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# Development Document for Effluent Limitations Guidelines and Standards for the

Final

# Metal Finishing

## Point Source Category

# DEVELOPMENT DOCUMENT

for

# EFFLUENT LIMITATIONS GUIDELINES
# NEW SOURCE PERFORMANCE STANDARDS

for the

# METAL FINISHING POINT SOURCE CATEGORY

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# SECTION I

# CONCLUSIONS

In order to establish uniformly applicable effluent limitations and standards, groupings can be established within each industrial category based on certain criteria. These criteria include raw waste characteristics, manufacturing processes, raw materials used, product type and/or production volume, size and age of facility, number of employees, water usage, and individual plant characteristics.

After consideration of these factors as applied to the metal finishing industry, it was concluded that a single metal finishing subcategory could be established. Thus, all process wastewaters in the Metal Finishing Category are amenable to treatment by a single system. One set of discharge limitations and standards results from the use of a single waste treatment technology system.

Effluent limitations and standards are expressed in concentration units (mg/l) without accompanying production based units. Basing limitations and standards on production based units was rejected after numerous attempts failed to find production related factors which could be correlated in a statistically reliable manner with wastewater flow. This lack of correlation is understandable in light of the number and complexity of metal finishing manufacturing operations.

# SECTION II
# RECOMMENDATIONS

On the basis of the toxic pollutant analysis and the evaluation of applicable technologies for discharge control and treatment, it is recommended that effluent limitation guidelines, new source performance standards and pretreatment standards for new and existing sources be promulgated for the Metal Finishing Point Source Category.

Tables 2-1 through 2-5 summarize the regulations for Best Practicable Control Technology Currently Available (BPT), Best Available Technology Economically Achievable (BAT), Pretreatment Standards for Existing Sources (PSES), Pretreatment Standards for New Sources (PSNS) and New Source Performance Standards (NSPS).

BCT limitations for this industry were proposed on October 29, 1982 (47 FR 49176). They were accompanied by a proposed methodology for the general development of BCT limitations. BCT limits for this industry will be promulgated with, or soon after the promulgation of the final methodology for BCT development. At that time EPA will respond to relevant comments filed in either that rulemaking or in this one.

## TABLE 2-1
## BPT LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Oil and Grease | 52 | 26 |
| TSS | 60 | 31 |
| pH | Within the range of 6.0 to 9.0 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

## TABLE 2-2
## BAT LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

## TABLE 2-3
## PSES LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO (interim) | 4.57 | |
| TTO (final) | 2.13 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

## TABLE 2-4
## PSNS LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.11 | 0.07 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

## TABLE 2-5
## NSPS LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.11 | 0.07 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Oil and Grease | 52 | 26 |
| TSS | 60 | 31 |
| pH | Within the range of 6.0 to 9.0 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

# SECTION III

# INTRODUCTION

## LEGAL AUTHORITY

This document is written under authority of Sections 301, 304, 306, 307, 308, and 501 of the Clean Water Act (the Federal Water Pollution Control Act Amendments of 1972, 33 USC 1251 *et seq.*, as amended by the Clean Water Act of 1977, P.L. 95-217) (the "Act"). The document is also in response to the Settlement Agreement in *Natural Resources Defense Council, Inc. et al v. Train*, 8 ERC 2120 (D.D.C 1976), modified March 9, 1979.

The Federal Water Pollution Control Act Amendments of 1972 established a comprehensive program to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters," Section 101(a). By July 1, 1977, existing industrial dischargers were required to achieve "effluent limitations requiring the application of the best practicable control technology currently available" ("BPT"), Section 301(b)(1)(A); and by July 1, 1983, these dischargers were required to achieve "effluent limitations requiring the application of the best available technology economically achievable ... which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants" ("BAT"), Section 301 (b)(2)(A). New industrial direct dischargers were required to comply with Section 306 new source performance standards ("NSPS"), based on best available demonstrated technology, and new and existing dischargers to publicly owned treatment works ("POTWs") were subject to pretreatment standards under Sections 307(b) and (c) of the Act. While the requirements for direct dischargers were to be incorporated into National Pollutant Discharge Elimination System (NPDES) permits issued under Section 402 of the Act, pretreatment standards were made enforceable directly against dischargers to POTWs (indirect dischargers).

Although section 402 (a)(1) of the 1972 Act authorized the setting of requirements for direct dischargers on a case-by-case basis, Congress intended that, for the most part, control requirements would be based on regulations promulgated by the Administrator of the EPA. Section 304(b) of the Act required the Administrator to promulgate regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of BPT and BAT. Moreover, Sections 304(c) and 306 of the Act required promulgation of regulations for NSPS, and Sections 304(f), 307(b), and 307(c) required promulgation of regulations for pretreatment standards.

In addition to these regulations for designated industry categories, Section 307(a) of the Act required the Administrator to promulgate effluent standards applicable to all dischargers of toxic pollutants. Finally, Section 501(a) of the Act authorized the Administrator to prescribe any additional regulations "necessary to carry out his functions" under the Act.

The EPA was unable to promulgate many of these regulations by the dates contained in the Act. In 1976, EPA was sued by several environmental groups, and in settlement of this lawsuit EPA and the plaintiffs executed a "Settlement Agreement" which was approved by the Court. This Agreement required EPA to develop a program and adhere to a schedule for promulgating for 21 major industries BAT effluent limitations guidelines, pretreatment standards, and new source performance standards for 65 "priority" pollutants and classes of pollutants. See Natural Resources Defense Council, Inc. et al v. Train, 8 ERC 2120 (D.D.C. 1976), modified March 9, 1979.

On December 27, 1977, the President signed into law the Clean Water Act of 1977. Although this law makes several important changes in the Federal water pollution control program, its most significant feature is its incorporation into the Act of several of the basic elements of the Settlement Agreement program for toxic pollution control. Sections 301(b)(2)(A) and 301(b)(2)(C) of the Act now require the achievement by July 1, 1984 of effluent limitations requiring application of BAT for "toxic" pollutants, including the 65 "priority" pollutants and classes of pollutants which Congress declared "toxic" under Section 307(a) of the Act. Likewise, EPA's programs for new source performance standards and pretreatment standards are now aimed principally at toxic pollutant controls. Moreover, to strengthen the toxics control program, Section 304(e) of the Act authorizes the Administrator to prescribe "best management practices" ("BMPs") to prevent the release of toxic and hazardous pollutants from plant site runoff, spillage or leaks, sludge or waste disposal, and drainage from raw material storage associated with, or ancillary to, the manufacturing or treatment process.

In keeping with its emphasis on toxic pollutants, the Clean Water Act of 1977 also revises the control program for non-toxic pollutants. Instead of BAT for "conventional" pollutants identified under Section 304(a)(4) (including biochemical oxygen demand, suspended solids, fecal coliform and pH), the new Section 301(b)(2)(F) requires achievement by July 1, 1984, of "effluent limitations requiring the application of the best conventional pollutant control technology" ("BCT"). The factors considered in assessing BCT for an industry include the costs of attaining a reduction in effluents and the effluent reduction benefits derived compared to the costs and effluent reduction benefits from the discharge of publicly owned treatment works (Section 304(b)(4)(B)). For non-toxic, nonconventional pollutants, Sections 301(b)(2)(A) and (b)(2)(F) require achievement of BAT effluent limitations within three years after their establishment or July 1, 1984, whichever is later, but not later than July 1, 1987.

## GUIDELINE DEVELOPMENT SUMMARY

The Metal Finishing Category (MFC) encompasses 46 unit operations involved in the machining, fabrication and finishing of products primarily associated with SIC groups 34 through 39. The effluent guidelines for the Metal Finishing Category were developed from data obtained from previous EPA studies, literature searches, plant surveys and evaluations, and long term self-monitoring data supplied by industry. Initially, all existing information from EPA records and data from literature searches were collected. This information was then compiled in a format that summarized the individual plant descriptions for the following information: manufacturing unit operations performed, water usage, process water discharges, wastewater treatment practices, and wastewater constituents.

In addition to providing a quantitative description of the Metal Finishing Category, this existing information was used to determine if the wastewater characteristics of the industry as a whole were uniform and thus amenable to one set of discharge standards. The discharge characteristics of all plants in the existing data base were not uniform; however, the discharge from these plants was amenable to the application of a common end-of-pipe treatment technology. Therefore, the entire Metal Finishing Category is represented by a single subcategory and is subject to one set of effluent discharge limitations. Seven classifications of raw waste are present and were studied to establish treatment requirements. These seven waste types are:

- Common Metals
- Precious Metals
- Complexed Metals
- Hexavalent Chromium
- Cyanide
- Oils
- Toxic Organics

To supplement existing data, data collection portfolios (DCP's) under the authority of Section 308 of the Federal Water Pollution Control Act as amended were transmitted by the EPA to a large number of manufacturing facilities in the Metal Finishing Category. In addition to the existing data base and the plant supplied information (via the completed DCP's), a sampling program was conducted at selected plant locations. The sampling program was used to establish the sources and quantities of pollutant parameters in the raw process wastewater and the treated effluent. The sites visited were chosen on the basis of either the specific manufacturing operations performed or the particular waste treatment technology employed. Historical effluent information in the form of long term self monitoring data, was requested by the EPA and was responded to by nearly 100 plants. All of the data collected were analyzed to correlate the pollutants generated with the manufacturing processes performed by each facility.

In addition to evaluating pollutant constituents and discharge rates, the full range of control and treatment technologies within the Metal Finishing Category was identified and examined. This was done considering the pollutants to be treated and their chemical, physical, and biological characteristics. Special attention was paid to in-process technology such as the recovery and reuse of process solutions, the recycle of process water, and the reduction of water use.

This information was then evaluated in order to determine the levels of technology appropriate as bases for effluent limitations for existing sources after July 1, 1977, ("Best Practicable Control Technology Currently Available") and after July 1, 1984 ("Best Available Technology Economically Achievable"). Levels of technology appropriate for direct discharge and pretreatment of wastewater to POTW's from both new and existing sources were also identified as were the demonstrated control technology, processes, operating methods, or other alternatives. Various factors were considered in the evaluation of these technologies. These factors included demonstrated effluent performance of treatment technologies, the total cost of application of the technology in relation to the pollution reduction benefits to be achieved, the production processes employed, the engineering aspects of the application of various types of control techniques and process changes, and non-water quality environmental impact (including energy requirements).

## SOURCES OF INDUSTRY DATA

Data for the Metal Finishing Category were gathered from literature surveys, previous studies of the industry by the EPA, inquiries to professional contacts, seminar and meeting attendance, the survey and evaluation of manufacturing facilities, and long term self-monitoring data provided by industry.

### Literature Study

Published literature in the form of books, periodicals, reports, papers, and promotional materials was examined. These sources are listed in Section XV. The material researched included manufacturing processes, recycling/reclamation techniques, pollutant characteristics, waste treatment technologies, and cost data.

## Previous EPA Studies

Previous EPA studies that contributed technical information to the Metal Finishing Category study were:

- Machinery & Mechanical Products Manufacturing Category
- Electroplating Category
- Electroless Plating & Printed Circuit Board Manufacturing Segments of the Electroplating Category
- Printing & Publishing Category
- Mechanical & Electrical Products Category
- Copper & Copper Alloy Manufacturing Category
- Aluminum & Aluminum Alloy Manufacturing Category
- Iron & Steel Manufacturing Category

These EPA studies provided information on the process raw wastes generated by each of the metal finishing operations listed in Table 3-1 and the treatment utilized by industry to control the pollutants in these wastes. Information from the Machinery and Mechanical Products Manufacturing study was used specifically to identify plants with segregated wastes for particular manufacturing unit operations and with treatment technology to control these wastes. Applicable plants were selected for sampling to establish waste characteristics and performance of existing wastewater treatment components and systems. Plant data from earlier studies of electroplating, electroless plating, and printed circuit board manufacturing were examined and incorporated into the current Metal Finishing data base. Data from the Printing and Publishing Category study were examined with the intent of including lithography and metallic plate making in the Metal Finishing Category. Plant data files from the Mechanical and Electrical Products study were incorporated directly into the Metal Finishing data base. Selected data from the copper, aluminum, and iron and steel studies were used to determine characteristics of oily raw waste streams and to determine performance of oily waste treatment technologies. Most of the preceding information was obtained directly from EPA files or EPA contractors rather than from published reports.

## TABLE 3-1
## METAL FINISHING CATEGORY UNIT OPERATIONS

UNIT OPERATIONS

1. Electroplating
2. Electroless Plating
3. Anodizing
4. Conversion Coating
5. Etching (Chemical Milling)
6. Cleaning
7. Machining
8. Grinding
9. Polishing
10. Tumbling (Barrel Finishing)
11. Burnishing
12. Impact Deformation
13. Pressure Deformation
14. Shearing
15. Heat Treating
16. Thermal Cutting
17. Welding
18. Brazing
19. Soldering
20. Flame Spraying
21. Sand Blasting
22. Other Abrasive Jet Machining
23. Electric Discharge Machining
24. Electrochemical Machining
25. Electron Beam Machining
26. Laser Beam Machining
27. Plasma Arc Machining
28. Ultrasonic Machining
29. Sintering
30. Laminating
31. Hot Dip Coating
32. Sputtering
33. Vapor Plating
34. Thermal Infusion
35. Salt Bath Descaling
36. Solvent Degreasing
37. Paint Stripping
38. Painting
39. Electrostatic Painting
40. Electropainting
41. Vacuum Metalizing
42. Assembly
43. Calibration
44. Testing
45. Mechanical Plating
46. Printed Circuit Board Manufacturing

### Professional Contacts

All Federal EPA regions and several state environmental agencies were contacted to obtain permit and monitoring data on plants that performed metal finishing processes.

Numerous suppliers and manufacturers for the metal finishing industry were contacted to collect information regarding the use and properties of materials, constituents of process chemicals, waste treatment equipment, waste contract haulers, and possible applications of process modifications to minimize the generation of pollutants.

### Seminars and Meetings

An Advanced Wastewater Treatment Seminar provided methods for accurately estimating waste treatment costs. The American Electroplaters Society Intensive Training Course in Electroplating and Surface Finishing was taken. The Eastern Plant Engineering Conference on lubricant management, conservation, recycling, and disposal was also attended.

In addition, jointly sponsored EPA/American Electroplaters' Society conferences on Advanced Pollution Control for the Metal Finishing Industry were attended. At these conferences various papers on metal finishing technology and waste treatment were presented by the industry and the EPA. A meeting of the Continuous Coil Anodizing Association was also attended. The EPA sponsored an informational meeting with the Association of Home Appliance Manufacturers, the Electrical Industries of America, the Motor Vehicles Manufacturers Association of the United States, the National Association of Manufacturers, and the National Electrical Manufacturers Association.

### Plant Survey and Evaluation

The collection of data pertaining to facilities in the metal finishing industry was accomplished via two primary mechanisms. The EPA conducted a survey wherein data collection portfolios (DCPs) in questionnaire form were mailed to production facilities. Also, a plant visit and sampling program was implemented to accumulate the specific data necessary for each waste characteristic subcategory.

Data Collection Portfolios - Data collection portfolios of three types were sent to various industries within the Metal Finishing Category. The first DCP was utilized during the Machinery and Mechanical Products Industries Study. Data were obtained from 339 production facilities that were selected from a group of 1,422 plants originally contacted by telephone. Requested information included general plant data, principal raw materials consumed, specific production processes employed, composition of effluent streams and wastewater treatment in use.

The second DCP, used during the M&EP study was sent to 900 facilities that were randomly selected from approximately 160,000 manufacturers listed in recent Dun & Bradstreet data. This DCP requested information pertinent to general plant characteristics, unit operations performed (including quantity, frequency, and method of liquid disposal), data related specifically to plating type operations, wastewater treatment facilities, and the contract hauling of wastes. A total of 365 useful responses resulted from the mailing of this questionnaire.

The third DCP was used during the Electroplating study. It was mailed to 1883 companies believed to operate plating facilities. This mailing list was randomly selected from among the approximately 13,000 facilities that perform plating in the United States. There were approximately 1190 usable responses (from 419 companies) to this questionnaire mailing. This survey requested information regarding general plant characteristics, production history, manufacturing processes, process and waste treatment, wastewater characteristics, treatment costs, and economic analysis data.

Plant Sampling Visits - During the study of the metal finishing industry, a total of 322 manufacturing facilities were visited. The criteria used to select plants for sampling visits were:

1. A large percentage of the plant's effluent discharge should result from the manufacturing processes listed in Table 3-1.

2. The physical layout of plant plumbing should facilitate .sampling of the wastewater type under study.

3. The plant must have waste treatment and control technology in place.

4. The mix of plants visited should contain dischargers to both surface waters and publicly owned treatment works (POTW).

5. The selected plants should provide a representative geographical distribution to avoid a data base that concentrates on a unique geographical condition.

The plant visits consisted of two major activities: collection of all pertinent technical information related to both the manufacturing processes and the treatment techniques and collection of wastewater samples. The technical data gathering effort entailed completion of the applicable data collection portfolio and obtaining information in the following specific areas:

1. Rinsing operations and their effect on water use and waste characteristics.

2. Water conservation techniques, both practiced and planned.

3. Overall performance of the waste treatment system and future plans or changes anticipated.

4. Current regulations under which the plant is operating and any difficulties in meeting them.

5. Process modifications which significantly alter the characteristics of the wastewater generated.

6. Particular pollutant parameters which plant personnel believe will be found in the waste stream.

7. Any problem or situation peculiar to the plant being visited.

The object of plant sampling was to determine by analysis which pollutants were present in the plant wastewater for each subcategory. The wastewater collection at the visited plants consisted of a composite sampling program performed over a two or three day period. Prior to the sampling visit, all available data pertaining to manufacturing processes and waste treatment were reviewed. Representative sample points were selected for the raw wastewater entering the treatment systems and for the final treated effluents. Finally a detailed sampling plan showing the selected sample points and the overall sampling procedure was prepared, reviewed, and approved by the EPA.

Composite samples (24 hour composites) were taken at each sample point. The plants which were sampled were divided into two sample analysis groups. Within each analysis group the samples were subjected to various levels of analysis depending on the stability of the parameters to be analyzed. These analysis groups and the various levels of analysis within were:

1. On-site analysis, local laboratory analysis, Chicago EPA laboratory analysis, GC/MS laboratory analysis, and central laboratory analysis.

2. On-site analysis, local laboratory analysis, EPA contracted laboratory metals analysis and EPA contracted laboratory organics analysis.

In the first analysis group, on-site analysis performed by the sampler at the facility determined flow rate, pH, and temperature. Several liters of water from each sample point were delivered to a laboratory in the locality of the subject plant and analyzed for total cyanide, cyanide amenable to chlorination, TSS, oil and grease, and phenols. This analysis was performed by local laboratories within a 24 hour period after the composite sample was prepared. Two liters of water from each sample point were sent to an EPA laboratory where screening analysis was run to establish metals present in the samples. Water samples from each point were also sent to a laboratory with GC/MS capabilities to determine organics that were present. The remainder of the wastewater was shipped to a central laboratory where analysis was performed to verify the levels of metals, organics, and total dissolved solids as appropriate. For some sampling visits the Chicago EPA laboratory and the GC/MS laboratory were eliminated. Analysis for certain special parameters such as palladium and rhodium was performed only if the facility being sampled utilized such materials in their process lines. Samples from electroless plating plants were also analyzed for the complexing agents which were being used by the plants. In addition to this sampling and analysis, special grab samples were collected from certain plants to obtain data related to specific unit operations, process variations, or rinsing operations. In the second analysis group, the on-site analysis remained the same as in the first group. The local laboratory analyzed for total cyanide, oil and grease, ammonia nitrogen, TOC, TSS, BOD, and phenols. These were analyzed within 24 hours after the composite or grab composite sample was prepared. Two liters of water were sent to an EPA contracted laboratory to perform analysis to determine metals present in the water samples. Additional water was sent to a second EPA contracted laboratory for analysis to determine organics present in the wastewater.

The acquisition, preservation, and analysis of the water samples were performed in accordance with methods set forth in 40 CFR Part 136. Sampling parameters are presented in Table 3-2.

# Table 3-2

## SAMPLING PARAMETERS

Toxic Pollutants

1 acenaphthene
2 acrolein
3 acrylonitrile
4 benzene
5 benzidine
6 carbon tetrachloride (tetrachloromethane)
7 chlorobenzene
8 1,2,4-trichlorobenzene
9 hexachlorobenzene
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
18 bis(2-chloroethyl) ether
19 2-chloroethyl vinyl ether (mixed)
20 2-chloronaphthalene
21 2,4,6-trichlorophenol
22 parachlorometa cresol
23 chloroform (trichloromethane)
24 2-chlorophenol
25 1,2-dichlorobenzene
26 1,3-dichlorobenzene
27 1,4-dichlorobenzene
28 3,3'-dichlorobenzidine
29 1,1-dichloroethylene
30 1,2-trans-dichloroethylene
31 2,4-dichlorophenol
32 1,2-dichloropropane
33 1,2-dichloropropylene (1,3-dichloropropene)
34 2,4-dimethylphenol
35 2,4-dinitrotoluene
36 2,6-dinitrotoluene
37 1,2-diphenylhydrazine
38 ethylbenzene
39 fluoranthene
40 4-chlorophenyl phenyl ether
41 4-bromophenyl phenyl ether
42 bis(2-chloroisopropyl) ether
43 bis(2-chloroethoxy) methane
44 methylene chloride (dichloromethane)
45 methyl chloride (chloromethane)

## Table 3-2 (CONT.)
## SAMPLING PARAMETERS

| | |
|---|---|
| 46 | methyl bromide (bromomethane) |
| 47 | bromoform (tribromomethane) |
| 48 | dichlorobromomethane |
| 51 | chlorodibromomethane |
| 52 | hexachlorobutadiene |
| 53 | hexachlorocyclopentadiene |
| 54 | isophorone |
| 55 | naphthalene |
| 56 | nitrobenzene |
| 57 | 2-nitrophenol |
| 58 | 4-nitrophenol |
| 59 | 2,4-dinitrophenol |
| 60 | 4,6-dinitro-o-cresol |
| 61 | N-nitrosodimethylamine |
| 62 | N-nitrosodiphenylamine |
| 63 | N-nitrosodi-n-propylamine |
| 64 | pentachlorophenol |
| 65 | phenol |
| 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 |
| 72 | 1,2-benzanthracene (benzo(a)anthracene) |
| 73 | benzo (a) pyrene (3,4-benzo-pyrene) |
| 74 | 3,4-benzofluoranthene (benzo(b)fluoranthene) |
| 75 | 11,12-benzofluoranthene (benzo(k)fluoranthene) |
| 76 | chrysene |
| 77 | acenaphthylene |
| 78 | anthracene |
| 79 | 1,12-benzoperylene (benzo(ghi)-perylene) |
| 80 | fluorene |
| 81 | phenanthrene |
| 82 | 1,2,5,6-dibenzanthracene (dibenzo (a,h) anthracene) |
| 83 | indeno (1,2,3-cd) pyrene (2,3-o-phenylene pyrene) |
| 84 | pyrene |
| 85 | tetrachloroethylene |
| 86 | toluene |
| 87 | trichloroethylene |
| 88 | vinyl chloride (chloroethylene) |
| 89 | aldrin |
| 90 | dieldrin |
| 91 | chlordane (technical mixture and metabolites) |
| 92 | 4,4'-DDT |

## Table 3-2 (CONT.)
## SAMPLING PARAMETERS

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 (BHC=hexachlorocyclohexane)
103 beta-BHC
104 gamma-BHC (lindane)
105 delta-BHC
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)
113 toxaphene
114 antimony
115 arsenic
116 asbestos
117 beryllium
118 cadmium
119 chromium, total and hexavalent
120 copper
121 cyanide, total & amenable to chlorination
122 lead
123 mercury
124 nickel
125 selenium
126 silver
127 thallium
128 zinc
129 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

### Conventional Pollutants

oil & grease
TSS
pH

## Table 3-2 (CONT.)
## SAMPLING PARAMETERS

### Nonconventional Pollutants

gold
fluoride
phosphorus
aluminum
barium
iridium
magnesium
molybdenum
osmium
palladium
platinum
rhodium
ruthenium
sodium
tin
titanium
vanadium
yttrium
total phenols
bis (chloromethyl) ether
trichlorofluoromethane
dichlorodifluoromethane

### Other Parameters

flow
temperature

Long-Term Self-Monitoring Data - During the study of the metal finishing industry, a request for long-term self-monitoring data was sent to various industries within the Metal Finishing Category. More than 50 plants responded with a full year of daily data that had been analyzed by an approved EPA method. The criteria used to select plants from whom data were requested were:

1. The plant was believed to monitor, via analysis, their effluent.

2. The plant was known to discharge wastewater that contained cadmium, chromium, copper, lead, nickel, silver, zinc, cyanide, or oils at levels that required treatment.

3. The plant had combinations of the following waste treatment control technologies in-place:

    a. Hydroxide precipitation and sedimentation
    b. Precipitation/sedimentation followed by filtration
    c. Emulsion breaking/oil separation for oily wastes
    d. Cyanide destruction
    e. Hexavalent chromium reduction

4. A large percentage of the wastewater discharge resulted from the manufacturing processes listed in Table 3-1.

5. The mix of plants contained discharges to both surface waters and publicly owned treatment works (POTW).

6. The selected plants covered a wide geographical distribution to avoid any geographical uniqueness.

Post Proposal Data - After publication of the proposed regulation, industry and control authorities submitted data as part of the comments. The data were not included in the derivation of the final limits. The reasons for exclusion were: inadequate treatment, i.e., high TSS; technology different from regulatory basis; and incomplete information. However, all the data were examined and a comparison made between the submitted data and the effluent limits. Where reasonable evidence was presented, modifications were made to the analysis of the data to address the comment.

