves®																												
SEDIMENTATION																														
Approximate Settling Rate		Thickeners, clarifiers																												
50 - 0.1 ft/hr																														
+1.0 ft/hr		Hydraulic classifiers																												
1 - 0.05 ft/hr		Hydraulic cyclones																												
CENTRIFUGATION																														
Density Dependent		Lower Solids Conc. Lt.		Solids Loss in Filtrate		Reciprocating pusher																								
No		15 wt%		50% solids below 100 μ																										
No		0 wt%		Small above 50 μ		High speed, automatic batch																								
Yes		0 wt%		Negligible		Solid bowl, scroll discharge																								
FILTRATION																														
Solids Concentration, wt%		Filter Rate, g/m/ft ²		Rotary vacuum drum																										
+20		+5																												
10 to 20		5 to 0.2		Tilting pan, scroll discharge																										
1 to 10		0.2 to 0.02		Rotary vacuum disc																										
-5		0.2 to 0.01		Continuous precoat or plate and frame																										

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(447035). Typical application and performance characteristics for several types of filters and centrifuges are summarized in Tables 4.7 and 4.8.

The capital investment to separate 6 tpd of zinc hydroxide sludge (4 wt%) from 36,000 gpd of metal plating wastewater by vacuum filtration on a rotary drum is estimated at \$240,000 (B-1394, adjusted to January 1979). Operating costs, principally labor and capital-related charges, including straight-line depreciation over 10 years, are \$43.00/ton of dry solids. The corresponding costs for centrifuging are placed at \$168,000 and \$38.50/ton.

Flotation

Flotation technology (which is widely used in the mineral industry) is used in waste treatment principally to separate solids from biological oxidation. It relies on the tendency of some solids to attach themselves to air bubbles rather than to water molecules. This hydrophobic tendency is enhanced by the addition of chemical agents or collectors, which usually have an anionic or cationic group attached to a hydrophobic hydrocarbon group. The ionic group is attracted to the surface of the solid, whereas the hydrocarbon portion repels water molecules. Thus, the particles are carried to the surface of the flotation vessel by rising air bubbles and are skimmed off. Typical collectors are sodium lauryl sulfate (30%) at 2¢/lb, tertiary-butyl amine at 86¢/lb, and 2-mercaptobenzothiazole at 94¢/lb.

Other reagents may be used to control pH, to promote frothing, or to suppress the flotation of other types of solids. Air is introduced into the suspension through a sparge tube, diffusion plate, or rotating agitator. Alternatively, air may be dissolved in the suspension under pressure and then the pressure is released to generate air bubbles in situ. Figure 4.6 illustrates a dissolved air flotation system for the concentration of a biological sludge. The advantage of the dissolved

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Table 4.7
SOME TYPICAL FILTER APPLICATIONS

<u>Typical Material</u>	<u>Material Character</u>	<u>Approx. Filter Capacity (lb/sq ft/day)</u>	<u>Filter Type</u>
Cyanide slime, flotation concentrates	Finely ground minerals	400-2,000	Continuous vacuum
Cement slurry	Finely ground limestone, shale and clay	400-200	Continuous vacuum
Pulp and paper	Free filtering fibers	200-1,200 (1½ to 20 gpm/ft ²)	Continuous vacuum
Crystals, salt, etc.	Granular, crystalline	3,000-12,000	Continuous vacuum
Pigments	Smeary, sticky, finely divided	200-500	Plate and frame or pressure tank
Sewage sludge	Colloidal, slimy	25-150	Continuous vacuum
Varnish	Cloudy, viscous liquid filtered hot with filter aid	(5 gal/sq ft/hr)	Plate and frame
Mineral oil	Removal of 1 to 20% bleaching clay from oil	(3-30 gal/sq ft/hr)	Pressure tank

Sources: B-1, 447034.

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Table 4.8

TYPICAL CENTRIFUGE PERFORMANCE CHARACTERISTICS

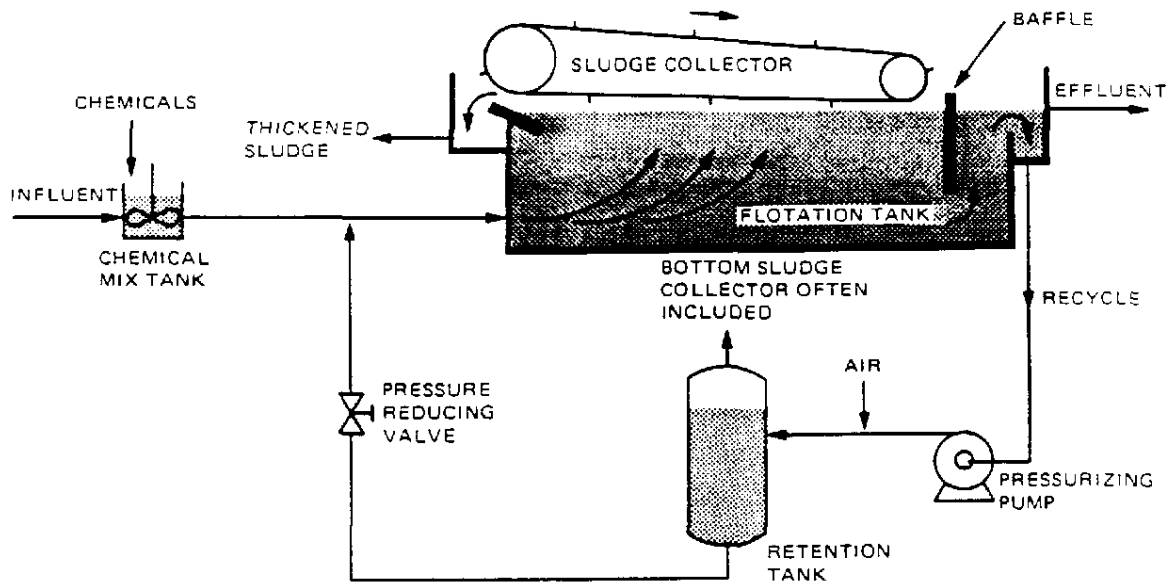
<u>Centrifuge Type</u>	<u>Bowl Dia. (inches)</u>	<u>Motor Horse- power</u>	<u>Throughput</u>	
			<u>Liquid (gpm)</u>	<u>Solids (tons/hr)</u>
Tubular	1-3/4		0.05-0.25	
	4-1/8	2	0.1-10	
	5	3	0.2-20	
Disc	7	1/3	0.1-10	
	13	6	5-50	
	24	7-1/2	20-200	
Helical conveyor	6	5	to 20	0.03-0.25
	18	15	to 50	0.5-1.5
	32	60	to 250	3-10
	54	150	to 750	20-60

Sources: B-1, 447033, 447036.

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Figure 4.6

SCHEMATIC DIAGRAM OF DISSOLVED-AIR FLOTATION TANK WITH RECYCLE



Source: B-1393.

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air flotation here is that it removes the small, light sludge particles more completely and in a shorter time than would be possible by sedimentation.

The typical air-to-solids weight ratio encountered in the thickening of wastewater biological sludges varies from 0.005 to 0.060 at pressures of 40 to 65 psig (B-1393). The cost of flotation cells ranges from \$35 to \$65/cu ft for cell sizes from 400 to 60 cu ft (B-1, adjusted to January 1979).

Solvent Extraction

Solvent extraction is not competitive with biological oxidation and thus it should be considered only for nonbiodegradable chemicals (B-1394). If these are dilute, active carbon is probably more economic. If they are concentrated, the choice may be between extraction and steam stripping.

Solvent extraction generally refers to the extraction of an organic chemical by an organic solvent. However, if a chelating agent is added to the extracting liquid, inorganic anions and cations can be separated from aqueous solutions. A chelating agent forms an ionic complex with the ions in solution. By changing the pH, the ions are released. Typical chelating agents are sodium tripolyphosphate and ethylenediaminetetraacetic acid contained in a solvent such as kerosene, chlorobenzene, or tridecyl alcohol. Their area of application is similar to that of the ion exchange resins. However, they lend themselves better to continuous flow systems and possibly to somewhat higher ion concentrations than does fixed bed ion exchange.

A system to recover zinc, copper, cyanide, and chromium ions by chelate extraction from 80,000 gal/day of dilute metal plating wastes is estimated to require a capital investment of \$325,000 (B-1394). Operating costs, principally labor, caustic, and capital charges (including 10%/yr depreciation) total \$4.32/1,000 gallons adjusted to January 1979.

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Crystallization

Crystallization today has only limited application to the treatment of industrial wastewater. One example of its current use is the reaction of aqueous sulfuric acid wastes from the caprolactam industry with ammonia to form ammonium sulfate, which is recovered by crystallization. As the controls on plant waste discharges become more strict, crystallization may find additional applications. Freeze crystallization has been suggested as a possible method for liquid waste streams containing concentrations of 1 to 10 wt% of hazardous materials (B-1394).

The design of crystallization operations and the equipment available for same have been covered in detail by Bamforth (B-13917) and Perry (B-1).

Adsorption on Activated Carbon

Adsorption on activated carbon is a practical, well established method for eliminating organic impurities in wastewater. It is most applicable to organic solutes with large molecules, low water solubility, low polarity, and a low degree of ionization (e.g., phenol, higher alcohols, and chlorinated hydrocarbons). Organics with low molecular weight (methanol), two or more hydrophylic groups (glycols), or high polarity (sugars) are usually poorly adsorbed. Very large molecules relative to the carbon pores, such as some dyes, may also be poorly adsorbed.

A number of inorganic elements and compounds, such as iodine, chlorine, sodium cyanide, copper, and ammonia are also adsorbed by active carbon. The degree of adsorption varies from one material to another; it is likely to be highly pH-dependent, and regeneration may require acid or alkali washes. Strong electrolytes--sodium chloride, hydrogen chloride, sulfuric acid--are not adsorbed on active carbon (B-1394).

In general, active carbon is most useful for the removal of non-biodegradable (refractory) organics or the residual organics remaining after biological treatment (B-1395).

Active carbon adsorption of impurities in aqueous streams may be carried out by various methods:

- Down-flow alternating fixed beds
- Up-flow expanded beds
- Countercurrent continuous moving beds
- Continuous circulating suspensions.

The first is the most common.

When the carbon beds are in a fluidized or circulating slurry, the equilibrium concentration of the adsorbate can be expressed by the Freundlich isotherm:

$$XM = KC_e^{1/n}$$

where: X = weight of adsorbed impurities, g
M = weight of activated carbon, g
C_e = equilibrium concentration of impurity in solution, mg/liter
K, n = experimentally determined constants.

Typical liquid flow rates are about 7 to 10 gpm/sq ft, and when backwashing is required to disengage solids, a flow rate of 15 to 20 gpm/sq ft is normal for 8 x 30 or 12 x 40 mesh granular carbon (B-13918). Typical contact times are 20 to 60 minutes for COD loadings of 0.2 to 0.5 lb/lb carbon (B-13914).

Activated carbon can be removed (or returned) from the column as a slurry. The solids are collected and regenerated by heating to 1500° to 1700°F in a multiple hearth furnace. Carbon losses due to attrition and burning are usually from 5 to 10%. If the adsorbate is sufficiently volatile, the carbon can be regenerated with steam (about 1 lb steam/lb carbon). Inorganics are removed by washing the activated carbon with a suitable solvent, acid or base.

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The costs of activated carbon treatment vary widely with the type and concentration of impurity to be removed. The removal of 1,000 ppm of phenol from 100,000 gpd of wastewater is estimated to require a capital investment of \$1.3 million. The cost of removal to 1 ppm, including 10%/yr, depreciation and carbon makeup at 50c/lb, is \$18/1,000 gallons (B-1394, adjusted to January 1979). For tertiary treatment of water in publicly owned sewage treatment plants, the cost can be as low as 12c/1,000 gallons at a 10 million gal/day rate.

Recent research has been directed toward the combining of carbon adsorption with biologically activated sludge treatment (447044, 357789). The addition of powdered activated carbon to biologically activated sludge systems has, in addition to lowering capital investments, the following advantages:

- Improved removal of organics
- Reduced carryover of effluent solids
- Reduced foaming in the aeration system
- Improved sludge settling characteristics
- Reduced shock from toxic impurities.

The addition of powdered activated carbon (0.076 to 0.20 lb/1,000 gal) to 600 gpm of a refinery wastewater is reported to reduce solids effluent by 50%, BOD by 75%, and suspended solids carryover by 40% (447044). Du Pont (357789) reported similar benefits for its Powdered Activated Carbon Treatment (PACT) process. Here the carbon is regenerated by burning-off the less dense surface sludge layer on the treatment solids. Capital investment for the combined operation was estimated to be 25% lower than the total for separate operations. Operating costs were 10% less. Gitchel (357785) proposes to regenerate the carbon in an aqueous carbon slurry by direct oxidation of the slurry at temperatures of 212° to 600°F (100° to 320°C) and pressures up to 3000 psig.

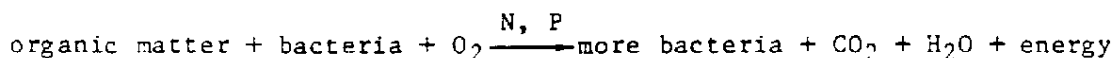
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The Rohm and Haas Company (447039) has developed a number of porous polymeric adsorbents with capabilities similar to those of active carbon. These adsorbents are cross-linked structures of polymethacrylate or polystyrene. They are easily regenerated by washing with a solvent such as acetone or methanol. The regenerant and the adsorbate are then recovered by distillation. There is little or no attrition or breakdown of cross-linked polymer in several years of operation. An estimated capital cost to treat 115,000 gpd waste stream containing 1.0% phenol is \$1.7 million as of January 1979 (447039). Operating costs are \$15.60 per 1,000 gallons treated, without the recovered phenol value, and minus \$5.30 if phenol is included at 25c/lb.

Secondary Treatment

Air-Activated Sludge

Certain bacteria or microorganisms, in the presence of oxygen and nutrients, feed upon organic liquids and solids in aqueous suspension or solution (aerobic digestion):

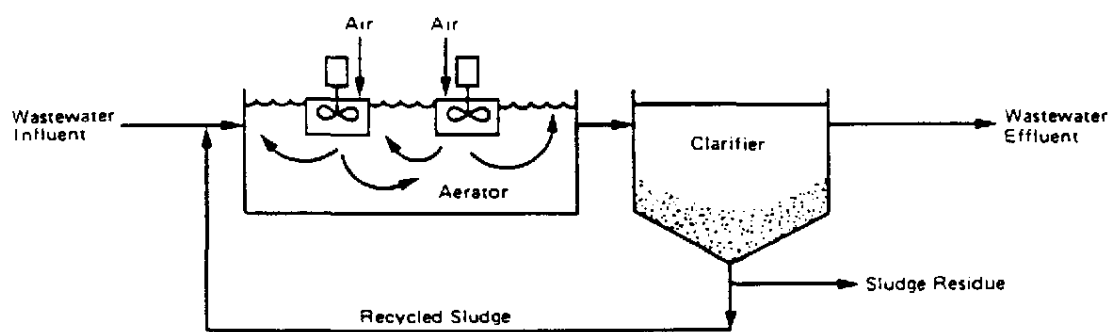


This is a widely used method for the destruction of organic wastes (B-13913). The conditions necessary for aerobic digestion include:

- Oxygen availability.
- pH level near neutral.
- Availability of nitrogen and phosphorus.
- Absence of bactericidal materials (e.g., halogenated compounds and heavy metals).
- Adequate mixing.

Figure 4.7 illustrates the basic operation of an activated sludge system. The wastewater influent is mixed with recycle sludge and air. The mixture is then settled to separate sludge solids. A portion of the solids is recycled and the balance is filtered and discarded. A

Figure 4.7
ACTIVATED SLUDGE SYSTEM



Source: B-1394

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number of variations are possible in equipment design and in the method and sequence of aeration and separation steps (B-1393, B-13920). The use of a deep shaft (5 ft dia by 500 ft deep) for aeration reduces ground area and capital requirements and is said to increase system efficiency or capacity (B-13921, 447040).

The design of activated sludge treatment systems requires data on the BOD reaction rate, the oxygen requirement, and the sludge yield (B-1395). If this information is not available from an existing treatment plant, it can be determined experimentally in the laboratory (B-13922). The aerator size, air requirement, mixing horsepower, and amount of sludge residue are then calculated (B-1395, B-13922, 447055). Typical design and operating characteristics for three types of activated sludge aeration systems are listed in Table 4.9.

The approximate investment, adjusted to January 1979, in conventional aerobic digestion, sludge thickening, and filtration are \$1.8, \$4.8, and \$7.5 for waste feed rates of 1.0, 5.0, and 10 mgd and a BOD reduction from 500 to 25 ppm (349186). The capital investment to treat 1 mgd of wastewater containing 10,000 ppm COD, and 4,000 ppm BOD was estimated at \$2.1 million (1979 dollars) (B-1394). This included primary clarification, equalization, aeration, and sludge separation. Operating costs, including depreciation (10%) and taxes and insurance were \$2.20/1,000 gal.

Oxygen-Activated Sludge

The use of oxygen in place of air for activated sludge biological treatment is said to have a number of advantages (357787):

- Higher BOD removal rates
- Faster sludge settling rates
- Reduced total oxygen consumption
- Lower sludge output
- Reduced aeration horsepower.

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Table 4.9
ACTIVATED SLUDGE PROCESS CHARACTERISTICS

Characteristic	Process Type		
	Conventional	Complete Mix	Step Aeration
Flow type	Plug flow	Completely mixed	Plug flow
Aeration	Diffused air	Diffused air	Diffused air
Agitation	Mechanical	Mechanical	None
BOD ₅ removal efficiency (%)	85-95	85-95	85-95
BOD ₅ removal (lb/day) per lb microorganisms	0.2-0.4	0.2-0.6	0.2-0.4
Volumetric loading (lb BOD ₅ /1,000 ft ³)	20-40	50-120	40-60
MLSS (mg liter)	1,500-3,000	3,000-6,000	2,000-3,500
Aeration volume/hourly feed rate	4-8	3-5	3-5
Application	Low strength, domestic wastes	General application, resistant to shock loads	General application to many wastes
Nutrients (total)			
N	1 lb per 50 lb BOD ₅		
P	0.2 lb per 50 lb BOD ₅		
Air required when BOD ₅ removal is			
Greater than 0.3	500-900 ft ³ of air per lb BOD ₅ removed		
Less than 0.3	1,200-1,800 ft ³ of air per lb BOD ₅ removed		
Agitation horsepower	1 hp for 45 lb BOD ₅ removal/day or 100 hp/10 ⁶ gal aerator volume		

Sources: B-1393, B-1395, B-13922.

MCD 000016461

There are also a number disadvantages (357784):

- Higher capital costs to enclose treatment tanks to contain oxygen-rich gases.
- pH lowering due to CO₂ buildup in solution may require caustic addition.
- Added cost of oxygen-rich gases.

A performance summary for air and oxygen systems is shown below (357786). Oxygen has the advantages of higher throughput and lower sludge production.

	<u>Air</u>	<u>Oxygen</u>
MLVSS (mg/liter)	3,440	4,270
Dissolved oxygen (mg/liter)	0.5-2.0	15
Biomass loading (mg BOD ₅ per mg MLVSS/day)	0.35	0.32
Clarifier overflow rate (m ³ /day-m ²)	0.5	2.0
Sludge production (mg TSS/mg BOD ₅ removed)	0.91	0.52

Eckenfelder (357784) has compared air and oxygen systems treating 60,000 lb/day of BOD. He reports that the added capital investment in closed oxygenation equipment was more than balanced by the savings in agitation power costs.

The dispersion of oxygen in open tanks through rotating microdiffusers, studied by FMC Corporation (357788), has the advantage of requiring minimal modification of existing equipment while still realizing higher capacity, reduced sludge production, and lower power consumption of the oxygen system. The capacity of an existing 10 mgd open tank biological oxidation system was doubled by converting to oxygen diffusion at a capital cost of \$400,000, adjusted to January 1979, average BOD removal and oxygen were both in excess of 90%, and power consumption was only 25 bhp/mgd.

Facultative Lagoons

Bacteria and microorganisms which use dissolved oxygen for the conversion of BOD to insoluble sludge are characterized as aerobic. Anaerobic organisms function without dissolved oxygen. Simple organic wastes, primarily carbohydrates, lipids, proteins, alcohols, and organic acids, are converted anaerobically to volatile acids by acid-forming bacteria and then to methane and carbon dioxide by methane bacteria (B-13923). Facultative lagoons, which operate without agitation or air oxygen injection, are anaerobic except for a surface zone a few inches deep, which is aerobic by air diffusion.

Facultative lagoons vary in depth from 3 to 20 feet. Periodically, it is necessary to remove accumulated sludge from the lagoon bottom or increase the height of the containing walls. Advantages are simplicity, low operating costs, and since a portion of the wastes are converted to methane and CO₂, reduced sludge volume.

Disadvantages are the reduced capacity (20 to 50 lb BOD₅/acre/day) and the large land area used. Methane-forming bacteria require a relatively narrow pH range (6.8 to 7.5). Long chain or cyclic hydrocarbons are not degradable, and microbial activity is inhibited by oil, fat, or grease. Under certain conditions algae growth can cause toxicity, odors, and a buildup in BOD₅ above that of the influent (B-13923).

Design of facultative lagoons has been reviewed by Middlebrooks (B-13923) and Clark (B-1393).

Trickle Filters

Trickle filters are porous beds of crushed stone or of plastic packing over which the wastewater flows. Sufficient void space allows the passage of air for the growth of aerobic bacteria which biodegrade organic impurities in the water. Beds may be up to 30 feet deep and 200 feet in diameter. Wastewater is distributed over the bed by a spray nozzle or rotating arm. High sidewalls are desirable so that the

media can be flooded with wastewater occasionally to eliminate stagnant volumes and to control fly larvae. Recirculation of the effluent wastes allows a higher loading (1,000 to 5,000 lb BOD₅/acre-ft-day) than a one-pass noncirculating operation (300 to 1,000 lb BOD₅/acre-ft-day. These are referred to as high and low rate filters.

Advantages of the trickle filter biological treatment are (B-13913):

- Simple construction and operation
- Low operating costs
- Resistance to organic or toxic shock
- Ability to handle high temperature wastewater.

Disadvantages are (B-13914):

- Reduced BOD capacity per unit volume [5 to 25 lb BOD₅/1,000 cu ft (low rate) and 25 to 300 lb BOD₅/1,000 cu ft (high rate)].
- BOD removal efficiencies usually in the range of 50-85%.
- Presence of odors and flies.

Filters are usually followed by a clarifier, and the recycle stream to a high rate filter can be taken before or after the clarifier (B-1393). Using two filters in series with separate recirculation to each filter improves removal efficiency.

Removal efficiency can be estimated from the following empirical equation (B-1393):

$$E_1 = \frac{1}{1 + 0.0085 \sqrt{W/VF}}$$

MCP 000016464

where

E_1 = Fractional efficiency of BOD removal for process, including recirculation and sedimentation.

W = BOD loading to filter, lb/day.

V = Volume of filter media, acre-ft.

$$F = \text{Recirculation factor} = \frac{1 + R}{(1 + R/10)^2}$$

R = Recirculation ratio, i.e., $\frac{\text{slurry recirculated}}{\text{slurry drawn off}}$

Thus, for 2 mgd of industrial wastewater having a BOD₅ of 600 mg/liter, the filter area necessary for 71% removal at a 6 ft depth and a recirculation ratio = 4 is as follows:

$$\text{Recirculation factor} = 1 + 4/(1.4)^2 = 2.55$$

$$\text{BOD}_5 \text{ loading} = 600 \times 8.34 \times 2 = 10,000 \text{ lb BOD/day.}$$

Then, from the formula above,

$$0.71 = \frac{1}{1 + 0.0085 \sqrt{10,000/2.55V}}$$

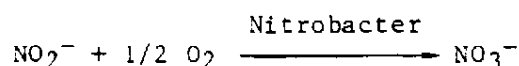
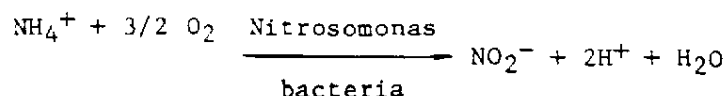
Solving for $V = 1.75$ acre-ft,

thus, at a 6 ft depth, the area = 0.292 acre.

Capital and operating costs to treat 2 mgd of wastewater containing 1,250 ppm BOD₅ with 50% removal have been estimated by Oliver (B-13920). The capital cost adjusted to January 1979 is \$384,000 and direct operating cost is 6¢/1,000 gal.

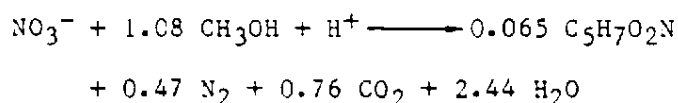
Nitrification-Denitrification

Nitrogen is present in sewage in the form of urea, proteinaceous matter, and ammonium or nitrate compounds. The first two are readily decomposed by bacteria to ammonia. This ammonia is converted further to nitrites and nitrates in an aerobic environment (B-1393):



Nitrification, given sufficient residence time, will occur in most aerobic biological treatment processes. While the nitrates are oxygen-resistant, they do support algae growth and other plant life with a consequent conversion back to ammonia. Thus, it is desirable to carry the nitrification one step further.

Under anaerobic conditions, and with the presence of methanol as a carbon source, nitrates are biologically converted to nitrogen and carbon monoxide:



The methanol requirement, mg/liter, is equal to:

$$C_m = 2.47 N_0 + 1.53 N_1 + 0.37 D_0$$

where

N_0 , N_1 , and D_0 = initial concentrations of nitrate-nitrogen, nitrite-nitrogen, and dissolved oxygen, in mg/liter.

Nitrification requires from 10 to 20 days at 20°C and, while it can take place in activated sludge systems, the additional time is often provided in a separate system following biological sludge removal to reduce sludge volume in the nitrification reactor. Nitrification has been applied to NH_3 concentrations as high as 500 mg/liter with 90% removal in a single stage and 97% in two stages. It is most efficient at temperatures of 28 to 32°C and a pH range of 7.8 to 8.3 (B-1395).

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Denitrification has been applied to nitrate levels as high as 10,000 mg/liter at pH of 6.5 to 7.0. Holding times are in the range of 1 to 5 days at 20°C. Design calculations and various possible arrangements for activated sludge, nitrification, and denitrification operations are described by Adams (B-1395).

Capital cost of a nitrification-denitrification system to treat 2.5 mgd of nylon plant nitrogen wastes was estimated at \$4 million (B-13914, adjusted to January 1979). Feed composition and percent removal were as follows:

<u>Feed Composition</u>	<u>% Removal</u>
Total organic carbon (TOC)	80-90
BOD	90-95
NO ₃ -N	60-80
NO ₂ -N	
NH ₃ -N	
Organic N	

The system consisted of an anaerobic reactor with 36 hr retention and an oxygen concentration less than 0.2 mg/liter. This was followed by an aerobic basin with a 5 day retention. Sludge was separated by dissolved air flotation and a portion of it was recycled to the anaerobic reactor. Effluent from the flotation was filtered for complete removal of solids.

Sand Filters

Gravity sand filters are widely used for water purification. They consist basically of a layer of sand through which water is passed. Suspended solids are retained by the sand bed. They are removed by scraping the top surface of the sand bed or by backwashing to expand the bed and wash out the filtered solids.

Sand filters have been classified as slow and fast (B-13915). The slow sand filter uses a fine sand (0.35 to 0.50 mm dia) with flow rates of 50 to 100 gpd/sq ft. The buildup of a bacterial layer on top of the

sand aids in the separation of particles as small as 0.5 μ . A disadvantage of the slow filter is that it uses only the top inch or two of the bed; therefore, it has to be cleaned frequently. The fast sand filter (2,000 to 3,000 gpd/ft²) uses a larger sand particle (0.50 to 0.60 mm). The addition of polyelectrolytes to promote agglomeration enables even larger sand particle sizes and faster filtration rates.

The use of several bed materials--sand, anthracite, and garnet--of progressively smaller size and greater density permits fuller use of the bed depth. Thus, when the bed is fluidized by backwashing, the coarse, light particles are reclassified on top of the bed, and the fine, heavy particles on the bottom (B-1, B-1393).

A continuous sand filter has been developed in which the flow is from bottom to top and a diaphragm continually moves the bed upward in plug-fashion as fresh sand flows in underneath (B-13911). Sand overflow from the top is washed to remove entrapped solids, then recycled. Thus, the entire filter bed depth is in continuous use.

A disadvantage of the sand filter is the fact that the solid-liquid feed is concentrated (by backwashing) rather than separated. In some instances, using air together with the backwash to expand the filter bed, reduces the volume of the collected slurry (B-13914). Typically backwash volumes are 5 to 10% of the feed volume, and solids separation efficiency is 65 to 95% of the feed solids.

The capital cost, for a 7.5 mgd sand filtration system--including automatic controls, auxiliary equipment, and building--is \$1.56 million (B-13911, adjusted to January 1979).

Tertiary Treatment

Foam Fractionation

Foam fractionation is the concentration of dissolved nonvolatile surface active agents (i.e., molecules with both hydrophobic and hydrophilic groups) which tend to concentrate at water-gas interfaces

(447046). Heavy metal ions may also be concentrated in the presence of surface active chelating or complexing agents (447045).

Foam fractionation columns operate with countercurrent flows of liquid and foam phases in a manner analogous to that of distillation columns. Similarly, they can be employed in stripping or enriching modes or in a combination of both. The design of foam fractionation columns is derived from the experimentally determined equilibrium curve for impurity concentrations in liquid and foam phases and from the height of a transfer unit (HTU) (B-1, 447047, 447048). In some cases, the separation can be made in a conventional bubble plate column.

Possible methods for the coalescence of the foam overflow or reflux include rotating paddles, nylon mesh contactors, or ultrasonic vibration.

Foam fractionation is most likely to be economic for the concentration of trace amounts of surfactants, dyes, phenolics, and heavy metals (447048). A tenfold concentration of toxic ions is said to be readily obtained by a simple mode fractionation (e.g., no reflux and feed to foam pool) (B-1).

The estimated capital investment (adjusted to January 1979) for 70% removal of a few ppm of alkyl benzene sulfonate in 1 mgd of municipal wastes is \$72,000. At 10 mgd, the investment is \$485,000 (447049).

Chlorination

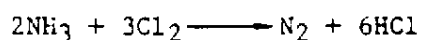
Water that is to be recycled for human or animal use must be disinfected. The most common disinfectant is chlorine gas, which is drawn into the aqueous stream as it passes through an ejector. Instruments maintain a constant proportion of chlorine to water to give a residual Cl_2 content of about 0.5 mg/liter (B-1393). Following mixing, a contact time of 15 to 30 minutes is usually required for disinfection.

Typical chlorine dosages for disinfection of wastewater at various stages of treatment are as follows:

<u>Source of Effluent</u>	<u>Dosage Range (mg/liter)</u>
Untreated water	6-25
Primary sedimentation	5-20
Activated sludge	2-8
Chemical precipitation	2-6
Multimedia filter following activated sludge	1-5

The capital investment required to chlorinate 1 mgd at a dosage of 10 mg/liter is estimated at \$90,000; at 10 mgd and the same dosage, this figure is \$130,000 (B-13924, adjusted to January 1979). Operating costs are the cost of chlorine plus capital-related charges.

Chlorine can also be used to eliminate ammonia from wastewater (B-1393):



Best results are obtained with a reaction time of 2 hours, a temperature of 45 to 48°F (7 to 9°C), and a pH between 7 and 9. Chlorine requirements are about 10 mg of Cl₂ per mg of NH₃.

Chlorination is effective for the removal of small quantities of ammonia (1 mg/liter or less). For higher quantities, the cost of chlorine becomes significant (B-13911). A disadvantage is the generation of by-product hydrogen chloride.

Ozonation

Ozone is a powerful oxidizing agent capable of destroying various toxic, or otherwise undesirable, organic and inorganic compounds. Table 4.10 lists some of these compounds. Ozone is generated as required and, since it is expensive to produce, it is most likely to be economic only for impurity concentrations of 100 ppm or less.

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Table 4.10

TYPICAL COMPOUNDS SUSCEPTIBLE TO OZONATION*

OrganicAromatic hydrocarbons

Biphenyl
 3,4-Benzpyrene
 1,2-Benzanthracene
 3,4-Benzfluoranthene

Microorganisms

Bacteria
 Viruses
 Algae
 Protozoa

Detergents

Alkyl benzene sulfonate
 Anionic detergent
 Nonionic detergent

Other

Color
 Odor
 Disinfection

Pesticides

Aldrin
 DDT
 -BHC
 Dieldrin
 Malathion
 Methyl parathion

Ozone Oxidation Combined withUV Radiation†

Acetic acid
 Ethanol
 Glycerol

Phenols

Phenol
 o-, m-, and p-Cresols
 Catechol
 Xylenol

Inorganic

Potassium cyanide
 Potassium ferricyanide
 Sodium thiocyanate
 Sodium thiosulfate

*Numerous other compounds are more economically handled by biological oxidation.

†Little or no oxidation without UV radiation.

Sources: B-1394, 447053, 447054.

Ozone is produced by passing air or oxygen through an electrical discharge. When air is used, the maximum ozone concentration attained is about 2% or less with an electrical expenditure of 7 to 9 kwh/lb ozone. When oxygen (50-75%) is used, ozone concentrations of 5 to 6% are possible with a power usage of 3.5 to 5 kwh/lb ozone (B-1394). With air, a once-through process is used and the air, following destruction of residual ozone by catalytic or thermal means, is discharged to the atmosphere. When oxygen is used, the value of the oxygen necessitates its being recycled. Union Carbide (447054) suggests that this latter system can be advantageously combined with an oxygen-activated sludge operation. Thus, there is only a single pass of oxygen through the ozone treatment process with the exiting unconverted oxygen stream going to a biological oxidation operation. This eliminates the oxygen treating and recycling.

Typically, ozone usage is in the range of 1.5 to 3.0 lb/lb of impurity with liquid residence times of 10 to 15 minutes. However, some hazardous materials may require retention times up to one hour with stagewise application of the ozone (B-1394). The optimum combination of ozone dose and contact time must be determined experimentally for each application.

Currently, ozone is most frequently used in tertiary treatments for disinfection, odor or color removal, and oxidation of residual trace contaminants (B-13912, 447052, 447050). Ozone is effective as a water disinfectant at dosages of 5 mg/liter or less (447050). Its advantage is the absence of any residual impurity. The principal disadvantage is the cost of equipment and operation. Recent evidence of the formation of carcinogenic compounds during chlorination of drinking water could, if verified, greatly expand the use of ozone for disinfection (447101). Increased generator efficiencies (lb ozone/kwh), lower investment cost, and/or stricter effluent regulation could increase the use of ozone for reduction of cyanides, phenols, metal plating wastes, etc. (B-13912).

Large volume (6,000 lb ozone/day) ozone generation systems require capital investments of about \$350 to \$450/lb ozone/day (B-13912). The capital investment for a small volume ozonation process to lower the phenol concentration in 800,000 gpd of refinery effluent water from 0.38 ppm to 0.012 ppm has been estimated at \$380,000. Ozone output was 190 lb/day and operating cost was about 53¢/1,000 gal (B-1394, adjusted to January 1979).

Toxic Liquids Disposal

Pumping into the ground at depths of several thousand feet has been used for the disposal of corrosive and toxic liquid wastes. Principal costs are those of well drilling, pumps, and power for pump operation. The capital investment for disposal of 500 gpm at a depth of 3,000 feet is estimated at \$2.4 million, including pumps with 900 psi discharge pressure (101272, adjusted to January 1979). However, the areas available for "deep-welling" are being increasingly restricted and, by the early or mid-1980s, this disposal method will probably not be acceptable for toxic wastes in most industrial nations.

Incineration is a generally acceptable method of disposal for toxic liquid wastes. For example, a fluidized silica bed operating at 1400 to 1500°F (760 to 815°C) has been used for the destruction of 4% of mixed organic compounds in 750 gph of aqueous solution (447008). Destruction of the organics was 99.9% efficient and the No. 2 fuel oil consumption was 0.33 to 0.43 gal/gal. Capital investment was \$6.0 million and operating costs--principally fuel and capital related items--was \$530 per 1,000 gallons of liquid wastes.

The Zimpro system of wet air oxidation, at elevated temperatures and pressures, of liquid chemical wastes has the lowest operating costs (447008). However, at 536°F (280°C), the destruction efficiency of some organics is less than 85%. A more recent paper on the Zimpro process (447074) shows that pentachlorophenol is 82% consumed at 527°F (275°C) and almost completely (99.88%) eliminated at 608°F (320°C).

4B GASEOUS WASTE TREATMENT AND DISPOSAL TECHNOLOGY

A variety of well established industrial techniques are suitable for the elimination of environmentally objectionable solids and vapors from inert gases. The most used methods are indicated by the block flow diagram of Figure 4.8. For example, hot combustion gases from a coal fired boiler might pass through the sequence of--spray cooler, cyclone separator, bag filter, SO₂ scrubber, and stack--before being released to the atmosphere.

Pretreatment

Waste gases may need to be compressed before treatment. If the gases are free of suspended solids and are at temperatures below about 200°F (100°C) they can be compressed directly--otherwise after cooling and separation of the solids from the gases. The required pressure is generally less than 25 psia. Figure 4.9 shows the brake horsepower required by a centrifugal compressor to increase the pressure of air, at various flow rates, to 17, 20 and 25 psig. Compressor costs are available from the literature (B-13927) or from the PEPCOST relation:

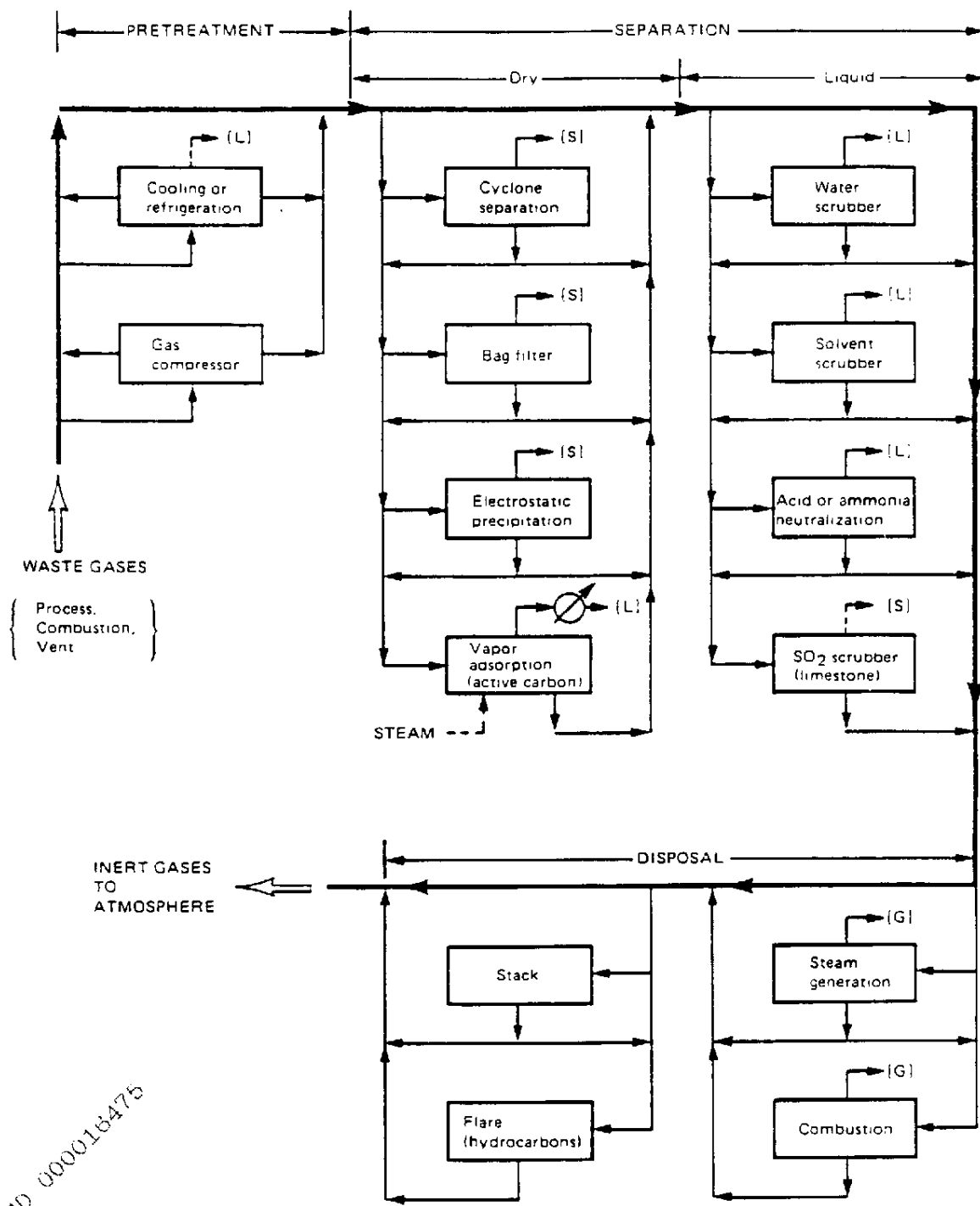
$$\text{Cost \$} = 3,894 \times 290 \times (\text{bhp}/4,500)^{0.76}$$

Feed gases can be precooled by either indirect or direct heat exchange to water. Typical values of U for heat transfer from gases to water are in the range of 10 to 50 (B-1).

For a counter current spray cooler, empirical equations for maximum allowable gas velocity and unit heat transfer rate are as follows (447060):

Figure 4.8

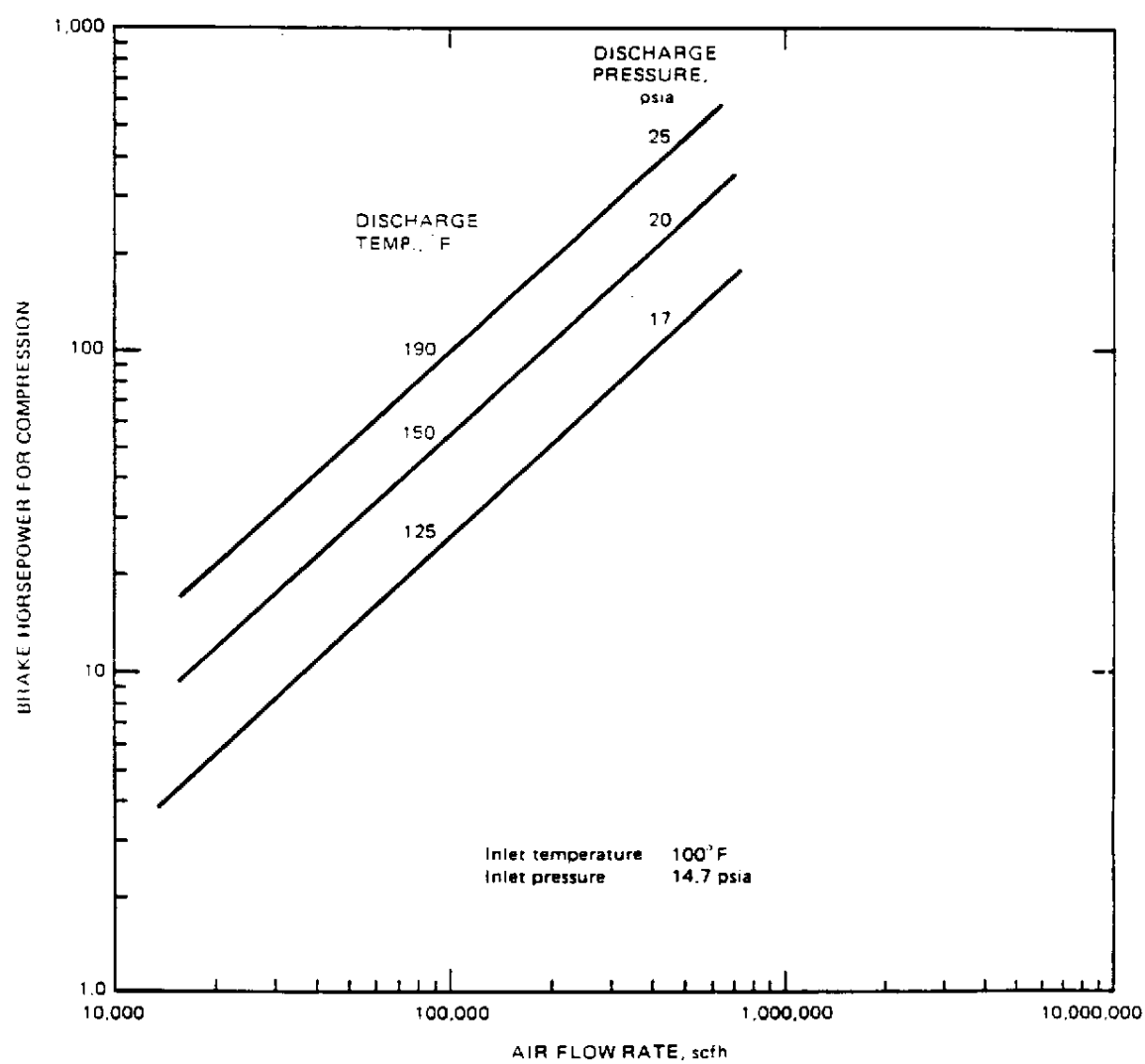
WASTE GAS TREATMENT ALTERNATIVES



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Figure 4.9

COMPRESSOR HORSEPOWER FOR VARIOUS AIR FLOW RATES



Source: B-13944.

$$V_{\max} = C \frac{\rho_l - \rho_g}{\rho_g}^{1/2}$$

$$h_{ga} = \frac{0.0146 G^{0.82} L^{0.47}}{Z_T^{0.38}}$$

where $V_{\max}$ = max gas velocity, ft/sec

C = a constant = 20

ρ_l, ρ_g = liquid and gas densities, lb/cu ft

h_{ga} = volumetric heat transfer coefficient, Btu/hr/cu ft/°F

G, L = gas and liquid mass velocities, lb/hr/ft²

Z_T = height of contacting zone, ft.

Knowing $V_{\max}$ and h_{ga} , one can readily calculate the cross-section and the height of the column. The cost can then be estimated conventionally.

Dry Systems

Gas-Solid Separation

The principal types of equipment for gas-solid separations are:

- Cyclones
- Bag filters
- Electrostatic precipitators.

The choice among these depends primarily on the particle size of the solid, the concentration of the solid in the gas, and the degree of separation desired, as indicated in Table 4.11. Electrostatic precipitators are the most efficient at particle sizes smaller than 2 microns.