## UTILIZATION OF INDUSTRY DATA

Data collected from the previously described sources are used throughout this report in the development of a basis for limitations. Subcategorization was not deemed necessary because all wastes were amenable to the same treatment scheme. However, seven distinct types of process raw wastes were found to occur in the Metal Finishing Category. These seven process raw waste types are: common metals, precious metals, complexed metals, hexavalent chromium, cyanide, oils, and solvents. The water usage and raw waste characteristics for each raw waste type, presented in Section V, were obtained from the analysis of raw wastewater samples taken from the process wastes discharged by the manufacturing unit operations. Selection of the pollutant parameters for control (Section VI) was made from these plant sampling results. This selection required that two criteria be met: first, the pollutant nature of the parameter must be significant; and second, it must be discharged at a significant concentration level. Based on the amount and types of pollutants requiring control, applicable treatment technologies were studied and are discussed in Section VII of this document. Wastewater treatment technologies utilized by the Metal Finishing Category plants and observed during plant visits were used to identify applicable treatment technologies. All performance data presented are for existing treatment installations. Both in-process control and end-of-pipe wastewater treatment were studied and are included in the discussion. Actual sampling data are used in Section VII to define treatment system performance and for the presentation of actual achievable effluent concentration levels for various treatment options. The cost of treatment (for both individual technologies and systems) based on literature surveys, on-site surveys, and data from equipment manufacturers is contained in Section VIII of this document. The guidelines and limitations for the Best Practicable Control Technology Currently Available (BPT) are presented in Section IX. Section X contains the guidelines and limitations for the Best Available Technology Economically Achievable (BAT). New Source Performance Standards (NSPS) are presented in Section XI. Pretreatment guidelines and limitations are discussed in Section XII. Innovative technologies and the provisions for their use in the regulations are detailed in Section XIII.

## INDUSTRY DESCRIPTION

The Metal Finishing Category is defined by manufacturing processes. The industries covered by the Metal Finishing Category are generally included in Standard Industrial Classification (SIC) Major Groups 34 through 39 and are those that perform some combination of the 46 manufacturing unit operations listed in Table 3-1. The specific industries covered by these Major Groups are listed in Table 3-3. Industries listed in Table 3-3 which are not exclusively in the Metal Finishing Category include porcelain enameling, coil coating, batteries manufacturing, electrical and electronic components, photographic equipment and supplies, iron and steel, aluminum and aluminum alloys, copper and copper alloys, and shipbuilding. For example, all of the industries listed under Major Group 36 are covered under both the Electrical and Electronics Component Category and the Metal Finishing Category. The Electrical and Electronic Components Category covers processes unique to electronics, and the Metal Finishing Category covers the remaining processes used to manufacture the products in Major Group 36.

## TABLE 3-3
## INDUSTRIES WITHIN THE METAL FINISHING CATEGORY

### Major Group 34 Fabricated Metal Products, Except Machinery and Transportation Equipment

341 Metal Cans and Shipping Containers.
342 Cutlery, Hand Tools, and General Hardware.
343 Heating Equipment (except Electric and Warm Air, Plumbing Fixtures).
344 Fabricated Structural Metal Products.
345 Screw Machine Products, and Bolts, Nuts, Screws, Rivets and Washers.
346 Metal Forgings and Stampings.
347 Coating, Engraving and Allied Services.
348 Ordnance and Accessories, except Vehicles and Guided Missiles.
349 Miscellaneous Fabricated Metal Products.

### Major Group 35 Machinery, Except Electrical

351 Engines and Turbines.
352 Farm and Garden Machinery and Equipment.
353 Construction, Mining and Materials Handling Machinery and Equipment.
354 Metalworking Machinery and Equipment.
355 Special Industry Machinery, except Metalworking Machinery.
356 General Industrial Machinery and Equipment.
357 Office, Computing, and Accounting Machines.
358 Refrigeration and Service Industry Machinery.
359 Miscellaneous Machinery, except Electrical.

### Major Group 36 Electrical and Electronic Machinery, Equipment and Supplies

361 Electric Transmission and Distribution Equipment.
362 Electrical Industrial Apparatus.
363 Household Appliances.
364 Electric Lighting and Wiring Equipment.
365 Radio and Television Receiving Equipment, except Communication Types.
366 Communication Equipment.
367 Electronic Components and Accessories.
369 Miscellaneous Electrical Machinery, Equipment, and Supplies.

### Major Group 37 Transportation Equipment

371 Motor Vehicles and Motor Vehicle Equipment.
372 Aircraft and Parts.

## TABLE 3-3 (Cont.)

### Major Group 37 Transportation Equipment (Cont.)

| | |
|---|---|
| 373 | Ship and Boat Building and Repairing. |
| 374 | Railroad Equipment. |
| 375 | Motorcycles, Bicycles, and Parts. |
| 376 | Guided Missiles and Space Vehicles and Parts. |
| 379 | Miscellaneous Transportation Equipment. |

### Major Group 38 Measuring, Analyzing and Controlling Instruments: Photographic, Medical and Optical Goods; Watches and Clocks

| | |
|---|---|
| 381 | Engineering, Laboratory, Scientific, and Research Instruments and Associated Equipment. |
| 382 | Measuring and Controlling Instruments. |
| 383 | Optical Instruments and Lenses. |
| 384 | Surgical, Medical, and Dental Instruments and Supplies. |
| 385 | Opthalmic Goods. |
| 386 | Photographic Equipment and Supplies |
| 387 | Watches, Clocks, Clockwork Operated Devices, and Parts. |

### Major Group 39 Miscellaneous Manufacturing Industries

| | |
|---|---|
| 391 | Jewelry, Silverware, and Plated Ware. |
| 393 | Musical Instruments. |
| 394 | Dolls. |
| 395 | Pens, Pencils, and Other Office and Artists' Materials. |
| 396 | Costume Jewelry, Costume Novelties, Buttons and Miscellaneous Notions, Except Precious Metal. |
| 399 | Miscellaneous Manufacturing Industries. |

Based upon industry journal mailing lists, there are approximately 13,500 manufacturing facilities in the United States which are covered by the Metal Finishing Category. These plants are engaged in the manufacturing of a variety of products that are constructed primarily by using metals. The operations performed (Table 3-1) usually begin with materials in the form of raw stock (rods, bars, sheet, castings, forgings, etc.) and can progress to the most sophisticated surface finishing operations. These facilities vary greatly in size, age, number of employees and number and type of operations performed. They range from very small job shops with less than 10 employees to large facilities employing thousands of production workers. Because of the differences in size and processes, production facilities are custom-tailored to the specific needs of each individual plant. Figure 3-1 illustrates the variation in number of unit operations that can be performed depending upon the complexity of the product. The possible variations of unit operations within the Metal Finishing Category are extensive. The unit operations (and their sequence) presented in Figure 3-1 are not actual plants but are representative of possible manufacturers within the Metal Finishing Category. Some complex products could require the use of nearly all 45 unit operations, while a simple product might require only a single operation.

Many different raw materials are used by the plants in the Metal Finishing Category. Basis materials are almost exclusively metals which range from common copper and steel to extremely expensive high grade alloys and precious metals. The solutions utilized in the various unit operations can contain acids, bases, cyanide, metals, complexing agents, organic additives, oils and detergents. All of these raw materials can potentially enter wastewater streams during the production sequence.

Water usage within the Metal Finishing Category, the processes that utilize water and the quantities of process wastewater generated by metal finishing are presented in Section V. Plating and cleaning operations are typically the biggest water users. While the majority of metal finishing operations use water, some of them are completely dry. The type of rinsing utilized can have a marked effect on water usage as can the flow rates within the particular rinse types. Product quality requirements often dictate the amount of rinsing needed for specific parts. Parts requiring extensive surface preparation will generally necessitate the use of larger amounts of water.

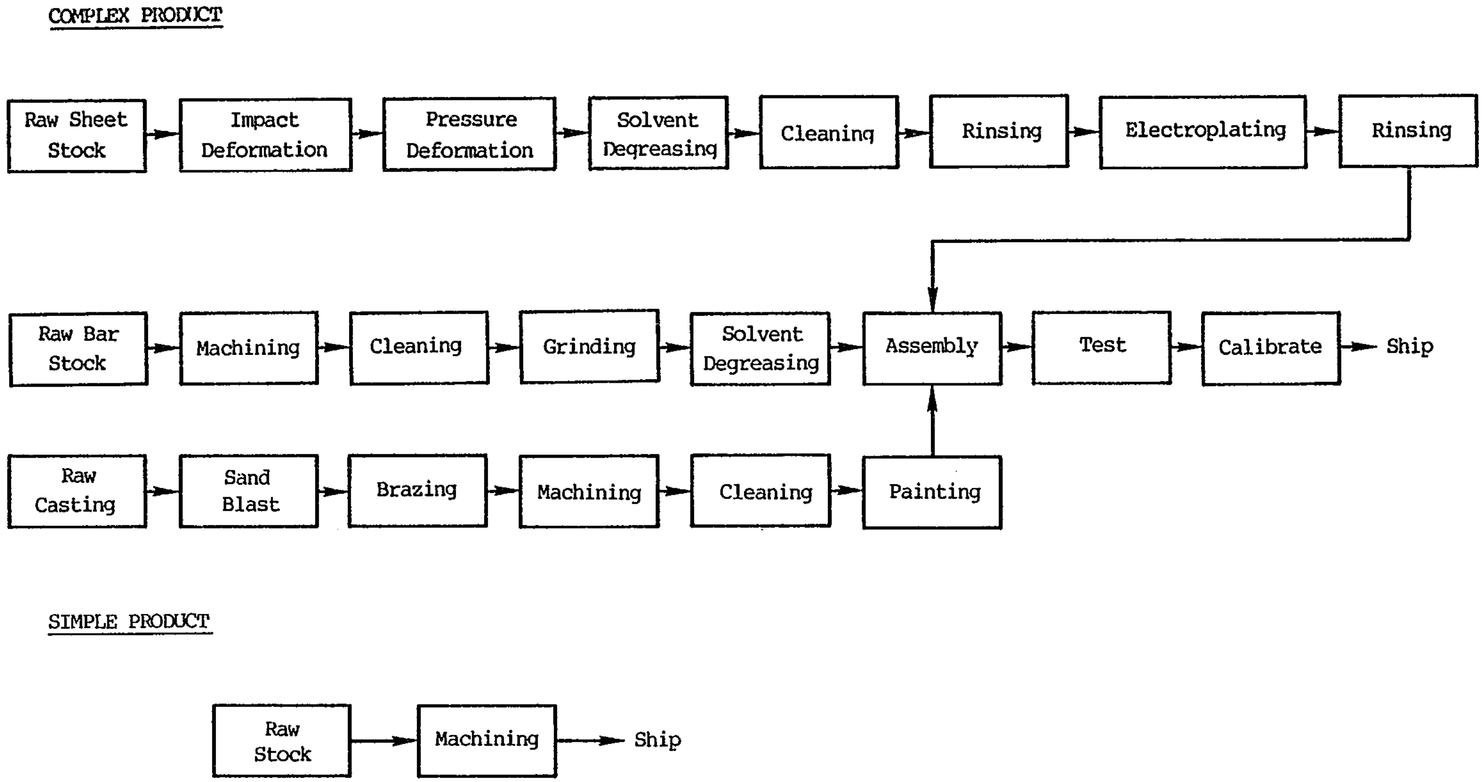


FIGURE 3-1

METAL FINISHING PROCESS APPLICATION

## UNIT OPERATIONS DESCRIPTIONS

This subsection describes each of the 46 individual unit operations that are included in the Metal Finishing Category.

1. Electroplating is the production of a thin surface coating of one metal upon another by electrodeposition. This surface coating is applied to provide corrosion protection, wear or erosion resistance, anti-frictional characteristics, or for decorative purposes. The electroplating of common metals includes the processes in which ferrous or nonferrous basis material is electroplated with copper, nickel, chromium, brass, bronze, zinc, tin, lead, cadmium, iron, aluminum or combinations thereof. Precious metals electroplating includes the processes in which a ferrous or nonferrous basis material is plated with gold, silver, palladium, platinum, rhodium, indium, ruthenium, iridium, osmium, or combinations thereof.

   In electroplating, metal ions in either acid, alkaline or neutral solutions are reduced on cathodic surfaces. The cathodic surfaces are the workpieces being plated. The metal ions in solution are usually replenished by the dissolution of metal from anodes or small pieces contained in inert wire or metal baskets. Replenishment with metal salts is also practiced, especially for chromium plating. In this case, an inert material must be selected for the anodes. Hundreds of different electroplating solutions have been adopted commercially but only two or three types are utilized widely for a particular metal or alloy. For example, cyanide solutions are popular for copper, zinc, brass, cadmium, silver, and gold. However, non-cyanide alkaline solutions containing pyrophosphate have come into use recently for zinc and copper. Zinc, copper, tin and nickel are plated with acid sulfate solutions, especially for plating relatively simple shapes. Cadmium and zinc are sometimes electroplated from neutral or slightly acidic chloride solutions. The most common methods of plating are in barrels, on racks, and continuously from a spool or coil.

2. Electroless Plating is a chemical reduction process which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of metal without the use of external electrical energy. It has found widespread use in industry due to several unique advantages over conventional electroplating. Electroless plating provides a

uniform plating thickness on all areas of the part regardless of the configuration or geometry of the part. An electroless plate on a properly prepared surface is dense and virtually non-porous. Copper and nickel electroless plating are the most common. The basic ingredients in an electroless plating solution are:

1. A source of metal, usually a salt.
2. A reducer to reduce the metal to its base state.
3. A complexing agent to hold the metal in solution (so the metal will not plate out indiscriminately).
4. Various buffers and other chemicals designed to maintain bath stability and increase bath life.

Electroless plating is an autocatalytic process where catalysis is promoted from one of the products of a chemical reaction. The chemistry of electroless plating is best demonstrated by examining electroless nickel plating. The source of nickel is a salt such as nickel chloride or nickel sulfate, and the reducer is sodium hypophosphite. There are several complexing agents can be used, the most common ones being citric and glycolic acid. Hypophosphite anions in the presence of water are dehydrogenated by the solid catalytic surface provided by nickel to form acid orthophosphite anions. Active hydrogen atoms are bonded on the catalyst forming a hydride. Nickel ions are reduced to metallic nickel by the active hydrogen atoms which are in turn oxidized to hydrogen ions. Simultaneously, a portion of the hypophosphite anions are reduced by the active hydrogen and adsorbed on the catalytic surface producing elemental phosphorus, water and hydroxyl ions. Elemental phosphorus is bonded to or dissolved in the nickel making the reaction irreversible. At the same time hypophosphite anions are catalytically oxidized to acid orthophosphite anions, evolving gaseous hydrogen. The basic plating reactions proceed as follows:

The nickel salt is ionized in water

$$NiSO_4 = Ni^{+2} + SO_4^{-2}$$

There is then a reduction-oxidation reaction with nickel and sodium hypophosphite.

$$Ni^{+2} + SO_4^{-2} + 2NaH_2PO_2 + 2\ H_2O =$$

$$Ni + 2NaH_2PO_3 + H_2 + H_2SO_4$$

The sodium hypophosphite also reacts in the following manner:

$$2NaH_2PO_2 + H_2 = 2P + 2NaOH + 2H_2O$$

As can be seen in the equations above, both nickel and phosphorus are produced, and the actual metal deposited is a nickel-phosphorus alloy. The phosphorus content can be varied to produce different characteristics in the nickel plate.

When electroless plating is done on a plastic basis material, catalyst application and acceleration steps are necessary as surface preparation operations. These steps are considered part of the electroless plating unit operation.

Immersion plating is a chemical plating process in which a thin metal deposit is obtained by chemical displacement of the basis metal. Unlike electroless plating, it is not an autocatalytic process. In immersion plating, a metal will displace from solution any other metal that is below it in the electromotive series of elements.

The lower (more noble) metal will be deposited from solution while the more active metal (higher in the series) will be dissolved. A common example of immersion plating is the deposition of copper on steel from an acid copper solution. Because of the similarity of the wastes produced and the materials involved, immersion plating is considered part of the electroless plating unit operation.

3. Anodizing is an electrolytic oxidation process which converts the surface of the metal to an insoluble oxide. These oxide coatings provide corrosion protection, decorative surfaces, a base for painting and other coating processes, and special electrical and mechanical properties. Aluminum is the most frequently anodized material, while some magnesium and limited amounts of zinc and titanium are also treated.

Although the majority of anodizing is carried out by immersion of racked parts in tanks, continuous anodizing is done on large coils of aluminum in a manner similar to continuous electroplating. For aluminum parts, the formation of the oxide occurs when the parts are made anodic in dilute sulfuric acid or dilute chromic acid solutions. The oxide layer begins formation at the extreme outer surface, and as the reaction proceeds, the oxide grows into the metal. The last formed oxide, known as the boundary layer, is located at the interface between the base metal and the oxide. The boundary is extremely thin and nonporous. The sulfuric acid process is typically used for all parts fabricated from aluminum alloys except for parts subject to stress or containing recesses in which the sulfuric acid solution may be retained and attack the aluminum. Chromic acid anodic coatings are more protective than sulfuric acid coatings and have a relatively thick boundary layer. For these reasons, a chromic acid bath is used if a complete rinsing of the part cannot be achieved.

4. Coating - This manufacturing operation includes chromating, phosphating, metal coloring and passivating. These coatings are applied to previously deposited metal or basis material for increased corrosion protection, lubricity, preparation of the surface for additional coatings or formulation of a special surface appearance. In chromating, a portion of the base metal is converted to one of the components of the protective film formed by the coating solution. This occurs by reaction with aqueous solutions containing hexavalent chromium and active organic or inorganic compounds. Chromate coatings are most frequently applied to zinc, cadmium, aluminum, magnesium, copper, brass, bronze and silver. Most of the coatings are applied by chemical immersion although a spray or brush treatment can be used. Changes in the solutions can impart a wide range of colors to the coatings from colorless to iridescent yellow, brass, brown, and olive drab. Additional coloring of the coatings can be achieved by dipping the parts in organic dye baths to produce red, green, blue, and other colors.

Phosphate coatings are used to provide a good base for paints and other organic coatings, to condition the surfaces for cold forming operations by providing a base for drawing compounds and lubricants, and to impart corrosion resistance to the metal surface by the coating itself or by providing a suitable base for rust-preventative oils or waxes. Phosphate conversion coatings are formed by the immersion of iron, steel, or zinc plated steel in a dilute solution of phosphoric acid plus other reagents. The method of applying the phosphate coating is dependent upon the size and shape of the part to be coated. Small parts are coated in barrels immersed in the phosphating solution. Large parts, such as steel sheet and strip, are spray coated or continuously passed through the phosphating solution. Supplemental oil or wax coatings are usually applied after phosphating unless the part is to be painted.

Metal coloring by chemical conversion methods produces a large group of decorative finishes. This operation covers only chemical methods of coloring in which the metal surface is converted into an oxide or similar metallic compound. The most common colored finishes are used on copper, steel, zinc, and cadmium.

Application of the color to the cleaned basis metal involves only a brief immersion in a dilute aqueous solution. The colored films produced on the metal surface are extremely thin and delicate. Consequently, they lack resistance to handling and the atmosphere. A clear lacquer is often used to protect the colored metal surface. A large quantity of copper and brass is colored to yield a wide variety of shades and colors. Shades of black, brown, gray, green and patina can be obtained on copper and brass by use of appropriate coloring solutions. The most widely-used colors for ferrous metals are based on oxides which yield black, brown, or blue colors. A number of colors can be developed on zinc depending on the length of immersion in the coloring solution. Yellow, bronze, dark green, black and brown colors can be produced on cadmium. Silver, tin, and aluminum are also colored commercially. Silver is given a gray color by immersion in a polysulfide solution such as ammonium polysulfide. Tin can be darkened to produce an antique finish of pewter by immersion in a solution of nitric acid and copper sulfate.

Passivation refers to forming a protective film on metals, particularly stainless steel and copper, by immersion in an acid solution. Stainless steel is passivated in order to dissolve any imbedded iron particles and to form a thin oxide film on the surface of the metal. Typical solutions for passivating stainless steel include nitric acid and nitric acid with sodium dichromate. Copper is passivated with a solution of ammonium sulfate and copper sulfate forming a blue-green patina on the surface of the metal.

5. Etching and Chemical Milling - These processes are used to produce specific design configurations and tolerances or surface appearances on parts (or metal-clad plastic in the case of printed circuit boards) by controlled dissolution with chemical reagents or etchants. Included in this classification are the processes of chemical milling, chemical etching and bright dipping. Chemical etching is the same process as chemical milling except the rates and depths of metal removal are usually much greater in chemical milling. Typical solutions for chemical milling and etching include ferric chloride, nitric acid, ammonium persulfate, chromic acid, cupric chloride, hydrochloric acid and combinations of these reagents. Bright dipping is a specialized form of etching and is used to remove oxide and tarnish from ferrous and nonferrous materials and is frequently performed just prior to anodizing. Bright dipping can produce a range of surface appearances from bright clean to brilliant depending on the surface smoothness desired for the finished part. Bright dipping solutions usually involve mixtures of two or more of sulfuric, chromic, phosphoric, nitric and hydrochloric acids. Also included in this unit operation is the stripping of metallic coatings.

6. Cleaning involves the removal of oil, grease and dirt from the surface of the basis material using water with or without a detergent or other dispersing agent. Alkaline cleaning (both electrolytic and non-electrolytic) and acid cleaning are both included.

Alkaline cleaning is used to remove oily dirt or solid soils from workpieces. The detergent nature of the cleaning solution provides most of the cleaing action with agitation of the solution and movement of the workpiece being of secondary importance. Alkaline cleaners are classified into three types: soak, spray, and electrolytic. Soak cleaners are used on easily removed soil. This type of cleaner is less efficient than spray or electrolytic cleaners. Spray cleaners combine the detergent properties of the solution with the impact force of the spray which mechanically loosens the soil. Electrolytic cleaning produces the cleanest surface available from conventional methods of alkaline cleaning. The effectiveness of this method results from the strong agitation of the solution by gas evolution and oxidation-reduction reactions that occur during electrolysis. Also, certain dirt particles become electrically charged and are repelled from the surface. Direct current (cathodic) cleaning uses the workpiece as the cathode, while for reverse current (anodic) cleaning the workpiece is the anode. In periodic reverse current cleaning, the current is periodically reversed from direct current to reverse current. Periodic reverse cleaning gives improved smut removal, accelerated cleaning and a more active surface for any subsequent surface finishing operation.

Acid cleaning is a process in which a solution of an inorganic (mineral) acid, organic acid, or an acid salt, in combination with a wetting agent or detergent, is employed to remove oil, dirt, or oxide from metal surfaces. Acid cleaning is done with various acid concentrations can be referred to as pickling, acid dipping, descaling, or desmutting. The solution may or may not be heated and can be an immersion or spray operation. Agitation is normally required with soaking, and spray is usually used with complex shapes. An acid dip operation may also follow alkaline cleaning prior to plating. Phosphoric acid mixtures are also in common use to remove oils and light rust while leaving a phosphate coating that provides a paint base or temporary resistance to rusting. Strong acid solutions are used to remove rust and scale prior to surface finishing.

7. Machining is the general process of removing stock from a workpiece by forcing a cutting tool through the workpiece, removing a chip of basis material. Machining operations such as turning, milling, drilling, boring, tapping, planing, broaching, sawing and cutoff, shaving, threading, reaming, shaping, slotting, hobbing, filing, and chamfering are included in this definition.

8. Grinding is the process of removing stock from a workpiece by the use of a tool consisting of abrasive grains held by a rigid or semirigid binder. The tool is usually in the form of a disk (the basic shape of grinding wheels), but may also be in the form of a cylinder, ring, cup, stick, strip, or belt. The most commonly used abrasives are aluminum oxide, silicon carbide, and diamond. The processes included in this unit operation are sanding (or cleaning to remove rough edges or excess material), surface finishing, and separating (as in cut-off or slicing operations).

9. Polishing is an abrading operation used to remove or smooth out surface defects (scratches, pits, tool marks, etc.) that adversely affect the appearance or function of a part. Polishing is usually performed with either a belt or wheel to which an abrasive such as aluminum oxide or silicone carbide is bonded. Both wheels and belts are flexible and will conform to irregular or rounded areas where necessary. The operation usually referred to as buffing is included in the polishing operation.

10. Barrel Finishing or tumbling is a controlled method of processing parts to remove burrs, scale, flash, and oxides as well as to improve surface finish. Widely used as a finishing operation for many parts, it obtains a uniformity of surface finish not possible by hand finishing. For large quantities of small parts it is generally the most economical method of cleaning and surface conditioning.

    Parts to be finished are placed in a rotating barrel or vibrating unit with an abrasive media, water or oil, and usually some chemical compound to assist in the operation. As the barrel rotates slowly, the upper layer of the work is given a sliding movement toward the lower side of the barrel, causing the abrading or polishing action to occur. The same results may also be accomplished in a vibrating unit, in which the entire contents of the container are in constant motion.

11. Burnishing is the process of finish sizing or smooth finishing a workpiece (previously machined or ground) by displacement, rather than removal, of minute surface irregularities. It is accomplished with a smooth point or line-contact and fixed or rotating tools.

12. Impact Deformation is the process of applying an impact force to a workpiece such that the workpiece is permanently deformed or shaped. Impact deformation operations include shot peening, peening, forging, high energy forming, heading, and stamping.

13. Pressure Deformation is the process of applying force (at a slower rate than an impact force) to permanently deform or shape a workpiece. Pressure deformation includes operations such as rolling, drawing, bending, embossing, coining, swaging, sizing, extruding, squeezing, spinning, seaming, staking, piercing, necking, reducing, forming, crimping, coiling, twisting, winding, flaring or weaving.

14. Shearing is the process of severing or cutting a workpiece by forcing a sharp edge or opposed sharp edges into the workpiece stressing the material to the point of shear failure and separation.

15. Heat Treating is the modification of the physical properties of a workpiece through the application of controlled heating and cooling cycles. Such operations as tempering, carburizing, cyaniding, nitriding, annealing, normalizing, austenizing, quenching, austempering, siliconizing, martempering, and malleabilizing are included in this definition.

16. Thermal Cutting is the process of cutting, slotting or piercing a workpiece using an oxyacetylene oxygen lance or electric arc cutting tool.

17. Welding is the process of joining two or more pieces of material by applying heat, pressure or both, with or without filler material, to produce a localized union through fusion or recrystallization across the interface. Included in this process are gas welding, resistance welding, arc welding, cold welding, electron beam welding, and laser beam welding.

18. Brazing is the process of joining metals by flowing a thin, capillary thickness layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term brazing is used where the temperature exceeds 425°C (800°F).

19. Soldering is the process of joining metals by flowing a thin (capillary thickness) layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount

of base metal in the molten filler metal, without fusion of the base metal. The term soldering is used where the temperature range falls below 425°C (800°F).

20. Flame Spraying is the process of applying a metallic coating to a workpiece using finely powdered fragments of wire, together with suitable fluxes, are projected through a cone of flame onto the workpiece.

21. Sand Blasting is the process of removing stock, including surface films, from a workpiece by the use of abrasive grains pneumatically impinged against the workpiece. The abrasive grains used include sand, metal shot, slag, silica, pumice, or natural materials such as walnut shells.

22. Abrasive Jet Machining is a mechanical process for cutting hard brittle materials. It is similar to sand blasting but uses much finer abrasives carried at high velocities (500-3000 fps) by a liquid or gas stream. Uses include frosting glass, removing metal oxides, deburring, and drilling and cutting thin sections of metal.

23. Electrical Discharge Machining is a process which can remove metal with good dimensional control from any metal. It cannot be used for machining glass, ceramics, or other nonconducting materials. The machining action is caused by the formation of an electrical spark between an electrode, shaped to the required contour, and the workpiece. Since the cutting tool has no contact with the workpiece, it can be made from a soft, easily worked material such as brass. The tool works in conjunction with a fluid such as mineral oil or kerosene, which is fed to the work under pressure. The function of this coolant is to serve as a dielectric, to wash away particles of eroded metal from the workpiece or tool, and to maintain a uniform resistance to flow of current.

    Electrical discharge machining is also known as spark machining or electronic erosion. The operation was developed primarily for machining carbides, hard nonferrous alloys, and other hard-to-machine materials.

24. Electrochemical Machining is a process based on the same principles used in electroplating except the workpiece is the anode and the tool is the cathode. Electrolyte is pumped between the electrodes and a potential applied with the result that metal is rapidly removed.

    In this process, electrode accuracy is important since the surface finish of the electrode tool will be reproduced in the surface of the workpiece. While copper is frequently used as the electrode, brass, graphite, and copper-tungsten are also used. The tool must be an electrical conductor, easy to machine, corrosion resistant, and able to conduct the quantity of current needed. Although there is no standard electrolyte, sodium chloride is more generally used than others.

25. Electron Beam Machining is a thermoelectric process. In electron beam machining, heat is generated by high velocity electrons impinging on part of the workpiece. At the point where the energy of the electrons is focused, it is transformed into sufficient thermal energy to vaporize the material locally. The process is generally carried out in a vacuum. While the metal-removal rate of electron beam machining is approximately 0.01 milligrams per second, the tool is accurate and is especially adapted for micro-machining. There is no heat affected zone or pressure on the workpiece and extremely close tolerances can be maintained. The process results in X-ray emission which requires that the work area be shielded to absorb radiation. At present the process is used for drilling holes as small as 0.0508 mm (0.002 in.) in any known material, cutting slots, shaping small parts, and machining sapphire jewel bearings.

26. Laser Beam Machining is the process whereby a highly focused monochromatic collimated beam of light is used to remove material at the point of impingement on a workpiece. Laser beam machining is a thermoelectric process, and material removal is largely accomplished by evaporation although some material is removed in the liquid state at high velocity. Since the metal removal rate is very small, they are used for such jobs as drilling microscopic holes in carbides or diamond wire drawing dies and for removing metal in the balancing of high-speed rotating machinery.

Lasers can vaporize any known material. They have small heat affected zones and work easily with nonmetallic hard materials.

27. Plasma Arc Machining is the process of material removal or shaping of a workpiece by a high velocity jet of high temperature ionized gas. A gas (nitrogen, argon, or hydrogen) is passed through an electric arc causing it to become ionzied and raised to temperatures in excess of 16,649°C (30,000°F). The relatively narrow plasma jet melts and displaces the workpiece material in its path. Because plasma machining does not depend on a chemical reaction

between the gas and the work material and because plasma temperatures are extremely high, the process can be used on almost any metal, including those that are resistant to oxygen-fuel gas cutting. The method is of commercial importance mainly for profile cutting of stainless steel and aluminum alloys.

28. Ultrasonic Machining is a mechanical process designed to effectively machine hard, brittle materials. It removes material by the use of abrasive grains which are carried in a liquid between the tool and the work and which bombard the work surface at high velocity. This action gradually chips away minute particles of material in a pattern controlled by the tool shape and contour. A transducer causes an attached tool to oscillate linearly at a frequency of 20,000 to 30,000 times per second at an amplitude of 0.0254 to 0.127 mm (0.001 to 0.005 in). The tool motion is produced by being part of a sound wave energy transmission line which causes the tool material to change its normal length by contraction and expansion. The tool holder is threaded to the transducer and oscillates linearly at ultrasonic frequencies, thus driving the grit particles into the workpiece. The cutting particles, boron carbide and similar materials, are of a 280-mesh size or finer, depending upon the accuracy and the finish desired. Operations that can be performed include drilling, tapping, coining, and the making of openings in all types of dies. Ultrasonic machining is used principally for machining materials such as carbides, tool steels, ceramics, glass, gem stones, and synthetic crystals.

29. Sintering is the process of forming a mechanical part from a powdered metal by fusing the particles together under pressure and heat. The temperature is maintained below the melting point of the basis metal.

30. Laminating is the process of adhesive bonding layers of metal, plastic, or wood to form a part.

31. Hot Dip Coating is the process of coating a metallic workpiece with another metal by immersion in a molten bath to provide a protective film. Galvanizing (hot dip zinc) is the most common hot dip coating.

32. Sputtering is the process of covering a metallic or nonmetallic workpiece with thin films of metal. The surface to be coated is bombarded with positive ions in a gas discharge tube, which is evacuated to a low pressure.

33. Vapor Plating is the process of decomposition of a metal or compound upon a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting point of either the deposit or the basis material.

34. Thermal Infusion is the process of applying a fused zinc, cadmium, or other metal coating to a ferrous workpiece by imbuing the surface of the workpiece with metal powder or dust in the presence of heat.

35. Salt Bath Descaling is the process of removing surface oxides or scale from a workpiece by immersion of the workpiece in a molten salt bath or a hot salt solution. Molten salt baths are used in a salt bath - water quench - acid dip sequence to clean hard-to-remove oxides from stainless steels and other corrosion-resistant alloys. The work is immersed in the molten salt (temperatures range from 400 - 540 degrees C), quenched with water, and then dipped in acid. Oxidizing, reducing, and electrolytic baths are available, and the particular type needed is dependent on the oxide to be removed.

36. Solvent Degreasing is a process for removing oils and grease from the surfaces of a workpiece by the use of organic solvents, such as aliphatic petroleums (eg-kerosene, naptha), aromatics (eg-benzene, toluene), oxygenated hydrocarbons (eg-ketones, alcohol, ether), halogenated hydrocarbons (eg-1,1,1-trichloroethane, trichloroethylene, methylene chloride), and combinations of these classes of solvents. Solvent cleaning can be accomplished by either the liquid or vapor phase. Solvent vapor degreasing is normally quicker than solvent liquid degreasing. However, ultrasonic vibration is sometimes used with liquid solvent so as to decrease the required immersion time with complex shapes. Solvent cleaning is often used as a precleaning operation such as prior to the alkaline cleaning that precedes plating, as a final cleaning of precision parts, or as a surface preparation for some painting operations.

Emulsion cleaning is a type of solvent degreasing that uses common organic solvents (eg-kerosene, mineral oil, glycols, and benzene) dispersed in an aqueous medium with the aid of an emulsifying agent. Depending on the solvent used, cleaning is done at temperatures from room temperature to 82°C (180°F). This operation uses less chemical than solvent degreasing because of the lower solvent concentration employed. The process is used for rapid superficial cleaning and is usually performed as emulsion spray cleaning.

37. Paint Stripping is the process of removing an organic coating from a workpiece. The stripping of such coatings is usually performed with caustic, acid, solvent, or molten salt.

38. Painting is the process of applying an organic coating to a workpiece. The application of coatings such as paint, varnish, lacquer, shellac, and plastics by processes such as spraying, dipping, brushing, roll coating, lithographing, and wiping are included. Spray painting is by far the most common and can be used with nearly all varieties of paint. The paint can be sprayed manually or automatically, hot or cold, and it may be atomized with or without compressed air to force the paint through an orifice. Other processes included under this unit operation are printing, silk screening and stenciling.

39. Electrostatic Painting is the application of electrostatically charged paint particles to an oppositely charged workpiece followed by thermal fusing of the paint particles to form a cohesive paint film. Usually the paint is applied in spray form and may be applied manually or automatically, hot or cold, and with or without compressed air atomization. Both waterborne and solvent-borne coatings can be sprayed electrostatically.

40. Electropainting is the process of coating a workpiece by either making it anodic or cathodic in a bath that is generally an aqueous emulsion of the coating material. The electrodeposition bath contains stabilized resin, dispersed pigment, surfactants, and sometimes organic solvents in water. Electropainting is used primarily for primer coats because it gives a fairly thick, highly uniform, corrosion resistant coating in relatively little time.

41. Vacuum Metalizing is the process of coating a workpiece with metal by flash heating metal vapor in a high-vacuum chamber containing the workpiece. The vapor condenses on all exposed surfaces.

42. Assembly is the fitting together of previously manufactured parts or components into a complete machine, unit of a machine, or structure.

43. Calibration is the application of thermal, electrical, or mechanical energy to set or establish reference points for a component or complete assembly.

44. Testing is the application of thermal, electrical, or mechanical energy to determine the suitability or functionality of a component or complete assembly.

45. Mechanical Plating is the process of depositing metal coatings on a workpiece via the use of a tumbling barrel, metal powder, and usually glass beads for the impaction media. The operation is subject to the same cleaning and rinsing operations that are applied before and after the electroplating operation.

46. Printed Circuit Board Manufacturing involves the formation of a circuit pattern of conductive metal (usually copper) on nonconductive board materials such as plastic or glass. There are five basic steps involved in the manufacture of printed circuit boards: cleaning and surface preparation, catalyst and electroless plating, pattern printing and masking, electroplating, and etching.

After the initial cutting, drilling and sanding of the boards, the board surface is prepared for plating electroless copper. This surface preparation involves an etchback (removal of built-up plastic around holes) and an acid and alkaline cleaning to remove grime, oils, and fingerprints. The board is then etched and rinsed. Following etching, the catalyst is applied, and rinsing operations following catalyst application. The entire board is then electroless copper plated and rinsed.

Following electroless copper plating, a plating resist is applied in non-circuit areas. Following application of a resist, a series of electroplates are applied. First the circuit is copper plated. A solder electroplate is applied next followed by a rinse. For copper removal in non-circuit areas, an etch step is next. After the etch operation, a variety of tab plating processes can be utilized depending on the board design requirements. These include nickel electroplating, gold electroplating, rhodium electroplating, and tin immersion plating.

There are presently three main production methods for printed circuit boards: additive, semi-additive, and subtractive. The additive method uses pre-sensitized, unclad material as the starting board; the semi-additive method uses unclad, unsensitized material as the starting board; and the subtractive method begins with copper clad, unsensitized material.

# SECTION IV
# INDUSTRY CATEGORIZATION

## INTRODUCTION

The primary purpose of industry categorization is to establish groupings within the Metal Finishing Category (MFC) such that each group (subcategory) has a uniform set of effluent limitations. This requires that the elements of each group be capable of using similar treatment technologies to achieve the effluent limitations. Thus, the same wastewater treatment and control technology is applicable within a subcategory and a uniform treated effluent results from the application of a specific treatment and control technology. This section presents the subcategorization established for the Metal Finishing Category and explains the selection rationale.

Proper industry subcategorization defines groups within an industrial category whose wastewater discharges can be controlled by the same concentration or mass based limitations. The subsections which follow deal with these considerations as they apply to the Metal Finishing Category.

## CATEGORIZATION BASIS

The following aspects of the Metal Finishing Category were considered for the bases of establishing subcategories:

1. Raw waste characteristics
2. Manufacturing processes
3. Raw materials (basis and process)
4. Product type or production volume
5. Size and age of facility
6. Number of employees
7. Water usage
8. Individual plant characteristics

After examination of the potential categorization bases, a single metal finishing subcategory was established. All process wastewaters in the Metal Finishing Category are amenable to treatment by a single system and one set of discharge standards results from the application of a single waste treatment technology.

Seven distinct types of raw wastes are present in metal finishing wastewaters. These raw wastes can be divided into two constituents, namely: inorganic and organic wastes. These can then be further subdivided into the specific types of waste that occur in each of the two major areas and are identified in Table 4-1.

## TABLE 4-1
## METAL FINISHING CATEGORY RAW WASTE CLASSIFICATIONS

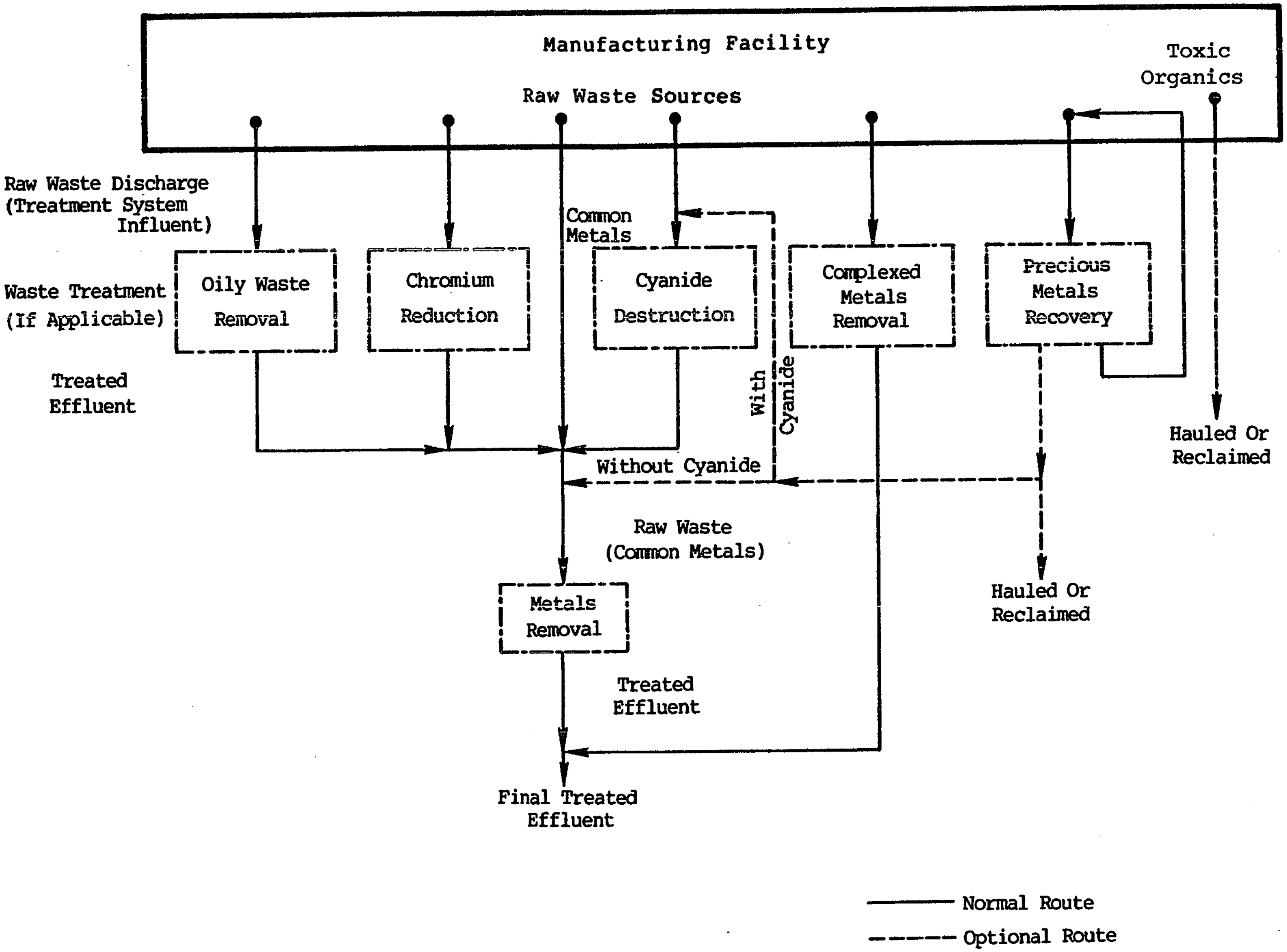
| MAJOR SUBDIVISION | RAW WASTE TYPE |
|---|---|
| INORGANIC WASTES | 1. Common metals<br>2. Precious metals<br>3. Complexed metals<br>4. Chromium (hexavalent) |
| ORGANIC WASTES | 5. Cyanide<br>6. Oils<br>7. Toxic organics |

Figure 4-1 presents the waste treatment requirement for the Metal Finishing Category and illustrates the effect of raw waste type upon the treatment technology requirements. All of the process raw wastes resulting from each of the 46 individual unit operations, previously defined and described in Section III, are encompassed by one or more of the raw waste types. Table 4-2 presents a tabulation of the manufacturing unit operations and the types of the raw waste that they have the potential to generate. Thus a direct relationship exists between the treatment system requirements and the unit operations performed at a manufacturing facility. Subsequent sections of this document further describe the specifics of the relationship between the unit operations performed, the wastes they produce, and the various levels of treatment technology and systems applicable to guideline limitations.

The following paragraphs discuss other approaches that were considered as bases for further subdividing the metal finishing subcategory and the rationale for further subdivision being unnecessary.

### Manufacturing Processes

The manufacturing processes employed by the Metal Finishing Category are fully represented by the 46 unit operations that were defined in Section III. Unit operation subdivision would be overly complex as a subcategorization basis due to the number of combinations of processes that exists in this category. In addition, subdivision on the basis of each of the unit operations is not unique since many operations generate the same waste constituents. Unit operations with similar waste characteristics could be combined to form individual subcategories and thus effectively provide a categorization based upon waste characteristics. However, as explained



Note: Discharge from precious metals recovery may be hauled in alternative ways, depending on the recovery method in use.

FIGURE 4-1

WASTE TREATMENT SCHEMATIC

# TABLE 4-2

## WASTE CHARACTERISTIC DISTRIBUTION

| WASTE CHARACTERISTICS / UNIT OPERATION | INORGANICS | | | | ORGANICS | | |
|---|---|---|---|---|---|---|---|
| | Common Metals | Precious Metals | Complexed Metals | Chromium (Hexavalent) | Cyanide | Oils | Toxic Organics |
| 1. Electroplating | x | x | | x | x | | |
| 2. Electroless Plating | x | x | x | | x | | |
| 3. Anodizing | x | | | x | | | |
| 4. Conversion Coating | x | x | | x | x | | |
| 5. Etching (Chem. Milling) | x | x | x | x | | | |
| 6. Cleaning | x | x | x | x | x | x | x |
| 7. Machining | x | | | | | x | |
| 8. Grinding | x | | | | | x | |
| 9. Polishing | x | x | | | | x | |
| 10. Tumbling | x | | | x | x | x | |
| 11. Burnishing | x | x | | | x | x | |
| 12. Impact Deformation | x | | | | | x | |
| 13. Pressure Deformation | x | | | | | x | |
| 14. Shearing | x | | | | | x | |
| 15. Heat Treating | x | | | | x | x | x |
| 16. Thermal Cutting | x | | | | | | |
| 17. Welding | x | | | | | | |
| 18. Brazing | x | | | | | | |
| 19. Soldering | x | | x | | | | |
| 20. Flame Spraying | x | | | | | | |
| 21. Sand Blasting | x | | | | | | |
| 22. Other Abr. Jet Machining | x | | | | | x | |
| 23. Elec. Discharge Machining | x | | | | | x | |
| 24. Electrochemical Machining | x | | | | x | x | x |
| 25. Electron Beam Machining | x | | | | | | |
| 26. Laser Beam Machining | x | | | | | | |
| 27. Plasma Arc Machining | x | | | | | | |
| 28. Ultrasonic Machining | x | | | | | | |

TABLE 4-2

WASTE CHARACTERISTIC DISTRIBUTION
(CONT.)

| WASTE CHARACTERISTICS / UNIT OPERATION | INORGANICS | | | | ORGANICS | | |
|---|---|---|---|---|---|---|---|
| | Common Metals | Precious Metals | Complexed Metals | Chromium (Hexavalent) | Cyanide | Oils | Toxic Organics |
| 29. Sintering | x | | | | | | |
| 30. Laminating | x | | | | | | |
| 31. Hot Dip Coating | x | | | | | | |
| 32. Sputtering | x | | | | | | |
| 33. Vapor Plating | x | | | | | | |
| 34. Thermal Infusion | x | | | | | | |
| 35. Salt Bath Descaling | x | | | | | x | |
| 36. Solvent Degreasing | x | | | | | x | x |
| 37. Paint Stripping | x | | | | | x | x |
| 38. Painting | x | | | | | x | x |
| 39. Electrostatic Painting | x | | | x | | x | x |
| 40. Electropainting | x | | | | | | x |
| 41. Vacuum Metalizing | x | | | | | | |
| 42. Assembly | x | | | | | x | x |
| 43. Calibration | x | | | | | x | |
| 44. Testing | x | | | | | x | |
| 45. Mechanical Plating | x | | | x | | | |
| 46. Printed Circuit Board Manufacturing | x | x | x | x | x | | x |

previously, a direct correlation exists between the unit operations performed and treatment technology needed via the selected metal finishing subcategorization. Therefore, manufacturing process variations are inherently accounted for by their waste characteristics and no further subdivision on the basis of manufacturing process is required.

## Raw Materials

There is a wide variation in basis materials, process materials, and process chemicals used within this industry and all wastes are a direct result of this material usage. Subcategorization on the basis of raw material usage would not result in industry subgroups whose wastes are amenable to treatment by different systems.

## Product Type or Production Volume

The products manufactured by the Metal Finishing Category cover virtually the entire spectrum of metallic goods. There are specific differences in manufacturing operations and many varieties of raw and process materials are used throughout the category. However, wastewaters resulting from the manufacture of many different products have the same waste treatment requirements and this is accounted for by the single metal finishing subcategory.

The production volume influences the mass of pollutants discharged but does not alter the waste constituents. Therefore, the quantity of work processed is not appropriate as a basis for subcategorization.

## Size and Age of Facility

The nature of the manufacturing processes for the Metal Finishing Category is the same in all facilities regardless of their size. Size is an insufficient criterion for further subdivision since the waste characteristics of a plant depend on the raw materials and the unit operations employed. Size, however, is an important consideration in determining the mass of pollutants discharged.

The relative age of plants is important but is not a suitable basis for subdividing the metal finishing subcategory because it does not consider those items which affect the effluent discharged. The age of a plant has no bearing on the resulting waste characteristics or the required waste treatment.

## Number of Employees

The number of employees is not an appropriate basis for subdivision since identical manufacturing operations can be performed manually or by automatic machinery. For example, a specific operation might be accomplished manually by several machine operators for a particular production level or, if automated, it might reguire only one operator to produce an equivalent production output. In both cases, the resulting waste characteristics are identical if all other factors are the same.

### Water Usage

Variations in water usage will not alter the identity of wastewater constituents but may affect their concentrations in the waste stream. These variations are due mainly to the different rinsing operations employed (i.e. single stage rinsing, series rinsing, countercurrent rinsing, etc). Since wastewater treatment systems are designed to remove groups of pollutants (having similar physical or chemical properties), subcategorization on the basis of water usage would not be appropriate.

### Individual Plant Characteristics

Individual plant characteristics, including geographical location, do not provide a proper basis for subcategorization because they do not affect the process wastewater characteristics of the plant.

### Summary of Categorization Bases

For this study, a single metal finishing subcategory which includes seven types of raw waste was established. The primary division of waste characteristics is the grouping of wastes into inorganic and organic compounds. These two groups are then subdivided into four inorganic and three organic raw waste types. The seven raw waste types encompass the pollutants contained in the wastewaters generated by all combinations of unit operations, raw materials, and process materials and chemicals employed in the Metal Finishing Category.

## EFFLUENT LIMITATION BASE

In addition to determining the necessity for subdividing the Metal Finishing Category, subcategorization also involves the selection of a parameter on which to base limitations.

Since pollutants are measured in terms of their concentration (mg/l), concentration itself is the obvious primary consideration for quantification of the limitations. Utilization of concentration has the following advantages:

1. Concentration is a directly measurable parameter using fundamental sampling and analysis techniques.

2. Industry, via its self-monitoring data, has the opportunity to rapidly recognize and respond to deviations from a given set of limitations.

3. Application of pertinent treatment and control systems to either new or existing manufacturing facilities is straightforward because these systems are designed to provide reduction to specific effluent concentration levels for specific pollutants.

A production related parameter for this industry, such as a combination of the product surface area and the number of particular wastewater producing operations performed, can be used in conjunction with the concentration and process flow rate to provide mass discharge limitations (e.g. limitation in terms of mg/operation-sq.m. for electroplating operations). Based on previous electroplating studies, the application of this type of parameter to quantify limitations has proven to be difficult to understand, implement, and enforce. Several specific problems associated with the use of a production related parameter for the Metal Finishing Category are:

1. Differences in part configuration are not accounted for by merely using a surface area basis such as was used in the past for electroplating.

2. It is often difficult to determine the production level. For example, the overall area of barrel plated items such as miscellaneous jewelry varies constantly throughout a normal production day. To determine production (surface area plated) requires measurement of each individual part.

3. Mass based limitations are difficult to implement if either the production sequence or processed parts are constantly changing, as is especially the case for job shops.

4. It is often difficult to establish what constitutes a single wastewater producing operation since operations may be dry or wet and the sequence of performing operations is subject to variation.

The use of concentration alone as the limitation criterion allows direct measurement and analysis of the treated effluent to verify compliance with the regulations. Thus concentration is selected as the limitations basis for the Metal Finishing Category.

# SECTION V
# WASTE CHARACTERIZATION

## INTRODUCTION

This section presents the water uses, identifies the waste constituents, and quantifies the pollutant parameters that originate in the Metal finishing Category. Published literature, data collection portfolio responses, and actual sampling data were reviewed in order to obtain data for this section. In general, quantitative raw waste information was not included in the data collection portfolios. When such information was included, it was fragmented, incomplete and nearly impossible to correlate. Therefore, the raw waste data presented are derived from an analysis of samples taken at visited plants, downstream of the manufacturing sources, and prior to waste treatment. All parameters analyzed were measured as total rather than dissolved and are expressed in terms of milligrams per liter (mg/ℓ).