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Table 4.11

APPLICATIONS OF GAS-SOLID SEPARATION EQUIPMENT

Characteristic	Cyclone	Bag Filter	Electrostatic Precipitator
Minimum size particle (microns)	10	0.2	2 (max)
Minimum solid particle loading (grains/cu ft)	10	0.1	0.1
Maximum collection efficiency (wt%)	85	99	99
Typical gas velocity (fpm)	2,000 to 4,000	1 to 20	100 to 600
Approx. pressure drop (inches H ₂ O)	1/2 to 3	2 to 6	0.2 to 1
Approx. upper size limit (1,000 cfm)	50	200	10 to 2,000
Installed cost (\$1,000)*	125	420	600
Power cost (\$/yr) [†]	9,040	7,480	4,000
Maintenance (%/yr of installed cost)	1.0	6.0	0.6

*January 1979 cost for typical systems handling 60,000 cfm of gas at 68°F with a loading of 5 grains per cubic foot, 30% smaller than 10 microns.

[†] Electricity at 20 mills/kwh.

Sources: B-1, B-13928, 447059.

They also have the lowest operating costs--largely for maintenance and power. However, the installed cost for an electrostatic precipitator treating 60,000 cfm of gas is \$600,000, compared with \$125,000 for a similar capacity cyclone and \$420,000 for a bag filter.

Adsorption on Activated Carbon

The removal of objectionable or valuable vapors from inert gases such as air is a well developed and widely used technology (447069, 447063). Vapors are attracted to the surface of the carbon by forces

believed to be similar to those of chemical combination. The amount of a particular vapor adsorbed by a specific sample of active carbon at a given temperature can be represented by a Langmuir isotherm (B-13929):

$$X/M = \frac{k \cdot K \cdot p}{1 + Kp}$$

where X/M = wt of vapor per unit wt of carbon

k and K = constants

p = partial pressure of vapor over carbon.

The constants " k " and " K " must be determined experimentally for each adsorption system. Table 4.12 shows the approximate amounts of various chemicals adsorbed by active carbon from air saturated at 20°C and 760 mm Hg. Generally, adsorbability varies directly with vaporization temperature. Typically, solvent recovery systems are designed for solvent capacities of 10 to 20 lb solvent/100 lb active carbon (B-12930).

Adsorption heat for various solvents ranges from about 12,000 to 15,000 cal/g-mol (21,500 to 27,000 Btu/lb-mol). Where this results in more than a 5 or 10°C rise in the temperature of gas stream, cooling of the bed may be necessary. The bed is regenerated by blowing with steam to vaporize the adsorbed solvent. Typical steam usage is 3 to 5 lb/lb of solvent (447058).

Typical pressure drops for air flowing through active carbon beds at 70°F and 760 mm Hg pressure are shown in Figure 4.10.

The installed cost of an active carbon adsorber to treat 1.2 million cfh of air containing 200 ppm of solvent is \$530,000 (447064, adjusted to January 1979). Steam requirements for this low solvent concentration can be as high as 30 lb/lb of recovered solvent.

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Table 4.12
VAPORS ADSORBED BY ACTIVATED CARBON*

High (20 to 50 wt%)	Medium (10 to 25 wt%)	Low (Less than 10%)	Very Low (Not suitable at specified conditions)
Acetic acid	Acetone	Acetaldehyde	Carbon dioxide
Alcohols	Acrolein	Acetylene	Carbon monoxide
Amyl acetate	Acrylic acid	Amines	Ethylene
Benzene	Butylether	Butane	Ethane
Bromine	Butyraldehyde	Butylene	Methane
Butyric acid	Carbon disulphide	Ethylene	
Caprylic acid	Chlorine	Formaldehyde	
Carbon tetrachloride	Ethyl chloride	Formic acid	
Chloroform	Ethyl ether	Methyl chloride	
Cresol	Hexane	Propane	
Disinfectants	Hydrogen sulfide	Propylene	
Ethyl acetate	Methyl acetate		
Gasoline	Methyl alcohol		
Mercaptans	Nitrogen dioxide		
Ozone	Pentane		
Phenol	Pentylene		
Pyridine	Sulfur dioxide		
Toluene	Sulfur trioxide		
Turpentine			

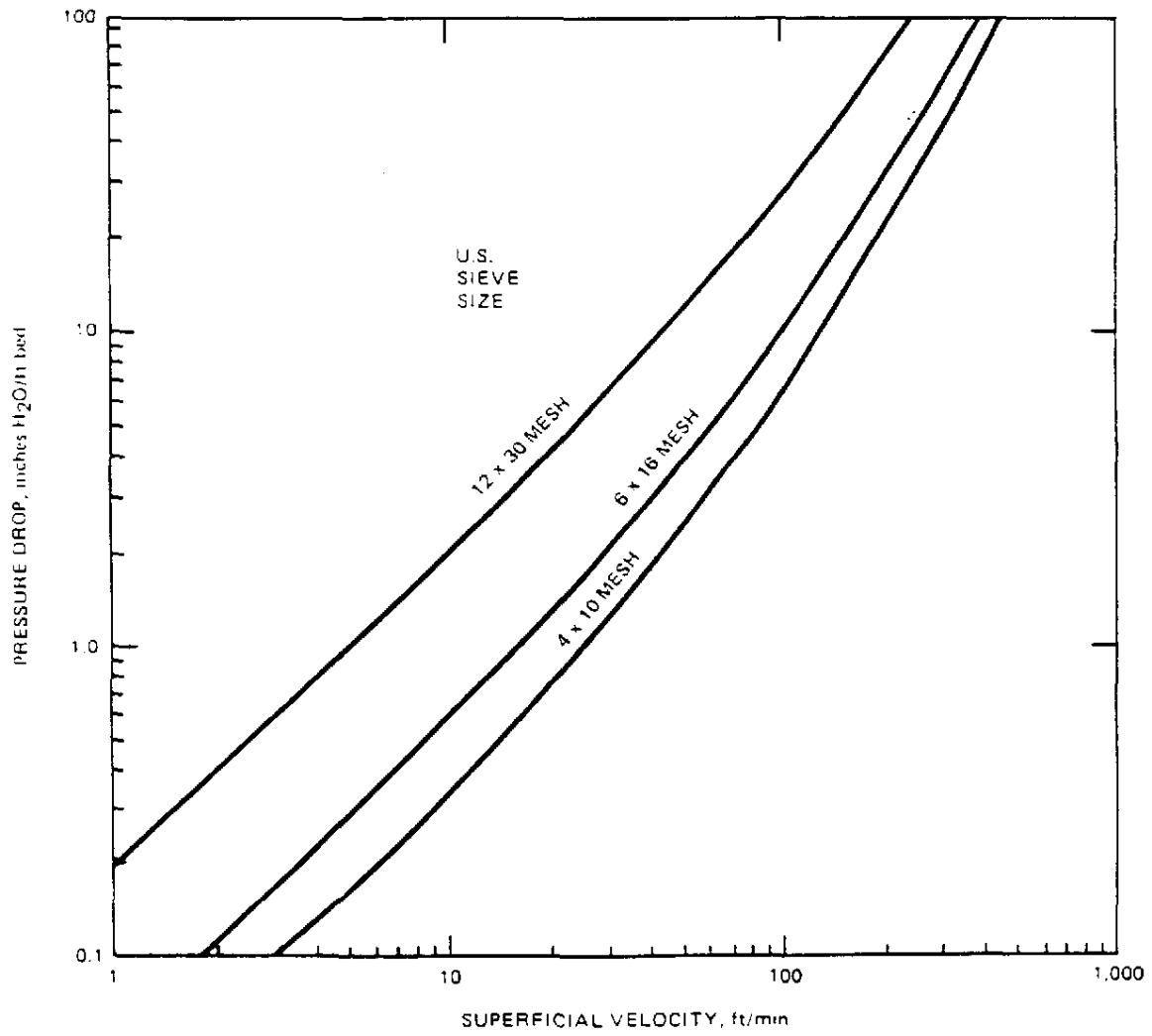
*Adsorption from saturated air at 20°C and 760 mm Hg.

Sources: B-13929, B-13930.

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Figure 4.10

PRESSURE DROP FOR AIR FLOW THROUGH ACTIVE CARBON
AT 70°F AND 760 mmHg



Source: Pittsburgh Activated Carbon

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Liquid Systems

Water and Solvent Scrubbing

Water-soluble gases such as hydrogen chloride, methanol, and formaldehyde are readily removed from insoluble gases by scrubbing with water in a packed or tray column. Similarly, organic vapors (such as benzene, ethane, and styrene) that are insoluble in water are easily removed by scrubbing with a low volatility hydrocarbon liquid.

The optimum design of scrubbers depends on the kind and composition of the gases being treated as well as on the type of solvent and its capacity for the gaseous components. However, for the average operation a scrubbing tower with 20 actual plates is usually adequate. Also the tower diameter is such that the vapor velocity up through the column is below flooding. Maximum solute concentration in water or solvent is 5 wt%.

Knowing the column size and circulation, one can readily estimate the capital and operating costs by the PEPCOST computer program or from published data (B-13927, B-13928).

Acid or Ammonia Neutralization

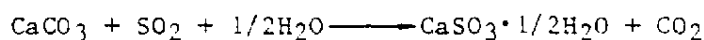
Gases containing acid or ammonia vapors are commonly neutralized by scrubbing with an aqueous slurry or solution of lime or sulfuric acid. Column sizing is similar to that of water and solvent scrubbers. However, the materials of construction must be acid- or alkali-resistant and additional facilities are needed for storage and mixing of neutralizing agents. Storage capacity is usually equivalent to 5 days' supply of acid or alkali.

Limestone Desulfurization

National ambient air quality standards require sulfur oxides concentrations of less than 0.5 ppm (447061). As more power plants convert from hydrocarbons to coal, the capacity requiring flue gas

desulfurization is expected to skyrocket from 4,000 MW in 1975 to over 130,000 MW by 1985 in the United States (447062).

While numerous flue gas desulfurization processes have been patented, less than ten are in large scale operation or construction. Of these, the limestone slurry process accounts for more than 50% of the total capacity. Limestone slurry (5 to 15 wt%) is sprayed into towers, where it reacts with sulfur dioxide to form hydrated calcium sulfate and carbon dioxide:



In practice, some SO_2 is oxidized to SO_3 and this combines to give mixed calcium gypsum crystals $[\text{Ca}(\text{SO}_3)_x(\text{SO}_4)_y \cdot z\text{H}_2\text{O}]$ (447061). Sulfur dioxide removal is about 80 to 95%. The most used method of sludge disposal is on-site ponding and landfill.

Investment and operating costs for the limestone desulfurization of flue gas were evaluated in PEP Report No. 63B. The fixed capital investment to desulfurize 13×10^6 scfh of flue gas from 2,500 vppm to 500 vppm is \$17.4 million. Limestone (93% CaCO_3) usage is 8,600 lb/hr and the resultant gypsum sludge output is 28,800 lb/hr. Operating requirements are principally labor (7 operators/shift), steam (21,000 lb/hr), and electricity (1,300 kw). Maintenance labor and materials is taken at 3%/yr of capital investment.

Waste Gas Disposal

Steam Generation and Incineration

When the waste gases contain combustible gases in concentrations greater than 100 Btu/scf, it may be preferable to burn them for steam generation. Thus, 100,000 scfh of low Btu gas (125 Btu/scf) could generate, at 60% efficiency, 8,000 lb/hr of steam, with a modular investment in burners and steam boiler of about \$155,000. At 500 Btu/scf, the comparable figures are 75% efficiency, 40,000 lb/hr steam, and an investment of \$450,000, as of January 1979.

When the waste gases contain a small quantity of an environmentally objectionable gas which is not readily eliminated by preceding methods but which is combustible (e.g., acetylenes), incineration may be desirable. In this case, auxiliary fuel would be added to produce combustion temperatures up to 2000°F (1100°C). Sensible heat in the combustion gases would be used for steam generation as before.

Emergency Flaring

In industrial nations, the gas flare serves mainly as a means of disposal for flammable gases during a process equipment failure or emergency plant shutdown. The exit velocity of hydrocarbon gases from a flare should not exceed 1/5 of the sonic velocity if a stable flame is to be maintained (447067):

$$V = 1/5 \sqrt{gkRT/M}$$

where V = gas exit velocity, ft/sec

g = gravity constant = 32.2

k = Cp/Cv = 1.2

R = gas constant, 1,546

T = vapor temperature, °R

M = molecular weight of vapor.

Knowing the gas escape velocity and the maximum volume of gas flow, one can calculate the stack diameter. The stack height is obtained from the following relation:

$$q = \frac{960 w \sqrt{M}}{4\pi [x^2 + h(h + 120 D)]}$$

where q = heat intensity on the ground at X ft from base of stack.

w = gas flow rate, lb/hr.

h = height of stack, ft.

D = stack diameter, ft.

M = molecular weight of vapor.

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Using a heat intensity "q" at the base of the stack ($X = 0$) of 1,500 Btu/hr/sq ft (approx maximum for 20 second human exposure), the stack height can be determined.

If steam is injected (0.3 lb/lb HC), carbon particles are converted to carbon oxides and smoke is eliminated (B-13931). Esso Research (447065) have proposed a smokeless multijet flare which does not require steam addition and which does not have to be elevated. Inside diameter of this stack in feet is equal to 0.825 times the square root of the heat release in million Btu/hr.

The erected capital cost to flare hydrocarbons (mol wt = 40) at a rate of 0.5 million scfh is estimated at \$190,000 for the elevated flare and, if steam is employed, an additional \$650,000 is required for steam generation. For the Esso multijet flare, the comparable cost is \$400,000.

Dispersion by a Stack

When environmentally objectionable impurities in the waste gases have been reduced to acceptable limits, the gases are discharged to the atmosphere. A study made many years ago by Moyer Thomas et al. (447068) determined the impurity concentrations downstream from dispersion stacks. The maximum concentration was found at a distance

$$X_{\max} = h/2 \ C_z$$

and the concentration at this distance was expressed by:

$$C_{\max} = \frac{4M}{\sqrt{2\pi} e^{2uh^2}} \cdot \frac{C_z}{C_y}$$

where h = stack height, cm.

C_z & C_y = vertical and horizontal diffusion coef., 0.05 to 0.07.

M = gaseous impurity emission, g/sec.

e = natural logarithm base = 2.718.

u = mean wind velocity, cm/sec.

Some additional guides to dispersion stack design are suggested by Ross (B-13913):

- Stack height should be 2.1/2 times that of surrounding buildings to minimize turbulence.
- Gas ejection velocity should be greater than 60 ft./sec so as to escape the turbulent wake of the stack.
- Ground concentration varies inversely as the square of the effective stack height.

The estimated installed cost of 100 foot steel stacks of 24 and 48 inches diameter is \$23,000 and \$70,000 (447057, adjusted to January 1979).

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4C SOLID WASTE TREATMENT AND DISPOSAL TECHNOLOGY

Solids generated in liquid and gaseous waste treatment are treated and/or disposed of as described in this section. Solid wastes such as catalyst residues and spent adsorbents are also handled as described here. Potential treatment and disposal means are illustrated by the block diagram of Figure 4.11. The treatment procedures are standard, widely used, industrial methods. This section briefly reviews their application to waste treatment.

Waste Solids Treatment

Dewatering

Dewatering centrifuges are applicable to relatively coarse (+100 mesh) granular, nonsticking materials. The capacity of these centrifuges is very dependent on the particle size of the feed solids, as shown in Figure 4.12. For example, for a KCl feed with a moisture content of 35 wt% and a top size of 1/8 inch, a 36 inch bowl centrifuge has a capacity of 44 tph of solids with an exit moisture content of less than 6 wt%. This exit moisture content increases with solids feed rate and decreases with increasing solids particle size, as illustrated by Figure 4.13.

The approximate purchase prices of helical-conveyor centrifuges are as follows (B-1, adjusted to January 1979):

<u>Bowl Diameter</u> <u>(Inches)</u>	<u>Purchase Price, (\$)</u>	
	<u>Steel</u>	<u>Stainless 316</u>
26	58,000	100,000
36	85,000	140,000

Figure 4.11

WASTE SOLID TREATMENT ALTERNATIVES

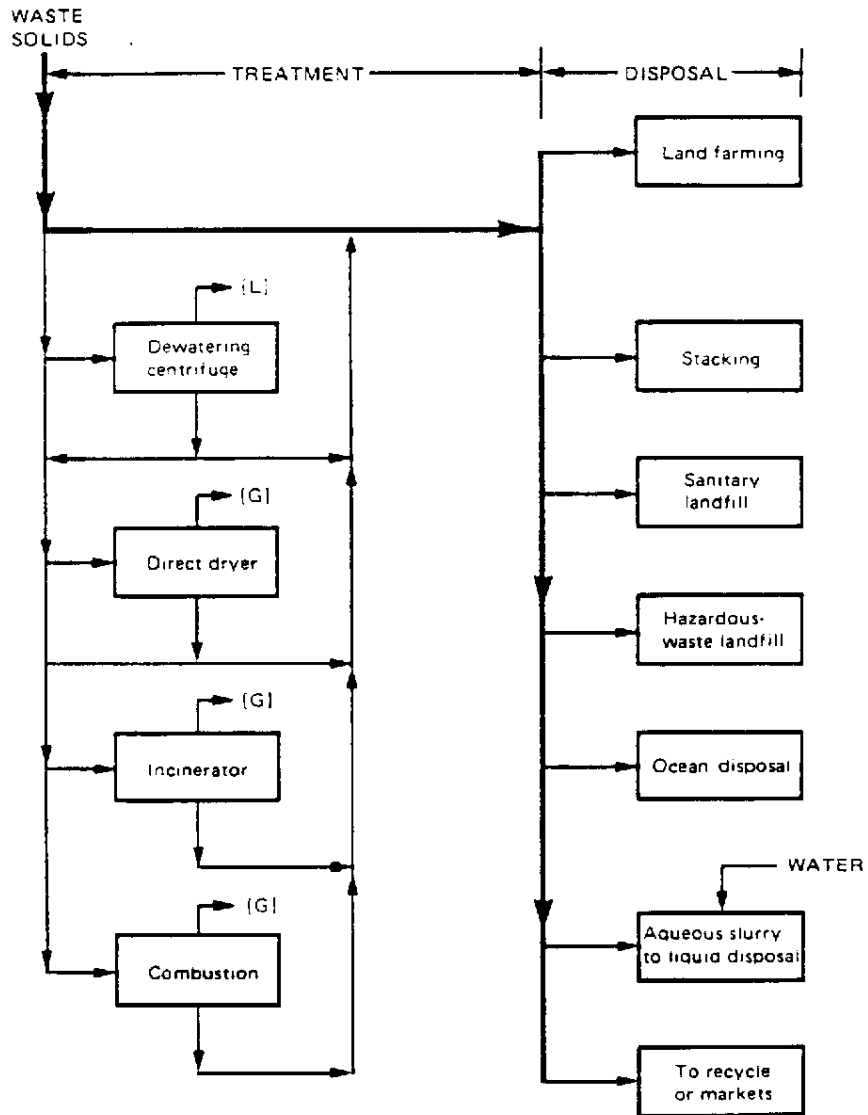
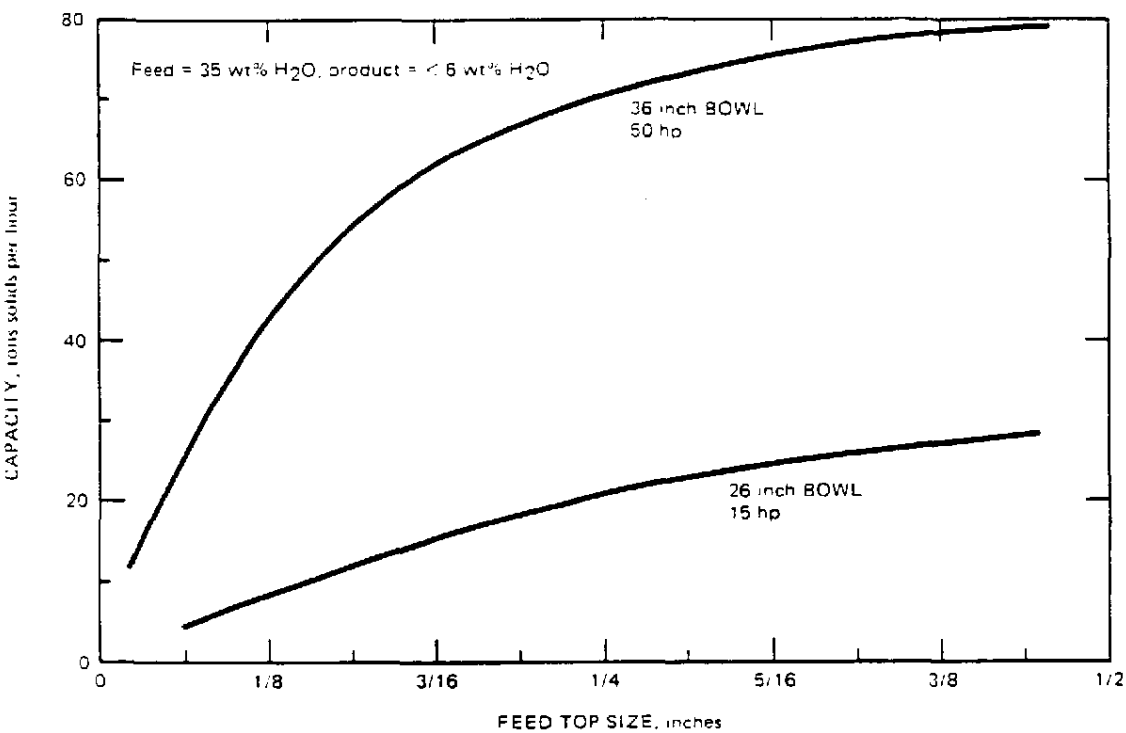


Figure 4.12

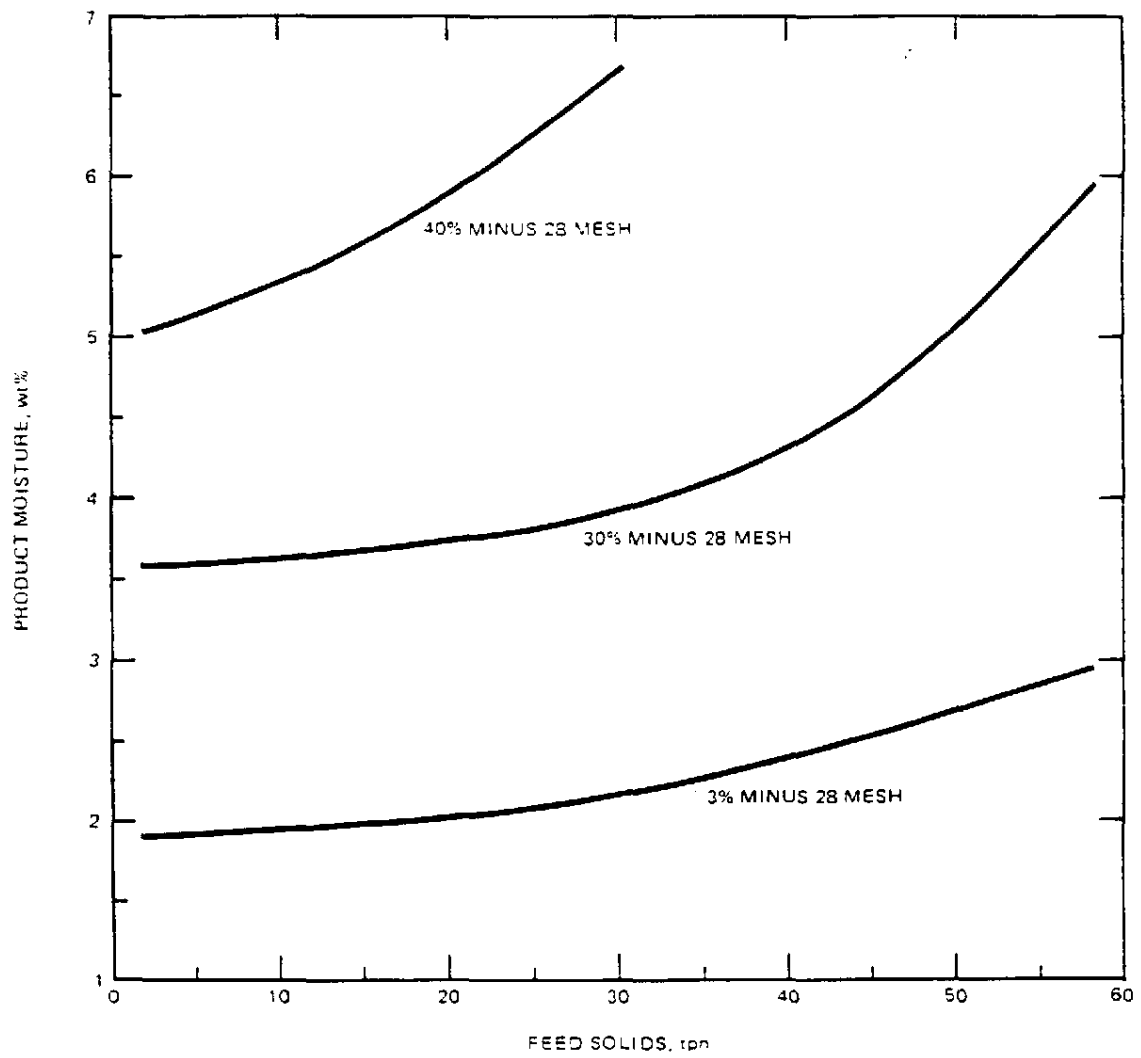
EFFECT OF FEED SIZE ON DRYING CENTRIFUGE CAPACITY



MCD 000016489

Figure 4.13

EFFECT OF FEED RATE AND SIZE ON DRYING CENTRIFUGE
PRODUCT MOISTURE



MCD 000016490

In addition to the dewatering centrifuge, the module would also contain a 20 foot screw feed conveyor, 5 hours' solids and water surge capacity, and a water pump.

Drying

The equipment applicable to the drying of waste solids includes rotary dryers, flash dryers, multiple hearths, and fluidized beds. Only the direct heat rotary dryer will be considered here.

The capacity of the dryer can be expressed by a heat transfer equation (B-1):

$$Q = U_a V (\Delta t)_m$$

where Q = total heat transfer, Btu/hr

V = volumetric heat transfer coefficient, Btu/hr/cu ft/°F

$(\Delta t)_m$ = mean temperature difference between hot gases and solids.

When the solids temperature is not known, the logarithmic mean of the wet bulb depressions of inlet and outlet air can be used. An empirical relation for the volumetric heat transfer coefficient is $U_a = 0.5G^{0.67}/D$ and replacing V by $\pi D^2 L/4$ changes the heat transfer equation to:

$$Q = 0.4LDC^{0.67}(\Delta t_m)$$

where L and D = dryer length and diameter, feet

G = gases mass velocity, lb/hr/sq ft.

Thus, knowing the quantity of heat to be transferred and the inlet and outlet air temperatures, one can calculate the mass of air required and the dryer length and diameter.

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Typical performance for direct warm air cocurrent rotary dryers is given below (B-1). Solids moisture is reduced from 25 wt% to 0.5 wt% with inlet and outlet air temperatures of 330°F and 160°F and inlet and outlet solids temperatures of 80°F and 150°F. Inlet air is heated by indirect heat exchange with steam.

Dryer size (D inches x L feet)	48 x 25	72 x 35	120 x 55
Heat load, Q (Btu/hr)	342,000	780,000	2,160,000
Steam, 150 psig (lb/hr)	700	1,600	4,500
Discharge solids (lb/hr)	900	2,100	5,700
Exhaust gas (cu ft/min)	2,250	5,100	14,100
Water evaporated (lb/hr)	300	700	1,900
Dryer fan and drive (hp)	8	20	80
Dryer purchase cost, Jan. 1979	\$63,000	\$105,000	\$210,000

Incineration

Incineration of solid waste is usually costly but, for many toxic organic materials, it may be the only safe method of disposal. Bayer AG in November 1977 commissioned a \$13 million incineration plant for chlorine and phosphorus organic compounds (447070). This plant can treat 25,000 metric tons of waste per annum at an average cost (in 1978) of \$190 per metric ton. For several years, two ships--Matthias III and Vulcanus--operating from Germany and Holland, have incinerated organic wastes such as vinyl chloride residues and herbicide orange, in selected ocean locations (447071).

In the United States, EPA has sponsored several demonstration plants for the destruction of chemical wastes, solid and liquid (447008, 447019). Five different systems have been tested: (1) sudden expansion liquid combustion chamber, (2) rotating hearth pyrolyzer, (3) fluidized bed combustor, (4) tandem autoclaves for decomposition of liquids at elevated pressures and temperatures, and (5) rotary kiln followed by an afterburner for evolved gases. Details of these tests together with estimates for commercial scale operation are summarized in Table 4.13.

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Table 4.13

U.S. EPA-SPONSORED WASTE INCINERATION DEMONSTRATION PLANTS

	The Marquardt Company, Van Nuys, Calif.	Midland Ross Corp. Surface Combustion Division, Toledo, Ohio	Systems Technology, Inc., Franklin, Ohio
Incinerator type	SUE ^o (sudden expansion) liquid combustion chamber followed by a caustic venturi scrubber, a scrub solution separator tank, a wire demister vessel, and a stack.	Rotating hearth pyrolyzer followed by a rich fume combustion chamber. Exhaust gases mixed with fresh air before exiting through a stack.	Fluidized bed combustor followed by a venturi scrubber, and an exhaust stack.
Incinerator capabilities	Liquids only	Solids, sludges, or tars	Liquids, slurries, or solids
Feed rate	50-60 gph	200-400 lb/hr	To 340 gpm
Operating temperature	To 1000°F (1650°C)	To 1400°F (760°C)	1100-1500°F (600-810°C)
Heat capacity (Btu/hr)	5.5 x 10 ⁶	2.0 x 10 ⁶	59 x 10 ⁶
Wastes treated (combustion heat)	(1) Ethylene plant wastes of unsaturated and aromatic hydrocarbons (18,000 Btu/lb) (2) Hexachlorocyclopentadiene plant wastes with waxy particulates (4,300 Btu/lb)	(1) API separator bottoms. Unsaturated and aromatic hydrocarbons (2,500 Btu/lb) (2) Solid SBR waste plus carbon and some sulfur and metals, 30% H ₂ O (9,800 Btu/lb)	(1) Methyl methacrylate waste liquid with gritty sediment (<2,700 Btu/lb) (2) Phenol and cresol wastes with 86% H ₂ O and 5% inorganic solids (2,700 Btu/lb)
Incinerator conditions			
Feed rate (lb/hr)	(1) 185-265 (2) 265-384	(1) 32-56 (2) 56-127	4,030-4,830 4,770-7,320
Temperature	(1) 240-2975°F (1349-1752°C) (2) 2458-2572°F (1348-1378°C)	(1) 1400°F (760°C) (2) 1400°F (760°C) (Comb. chamber, 1525°F)	(1) 1425-1550°F (774-843°C) (2) 1364-1652°F (740-900°C)
Residence time	(1) 0.14-0.19 sec (2) 0.17-0.18 sec	(1) 12.5 min (2) 15 min	(1) 13 sec (2) 12-14 sec
Incinerator performance			
Stack particulates (cg/m ³)	(1) 20-25* (2) 36-113*	(1) 28-88 (2) 9-14	(1) 560-630* (2) 1,280-1,430*
Trace metals, ng/m ³	(1) 0.001-0.003 Pb (2) 0.005 Pb 0.05 Mn	(1) Zn, Pb-0.05 SO ₂ 30-50 ppm (2) SO ₂ 25 ppm	(1) Pb 0.55-2.2 (2) Pb 0.44-0.87
Destruction efficiency (%)	(1) 99.5 (2) 99.95	(1) 96 (2) 80-90	(1) 99.93 (2) 99.93
Estimated commercial plant size (short tons/hr)	(1) 16,500 (2) 4,950	(1) 320 (2) 2,200	(1) 14,800 (2) 28,700
Est. capital investment, adjusted to January 1979 (\$ millions)	(1) 1.92 (2) 1.72	(1) 0.47 (2) 0.97	(1) 6.32 (2) 6.40
Operating cost, adjusted to January 1979 (\$/short ton)	(1) (2)	(1) (2)	(1) (2)
Labor, \$12.70 man-hr	26.2 82.3	441.8 185.1	11.0 7.8
Auxiliary fuel, \$2.60 million Btu	— 94.0	52.7 21.5	35.7 35.7
Chemicals and utilities	5.9 201.3	5.3 5.1	34.8 5.7
Maintenance	11.2 112.9	136.5 42.8	42.2 24.8
Capital-related costs, 22% investment	25.5 76.0	310.7 97.2	95.7 53.8
Total operating cost	68.8 566.5	947.0 351.7 -50.7 -48.1† 896.3 303.6	219.4 127.8
Net cost			

*No organic waste materials detected in scrubber water.

†Fuel credit.

‡Follow-up treatment.

Source: 447008.

Table 4.13 (Concluded)
U.S. EPA-SPONSORED WASTE INCINERATION DEMONSTRATION PLANTS

	Zimpro, Inc., Rothschild, Wisc.	3M Company, Cottage Grove, Minn.	Rollins Environmental Service Inc., Deer Park, Texas
Incinerator type	Two continuous autoclaves in series with air bubbled through the liquid wastes at elevated temperatures and pressures (to 1600 psig) in the presence of a copper catalyst.	Rotary kiln followed by a secondary combustion chamber, a water quench tower, a water scrub tower, and an exhaust stack.	Rotary kiln followed by an afterburner chamber, venturi and tray tower scrubbers, and an exhaust stack.
Incinerator capabilities	Liquids with low heating values	Pumpable liquids and drummed solids	Pumpable liquids wastes and drummed solids
Feed rate	5-100 gph	4,000 lb/hr	725 lb/hr PCB capacitors in drums
Operating temperature	450-620°F (230-325°C)	980-1090°C (1800-2000°F)	2400-2700°F (1300-1500°C)
Heat capacity (Btu/hr)	--	90 x 10 ⁶	110 x 10 ⁶
Wastes treated (combustion heat)	(1) Coke plant aqueous wastes containing phenols, cresols, ammonia, and particulates; OD = 5,520 ppm (100 Btu/lb) (2) Aqueous waste soln of dichloronitrobenzene (20g/l) and 6-7% dissolved solids (100 Btu/lb)	(1) Aqueous (72%) slurry of polyvinyl chloride solids (28%) with traces of vinyl chloride and aliphatic hydrocarbons (1,300 Btu/lb)	(1) 725 lb/hr milled PCB capacitors in fiber drums (<5,000 Btu/lb) (2) Nitrochlorobenzene (95%) wastes plus 5% isomers (9,100 Btu/lb)
Incinerator conditions			
Feed rate (lb/hr)	(1) 46 (2) 53.4	Primary zone: 1600°F (870°C) Secondary zone: 2000°F (1095°C)	(1) 725 (2) 1,025
Temperature	(1) 536°F (280°C) (2) 536°F (280°C) Pressure, 107 atm		(1) Kiln, 2280°F not used Afterburner, 2-30°F (2) Kiln not used afterburner, 2430°F
Residence time	(1) 1.0 hr (2) 1.0 hr	Solids, 2 hr Gases, 2 sec	(1) 3.2 sec (2) 2.3 sec
Incinerator performance			
Stack particulates (mg/m ³)	Further water treatment needed to remove catalyst and residual organics.	71* (HCl, 15)	(1) 35* (2) 14*
Trace metals, µg/m ³	(1) 99.4% of dichloronitrobenzene (2) 99% phenol 66% quinoline	Scrubber water 720 mg HCl/liter	(1) Pb 2.7 (2) None detected
Destruction efficiency (%)	83% of COD	(1) 99.99 (2) 99.99	(1) 99.96 (2) 99.99
Estimated commercial plant size (short tons/hr)	(1) 770,000 (2) 53,000	74,000	(1) 5,500 (2) 5,000
Est. capital investment, adjusted to January 1979 (\$ million)	(1) 11.3 (2) 2.3	8.3	(1) 3.9 (2) 3.0
Operating cost, adjusted to January 1979 (\$/short ton)	(1) (2)		(1) (2)
Labor, \$12.70 man-hr	0.42 2.95	52.5	93.6 54.4
Auxiliary fuel, \$2.60 million Btu	1.00 0.50	185.5	307.0 20.2
Chemicals and utilities	0.45 1.09	31.5	96.3 18.9
Maintenance	0.64 1.95	40.7	71.6 31.8
Capital-related costs	3.27 9.23	223.4	154.2 130.9
12% investment			
Total operating cost	5.78 15.70	533.6	722.7 258.2
Net cost	3.58 [†] 0.30		
	9.36 16.10		

*No organic waste materials detected in scrubber water.

[†]Fuel credit.

[‡]Follow-up treatment.

Source: 447008.

The rotary kiln followed by a secondary combustion chamber or afterburner offers the greatest flexibility for handling both liquid and solid wastes with destruction efficiencies of greater than 99.99%. However, the capital investment for this system (\$600 to \$1,100/annual ton capacity) is the highest of the five systems considered. For those wastes with less than 5,000 Btu combustion heat per lb, auxiliary fuel costs can be appreciable.

The design of direct fired rotary kilns is similar to that for direct heat dryers. Heat efficiencies usually range from 55 to 75% with heat transfer rates of about 2,500 to 6,000 Btu/hr/cu ft (B-1). Heat efficiency can be improved by the use of heat exchangers or recuperators to recover sensible heat from the exhaust gases.

Zimmerman (447076) has described the Kelly-Hoskinson batch incinerator, which ranges from 2 to 12 cu yd capacity. It has a primary combustion chamber that operates at 2200°F (1200°C) and provides secondary fume combustion in the base of the exhaust stack. It operates without precipitators, scrubbers, or grates on combustible wastes and gases which are noncorrosive and nontoxic. Purchase cost ranges from about \$12,000 to \$62,000 (January 1979). Natural gas fuel consumption is between 100,000 and 300,000 Btu/hr.

Combustion

Solid wastes containing less than 2 to 3 lb of water per lb of combustible material can usually be incinerated without auxiliary fuel and possibly with some heat recovery. For example a solid waste containing 52.3 wt% carbon, 6.2% hydrogen, 40.5% oxygen, and 1.0% ash, has a gross heat of combustion of 9,000 Btu/lb. The available net heat from burning 1,000 lb/hr of this material, accompanied by 100 lb/hr of moisture, is as follows:

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	<u>Btu/hr</u>
• Gross heat input (9,000 x 1,000)	9,000,000
• Less evaporation of free water (1,060 x 100)	106,000
• Less evaporation of formed water (0.563 x 1,060 x 1,000)	597,000
• Less losses, assume 80% heat trans. effic. (9.0 x 10 ⁶ x 0.2)	<u>1,800,000</u>
Net heat	6,497,000

This is equivalent to 5,700 lb/hr of saturated steam at 125 psig.

Detailed considerations of the design of municipal waste treatment incinerators have been published by the Research and Education Association (B-13933). Capital investment for a multiple chamber batch incinerator is said to be about \$15,000 to \$40,000 per daily ton of waste capacity. This is exclusive of any combustion gases treatment.

By comparison, costs by Babcock and Wilcox Company (447075, adjusted to January 1979) for a coal fired steam generator are as follows (\$1,000):

	<u>Steam Capacity (lb/hr)</u>		
	<u>50,000</u>	<u>100,000</u>	<u>200,000</u>
Equipment cost			
Boiler, furnace, fans, economizer and firing equipment	675	1,100	2,000
Metering and control inst.	25	30	40
Deaerator and water treatment	60	91	147
Boiler feed pump	<u>5</u>	<u>9</u>	<u>13</u>
Total equipment	765	1,230	2,200
Estimated module cost (f ^M = 3.0)	2,300	3,700	6,600

Assuming a waste sludge feed of 5,000 Btu/lb net heating value (i.e., equivalent to 3.7 lb steam/lb sludge), the above module costs range from \$10,000 to \$15,000 per daily ton of sludge feed.

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Waste Solids Disposal

Land Farming

Land farming has been used in the United States for over 25 years as a means of disposal of refinery sludges. Over the next several years, the quantity of sludge disposed of by this method could double or triple (447079). Land farming is applicable to biodegradable hydrocarbon sludges which are nontoxic, nonreactive, and nonvolatile and have flash points below 140°F (60°C) (447088). These are principally oil refinery wastes such as API separator bottoms, treating clays, and tank and separator cleanings.

Land farming consists of spreading the hydrocarbon waste over bare soil in layers up to several inches. The land is then cultivated at regular intervals to provide closer contact between the waste and the soil. Bacteria convert the waste to humus, which may actually improve the original land's ability to sustain vegetation. Typical application rates for oil refinery wastes range from about 200 to 600 barrels/year/acre (30 to 90 tons/year/acre) (447017).

Regulations for the selection and operation of land farming sites (447088) stipulate that land farms be located on stable, level land at least 5 feet above the historic high water table, with no possibility of migration to livestock or public water supplies. Wastes must not be applied when the soil is saturated with water or when its temperature is less than freezing. The pH of the soil should be between 7 and 9 to prevent leaching of heavy metals and to encourage bacterial or algae growth. The use of supplemental nitrogen and phosphorus may also be needed to assist the growth of microorganisms. The site must be monitored to detect any migration of waste impurities.

A typical cost for land farming operations, exclusive of land, is reported to be about \$16.50 per ton of waste (447088, February 1979).

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Stacking

Waste stacking is applicable mainly to gypsum from wet process phosphoric acid plants or from power plant flue gas scrubbers (447091). To start the stack, an area is enclosed by an earthen dike, and the aqueous slurry is pumped inside. The gypsum settles and the water overflows and is recycled or neutralized. As the gypsum settles and consolidates, it is used to raise the retaining wall for the gypsum pond as shown in Figure 4.14.

Gypsum has a sedimented density of about 100 lb/cu ft; therefore, one acre foot has a storage capability of 2,000 tons. Thus, a 1,000 tons/day wet process phosphoric acid plant producing 4,500 tons/day of gypsum that is stacked to a depth of 20 ft would require 40 new acres every year.

Regulations for stacking as well as those for sanitary disposal (discussed next) are generally similar to those for land farming (447088).

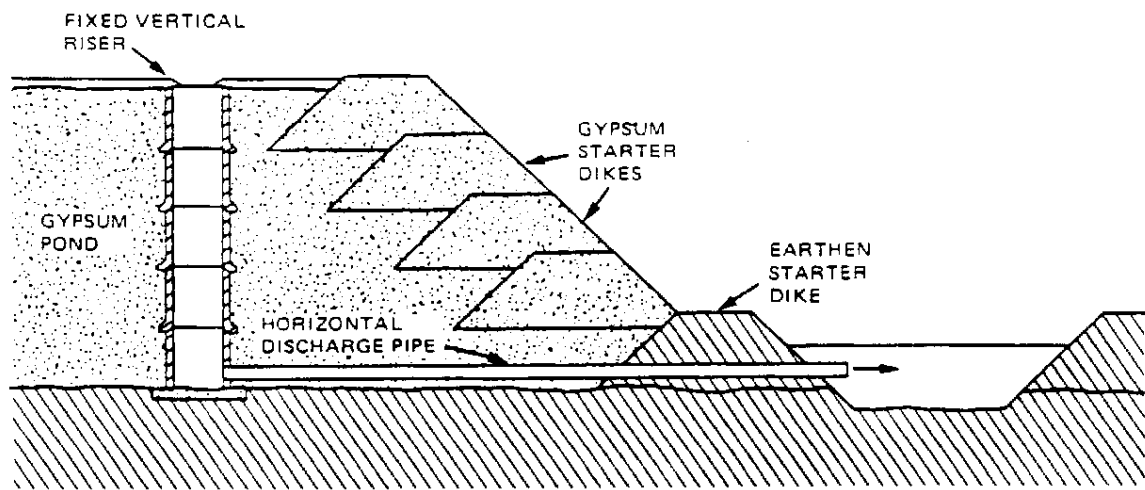
Disposal costs are principally land costs. Added to this is the cost of a dragline or mechanical shovel for building dikes and possibly a rubber or plastic liner to prevent contamination of ground water sources.

Sanitary Landfill

Sanitary landfill is the placing of compacted wastes into earth cells which are later covered with soil. The wastes must be inert to begin with or be capable of microbial conversion to harmless compounds. The landfill should be designed to prevent leaching from the fill and contamination of surrounding streams. This may be accomplished by providing drainage from the fill to a collection and treatment point or by enclosing the fill in an impervious liner (447090).

Figure 4.14

STACKING PROCEDURE FOR WASTE GYPSUM



Source: 447091.

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Disposal costs for landfill operations, where cover material is available on site, are estimated to range from about \$10/ton at 20 tons per day, to \$4.5 at 50 tons and \$2.5 at 200 tons per day (383522, adjusted to January 1979).

Hazardous-Waste Landfill

Hazardous wastes are those materials which pose substantial present or potential hazard to human health or living organisms because they are lethal, nondegradable, persistent in nature, or cause detrimental cumulative effects (447007). These include toxic, radioactive, flammable, and explosive materials.

Numerous restrictions apply to the selection of a hazardous-waste disposal site, permits are necessary for dumping wastes at these sites, and long term monitoring is required to detect any leakage from the containment area (447015). Finally, severe penalties are provided for noncompliance with these regulations.

The complexity of regulations and the costs of compliance tend to restrict ownership of hazardous-waste disposal facilities to those companies with appreciable quantities of hazardous wastes or to companies specializing in services.

A 1977 EPA publication (447092) lists over 100 hazardous-waste management facilities across the United States. These include service operations for incineration, deep-welling, and land disposal of hazardous wastes as well as for solvent reclaiming and metal reprocessing. A resume of the background, capabilities, and service charges for many of these operations is contained in another EPA publication (447078).

Secure landfill disposal costs are in the range of \$20 to \$60/short ton. The estimated costs for a 20 year operation of a hazardous-waste facility (4,000 tons/yr) owned and operated by Union Carbide are as follows (447007, adjusted to January 1979):

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Study and design	\$ 114,000
Land	147,000
Equipment	367,000
Operating costs (20 years)	<u>4,242,000</u>
Total	\$4,870,000 (\$61/ton)

An industry source estimates that pending regulations and inflation will double hazardous-waste landfill disposal costs by 1985.