This section is organized in the following manner. First is a discussion of water usage within the Metal Finishing Category. This is followed by a discussion of waste characteristics for each of the forty-six unit operations. Finally, there is a description of the parameters found in the total plant process wastewaters discharged prior to end-of-pipe treatment, and a description of the parameters found in each of the seven waste types that were outlined in Section IV:

- Common metals
- Precious metals
- Complexed metals
- Hexavalent chromium
- Cyanide
- Oils
- Toxic organics

## WATER USAGE IN THE METAL FINISHING CATEGORY

Water is used for rinsing workpieces, washing away spills, air scrubbing, process fluid replenishment, cooling and lubrication, washing of equipment and workpieces, quenching, spray booths, and assembly and testing. Descriptions of these uses follow.

### Rinsing

A large proportion of the water usage in the Metal Finishing Category is for rinsing. This water is used to remove the film (fluids and solids) that is deposited on the surfaces of the workpieces during the preceding process. As a result of this rinsing, the water becomes contaminated with the constituents of the film. Rinsing can be used in some capacity after virtually all of the unit operations covered by the Metal Finishing Category and is considered to be an integral part of the unit operation that it follows.

## Spills and Air Scrubbing

Water is used for washing away floor spills and for scrubbing of ventilation exhaust air. In both cases these wastewaters are contaminated with constituents of process materials and dirt.

## Process Fluid Replenishment

As process fluids (e.g. - cleaning solutions, plating solutions, paint formulations, etc.) become exhausted or spent, new solutions have to be made up, with water a major constituent of these solutions. When a fluid is used at high temperature, water must be added periodically to make up for evaporative losses. Exhausted or spent process solutions to be dumped are either collected in sumps for batch processing or are slowly metered into discharged rinse water prior to treatment.

## Cooling and Lubrication

Coolants and lubricants in the form of free oils, emulsified oils, and grease are required by many metal removal operations. The films and residues from these fluids are removed during cleaning, washing, or rinsing operations and these constituents contaminate other fluids. In addition, spent fluids in the sumps represent a further waste contribution that is processed either batchwise (segregated) or is discharged to other waste streams.

## Water from Auxiliary Operations

Auxiliary operations such as stripping of plating or painting racks are essential to plant operations; waters used in these operations do become contaminated and require treatment.

## Washing

Water used for washing workpieces or for washing equipment such as filters, pumps and tanks picks up residues of concentrated process solutions, salts, or oils and is routed to an appropriate wastewater stream for treatment.

## Quenching

Workpieces which have undergone an operation involving intense heat such as heat treating, welding, or hot dip coating are frequently quenched or cooled in aqueous solutions to achieve the desired properties or to facilitate subsequent handling of the part. These solutions become contaminated and require treatment.

### Spray Booths

Plants which employ spray painting processes use spray booths in order to capture oversprayed paint in a particular medium. Many of these booths use water curtains to capture the paint overspray. The paint is directed against a flowing stream of water, which scrubs the air so that paint and solvents are not exhausted to the outside atmosphere. The paint collected in the water is removed by skimming or by use of an ultrafilter and the water is reused in the curtain. This water will periodically be dumped.

### Testing and Calibration

Many types of testing such as leak, pressure, and performance testing, make use of large quantities of water that become contaminated.

## WATER USAGE BY OPERATIONS

Table 5-1 is a listing of the unit operations covered in the Metal Finishing Category and shows the operations that tend to utilize water. The table is broken down according to degree of water use: significant water usage, minimal water usage and zero discharge. The operations found to have zero discharge were determined by an analysis of visited plants in the Metal Finishing Category data base; the data are shown in Table 5-2. The data shown include total number of occurrences of each unit operation, number of zero discharges and the percentage of the total occurrence with zero discharge. The unit operations which tend to have zero discharge are electron beam machining, laser beam machining, plasma arc machining, ultrasonic machining, sintering, sputtering, vapor plating, thermal infusion, vacuum metalizing and calibration. Table 5-3 shows the zero discharge data from the DCP data bases for comparison. While an operation may tend to be zero discharge, associated preparatory operations, i.e., cleaning, may have discharges.

Figures 5-1a and 5-1b display the ranges of flows which may be found within the Metal Finishing Category. This figure is based on flow information obtained from visited plants and the majority of the plants fall within a flow range of zero to 100,000 gallons per day, which is expanded in the figure.

## Table 5-1
## WATER USAGE BY METAL FINISHING OPERATIONS

| Unit Operation | Major Water Usage | Minimal Water Usage | Zero Discharge |
|---|---|---|---|
| 1. Electroplating | x | | |
| 2. Electroless Plating | x | | |
| 3. Anodizing | x | | |
| 4. Conversion Coating | x | | |
| 5. Etching (Chemical Milling) | x | | |
| 6. Cleaning | x | | |
| 7. Machining | x | | |
| 8. Grinding | x | | |
| 9. Polishing | | x | |
| 10. Tumbling (Barrel Finishing) | x | | |
| 11. Burnishing | | x | |
| 12. Impact Deformation | | x | |
| 13. Pressure Deformation | | x | |
| 14. Shearing | | x | |
| 15. Heat Treating | x | | |
| 16. Thermal Cutting | | x | |
| 17. Welding | x | | |
| 18. Brazing | | x | |
| 19. Soldering | | x | |
| 20. Flame Spraying | | x | |
| 21. Sand Blasting | x | | |
| 22. Other Abr. Jet Machining | | x | |
| 23. Elec. Discharge Machining | | x | |
| 24. Electrochemical Machining | | x | |
| 25. Electron Beam Machining | | | x |
| 26. Laser Beam Machining | | | x |
| 27. Plasma Arc Machining | | | x |
| 28. Ultrasonic Machining | | | x |
| 29. Sintering | | | x |
| 30. Laminating | | x | |
| 31. Hot Dip Coating | | x | |
| 32. Sputtering | | | x |
| 33. Vapor Plating | | | x |
| 34. Thermal Infusion | | | x |
| 35. Salt Bath Descaling | x | | |
| 36. Solvent Degreasing | | x | |
| 37. Paint Stripping | x | | |
| 38. Painting | x | | |
| 39. Electrostatic Painting | x | | |
| 40. Electropainting | x | | |
| 41. Vacuum Metalizing | | | x |
| 42. Assembly | | x | |
| 43. Calibration | | | x |
| 44. Testing | x | | |
| 45. Mechanical Plating | x | | |
| 46. Printed Circuit Board Manufacturing | x | | |

## TABLE 5-2
## DETERMINATION OF ZERO DISCHARGE OPERATIONS

| | Unit Operation | Number of Occurences | Number of Zero Dischargers | Percentage of Zero Dischargers |
|---|---|---|---|---|
| * 1. | Electroplating | 32 | 0 | 0.0 |
| * 2. | Electroless Plating | 9 | 0 | 0.0 |
| * 3. | Anodizing | 12 | 0 | 0.0 |
| * 4. | Conversion Coating | 11 | 0 | 0.0 |
| * 5. | Etching & Chemical Milling | 8 | 0 | 0.0 |
| * 6. | Cleaning | 41 | 0 | 0.0 |
| 7. | Machining | 60 | 8 | 13.3 |
| 8. | Grinding | 62 | 31 | 50.0 |
| 9. | Polishing | 42 | 30 | 71.4 |
| 10. | Tumbling (Barrel Finishing) | 53 | 20 | 37.8 |
| 11. | Burnishing | 16 | 10 | 62.5 |
| 12. | Impact Deformation | 20 | 18 | 90.0 |
| 13. | Pressure Deformation | 39 | 34 | 87.2 |
| 14. | Shearing | 37 | 33 | 89.2 |
| 15. | Heat Treating | 37 | 17 | 45.9 |
| 16. | Thermal Cutting | 18 | 17 | 94.4 |
| 17. | Welding | 52 | 46 | 88.5 |
| 18. | Brazing | 28 | 25 | 89.3 |
| 19. | Soldering | 38 | 33 | 86.8 |
| 20. | Flame Spraying | 5 | 3 | 60.0 |
| 21. | Sand Blasting | 20 | 18 | 90.0 |
| 22. | Other Abrasive Jet Machining | 20 | 18 | 90.0 |
| 23. | Electrical Discharge Machining | 12 | 9 | 75.0 |
| 24. | Electrochemical Machining | 9 | 3 | 33.3 |
| 25. | Electron Beam Machining | 6 | 6 | 100.0 |
| 26. | Laser Beam Machining | 5 | 5 | 100.0 |
| 27. | Plasma Arc Machining | 4 | 4 | 100.0 |
| 28. | Ultrasonic Machining | 2 | 2 | 100.0 |
| 29. | Sintering | 4 | 4 | 100.0 |
| 30. | Laminating | 11 | 10 | 91.0 |
| 31. | Hot Dip Coating | 4 | 3 | 75.0 |
| 32. | Sputtering | 2 | 2 | 100.0 |
| 33. | Vapor Plating | 3 | 3 | 100.0 |
| 34. | Thermal Infusion | 3 | 3 | 100.0 |
| 35. | Salt Bath Descaling | 13 | 2 | 15.4 |
| **36. | Solvent Degreasing | - | - | 0.0 |
| 37. | Paint Stripping | 50 | 3 | 6.0 |
| 38. | Painting | 18 | 0 | 0.0 |
| 39. | Electrostatic Painting | 15 | 0 | 0.0 |
| 40. | Electropainting | 15 | 0 | 0.0 |
| 41. | Vacuum Metalizing | 7 | 7 | 100.0 |
| 42. | Assembly | 61 | 57 | 93.4 |
| 43. | Calibration | 24 | 24 | 100.0 |
| 44. | Testing | 70 | 40 | 57.0 |
| ***45. | Mechanical Plating | - | - | - |

*These data are from a 41 plant sampled data base. All other data are from a separate 99 plant sampled data base.

**Not included in the 99 plant data base. Other data indicate that this operation consistently generates wastewater.

***Not included in survey at time of plant visits.

## TABLE 5-3
## DETERMINATION OF ZERO DISCHARGE OPERATIONS
## (DCP DATA BASES)

| | Unit Operation | Number of Occurences | Number of Zero Dischargers | Percentage of Zero Dischargers |
|---|---|---|---|---|
| * 1. | Electroplating | 1100 | 0 | 0.0 |
| * 2. | Electroless Plating | 207 | 0 | 0.0 |
| * 3. | Anodizing | 233 | 0 | 0.0 |
| * 4. | Conversion Coating | 490 | 0 | 0.0 |
| * 5. | Etching & Chemical Milling | 177 | 0 | 0.0 |
| * 6. | Cleaning | 1221 | 0 | 0.0 |
| 7. | Machining | 241 | 200 | 83.0 |
| 8. | Grinding | 204 | 166 | 81.5 |
| 9. | Polishing | 80 | 79 | 98.8 |
| 10. | Tumbling (Barrel Finishing) | 41 | 15 | 36.6 |
| 11. | Burnishing | 11 | 8 | 72.7 |
| 12. | Impact Deformation | 36 | 35 | 97.2 |
| 13. | Pressure Deformation | 48 | 46 | 95.8 |
| 14. | Shearing | 96 | 95 | 98.9 |
| 15. | Heat Treating | 38 | 29 | 76.3 |
| 16. | Thermal Cutting | 32 | 30 | 93.7 |
| 17. | Welding | 162 | 158 | 97.5 |
| 18. | Brazing | 75 | 75 | 100.0 |
| 19. | Soldering | 87 | 82 | 94.2 |
| 20. | Flame Spraying | 7 | 7 | 100.0 |
| 21. | Sand Blasting | 44 | 44 | 100.0 |
| 22. | Other Abrasive Jet Machining | 8 | 7 | 87.5 |
| 23. | Electrical Discharge Machining | 12 | 9 | 75.0 |
| 24. | Electrochemical Machining | 3 | 1 | 34.0 |
| 25. | Electron Beam Machining | 0 | 0 | - |
| 26. | Laser Beam Machining | 1 | 1 | 100.0 |
| 27. | Plasma Arc Machining | 4 | 4 | 100.0 |
| 28. | Ultrasonic Machining | 2 | 0 | 100.0 |
| 29. | Sintering | 3 | 3 | 100.0 |
| 30. | Laminating | 17 | 16 | 94.1 |
| 31. | Hot Dip Coating | 7 | 3 | 42.8 |
| 32. | Sputtering | 1 | 1 | 100.0 |
| 33. | Vapor Plating | 0 | 0 | - |
| 34. | Thermal Infusion | 0 | 0 | - |
| 35. | Salt Bath Descaling | 2 | 1 | 50.0 |
| 36. | Solvent Degreasing | 77 | 28 | 36.4 |
| 37. | Paint Stripping | 16 | 8 | 50.0 |
| 38. | Painting | 97 | 84 | 86.6 |
| 39. | Electrostatic Painting | 9 | 9 | 100.0 |
| 40. | Electropainting | 2 | 2 | 100.0 |
| 41. | Vacuum Metalizing | 2 | 2 | 100.0 |
| 42. | Assembly | 167 | 165 | 98.8 |
| 43. | Calibration | 46 | 45 | 97.8 |
| 44. | Testing | 93 | 82 | 88.0 |
| * 45. | Mechanical Plating | 2 | 0 | 0.0 |

*These data are from a 1221 plant DCP data base. All other data are from a separate 365 plant DCP data base.

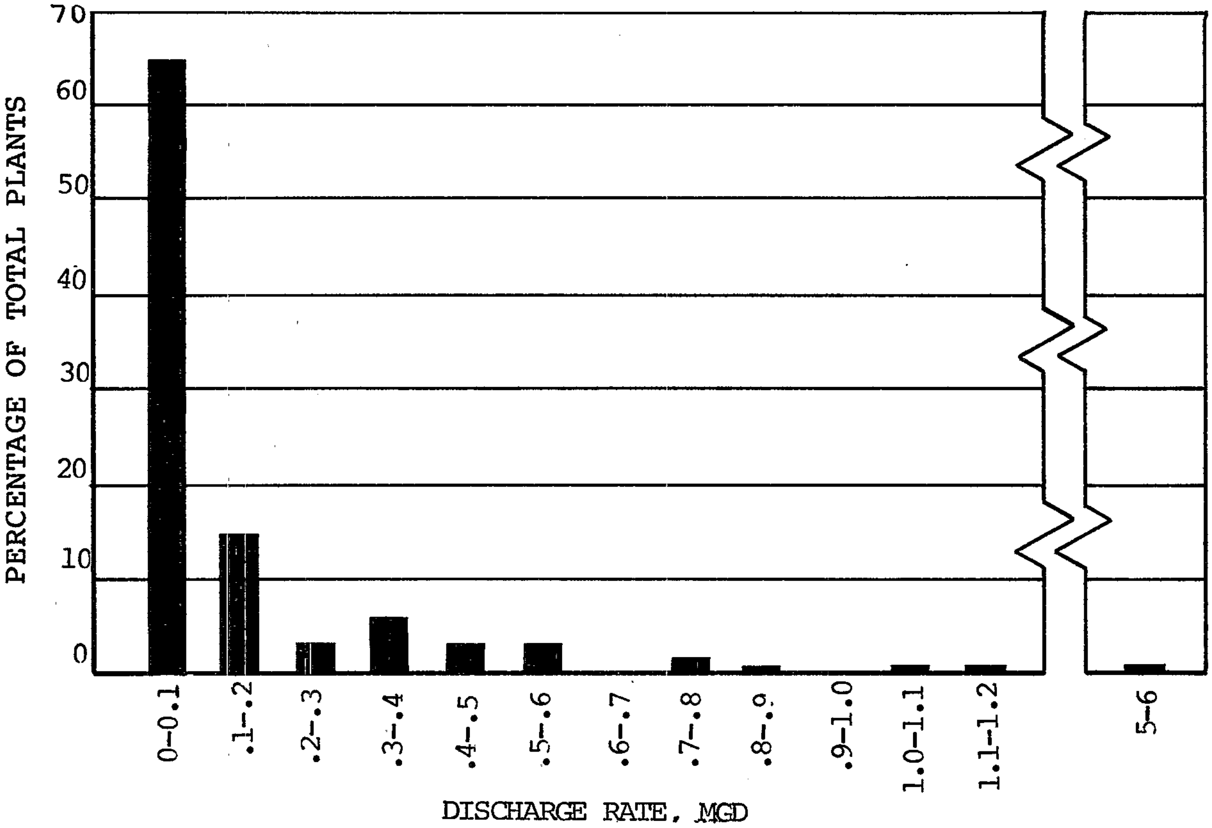


FIGURE 5-1a

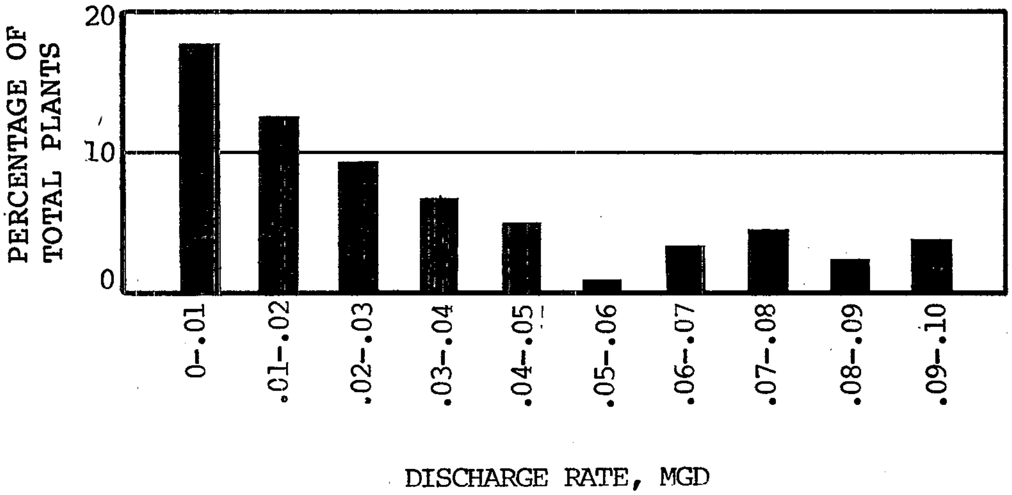


FIGURE 5-1b

FIGURE 5-1

FLOW DISTRIBUTION WITHIN THE
METAL FINISHING CATEGORY

## WATER USAGE BY WASTE TYPE

Tables 5-4 through 5-9 present data on the contribution of the various types of waste streams toward the total flow of a plant. For each visited plant where flows of discrete types of waste streams could be measured, the tables present total wastewater flow, waste type stream flow and percentage contribution of the waste type stream flow.

Table 5-4 shows flow data for those visited plants which had common metals waste streams measured prior to mixing with other pretreated wastewaters. The average contribution of these streams to the total wastewater flow is 67.6% (range of 1.4-100%). All of the plants visited and sampled had a waste stream requiring common metals treatment.

Table 5-5 contains flow data for those plants with precious metals wastewater. Of the plants in the data set used for these tables, 6.3% of them had production processes which generated precious metals wastewater. The typical precious metals wastewater flow contribution is 20.1%.

Table 5-6 presents flow data for those plants with segregated complexed metals waste streams. Although additional plants have processes which generate complex metal wastes, their wastes are not segregated. The average contribution of the complexed metal streams at those plants listed in the table is 11.9%, and 13.9% of the plants in the data set used for these tables have complexed metal streams.

Table 5-7 presents the flow contribution of hexavalent chromium wastewater streams. Of the plants in the data set used for these tables, 24.1% have segregated hexavalent chromium waste streams. The average flow contribution of these waste streams to the total wastewater stream is 23.4%. Of the plants having hexavalent chromium streams, 100% segregate those streams for treatment.

Table 5-8 presents flow data on cyanide bearing waste streams. As shown on the table, at those plants with cyanide wastes, the average contribution of the cyanide bearing stream toward the total wastewater generated is 14.6% (range: 1.4-29.6%). Of the plants in the data set used for these tables, 13.9% have segregated cyanide bearing wastes.

Table 5-9 presents data for the flow of segregated oily wastewater. Segregated oily wastewater is defined as oil waste collected from machine sumps and process tanks that is kept segregated from other wastewaters until it has been treated by an oily waste removal system. The plants identified in Table 5-9 , which make up 12.9% of the plants in the data set used for these tables, are known to segregate their oily wastes. The average contribution of their oily wastes to this total wastewater flow is 6.4%, with a range of nearly zero to 31.7%.

## TABLE 5-4
## COMMON METALS STREAM CONTRIBUTION

| Plant ID | Common Metals Stream Flow (gpd) | Total Process Water Discharge (gpd) | Percent Of Total Flow |
|---|---|---|---|
| 1003 | 16,590 | 16,590 | 100.0 |
| 2032 | 56,987 | 77,995 | 73.1 |
| 2033 | 37,680 | 59,136 | 63.7 |
| 2062 | 18,000 | 50,400 | 35.7 |
| 4069 | 145,800 | 183,816 | 79.3 |
| 4071 | 93,600 | 194,320 | 48.2 |
| 6091 | 53,280 | 244,080 | 21.8 |
| 6110 | 304,800 | 304,800 | 100.0 |
| 6679 | 8,269 | 8,269 | 100.0 |
| 6960 | 24,280 | 42,780 | 56.8 |
| 7001 | 165,000 | 825,000 | 20.0 |
| 8006 | 3,200 | 3,200 | 100.0 |
| 8007 | 3,600 | 4,880 | 73.8 |
| 9052 | 272,400 | 272,400 | 100.0 |
| 11103 | 152,912 | 186,712 | 81.9 |
| 11108 | 83,536 | 83,536 | 100.0 |
| 12061 | 252,822 | 593,280 | 42.6 |
| 12065 | 50,400 | 723,432 | 7.0 |
| 12075 | 719,248 | 5,352,000 | 13.4 |
| 15608 | 80,827 | 95,634 | 84.5 |
| 17050 | 5,280 | 5,280 | 100.0 |
| 17061 | 255,672 | 292,080 | 87.5 |
| 18538 | 151,264 | 829,192 | 18.2 |
| 19068 | 6,421 | 8,117 | 79.1 |
| 20022 | 599,232 | 603,786 | 99.2 |
| 20083 | 65,067 | 89,840 | 72.4 |
| 21003 | 1,600 | 13,360 | 12.0 |
| 21066 | 55,600 | 82,576 | 67.3 |
| 25010 | 400 | 400 | 100.0 |
| 27046 | 46,080 | 50,400 | 91.4 |
| 30054 | 303 | 21,842 | 1.4 |
| 33028 | 1,320 | 1,320 | 100.0 |
| 36048 | 6,241 | 6,819 | 91.5 |
| 38052 | 5,000 | 14,750 | 33.9 |
| 40060 | 76,320 | 76,320 | 100.0 |
| 40063 | 9,080 | 103,522 | 8.8 |
| 41051 | 210,880 | 217,280 | 97.1 |
| 44062 | 54,800 | 74,320 | 73.7 |
| 46025 | 96 | 96 | 100.0 |

Average common metals stream contribution = 67.6%

## TABLE 5-5
## PRECIOUS METALS STREAM CONTRIBUTION

| Plant ID | Precious Metals Stream Flow (gpd) | Total Process Water Discharge (gpd) | Percent Of Total Flow |
|---|---|---|---|
| 02033 | 12,720 | 59,136 | 21.5 |
| 06090 | 2,400 | 171,600 | 2.8 |
| 21003 | 4,080 | 13,360 | 30.5 |
| 30054 | 5,406 | 21,908 | 24.7 |
| 36623 | 77,040 | 364,560 | 21.1 |

Average precious metals stream contribution = 20.1%

## TABLE 5-6
## COMPLEXED METALS STREAM CONTRIBUTION

| Plant ID | Complexed Metals Stream Flow (gpd) | Total Process Water Discharge (gpd) | Percent Of Total Flow |
|---|---|---|---|
| 02032 | 6,080 | 77,995 | 7.8 |
| 02033 | 7,667 | 59,136 | 13.0 |
| 04069 | 20,016 | 183,816 | 10.9 |
| 04071 | 100,720 | 194,320 | 51.8 |
| 06097 | 5,232 | 61,424 | 8.5 |
| 12065 | 17,280 | 723,432 | 2.4 |
| 15608 | 10,768 | 95,634 | 11.3 |
| 17061 | 10,320 | 292,080 | 3.5 |
| 20083 | 11,773 | 89,840 | 13.1 |
| 34051 | 960 | 14,400 | 6.7 |
| 36048 | 131 | 6,819 | 1.9 |

Average complexed metals stream contribution = 11.9%

## TABLE 5-7
## HEXAVALENT CHROMIUM STREAM CONTRIBUTION

| Plant ID | Hexavalent Chromium Stream Flow (gpd) | Tptal Process Water Discharge (gpd) | Percent Of Total Flow |
|---|---|---|---|
| 06072 | 9,480 | 51,720 | 18.3 |
| 06091 | 106,560 | 244,080 | 43.7 |
| 06960 | 10,175 | 42,780 | 23.8 |
| 12075 | 147,480 | 5,384,072 | 2.7 |
| 18538 | 172,016 | 829,192 | 20.7 |
| 20082 | 91,609 | 129,859 | 70.5 |
| 20083 | 5,187 | 89,840 | 5.8 |
| 21066 | 14,528 | 82,576 | 17.6 |
| 30050 | 7,308 | 564,000 | 1.3 |
| 30054 | 1,680 | 21,908 | 7.7 |
| 30074 | 25,920 | 43,392 | 47.2 |
| 31050 | 600 | 4,600 | 13.0 |
| 33024 | 2,952 | 34,896 | 8.5 |
| 35061 | 70,000 | 785,000 | 8.9 |
| 38052 | 9,750 | 14,750 | 66.1 |
| 40061 | 48,600 | 59,400 | 81.8 |
| 40062 | 2,160 | 571,680 | 0.4 |
| 44050 | 11,040 | 113,760 | 9.7 |
| 44062 | 15,752 | 74,320 | 21.2 |

Average hexavalent chromium stream contribution = 23.4%

## TABLE 5-8
## CYANIDE BEARING STREAM CONTRIBUTION

| Plant ID | Cyanide Bearing Stream Flow (gpd) | Total Process Water Discharge (gpd) | Percent Of Total Flow |
|---|---|---|---|
| 02033 | 17,496 | 59,136 | 29.6 |
| 06072 | 3,280 | 51,720 | 6.3 |
| 06090 | 2,400 | 171,600 | 1.4 |
| 11103 | 21,704 | 186,712 | 11.6 |
| 19050 | 3,480 | 25,264 | 13.8 |
| 20083 | 3,960 | 89,840 | 4.4 |
| 21066 | 12,448 | 82,576 | 15.1 |
| 30022 | 11,520 | 48,960 | 23.5 |
| 33024 | 5,256 | 26,688 | 15.1 |
| 35061 | 150,000 | 785,000 | 19.1 |
| 36623 | 77,040 | 364,560 | 21.1 |

Average cyanide stream contribution = 14.6%

## TABLE 5-9
## SEGREGATED OILY WASTEWATER CONTRIBUTION

| Plant ID | Segregated Oily Waste Discharge (gpd) | Total Plant Discharge (gpd) | Percent Of Total Flow |
|---|---|---|---|
| 01058 | 125,000 | 2,590,000 | 4.83 |
| 03043 | 2,081 | 118,650 | 1.75 |
| 04892 | 33,600 | 285,200 | 11.8 |
| 06019 | 30,800 | 1,810,000 | 1.70 |
| 11477 | 21,600 | 1,090,000 | 1.98 |
| 12078 | 15,300 | 1,064,900 | 1.44 |
| 13042 | 60,000 | 223,400 | 26.9 |
| 13324 | 14,400 | 144,900 | 9.94 |
| 14062 | 14,362 | 609,700 | 2.36 |
| 15010 | 13,000 | 1,100,000 | 1.18 |
| 15055 | 30,000 | 600,000 | 5.00 |
| 19462 | 2,200 | 250,000 | 0.88 |
| 20005 | 174,990 | 1,500,000 | 11.7 |
| 20103 | 11,100 | 150,000 | 7.42 |
| 23041 | 3,090 | 900,000 | 0.34 |
| 28699 | 190,280 | 600,000 | 31.7 |
| 30012 | 4,845 | 312,440 | 1.55 |
| 30166 | 249 | 11,250 | 2.21 |
| 30516 | 31,700 | 20,000,000 | 0.16 |
| 30698 | 2,500 | 20,000 | 12.5 |
| 31031 | 286 | 2,160,000 | 0.01 |
| 33050 | 2,558 | 320,000 | 0.80 |
| 33692 | 68,000 | 500,000 | 13.6 |
| 38040 | 693 | 117,000 | 0.59 |

Average segregated oily waste contribution = 6.4%

## WASTE CHARACTERISTICS FROM METAL FINISHING UNIT OPERATIONS

The waste constituents most commonly found in wastewaters generated by the forty-six metal finishing unit operations are described in the following subsections. Information from 1,048 data collection portfolios on the presence of priority pollutants in metal finishing wastewaters are summarized in Tables 5-10 and 5-11. Table 5-10 shows the number and type of responses given for each of the 129 pollutant parameters. (KTBP is known to be present, BTBP is believed to be present, BTBA is believed to be absent, and KTBA is known to be absent.) Table 5-11 indicates reported sources of the pollutants known to be present. Table 5-12 summarizes the waste characteristic distribution for the 46 unit operations. Operations which have been designated as generally zero dischargers are omitted from this discussion. Included in each of the unit operation presentations is a listing of each waste type to which the particular operation's wastewater could contribute.

### ELECTROPLATING

Electroplating baths contain metal salts, acids, alkalies, and various bath control compounds. All of these materials contribute to the wastewater stream either through part dragout, batch dump, or floor spill. Electroplating baths can contain copper, nickel, silver, gold, zinc, cadmium, palladium, platinum, chromium, lead, iron and tin. In addition to these metals, common cationic components of plating baths are ammonia, sodium and potassium. Anions likely to be present are chromate, borate, cyanide, carbonate, fluoride, fluoborate, phosphates, chloride, nitrate, sulfate, sulfide, sulfamate and tartrate.

Many plating solutions contain metallic, metallo-organic and organic additives to induce grain refining, leveling of the plating surface and deposit brightening. Arsenic, cobalt, molybdenum and selenium are used in this way, as are saccharin and various aldehydes. These additives are generally present in a bath at concentrations of less than one percent by volume or weight. Table 5-13 presents a selection of plating baths and their major constituents. The processes covered under the electroplating unit operation and the type of wastewater are listed below:

Common metals - Electroplating of aluminum, brass, bronze, cadmium, acid copper, fluoborate copper and copper pyrophosphate, iron, lead, nickel, solder, tin and zinc.

Precious metals - Electroplating of gold, silver, rhodium, palladium, platinum, indium, ruthenium, iridium, and osmium.

Cyanide wastes - Cyanide plating of copper, cadmium, zinc, brass, gold, silver, indium, and irridium.

Hexavalent chromium wastes - chromium plating.

## Table 5-10

## POLLUTANT PARAMETER QUESTIONNAIRE DCP RESPONSES

| Pollutant Parameter | | Number of Responses | KTBP | BTBP | BTBA | KTBA |
|---|---|---|---|---|---|---|
| 001 | Acenaphthene | 1011 | 0 | 2 | 762 | 221 |
| 002 | Acrolein | 1011 | 0 | 1 | 760 | 224 |
| 003 | Acrylonitrile | 1013 | 2 | 12 | 755 | 218 |
| 004 | Benzene | 1014 | 9 | 16 | 734 | 229 |
| 005 | Benzidine | 1011 | 1 | 5 | 746 | 233 |
| 006 | Carbon tetrachloride (tetrachloromethane) | 1012 | 3 | 10 | 737 | 236 |
| 007 | Chlorobenzene | 1010 | 1 | 8 | 751 | 224 |
| 008 | 1,2,4-trichlorobenzene | 1010 | 0 | 9 | 749 | 226 |
| 009 | Hexachlorobenzene | 1010 | 0 | 4 | 756 | 224 |
| 010 | 1,2-dichloroethane | 1011 | 2 | 11 | 752 | 220 |
| 011 | 1,1,1-trichloroethane | 1020 | 53 | 77 | 666 | 198 |
| 012 | Hexachloroethane | 1010 | 0 | 7 | 752 | 225 |
| 013 | 1,1-dichloroethane | 1010 | 1 | 8 | 758 | 217 |
| 014 | 1,1,2-trichloroethane | 1010 | 5 | 17 | 742 | 220 |
| 015 | 1,1,2,2-tetrachloroethane | 1010 | 0 | 12 | 746 | 226 |
| 016 | Chloroethane | 1010 | 9 | 14 | 744 | 217 |
| 017 | Bis(chloromethyl) ether | 1010 | 0 | 1 | 756 | 227 |
| 018 | Bis(2-chloroethyl) ether | 1009 | 0 | 1 | 755 | 227 |
| 019 | 2-chloroethyl vinyl ether (mixed) | 1009 | 1 | 1 | 756 | 225 |
| 020 | 2-chloronaphthalene | 1009 | 0 | 3 | 758 | 222 |
| 021 | 2,4,6-trichlorophenol | 1008 | 1 | 4 | 754 | 222 |
| 022 | Parachlorometa cresol | 1009 | 0 | 4 | 756 | 223 |
| 023 | Chloroform (trichloromethane) | 1009 | 7 | 13 | 743 | 221 |

Table 5-10 (Continued)

| Pollutant Parameter | | Number of Responses | KTBP | BTBP | BTBA | KTBA |
|---|---|---|---|---|---|---|
| 024 | 2-chlorophenol | 1008 | 1 | 3 | 760 | 218 |
| 025 | 1,2-dichlorobenzene | 1009 | 1 | 2 | 756 | 223 |
| 026 | 1,3-dichlorobenzene | 1009 | 0 | 2 | 758 | 223 |
| 027 | 1,4-dichlorobenzene | 1009 | 1 | 3 | 756 | 223 |
| 028 | 3,3-dichlorobenzidine | 1009 | 0 | 1 | 755 | 227 |
| 029 | 1,1-dichloroethylene | 1010 | 2 | 2 | 763 | 217 |
| 030 | 1,2-trans-dichloroethylene | 1010 | 1 | 2 | 760 | 221 |
| 031 | 2,4-dichlorophenol | 1009 | 0 | 4 | 757 | 222 |
| 032 | 1,2-dichloropropane | 1010 | 1 | 1 | 756 | 226 |
| 033 | 1,2-dichloropropylene (1,3-dichloropropene) | 1010 | 0 | 1 | 760 | 223 |
| 034 | 2,4-dimethylphenol | 1008 | 0 | 3 | 757 | 222 |
| 035 | 2,4-dinitrotoluene | 1008 | 0 | 1 | 759 | 222 |
| 036 | 2,6-dinitrotoluene | 1008 | 0 | 1 | 759 | 222 |
| 037 | 1,2-diphenylhydrazine | 1008 | 1 | 1 | 758 | 222 |
| 038 | Ethylbenzene | 1010 | 3 | 5 | 758 | 218 |
| 039 | Fluoranthene | 1006 | 0 | 2 | 758 | 221 |
| 040 | 4-chlorophenyl phenyl ether | 1007 | 0 | 2 | 755 | 225 |
| 041 | 4-bromophenyl phenyl ether | 1010 | 0 | 2 | 755 | 225 |
| 042 | Bis(2-chloroisopropyl) ether | 1009 | 0 | 2 | 756 | 225 |
| 043 | Bis(2-chloroethoxy) methane | 1010 | 0 | 4 | 755 | 225 |
| 044 | Methylene chloride (dichloromethane) | 1015 | 38 | 49 | 695 | 206 |
| 045 | Methyl chloride (chloromethane) | 1011 | 5 | 11 | 747 | 223 |
| 046 | Methyl bromide (bromomethane) | 1012 | 2 | 1 | 759 | 224 |

## Table 5-10 (Continued)

| Pollutant Parameter | | Number of Responses | KTBP | BTBP | BTBA | KTBA |
|---|---|---|---|---|---|---|
| 047 | Bromoform (tribromomethane) | 1014 | 0 | 2 | 759 | 227 |
| 048 | Dichlorobromomethane | 1014 | 1 | 2 | 758 | 227 |
| 050 | Dichlorodifluoromethane | 1014 | 4 | 15 | 748 | 221 |
| 051 | Chlorodibromomethane | 1014 | 1 | 1 | 759 | 227 |
| 052 | Hexachlorobutadiene | 1014 | 0 | 2 | 761 | 225 |
| 053 | Hexachlorocyclopentadiene | 1012 | 0 | 1 | 760 | 225 |
| 054 | Isophorone | 1012 | 1 | 9 | 755 | 221 |
| 055 | Naphthalene | 1015 | 2 | 14 | 748 | 225 |
| 056 | Nitrobenzene | 1015 | 0 | 9 | 755 | 225 |
| 057 | 2-nitrophenol | 1013 | 0 | 2 | 758 | 227 |
| 058 | 4-nitrophenol | 1013 | 0 | 2 | 758 | 227 |
| 059 | 2,4-dinitrophenol | 1013 | 0 | 2 | 757 | 228 |
| 060 | 4,6-dinitro-o-cresol | 1012 | 0 | 1 | 759 | 226 |
| 061 | N-nitrosodimethylamine | 1012 | 0 | 1 | 762 | 224 |
| 062 | N-nitrosodiphenylamine | 1014 | 0 | 1 | 762 | 224 |
| 063 | N-nitrosodi-n-propylamine | 1014 | 0 | 2 | 759 | 227 |
| 064 | Pentachlorophenol | 1012 | 0 | 8 | 754 | 224 |
| 065 | Phenol | 1020 | 71 | 40 | 677 | 206 |
| 066 | Bis(2-ethylhexyl) phthalate | 1014 | 2 | 4 | 760 | 222 |
| 067 | Butyl benzyl phthalate | 1014 | 2 | 4 | 759 | 223 |
| 068 | Di-n-butyl phthalate | 1014 | 2 | 4 | 758 | 223 |
| 069 | Di-n-octyl phthalate | 1013 | 1 | 4 | 758 | 224 |
| 070 | Diethyl phthalate | 1012 | 2 | 2 | 759 | 223 |

## Table 5-10 (Continued)

| Pollutant Parameter | | Number of Responses | KTBP | BTBP | BTBA | KTBA |
|---|---|---|---|---|---|---|
| 071 | Dimethyl phthalate | 1014 | 2 | 2 | 759 | 225 |
| 072 | 1,2-benzanthracene (benzo(a)anthracene) | 1014 | 1 | 2 | 759 | 226 |
| 073 | Benzo(a)pyrene (3,4-benzo-pyrene) | 1014 | 0 | 2 | 757 | 229 |
| 074 | 3,4-benzofluoranthene (benzo(b)fluoranthene) | 1014 | 0 | 1 | 759 | 228 |
| 075 | 11,12-benzofluoranthene (benzo(k)fluoranthene) | 1014 | 0 | 1 | 759 | 228 |
| 076 | Chrysene | 1014 | 0 | 1 | 760 | 227 |
| 077 | Acenaphthylene | 1014 | 0 | 1 | 759 | 228 |
| 078 | Anthracene | 1012 | 0 | 2 | 756 | 227 |
| 079 | 1,12-benzoperylene (benzo(ghi)-perylene) | 1012 | 0 | 1 | 759 | 226 |
| 080 | Fluorene | 1011 | 1 | 1 | 760 | 223 |
| 081 | Phenanthrene | 1010 | 0 | 1 | 759 | 224 |
| 082 | 1,2,5,6-dibenzanthracene (dibenzo(a,h)anthracene) | 1009 | 1 | 1 | 755 | 225 |
| 083 | Indeno(1,2,3-cd) pyrene (2,3-o-phenylene pyrene) | 1009 | 0 | 1 | 755 | 227 |
| 084 | Pyrene | 1009 | 1 | 3 | 756 | 223 |
| 085 | Tetrachloroethylene | 1008 | 8 | 19 | 740 | 215 |
| 086 | Toluene | 1016 | 37 | 69 | 694 | 190 |
| 087 | Trichloroethylene | 1011 | 27 | 71 | 683 | 204 |
| 088 | Vinyl chloride (chloroethylene) | 1009 | 4 | 8 | 757 | 214 |
| 089 | Aldrin | 1010 | 0 | 3 | 752 | 229 |

Table 5-10 (Continued)

| Pollutant Parameter | Number of Responses | KTBP | BTBP | BTBA | KTBA |
|---|---|---|---|---|---|
| 090 Dieldrin | 1008 | 0 | 2 | 753 | 227 |
| 091 Chlordane (technical mixture and metabolites) | 1008 | 0 | 2 | 756 | 224 |
| 092 4,4-DDT | 1008 | 0 | 2 | 749 | 231 |
| 093 4,4-DDE (p,p-DDX) | 1008 | 0 | 3 | 751 | 228 |
| 094 4,4-DDD (p,p-TDE) | 1008 | 0 | 3 | 755 | 224 |
| 095 Alpha-endosulfan | 1008 | 0 | 2 | 756 | 224 |
| 096 Beta-endosulfan | 1008 | 0 | 2 | 756 | 224 |
| 097 Endosulfan sulfate | 1008 | 0 | 2 | 758 | 222 |
| 098 Endrin | 1008 | 0 | 2 | 751 | 229 |
| 099 Endrin aldehyde | 1008 | 0 | 2 | 756 | 224 |
| 100 Heptachlor | 1008 | 0 | 3 | 754 | 225 |
| 101 Heptachlor epoxide (BHC-hexachlorocyclohexane) | 1008 | 0 | 2 | 755 | 225 |
| 102 Alpha-BHC | 1008 | 0 | 2 | 753 | 227 |
| 103 Beta-BHC | 1008 | 0 | 2 | 753 | 227 |
| 104 Gamma-BHC | 1008 | 0 | 2 | 750 | 230 |
| 105 Delta-BHC | 1009 | 0 | 4 | 750 | 229 |
| 106 PCB-1242 (Aroclor 1242) | 1010 | 6 | 10 | 731 | 237 |
| 107 PCB-1254 (Aroclor 1254) | 1009 | 3 | 6 | 736 | 238 |
| 108 PCB-1221 (Aroclor 1221) | 1009 | 1 | 4 | 744 | 234 |
| 109 PCB-1232 (Aroclor 1232) | 1009 | 2 | 4 | 745 | 232 |
| 110 PCB-1248 (Aroclor 1248) | 1008 | 2 | 5 | 741 | 234 |
| 111 PCB-1260 (Aroclor 1260) | 1006 | 3 | 6 | 733 | 238 |

TABLE 5-10 (Continued)

| Pollutant Parameter | | Number of Responses | KTBP | BTBP | BTBA | KTBA |
|---|---|---|---|---|---|---|
| 112 | PCB-1016 (Aroclor 1016) | 990 | 1 | 5 | 729 | 231 |
| 113 | Toxaphene | 990 | 0 | 3 | 737 | 226 |
| 114 | Antimony | 990 | 33 | 37 | 696 | 200 |
| 115 | Arsenic | 996 | 39 | 18 | 689 | 226 |
| 116 | Asbestos | 987 | 10 | 22 | 713 | 218 |
| 117 | Beryllium | 986 | 33 | 37 | 685 | 208 |
| 118 | Cadmium | 1012 | 272 | 56 | 479 | 179 |
| 119 | Chromium | 1048 | 633 | 96 | 219 | 74 |
| 120 | Copper | 1038 | 577 | 105 | 248 | 82 |
| 121 | Cyanide | 1032 | 457 | 86 | 330 | 133 |
| 122 | Lead | 1017 | 280 | 84 | 477 | 150 |
| 123 | Mercury | 1002 | 88 | 25 | 630 | 233 |
| 124 | Nickel | 1039 | 531 | 110 | 276 | 98 |
| 125 | Selenium | 990 | 37 | 28 | 686 | 215 |
| 126 | Silver | 1007 | 185 | 54 | 562 | 182 |
| 127 | Thallium | 990 | 25 | 13 | 702 | 227 |
| 128 | Zinc | 1032 | 520 | 74 | 304 | 112 |
| 129 | 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) | 990 | 0 | 6 | 733 | 224 |

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KTBP - Known to be present
BTBP - Believed to be present
KTBA - Known to be absent
BTBA - Believed to be absent

## TABLE 5-11

## SOURCE IDENTIFICATION FOR KTBP (KNOWN TO BE PRESENT) POLLUTANT PARAMETERS

| Pollutant Parameter | KTBP Responses | Sources of Pollutant Parameters |
|---|---|---|
| 003 Acrylonitrile | 2 | ABS components manufactured |
| 004 Benzene | 9 | Fuel component; solvent; raw material; contaminant in toluene; water supply |
| 005 Benzidine | 1 | Solvent and cleaner |
| 006 Carbon tetrachloride | 3 | Water supply |
| 007 Chlorobenzene | 1 | Spray booth wall coating |
| 010 1,2-Dichloroethane | 2 | Photoresist developer; water supply |
| 011 1,1,1-Trichloroethane | 53 | Degreaser; photoresist developer; cleaner; hand washing operations; plating; maintenance solvent; milling; water supply |
| 013 1,1-Dichloroethane | 1 | Plant lab facilities; cleaning |
| 014 1,1,2-Trichloroethane | 5 | Degreaser; cleaning; plant lab facilities |
| 016 Chloroethane | 9 | Raw material; degreaser; wash tanks; floor cleaner; solvent cleaning |
| 019 2-Chloroethyl vinyl ether | 1 | Water supply |
| 021 2,4,6-Trichlorophenol | 1 | Unknown (detected by sample analysis) |
| 023 Chloroform | 7 | Raw material; degreaser; nickel brightener constituent; water supply |
| 024 2-Chlorophenol | 1 | Water supply |
| 025 1,2-Dichlorobenzene | 1 | Gum solvent |
| 027 1,4-Dichlorobenzene | 1 | Unknown (detected by sample analysis) |
| 029 1,1-Dichloroethylene | 2 | Water supply |
| 030 1,2-trans-Dichloroethylene | 1 | Water supply |

TABLE 5-11 (Continued)

| Pollutant Parameter | | KTBP Responses | Sources of Pollutant Parameters |
|---|---|---|---|
| 032 | 1,2-Dichloropropane | 1 | Water supply |
| 037 | 1,2-Diphenylhydrazine | 1 | Coolant biocide |
| 038 | Ethylbenzene | 3 | Fuel constituent |
| 044 | Methylene chloride | 38 | Paint stripper; photoresist stripper; cleaner; plastic; injection molding and extrusion; etch resist stripper; solvent; painting; electroplating; rubber primer |
| 045 | Methyl chloride | 5 | Raw material; cleaner; paint stripper |
| 046 | Methyl bromide | 2 | Constituent of chrome plating bath |
| 048 | Dichlorobromomethane | 1 | Water supply |
| 050 | Dichlorodifluoromethane | 4 | Refrigerant; anodizing bath coolant; water supply |
| 051 | Chlorodibromomethane | 1 | Water supply |
| 054 | Isophorone | 1 | White paint |
| 055 | Naphthalene | 2 | Painting |
| 065 | Phenol | 71 | Lubricating oils; post metal finishing operations; paper and molding compounds; photoresist stripper coolant; creosote floor blocks; iron phosphatizing; etch resist stripper; adhesives; gasoline; paint stripper; painting; washers; hydraulic oils; wire insulation stripping; rinsing; plating; emulsion breaker; varnish; coolant biocide; spindle oil; DTE oil; spray paint; adhesives; electropainting; integrated circuit lab; paint; conformal coating; cast iron making (coke); paint gun cleaner; cleaners tin plating additive; phosphate esters; phenolic resins; water supply |

TABLE 5-11 (Continued)

| Pollutant Parameter | | KTBP Responses | Sources of Pollutant Parameters |
|---|---|---|---|
| 066 | Bis (2-ethylhexyl) phthalate | 2 | Sealants; paints; adhesives; water supply |
| 067 | Butylbenzyl phthalate | 2 | Sealants; paints; adhesives; water supply |
| 068 | Di-n-butyl phthalate | 2 | Sealants; paints; adhesives; water supply |
| 069 | Di-n-octyl phthalate | 1 | Sealants; paints; adhesives |
| 070 | Diethyl phthalate | 2 | Sealants; paints; adhesives; water supply |
| 071 | Dimethyl phthalate | 2 | Sealants; paints; adhesives; water supply |
| 072 | 1,2-Benzanthrancene | 1 | Water supply |
| 080 | Fluorene | 1 | Unknown (detected by sample analysis) |
| 082 | 1,2,5,6-Dibenzanthracene | 1 | Unknown (detected by sample analysis) |
| 084 | Pyrene | 1 | Unknown (detected by sample analysis) |
| 085 | Tetrachloroethylene | 8 | Degreaser; photoresist stripper; ceramic tinning; electroplating; cleaner; solvent recovery; water supply |
| 086 | Toluene | 37 | Painting; paint thinner; varnish thinner; paint booth cleanup; thinner for printed circuit protective coating; cleaning solvent; adhesive; water supply |
| 087 | Trichloroethylene | 27 | Degreaser; paint thinner; photoresist developer; electroplating operations; lab solvent; machine solvent; electrical contact cleaner; welding tip cleaner; water supply |
| 088 | Vinyl chloride | 4 | Plastic molding; sealers; adhesives; coating for manufactured parts; water supply |
| 106 | PCB-1242 | 6 | Lighting fixtures; power correction units; transformers; previous usage hydraulic fluid; water supply |

## TABLE 5-11 (Continued)

| Pollutant Parameter | | KTBP Responses | Sources of Pollutant Parameters |
|---|---|---|---|
| 107 | PCB-1254 | 3 | Process capacitors; previous usage; water supply |
| 108 | PCB-1221 | 1 | Process capacitors; water supply |
| 109 | PCB-1232 | 2 | Lighting fixtures; power correction units; transformers; process capacitors; water supply |
| 110 | PCB-1248 | 2 | Lighting fixtures; power correction units; transformers; process capacitors; water supply |
| 111 | PCB-1260 | 3 | Process capacitors; previous usage; water supply |
| 112 | PCB-1016 | 1 | Water supply |
| 116 | Asbestos compounds | 10 | Aluminum dip braze; pipe covering; brakeband operations; furnace seals; sealer compound; plaster molds; nickel electroplating bath filter; water supply |

## TABLE 5-12
## WASTE CHARACTERISTIC DISTRIBUTION

| WASTE CHARACTERISTICS / UNIT OPERATION | INORGANICS | | | | ORGANICS | | | |
|---|---|---|---|---|---|---|---|---|
| | Common Metals | Precious Metals | Complexed Metals | Chromium (Hexavalent) | Cyanide | Oils | Toxic Organics | Zero Discharge |
| 1. Electroplating | x | x | | x | x | | | |
| 2. Electroless Plating | x | x | x | x | | | | |
| 3. Anodizing | x | | | x | | | | |
| 4. Conversion Coating | x | x | | x | x | | | |
| 5. Etching (Chem. Milling) | x | x | x | x | x | | | |
| 6. Cleaning | x | x | x | x | x | x | x | |
| 7. Machining | x | | | | | x | | |
| 8. Grinding | x | | | | | x | | |
| 9. Polishing | x | x | | | | x | | |
| 10. Tumbling | x | | | x | x | x | | |
| 11. Burnishing | x | x | | | x | x | | |
| 12. Impact Deformation | x | | | | | x | | |
| 13. Pressure Deformation | x | | | | | x | | |
| 14. Shearing | x | | | | | x | | |
| 15. Heat Treating | x | | | | x | x | | |
| 16. Thermal Cutting | x | | | | | | | |
| 17. Welding | x | | | | | | | |
| 18. Brazing | x | | | | | | | |
| 19. Soldering | x | | x | | | | | |
| 20. Flame Spraying | x | | | | | | | |
| 21. Sand Blasting | x | | | | | | | |
| 22. Other Abr. Jet Machining | x | | | | | x | | |
| 23. Elec. Discharge Mach. | x | | | | | x | | |
| 24. Electrochemical Mach. | x | | | | x | | x | |
| 25. Electron Beam Mach. | | | | | | | | x |
| 26. Laser Beam Mach. | | | | | | | | x |
| 27. Plasma Arc Mach. | | | | | | | | x |
| 28. Ultrasonic Machining | | | | | | | | x |