Other Disposal Methods

Ten years ago the oceans were the recipients of large volumes of solid industrial wastes (447029). However, increasing regulation is gradually reducing the quantity and kind of industrial wastes which may be dumped in the oceans (419299). In the United States, EPA regulations are expected to terminate the discharge of waste to coastal waters by the end of 1981 (447082). In Western Europe a 95% reduction of ocean dumped wastes by 1985 is proposed.

Another alternative for disposing of solid waste is to slurry it in water and inject it deep into the ground where it is isolated from potable-water aquifers by impervious and fracture-resistant strata of shale, limestone, or dolomite (447087). Currently, there are approximately 380 deep welling sites in the United States. By the end of 1979, all such sites in the United States are expected to come under EPA regulations for inspection, monitoring, record keeping, and reporting. Thus, deep-welling is likely to continue for some time as a waste disposal method in suitable locations but with increased control and regulation.

The average investment for a deep well--including casing, surface facilities, pumps, etc.--is about \$75 to \$90 per foot (447087, adjusted to January 1979). Maintenance costs for an injection rate of 6 million gal/mo (140 gal/min) into a 10,000 ft well are reported to run about \$60,000/yr and energy at 2c/gal (447087).

5 COST CALCULATIONS FOR WASTE TREATMENT MODULES

There are a number of methods for the development of preliminary capital cost estimates for chemical or waste treatment processes. The Hirsch and Glazier method (289) totals the purchase costs of all the major equipment. This total is multiplied by given factors--depending on the amount and type of equipment--to obtain the battery limits investment for the process. This figure represents the capital cost of the complete, ready-to-operate processing unit. It includes foundations, piping, instruments, housing, erection costs, and contractors fee, but excludes land, utilities, feed and product storage, and start-up costs. This method has been adapted to PEP estimating procedures.

The Miller method (10039) for estimating the cost of a chemical plant totals the costs of major equipment items and then adds percentages for the foundation, erection, piping, insulation, electrical work, and building requirements. These percentages are selected on the basis of the type of process and the average value of the major equipment items. They allow the estimator some leeway in deciding whether each requirement is minimal, moderate, or extensive. This method, has also been adapted to the PEP computer program.

A third method (used by Guthrie) estimates the installed or modular cost for individual processing operations (distillation, drying, etc.) by multiplying the purchase cost of the equipment by factors for installation labor and materials. The battery limits cost is the sum of the modular values plus a percentage for indirect costs. This method requires slightly more time and effort than the others but it correlates installation costs with specific operations better than the others do.

Waste treatment processing consists of only a few standard chemical and physical operations. Thus, the use of process modules is possibly the simplest means for estimating the investment for treating a given waste flow.

Guthrie (B-13926, 76481) has applied the modular approach to the evaluation of chemical process capital investments. In Guthrie's method the costs of installation materials (M) and labor (L) are estimated as fractions of the purchase cost of the equipment (E). Thus, the direct or installed cost of an item of equipment is $E + M + L$. This sum is then multiplied by an indirect factor (I) (which depends on the size of the direct cost) to obtain the modular cost of that equipment item, as illustrated schematically in Figure 5.1. Excluded from the modular cost is the cost of land, site preparation, contractor's fee, and contingencies.

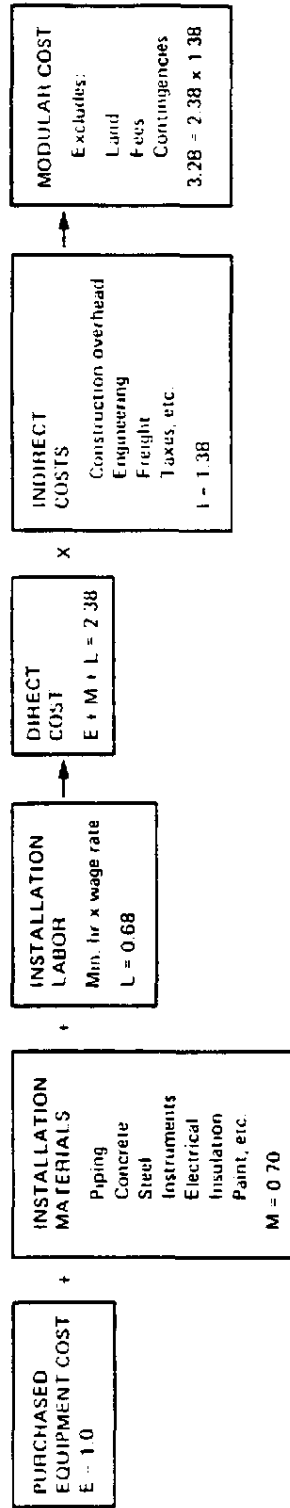
Guthrie supplies M and L factors for specific items of chemical equipment in various sizes. Adjustment factors are supplied for alternative materials of construction and for locations other than the U.S. Gulf Coast. The effects of inflation from the base year to the present are handled by applying the appropriate cost indices to both materials cost and labor cost. A disadvantage of the Guthrie method is that L and M factors are not available for all types of process equipment--particularly some of the equipment used in waste treatment--and the procedure to develop them is complex.

Icarus Corporation (447001, 447056, 447057) has applied a modular cost estimating technique to waste treatment systems. The Icarus method is much more detailed than the Guthrie method. Equipment costs are obtained, together with the cost of materials for installation. Allowance is then made for labor cost and productivity, to obtain a direct cost. Adding construction overhead and engineering costs results in a base module cost comparable with that for chemical equipment by the Guthrie procedure. Icarus also provides location, design,

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Figure 5.1

GUTHRIE METHOD FOR MODULAR COST ESTIMATES



Sources: B-13926, 76481.

and material factors for adjusting the module costs. It has also been adapted to a computer program. However, this program has several disadvantages:

- The amount of detail and effort necessary to estimate module costs is more appropriate to an engineering design than to a preliminary estimate.
- There is no separation of the modular cost components to permit user modifications or to enable users to derive their own module costs for special equipment.

We have developed a simple and quick procedure for estimating modular costs for waste treatment operations which is independent of both Guthrie and Icarus modules.

Capital Cost Methods Used in this Study

The modular costs developed by both Icarus and Guthrie are generally 1.8 to 5.0 times the purchase price of the equipment. This is also true for the PEPCOST estimates of battery limits investment. Equipment items with "little" requirement for (A) foundations and support, (B) connecting piping, (C) electrical connections, insulation, and instrumentation, and (D) enclosure are close to the lower limit, while those with "extensive" amounts of these additions tend toward the upper limit. If, as shown in Table 5.1, we arbitrarily assign values of 0.2, 0.6, and 1.0 to represent "little", "some", and "extensive" needs for each of the four categories of installation activity, we have a quick way of estimating modular costs. For example, a tank and pump erected outside on the ground, with only inlet and outlet pipes, would have a module cost factor (f_M) = $1 + 0.2 + 0.2 + 0.2 + 0.2 = 1.8$. A distillation operation erected indoors on steel supports, with inter-connecting piping to condensers and reboiler and with extensive instrumentation and insulation, would have an $f_M = 1 + 1 + 1 + 1 + 1 = 5$.

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Table 5.1

SRI MODULE INVESTMENT ESTIMATION FACTORS

	<u>Installation Requirement</u>		
	<u>Little</u>	<u>Some</u>	<u>Extensive</u>
Base factor	1.0	1.0	1.0
(A) Foundations, steel supports, and field labor	0.2	0.6	1.0
(B) Connecting piping	0.2	0.6	1.0
(C) Insulation, electrical connections, and instruments	0.2	0.6	1.0
(D) Building or enclosure	<u>0.2</u>	<u>0.6</u>	<u>1.0</u>
Totals	1.8	3.4	5.0

Notes: (1) Module cost factor (f_M) = $1 + A + B + C + D$.

(2) Module cost = purchased equipment cost (f.o.b.) $\times f_M$.

Table 5.2 compares Icarus and Guthrie module costs with those estimated by SRI's simplified procedure. While considerable variation occurs in the cost of similar equipment items by the three modular estimating procedures, the equipment cost totals are very close. For example, the estimate for a 10,000 gal vertical cylindrical stainless steel tank is \$108,000 by the SRI method and \$190,000 by the Guthrie. This is equal to a plus or minus mean deviation of $(190 - 108)/(190 + 108) \times 100 = 27.5\%$. However, the totals for the nine modules listed show a mean deviation of only $(1,872 - 1,703)/(1,872 + 1,703) \times 100 = 4.7\%$. Thus, for a multimodule treatment system, the individual deviations appear to counteract one another. Also the modules developed above appear to offer sufficient accuracy for an approximate cost estimation.

Table S.2

COMPARISON OF CHEMICAL EQUIPMENT MODULE COSTS ESTIMATED BY DIFFERENT METHODS

Basis: PEP Cost Index = 290
Time = January 1979

Equipment Description	Icarus Module Cost* (\$)	Guthrie		SRI		Module Factor	Module Cost (\$)
		Equipment Purchase Cost (\$)	Module Factor	Equipment Purchase Cost (\$)	Module Factor		
Air cooled exchanger 500 sq ft Steel tubes	45,000	16,400	2.17	35,500	2.2		32,000
Column, valve trays 5 ft dia. x 30 ft high 15 trays Carbon steel	165,000	72,000	3.05	220,000	4.2		200,000
Compressor, centrifugal 1,000 hp Turbine drive	700,000	320,000	2.15	690,000	2.6		890,000
Furnace, cylindrical Carbon steel 10 million Btu/hr	250,000	82,000	2.19	180,000	3.4		255,000
Heat exchanger, fixed tube 1,000 sq ft 100 psi Carbon steel	58,500	14,300	3.17	45,000	4.2		40,700
Pump and driver, centrifugal 100 gpm 70 ft head Iron	10,900	1,950	3.30	6,400	3.8		7,600
Tank, horizontal, cylindrical 10,000 gal Carbon steel	47,000	15,000	3.05	46,000	2.2		31,000
Tank, vertical, cylindrical 10,000 gal Stainless steel	150,000	45,700	4.16	190,000	1.8		108,000
Thickener, 100 ft dia. 7,800 sq. ft.	390,000	—	—	290,000†	2.2		307,700
Totals	1,816,400			1,702,900			1,872,000

*Equipment purchase cost and module factors are not readily separable from the Icarus Corporation module cost.

†This figure was derived from the Cost Engineering Quarterly in order to complete the comparative column.

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Operating Costs

Operating costs for waste treatment--like those for chemical processing--are a function of the following three variables:

<u>Variable</u>	<u>Dependent Operating Costs</u>
Capital cost	Maintenance, taxes, and insurance, amortization, return on investment.
Feed or production rate	Process materials, utilities.
Process complexity	Labor (operators/shift), control analysts, overhead, supplies.

G&A (administration), sales, and research costs, and working capital interest, which are usually included in chemical plant operating costs, are believed to be small enough to be neglected for most waste treatment systems.

Capital-related charges, maintenance costs excepted, are normally taken as a predetermined fixed percentage of the capital investment. PEPCOST customarily uses 2% for taxes and insurance, 10% for amortization, and 25% for return on investment. The maintenance percentage depends upon the nature of the equipment and the stream being processed. Table 5.3 suggests a procedure for estimating annual module maintenance cost as a percentage of the module investment. Thus, a mixing tank or system handling noncorrosive liquid with some agitation and connected to inlet and outlet pumps would have a percentage maintenance = $0 + 0 + 1 + 1 + 0 = 2\%$. A filter or centrifuge processing a sulfuric acid slurry would have a figure of 7 or 8%.

Other operating costs which are a function of feed rate or process complexity are specific to each treatment operation and no generalized correlations are possible. Thus, the applicable process materials and utility requirements for each waste treatment operation is listed on the same page as the module cost. Where the labor requirement (operators/shift) is shown as a range (e.g., 0.2 to 0.5 operator/shift), the lower figure at the low end of the waste stream flow rate and the upper figure at the high end.

Module Cost Curves

We have derived module capital costs and maintenance percentages from published or quoted equipment prices and modular cost factors (f_M) as described above. For some specialized equipment--e.g., ozone generators, and electrodialysis or reverse osmosis cells--we used published installed capital and operating cost data directly for the modular costs.

These costs apply to a point in time of January 1, 1979 and a PEP Cost Index of 290. Cost curves have, where possible, been based on waste stream flow rates to enable direct reading of the modular cost. Where these costs are given as a function of equipment size, descriptive information in Section 4 of this study will enable a conversion from size to waste stream flow rate.

In instances where the desired module cost curve and operation table are not available, the procedures outlined above will enable the interested user to construct them.

Table 5.3

SRI MODULE MAINTENANCE COST ESTIMATION FACTORS

Conditions Contributing to the Cost of Maintenance	Annual Maintenance Cost (% of module cost)		
	None	Some	Appreciable
(A) Corrosivity, special const. materials	0	1	2
(B) Temperature above normal	0	1	2
(C) Power usage and moving parts	0	1	2
(D) Connecting equipment	0	1	2
(E) Solids handling, abrasion	<u>0</u>	<u>1</u>	<u>2</u>
Totals	0	5	10

Note: Annual maintenance cost (M_A) = (A + B + C + D + E) x module cost

The module capital cost curves and operation tables we developed are shown in Figures 5.2 through 5.53, as follows:

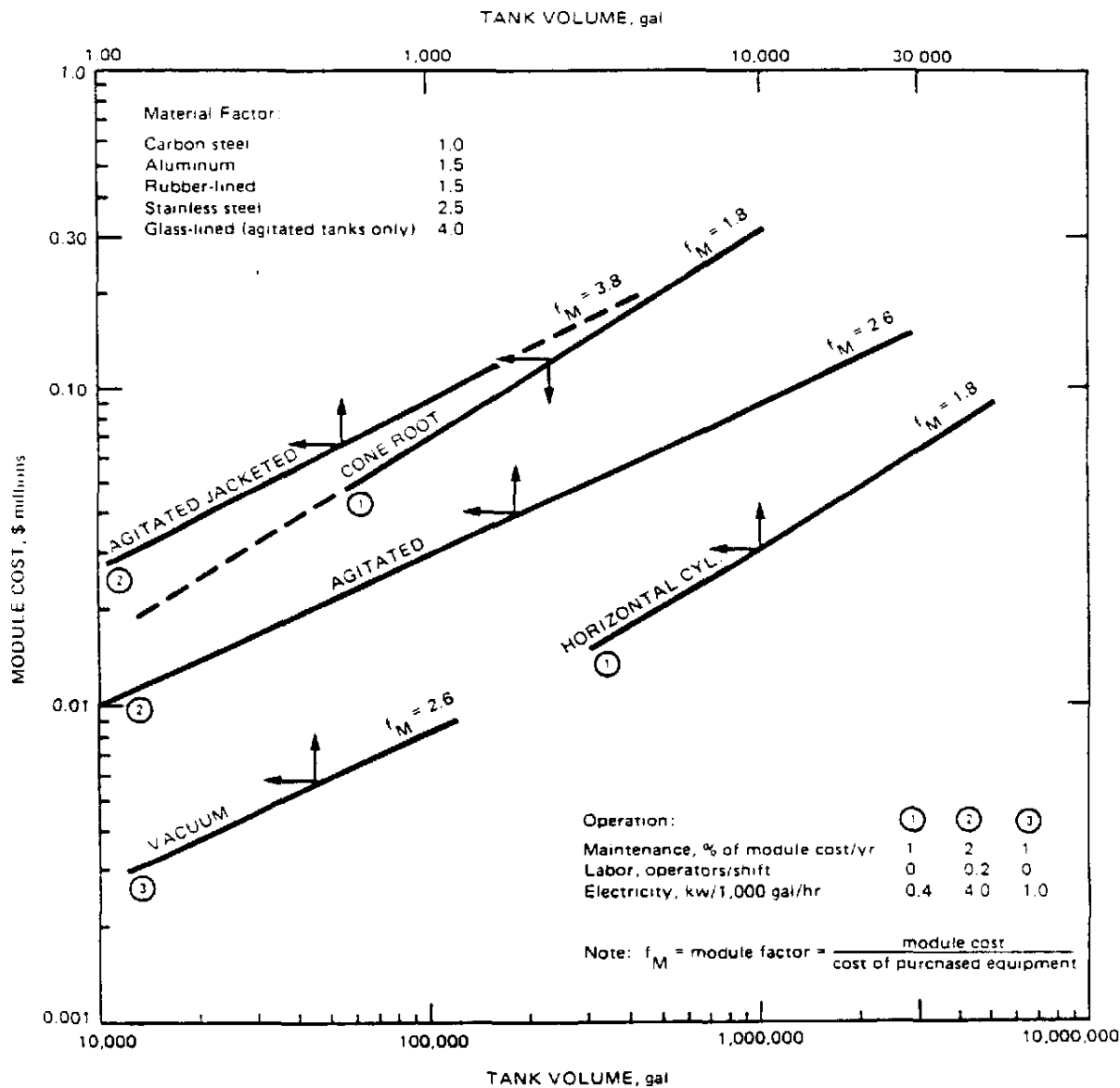
	<u>Figures</u>
Waste Stream	
Aqueous	5.2- 5.31
Gaseous	5.32-5.44
Solid	5.45-5.53

The application of these modules to the estimation of capital and operating costs for the treatment of chemical industry wastes is demonstrated in Section 6.

MCD 000016510

Figure 5.2

MODULE COST: TANKS



MCD 000016511

Figure 5.3

MODULE COST: THICKENER, CLARIFIER

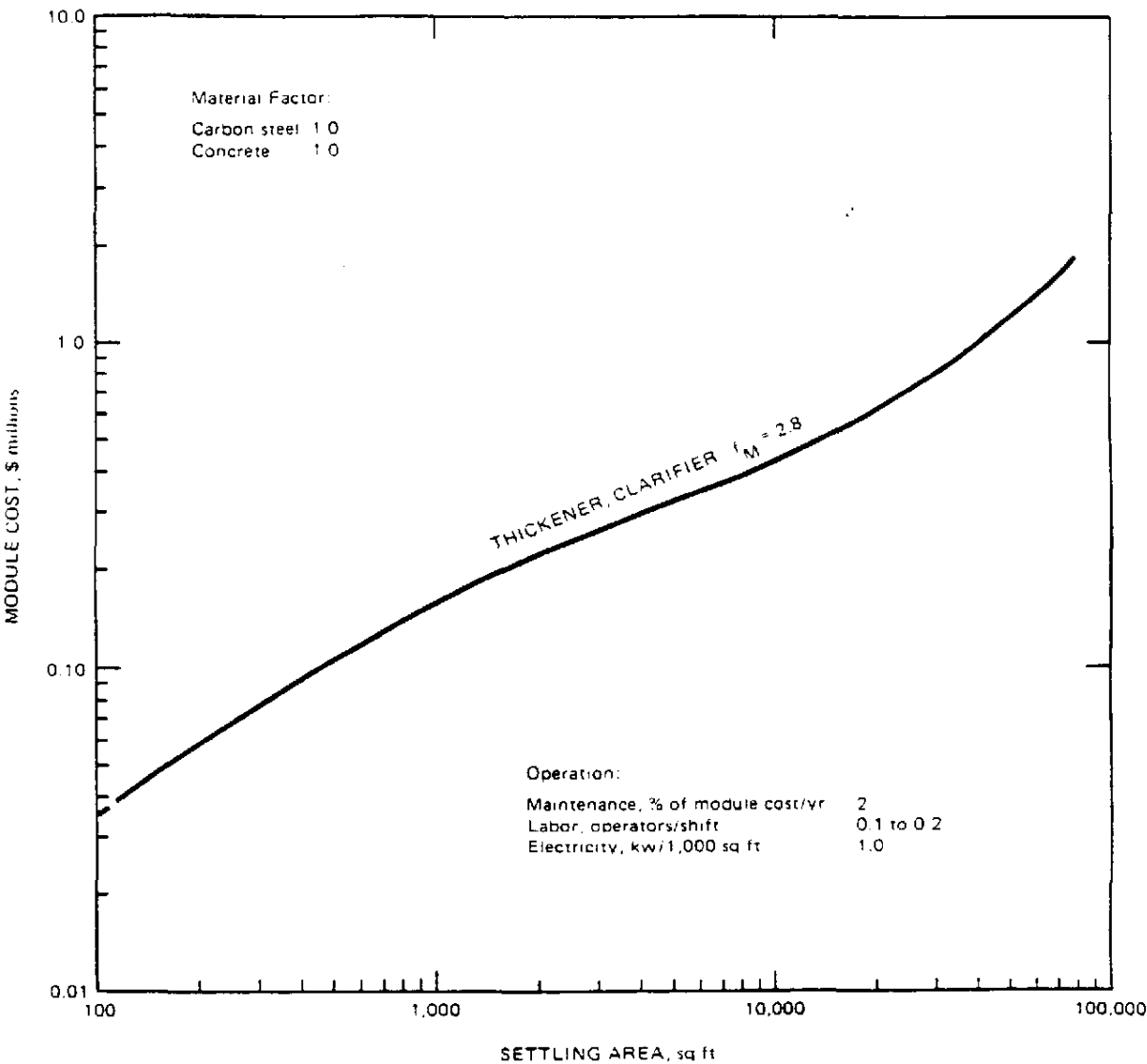
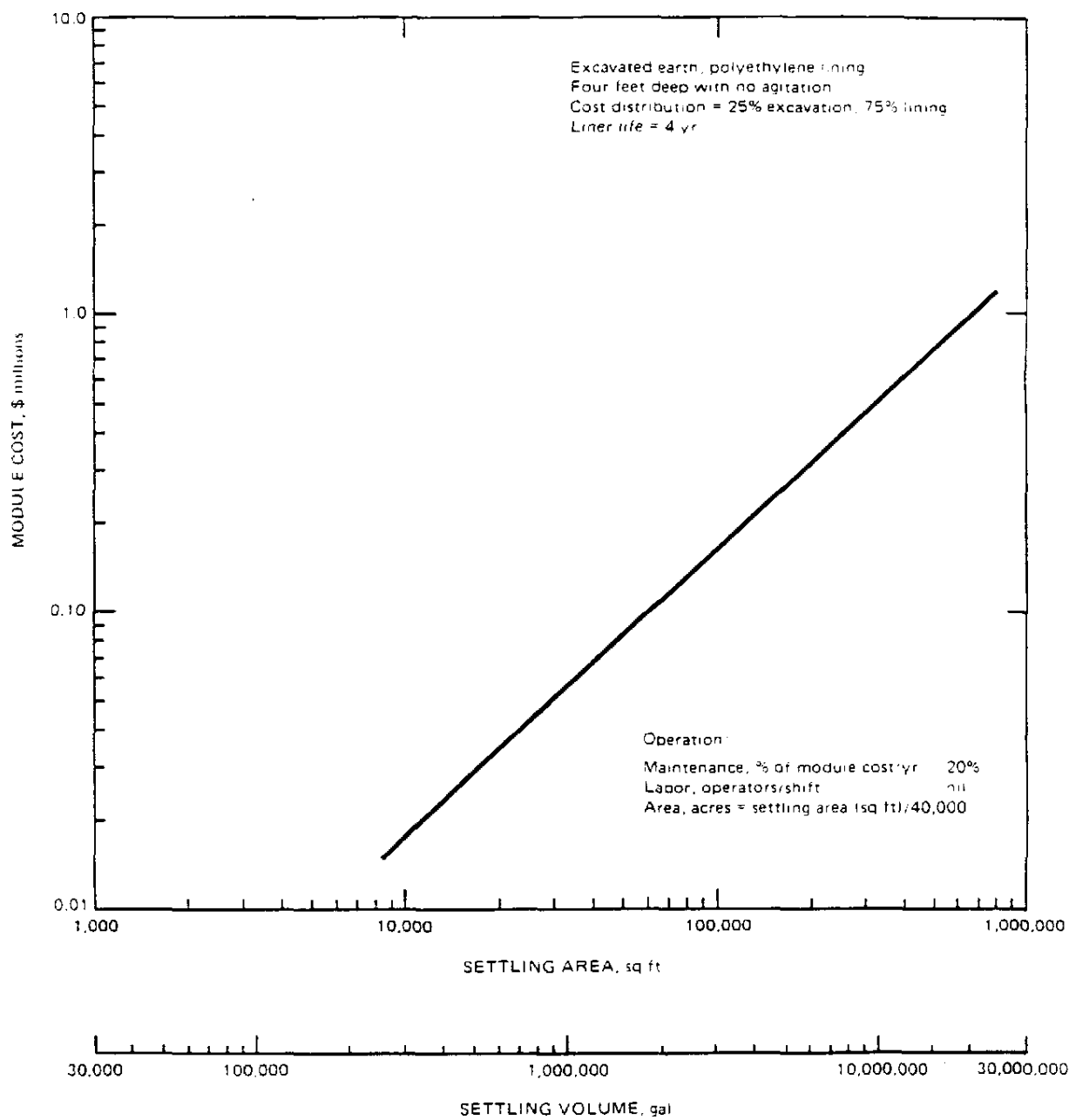


Figure 5.4

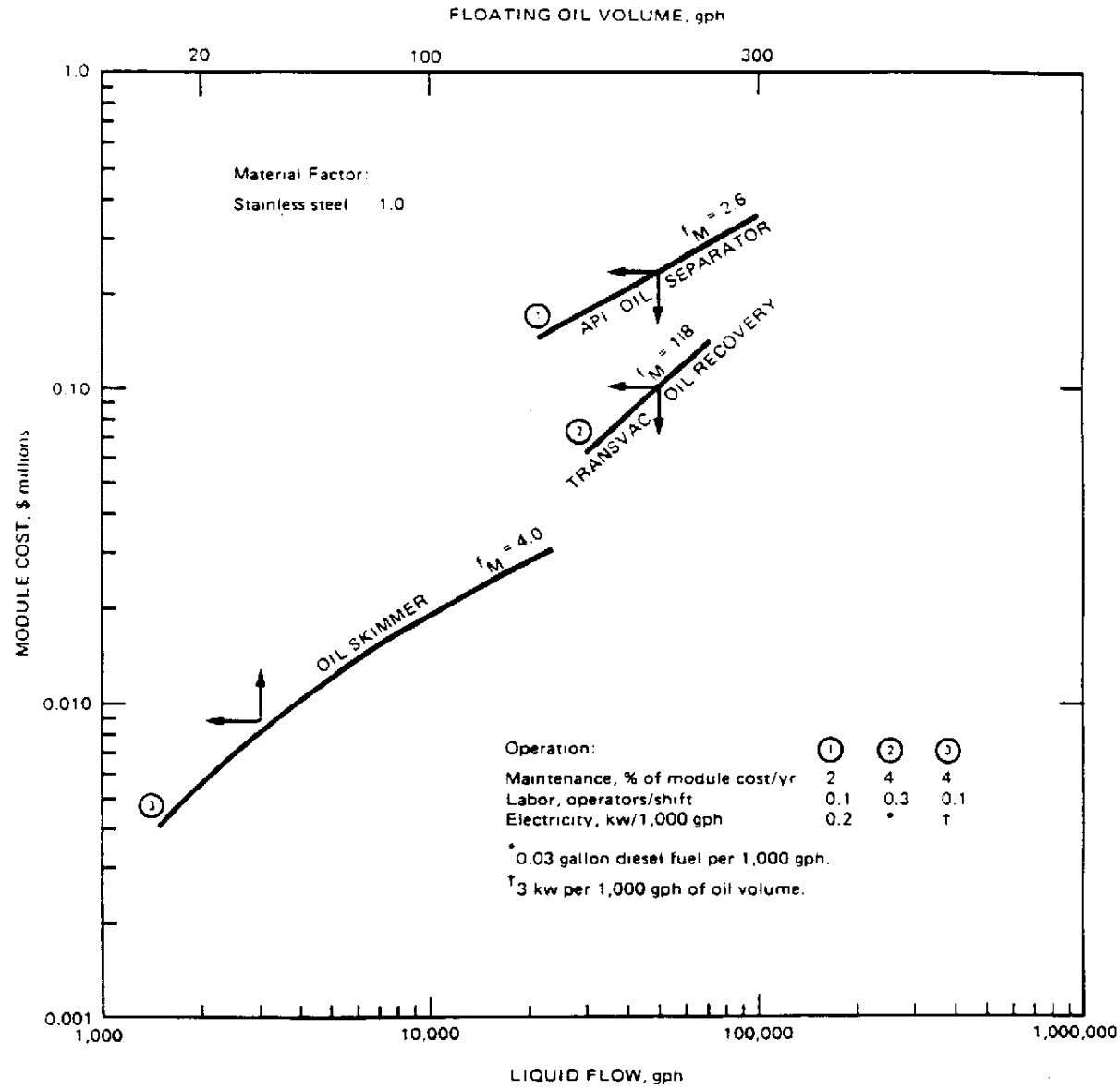
MODULE COST: SETTLING LAGOON



MCD 000016513

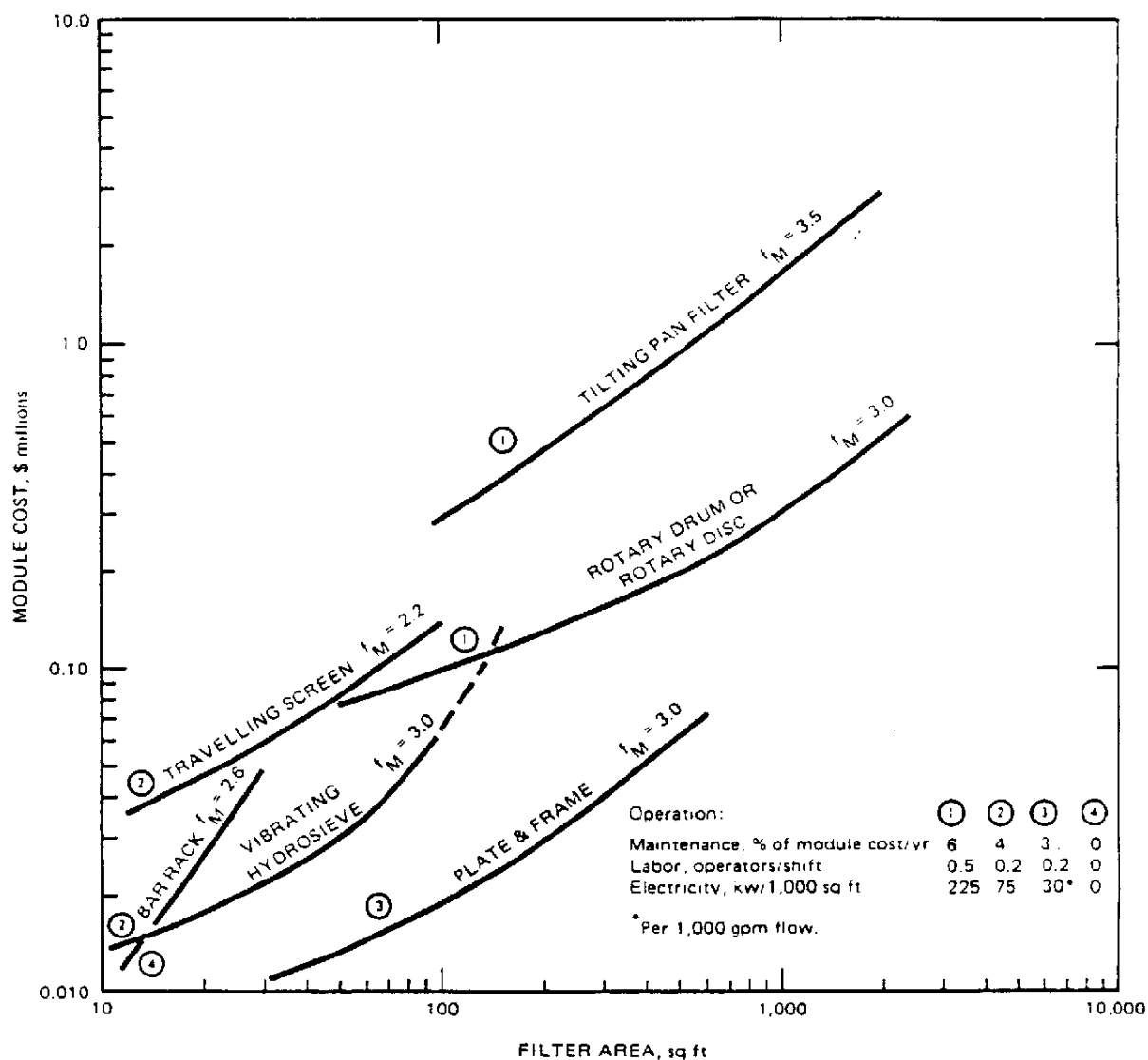
Figure 5.5

MODULE COST: OIL SEPARATORS



MCD 000016514

Figure 5.6
MODULE COST: FILTERS



MCD 000016515

Figure 5.7

MODULE COST: CENTRIFUGES

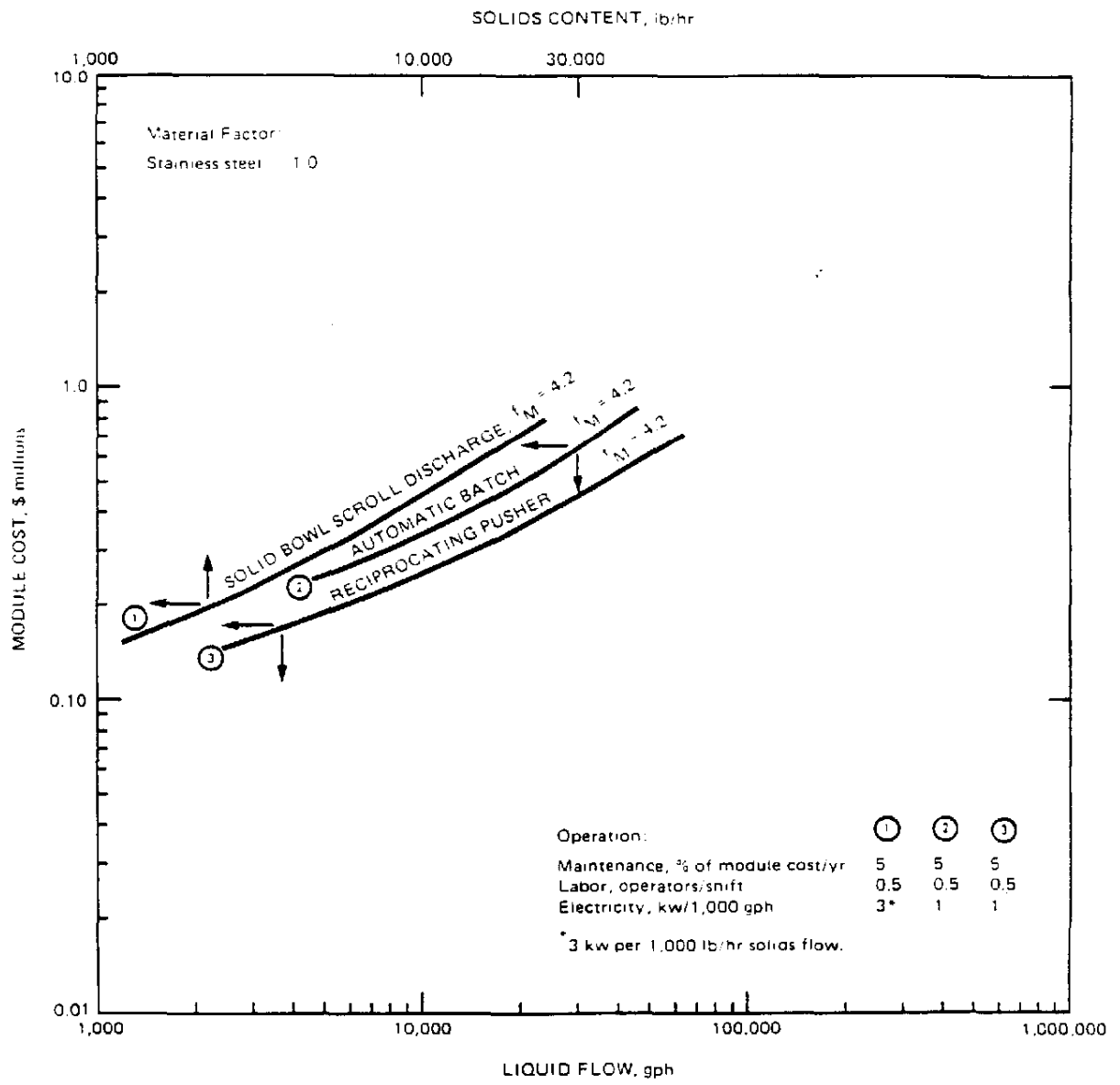
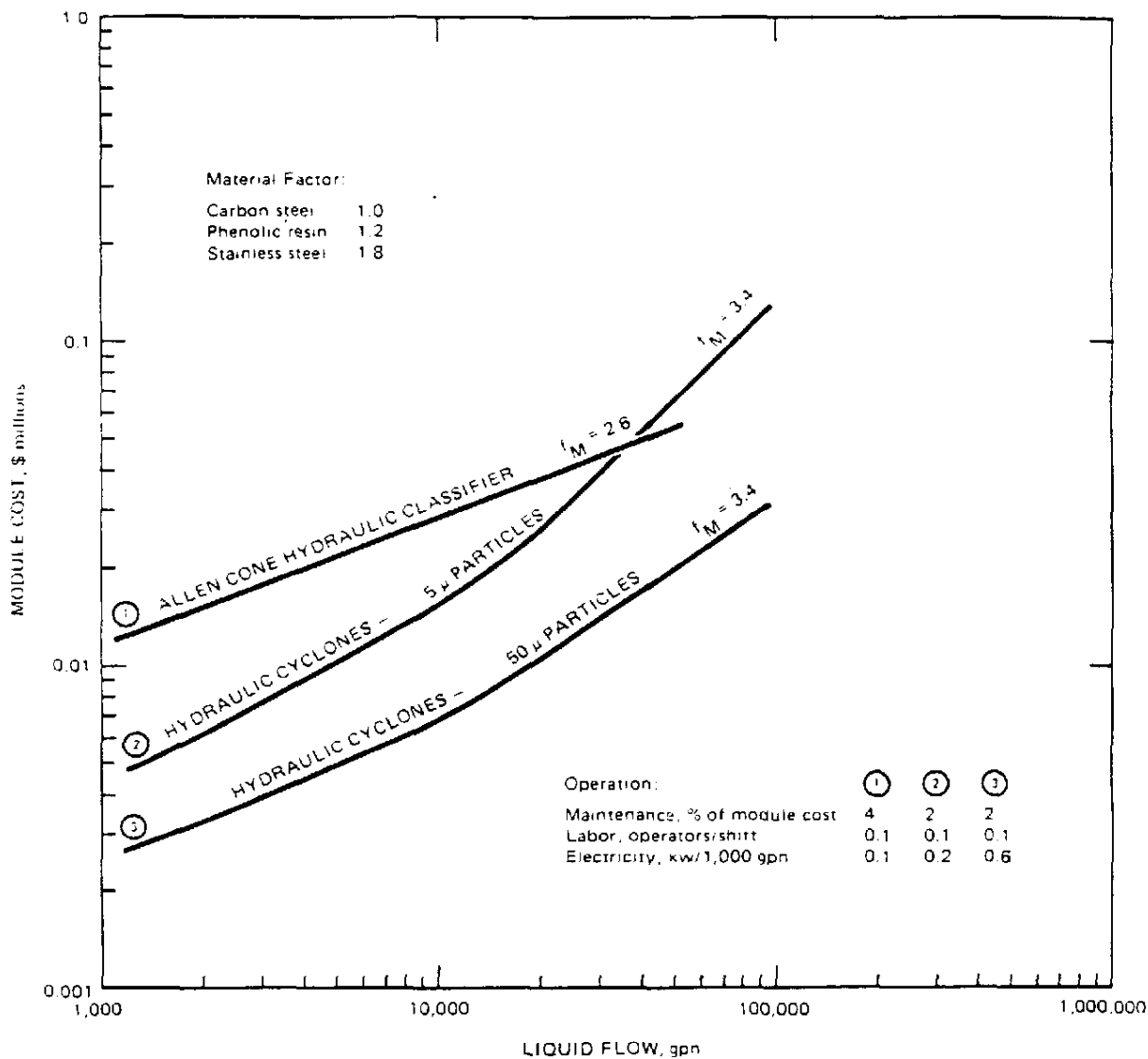


Figure 5.8

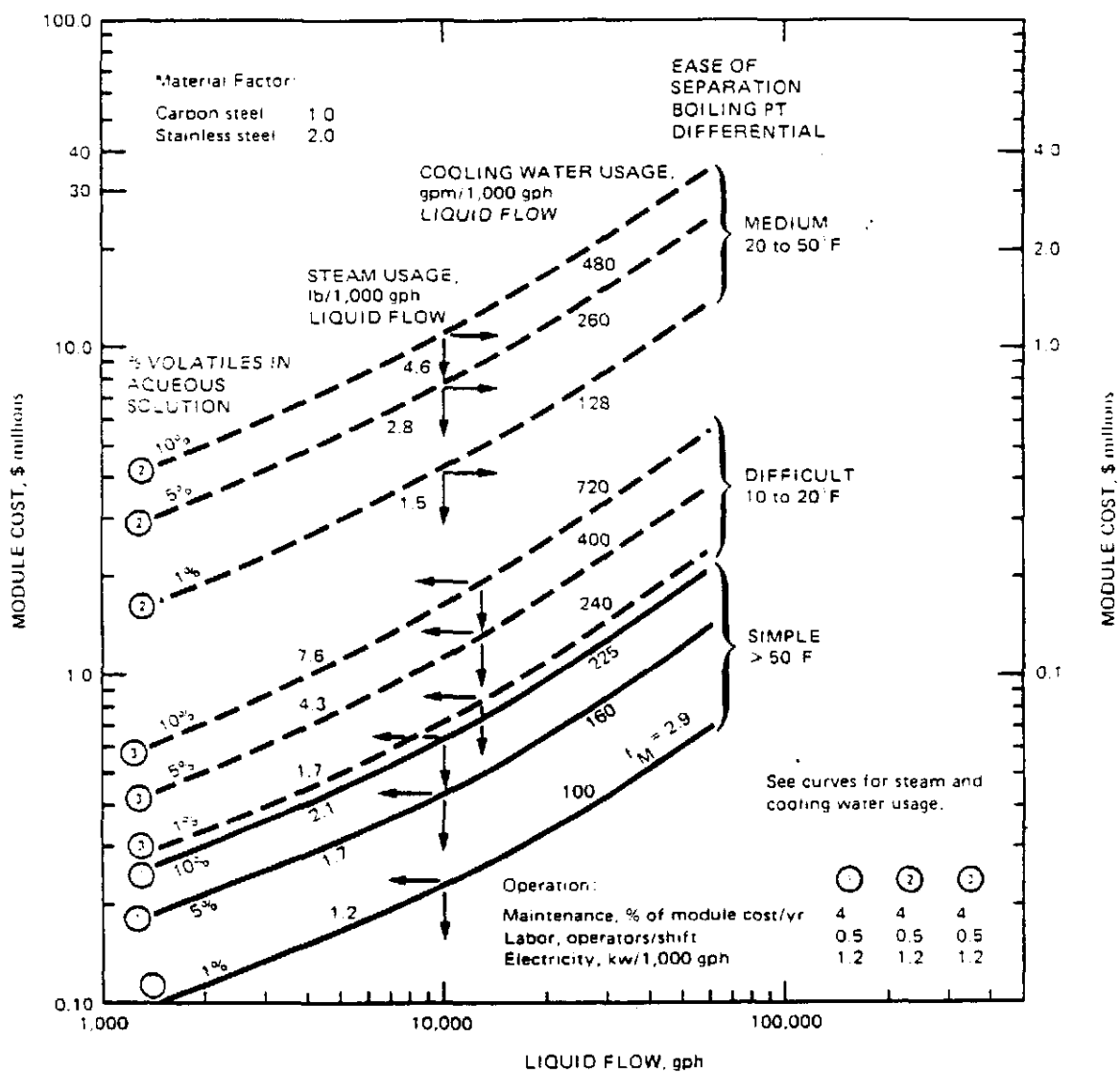
MODULE COST: HYDRAULIC CYCLONES



MOB 000016b17

Figure 5.9

MODULE COST: DISTILLATION SYSTEM



MCD 000016518

Figure 5.10

MODULE COST: EVAPORATORS

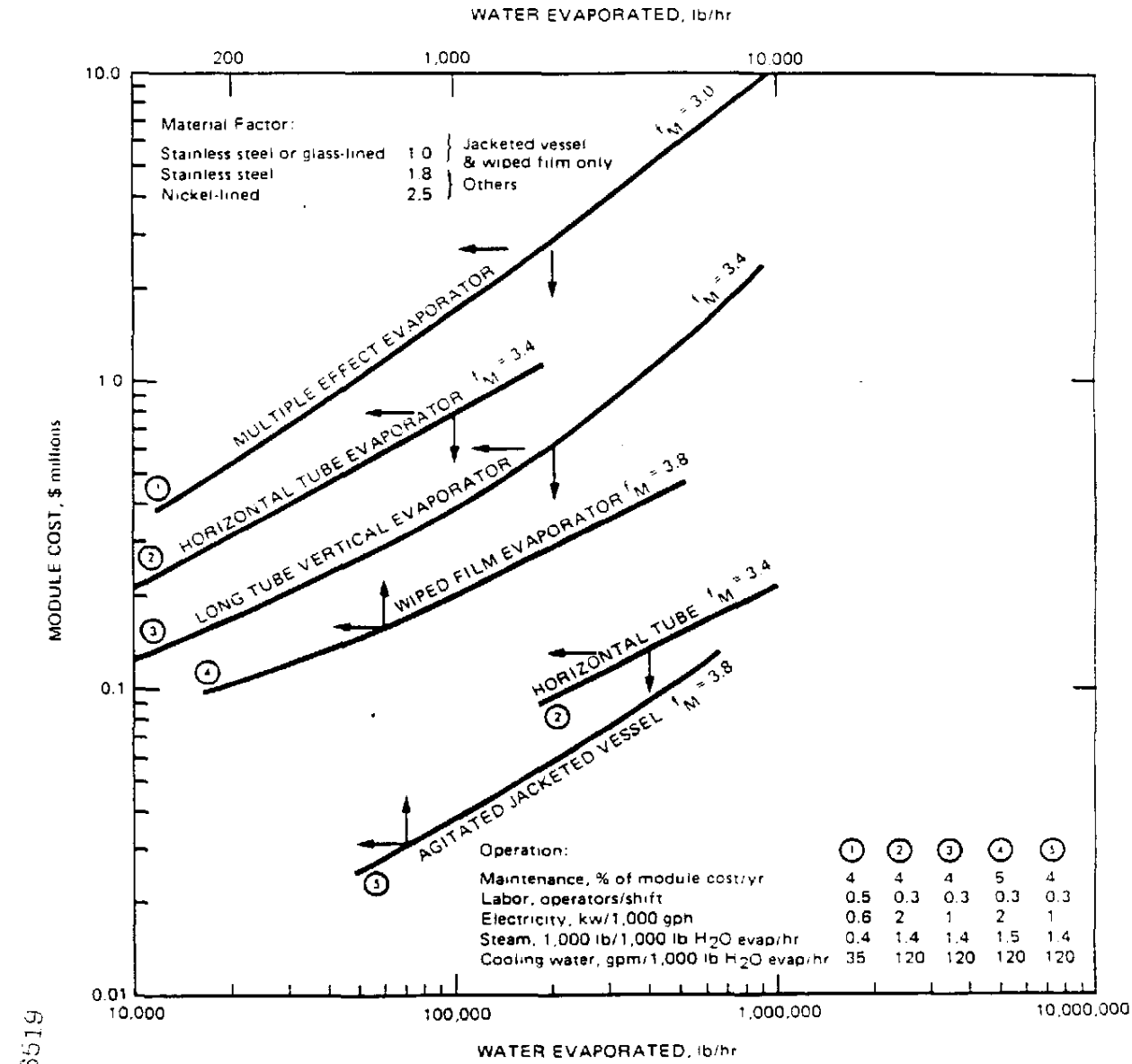
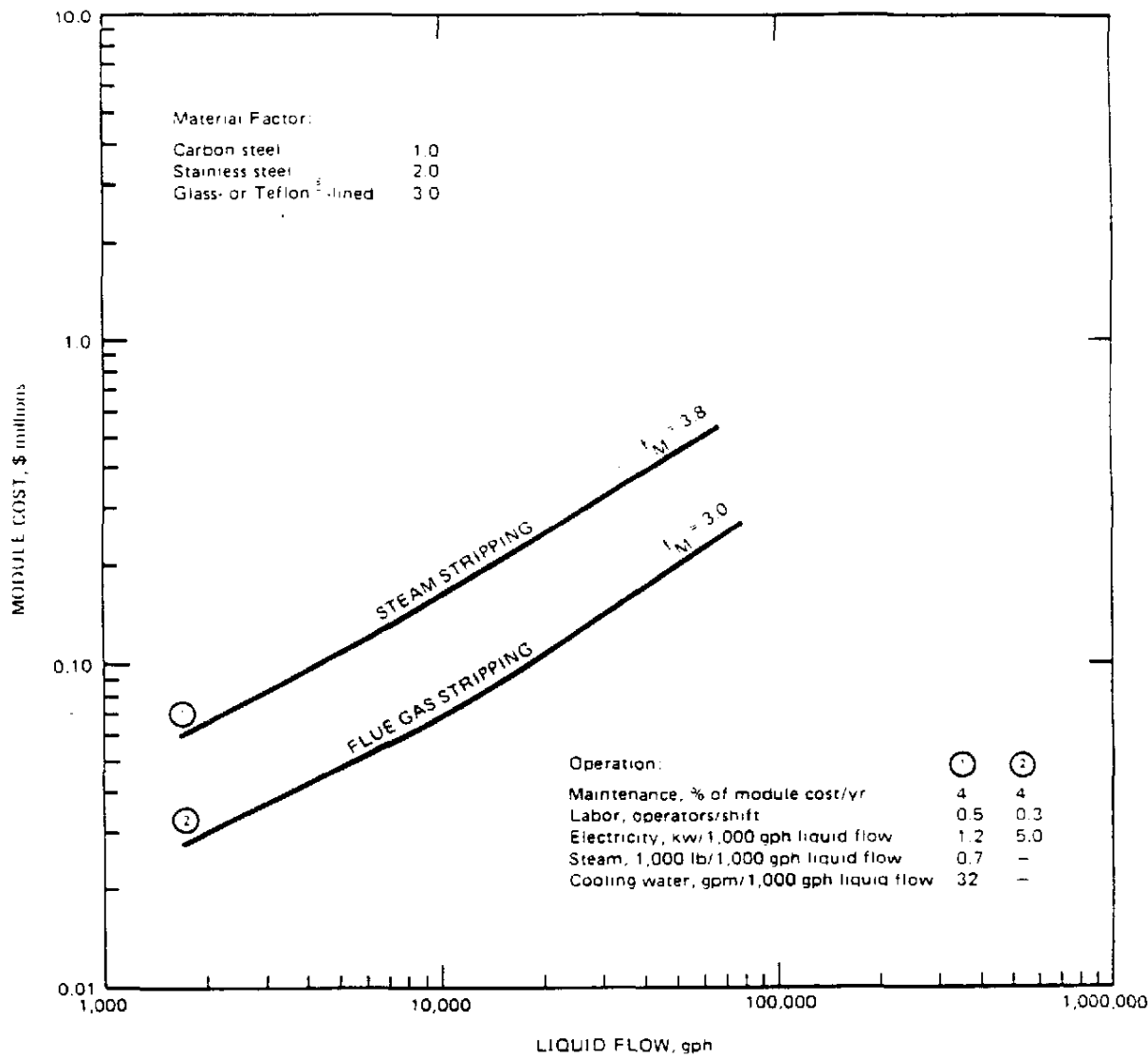


Figure 5.11

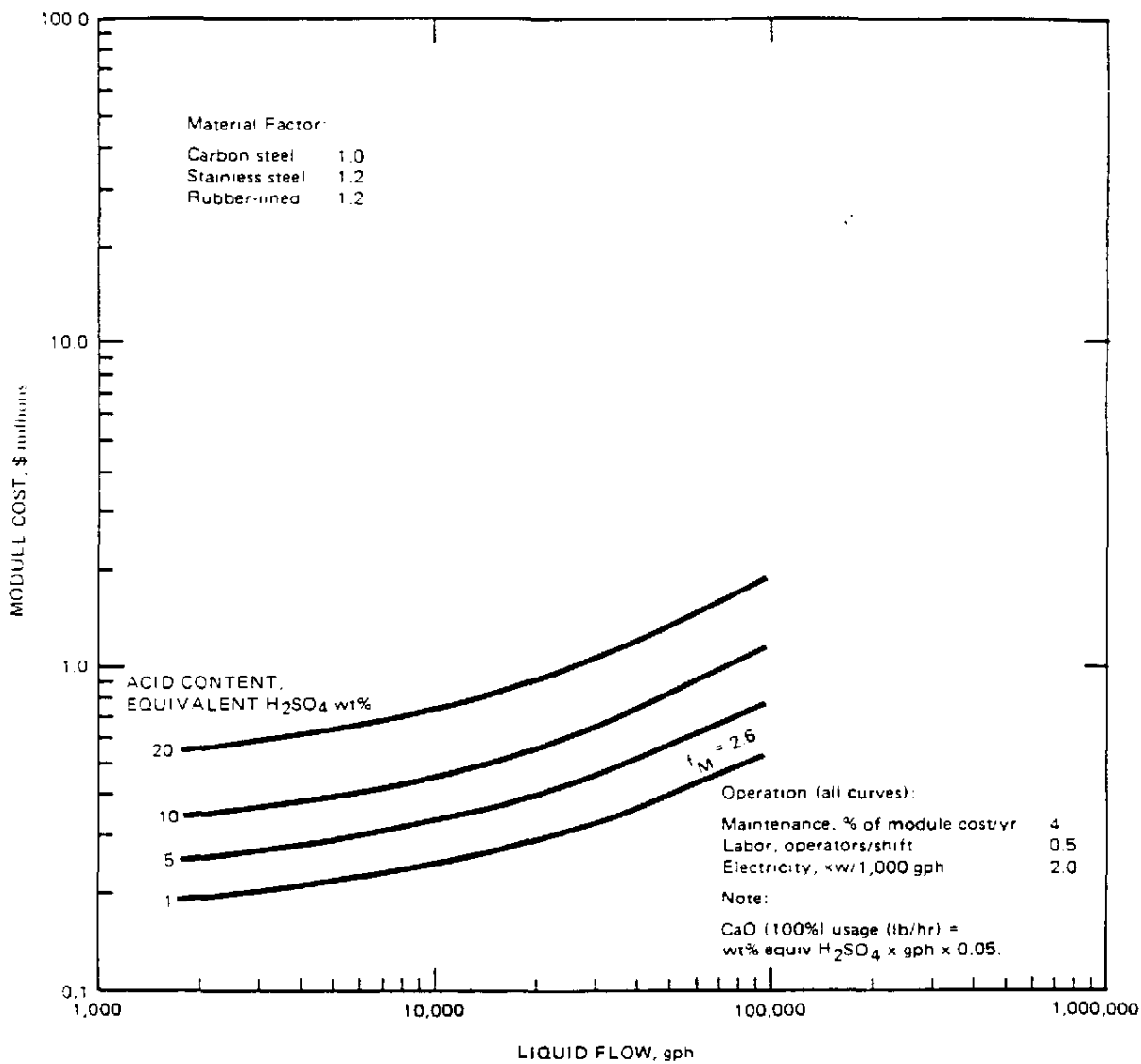
MODULE COST: STRIPPER, STEAM OR FLUE GAS



MCD 000016520

Figure 5.12

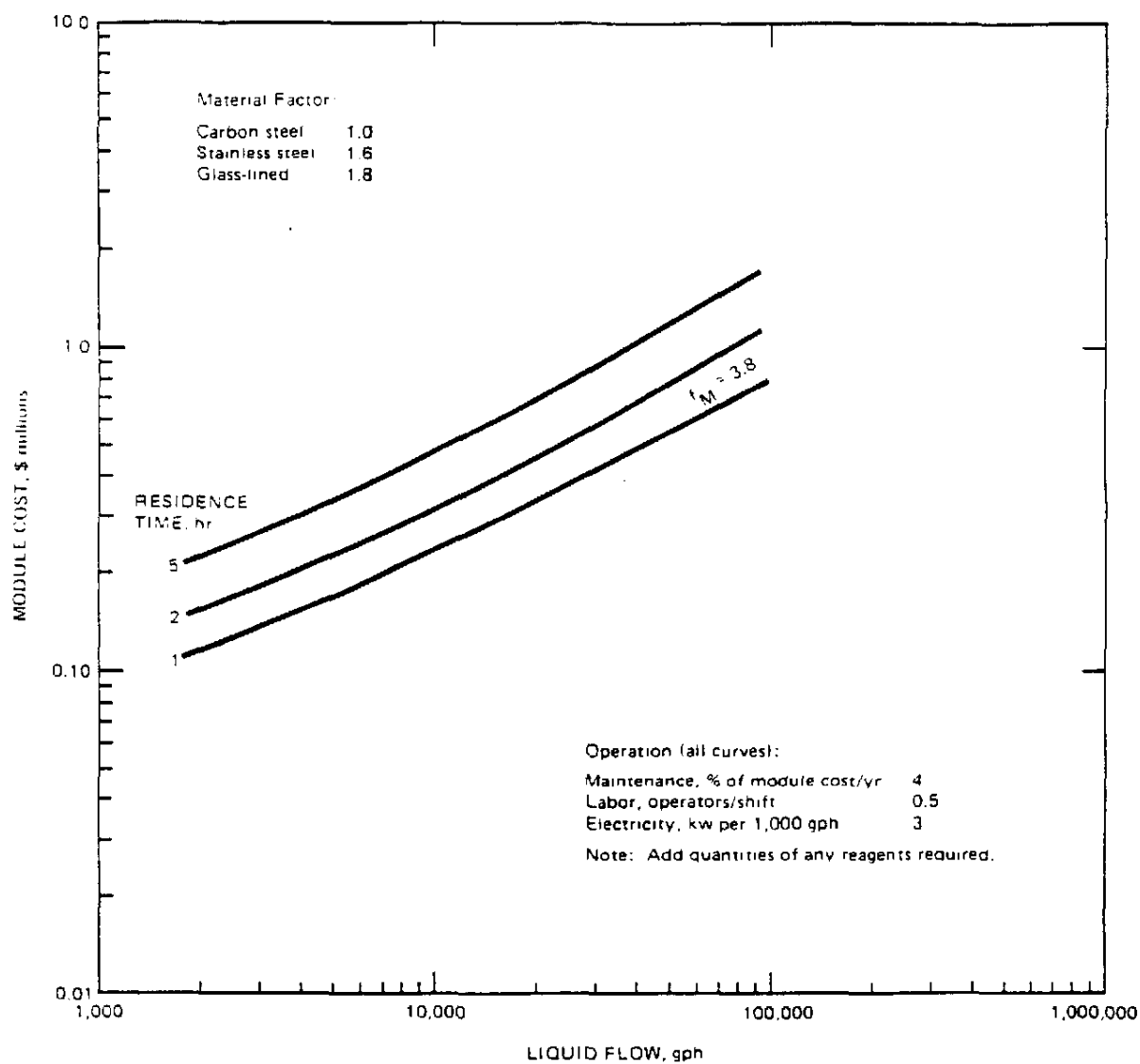
MODULE COST: LIME NEUTRALIZER



MCD 000016521

Figure 5.13

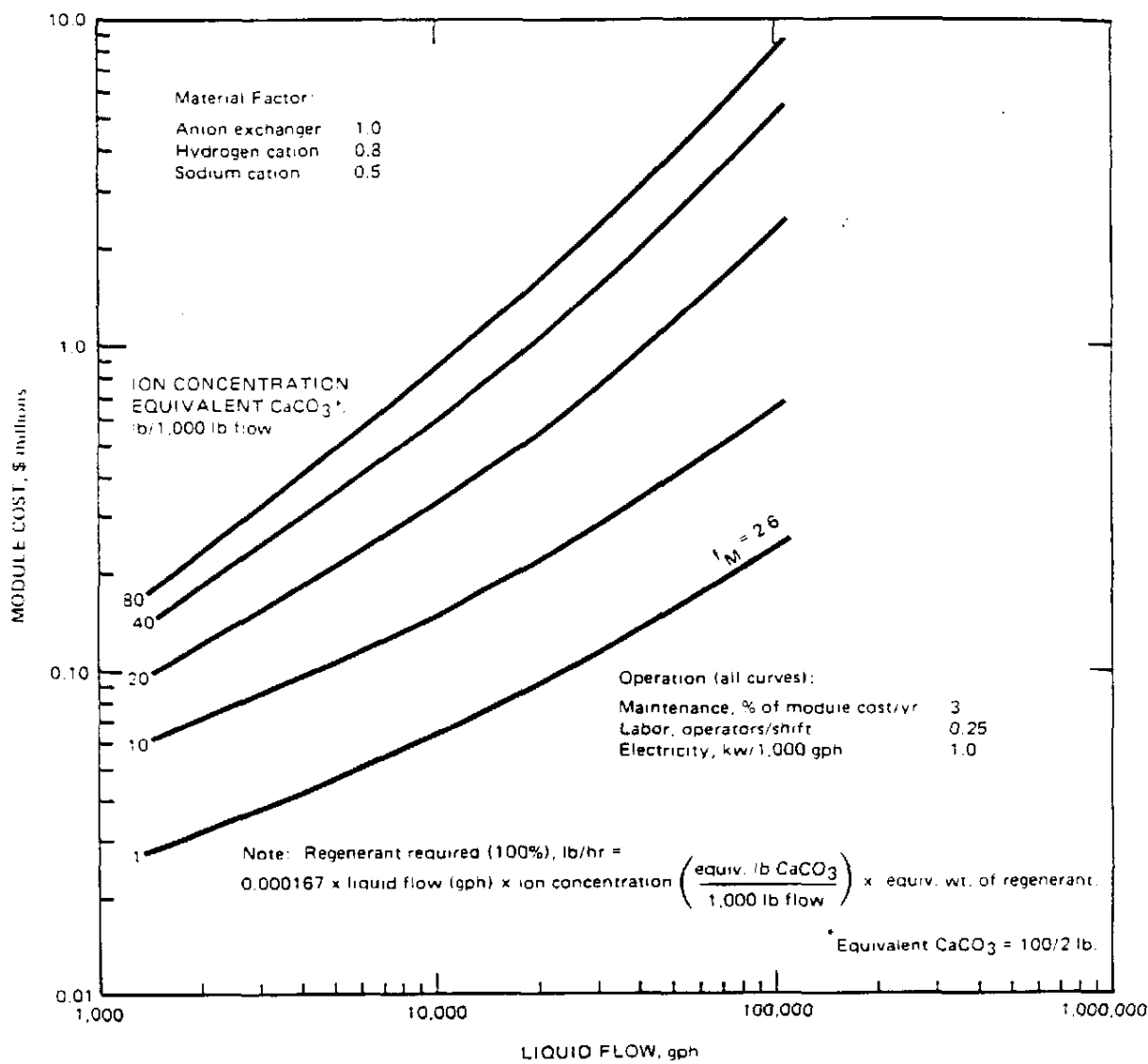
MODULE COST: SYSTEM FOR CHEMICAL REACTION OR PRECIPITATION



MCD 000016522

Figure 5.14

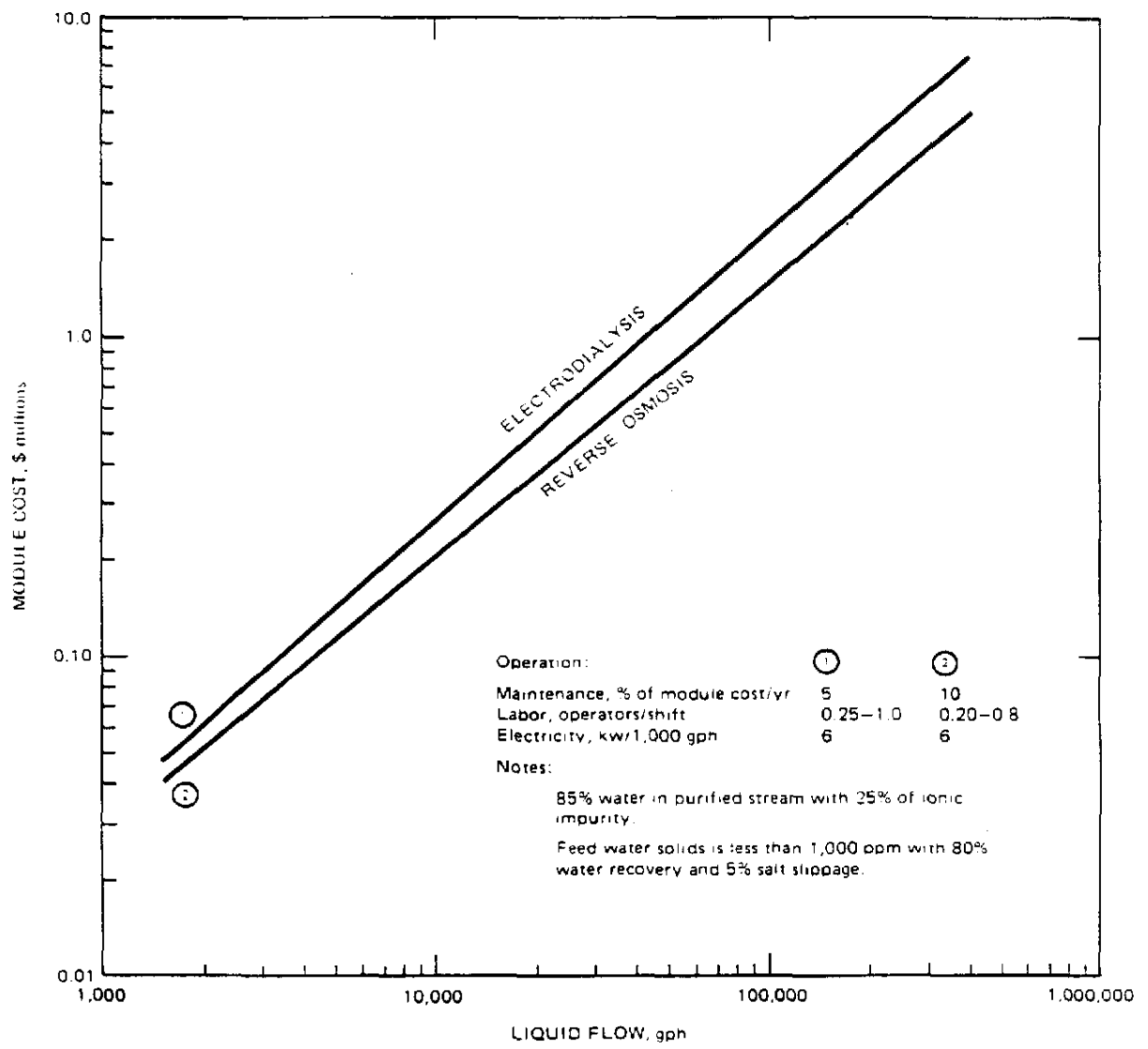
MODULE COST: ION EXCHANGE SYSTEM



MCD 000016523

Figure 5.15

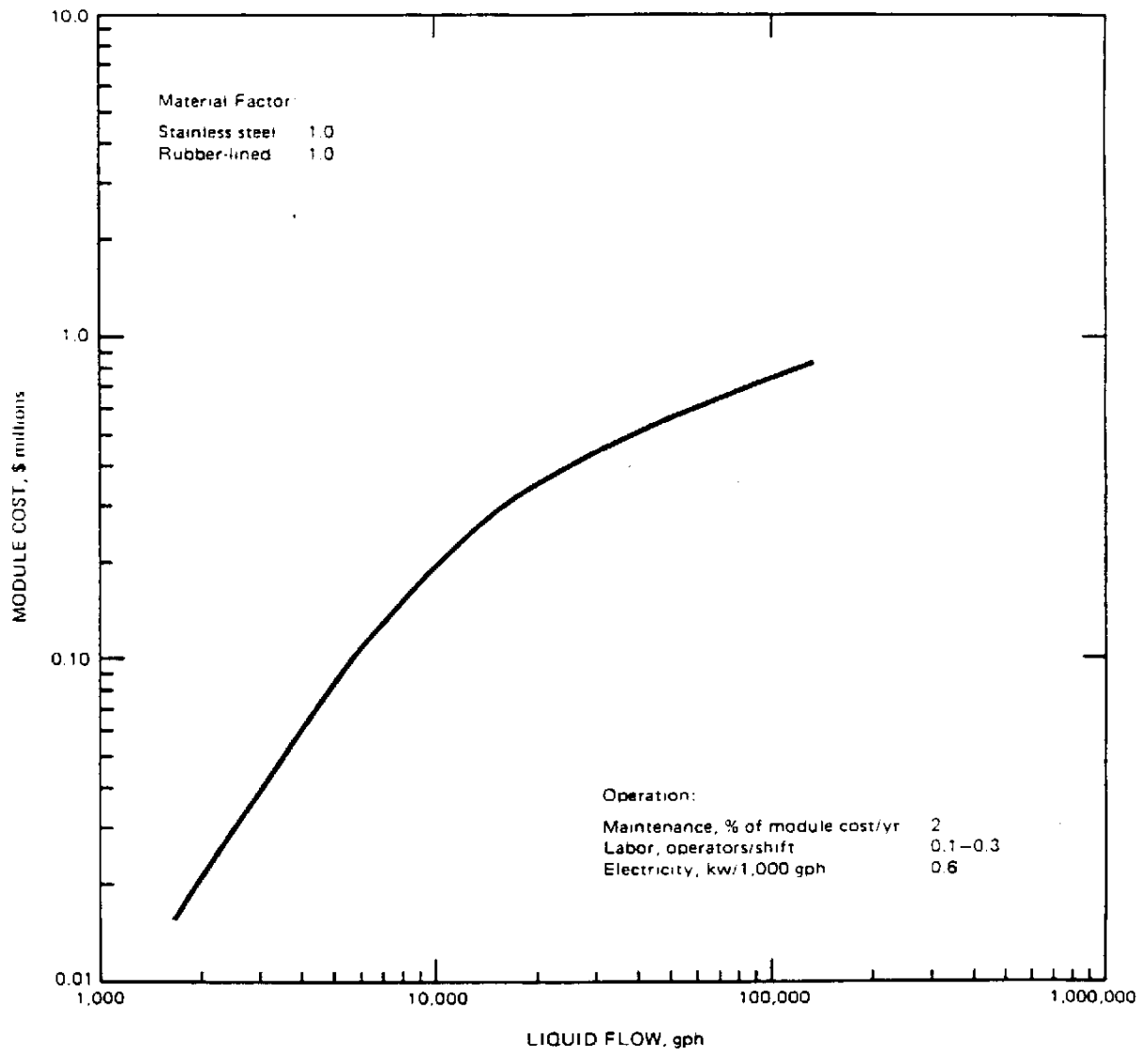
MODULE COST: ELECTRODIALYSIS AND REVERSE OSMOSIS CELLS



MCD 000016524

Figure 5.16

MODULE COST: DISSOLVED-AIR FLOTATION CELL



MCD 000016525

Figure 5.17

MODULE COST: CRYSTALLIZATION SYSTEM

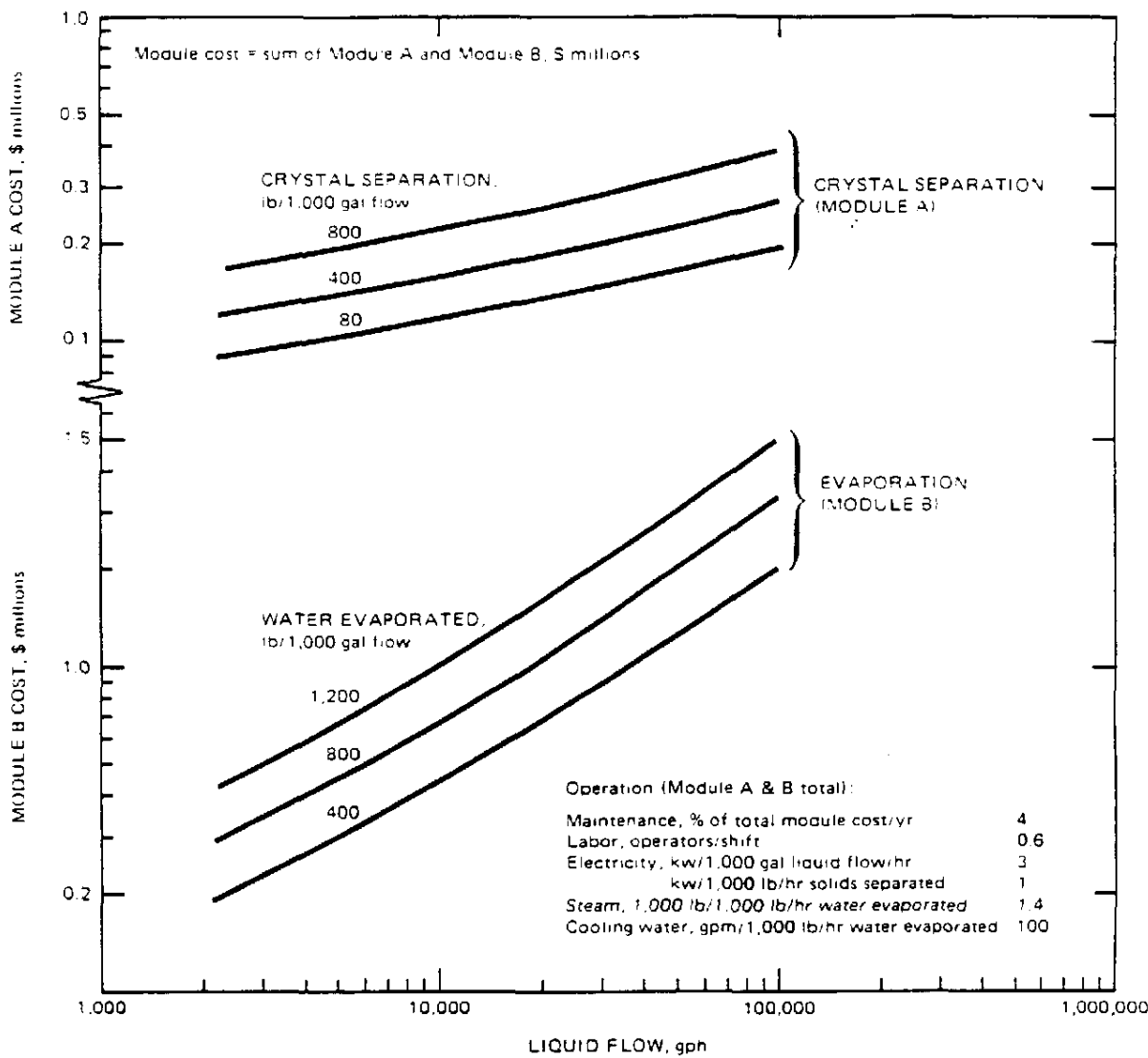
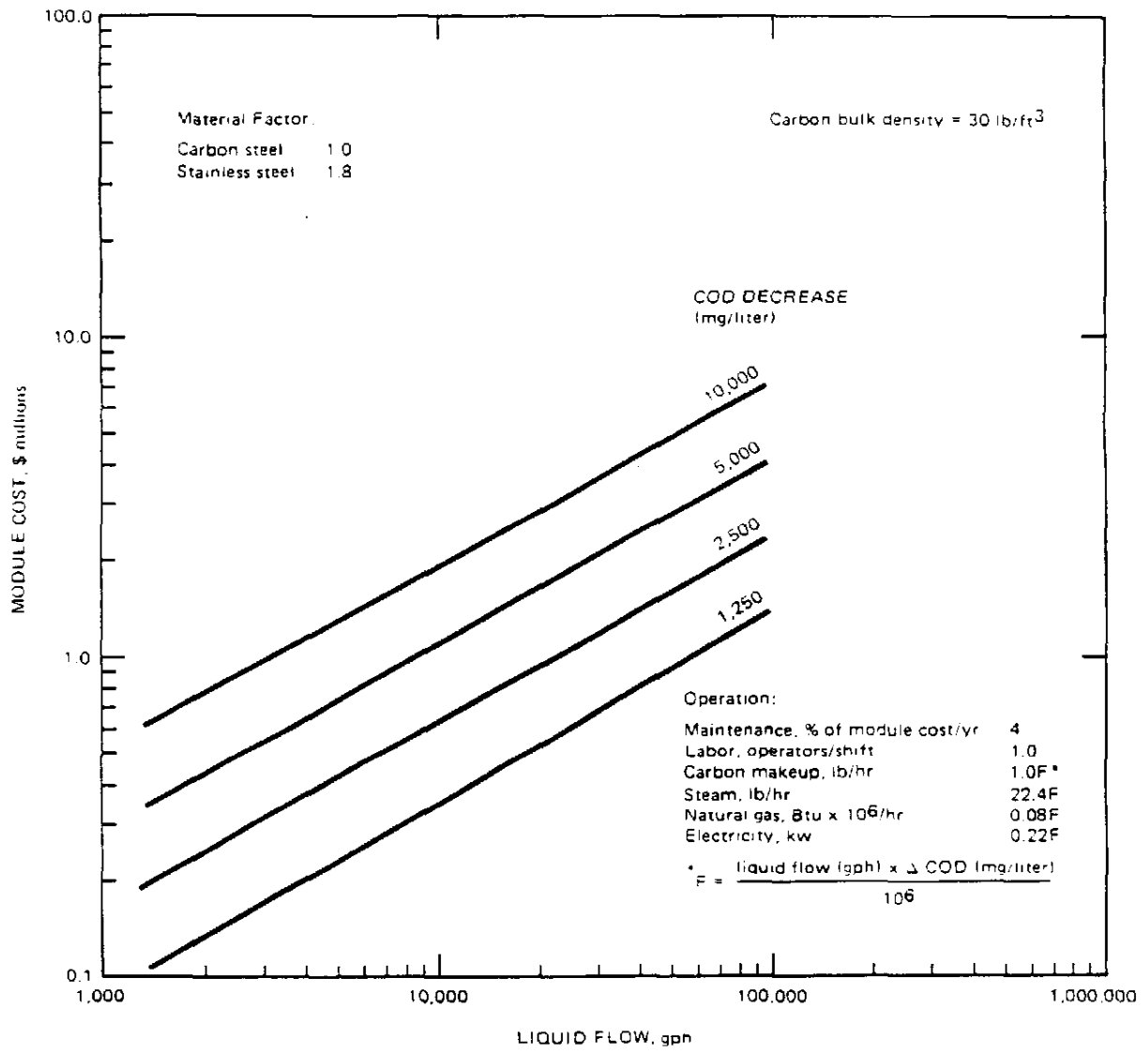