## TABLE 5-12 Cont.
## WASTE CHARACTERISTIC DISTRIBUTION

| WASTE CHARACTERISTICS / UNIT OPERATION | INORGANICS | | | | ORGANICS | | | |
|---|---|---|---|---|---|---|---|---|
| | Common Metals | Precious Metals | Complexed Metals | Chromium (Hexavalent) | Cyanide | Oils | Toxic Organics | Zero Discharge |
| 29. Sintering | | | | | | | | x |
| 30. Laminating | x | | | | | | | |
| 31. Hot Dip Coating | x | | | | | | | |
| 32. Sputtering | | | | | | | | x |
| 33. Vapor Plating | | | | | | | | x |
| 34. Thermal Infustion | | | | | | | | x |
| 35. Salt Bath Descaling | x | | | | | x | | |
| 36. Solvent Degreasing | x | | | | | x | x | |
| 37. Paint Stripping | x | | | | | x | x | |
| 38. Painting | x | | | | | | x | |
| 39. Electrostatic Painting | x | | | x | | | x | |
| 40. Electroplating | x | | | | | | x | |
| 41. Vacuum Metalizing | | | | | | | | x |
| 42. Assembly | x | | | | | x | x | |
| 43. Calibration | | | | | | | | x |
| 44. Testing | | | | | | x | | |
| 45. Mechanical Plating | x | | | x | | | | |
| 46. Printed Circuit Board Manufacturing | x | | x | | | | x | |

## TABLE 5-13
## CONSTITUENTS OF PLATING BATHS

| Electroplating Bath | Composition |
|---|---|
| Brass & Bronze: | Copper cyanide<br>Zinc cyanide<br>Sodium cyanide<br>Sodium carbonate<br>Ammonia<br>Rochelle salt |
| Cadmium Cyanide: | Cadmium cyanide<br>Cadmium oxide<br>Sodium cyanide<br>Sodium hydroxide |
| Cadmium Fluoborate: | Cadmium fluoborate<br>Fluoboric acid<br>Boric acid<br>Ammonium fluoborate<br>Licorice |
| Copper Cyanide: | Copper cyanide<br>Sodium cyanide<br>Sodium carbonate<br>Sodium hydroxide<br>Rochelle salt |
| Copper Fluoborate: | Copper fluoborate<br>Fluoboric acid |
| Acid Copper Sulfate: | Copper sulfate<br>Sulfuric acid |
| Copper Pyrophosphate: | Copper pyrophosphate<br>Potassium hydroxide<br>Ammonia |
| Fluoride Modified Copper Cyanide: | Copper cyanide<br>Potassium cyanide<br>Potassium fluoride |
| Chromium: | Chromic acid<br>Sulfuric acid |
| Chromium with Fluoride Catalyst: | Chromic acid<br>Sulfate<br>Fluoride |
| Gold Cyanide: | Metallic gold<br>Potassium cyanide<br>Sodium phosphate |

## TABLE 5-13 (Con't)
## CONSTITUENTS OF PLATING BATHS

| Electroplating Bath | Composition |
|---|---|
| Iron: | Ferrous sulfate<br>Ferrous chloride<br>Ferrous fluoborate<br>Calcium chloride<br>Ammonium chloride<br>Sodium chloride<br>Boric acid |
| Lead Fluoborate: | Lead fluoborate<br>Fluoboric acid<br>Boric acid<br>Gelatin or glue<br>Hydroquinone |
| Lead-Tin: | Lead fluoborate<br>Tin fluoborate<br>Boric acid<br>Fluoboric acid<br>Glue<br>Hydroquinone |
| Nickel (Watts): | Nickel sulfate<br>Nickel chloride<br>Nickel fluoborate<br>Boric acid<br>Nickel sulfate<br>Nickel chloride<br>Nickel sulfamate<br>Boric acid<br>Phosphoric acid<br>Phosphorous acid<br>"Stress-reducing agents" |
| Nickel-Acid Fluoride: | Hydrofluoric acid<br>Nickel carbonate<br>Citric acid<br>Sodium lauryl sulfate (wetting agent) |
| Black Nickel: | Nickel ammonium sulfate<br>Nickel sulfate<br>Zinc sulfate<br>Ammonium sulfate<br>Sodium thiocyanate |

## TABLE 5-13 (Con't)
## CONSTITUENTS OF PLATING BATHS

| Electroplating Bath | Composition |
|---|---|
| Silver: | Silver cyanide |
| | Potassium cyanide or Sodium cyanide |
| | Potassium carbonate or Sodium carbonate |
| | Potassium hydroxide |
| | Potassium nitrate |
| | Carbon disulfide |
| Acid Tin: | Tin fluoborate |
| | Fluoboric acid |
| | Boric acid |
| | Stannous sulfate |
| | Sulfuric acid |
| | Cresol sulfonic acid |
| | Beta naphthol |
| | Gelatin |
| Stannate Tin: | Sodium stannate |
| | Sodium hydroxide |
| | Sodium acetate |
| | Hydrogen peroxide |
| Tin-Copper Alloy: | Copper cyanide |
| | Potassium stannate |
| | Potassium cyanide |
| | Potassium hydroxide |
| | Rochelle salt |
| Tin-Nickel Alloy: | Stannous chloride |
| | Nickel chloride |
| | Ammonium fluoride |
| | Ammonium bifluoride |
| | Sodium fluoride |
| | Hydrochloric acid |
| Tin-Zinc Alloy: | Potassium stannate |
| | Zinc cyanide |
| | Potassium cyanide |
| | Potassium hydroxide |
| Acid Zinc: | Zinc sulfate |
| | Ammonium chloride |
| | Aluminum sulfate or Sodium acetate |
| | Glucose or Licorice |
| Zinc Cyanide: | Zinc oxide |
| | Sodium cyanide |
| | Sodium hydroxide |
| | Zinc cyanide |

## ELECTROLESS PLATING

Electroless plating (autocatalytic) is most often used on printed circuit boards, as a base plate for plating on plastics, and as a protective coating on metal parts. Copper and nickel are the metals most often plated autocatalytically, although iron, cobalt, gold, palladium, and arsenic can also be plated in this manner. The components of several electroless plating baths are listed in Table 5-14. The principle components are the metal being deposited, a reducing agent such as sodium hypophosphite or formaldehyde, and various complexing (or chelating) agents such as Rochelle salt, EDTA, or sodium citrate. Bath constituents enter the waste stream by way of dragout or batch dumping of the process bath.

Immersion plating, which is categorized with electroless plating, generates waste by basis material dissolution and process solution dragout. Table 5-15 lists the different immersion plating solutions as well as the base material upon which each can be deposited. Immersion plating baths are usually simple formulations of metal salts, alkalies and complexing agents. The complexing agents are typically cyanide or ammonia and are used to raise the deposition potential of the metal. Because of the displacement action involved in the immersion plating operation, more basis material ends up in the waste stream than the metal being deposited. Electroless plating wastewaters are contributed to the discrete process wastes by the following operations:

Precious metals - Electroless gold, electroless silver, electroless palladium, immersion gold, immersion palladium, immersion platinum, immersion rhodium, immersion silver.

Complexed metals - All electroless plating operations, all immersion plating operations.

Cyanide - Electroless gold, electroless arsenic, electroless silver, immersion brass, immersion silver, immersion tin.

## ANODIZING

The wastewaters generated by anodizing contain the basis material being anodized (aluminum or magnesium) as well as the constituents of the processing baths. Anodizing is done using solutions of either chromic or sulfuric acid. In addition, it is common to dye or color anodized coatings. A number of these dyes contain chromium (which will be found in wastewaters when the dyes are used) and other metals. Nickel acetate is widely used to seal anodic coatings and is therefore another potential pollutant associated with anodizing. Other complexes and metals originating from dyes, coloring solutions and sealers could possibly be found in anodizing wastewaters.

## TABLE 5-14
## CONSTITUENTS OF ELECTROLESS PLATING BATHS

| Process | Composition |
|---|---|
| Electroless Nickel: | Nickel chloride |
| | Sodium glycollate |
| | Sodium hypophosphite |
| | or |
| | Nickel carbonate |
| | Hydrofluoric acid |
| | Citric acid |
| | Ammonium acid fluoride |
| | Sodium hypophosphate |
| | Ammonium hydroxide |
| Electroless Copper: | Copper nitrate |
| | Sodium bicarbonate |
| | Rochelle salt |
| | Sodium hydroxide |
| | Formaldehyde |
| | or |
| | Copper sulfate |
| | Sodium carbonate |
| | Rochelle salt |
| | Versene-T |
| | Sodium hydroxide |
| | Formaldehyde |
| Electroless Cobalt-Nickel: | Cobalt chloride |
| | Nickel chloride |
| | Rochelle salt |
| | Ammonium chloride |
| | Sodium hypophosphite |
| Electroless Gold: | Potassium gold cyanide |
| | Ammonium chloride |
| | Sodium citrate |
| | Sodium hypophosphite |
| Electroless Gold over Cu, Ni, Kovar: | Potassium gold cyanide |
| | Citric acid |
| | Monopotassium acid phthalate |
| | Tungstic acid |
| | Sodium hydroxide |
| | N,N diethylglycine (Na salt) |

TABLE 5-14 (CONTINUED)

| Process | Composition |
|---|---|
| Electroless Iron: | Ferrous sulfate<br>Rochelle salt<br>Sodium hypophosphite |
| Electroless Palladium: | Tetramine palladium chloride<br>Disodium EDTA<br>Ammonium hydroxide<br>Hydrazine |
| Electroless Arsenic: | Zinc sulfate<br>Arsenic trioxide<br>Sodium citrate<br>Sodium cyanide<br>Sodium hydroxide<br>Ammonium hydroxide<br>Sodium hypophosphite |
| Electroless Chromium (acidic): | Chromic bromide<br>Chromic chloride<br>Potassium oxalate<br>Sodium acetate<br>Sodium hypophosphite |
| Electroless Chromium (alkaline): | Chromic bromide<br>Chromic iodide<br>Sodium oxalate<br>Sodium citrate<br>Sodium hypophosphite |
| Electroless Cobalt: | Cobalt chloride<br>Sodium citrate<br>Ammonium chloride<br>Sodium hypophosphite |
| Electroless Silver: | Silver cyanide<br>Sodium cyanide<br>Sodium hydroxide<br>Dimethylamine borane<br>Thiourea |

## TABLE 5-15
## CONSTITUENTS OF IMMERSION PLATING BATHS

| Process | Composition |
|---|---|
| Immersion Plating - | |
| Copper on Steel: | Copper sulfate<br>Sulfuric acid |
| Copper on Zinc: | Copper sulfate<br>Tartaric acid<br>Ammonia |
| Gold on Copper Alloys: | Potassium gold cyanide<br>Sodium cyanide<br>Sodium carbonate |
| Gold on Iron & Steel: | Denatured alcohol<br>Gold chloride |
| Lead on Copper Alloys and on Zinc: | Lead monoxide<br>Sodium cyanide<br>Sodium hydroxide |
| Lead on Steel: | Lead nitrate<br>Sodium cyanide<br>Sodium hydroxide |
| Nickel on Aluminum: | Nickel sulfate<br>Ammonium chloride |
| Nickel on Copper Alloys: | Nickel sulfate<br>Nickel ammonium sulfate<br>Sodium thiosulfate |
| Nickel on Steel: | Nickel chloride<br>Boric acid |
| Nickel on Zinc: | Nickel sulfate<br>Sodium chloride<br>Sodium carbonate |
| Palladium on Copper Alloys: | Palladium chloride<br>Hydrochloric acid<br>Ammonia (sealant) |
| Platinum on Copper Alloys: | Platinum chloride<br>Hydrochloric acid |
| Rhodium on Copper Alloys: | Rhodium chloride<br>Hydrochloric acid |

TABLE 5-15 (Continued)

| Process | Composition |
|---|---|
| Immersion Plating - | |
| Arsenic on Aluminum: | White aresenic<br>Sodium carbonate |
| Arsenic on Copper Alloys: | White arsenic<br>Ferric chloride<br>Muriatic acid |
| Arsenic on Steel: | White arsenic<br>Muriatic acid |
| Brass on Aluminum: | Zinc oxide<br>Sodium hydroxide<br>Copper cyanide<br>Sodium cyanide<br>Lead carbonate |
| Brass on Steel: | Stannous sulfate<br>Copper sulfate<br>Sulfuric acid |
| Cadmium on Aluminum: | Cadmium sulfate<br>Hydrofluoric acid |
| Cadmium on Copper Alloys: | Cadmium oxide<br>Sodium cyanide |
| Cadmium on Steel: | Cadmium oxide<br>Sodium hydroxide |
| Copper on Aluminum: | Copper sulfate<br>Ammonia<br>Potassium cyanide |
| | Copper sulfate<br>Hydrofluoric acid |
| | Copper sulfate<br>Ethylene diamine |
| Ruthenium on Copper Alloys: | Ruthenium chloride<br>Hydrochloric acid |
| Silver on Copper Alloys: | Silver cyanide<br>Sodium cyanide |
| | Silver nitrate<br>Ammonia<br>Sodium thiosulfate |

TABLE 5-15 (Continued)

| Process | | Composition |
|---|---|---|
| Immersion Plating - | | |
| | Silver on Zinc: | Silver cyanide<br>Potassium |
| | Tin on Aluminum: | Sodium stannate |
| | Tin on Copper Alloys: | Tin chloride<br>Sodium cyanide<br>Sodium hydroxide |
| | Tin on Steel: | Stannous sulfate<br>Sulfuric acid<br>Cream of tartar<br>Tin chloride |
| | Tin on Zinc: | Tin chloride |

Wastewaters are generated by the following anodizing operations:

Common metals - Sulfuric acid anodizing, phosphoric acid anodizing, oxalic acid anodizing, dyeing, nickel acetate sealing.

Cyanide - Ferrocyanide pigment impregnation

Hexavalent chromium - Chromic acid anodizing, dichromate sealing.

## COATING

Several types of conversion coating operations such as phosphating, chromating, coloring, and passivating contribute pollutants to raw waste streams. These pollutants may enter the waste stream through rinsing after coating operations and batch dumping of process baths. Coating process baths usually contain metal salts, acids, bases, and dissolved basis materials and various additives.

The phosphates of zinc, iron, manganese, nickel, and calcium are most often used for phosphate coatings. Strontium and cadmium phosphates are used in some baths, and the elements aluminum, chromium, fluorine, boron, and silicon are also common bath constituents. Phosphoric acid is used as the solvent in phosphating solutions.

Coloring can be done with a large variety of solutions. Several metals may be contributed to the waste stream by coloring operations, among them copper, nickel, lead, iron, zinc and arsenic. Passivation can be done in a nitric acid solution (for stainless steel) or a caustic solution (for copper). In both cases, dissolved basis materials enter the wastewater.

There are a number of conversion coating processes which utilize chromium-containing solutions. These include chromating, black oxidizing and sealing rinses. Chromating baths are usually proprietary solutions which contain concentrated chromic acid and active organic or inorganic compounds (even cyanide in some instances). Both hexavalent and trivalent chromium will be found in chromate conversion coating baths and in the rinses associated with them. Black oxidizing is done in solutions containing dichromate while sealing rinses used extensively following phosphating are usually made up of very dilute chromic acid. Any of these conversion coating operations will also contribute small amounts of basis material to their respective wastewater streams.

The wastewater contribution of conversion coating operations is as follows:

Common metals - Phosphating, nitric acid or caustic passivation, coloring.

Precious metals - Chromating of silver

Cyanide - Some chromating processes

Hexavalent chromium - Chromating, dichromate passivation, chromic acid sealing of phosphate coatings.

## ETCHING

Wastewater is produced in this unit operation by etching, chemical milling, bright dipping and related operations. As demonstrated by the list of etching solutions in Table 5-16, the majority of etching solutions are acidic while sodium hydroxide is used quite frequently as a caustic etch on aluminum. The constituents in the waste stream produced by etching operations are predominatly dissolved basis materials. Among the basis materials commonly etched are stainless steel, aluminum and copper. In addition to these materials, metals such as zinc and cadmium may appear in the waste stream due to bright dipping of these metals.

Certain etching baths contain concentrated chromic acid and are usually employed prior to plating steps. Chromic acid etches are used extensively on plastics prior to electroless plating of copper or nickel. These etching solutions and their associated rinses can contain hexavalent and trivalent chromium, small amounts of organic compounds (when used for etching plastics) and metals which originate in the basis material being etched. Chromic acid (in conjunction with other acids) is also used for the bright dipping of copper and copper alloys as well as zinc and cadmium plated parts.

An increasing number of etching solutions incorporate ammonia compounds. Ammonium hydroxide and ammonium chloride are the most common constituents of these baths. The ammonia contributed by these compounds acts as a metal-complexing agent in solution. Dumps of these baths or discharge of rinses following ammoniacal etches will therefore contain complexed wastes. These etchants are most widely used in the manufacture of printed circuit boards and their associated discharges can include complexed copper as well as various organic compounds (from the epoxy board and from etch resist formulations).

Cyanides are not generally used as constituents in etching baths. However, at least one bright dipping solution (for silver) does contain a mixture of sodium cyanide and hydrogen peroxide. The use of this particular bath will yield wastewater containing the above-mentioned constituents as well as silver.

## TABLE 5-16
## CONSTITUENTS OF PROCESS BATHS USED IN ETCHING

| Process | | Composition |
|---|---|---|
| Chemical Etching - | | |
| | Ferric chloride solns: | Ferric chloride<br>Hydrochloric acid<br>Base material |
| | Ammonium persulfate solns: | Ammonium persulfate<br>Mercuric chloride<br>Sulfuric acid<br>Ammonium chloride<br>Sodium chloride<br>Copper<br>Base material |
| | Cupric chloride solns: | Cupric chloride<br>Hydrochloric acid<br>Sodium chloride<br>Ammonium chloride<br>Base material |
| | Chromic-sulfuric acid solns: | Chromic acid<br>Sodium sulfate<br>Sulfuric acid<br>Copper<br>Base material |
| Chemical Milling - | For various metals: | Nitric acid<br>Chromic acid<br>Hydrochloric acid<br>Base metal |
| | For aluminum: | Sodium hydroxide |
| Electrochemical Milling - | | |
| | on steel, cobalt, copper, chromium: | Sodium chloride<br>Sodium nitrate<br>Base metal |
| | for tungsten & molybdenum alloys: | Sodium hydroxide<br>Sodium chloride<br>Base metal |

## TABLE 5-16 (Continued)

| Process | | Composition |
|---|---|---|
| Bright Dip - | | |
| | for Copper: | Nitric acid<br>Acetic acid<br>Phosphoric acid<br>Hydrochloric acid |
| | for Aluminum: | Phosphoric acid<br>Nitric acid<br>Glacial acetic acid |
| | also for Nickel: | Phosphoric acid<br>Sulfuric acid<br>Nitric acid<br>Phosphoric acid<br>Nitric acid<br>Titanium chloride |
| | for Zinc and Cadmium: | Chromium acid<br>Sulfuric acid |
| | for Silver: | Sodium cyanide<br>Hydrogen peroxide |

Etching operations contribute wastewater to the various waste types in the following manner:

Common metals - Etching, bright dipping and chemical milling of common metals basis materials with solutions such as ferric chloride, cupric chloride, nitric acid, hydrochloric acid, phosphic acid, sulfuric acid, hydrofluoric acid; stripping of common metal platings.

Precious metals - Any etching or bright dipping of precious metals; stripping of precious metal platings.

Complexed metals - Etching with ammoniated solutions such as ammonium hydroxide and ammonium chloride.

Cyanide - Certain bright dipping operations; cyanide stripping operations.

Hexavalent chromium - Etching, bright dipping, or chemical milling with solutions containing chromic acid; stripping with chromic acid or stripping of chromium platings.

## CLEANING

Cleaning operations are used throughout the Metal Finishing Category and provide the bulk of the wastewater generated by the industry. The purpose of cleaning is to remove the bulk of all of the soils (oils and dirt) prior to phosphating, electroplating, painting, pre and post penetrant inspection, burnishing and polishing, or after any other operation that produces an oil bearing part. Cleaning is often a necessary antecedent for several of the metal finishing operations. This cleaning does not include solvent cleaning which in itself is a separate unit operation.

Alkaline cleaning solutions usually contain one or more of the following chemicals: sodium hydroxide, sodium carbonate, sodium metasilicate, sodium phosphate (di- or trisodium), sodium silicate, sodium tetraphosphate, and a wetting agent. The specific content of cleaners varies with the type of soil being removed. For example, compositions for cleaning steel are more alkaline and active than those for cleaning brass, zinc die castings, and aluminum. Wastewaters from cleaning operations contain not only the chemicals found in the alkaline cleaners but also soaps from the saponification of greases left on the surface by polishing and buffing operations. Some oils and greases are not saponified but are, nevertheless, emulsified. The raw wastes from cleaning show up in rinse waters, spills and dumps of concentrated solutions.

The concentrations of dissolved basis metals in rinses following alkaline cleaning are usually small relative to acid dip rinses.

Organic chelating agents are utilized in some alkaline cleaning solutions in order to help soften the water. Hardness constituents such as calcium and magnesium salts are chelated as inert soluble complexes. This facilitates their removal from the surface of a part and prevents the formation of insoluble scums (from calcium and magnesium soaps). Therefore, some alkaline cleaning baths and their subsequent rinses contain complexed metals, phosphates in various forms and organic compounds including oils and greases.

Solutions for pickling or acid cleaning usually contain one or more of the following: hydrochloric acid (most common), sulfuric acid, nitric acid, chromic acid, fluoboric acid, and phosphoric acid. The solution compositions vary according to the nature of the basis metals and the type of tarnish or scale to be removed. These acid solutions accumulate appreciable amounts of metal as a result of dissolution of metal from workpieces or uncoated areas of plating racks that are recycled repeatedly through cleaning, acid treating, and electroplating baths.

As a result, the baths usually have a relatively short life, and when they are dumped and replaced, large amounts of chemicals must be treated or reclaimed. These chemicals also enter the waste stream by way of dragout from the acid solutions into rinse waters.

The amount of waste contributed by acid cleaners and alkaline cleaners varies appreciably from one facility to another depending on the substrate material, the formulation of the solution used for cleaning or activating the material, the solution temperature, the cycle time, and other factors. The initial condition of the substrate material affects the amount of waste generated during treatment prior to finishing. A dense, scale-free copper alloy part can be easily prepared for finishing by using a mild hydrochloric acid solution that dissolves little or no copper, whereas products with a heavy scale require stronger and hotter solutions and longer treating periods for ensuring the complete removal of any oxide prior to finishing.

Electrocleaners are basically heavy duty alkaline types that are employed with an electrical current. They are designed both for soil removal and metal activation. A dilute mineral acid dip usually follows the final cleaners to neutralize the alkaline film on the metal surface.

Emulsion cleaning removes soils from the surface of metals by the use of common organic solvents (e.g. kerosene, mineral oil, glycols, and benzene) dispersed in an aqueous medium with the aid of an emulsifying agent. Parts which have been emulsion cleaned are not normally rinsed following the cleaning operation. Wastes come from leaks and floor spills and can contain removed soils plus any of the cleaner constituents listed above.

Phosphates are used in some cleaners and function as water softeners, rinsing aids, soil suspending agents, and detergency boosters. Common cleaners include trisodium phosphate, sodium tripolyphosphate, tetrasodium and tetrapotassium pyrophosphates, and "glassy" phosphates such as sodium hexametaphosphate.

Diphase cleaning involves two immiscible liquid phases. One phase consists of water plus water soluble wetting agents, and may also include inorganic salts and emulsified oil. The other phase usually is a layer of some suitable organic solvent or solvents.

In general, cleaning baths and their associated rinses can contain oils, greases, grit, base metals, complexing agents, cyanides, acids, alkalies and miscellaneous additives. Cleaning operations contribute to the raw waste types in the following way:

Common metals - Most acid and alkaline cleaning operations.
Precious metals - Cleaning operations done on a precious metal basis material.
Complexed metals - Cleaning operations done with heavily chelated alkaline cleaners.
Hexavalent chromium - Cleaning done with chromated cleaners.
Cyanide - Cleaning done with cyanide cleaners.
Oily Waste - Cleaning of very oily parts.
Toxic organics - Solvent wiping, emulsion cleaning, vapor degreasing.

## MACHINING

Machining operations performed in the Metal Finishing Category incorporate the use of natural and synthetic oils for cooling and lubrication. Spills and leakage onto floor areas may be washed away with water and contribute oil/water emulsions to wastewater streams. Chip removal techniques produce large amounts of metal solids and clinging oils. Chip storage areas may include oil recovery facilities if the production level warrants them. If properly contained, these oily wastes will not normally enter wastewater streams. Any wastewaters which are generated belong to the common metals and oily waste types.

## GRINDING

Natural and synthetic oils are used in many grinding operations. Soluble oil emulsions and other fluids are used for cooling and lubrication, in a similar manner to that for machining. Some of these fluids are highly chlorinated and sulfochlorinated water soluble oils that contain wetting agents and rust inhibitors. Grinding system sumps contain ground metallic dust (or swarf) which is an oily sludge requiring periodic removal. This sludge does not mix with wastewater; however, grinding area spills and leaks may be washed into wastewater streams. They can contain any of the oily and additive constituents mentioned above. These wastes could contribute to the common metals, oily waste and solvent waste types.

## POLISHING

The wastes generated include polishing and buffing compounds, greases, metallic soaps, wafers, mineral oils, and dispersing agents. Greases with stearic acid addition, hydrogenated glycerides, and petroleum waxes are also used in these operations. Abrasives and fine metal particles accumulate and must be periodically removed. Area cleaning and washdown can produce wastes that enter wastewater streams. They would belong to the common metals and oily waste types.

## BARREL FINISHING

Abrasives, cleaners, soaps, anti-rust agents, emulsified oils, and water are used in barrel finishing (tumbling) operations. Caustic and alkaline cleaners are also used. Chemical solutions used in barrel finishing include maleic acid, tartaric acid, citric acid, sodium cyanide and sodium dichromate. Wastes from tumbling consist of dilute oils, process chemicals, fine clays, scale, and abrasive grit. Wastewater is generated by rinsing of parts following the finishing operation and by periodic dumping of process solutions. Contributions to the common metals, hexavalent chromium, cyanide and oily waste types could be made by this operation, depending upon the chemical solutions employed.

## BURNISHING

Lubricants and soap solutions are used to cool tools used in burnishing operations. Because burnishing provides a smoother surface, light spindle oil or rich soluble oil is usually used. Wastes may come from spills, leaks, process solution dumps and post-finish rinsing. The wastes could contribute to the common metals, precious metals and oily waste types depending upon the basis material finished. In addition, sodium cyanide (NaCN) may be used as a wetting agent and rust inhibitor (for steel), contributing to cyanide wastes from this operation.

## IMPACT DEFORMATION, PRESSURE DEFORMATION, AND SHEARING

Natural and synthetic oils, light greases, and pigmented lubricants are used in deformation and shearing operations. Pigmented lubricants include: whiting, lithapone, mica, zinc oxide, molybdenum disulfide, bentonite, flour, graphite, white lead, and soap-like materials. The presses commonly used for these operations incorporate hydraulic lines and incur fluid leakage that contributes oily waste. Spills and leaks in work areas may be cleaned with water and combined with other wastewater streams.