Figure 5.18

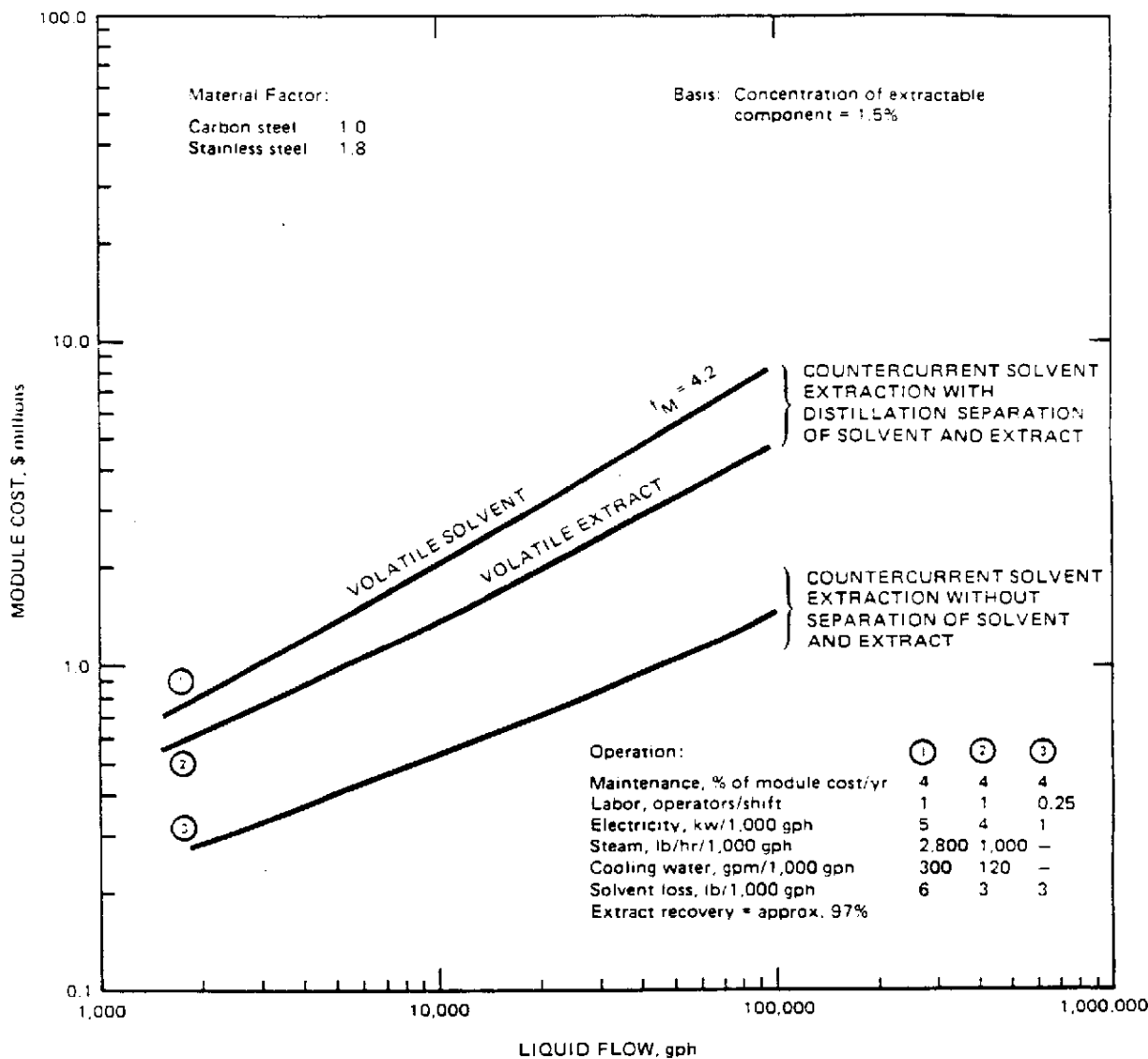
MODULE COST: ACTIVE CARBON ADSORBER FOR LIQUID STREAM



MCD 000018527

Figure 5.19

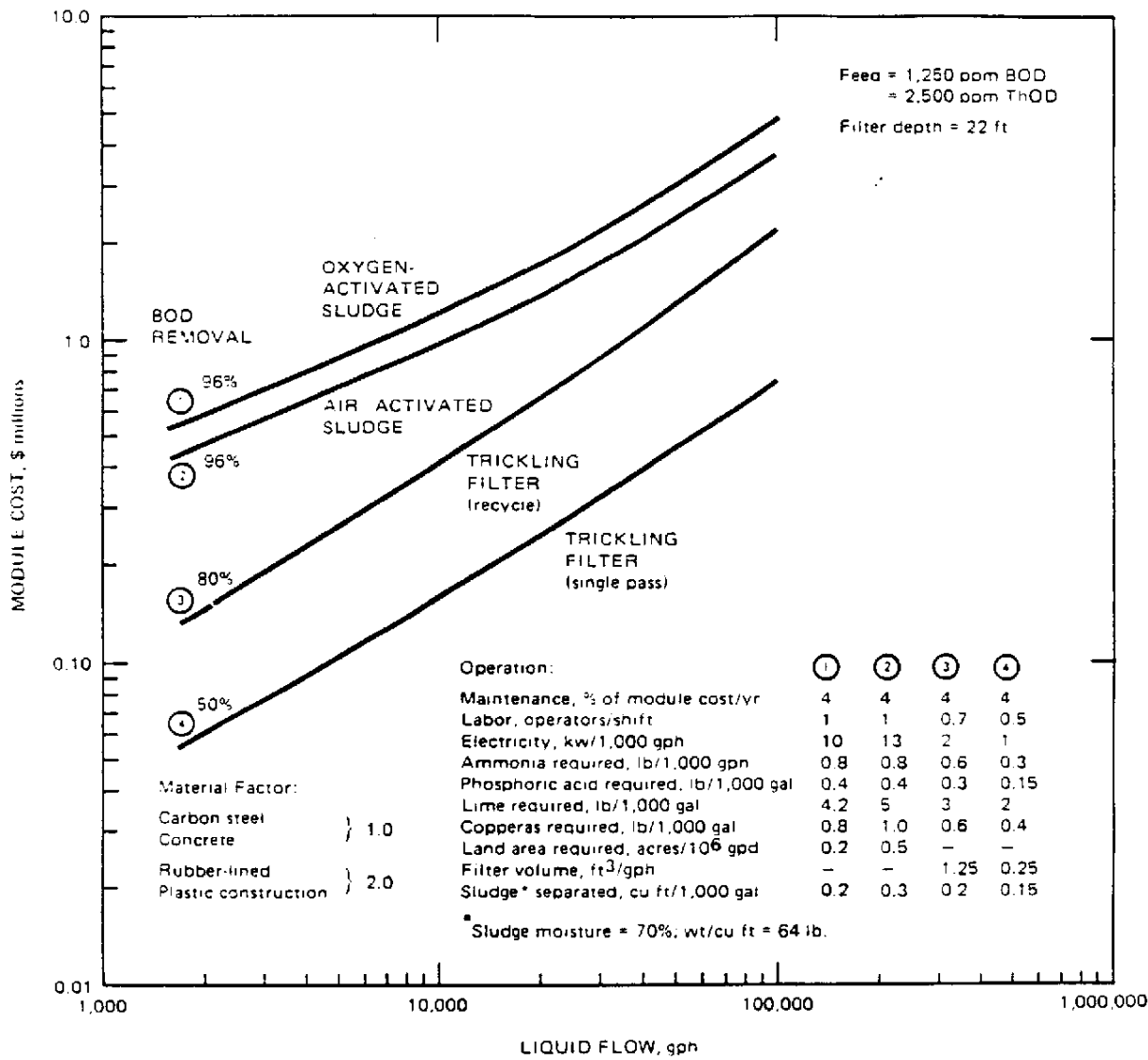
MODULE COST: SOLVENT EXTRACTION SYSTEM



MCD 000016528

Figure 5.20

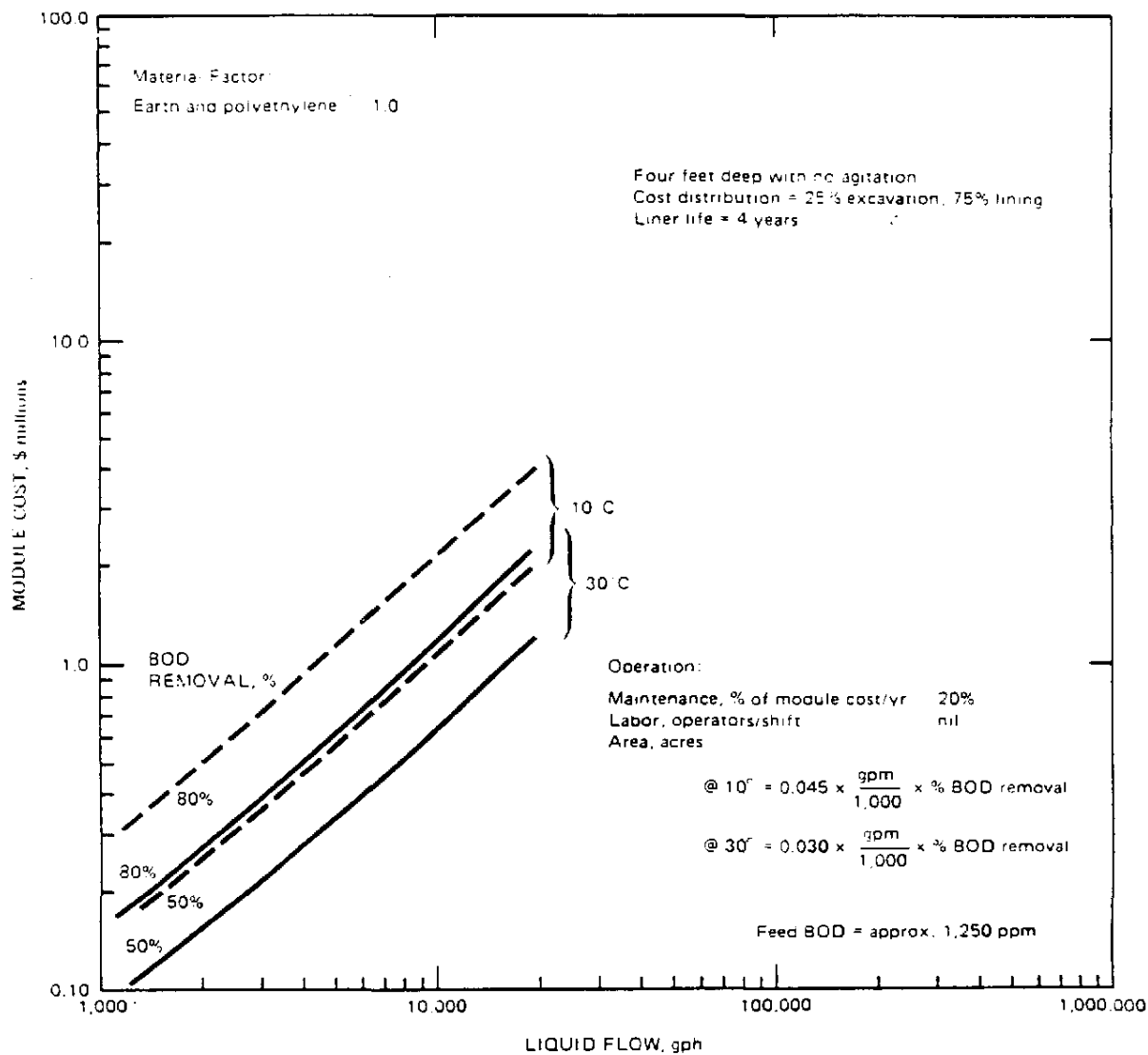
MODULE COST: BIOLOGICAL OXIDATION SYSTEM
INCLUDING SLUDGE SEPARATION



MCD 000016529

Figure 5.21

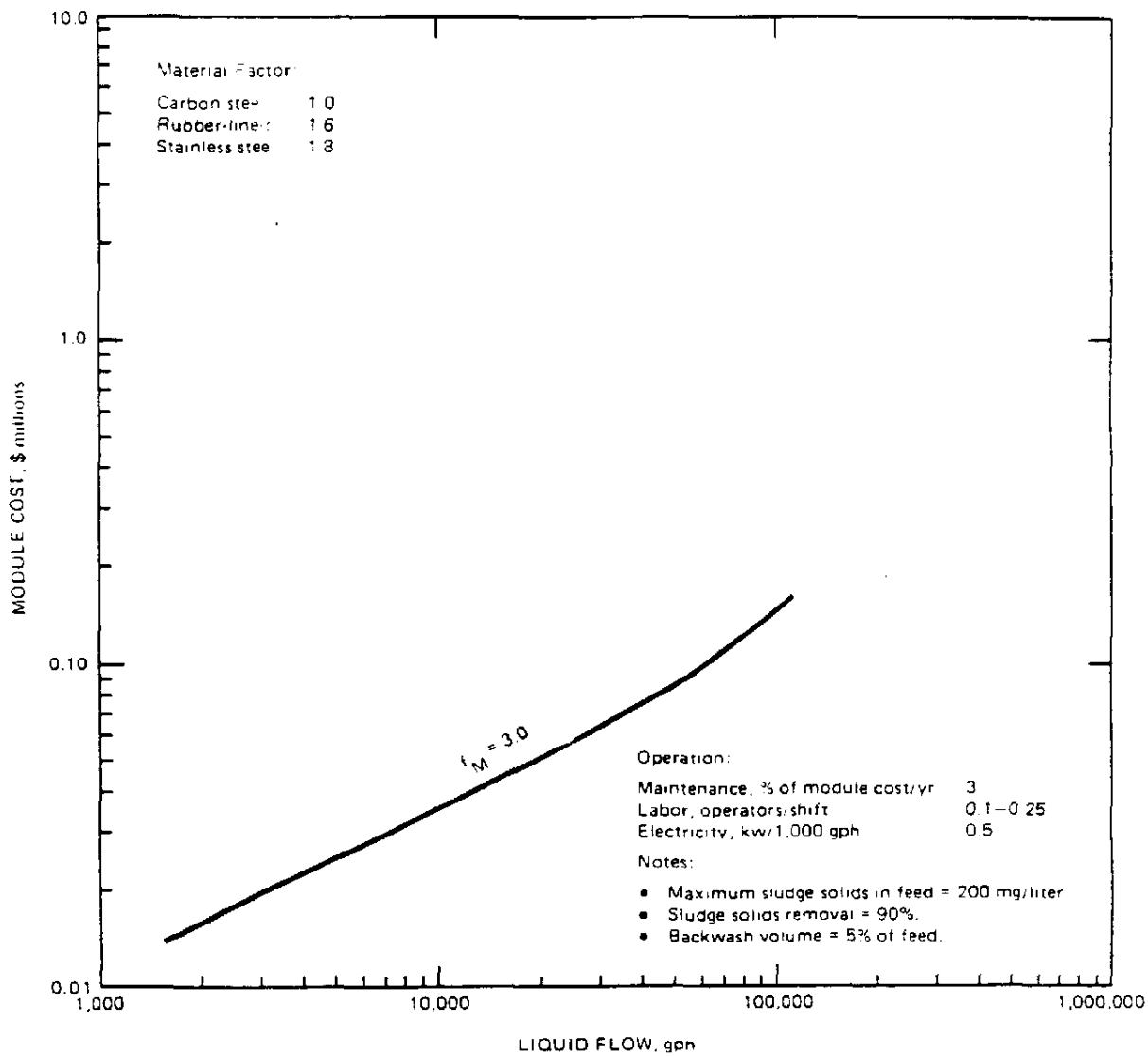
MODULE COST: FACULTATIVE LAGOON



MCD 000018530

Figure 5.22

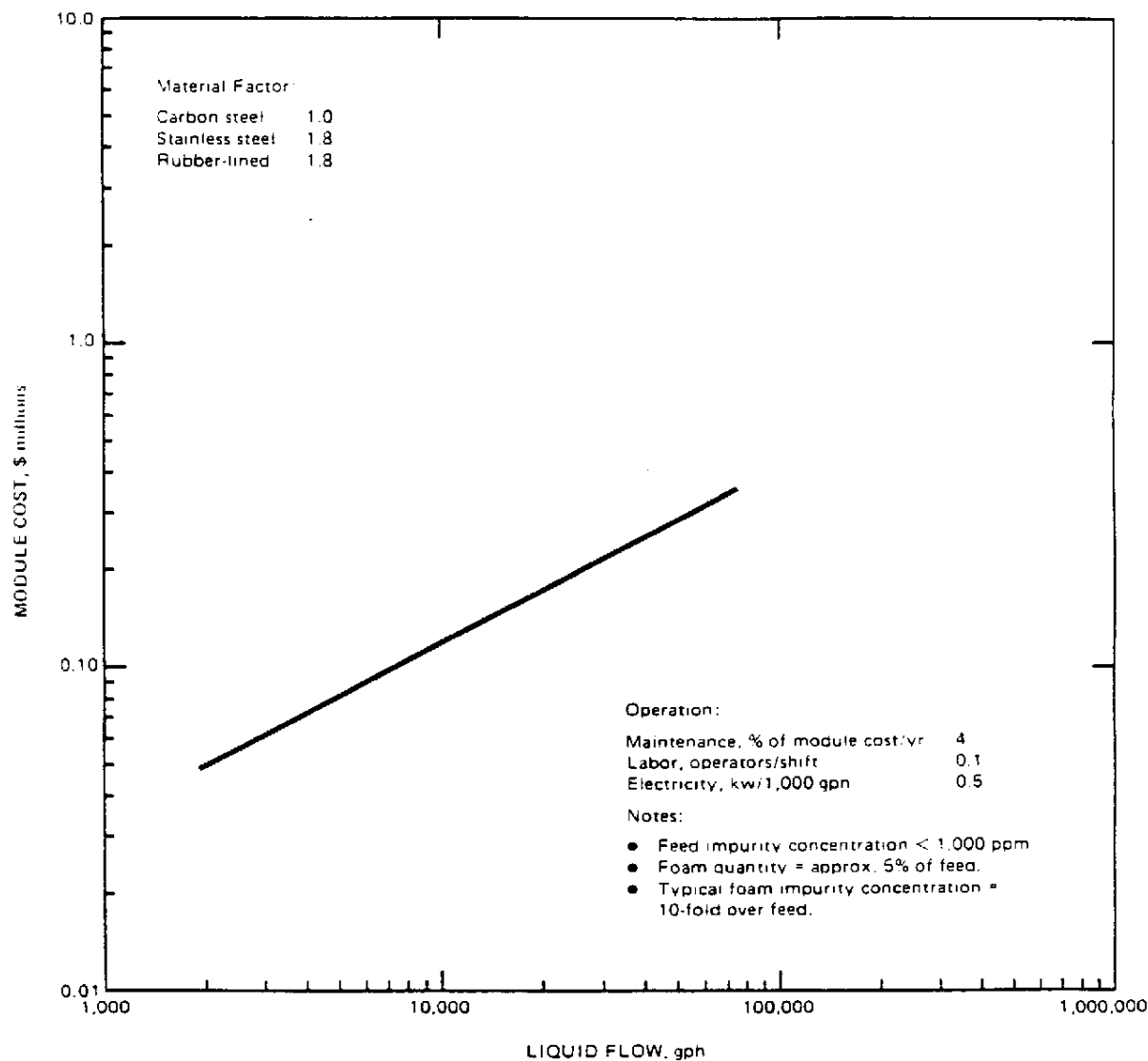
MODULE COST: FILTERS, DUAL MEDIA AND SAND



MCD 000016531

Figure 5.23

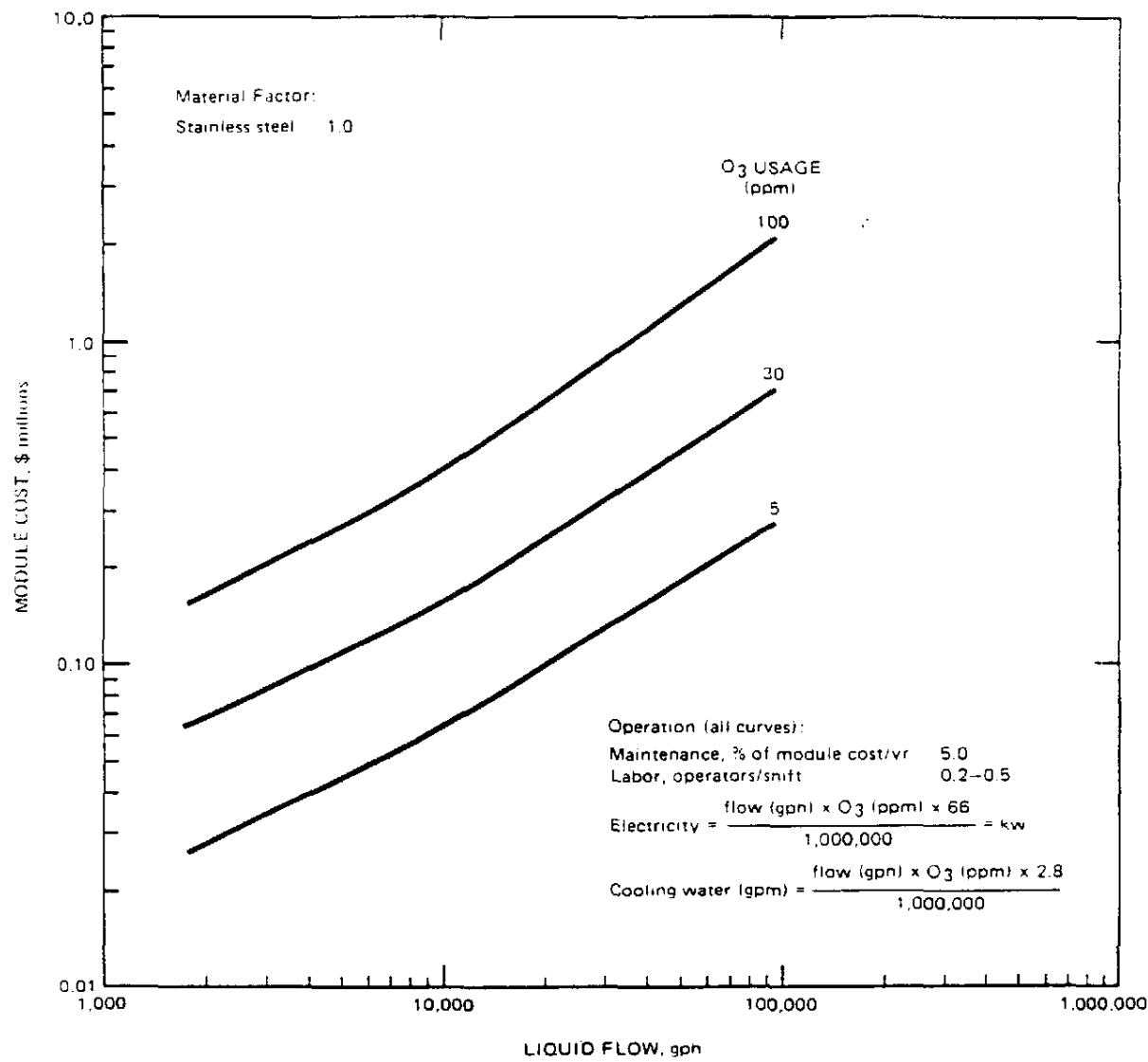
MODULE COST: FOAM FRACTIONATOR



MCD 000016532

Figure 5.24

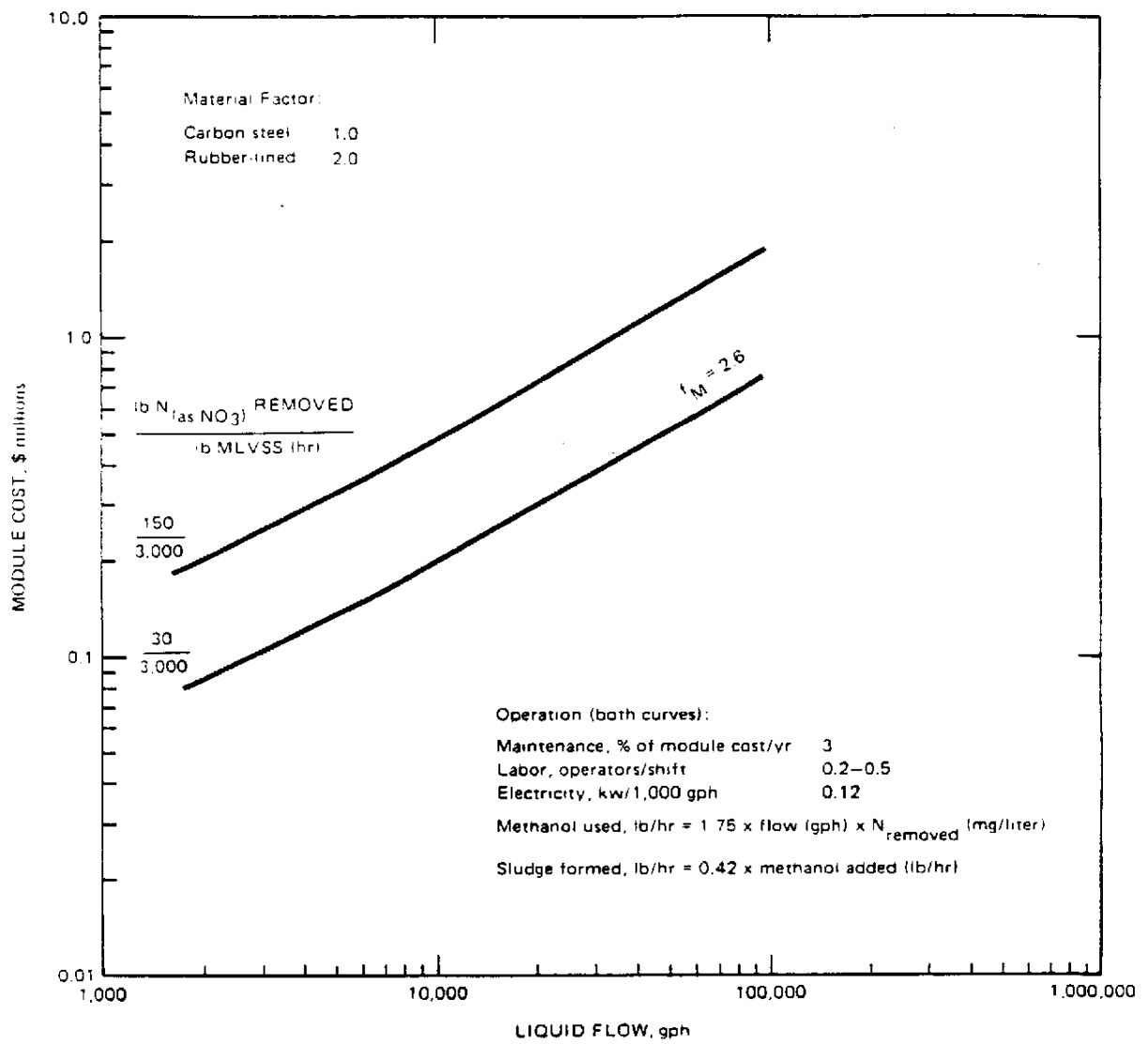
MODULE COST: OZONATION SYSTEM



MCD 000016533

Figure 5.25

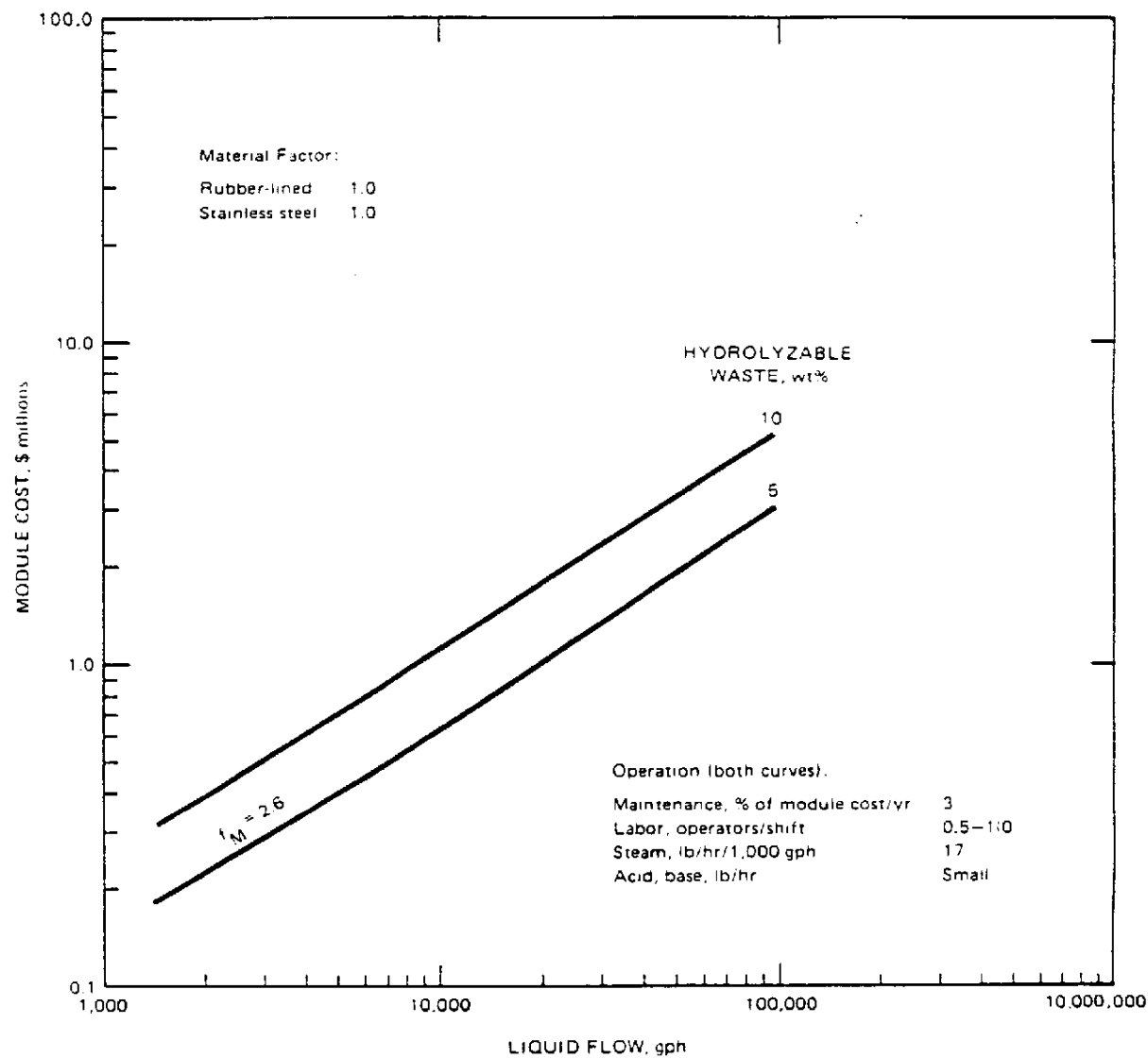
MODULE COST: DENITRIFICATION SYSTEM



MCD 000018534

Figure 5.26

MODULE COST: HYDROLYZER



MCI: 000016535

Figure 5.27

MODULE COST: CHLORINATOR FOR AMMONIA REMOVAL

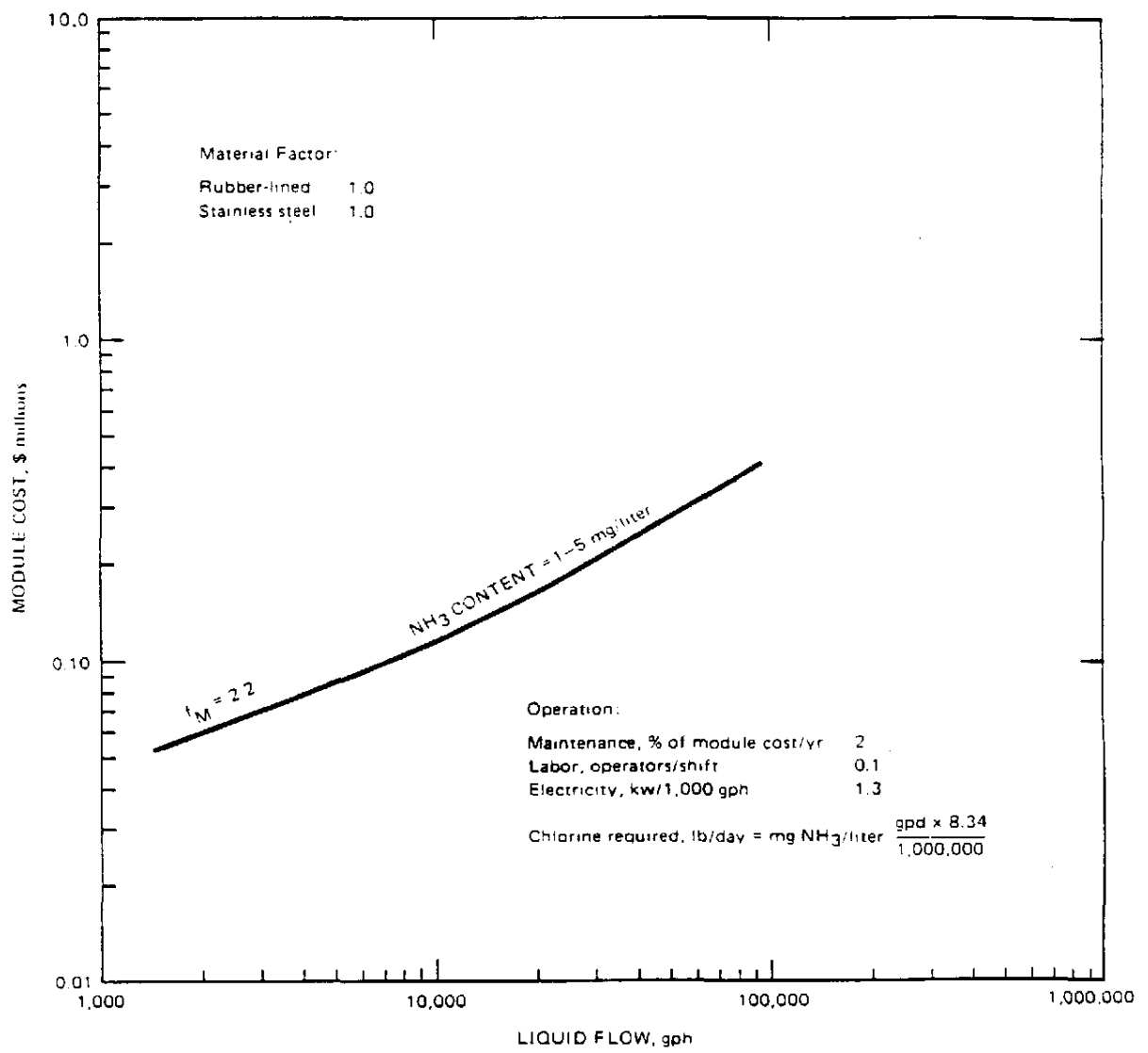
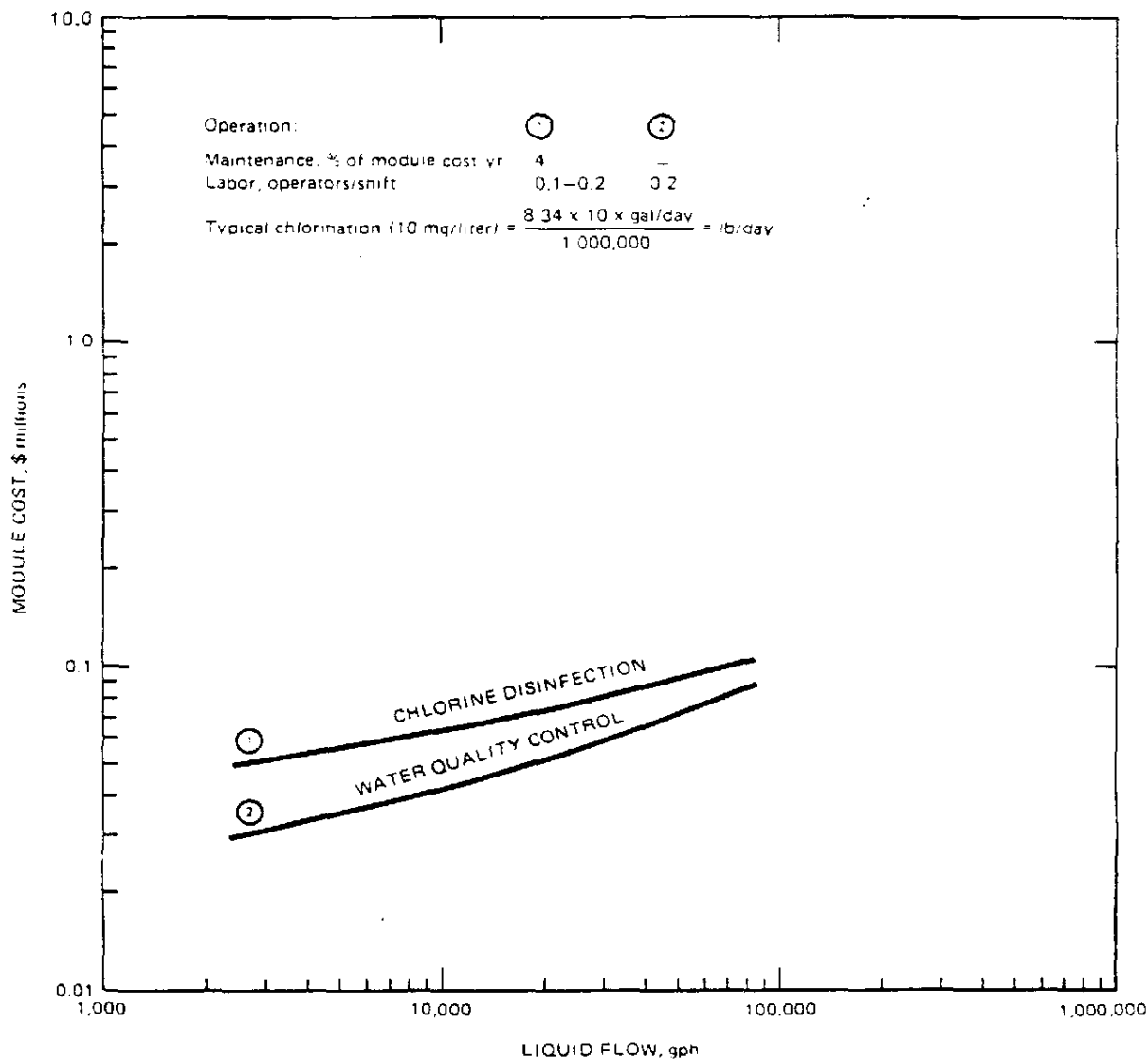


Figure 5.28

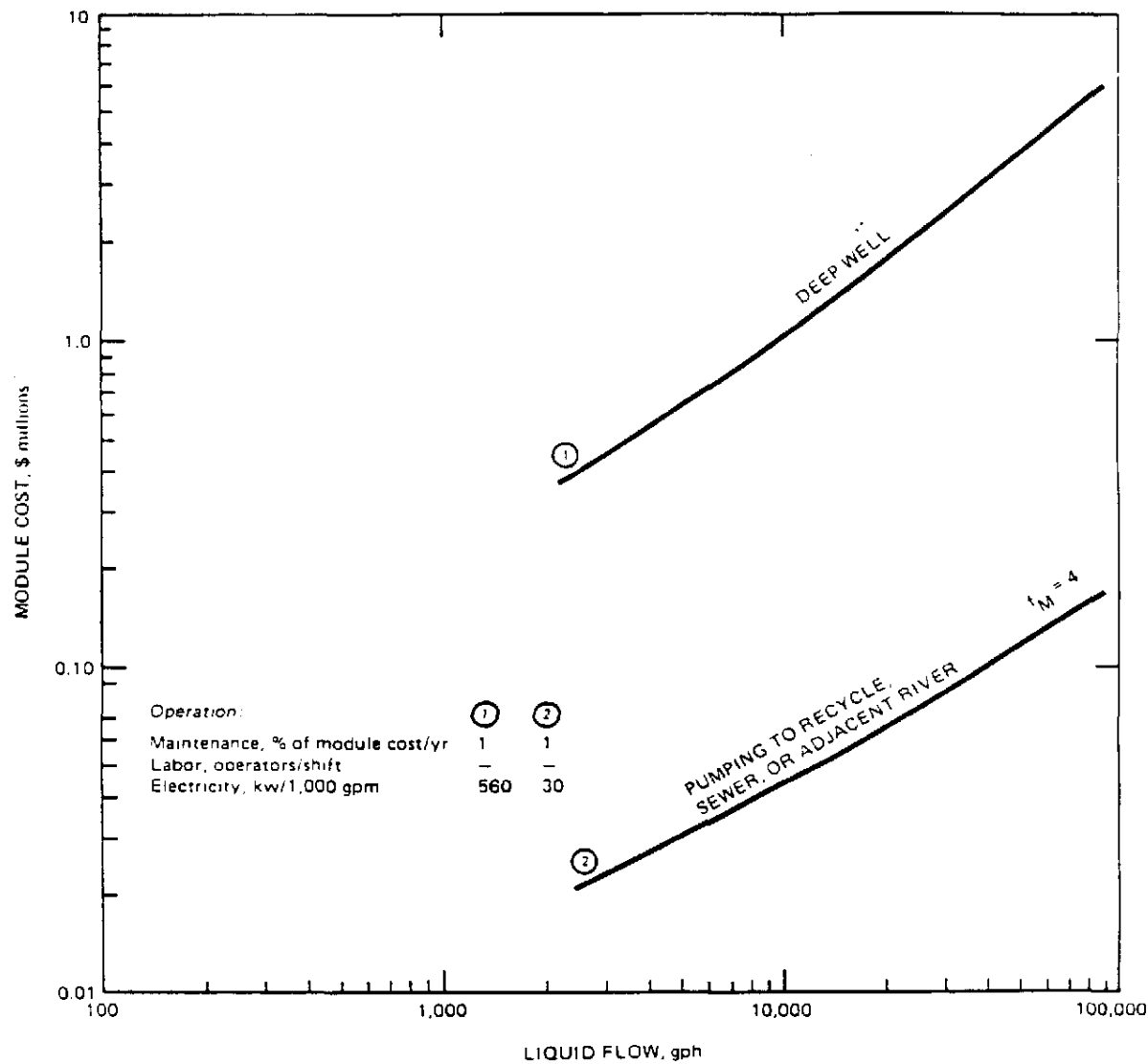
MODULE COST: CHLORINATOR FOR DISINFECTION
AND EQUIPMENT FOR WATER QUALITY CONTROL