Wastes from these operations would belong to the common metals and oily waste types.

## HEAT TREATING

Quenching oils are of three general types: Conventional, fast, and water/oil emulsions (10-90% oil). A conventional oil contains no additives that will alter cooling characteristics. Fast quenching oils are blends which may contain specially developed proprietary additives such as nickel-zinc dithiophosphate. The wastes generated will contain the solution constituents as well as various scales, oxides and oils. Wastewater is generated through rinses, bath discharges (including batch dumps), spills and leaks. Included among the solutions used are:

- Brine solutions (used in quenching) which can contribute sodium chloride, calcium chloride, sodium hydroxide, sodium carbonate, hydrochloric acid and sulfuric acid to waste streams.

- Water and water-based solutions (for quenching and rinsing) which may contain dissolved salts, soaps, alcohols, oils, emulsifiers, slimes and algae.

- Cyaniding (liquid carburizing and carbonitriding) solutions for heat treating containing sodium cyanide, inert salts (sodium carbonate and sodium chloride), detergents, rust preventatives, carbon, alkali carbonate, nitrogen, carbon monoxide, carbon dioxide, cyanide, cyanate and oils (from subsequent quenching).

- High temperature baths containing sodium cyanide, potassium chloride, sodium chloride, sodium carbonate, calcium and strontium chlorides, manganese dioxide, boron oxide, sodium fluoride and silicon carbide.

- Unalloyed molten lead used for heat treating steel.

Most heat treating operations contribute wastewater to the common metals or oily wastes subcategory. Cyaniding operations contribute wastewaters to the cyanide waste type and the oily waste type.

## THERMAL CUTTING

Water may be used for rinsing or cooling of parts and equipment following this operation. Wastewaters produced would contribute to the common metals and oily waste types.

## WELDING, BRAZING, SOLDERING, FLAME SPRAYING

These operations are normally not wastewater producers. However, each of them can be followed by quenching, cooling or annealing in a solution of water or emulsified oils. When this is done, wastes produced can belong to the common metals waste type.

## OTHER ABRASIVE JET MACHINING

Abrasive slurries in alkaline or emulsified oil solutions and abrasives in air, nitrogen, or $CO_2$ are used. Aluminum oxide, silicon carbide, dolomite, calcium magnesium carbonate, sodium bicarbonate and glass beads are common abrasives used in this operation. Wastewater can be produced through solution dumps, spills, leaks or washdowns of work areas and contributes to the common metals and oily waste types.

## ELECTRICAL DISCHARGE MACHINING

Dielectric fluids are used in this operation. Common fluids include: hydrocarbon-petroleum oils, kerosene, silicone oils, deionized water, polar liquids, and aqueous ethylene glycol solutions. Rinsing of machined parts and work area cleanups can generate wastewaters which also contain base materials. These wastewaters contribute to the common metals and oily waste types.

## ELECTROCHEMICAL MACHINING

In addition to standard chemical formulations, inorganic and organic solvents are sometimes used as electrolytes for electrochemical machining. Solvents used include water, ammonia, hydrocyanic acid, sulfur dioxide, acetone, benzene, ethanol, diethyl ether, methanol and pyridine. Any of the constituents listed as well as the basis material being machined can enter waste streams via rinse discharges, bath dumps and floor spills. Generated wastes can belong to the common metals, cyanide, and solvent waste types depending upon the solvent used.

## LAMINATING

Water is not often used by this operation. However, occasional rinsing or cooling may occur in conjunction with laminating. The waste generated could contribute to the common metals and oily waste types.

## HOT DIP COATING

Hot dipping involves the immersion of metal parts in molten metal. The molten metal coats the part and an alloy is formed at the interface of the two metals. Water is used for rinses following precleaning and sometimes for quenching after coating. Aluminum, zinc, lead and tin are the metals most commonly used. Hot zinc coating (galvanizing) is probably used more extensively than any others. Galvanizing (as well as the other coatings) is done mainly for corrosion protection; in a few instances, hot dip coatings are also used for decorative purposes. Most hot dip coatings require fluxing. In galvanizing, a zinc ammonium chloride flux is normally used prior to the actual coating step. These wastewaters can contribute to the common metals waste type.

## SALT BATH DESCALING

These baths contain molten salts, caustic soda, sodium hydride and chemical additives. They are designed to remove rust, scale and resolidified glass. These contaminants (and a small amount of base material and oils) enter wastewater streams through rinsing, spills, leaks, batch dumps of process solutions and improper handling of sludge produced by the process. Wastewaters produced by salt bath descaling contribute to the common metals and oily waste types.

## SOLVENT DEGREASING

Solvent degreasing uses organic solvents such as aliphatic petroleums (eg-kerosene, naptha), aromatics (eg-benzene, toluene), oxygenated hydrocarbons (eg-ketones, alcohol, ether), halogenated hydrocarbons (1,1,1-trichloroethane, trichloroethylene, methylene chloride), and combinations of these classes of solvents. The degreasing equipment, sumps, and stills contain spent solvents and sludges along with removed oils, greases, and metallic particles. These pollutants can enter wastewater streams and contribute to the toxic organic waste type.

## PAINT STRIPPING

The stripping of paint films from rejected parts, hooks, hangers, masks, and other conveyor equipment is included in this operation. All the stripping wastes can contain any of the constituents of the paint being removed, as well as a small amount of the basis material beneath the paint and the constituents of the stripping solution. Stripping solutions may contain caustic soda, wetting agents, detergents, emulsifiers, foam soaps, alcohol, amines, ammonia or solvents. Solvents used include chlorinated solvents (such as methylene chloride) and highly polar solvents (such as acetone, methyl ethyl ketone, benzene and toluene). Other solvents employed in paint stripping operations include carbon tetrachloride, trichloroethylene, and orthodichlorobenzene. Wastes are primarily generated by rinsing and can also contain small amounts of emulsified oils. Spills, leaks, and solution dumps can also contribute to wastewater streams. Wastes produced belong to the common metals and oily waste types.

## PAINTING, ELECTROPAINTING, ELECTROSTATIC PAINTING

The sources of wastewater associated with industrial painting processes include scrubbing water dumps, discharge of ultrafilter permeate and discharge of rinse waters. Scrubbing (water curtain) discharges vary widely in frequency of occurrence, from once a week up to once every six to twelve months. A dump schedule of once a month is not unusual for painters using water curtains. These wastewater dumps may contain any of the common paint ingredients (which often involve common metals) such as solvents, pigments, resins and other additives. Dumps are usually necessitated by buildups in the water of dissolved salts, odor-causing anaerobic bacteria, and suspended solids that clog the water curtain nozzles.

Ultrafiltration is used in connection with electropainting to concentrate paint solids. The permeate contains pollutants from the spent bath. However, the ultrafilter permeate is commonly used as a water source for rinses immediately following the electrodeposition process, and the ultrafilter concentrate is returned to the painting bath. A final deionized water rinse is used in electrodeposition painting, and the rinse water is eventually discharged to a waste stream. This wastewater will contain pollutants present in the paint bath.

In the dip coating process, wastewaters containing paint pigments and solvents are generated by selective spray rinsing following the paint bath. Electrodeposition rinses generate wastewaters and are described above. Rinses following autodeposition are normally discharged to waste streams and commonly contain chromium in addition to paint constituents. Wastewaters from these unit operations can contribute to the common metals, hexavalent chromium and solvent waste types.

## TESTING

Fuels, lubricating oils, and hydraulic fluids are commonly used in non-destructive performance testing for many products such as engines, valves, controls, and pressure vessels. Oily penetrants are used in dye-penetrant inspection and testing operations. Common penetrants include water, kerosene, ethylene glycol, neutral oil, SAE 10W or SAE 40W oils, water-washable penetrants, color-contrast penetrants, and emulsifiers. Leak testing, final washing (automobiles, etc.) and test area washdowns enter waste streams and may contain oils and fluids used at testing stations as well as heavy metal contamination derived from the component being tested. These wastewaters contribute to the common metals and oily waste types.

## MECHANICAL PLATING

Cadmium, zinc, and tin, singly or in combination, may be applied by mechanical plating. The parts are first precleaned by any of the conventional methods such as solvent degreasing or alkaline washing. They are then plated in a rotating, rubber lined barrel containing an acid solution, inert impact media, and the metal to be plated in powder form. The plated parts are rinsed and sometimes go through a chromating step before drying. Thus, the plating solution and rinse water contain common metals, while rinse water from the chromating step contains mainly hexavalent chromium.

## PRINTED CIRCUIT BOARD MANUFACTURING

Wastewater is produced in the manufacturing of printed circuit boards from the following processes:

1. Surface preparation - The rinses following scrubbing, alkaline cleaning, acid cleaning, etchback, catalyst application and activation.

2. Electroless plating - Rinses following the electroless plating step.

3. Pattern plating - Rinse following acid cleaning, alkaline cleaning, copper plating, and solder plating.

4. Etching - Rinses following etching and solder brightening.

5. Tab plating - Rinses following solder stripping, scrubbing, acid cleaning, and nickel, gold, or other plating operations.

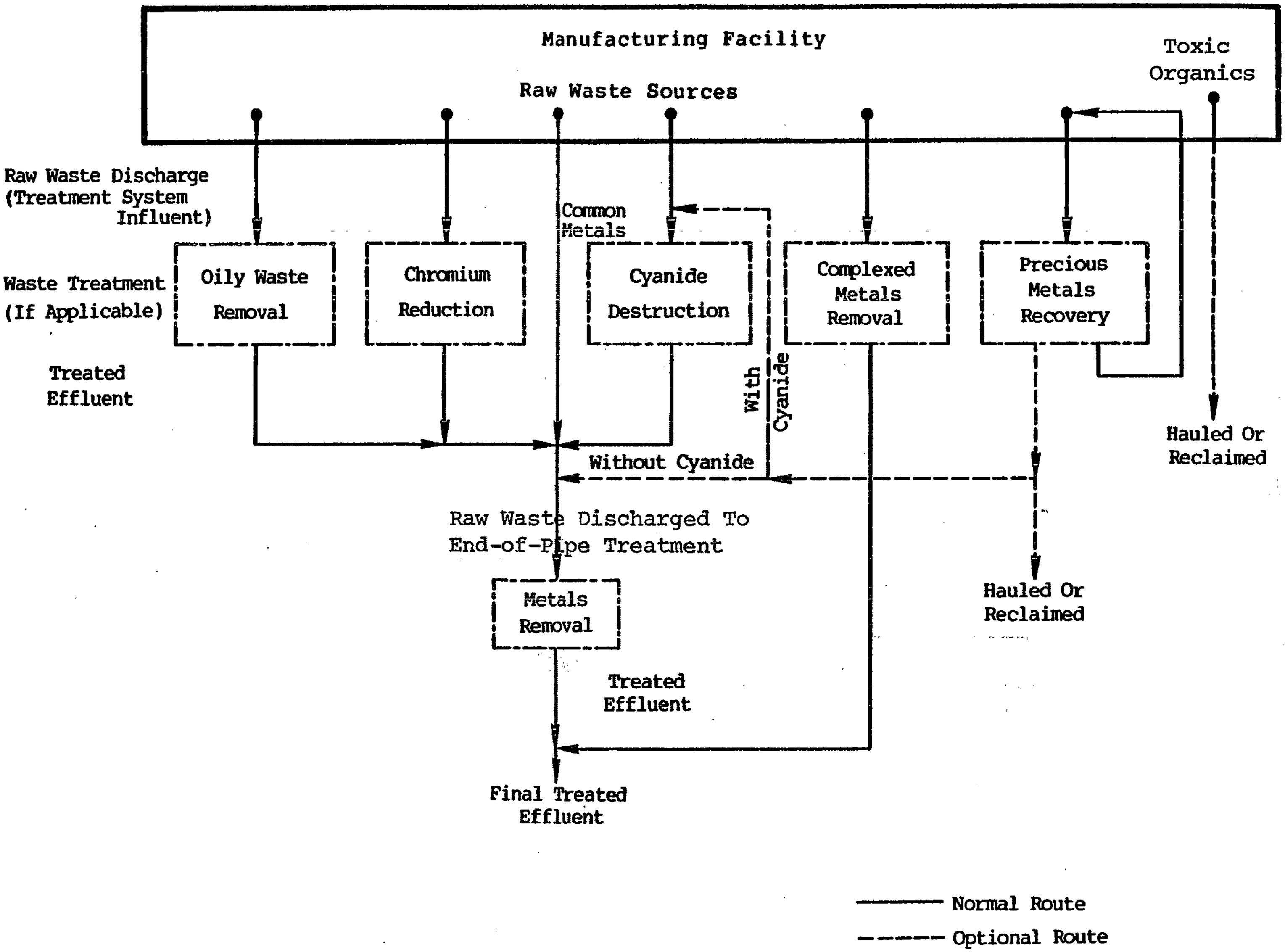
6. Immersion plating - Rinses following acid cleaning and immersion tin plating.

Additionally, water may be used for subsidiary purposes such as rinsing away spills, air scrubbing water, equipment washing, and dumping spent process solutions.

The principal constituents of the waste streams from the printed board industry are suspended solids, copper, fluorides, phosphorus, tin, palladium, and chelating agents. Low pH values are characteristic of the wastes because of the acid cleaning and surface pretreatment necessary. The suspended solids are comprised primarily of metals from plating and etching oprations and dirt which is removed during the cleaning processes prior to plating. The large amount of copper present in the waste stream comes from the electroless copper plating as well as copper electroplating and etching operations. Fluorides are primarily the result of cleaning and surface treatment processes utilizing hydrofluoric and fluorboric acids. Phosphorus results from the large amount of cleaning that is performed on the boards. Tin results from operations involving catalyst application and solder electroplating, and palladium is a waste constituent from catalyst application. The chelating agents present are primarily from the electroless plating operations, although others may have been added by the cleaning, immersion plating, and gold plating operations.

## CHARACTERISTICS OF WASTE TYPE STREAMS

The waste effluent schematic in Figure 5-2 is applicable to raw waste streams generated by operations within the Metal Finishing Category. In this scheme, oily waste, hexavalent chromium waste, cyanide waste, and precious metals waste are treated prior to combining with other plant wastewaters (i.e., common metals waste) for end-of-pipe treatment. Complexed metals waste are segregated and treated separately and toxic organics waste are hauled or reclaimed. In some cases a waste stream will contain pollutants belonging to more than one waste type. When this occurs, it is expected that the waste stream will receive the appropriate specialized treatment prior to joining other streams and receiving treatment for metals removal. For example, a waste stream from a copper cyanide electroplating operation must receive treatment for cyanide destruction before passing on to metals removal.



Note: Discharge from precious metals recovery may be hauled in alternative ways, depending on the recovery method in use.

FIGURE 5-2

WASTE TREATMENT SCHEMATIC

Oil-bearing streams containing common metals must pass through oil removal before going to metals removal. Selection of pollutant parameters for regulation is covered in Section VI. Specific details of appropriate waste treatment techniques are discussed in Section VII.

In order to characterize the waste streams for each waste type, raw waste data were gathered from the sampling visits. Discrete samples of raw wastes were taken for each waste type and analysis was done as explained previously in this section.

The minimum detectable limits for the priority pollutants, the conventional pollutants TSS and Oil and Grease, and selected non-conventional pollutants as published by EPA in March 1979 and December 1979 are presented in Table 5-17.

Individual laboratories can vary in their detection limits for various parameters and can often achieve lower detection limits than the ones presented in Table 5-17. Laboratories under contract to EPA for pollutant analysis for this program reported detection limits that were generally at or below the minimum detectable limits. The results of the analyses from sample visits are presented in this section.

The raw waste characteristics of the total plant raw waste discharged to end-of-pipe treatment and the individual waste types - common metals, precious metals, complexed metals, cyanide, hexavalent chromium, oily, and toxic organics wastes - are discussed in this section, and the sample visit data are presented. The data tables include the following terms:

- Minimum concentrations found in the analysis of each appropriate waste stream.
- Maximum concentrations found in the analysis of each appropriate waste stream.
- Mean concentrations calculated from the results of the analysis of each appropriate waste stream.
- Median concentrations selected by ranking appropriate waste stream concentration values.
- # of pts represents the number of streams used in the preceding computations.
- # of zeros is the number of times that a parameter was not detected. Zeros were used in the generation of statistics for the minimum, mean, median, and flow proportioned average concentrations.
- Flow Proportioned Mean Concentrations obtained by multiplying concentration times flow rate for each plant, summing these products, and dividing by the sum of the flow rates.

## TABLE 5-17

## MINIMUM DETECTABLE LIMITS*

| | PARAMETER | MINIMUM DETECTABLE LIMIT mg/ℓ |
|---|---|---|
| 1. | Acenaphthene | 0.01 |
| 2. | Acrolein | 0.1 |
| 3. | Acrylonitrile | 0.1 |
| 4. | Benzene | 0.005 |
| 5. | Benzidine | 0.04 |
| 6. | Carbon Tetrachloride (Tetrachloromethane) | 0.005 |
| 7. | Chlorobenzene | 0.005 |
| 8. | 1,2,4-Trichlorobenzene | 0.01 |
| 9. | Hexachlorobenzene | 0.01 |
| 10. | 1,2-Dichlorethane | 0.001 |
| 11. | 1,1,1-Trichloroethane | 0.005 |
| 12. | Hexachloroethane | 0.01 |
| 13. | 1,1-Dichloroethane | 0.005 |
| 14. | 1,1,2-Trichloroethane | 0.005 |
| 15. | 1,1,2,2-Tetrachloroethane | 0.01 |
| 16. | Chloroethane | 0.01 |
| 18. | Bis(2-chloroethyl)ether | 0.01 |
| 19. | 2-Chloroethyl Vinyl Ether (Mixed) | 0.01 |
| 20. | 2-Chloronaphthalene | 0.01 |
| 21. | 2,4,6-Trichlorophenol | 0.01 |
| 22. | p-Chloro-m-cresol | 0.01 |
| 23. | Chloroform (Trichloromethane) | 0.005 |
| 24. | 2-Chlorophenol | 0.01 |
| 25. | 1,2-Dichlorobenzene | 0.01 |
| 26. | 1,3-Dichlorobenzene | 0.01 |
| 27. | 1,4-Dichlorobenzene | 0.01 |
| 28. | 3,3'-Dichlorobenzidine | 0.02 |
| 29. | 1,1-Dichloroethylene | 0.005 |
| 30. | 1,2-trans-Dichloroethylene | 0.005 |
| 31. | 2,4-Dichlorophenol | 0.01 |
| 32. | 1,2-Dichloropropane | 0.01 |
| 33. | 1,3-Dichloropropylene(1,3-Dichloropropene) | 0.005 |
| 34. | 2,4-Dimethyl Phenol | 0.01 |
| 35. | 2,4-Dinitrotoluene | 0.02 |
| 36. | 2,6-Dinitrotoluene | 0.02 |
| 37. | 1,2-Diphenylhydrazine | 0.02 |

* References: USEPA Environmental Monitoring and Support Laboratory. Methods for Chemical Analysis of Water and Wastes. March 1979; and USEPA Guidelines Establishing Test Procedures for the Analysis of Pollutants, Proposed Regulations. Federal Register Vol. 44, No. 233. Monday, December 3, 1979.

## TABLE 5-17 (Continued)

## MINIMUM DETECTABLE LIMITS*

| | PARAMETER | MINIMUM DETECTABLE LIMIT mg/ℓ |
|---|---|---|
| 38. | Ethylbenzene | 0.005 |
| 39. | Fluoranthene | 0.01 |
| 40. | 4-Chlorophenyl Phenyl Ether | 0.01 |
| 41. | 4-Bromophenyl Phenyl Ether | 0.01 |
| 42. | Bis(2-chloroisopropyl)ether | 0.02 |
| 43. | Bis(2-chloroethoxy)methane | 0.02 |
| 44. | Methylene Chloride(Dichloromethane) | 0.005 |
| 45. | Methyl Chloride(Chloromethane) | 0.01 |
| 46. | Methyl Bromide (Bromomethane) | 0.01 |
| 47. | Bromoform (Tribromomethane) | 0.01 |
| 48. | Dichlorobromomethane | 0.005 |
| 51. | Chlorodibromomethane | 0.005 |
| 52. | Hexachlorobutadiene | 0.01 |
| 53. | Hexachlorocyclopentadiene | 0.01 |
| 54. | Isophorone | 0.01 |
| 55. | Naphthalene | 0.01 |
| 56. | Nitrobenzene | 0.01 |
| 57. | 2-Nitrophenol | 0.02 |
| 58. | 4-Nitrophenol | 0.05 |
| 59. | 2,4-Dinitrophenol | 0.05 |
| 60. | 4,6-Dinitro-o-cresol | 0.02 |
| 61. | N-Nitrosodimethylamine | 0.01 |
| 62. | N-Nitrosodiphenylamine | 0.01 |
| 63. | N-Nitrosodi-n-propylamine | 0.01 |
| 64. | Pentachlorophenol | 0.01 |
| 65. | Phenol | 0.01 |
| 66. | Bis(2-ethylhexyl) Phthalate | 0.01 |
| 67. | Butyl Benzyl Phthalate | 0.01 |
| 68. | Di-n-butyl Phthalate | 0.01 |
| 69. | Di-n-octyl Phthalate | 0.01 |
| 70. | Diethyl Phthalate | 0.01 |
| 71. | Dimethyl Phthalate | 0.01 |
| 72. | 1,2-Benzanthracene [Benzo(a)anthracene] | 0.01 |
| 73. | Benzo(a)Pyrene (3,4-Benzopyrene) | 0.02 |

* References: USEPA Environmental Monitoring and Support Laboratory. Methods for Chemical Analysis of Water and Wastes. March 1979; and USEPA Guidelines Establishing Test Procedures for the Analysis of Pollutants, Proposed Regulations. Federal Register Vol. 44, No. 233. Monday, December 3, 1979.

## TABLE 5-17 (Continued)

## MINIMUM DETECTABLE LIMITS*

| | PARAMETER | MINIMUM DETECTABLE LIMIT mg/ℓ |
|---|---|---|
| 74. | 3,4-Benzofluoranthene [Benzo(b)fluoranthene] | 0.02 |
| 75. | 11,12-Benzofluoranthene [Benzo(k)fluoranthene] | 0.02 |
| 76. | Chrysene | 0.02 |
| 77. | Acenaphthylene | 0.01 |
| 78. | Anthracene | 0.01 |
| 79. | 1,12-Benzoperylene [Benzo(ghi)perylene] | 0.02 |
| 80. | Fluorene | 0.01 |
| 81. | Phenanthrene | 0.01 |
| 82. | 1,2,5,6-Dibenzathracene [Dibenzo(a,h)anthracene] | 0.02 |
| 83. | Indeno(1,2,3-cd)pyrene (2,3-O-Phenylenepyrene) | 0.02 |
| 84. | Pyrene | 0.01 |
| 85. | Tetrachloroethylene | 0.005 |
| 86. | Toluene | 0.005 |
| 87. | Trichloroethylene | 0.005 |
| 88. | Vinyl Chloride (Chloroethylene) | 0.01 |
| 89. | Aldrin | 0.005 µg/ℓ |
| 90. | Dieldrin | 0.005 µg/ℓ |
| 91. | Chlordane (Technical Mixture and Metabolites) | 0.05 µg/ℓ |
| 92. | 4,4'-DDT | 0.01 µg/ℓ |
| 93. | 4,4'-DDE(P,P'-DDX) | 0.005 µg/ℓ |
| 94. | 4,4'-DDD(P,P'-TDE) | 0.01 µg/ℓ |
| 95. | Alpha-Endosulfan | 0.005 µg/ℓ |
| 96. | Beta-Endosulfan | 0.005 µg/ℓ |
| 97. | Endosulfan Sulfate | 0.01 µg/ℓ |
| 98. | Endrin | 0.005 µg/ℓ |
| 99. | Endrin Aldehyde | 0.01 µg/ℓ |
| 100. | Heptachlor | 0.005 µg/ℓ |
| 101. | Heptachlor Epoxide(BHC-Hexachlorocyclohexane) | 0.005 µg/ℓ |
| 102. | Alpha-BHC | 0.005 µg/ℓ |
| 103. | Beta-BHC | 0.005 µg/ℓ |
| 104. | Gamma-BHC(Lindane) | 0.005 µg/ℓ |
| 105. | Delta-BHC (PCB-Polychlorinated Biphenyls) | 0.005 µg/ℓ |
| 106. | PCB-1242 (Aroclor 1242) | 0.05 µg/ℓ |
| 107. | PCB-1254 (Aroclor 1254) | 0.10 µg/ℓ |
| 108. | PCB-1221 (Aroclor 1221) | 0.10 µg/ℓ |
| 109. | PCB-1232 (Aroclor 1232) | 0.10 µg/ℓ |
| 110. | PCB-1248 (Aroclor 1248) | 0.10 µg/ℓ |

* References: USEPA Environmental Monitoring and Support Laboratory. Methods for Chemical Analysis of Water and Wastes. March 1979; and USEPA Guidelines Establishing Test Procedures for the Analysis of Pollutants, Proposed Regulations. <u>Federal Register</u> Vol. 44, No. 233. Monday, December 3, 1979.