MCD 000018517

Figure 5.29

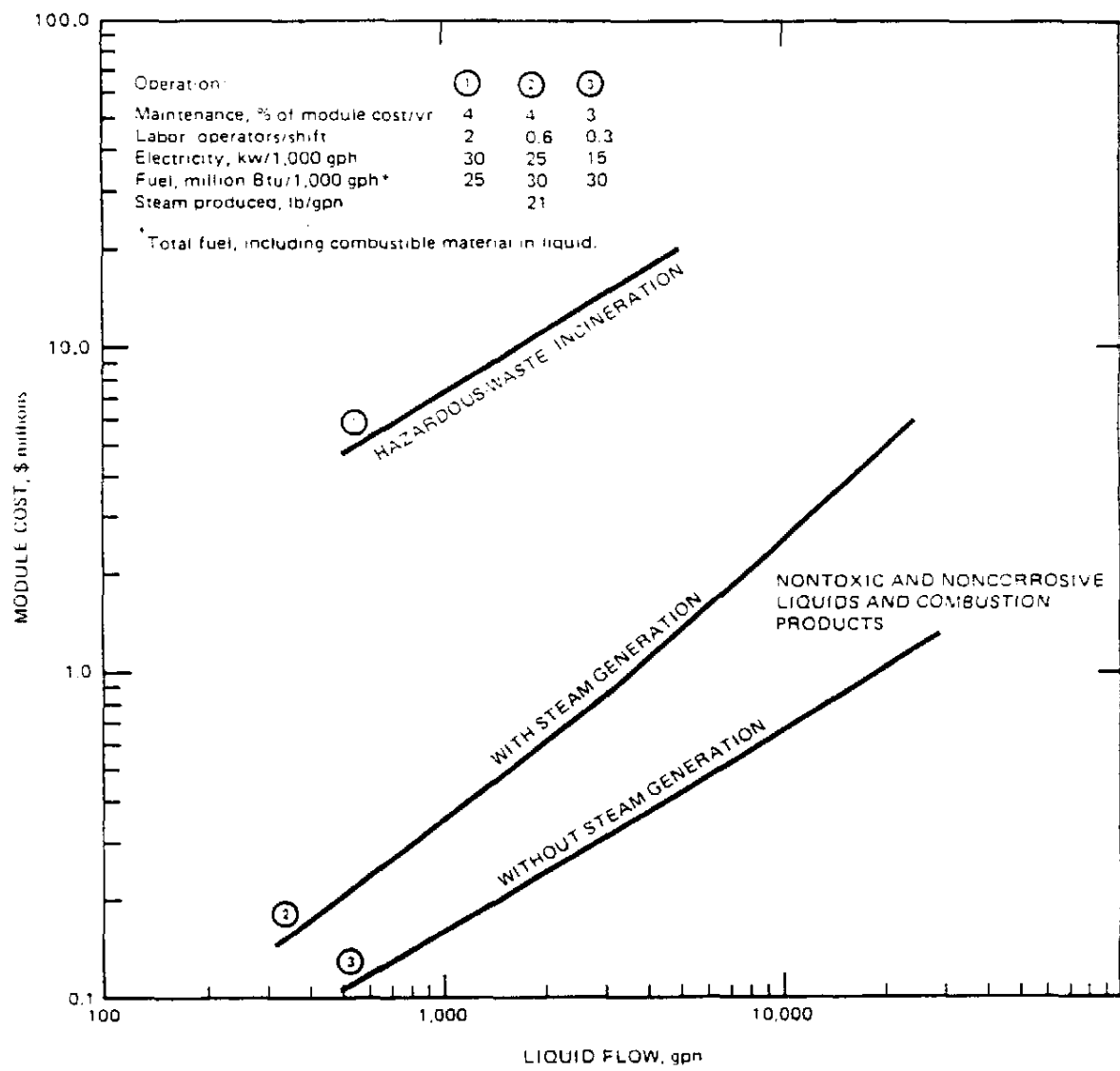
MODULE COST: PUMPING SYSTEM AND DEEP-WELLING SYSTEM



MCD 000016538

Figure 5.30

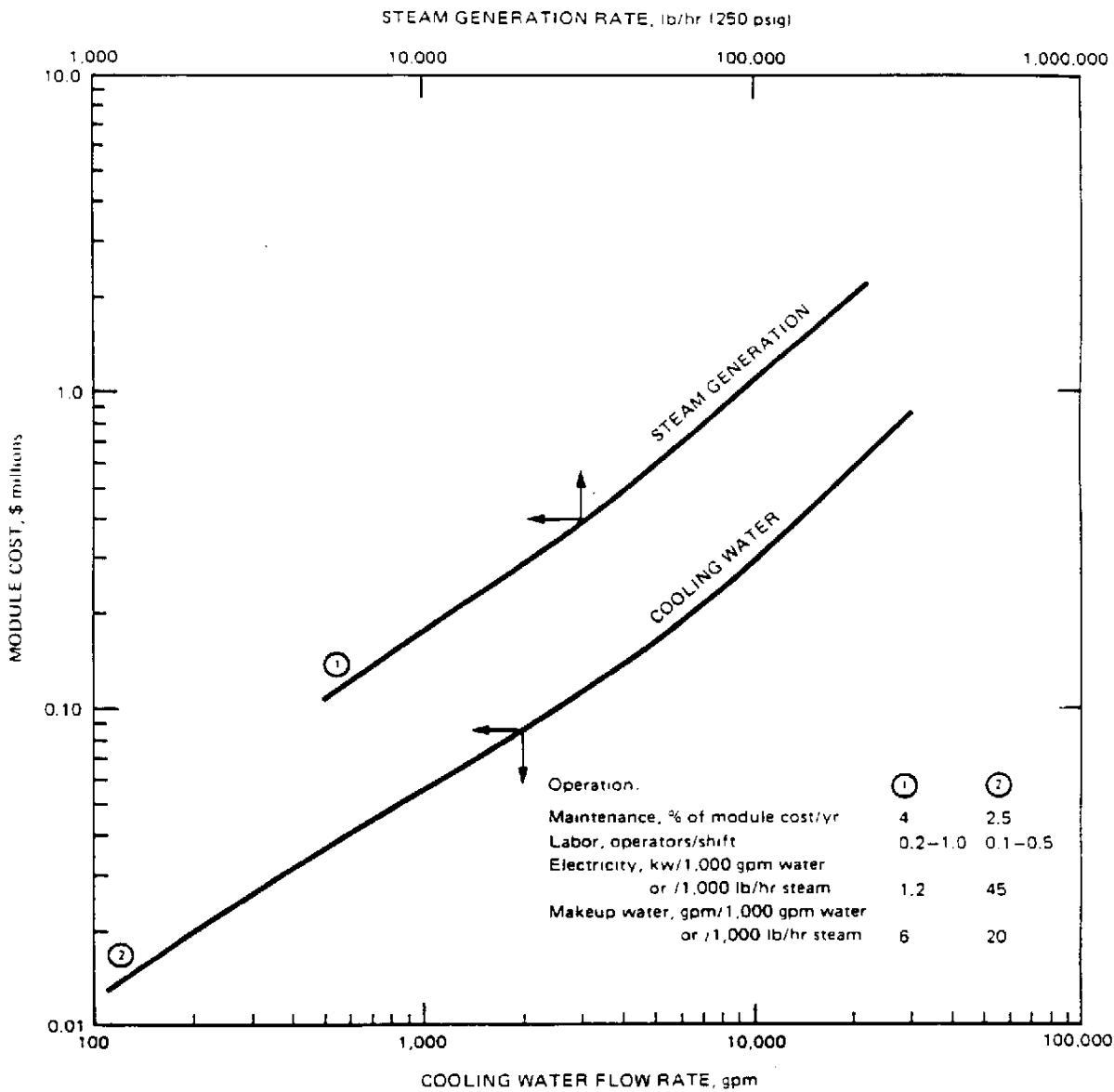
MODULE COST: LIQUID INCINERATOR



MCD 000018539

Figure 5.31

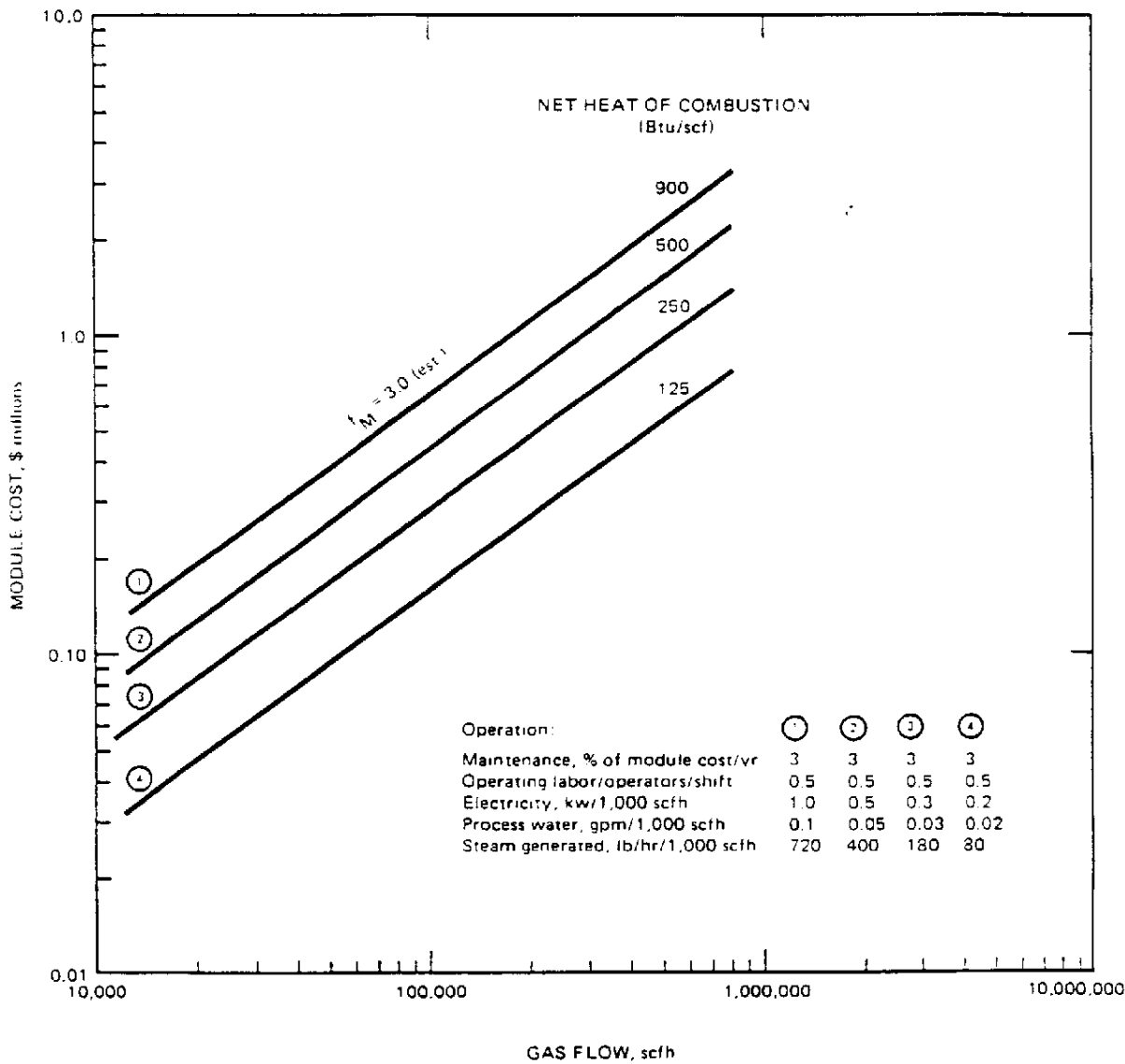
MODULE COST: STEAM AND COOLING WATER UTILITIES



MCD 000016540

Figure 5.32

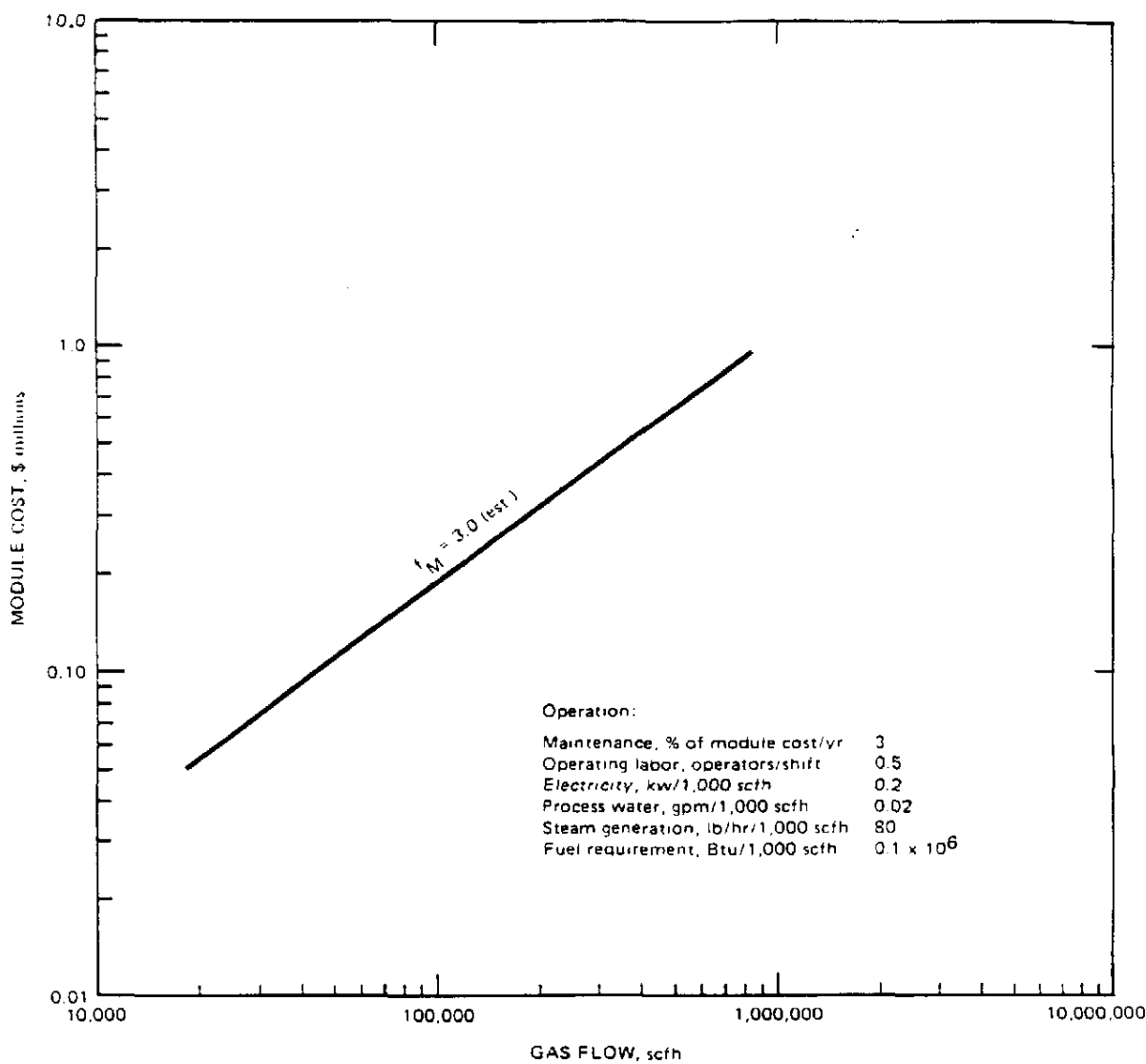
MODULE COST: GAS COMBUSTOR FOR STEAM GENERATION



MCD 000016541

Figure 5.33

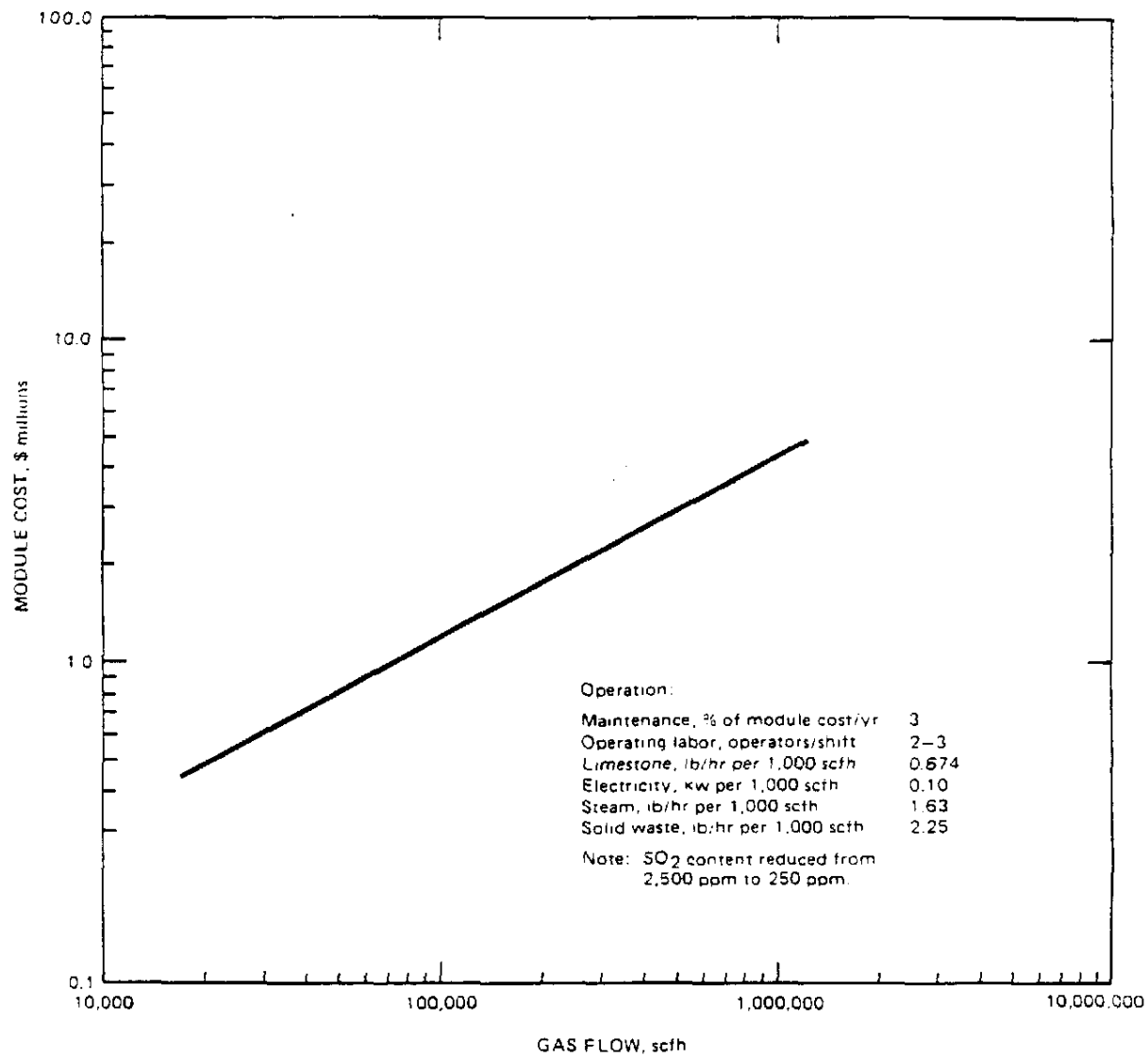
MODULE COST: GAS INCINERATOR



MCD 000016542

Figure 5.34

MODULE COST: FLUE GAS DESULFURIZATION SYSTEM



MCD 000018543

Figure 5.35

MODULE COST: HYDROCARBON GAS FLARE

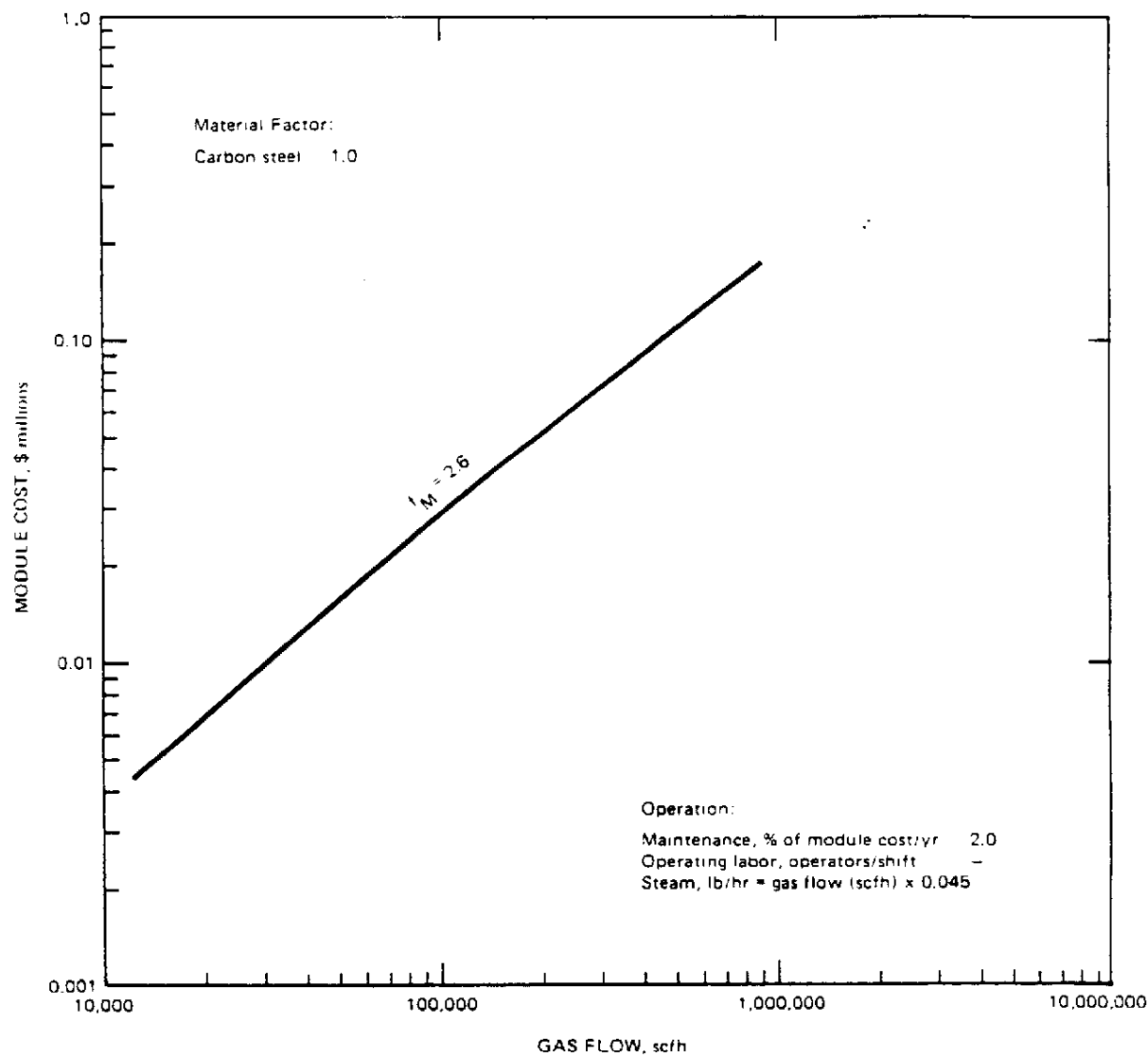
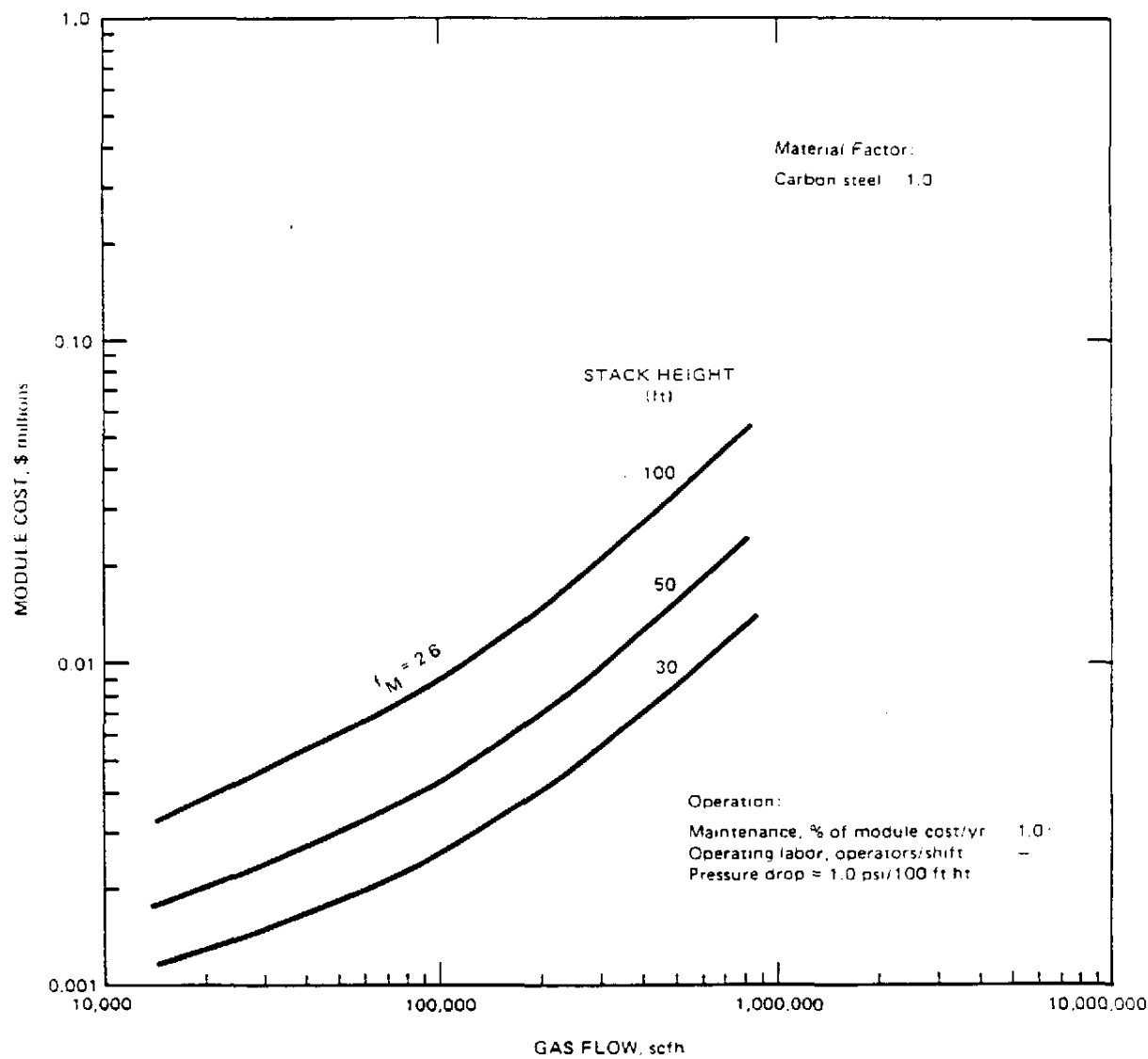


Figure 5.36

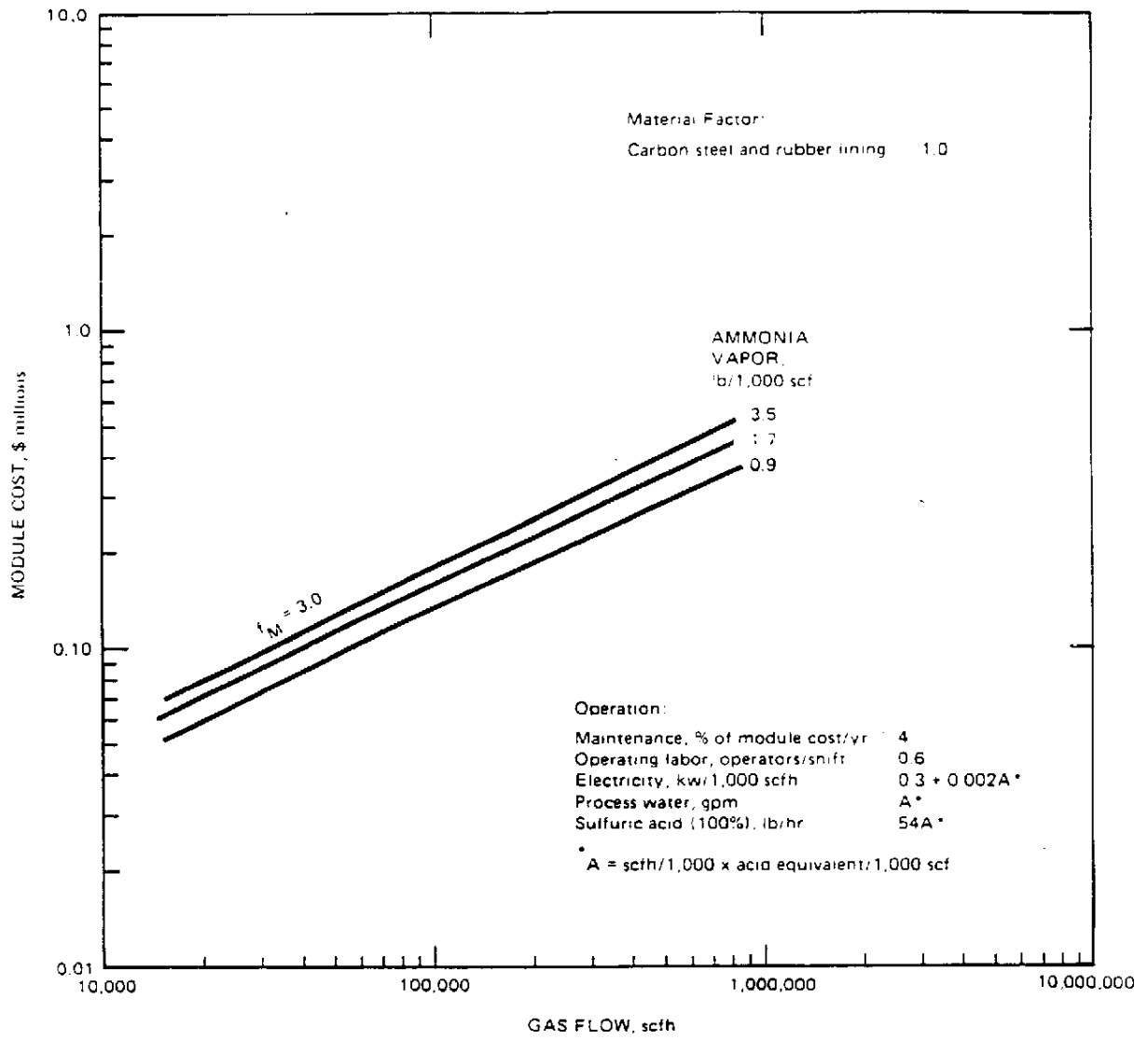
MODULE COST: GAS DISPERSION STACK



MCD 000016545

Figure 5.37

MODULE COST: AMMONIA NEUTRALIZER



MCD 000016546

Figure 5.38

MODULE COST: ACID GAS NEUTRALIZER

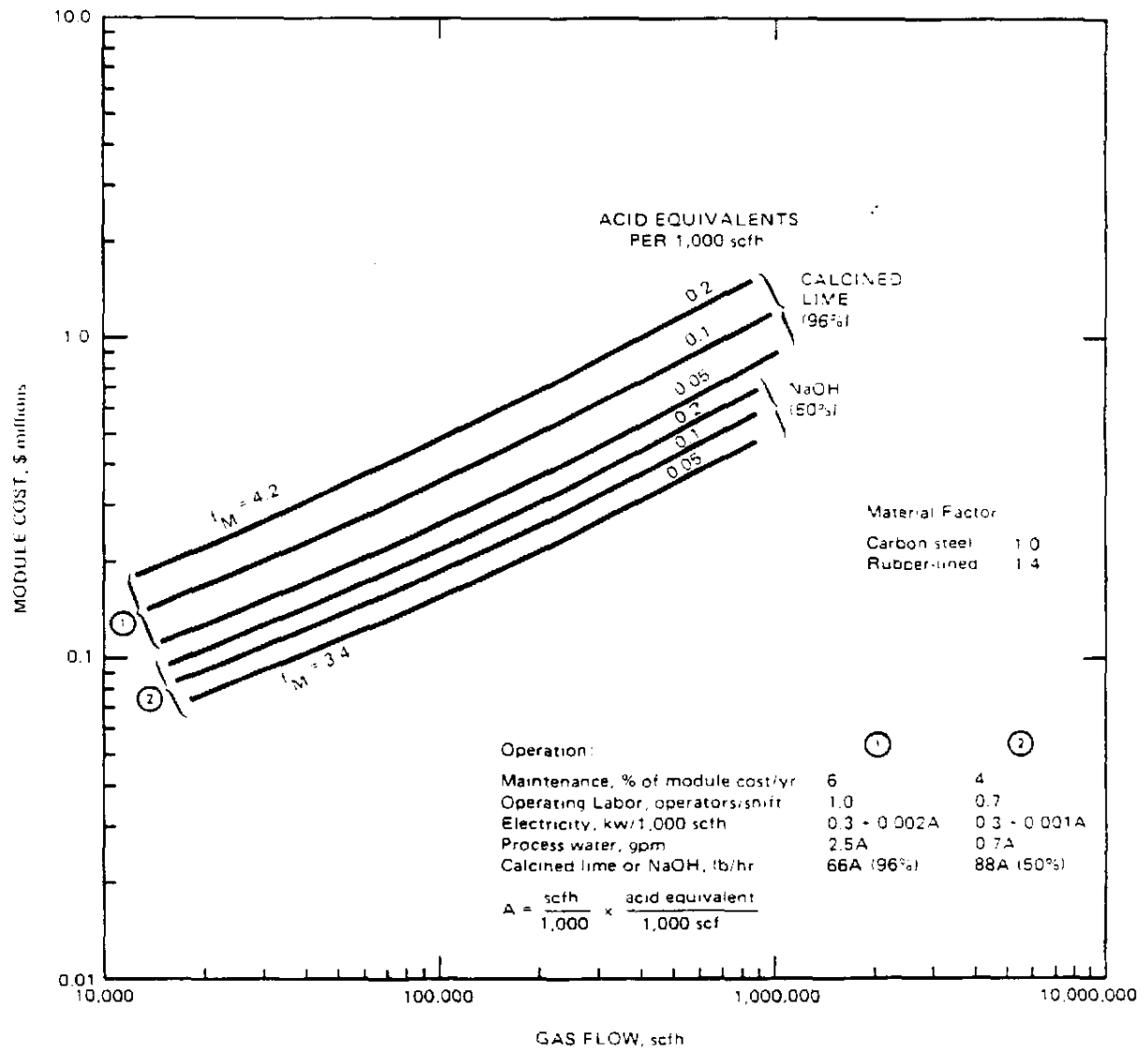
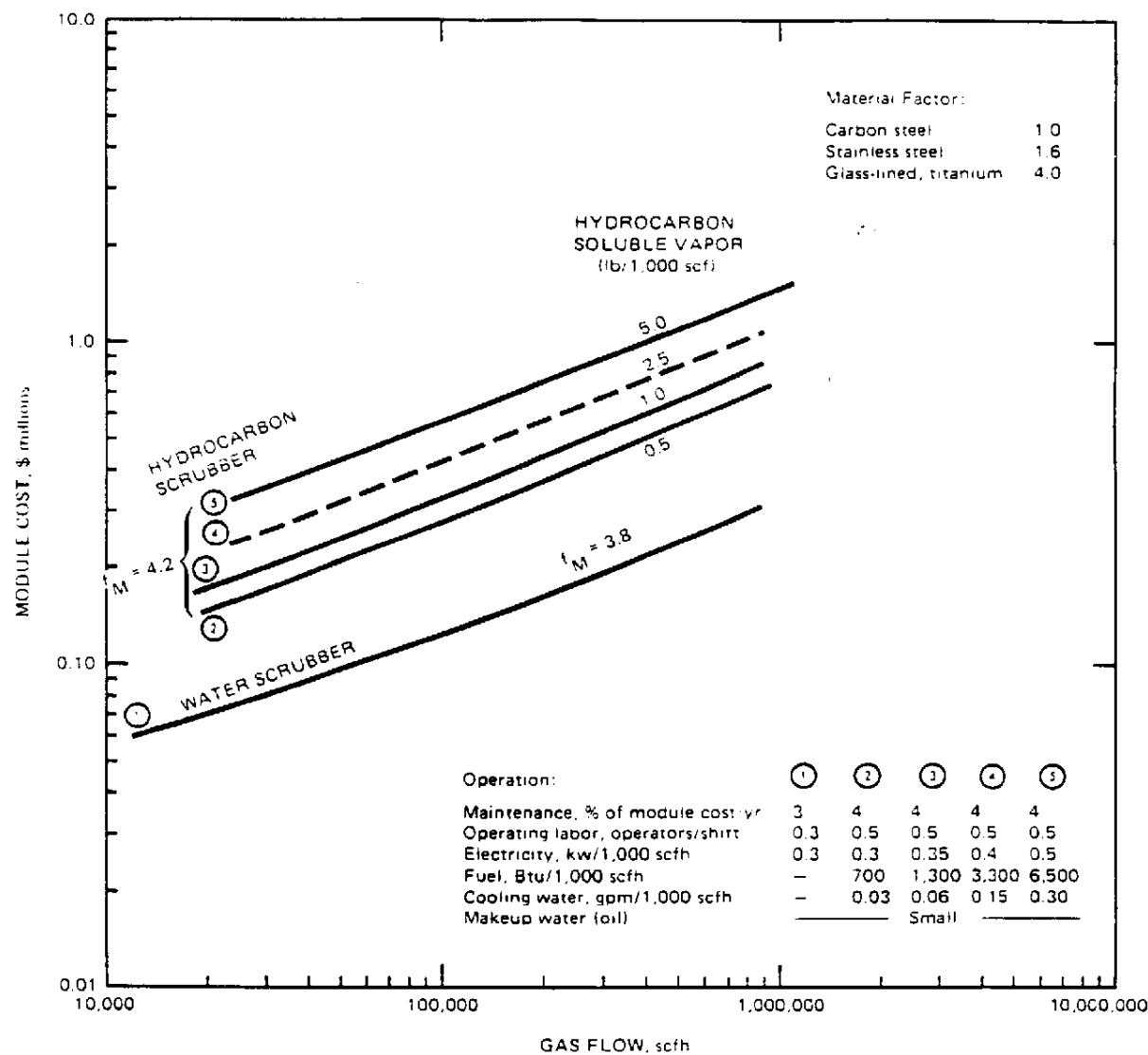


Figure 5.39

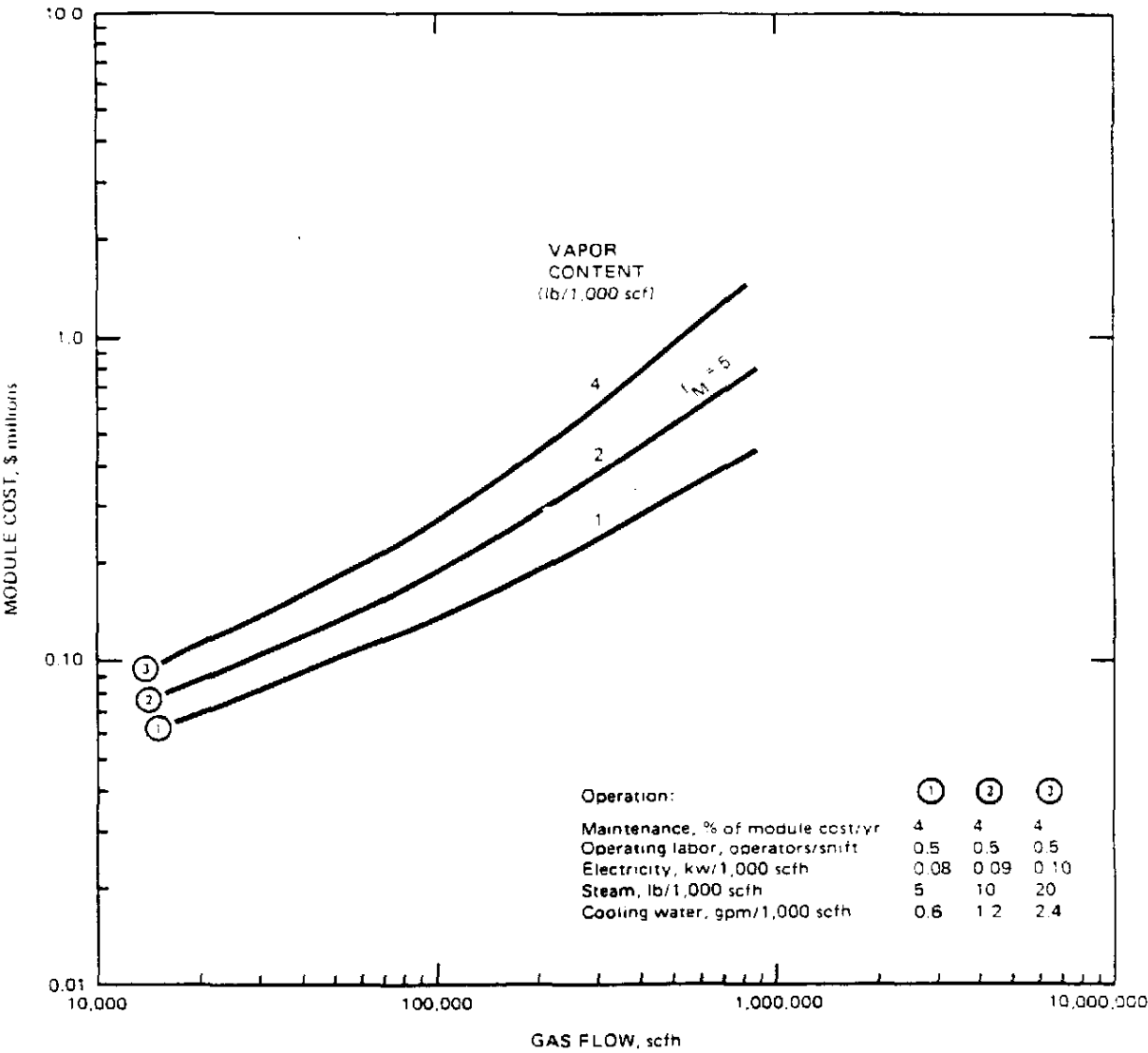
MODULE COST: SCRUBBERS, HYDROCARBON OR WATER



MCD 000016548

Figure 5.40

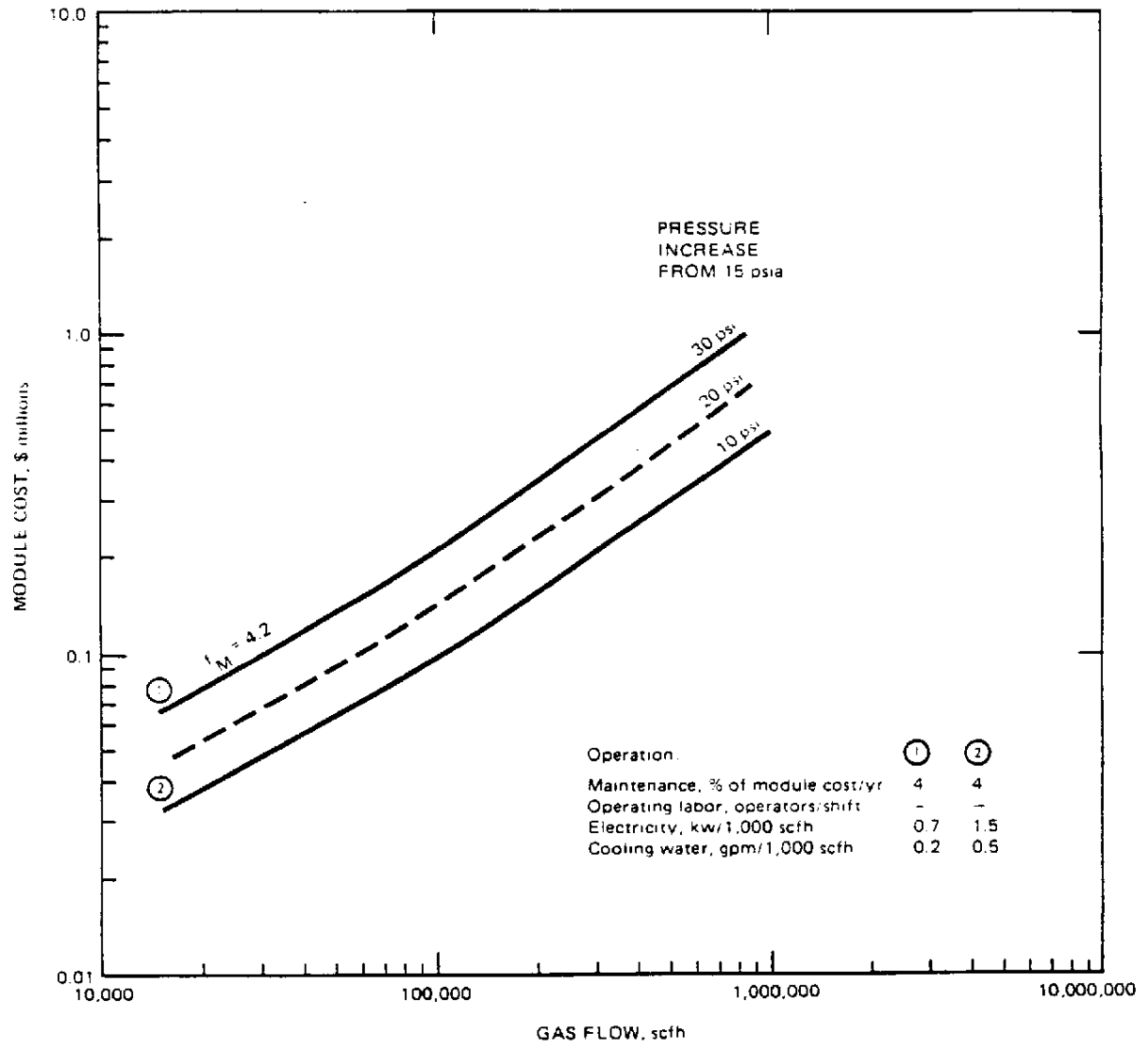
MODULE COST: ACTIVE CARBON ADSORBER FOR GASEOUS STREAM



MCD 000016549

Figure 5.41

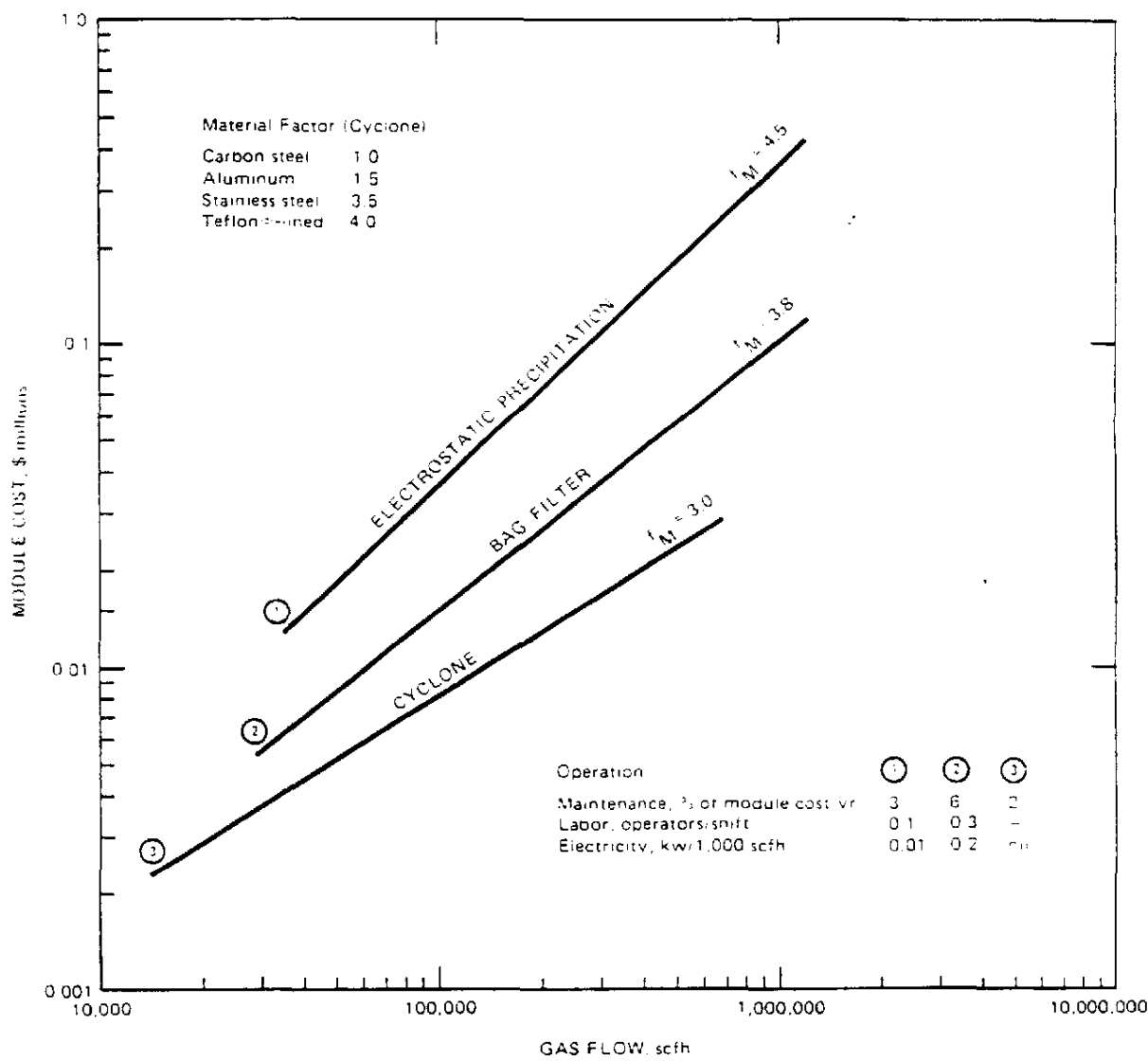
MODULE COST: GAS COMPRESSOR



MCD 000016550

Figure 5.42

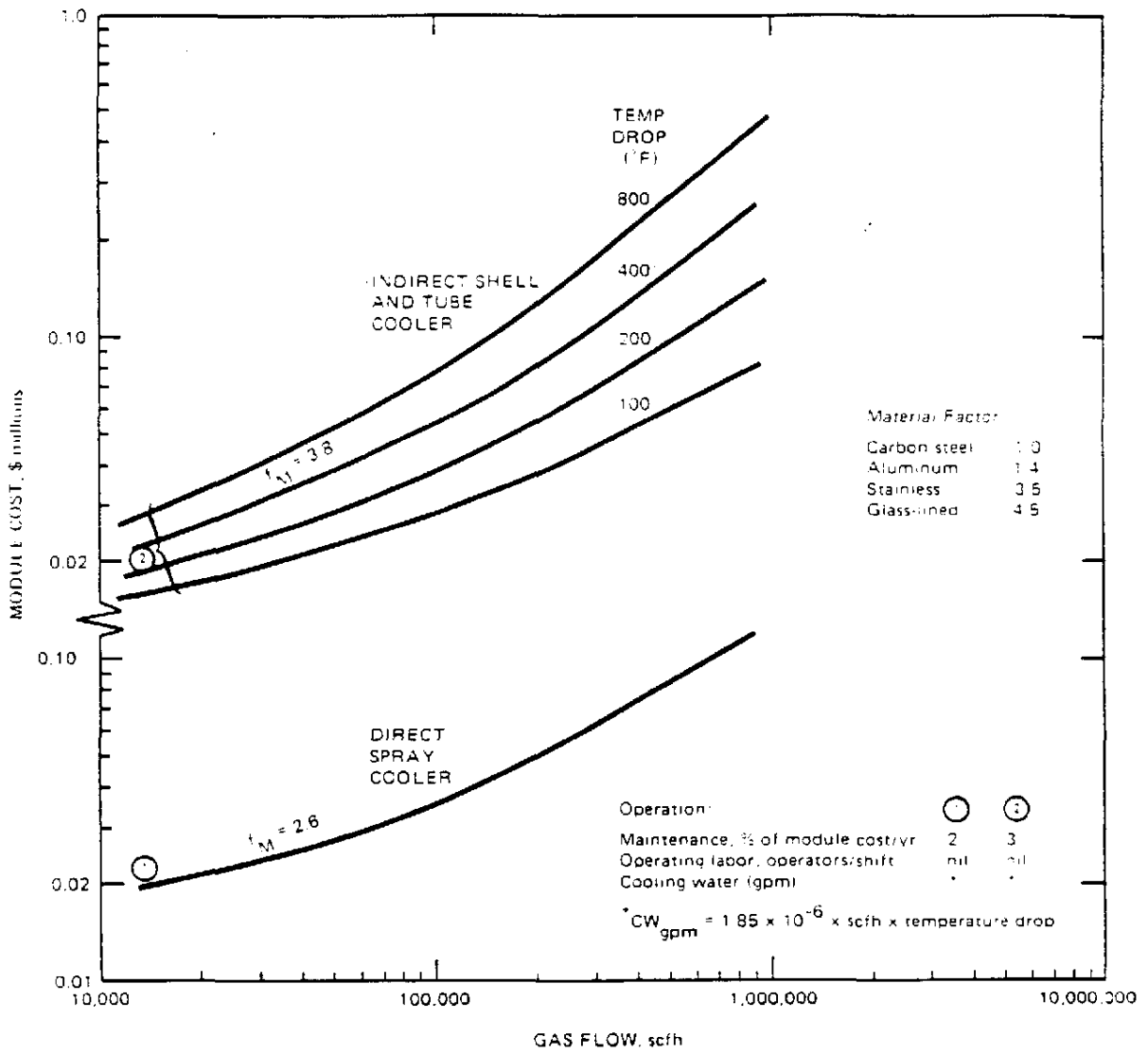
MODULE COST: DUST SEPARATOR



MCD 000016551

Figure 5.43

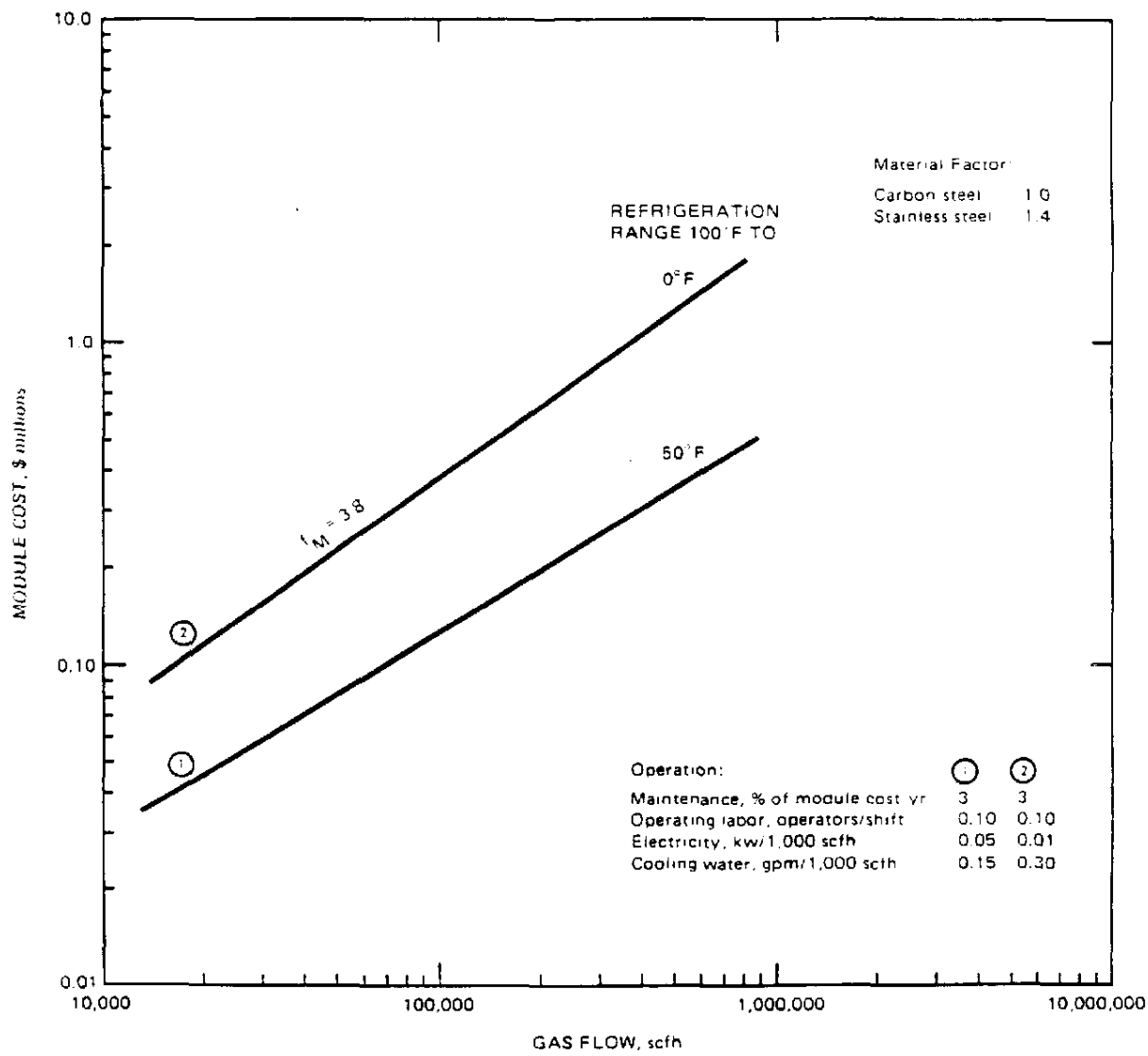
MODULE COST: GAS COOLERS



MCD 000016552

Figure 5.44

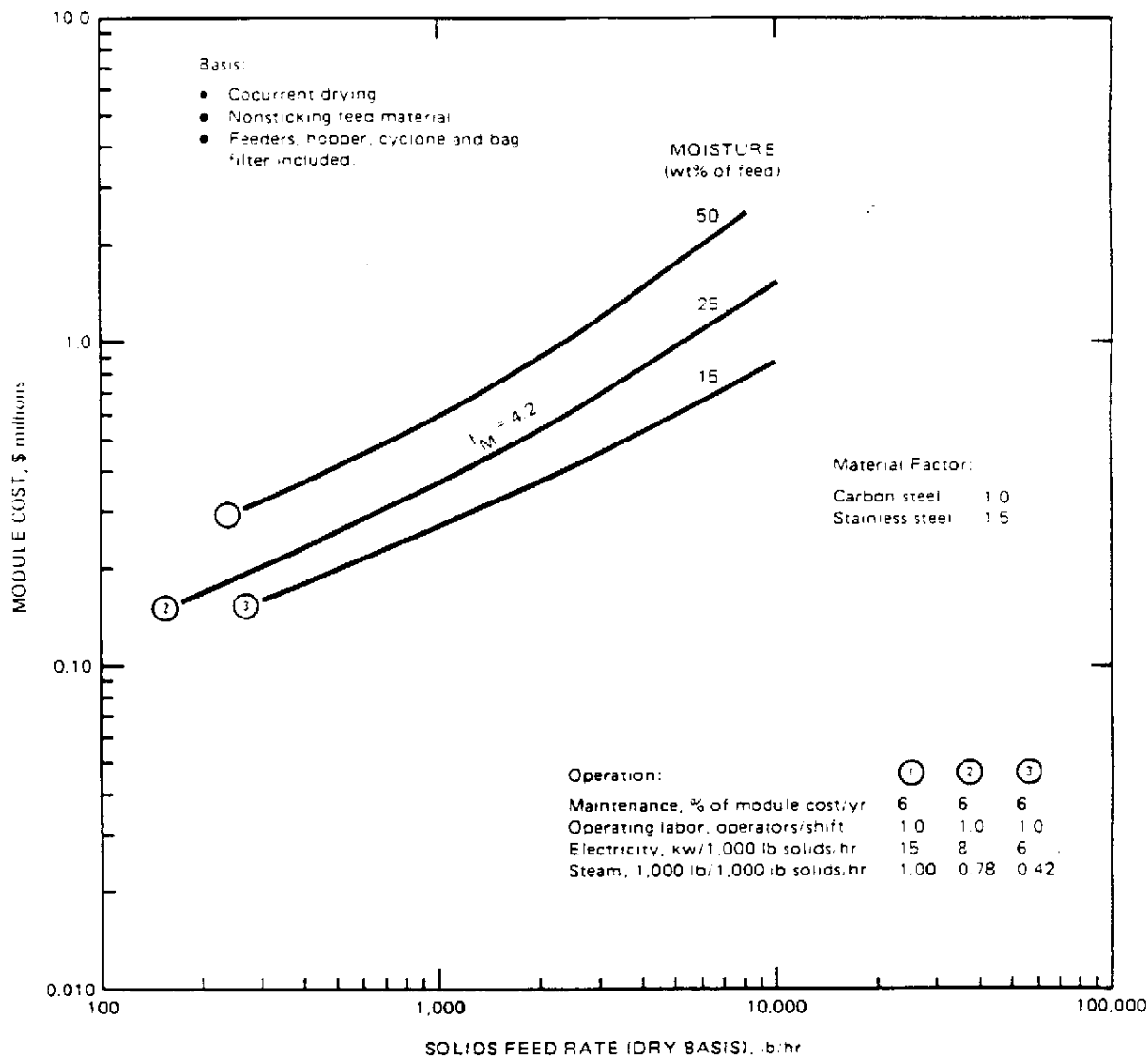
MODULE COST: GAS REFRIGERATION SYSTEM



MCD 000016553

Figure 5.45

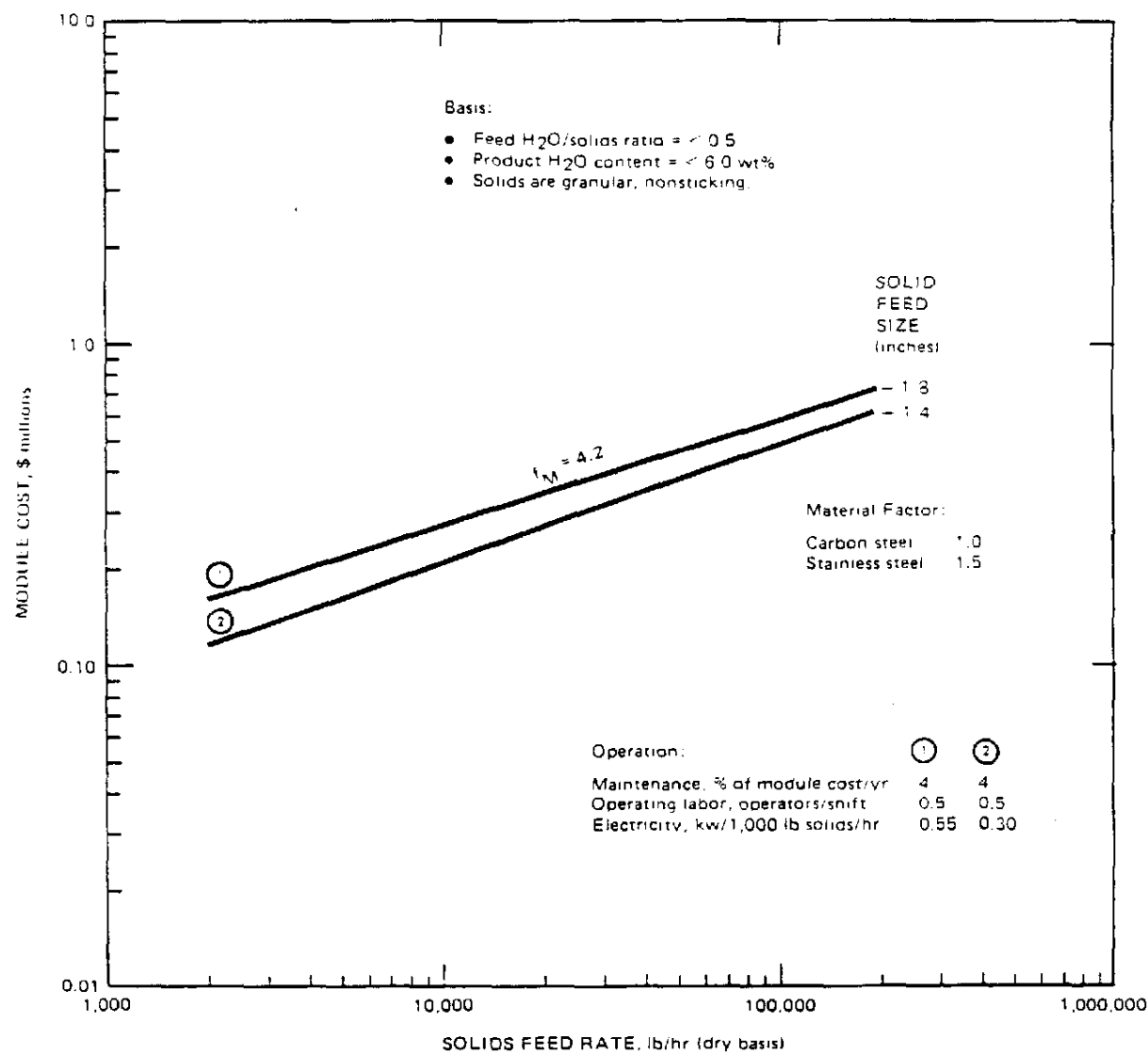
MODULE COST: ROTARY DIRECT DRYER



MCD 000016554

Figure 5.46

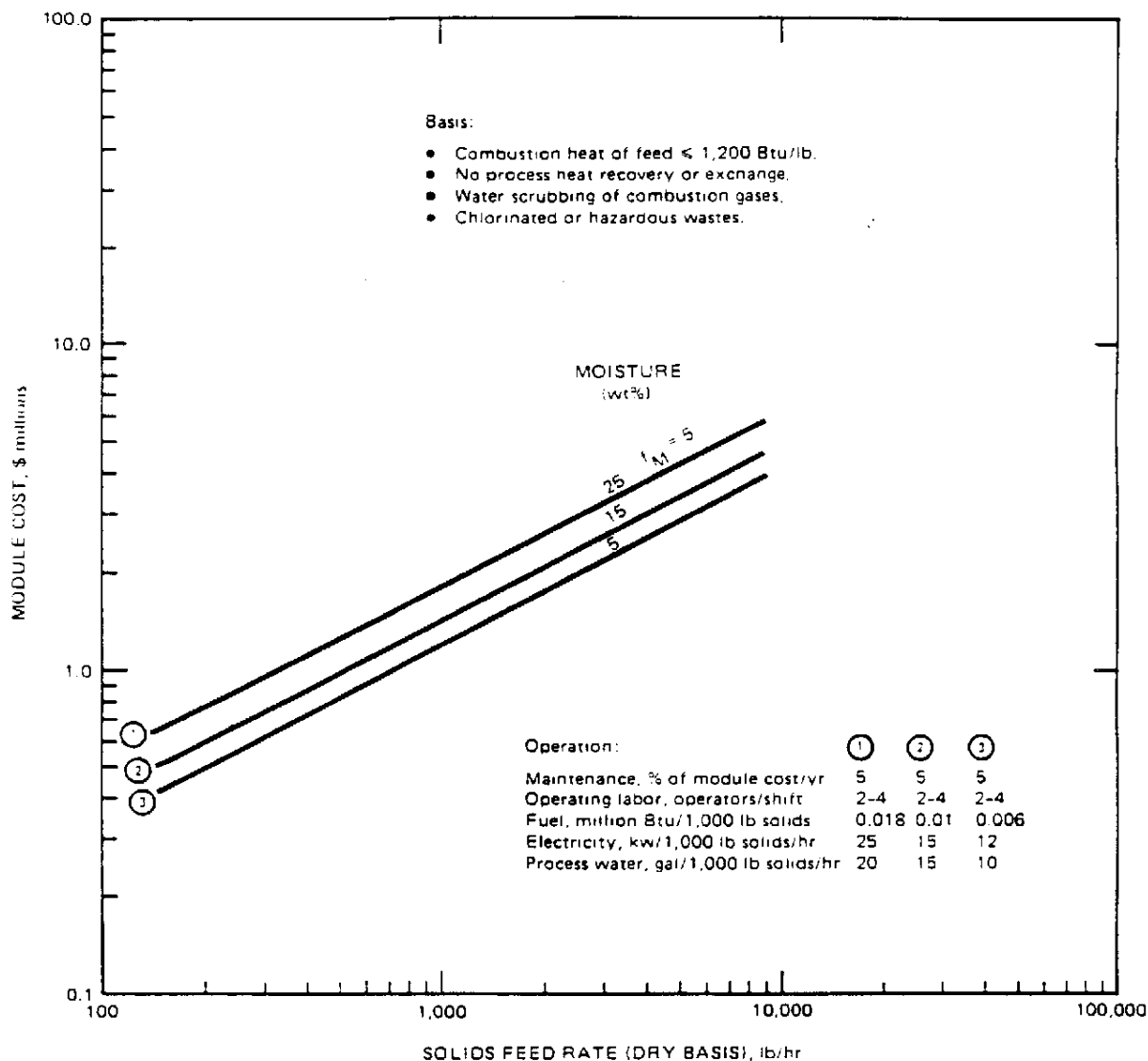
MODULE COST: DEWATERING CENTRIFUGE



MCD 000016555

Figure 5.47

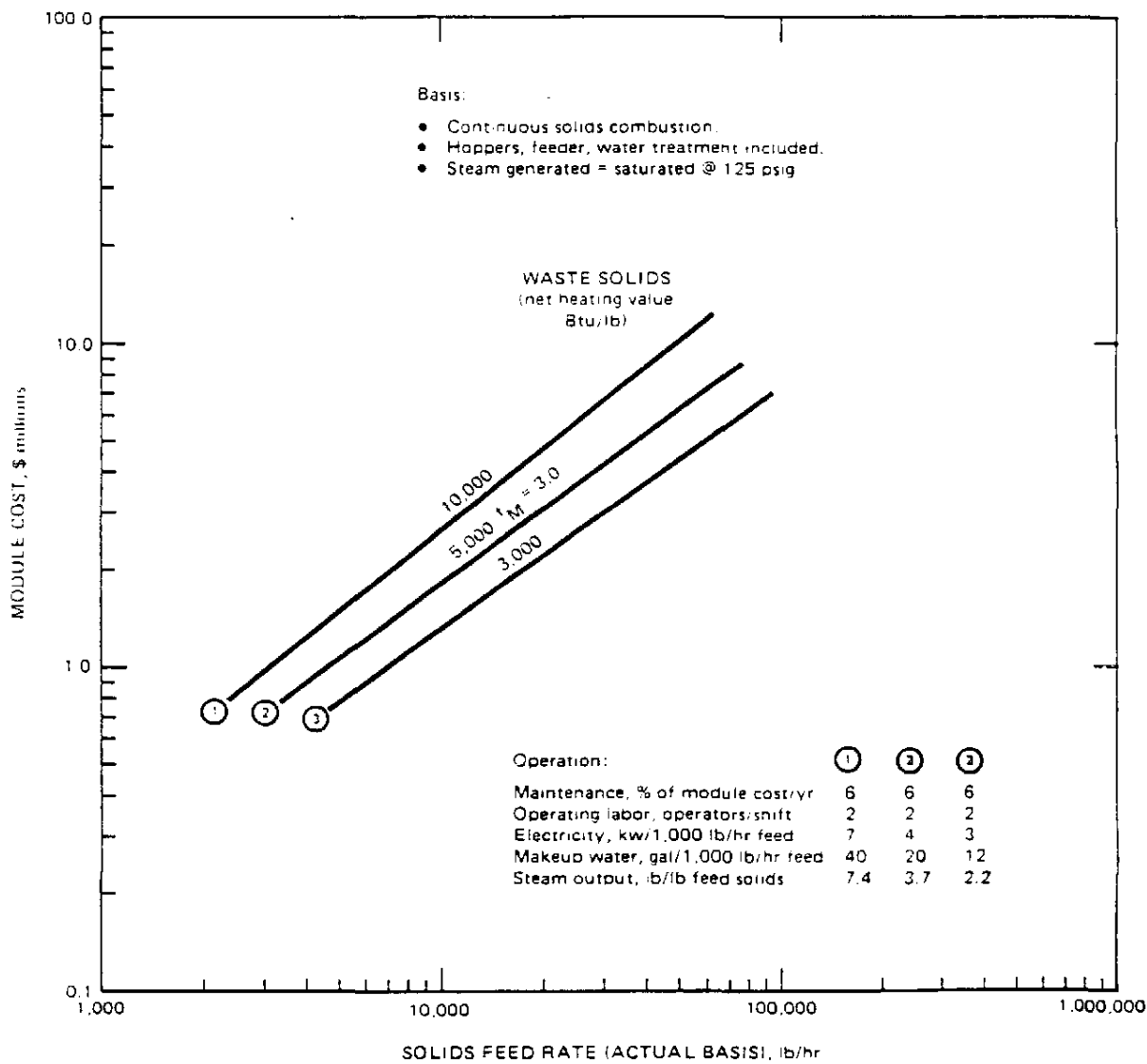
MODULE COST: SOLIDS INCINERATOR



MCD 000018556

Figure 5.48

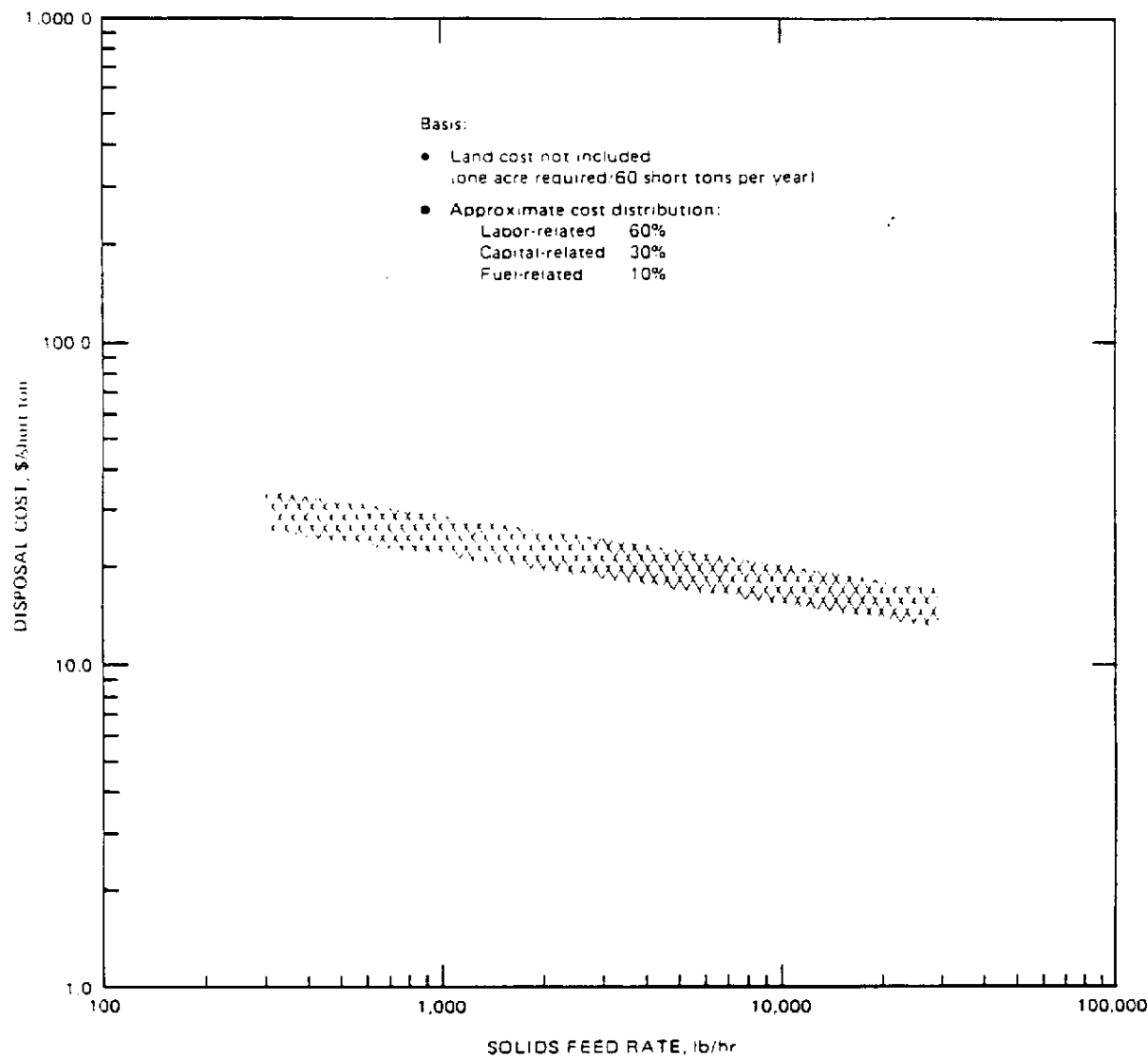
MODULE COST: SOLIDS COMBUSTOR



MCD 000016557

Figure 5.49

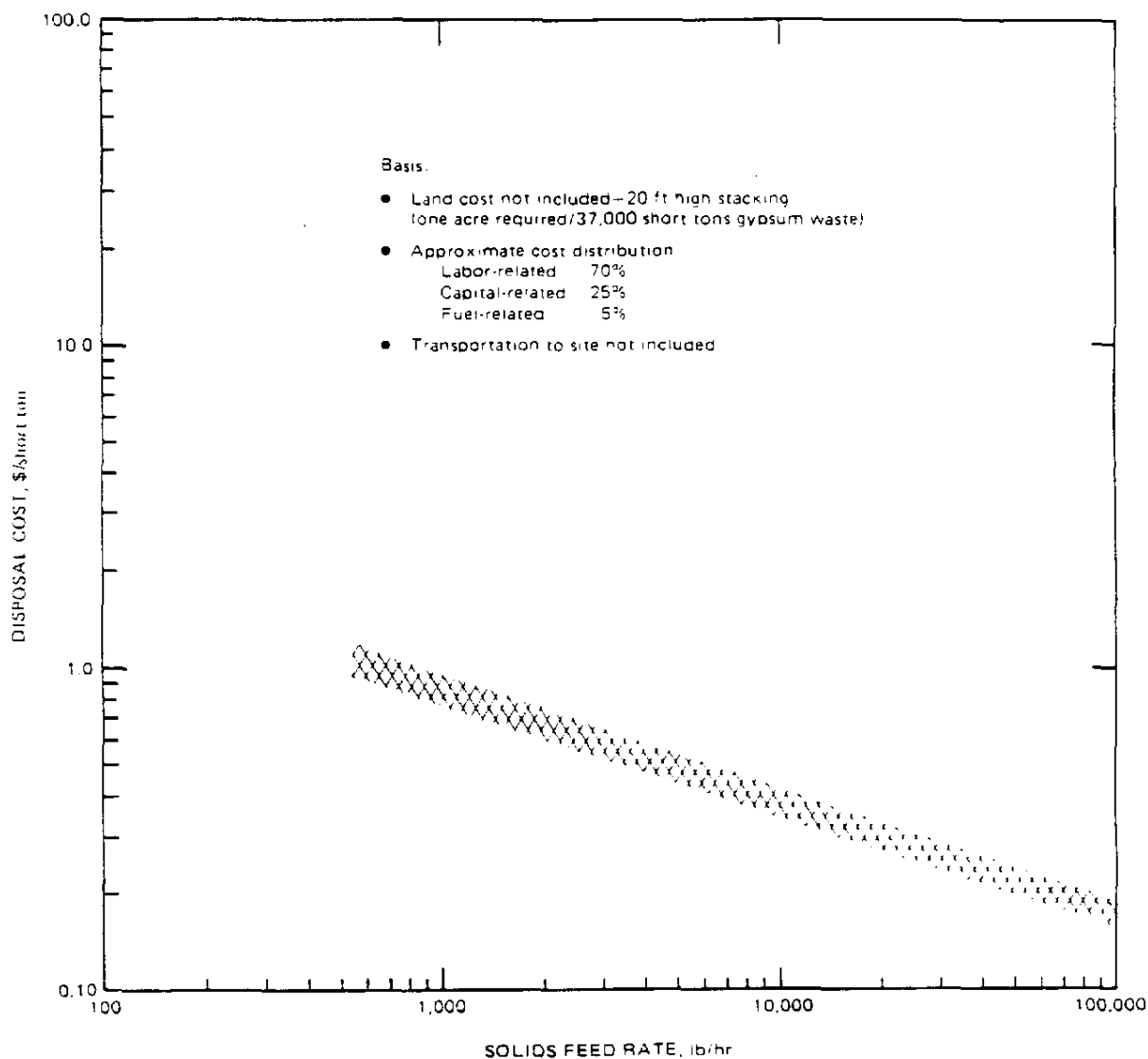
DISPOSAL COST: LAND FARMING



MCD 000016558

Figure 5.50

DISPOSAL COST: GYPSUM STACKING



MCD 000016559

Figure 5.51

DISPOSAL COST: SANITARY LANDFILL

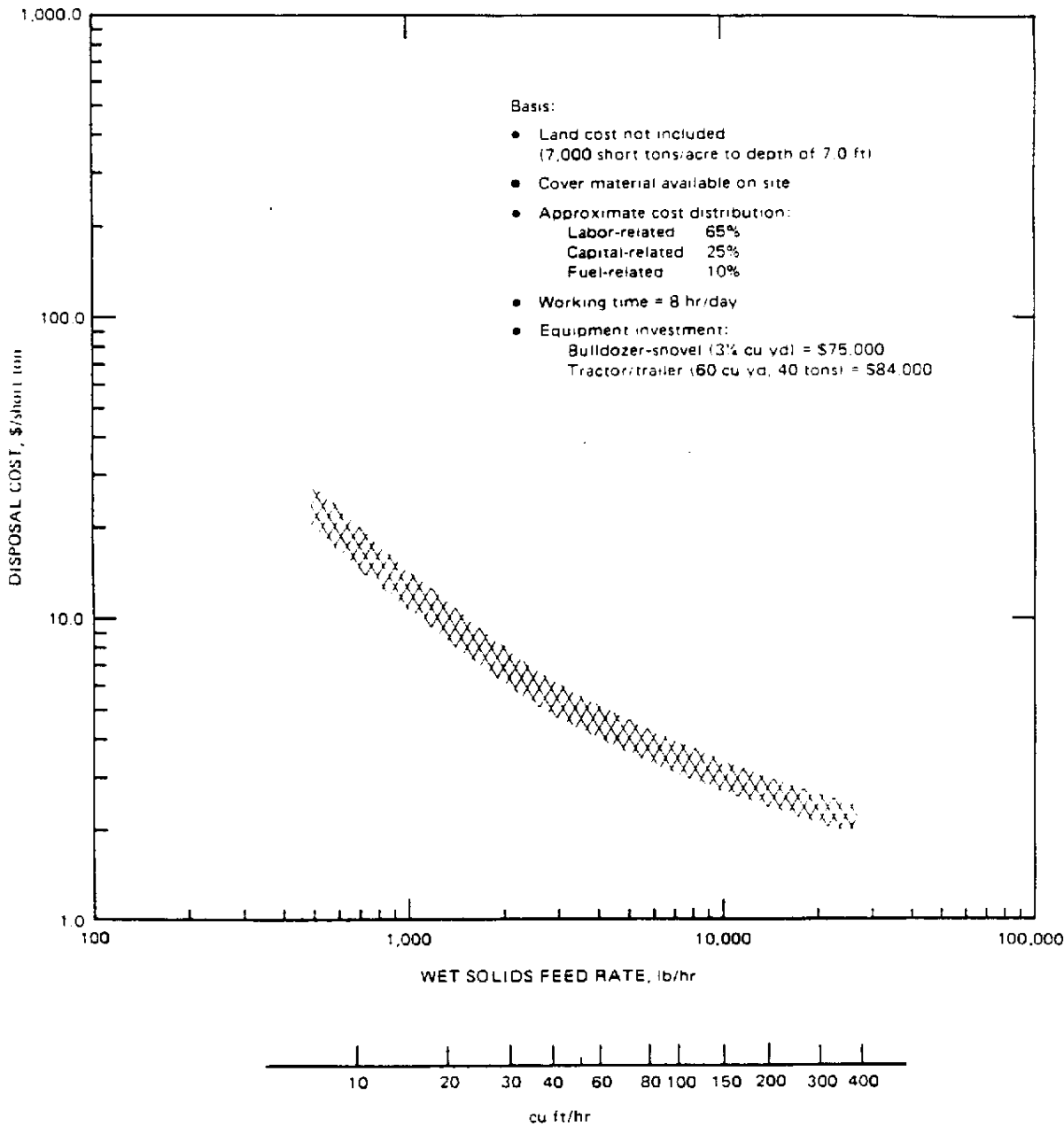
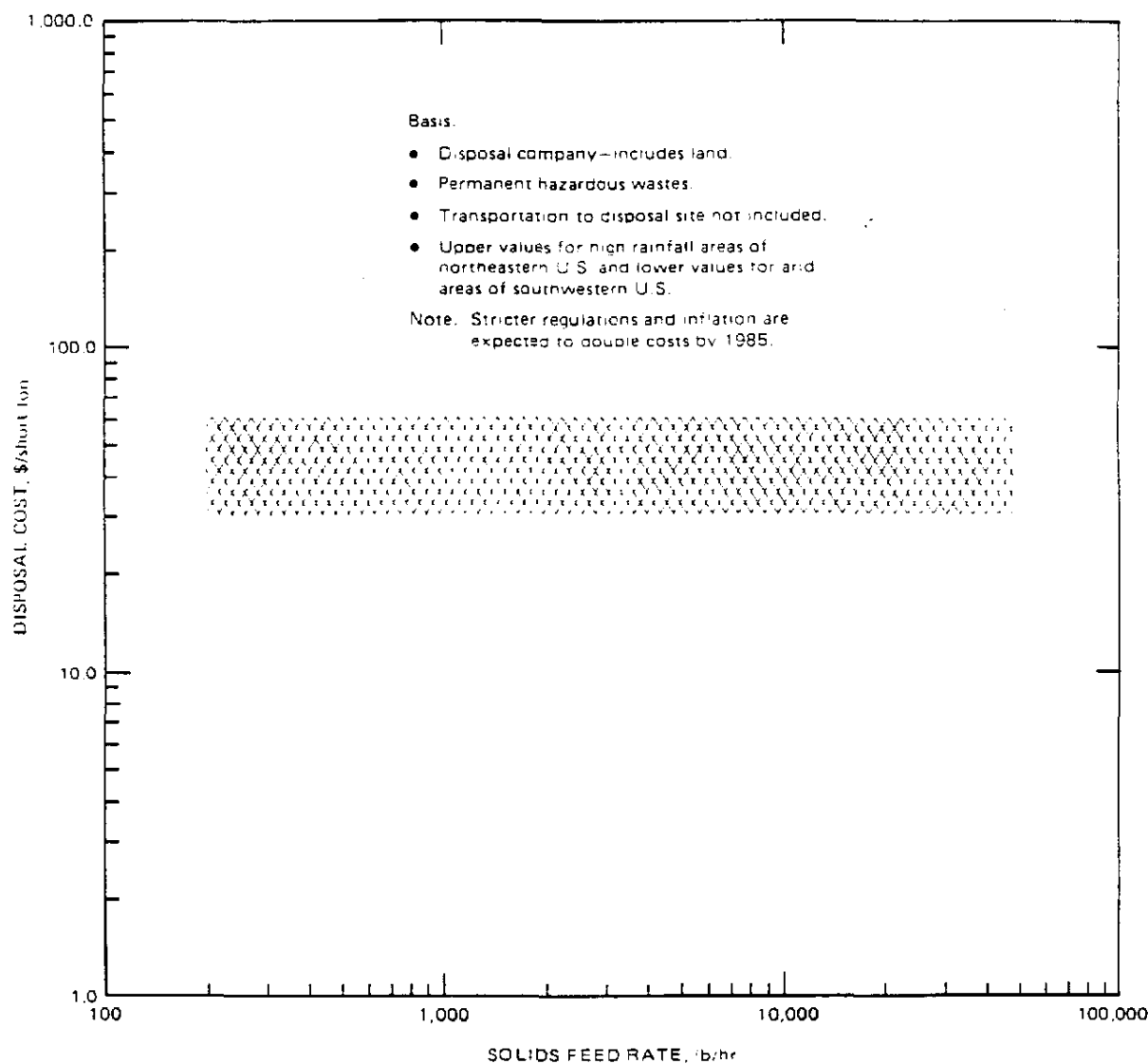


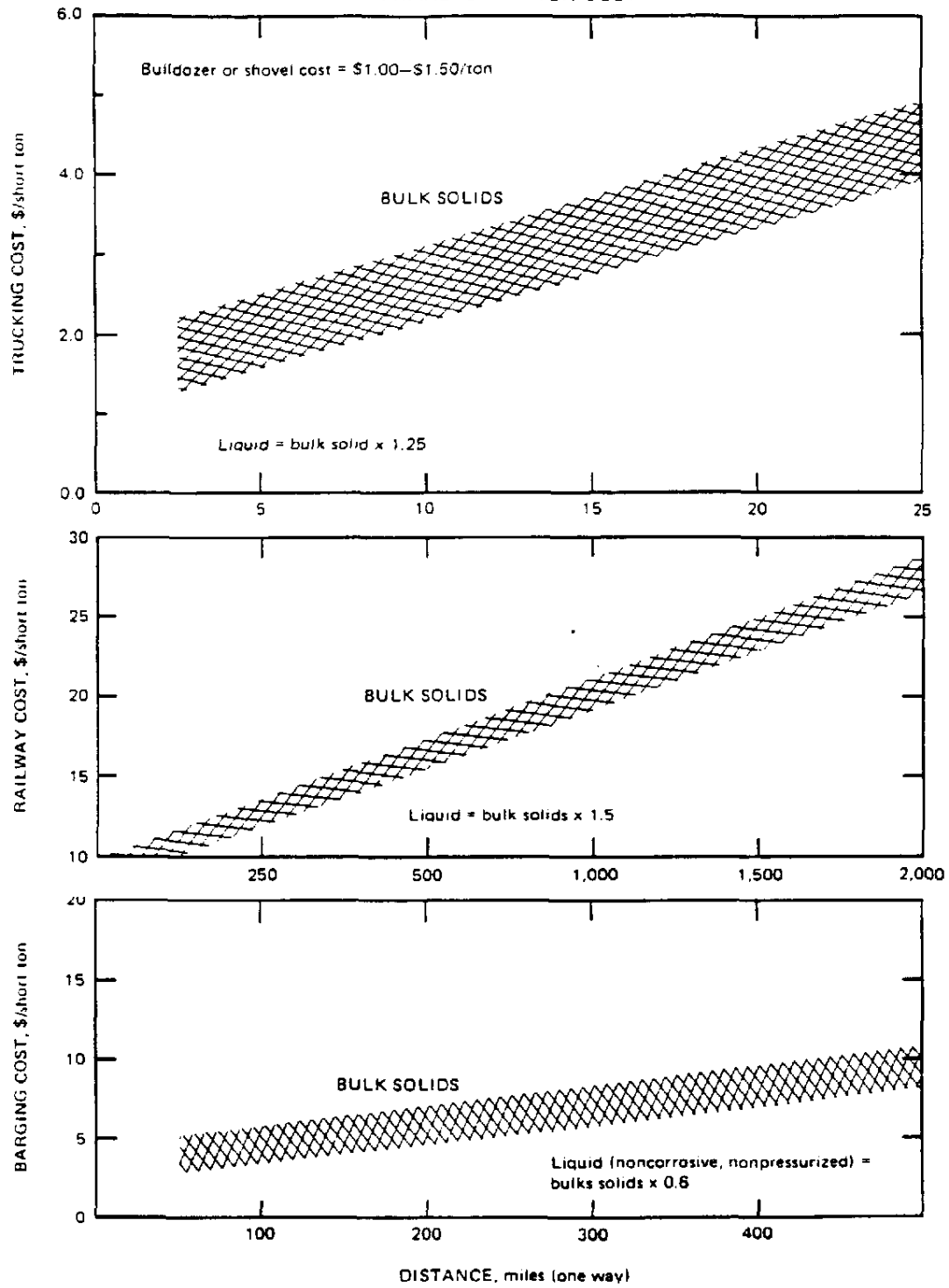
Figure 5.52

DISPOSAL COST: HAZARDOUS-WASTE LANDFILL



MCD 000016561

Figure 5.53
TRANSPORTATION COST



Source: Author estimates based on articles in *Chemical Week*, Nov. 1, 1978 and Oct. 11, 1972.

6 WASTE TREATMENT COSTS FOR SELECTED CHEMICAL INDUSTRIES

The waste treatment (and disposal) investment and operating costs for a specific chemical plant depend on several factors:

- The composition and quantity of waste streams.
- The area within which the wastes are generated and disposed of.
- The availability of existing public or licensed disposal facilities.
- The extent of local or national regulations pertaining to the disposal of waste materials.
- The nature of the chemical process.
- The kind and purity of the raw materials.

The purpose of this section is to demonstrate the application of the SRI-developed modular costs (see Section 5) to the estimation of capital and operating costs for the treatment of chemical plant wastes. To this end, the following chemical plants or complexes will be evaluated:

- A 1,000 tpd methanol plant.
- A one billion lb/yr ethylene plant.
- A multiplant complex for adiponitrile (280 tpd), ethylene propylene (1,200 tpd), hexamethylenediamine (270 tpd), and methanol (1,000 tpd).
- A 150 tpd phosphoric wet process phosphoric acid plant.

So far as possible, these estimates are compared with values derived independently elsewhere.

MCD 000016563

Methanol Plant Wastes

Treatment Methods

The volume and composition of the waste streams from a 1,000 tpd methanol plant (PEP Report No. 43A) are shown on the left hand side of Figure 6.1 and the suggested methods of treatment are indicated by the schematic blocks to the right.

Gaseous wastes--consisting of H_2S -rich methane purge gases from the active carbon adsorber, and the light-ends from the methanol purification--are combined and fed to a combustion furnace to generate export steam. Combustion gases are scrubbed to remove sulfur dioxide as calcium sulfite/sulfate solids and are then discharged to the atmosphere.

Liquid wastes, consisting of the bottoms from the methanol distillation column, are combined with miscellaneous process washing, leaks, and site runoff for biological oxidation. The resulting sludge is used for landfill, together with the calcium solids from the stack gas scrubber. Spent active carbon, and zinc oxide from the natural gas feed desulfurization are also sent to landfill disposal.

The BOD_5 content of the 3,000 gph of liquid discharge from the biological oxidation is 50 ppm or 30 lb/day. This compares with the EPA standard for new methanol plants (B-13935) of 0.12 lb/ton of methanol production, or 120 lb/day.

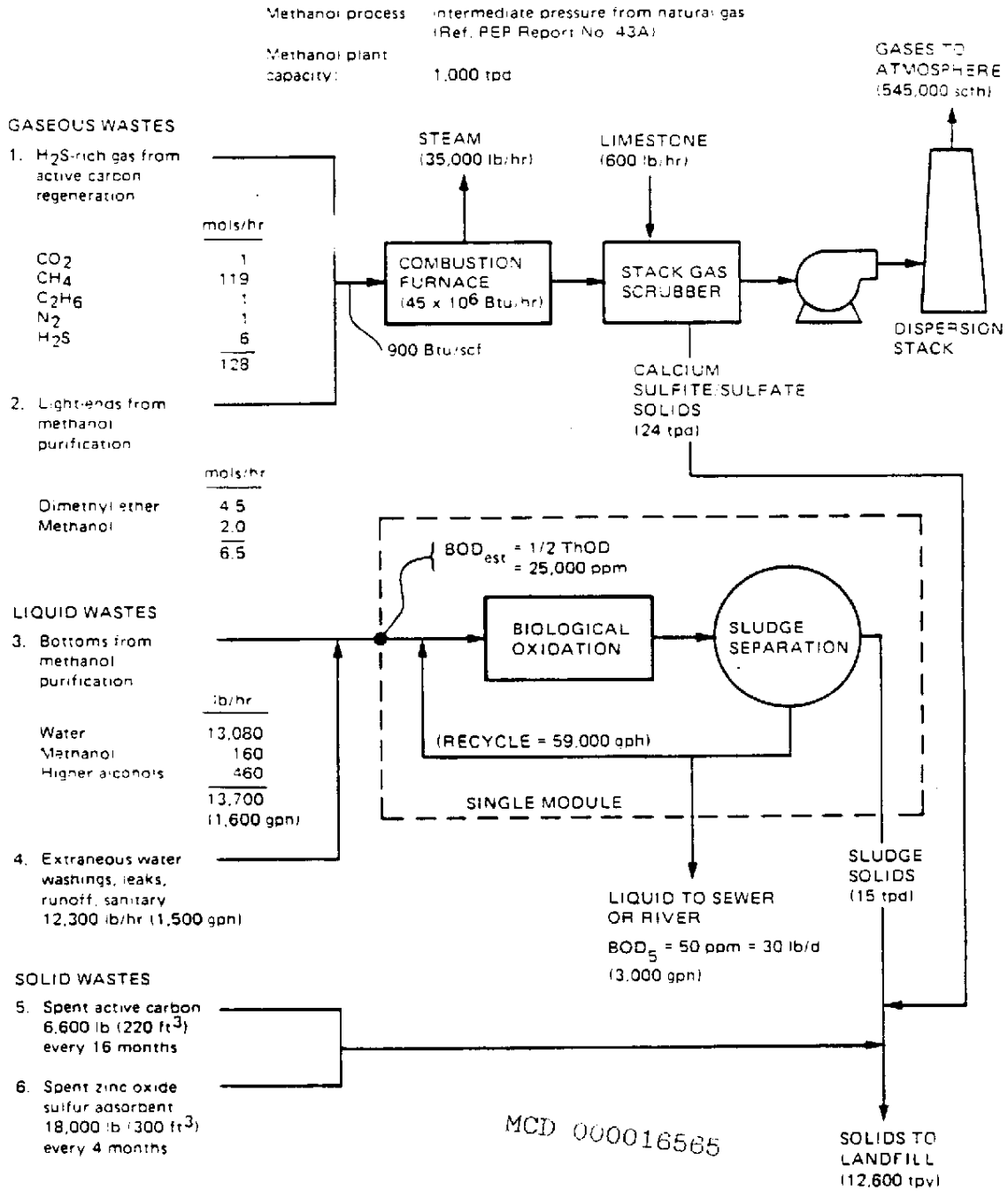
Treatment Costs

Capital investment and operating costs for the four equipment modules shown in Figure 6.1 are listed in Table 6.1. Module costs were read from the appropriate liquid, gas or solid treatment modules of Section 5. An additional 30% was included in the modular costs to allow for indirect expenses (e.g., contractors fees and overhead) as well as for general facilities (stores, maintenance shops, change rooms, etc.). Thus, the total waste treatment fixed capital is estimated at \$8.2 million, with the stack gas scrubber accounting for 50%

MCD 000016564

Figure 6.1

TREATMENT OF METHANOL PLANT WASTES



Reference: PEP Report No. 43A

Table 6.1
TREATMENT COSTS FOR METHANOL PLANT WASTES

Methanol Plant Capacity: 1,000 tpd; 0.9 Annual Stream Factor
Methanol Plant Investment: \$50 million
PEP Cost Index: 190
Time Base: January 1979

	Combustion Furnace	Stack Gas Scrubber	Dispersal Stack	Biological Oxid. and Sludge Sepn.	Totals
Capital Investment (\$1,000)					
Module costs	375	3,100	17	2,800	6,292
Indirect costs, general facilities, & contingencies, 30%	113	930	5	840	1,888
Total fixed capital	488	4,030	22	3,640	8,180
Operating costs (\$1,000/yr)					
Labor (men/shift) @ \$14.20/man-hr	(1) 60	(2) 240	—	(1) 120	(3 1/2) 420
Maintenance* (% module cost)	(3) 11	(3) 93	(1) Negl.	(4) 112	216
Materials					
Limestone @ \$20/ton	—	47	—	—	47
Line @ \$30/ton	—	—	—	37	37
Ammonia @ \$120/ton	—	—	—	24	24
Phosphoric acid @ \$150/ton	—	—	—	15	15
Copperas @ \$35/ton	—	—	—	7	7
Subtotal, materials	—	47	—	83	130
Utilities					
Electricity @ 2.6¢/kwh	10	11	—	168	189
Process water @ 60¢/1,000 gal	14	—	—	—	14
Steam @ \$5.00/1,000 lb	-1,386	—	—	—	-1,386
Subtotal, utilities	-1,362	11	—	168	-1,183
Overhead, 50% of labor	30	120	—	60	210
Depreciation, 10%/yr of fixed capital	49	403	2	364	818
Solids disposal, @ \$6.50/ton†	—	50	—	32	82
TOTAL OPERATING COST	-1,212	964	2	939	693

*Labor and materials.

†5 mile round trip @ \$2.00/ton plus \$4.50/ton landfill operation.

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of this and biological oxidation for 44%. The combustion furnace and the dispersal stack account for the remaining 6%. The above investment in waste treatment represents about 15% of the methanol plant fixed capital requirement.

Labor, material, and utility requirements for each equipment module are read from the table accompanying each module cost curve and entered in Table 6.1 at their current value or list price. Next, overhead costs, equal to 50% of operating labor, is added on the assumption that the waste treatment facilities are an integral part of a larger chemical unit or complex. Depreciation, is included at a rate of 10%/yr of fixed capital. Finally, a charge of \$6.50/ton is made for disposal of solids on the basis of the assumed hauling distance and disposal method. Thus, total treatment cost, after a credit of \$1.36 million/yr for the steam generated by the combustion furnace, is \$693,000/yr. This is equal to about 1.0% on a methanol sales price of 70¢/gal.

Discussion of Costs

The BOD₅ content of the 3,000 gph liquid feed to the biological oxidation is too high for a direct reading on the cost module curve. Thus, a recycle stream of 59,000 gph is assumed in order to reduce the BOD₅ content in the feed to 1,250 ppm. Then the modular cost for biological oxidation and sludge separation of \$2.8 million is read from the curve at a flow rate of 62,000 gph and a BOD content of 1,250 ppm.

A considerable reduction in these waste treatment costs is possible with planning. For example, if desulfurized natural gas is available as the raw material, the first three treatment modules-- combustion furnace, stack gas scrubber, and dispersal stack--would not be required. They could be replaced by a small flare to incinerate the light-ends from the methanol purification. Also, if the plant location is within a reasonable distance of a publicly owned treatment works (POTW) it may be more economic to treat the small volume of aqueous

organics in the public facility. A typical POTW fee of \$250/million gal/yr, 5¢/lb BOD, and 10¢/lb suspended solids plus a proportionate share of capital depreciation could result in an alternative annual cost in the range of \$600,000 to \$700,000.

An independent estimate (B-13934) of the capital investment to treat 4,200 gal/hr of aqueous methanol waste ($BOD_5 = 1,200$ ppm) by the best practicable technology (BPT) adjusted to a January 1979 basis, is \$712,000. Operating charges--exclusive of depreciation, overhead, and sludge disposal--are \$116,000/yr. Comparative costs for the same stream read from the biological oxidation (air-activated sludge) curve (Figure 5.20) are \$858,000 for capital investment (+17%) and \$162,000 annual operating charge (+28%).

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Ethylene Plant Wastes

Treatment Methods

The composition and quantity of gaseous and liquid ethylene plant waste streams, together with their proposed treatment sequence, is illustrated by Figure 6.2. The stream quantities and compositions are constructed from published information on ethylene plant wastes (PEP Report No. 29B and references 358765 and 358811). The treatment methods are selected from the available technology described in Section 4 of the current study.

Gaseous wastes, consisting of hydrocarbons containing purge and vent gases, are flared. Also in the event of an emergency shutdown, feed gases can be diverted to the flare stack until their flow can be stopped. Green oil liquid waste from the acetylene converter, together with oil skimmed from the process vaporizer blow-down is burned to generate steam. The combustion gases are discharged through the flare stack.

Process vaporizer blow-down following the flow equalization-settling-skimming tank is treated by anion exchanger to remove S, Cl, and CN ions. The effluent from the ion exchanger is combined with the condensate from the glycol stripper. This combined stream is then added to neutralized spent caustic wastes and the mixture is subjected to biological oxidation to reduce the organic contaminants. Finally, in accordance with the best available technology (BAT), the aqueous effluent from the biological oxidation is treated with active carbon to eliminate residual phenol, cyanide, and BOD. Runoff water capacity equivalent to 50% of the 2 year maximum one-hour rainfall (U.S. Gulf Coast) is included but not treated.

Treatment Costs

Capital and operating costs for the eight equipment modules described above are obtained from the modular cost curves and their associated operating tables of Section 5. These are listed in Table 6.2 for each module. Thus, the total module cost is \$1.06 million.

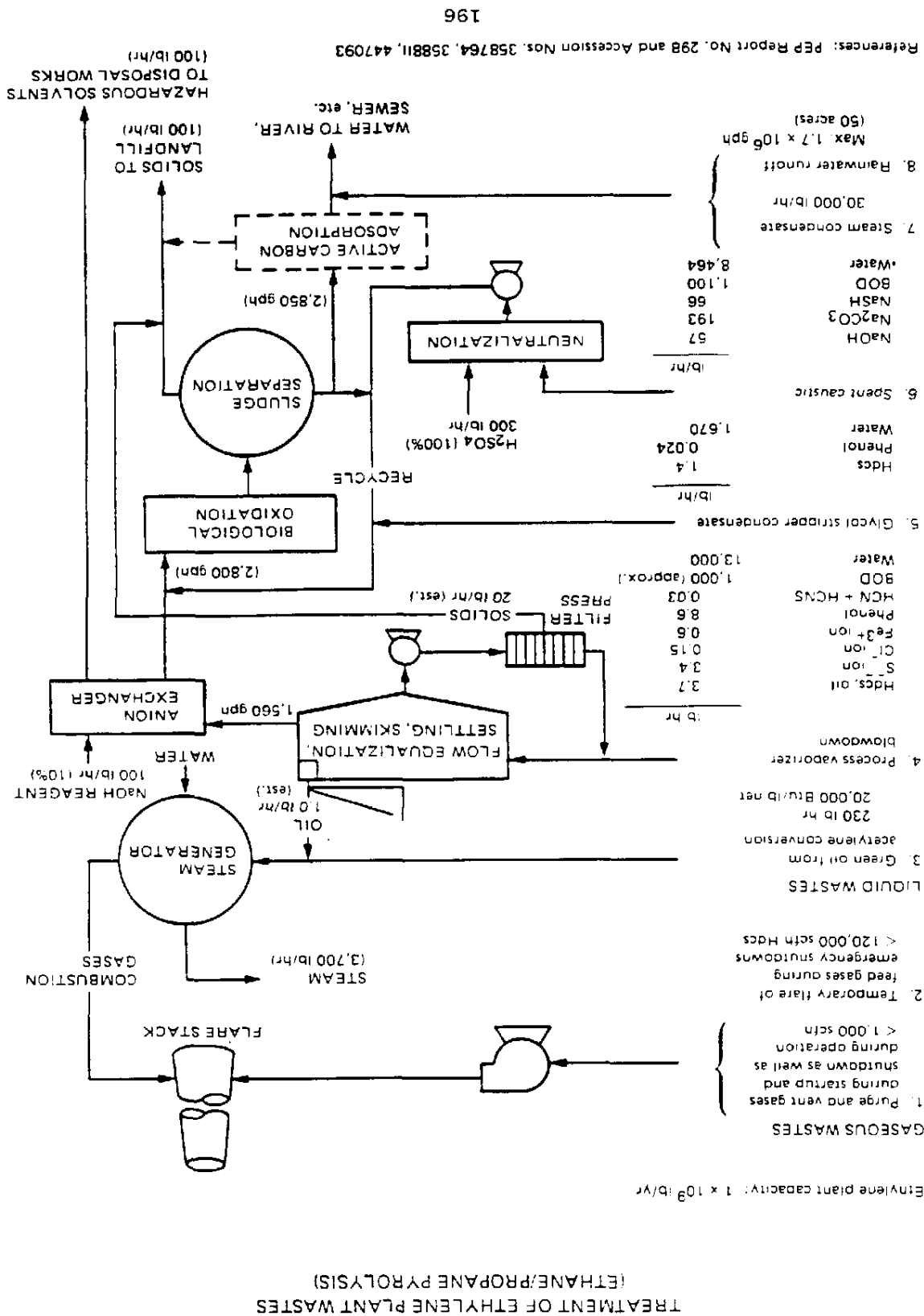


Table 6.2
TREATMENT COSTS FOR ETHYLENE PLANT WASTES

Ethylene Plant Capacity: 1.0×10^9 lb/yr at 0.9 Stream Factor
Ethylene Plant Investment: \$190 million
Pep Cost Index: 290
Time Base: January 1979

	Flare Stack	Steam Generator	Settler-Skimmer	Filter Press	Anion Exchanger
Capital investment (\$1,000)					
Module costs	34	46	120	30	30
Indirect costs, general facilities, & contingencies, 30%	10	14	36	9	9
Total fixed capital	44	60	156	39	39
Operating cost (\$1,000/yr)					
Labor (men/shift) @ \$14.20/man-hr	—	(0.5) 60	(0.1) 12	(0.2) 24	(0.3) 36
Maintenance* (% of module cost)	(2) 1	(4) 2	(2) 2	(3) 1	(3) 1
Materials					
NaOH (50%) @ 10c/lb	—	—	—	—	16
Ammonia (anhydrous) @ \$120/ton	—	—	—	—	—
Phosphoric acid (100%) @ \$150/ton	—	—	—	—	—
Lime (CaO) @ \$30/ton	—	—	—	—	—
Copperas @ \$35/ton	—	—	—	—	—
Sulfuric acid (100%) @ \$60/ton	—	—	—	—	—
Active carbon @ 60c/lb	—	—	—	—	—
Subtotal, materials	—	—	—	—	16
Utilities					
Electricity @ 2.6c/kwh	—	1	—	1	—
Steam @ \$5.00/1,000 lb	2	-146	—	—	—
Subtotal, utilities	2	-145	—	1	—
Overhead, 50% of labor	—	30	6	12	18
Depreciation, 10%/yr of fixed capital	4	6	16	4	4
Waste disposal					
Solids @ \$6.50/ton†	—	—	—	—	—
Liquid @ \$25/1,000 lb‡	—	—	—	—	20
TOTAL OPERATING COST	7	-47	36	42	95

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Table 6.2 (Concluded)

TREATMENT COSTS FOR ETHYLENE PLANT WASTES

Ethylene Plant Capacity: 1.0×10^9 lb/yr at 0.9 Stream Factor
 Ethylene Plant Investment: \$190 million
 PEP Cost Index: 290
 Time Base: January 1979

	Biol. Oxidn. & Sludge Sepn.	Neutralization	Active Carbon Adsorption	Totals
Capital investment (\$1,000)				
Module costs	530	100	165	1,055
Indirect costs, general facilities, & contingencies, 30%	157	30	50	215
Total fixed capital	687	130	215	1,370
Operating cost (\$1,000/yr)				
Labor (men/shift) @ \$14.20/man hr	(1) 120	(0.5) 60	(0.5) 60	372
Maintenance* (% of module cost)	(4) 21	(4) 4	(4) 6	(3.65) 38
Materials				
NaOH (50%) @ 10¢/lb	--	--	--	16
Ammonia (anhydrous) @ \$120/ton	1	--	--	1
Phosphoric acid (110%) @ \$15¢/ton	1	--	--	1
Lime (CaO) @ \$30/ton	2	--	--	2
Copperas @ \$35/ton	1	--	--	1
Sulfuric acid (100%) @ \$6¢/ton	--	71	--	71
Active carbon @ 60¢/lb	--	--	19	19
Subtotal, materials	5	71	19	111
Utilities				
Electricity @ 2.6¢/kwh	8	1	1	12
Steam @ \$5.00/1,000 lb	--	--	--	-144
Subtotal, utilities	8	1	1	-132
Overhead, 50% of labor	60	30	30	186
Depreciation, 10% of fixed capital	69	13	21	137
Waste disposal				
Solids † \$6.50/ton†	3	--	--	3
Liquid ‡ \$25/1,000 lb‡	--	--	--	20
TOTAL OPERATING COST	286	179	137	735

*Labor and materials.

†5 mile round trip at \$2.50/ton plus \$4.50/ton landfill operation.

‡Charge for disposal to hazardous-waste management facility.

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When indirect costs, general facilities, and contingencies are added, the total fixed capital reaches \$1.37 million. This represents about 0.7% of the investment for an ethylene plant.

Operating costs for the eight equipment modules, including a \$146,000 credit for steam generation, totals \$735,000/yr. This is an almost insignificant charge of 0.07¢/lb of ethylene/propylene product.

Discussion of Costs

A study sponsored by the U.S. National Commission on Water Quality (B-13934) gives three major sources of ethylene plant wastes:

- (1) Water quench tower draw-off
- (2) Aqueous bleed from the acid gas scrubbing system
- (3) Condensate from compressor interstage coolers.

The combined quantity of these streams is said to be 44,800 gph with a BOD of 1,000 ppm and a COD of 2,360 ppm.

The estimated capital investment in equalization, neutralization, biological oxidation, and active carbon facilities to treat the above streams according to the best available demonstrated technology (BADT) was \$2.24 million in 1973 or about \$4.48 million as of January 1979. Scaling this down by 85% to correspond to the major flow stream quantities in the preceding modular estimate, gives a comparable capital investment of $4.48 \times 1/(7)^{0.6} = \1.40 million (i.e., a 2% difference).

Direct annual operating cost, excluding depreciation, for the larger flows was reported as \$310,000 in 1973—equivalent to approximately \$620,000 in 1979. This compares with a scaled-up modular cost of \$694,000/yr (+12%).

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Multiplant Wastes

Treatment Methods

A treatment sequence for the combined wastes from acrylonitrile, ethylene/propylene, hexamethylenediamine, and methanol plants has been proposed by the U.S. National Commission on Water Quality (B-13934). This scheme is illustrated by the block flow diagram of Figure 6.3 along with stream quantities and compositions. The adiponitrile wastes containing appreciable amounts of organics and cyanides are divided between incineration and deep-well disposals. Hexamethylenediamine wastes are steam stripped to remove ammonia, ozonated to reduce cyanide concentration, and then treated to separate an oil phase. The remaining waste stream is combined in an equalization and surge tank with the wastes from ethylene and methanol plants. This combined stream, amounting to 71,700 gph, is next neutralized with sulfuric acid, treated by activated sludge biological oxidation to reduce BOD, filtered in a dual media filter, and then passed through activated carbon to remove the last traces of cyanides. The effluent can be discharged to an adjacent river or ocean.

1

Treatment Costs

Capital investment for the above system was estimated in 1973 at \$4.5 million for best available demonstrated technology (BADT) and \$7.05 for best available technology (BAT). Converted to January 1979 costs, these figures become \$9.0 and \$14.1 million, respectively. Operating costs, excluding depreciation, in 1973 were \$0.82 million for BADT and \$1.55 million for BAT—equivalent in 1979 dollars, to approximately \$1.6 and \$3.1 million/yr respectively.

We have reestimated the capital and operating costs for the same multiplant waste treatment sequence on the basis of the waste treatment modular cost and quantities for Section 5 of this study. The total modular cost is \$9.5 million and the total fixed capital investment is \$12.4 million (Table 6.3). Total operating costs are \$3.2 million annually—\$2.0 million if depreciation is excluded.

TREATMENT OF MULTIPLANT WASTES

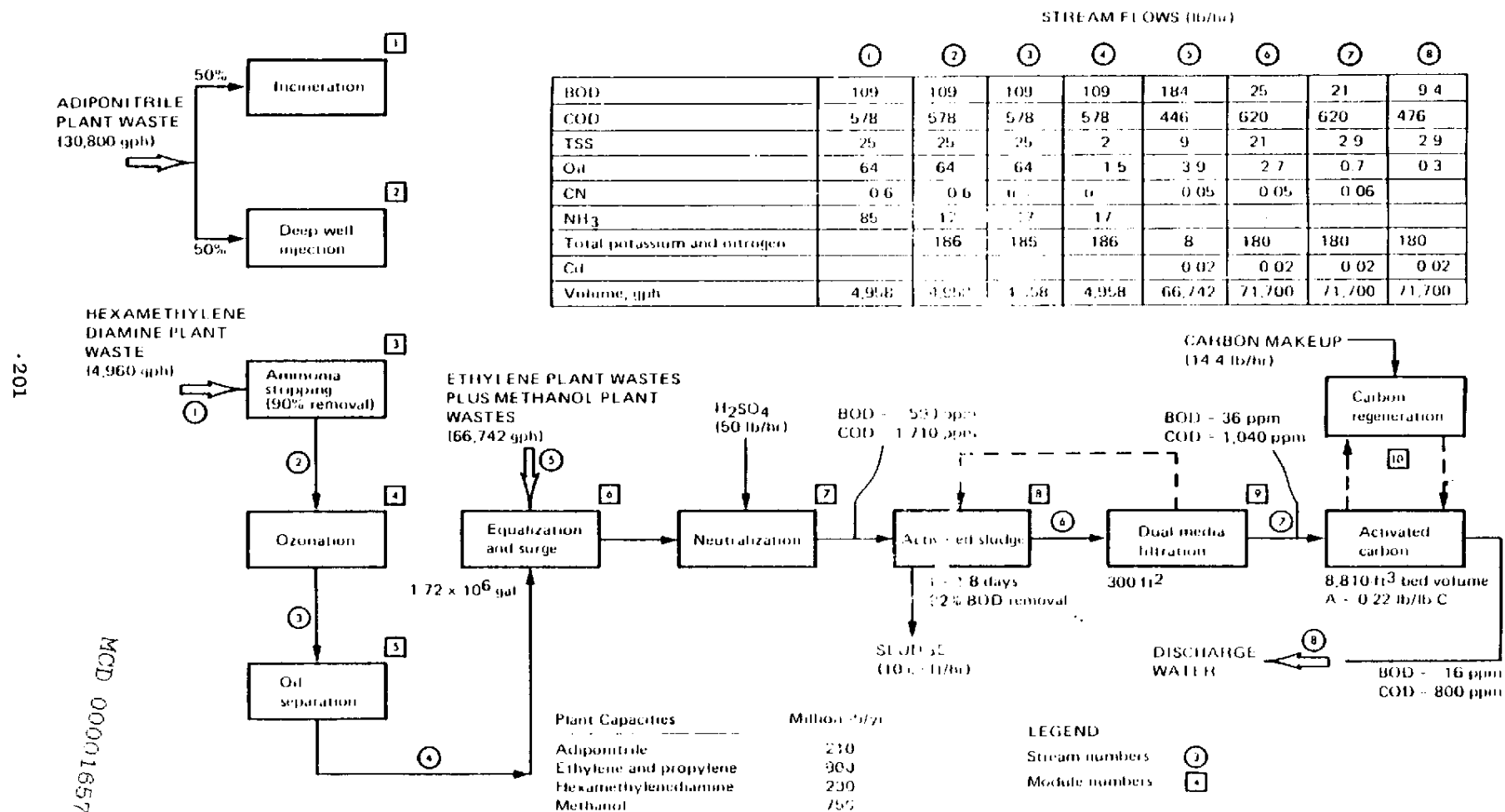


Table 6.3
TREATMENT COSTS FOR COMBINED MULTIPANT WASTES

Plant Capacities (million lb/yr at 0.9 stream factor):
 Ethylene & propylene = 900
 Adiponitrile = 200
 Hexamethylenediamine = 200
 Methanol = 750
 Plant Investment: 5085 million
 PEP Cost Index: 190
 Time Base: January 1979

	Incineration	Deep-Well Injection	Ammonia Stripping	Ozonation	Oil Separation	Equalization and surge
Capital investment (\$1,000)						
Module costs	4,000	1,450	100	150	5*	540
Cooling water utility	--	--	30	--	--	--
Indirect costs, 30%	1,200	435	35	45	--	160
Total fixed capital	5,200	1,885	135	195	5	700
Operating costs (\$1,000/yr)						
Labor (men/shift) @ \$14.20/man-hr	(1) 120	--	(0.5) 60	(0.2) 24	(0.1) 12	--
Maintenance (2% of module cost)	(+) 160	(1) 15	(+) --	(5) 8	(+) Negl	(1) 5
Materials†						
Sulfuric acid (100%) @ \$60/ton	--	--	--	--	--	--
Phosphoric acid (100%) @ \$150/ton	--	--	--	--	--	--
Lime (CaO) @ \$30/ton	--	--	--	--	--	--
Copperas @ \$15/ton	--	--	--	--	--	--
Active carbon @ 60¢/lb	--	--	--	--	--	--
Utilities						
Electricity @ 2.6¢/kwh	76	30	2	4	--	6
Fuel @ \$2.30/Million Btu	164\$	--	**	--	--	--
Overhead, 50% of labor	60	--	30	12	6	--
Depreciation, 10%/yr of F.C./yr	520	190	15	20	--	70
Solid waste disposal††						
Land spreading of bio-solids @ 2.50/ton	--	--	--	--	--	--
Landfill of carbon @ 6.50/ton	--	--	--	--	--	--
TOTAL OPERATING COST	1,300	235	111	68	18	81

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Table 6.3 (Concluded)
TREATMENT COSTS FOR COMBINED MULTIPANT WASTES

Plant Capacities (million lb/yr at 0.9 stream factor):
Ethylene & propylene = 900
Adiponitrile = 210
Hexamethylenediamine = 200
Methanol = 750
Plant Investment: \$385 million
PEP Cost Index: 290
Time Base: January 1979

	Neutralization	Activated Sludge	Dual Media Filtration	Activated Carbon	Totals
Capital Investment (\$1,000)					
Module costs	70	2,000	230	1,000	9,545
Cooling water utility	--	--	--	--	20
Indirect costs, 30%	22	600	70	300	2,855
Total fixed capital	90	2,600	300	1,300	12,430
Operating costs (\$1,000/yr)					
Labor (men/shift) @ \$14.20/man-hr	(0.5) 60	(1) 120	(0.5) 60	(1) 120	(4.8) 576
Maintenance (2% of module cost)	(4) 3	(4) 80	(5) 12	(4) 40	(13.5) 167
Materials*					
Sulfuric acid (100%) @ \$60/ton	12	--	--	--	12
Phosphoric acid (100%) @ \$150/ton	--	8	--	--	8
Slime (Gals) @ \$30/ton	--	21	--	--	21
Copperas @ \$35/ton	--	3	--	--	5
Active carbon @ 60¢/lb	--	--	--	58	68
Utilities					
Electricity @ 2.6¢/kwh	43	93	7	1	262
Fuel @ \$2.35/million Btu	--	--	--	21	385
Overhead, 50% of labor	30	60	30	60	288
Depreciation, 10%/yr of P.C./yr	9	260	30	130	1,244
Solid Waste Disposal**					
Land spreading of bio-solids @ 2.50/ton	--	10	--	--	14
Landfill of carbon @ 6.50/ton	--	--	--	4	--
TOTAL OPERATING COST	157	657	139	444	3,210

* An oil skimmer attached to the top of the equalization tank.

* Ammonia from the ammonia stripping is used in the activated sludge section. No credit is allowed for excess ammonia.

\$ Incinerable wastes assumed to have combustible content equal to 3,000 Btu/lb of waste.

**Excess steam from incineration is used for ammonia stripping. No credit taken for steam generation above this amount.

**Waste disposal is assumed to be adjacent to plant; therefore hauling charges are insignificant.

Comparison reference: 3-13934, Generalized Plant No. 18.

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Discussion of Costs

The difference between the above BADT and BAT costs is the addition of the activated carbon adsorber to the final waste treatment sequence so as to eliminate residual toxic impurities. The modular cost estimating procedures in this report do not distinguish among BADT, BAT, and BPT. Thus, it might be expected that the modular cost estimated here would occupy an intermediate position, as shown below:

	<u>Estimated Capital Investment (\$ millions)</u>	<u>Annual Operating Cost-- Excl. Deprec. (\$ millions)</u>
Modular costs	\$ 12.4	\$ 2. 0
Comparative costs		
BPT	8.6	1.58
BADT	9.1	1.63
BAT	14.1	3. 1

Thus, the BADT investment is 26% below the modular investment while the BAT figure is 14% above. The same comparative percentages for operating costs are -23% and +55% respectively.

The \$12 million investment in waste treatment facilities represents about 3% of the capital investment required for the four production units. The waste treatment operating costs of \$3.2 million/yr is equivalent to a charge of 0.16¢/lb on the combined product outputs of two billion lb/yr.

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Phosphoric Acid Plant Wastes

Treatment Methods

The wet process phosphoric acid industry, unlike the organic chemical industries above, has very sizable volumes of wastes for treatment and disposal. Also, it is difficult to make a sharp separation between processing operations and waste treatment functions.

Figure 6.4 illustrates a four stage system for handling the liquid and solid wastes after their separation from the process streams of a 150 tpd dihydrate wet process phosphoric acid plant. Aqueous wastes consist of the fluoride- and silica-rich solution from the phosphate dissolver off-gases scrubber. In addition, an allowance is made for 15,000 gph of runoff water consisting of the average rate of rainfall over the gypsum stack and the settling lagoon areas. An arbitrary allowance of 1,000 gph is also included for plant washings, spills, and leaks. Solid wastes consist of the gypsum filter cake from the phosphoric acid filtration plus sludge which settles out of the acid product following concentration before shipment. The quantities and compositions of liquid and solid wastes correspond to those in PEP Report No. 8B on wet process phosphoric acid, except for the settled sludge, which is derived from a paper by Kealy (432007).

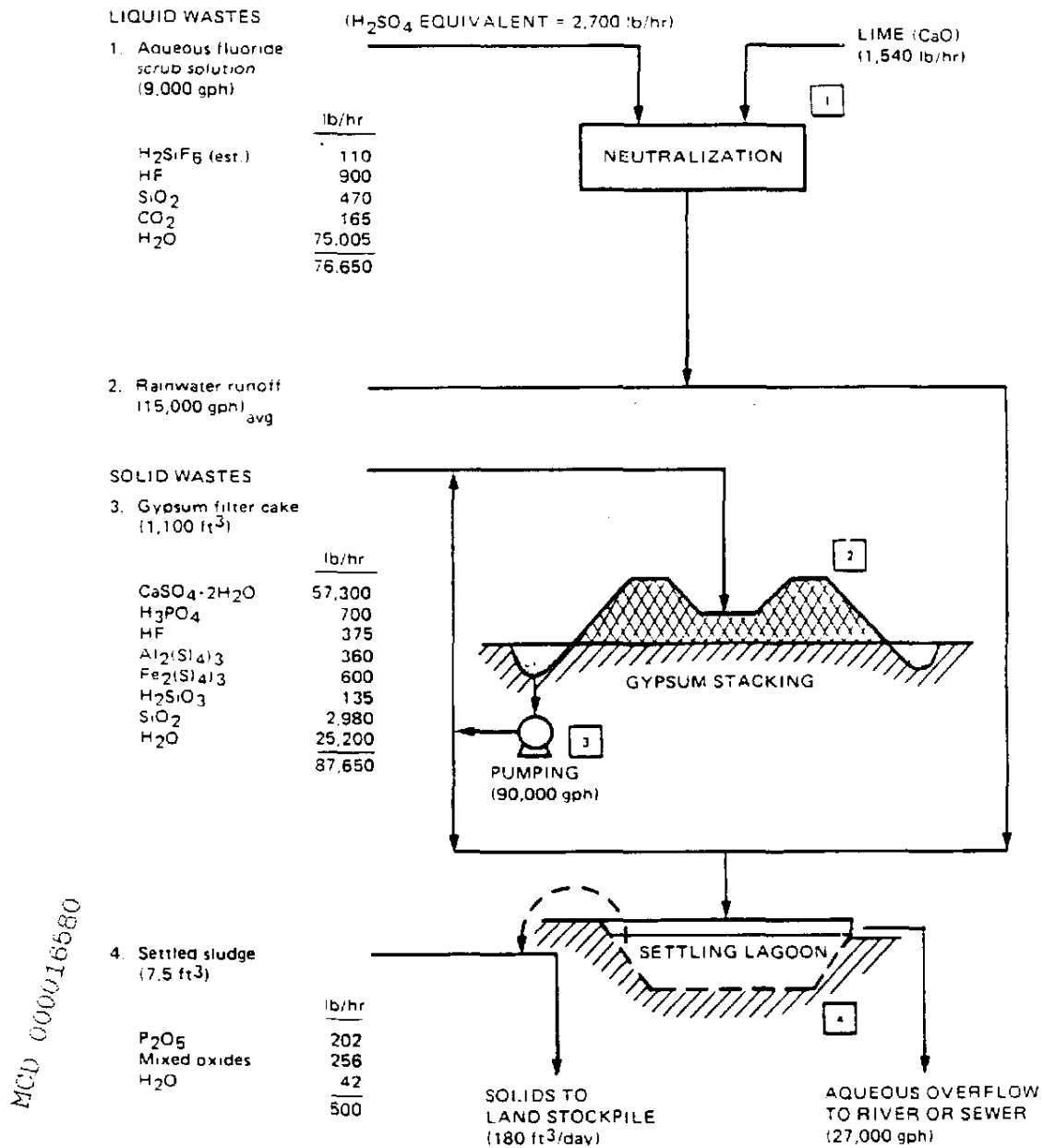
The aqueous fluoride scrub solution is neutralized with lime, and the neutral solution is combined with aqueous runoff and washings for disposal to river or sewer by way of a settling lagoon. The gypsum solids are entrained in a circulating aqueous slurry and carried 1/4 mile to the gypsum stacking area. Circulating liquor volume is kept constant by bleeding the excess to the settling lagoon. Settled solids are periodically removed from the lagoon and, together with the settled sludge from phosphoric acid, is stockpiled pending future use or recovery of contained fertilizer values.

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Figure 6.4

TREATMENT OF PROCESS PHOSPHORIC ACID PLANT WASTES
(DIHYDRATE WET PROCESS)

Phosphoric acid plant capacity: 150 tpd



Reference: PEP Report No. 8B, B-13936.

LEGEND

Module numbers

Treatment Costs

Capital and operating costs for the above waste treatment scheme are tabulated in Table 6.4. These were read from the appropriate liquid and solid treatment module curves and tables of Section 5. The 4 foot deep settling lagoon is sized for a 40 hour holding time to correspond to the minimum thickener settling rate in Figure 4.5 of 0.1 ft/hr. Other costs are read directly from the appropriate graphs and tables.

Thus, the total module costs are \$510,000. When indirect costs and service facilities are included, the fixed investment for waste treatment reaches \$664,000. This is divided 50% to neutralization, 35% to pumping, and 15% to the settling lagoon. It represents about 5% of the investment, exclusive of land, for the dihydrate wet process phosphoric acid plant. Land requirement, excluding that for process plant and utilities, is about 100 acres.

Operating costs are estimated at \$430,000/yr, with neutralization taking the lion's share (75%) of this. At a capacity phosphoric acid output of 50,000 tons/yr P_2O_5 , worth \$300/ton, this represents a charge of \$8.60/ton (3%) against the acid product.

Discussion of Costs

The capital investment for treatment of wastes from a 50,000 ton/yr P_2O_5 wet process phosphoric acid plant was independently estimated at \$292,000 in 1975 (B-13936)--equivalent to about \$368,000 in 1979. Treatment consisted of (a) sulfuric acid plant leakage containment, (b) gypsum pond seepage control, and (c) lime treatment and clarification of gypsum pond overflow.

Since no pumping costs were included, this cost probably compares more closely with the modular total fixed capital for neutralization, gypsum stacking, and settling lagoon--\$430,000 (-15%).

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Comparative operating costs were estimated at \$343,000/yr in 1975 (B-13936), or about \$400,000 in 1979. This compares well with the modular estimates in Table 6.4, excluding pumping--\$394,000/yr (+1.5%).

Conclusion

The modular values developed in this report appear capable of providing an easy first rapid approximation of chemical plant waste treatment costs.

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Table 6.4
TREATMENT COSTS FOR PHOSPHORIC ACID PLANT WASTES
(DIHYDRATE WET PROCESS)

Phosphoric Acid Plant Capacity: 150 tpd P_2O_5
at 0.9 Annual Stream Factor
Phosphoric Acid Plant Investment: \$10 million
PEP Cost Index: 290
Time Base: January 1979

	Neutralization	Gypsum Stacking	Pumping	Settling Lagoon	Total
Capital investment (\$1,000)					
Module cost	260	—	180	70	510
Indirect costs & service facilities 30%	78	—	54	22	154
Total fixed capital	338	0	234	92	664
Operating costs (\$1,000/yr)					
Labor (men/shift) @ \$14.20/man-hr	(0.5) 60	—	—	—	(0.5) 60
Maintenance (% of module cost)	(4) 10	—	(1) 2	(20) 14*	26
Materials, lime @ \$30/ton	183	—	—	—	183
Electricity @ 2.6¢/kwh	4	—	10	—	14
Overhead @ 50% of labor	30	—	—	—	30
Depreciation, 10% of F.C./yr	34	—	24	9	67
Sludge to stockpile @ 2.50/ton†	—	—	—	5	5
Gypsum stacking @ 18¢/ton‡	—	45	—	—	45
TOTAL OPERATING COST	321	45	36	28	\$430

*Polyethylene lagoon liner replaced every 4 years.

†Two mile haul (one way) at \$1.50/ton plus leveling at \$1.00/ton.

‡Stacking cost for 32 ton/hr solids. Including labor, material, overhead, and depreciation.

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Appendix A

COST BASIS

The module costs developed in this report are based on the equipment purchase price data used by the Process Economics Program (PEP) to estimate chemical plant investments. These apply to a U.S. Gulf Coast location near Houston, Texas, and to a PEP Cost Index of 290 corresponding to a time base of January 1, 1979.

Specialized operations such as electrodialysis, reverse osmosis, and biological oxidation are derived from published costs of installation within the United States. These, as well as quoted cost information, are also adjusted to a PEP Cost Index of 290.

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Appendix B

CALCULATIONS FOR THE EQUALIZATION OF A WASTE STREAM FLOW VARIABLE (Reference B-1395)

Samples of the wastewater stream are taken at regular intervals over a complete cycle of the variable to be controlled--in this case BOD content. The concentrations in each sample are plotted against the probability for a given or lower value to occur (see Figure B.1). Now, the standard deviation in the feed " σ_f " is equal to one-half of the difference of the values occurring at probability percentages of 15.9% and 84.1%. That is:

$$\sigma_f = \frac{\text{BOD } 84.1\% - \text{BOD } 15.9\%}{2} = \frac{980 - 380}{2} = 300.$$

The mean BOD value at 50% probability is 680 mg/liter.

If the maximum BOD leaving the equalization pond or vessel is to be 895 mg/liter at a probability of 95%--corresponding to a cumulative normal distribution " Y " = 1.65 (Table B.1), the standard effluent deviation:

$$"\sigma_e" = \frac{895 - 680}{1.65} = 130 \text{ mg/liter.}$$

The required residence time in the equalization vessel is:

$$\begin{aligned} t &= \frac{\Delta t}{2} \times \frac{(\sigma_f)^2}{(\sigma_e)^2} \\ &= \frac{12}{2} \times \frac{(300)^2}{(130)^2} \\ &= 32 \text{ hr or } 1.33 \text{ days} \end{aligned}$$

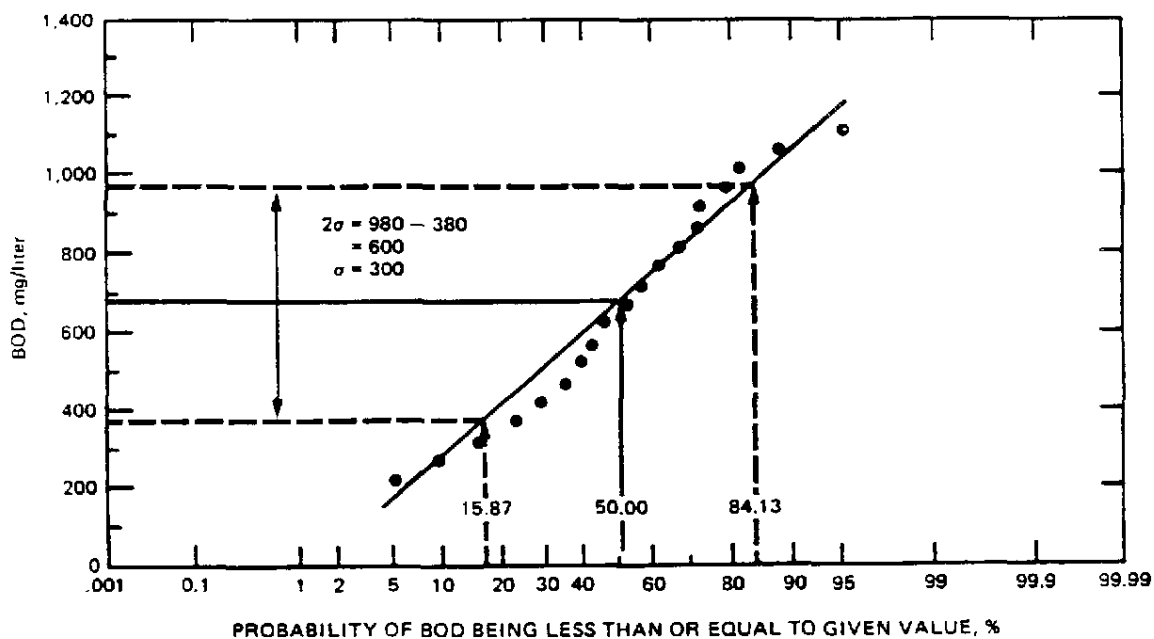
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where: Δt = cycle time of the variable from a mean value
 σ_f and σ_e = feed and effluent standard deviation, mg/liter
 t = equalization residence time, hr.

For a waste flow of one million gallons per day, the equalization capacity = $10^6 \times 1.33$ gallons or 177,000 ft³. This is equivalent to a container 137 ft in diameter with a liquid depth of 12 ft.

Figure B.1

PROBABILITY PLOT OF BOD VALUE



Source: B-1395.

Table B.1

CUMULATIVE NORMAL PROBABILITY DISTRIBUTION

<u>Y</u>	<u>P(X)*</u>	<u>Y</u>	<u>P(X)*</u>	<u>Y</u>	<u>P(X)*</u>
.00	.5000	1.30	.9032	2.55	.9946
.05	.5199	1.35	.9115	2.60	.9953
.10	.5398	1.40	.9192	2.65	.9960
.15	.5596	1.45	.9265	2.70	.9965
.20	.5793	1.50	.9332	2.75	.9970
.25	.5987				
.30	.6179	1.55	.9394	2.80	.9974
.35	.6368	1.60	.9452	2.85	.9978
.40	.6554	1.65	.9505	2.90	.9981
.45	.6736	1.70	.9554	2.95	.9984
.50	.6915	1.75	.9599	3.00	.9987
.55	.7088	1.80	.9641	3.05	.9989
.60	.7257	1.85	.9678	3.10	.9990
.65	.7422	1.90	.9713	3.15	.9992
.70	.7580	1.95	.9744	3.20	.9993
.75	.7734	2.00	.9772	3.25	.9994
.80	.7881	2.05	.9798	3.35	.9996
.85	.8023	2.10	.9821	3.45	.9997
.90	.8159	2.15	.9842	3.55	.9998
.95	.8289	2.20	.9861	3.75	.9999
1.00	.8413	2.25	.9878	4.00	1.0000
1.05	.8531	2.30	.9893		
1.10	.8643	2.35	.9906		
1.15	.8749	2.40	.9918		
1.20	.8849	2.45	.9929		
1.25	.8944	2.50	.9938		

*P(X) = confidence level.

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Appendix C

DESIGN STEPS FOR A COMPLETELY MIXED ACTIVATED SLUDGE SYSTEM (References B-1393 and B-1395)

1. BOD (or COD) removal rate is determined in the laboratory for various feed rates and mixed liquor volatile suspended solids (MLVSS) concentrations. The slope of the graph of $S_0 (S_0 - S_e) \times v t$ versus S_e (Figure C.1) gives the removal rate coefficient "K".

$$K (S_e - y) = \frac{S_0 (S_0 - S_e)}{X_v t}$$

where: S_0 = influent BOD, COD, or total oxygen demand (TOD), mg/liter
 S_e = effluent soluble BOD, COD, or TOD, mg/liter
 X_v = average MLVSS concentration--mg/liter (for conventional biological oxidation, $X_v \cong 1,500$ to 3,500)
 t = aeration time, day⁻¹
 K = organic removal rate coefficient, day⁻¹
 y = concentration of nonbiodegradable organics, mg/liter.

2. The variation of the removal rate coefficient with temperature is given by the equation:

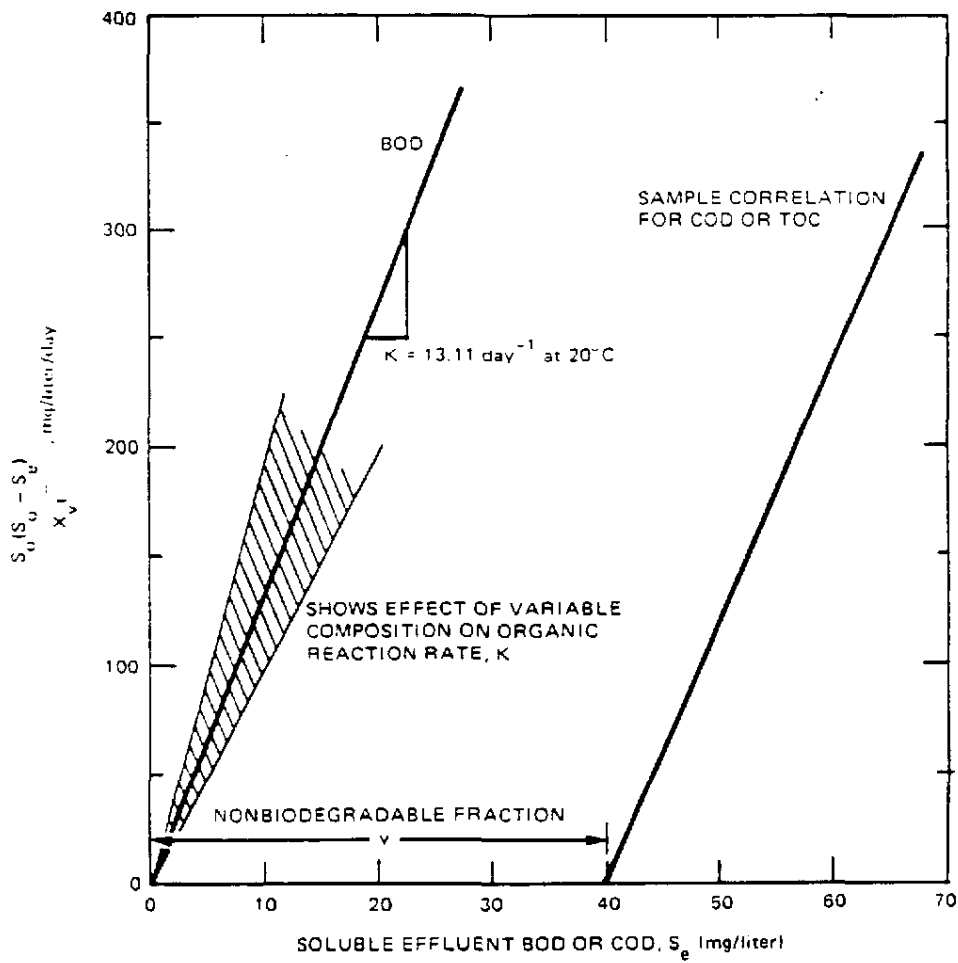
$$K_2 = K_1 \theta^{(T_2 - T_1)}$$

where: K_1 = coefficient at temp. T_1 , °C
 K_2 = coefficient at temp T_2 , °C
 θ = temperature coefficient ($\cong 1.03$ to 1.09)

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Figure C.1

DETERMINATION OF BOD REMOVAL RATE COEFFICIENT



Source: B-1395.

3. Plotting the oxygen usage per day for a known quantity of biodegradable matter (R_T/xX_Vt) versus the amount of BOD removal per day (S_T/xX_Vt), as shown in Figure C.2, gives the a' and b' constants for the equation:

$$R_T = a' S_T + b' x X_V$$

where: R_T = total oxygen usage, lb/O₂/day
 a' & b' = oxygen utilization coefficients
 S_T = BOD (COD or TOC) removed, lb/day
 X_V = average MLVSS concentration, mg/liter
 x = biodegradable fraction of MLVSS
 t = aeration time, days.

4. Constants in the equation for sludge production are determined from a graph of sludge formation ($\Delta X_V/xX_V$) against BOD removal per day (S_T/xX_Vt) as shown in Figure C.3.

$$\Delta X_V = a S_T - b x X_V$$

where: X_V = excess biological sludge production, lb/day
 a & b = sludge production coefficients.

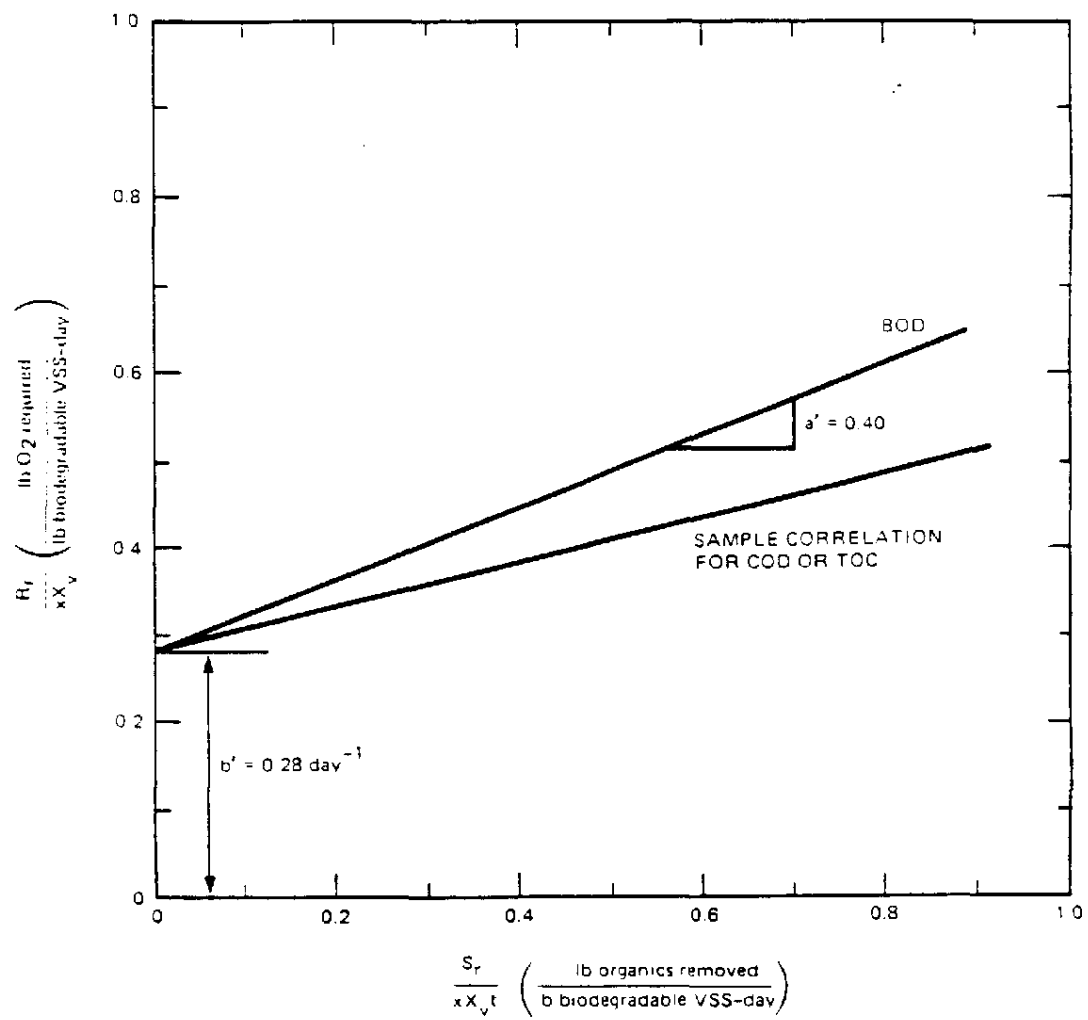
5. The biodegradable fraction (x) of MLVSS is calculated from the following equation:

$$x = \frac{aS_T + bX_V - \sqrt{(aS_T + bX_V)^2 - (4bX_V) 0.77aS_T}}{2bX_V}$$

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Figure C.2

DETERMINATION OF OXYGEN UTILIZATION COEFFICIENT

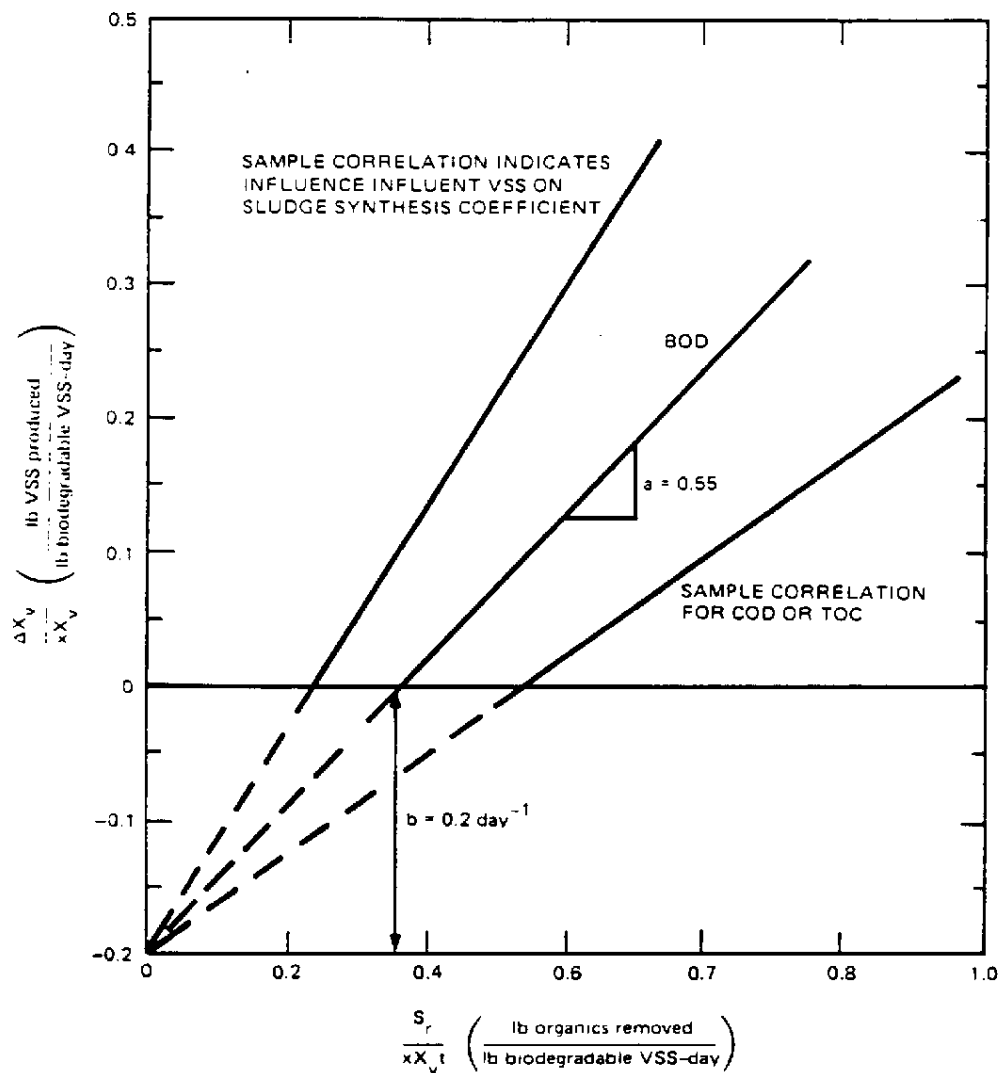


Source: B-1395.

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Figure C.3

DETERMINATION OF SLUDGE PRODUCTION COEFFICIENT



Source: B-1395.

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6. Nutrient requirements are estimated from the following two equations:

$$N = \frac{0.123 \times X_v}{0.77} + \frac{0.07 (0.77-x) X_v}{0.77}, \text{ lb/day}$$

$$P = \frac{0.026 \times X_v}{0.77} + \frac{0.01 (0.77-x) X_v}{0.77}, \text{ lb/day}$$

7. Aerator horsepower is approximated from the relation:

$$hp = \frac{\text{lb BOD removed per day}}{45}$$

8. Finally, the clarifier size is determined as indicated for sedimentation separation under "Primary Treatment" (page 67).

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Appendix D

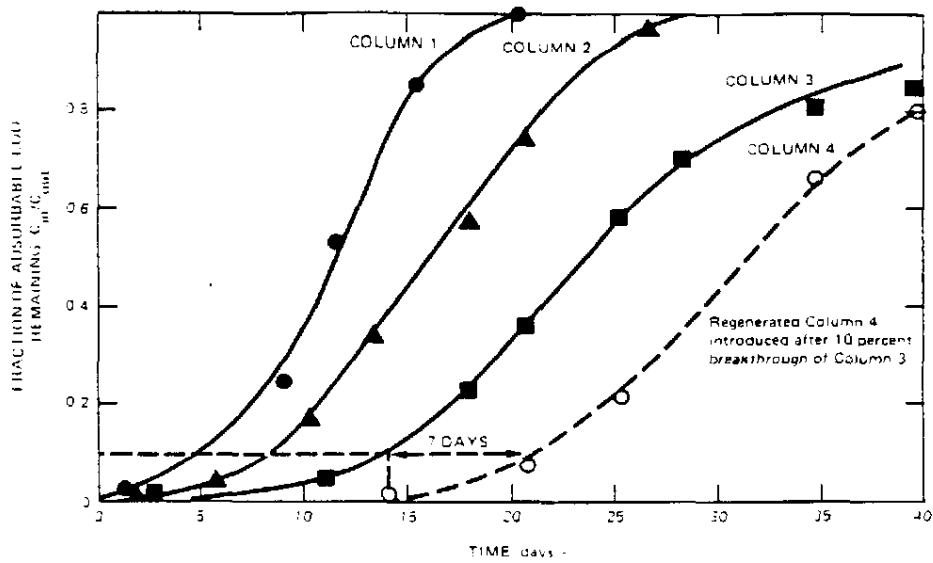
FIXED BED ACTIVE CARBON ADSORBER CAPACITY

The design of fixed bed adsorbers requires experimental data for the adsorbability of the component or components to be removed (B-1395). Figure D.1 shows the breakthrough curves for three 7.5 foot columns in series. When the third column reaches 10% effluent concentration, the first column is removed from the series and the fourth column is added. From these curves service time can be plotted as a function of bed depth, as shown in Figure D.2. Thus, for three 7.5 foot beds in series and for 10% breakthrough, the service time is 14.5 days. Four beds are required, with one bed being replaced every 5 days.

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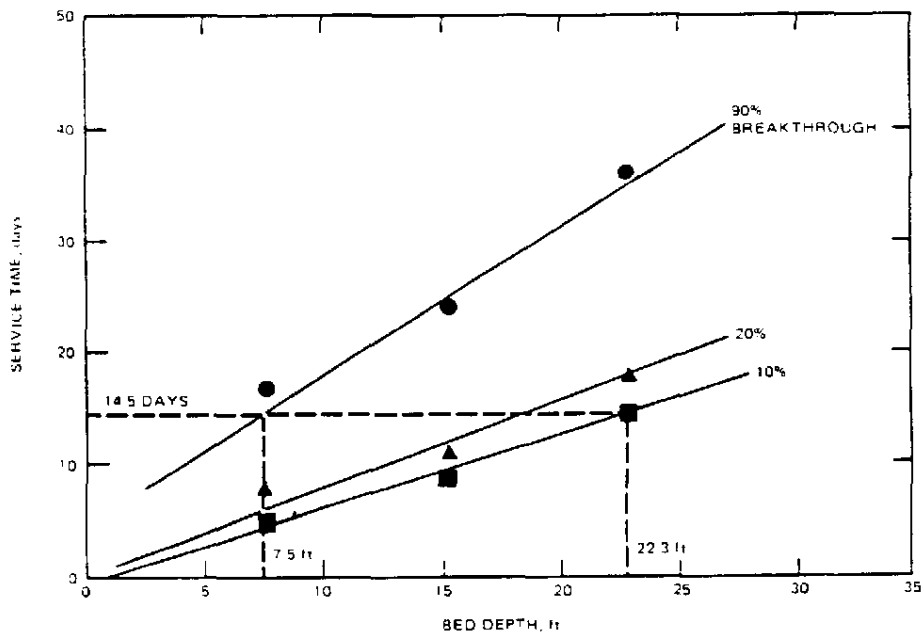
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Figure D.1
BREAKTHROUGH CURVES FOR THREE COLUMNS IN SERIES



Source B 1395

Figure D.2
SERVICE TIME AS A FUNCTION OF BED DEPTH



Source B 1395

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