## TABLE 5-17 (Continued)

## MINIMUM DETECTABLE LIMITS*

| | PARAMETER | MINIMUM DETECTABLE LIMIT mg/ℓ |
|---|---|---|
| 111. | PCB-1260 (Aroclor 1260) | 0.20 μg/ℓ |
| 112. | PCB-1016 (Aroclor 1016) | 0.05 μg/ℓ |
| 113. | Toxaphene | 0.05 μg/ℓ |
| 114. | Antimony | 0.2 |
| 115. | Arsenic | 0.002 |
| 116. | Asbestos | --- |
| 117. | Beryllium | 0.005 |
| 118. | Cadmium | 0.005 |
| 119. | Chromium | 0.05 |
| 120. | Copper | 0.02 |
| 121. | Cyanide | 0.02-0.005 |
| 122. | Lead | 0.1 |
| 123. | Mercury | 0.0002 |
| 124. | Nickel | 0.04 |
| 125. | Selenium | 0.002 |
| 126. | Silver | 0.01 |
| 127. | Thallium | 0.1 |
| 128. | Zinc | 0.005 |
| 129. | 2,3,7,8-Tetrachlorodibenzo-p-dioxin(TCDD) | 0.005 μg/ℓ |
| | Iron | 0.03 |
| | Gold | 0.1 |
| | Iridium | 3.0 |
| | Osmium | 0.3 |
| | Palladium | 0.1 |
| | Platinum | 0.2 |
| | Rhodium | 0.05 |
| | Ruthenium | 0.2 |
| | Tin | 0.8 |
| | Hexavalent Chromium | 0.001 |
| | Phosphorus (total) | 0.01 |
| | Fluoride | 0.1 |
| | Cyanide Amenable to Chlorination | 0.005 |
| | Total Phenols | 0.005 |
| | TSS | 10.0 |
| | Oil and Grease | 5.0 to 0.2 |

* References: USEPA Environmental Monitoring and Support Laboratory. Methods for Chemical Analysis of Water and Wastes. March 1979; and USEPA Guidelines Establishing Test Procedures for the Analysis of Pollutants, Proposed Regulations. <u>Federal Register</u> Vol. 44, No. 233. Monday, December 3, 1979.

## TOTAL PLANT RAW WASTE DISCHARGED TO END-OF-PIPE TREATMENT

Analysis of data the from sampled plants representing the raw waste stream discharged prior to end-of-pipe treatment is presented in Table 5-18. The major constituents of metal finishing raw waste discharged to end-of-pipe treatment are toxic metals contributed primarily from the common metals waste stream and the chromium waste stream after reduction. Cyanide, precious metals, and oil and grease appear as minor constituents in the raw waste to end-of-pipe treatment because (as shown in Figure 5-2) these streams, like chromium, are combined with the common metals waste after segregated treatment. The concentrations of these constituents in the individual raw waste streams prior to initial treatment, however, are significant.

## TABLE 5-18

## POLLUTANTS FOUND IN TOTAL PLANT RAW WASTE DISCHARGED TO END-OF-PIPE TREATMENT

| PARAMETER | | Flow Proportioned Mean Concentration |
|---|---|---|
| 114. | Antimony | 0.009 |
| 115. | Arsenic | 0.008 |
| 117. | Beryllium | 0.001 |
| 118. | Cadmium | 0.283 |
| 119. | Chromium | 27.46 |
| | Chromium, Hexavalent | 0.931 |
| 120. | Copper | 12.63 |
| 121. | Cyanide | 1.856 |
| | Cyanide, Amenable to Chlorination | 1.168 |
| 122. | Lead | 0.331 |
| 123. | Mercury | 0.001 |
| 124. | Nickel | 15.47 |
| 125. | Selenium | 0.001 |
| 126. | Silver | 0.023 |
| 127. | Thallium | 0.009 |
| 128. | Zinc | 12.47 |
| | Oil and Grease | 391.60 |
| | Total Suspended Solids | 539.09 |

## COMMON METALS WASTE TYPE

Table 5-19 shows the concentrations of metals in common metals raw waste streams from sampled plants. The major constituents in common metals waste are parameters which originate in process solutions such as from plating or galvanizing and enter the wastewater by dragout to rinses. These include cadmium, chromium, copper, cyanide, lead, nickel, zinc, and tin, and these pollutants appear in common metals waste streams in widely varying concentrations.

## PRECIOUS METALS WASTE TYPE

Table 5-20 shows the concentrations of silver, gold, palladium, and rhodium found in precious metals raw waste streams. All of the precious metals shown are used in Metal Finishing Category operations. The major constituents are silver and gold, which are much more commonly used than palladium and rhodium. Because of their high cost, metal finishers generally attempt to recover these metals from wastewaters.

## COMPLEXED METALS WASTE TYPE

The concentrations of toxic metals found in complexed metals raw waste streams are presented in Table 5-21. Complexed metals may occur in a number of unit operations but come primarily from electroless and immersion plating. The most commonly used metals in these operations are copper, nickel and tin. Wastewaters containing complexing agents must be segregated and treated independently of other wastes in order to prevent further complexing of free metals in the other streams.

## CYANIDE WASTE TYPE

The cyanide concentrations found in cyanide raw waste streams are shown in Table 5-22. Streams with high cyanide concentrations normally originate in electroplating and heat treating processes. Other unit operations can also contribute cyanide wastes. Cyanide-bearing waste streams should be segregated and treated before being combined with other raw waste streams.

## HEXAVALENT CHROMIUM WASTE TYPE

Concentrations of hexavalent chromium from metal finishing raw wastes are shown in Table 5-23. Hexavalent chromium enters

## TABLE 5-19
## POLLUTANT CONCENTRATIONS FOUND IN THE COMMON METALS RAW WASTE STREAM
## (Average Daily Values (mg/liter)

| Toxic Pollutant | Minimum | Maximum | Mean | Median | # Zeros | # Points | Flow Proportioned Mean Concentration |
|---|---|---|---|---|---|---|---|
| 114 Antimony | 0.0 | 0.430 | 0.007 | 0.0 | 84 | 106 | .0007 |
| 115 Arsenic | 0.0 | 0.064 | 0.005 | 0.0 | 75 | 105 | 0.015 |
| 117 Beryllium | 0.0 | 0.044 | 0.008 | 0.005 | 4 | 27 | 0.016 |
| 118 Cadmium | 0.0 | 21.5 | 0.613 | 0.001 | 48 | 119 | 0.070 |
| 119 Chromium | 0.0 | 35.4 | 2.10 | 0.105 | 16 | 116 | 1.39 |
| 120 Copper | 0.0 | 500. | 14.2 | 0.175 | 3 | 119 | 1.84 |
| 121 Cyanide | 0.0 | 2370. | 42.1 | 0.016 | 29 | 99 | 0.834 |
| 122 Lead | 0.0 | 42.3 | 1.25 | 0.053 | 35 | 122 | 0.738 |
| 123 Mercury | 0.0 | 0.400 | 0.005 | 0.0 | 67 | 109 | 0.001 |
| 124 Nickel | 0.0 | 415. | 19.4 | 0.078 | 20 | 111 | 4.16 |
| 125 Selenium | 0.0 | 0.060 | 0.007 | 0.005 | 5 | 26 | 0.003 |
| 126 Silver | 0.0 | 0.080 | 0.006 | 0.0 | 59 | 103 | 0.001 |
| 127 Thallium | 0.0 | 0.062 | 0.008 | 0.003 | 5 | 26 | 0.003 |
| 128 Zinc | 0.0 | 16,500. | 312. | 0.393 | 1 | 122 | 41.3 |
| Aluminum | 0.0 | 200. | 27.4 | 1.27 | 2 | 16 | 85.6 |
| Barium | 0.0 | 0.017 | 0.032 | 0.029 | 1 | 4 | 0.031 |
| Boron | 1.67 | 4.0 | 31.4 | 3.76 | 0 | 3 | 3.13 |
| Calcium | 25.0 | 76.2 | 51.4 | 52.2 | 0 | 4 | 58.5 |
| Cobalt | 0.0 | 0.023 | 0.007 | 0.0 | 4 | 7 | 0.010 |
| Fluorides | 0.0 | 36.1 | 4.31 | 0.876 | 9 | 99 | 6.15 |
| Iron | 0.0 | 13,100. | 500. | 2.44 | 1 | 102 | 84.7 |
| Magnesium | 5.6 | 31.1 | 16.1 | 13.8 | 0 | 4 | 17.4 |
| Manganese | 0.059 | 0.500 | 0.233 | 0.085 | 0 | 7 | 0.337 |
| Molybdenum | 0.0 | 0.300 | 0.102 | 0.018 | 1 | 6 | 0.109 |
| Phosphorus | 0.0 | 76.7 | 7.72 | 3.06 | 1 | 98 | 8.00 |
| Sodium | 16.7 | 310. | 151. | 138. | 0 | 4 | 211. |
| Tin | 0.0 | 14.7 | 1.04 | 0.0 | 60 | 98 | 3.35 |
| Titanium | 0.0 | 4.30 | 0.493 | 0.006 | 4 | 9 | 0.046 |
| Vanadium | 0.0 | 0.216 | 0.066 | 0.023 | 1 | 4 | 0.069 |
| Yttrium | 0.0 | 0.020 | 0.010 | 0.010 | 1 | 4 | 0.010 |
| Oil and Grease | 4.70 | 802,000. | 40,700. | 6,060. | 0 | 37 | 11,600. |

## TABLE 5-20
## POLLUTANT CONCENTRATIONS FOUND IN THE PRECIOUS METALS RAW WASTE STREAM

Average Daily Values (mg/liter)

| Toxic Pollutant | Minimum | Maximum | Mean | Median | # Zeros | # Points | Flow Proportioned Mean Concentration |
|---|---|---|---|---|---|---|---|
| 126 Silver | 0.0 | 600. | 69.0 | 0.243 | 3 | 15 | 8.09 |
| Gold | 0.0 | 42.7 | 9.27 | 0.560 | 6 | 15 | 6.11 |
| Palladium | 0.0 | 0.120 | 0.023 | 0.0 | 10 | 13 | 0.003 |
| Rhodium | 0.0 | 0.220 | 0.018 | 0.0 | 11 | 12 | 0.005 |

## TABLE 5-21
## POLLUTANT CONCENTRATIONS FOUND IN THE COMPLEXED METALS RAW WASTE STREAM

Average Daily Values (mg/liter)

| Toxic Pollutant | Minimum | Maximum | Mean | Median | # Zeros | # Points | Flow Proportioned Mean Concentration |
|---|---|---|---|---|---|---|---|
| 118 Cadmium | 0.0 | 3.65 | 0.247 | 0.0 | 22 | 31 | 0.173 |
| 120 Copper | 0.0 | 62.6 | 10.3 | 5.90 | 3 | 31 | 9.68 |
| 122 Lead | 0.0 | 3.61 | 0.372 | 0.0 | 21 | 31 | 0.240 |
| 124 Nickel | 0.0 | 294. | 22.5 | 0.550 | 6 | 31 | 18.8 |
| 128 Zinc | 0.023 | 17.6 | 3.05 | 0.210 | 0 | 31 | 2.52 |

## TABLE 5-22
## POLLUTANT CONCENTRATIONS FOUND IN THE CYANIDE RAW WASTE STREAM

Average Daily Values (mg/liter)

| Toxic Pollutant | Minimum | Maximum | Mean | Median | # Zeros | # Points | Flow Proportioned Mean Concentration |
|---|---|---|---|---|---|---|---|
| 121 Cyanide, Total | 0.045 | 1680. | 298. | 77.4 | 0 | 23 | 96.3 |
| Cyanide, Amen. to Chlor. | 0.0 | 1560. | 266. | 7.63 | 1 | 22 | 86.8 |

## TABLE 5-23
## POLLUTANT CONCENTRATIONS FOUND IN THE HEXAVALENT CHROMIUM RAW WASTE STREAM

Average Daily Values (mg/liter)

| Toxic Pollutant | Minimum | Maximum | Mean | Median | # Zeros | # Points | Flow Proportioned Mean Concentration |
|---|---|---|---|---|---|---|---|
| Chromium, Hexavalent | 0.005 | 12900. | 377. | 16.4 | 0 | 46 | 54.6 |

wastewaters as a result of many unit operations and can be very concentrated. Hexavalent chromium is highly toxic and should be segregated and treated before combining with other raw waste streams.

## OILY WASTE TYPE

Table 5-24 shows the concentrations of oil and grease in oily waste streams from sampled plants. Oily waste in the metal finishing industry consists of free oils, emulsified or water soluble oils and greases in a concentrated or dilute form. The relationship between the unit operations and type of oily waste generated (concentrated or dilute) is illustrated in Table 5-25. Applicable treatment of oily waste streams can vary dependent upon the concentration levels of the waste. Concentrated oily wastes typically include machining oils and process coolants and lubricants. Concentrated oily wastes are generally characterized by very high concentrations of oil and grease and should be segregated for oil removal prior to combining with other plant wastewaters for treatment. Dilute oily wastes include wastes from cleaning operations. The concentrations of oil and grease in these waste streams is generally much lower than that of segregated oily wastes and these streams typically do not receive segregated treatment before combining with other process wastewaters.

## TOXIC ORGANICS WASTE TYPE

Toxic organics raw wastes are generated in the Metal Finishing Category primarily by the dumping of spent solvents from degreasing equipment (including its sumps, water traps, and stills). These solvents are predominately comprised of compounds that are classified by the EPA as toxic pollutants. Table 5-26, extracted from the literature, illustrates specific solvents employed and shows their annual consumption for 1974. Spent solvents should be segregated, hauled for disposal or reclamation, or reclaimed on site. These and other sources of toxic organics enter various metal finishing wastewaters.

Table 5-26 shows that in 1974 this degreasing solvent consumption amounted to 1600 million pounds/yr (6.4 million lb/day) and is expected to be in the order of 2300 million pounds/yr (9.3 million lb/day) by 1985. Literature indicates that nearly 100% of all solvents consumed reach the atmosphere, either by direct evaporation from degreasing equipment or by evaporation subsequent to improper disposal. (Reference: Organic Solvent Cleaning - Background Information for Proposed Standards; USEPA; EPA-450/278-045; May 1979). In addition, the same reference estimates that approximately 75% of the incidence of solvent degreasing occurs in the metal finishing and related industries. Since degreasing solvents are predominantly concentrated priority pollutants that are discharged to the environment from a single unit operation, solvent degreasing, the reduction of this source will significantly improve the environment.

## TABLE 5-24

## POLLUTANT CONCENTRATIONS FOUND IN THE OILY RAW WASTE STREAM

| | Average Daily Values (mg/ℓ) | | | | | | |
|---|---|---|---|---|---|---|---|
| Toxic Pollutant | Minimum | Maximum | Mean | Median | No. Zeros | No. Points | Flow Proportioned Mean Concentration |
| Oil & Grease | 4.7 | 802,000 | 40,700 | 6,060 | 0 | 37 | 11,600 |

## TABLE 5-25
## OILY WASTE CHARACTERIZATION

| Unit Operation | Character of Oily Waste Generated | |
|---|---|---|
| | Concentrated | Dilute |
| Cleaning | | x |
| Machining | x | x |
| Grinding | x | x |
| Polishing | | x |
| Tumbling (Barrel Finishing) | | x |
| Burnishing | x | |
| Impact Deformation | x | |
| Pressure Deformation | x | |
| Shearing | x | |
| Heat Treating | x | x |
| Welding | x | |
| Brazing | x | |
| Soldering | x | |
| Flame Spraying | x | |
| Other Abrasive Jet Machining | x | |
| Electrical Discharge Machining | x | |
| Salt Bath Descaling | | x |
| Solvent Degreasing | x | |
| Paint Stripping | | x |
| Assembly | | x |
| Testing | x | x |

## TABLE 5-26
## 1974 DEGREASING SOLVENT CONSUMPTION

| | Solvent Consumption (Millions of Pounds/Yr). | | |
|---|---|---|---|
| Solvent Type | Cold Cleaning | Vapor Degreasing | All Degreasing |
| **Halogenated:** | | | |
| Trichloroethylene | 55 | 282 | 337 |
| 1,1,1-trichloroethane | 180 | 176 | 356 |
| Perchloroethylene | 29 | 90 | 119 |
| Methylene Chloride | 51 | 16 | 67 |
| Trichlorotrifluoroethane | 22 | 44 | 66 |
| | 337 | 608 | 945 |
| **Aliphatics:** | | | |
| (Kerosenes, Napthas) | 489 | 0 | 489 |
| **Aromatics:** | | | |
| Benzene | 15 | 0 | 15 |
| Toluene | 31 | 0 | 31 |
| Xylene | 27 | 0 | 27 |
| Cyclohexane | 2 | 0 | 2 |
| Heavy Aromatics | 27 | 0 | 27 |
| | 102 | 0 | 102 |
| **Oxygenated:** | | | |
| Ketones | | | |
| Acetone | 22 | 0 | 22 |
| Methyl Ethyl Ketone | 18 | 0 | 18 |
| Alcohols | | | |
| Butyl | 11 | 0 | 11 |
| Ethers | 13 | 0 | 13 |
| | 64 | 0 | 64 |
| Total Solvents: | 992 | 608 | 1600 |

The primary source of data for this report was 365 Data Collection Portfolios (DCP's) produced from a random survey of 900 manufacturers having Standard Industrial Classification (SIC) Codes between 3400 and 3999. These cover the manufacturing of: Fabricated Metal Products, Machinery, Electrical and Electronics Machinery, Transportation Equipment, Measuring Instruments, and Miscellaneous Products. The requested information concerning manufacturing unit operations and waste treatment methods provided solvent degreasing unit operation data including waste solvent consumption quantities and frequencies of disposition. Additional or missing data were obtained by telephone survey. Since the manufacturers were selected at random, the survey data was considered representative of the entire population of manufacturers within those SIC Codes.

A summary of the DCP data is presented in Table 5-27. These data show that 24% of the respondents perform the solvent degreasing operation, and that 73% of these have their waste solvents contract hauled while 27% discharge their waste directly to the environment. Based upon a mean discharge rate of 49.4 lb/day (as shown in Table 5-27) and a population of 13,470 metal finishing plants, approximately 43,000 lb/day of solvent are discharged directly to the environment.

13,470 (metal finishing plants)
x 24% (percent of plants which do solvent degreasing)
3,233 (number of plants performing solvent degreasing)
x 27% (percent of degreasing operations discharging to environment)
873 (number of degreasing operations discharging to environment)
x 49.4 (mean spent solvent discharge rate (lb/day)
43,126 spent solvent discharged to environment (lb/day)

In addition, approximately 3,300,000 lb/day are contract hauled.

3,233 (number of plants doing solvent degreasing)
x73% (percent of plants whose solvent wastes are contract hauled)
2,360 (number of plants whose solvents are contract hauled)
x 118.7 mean amount of solvents hauled (lb/day)
280,143 Total spent solvents hauled (lb/day)

The total solvent consumption based upon estimates in the literature is 4.8 million lb/day.

In addition to the DCP information, plant visits provided data that identified the particular solvents used by relatively large manufacturing facilities. These data show that 43 of the 84 manufacturers visited (51%) performed solvent degreasing. Although the quantity, frequency, and disposal data are incomplete, 93% of the manufacturers who reported a disposal method either used contract hauling or reclaimed their waste solvents. Comparing this with the random survey data (73% reporting contract haulers) indicates that larger manufacturers may be more likely to haul or reclaim their spent solvents.

## TABLE 5-27
## SUMMARY OF DCP SOLVENT DEGREASING DATA

| | |
|---|---|
| DCP's Issued | 900 |
| DCP Respondents | 365 |
| DCP Respondents Performing Solvent Degreasing | 88 (24%) |
| DCP Respondents with Supportive Plant Visit Data | 14 |
| DCP Respondents Contacted via Telecon | 28 |
| Degreasers - Waste Solvent Disposal Specified | 74 |
| Degreasers - Waste Solvent Disposal Unspecified | 14 |
| Degreasers That Have Waste Solvent Contract Hauled | 54 (73%) |
| Maximum hauled | 960 lbs/day |
| Minimum hauled | 0.4 lbs/day |
| Mean | 118.7 lbs/day |
| Degreasers Discharging to Sewer or Surface | 20 (27%) |
| Maximum discharged | 399 lbs/day |
| Minimum discharged | 0.5 lbs/day |
| Mean | 49.4 lbs/day |

The results of the analysis for total toxic organics (TTO) in the raw waste from sampled plants is presented in Table 5-28. Data on TTO concentrations in various operations and waste streams at sampled plants are presented in Tables 5-29 through 5-47.

## TABLE 5-28

## TOTAL TOXIC ORGANICS (TTO) CONCENTRATIONS IN METAL FINISHING RAW WASTE

| Raw Waste TTO Concentration (mg/ℓ) | Plant ID | Raw Waste TTO Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| NA | 6019 | 0.006 | 12061-15-2 |
| NA | 6091-15-0 | 0.007 | 11108-15-2 |
| NA | 6091-15-1 | 0.007 | 20022-15-2 |
| NA | 6091-15-2 | 0.008 | 40060-15-0 |
| NA | 12061-14-0 | 0.008 | 20022-15-1 |
| NA | 12065-14-1 | 0.009 | 18538-15-5 |
| NA | 12065-15-2 | 0.009 | 40060-15-1 |
| NA | 12065-15-4 | 0.009 | 6110-15-1 |
| NA | 13042-21-1 | 0.009 | 6110-15-2 |
| NA | 17050-14-0 | 0.009 | 9052-15-0 |
| NA | 19068-14-0 | 0.010 | 11103-15-2/3 |
| NA | 19069-15-0 | 0.010 | 6110-15-0 |
| NA | 19069-15-1 | 0.011 | 2033-15-4/5 |
| NA | 19069-15-2 | 0.011 | 11108-15-0 |
| NA | 20005-21-0 | 0.011 | 21066-15-1 |
| NA | 27046-15-2 | 0.012 | 18538-15-3 |
| NA | 34050-15-0 | 0.012 | 21066-15-0 |
| NA | 34050-15-1 | 0.012 | 9052-15-2 |
| NA | 34050-15-2 | 0.013 | 11103-15-4 |
| NA | 36048-15-0/1 | 0.014 | 21066-15-3 |
| NA | 36048-15-2/3 | 0.014 | 21003-15-2 |
| NA | 36048-15-4/5 | 0.014 | 41051-15-0 |
| NA | 38040-23-0 | 0.017 | 15608-15-2 |
| NA | 38040-23-1 | 0.019 | 15608-15-0 |
| NA | 38217-23-0 | 0.020 | 20022-15-0 |
| 0 | 9025-15-0 | 0.020 | 41051-15-1 |
| 0.002 | 20083-15-0/1 | 0.021 | 12075-15-2/3 |
| 0.003 | 20083-15-2/3 | 0.022 | 4069-15-0/1 |
| 0.003 | 20083-15-4/5 | 0.023 | 41051-15-2 |
| 0.005 | 11108-15-1 | 0.028 | 12075-15-0/1 |
| 0.006 | 12061-15-0 | 0.028 | 2033-15-0/1 |

NA = Total raw waste TTO not available; total effluent TTO presented in Section VII.

TABLE 5-28 (Continued)

## TOTAL TOXIC ORGANICS (TTO) CONCENTRATIONS IN METAL FINISHING RAW WASTE

| Raw Waste TTO Concentration (mg/ℓ) | Plant ID | Raw Waste TTO Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 0.030 | 2033-15-2/3 | 0.178 | 4069-15-4 |
| 0.030 | 12061-15-1 | 0.192 | 38052-15-1 |
| 0.031 | 2032-15-2 | 0.200 | 38052-15-2 |
| 0.034 | 21003-15-0 | 0.202 | 19068-15-2 |
| 0.036 | 17061-15-1 | 0.204 | 6960-15-2/3 |
| 0.038 | 15608-15-1 | 0.224 | 38051-15-0 |
| 0.040 | 9052-15-1 | 0.251 | 9025-15-1 |
| 0.040 | 21003-15-1 | 0.259 | 38051-15-1 |
| 0.042 | 12075-15-4/5 | 0.283 | 4282-21-0 |
| 0.043 | 4071-15-0 | 0.285 | 36178-21-0 |
| 0.059 | 6960-15-4/5 | 0.289 | 9025-15-2 |
| 0.064 | 18538-14-0 | 0.326 | 36178-21-1 |
| 0.084 | 11103-15-0 | 0.364 | 30054-15-0 |
| 0.091 | 34051-15-0 | 0.400 | 27046-15-1 |
| 0.095 | 34051-15-1 | 0.426 | 27046-15-0 |
| 0.097 | 6090-14-0 | 0.473 | 6019 |
| 0.097 | 38051-15-2 | 0.477 | 17050-15-1 |
| 0.098 | 44062-15-0 | 0.486 | 6090-15-1 |
| 0.099 | 38052-15-0 | 0.769 | 30054-15-1 |
| 0.104 | 6960-15-0/1 | 0.888 | 17061-14-1 |
| 0.107 | 44062-15-2 | 1.083 | 17050-15-0 |
| 0.109 | 2032-15-5 | 1.09 | 33692-23-0 |
| 0.110 | 44062-15-1 | 1.161 | 2032-15-0 |
| 0.111 | 34051-15-2 | 1.287 | 30054-15-2 |
| 0.113 | 4069-15-2/3 | 1.619 | 28699-21-0 |
| 0.120 | 19068-15-1 | 1.938 | 20103-21-0 |
| 0.130 | 4071-15-3 | 2.005 | 36178-21-2 |
| 0.133 | 4071-15-1 | 8.466 | 6090-15-2 |
| 0.140 | 30165-21-0 | 12.866 | 20103-21-1 |
| 0.141 | 17061-15-3 | 13.50 | 33692-23-1 |

## TABLE 5-29
## TTO CONCENTRATIONS IN RAW WASTE FROM ELECTROPLATING LINES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 21051-15-0 | Wastes from nickel and zinc plating lines | 43 | .625 |
| 21051-15-1 | Wastes from nickel and zinc plating lines (after copper reduction) | 86 | .396 |
| 12075-15-0 | Rinses from tin plating lines | 8.86 | .013 |
| 12075-15-2 | Rinses from tin plating lines | 7.1 | .006 |
| 12075-15-4 | Rinses from tin plating lines | 10.5 | .008 |
| 12075-15-0 | Rinses from tin plating lines | .9 | .01 |
| 12075-15-2 | Rinses from tin plating lines | .6 | .020 |
| 12075-15-4 | Rinses from tin plating lines | .4 | 0 |
| 18538-15-3 | Acid/Alkali rinses from nickel and zinc electroplating | 69.4 | .010 |
| 18538-15-5 | Acid/Alkali rinses from nickel and zinc electroplating | 63.8 | .010 |
| 2033-15-0 | Acid rinses from nickel plating | 53.77 | .011 |
| 2033-15-2 | Acid rinses from nickel plating | 53.77 | .015 |
| 2033-15-4 | Acid rinses from nickel plating | 53.77 | .014 |
| 12065-15-1 | Parts strip & rack strip rinses on common metals plating line | 54 | .026 |
| 12065-15-2 | Parts strip & rack strip rinses on common metals plating line | 54 | .016 |
| 12065-15-4 | Parts strip & rack strip rinses on common metals plating line | 54 | .035 |
| 19069-15-0 | Rinses from common metals plating (after partial treatment of wastewater) | 42 | .282 |

## TABLE 5-29 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM ELECTROPLATING LINES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 19069-15-1 | Rinses from common metals plating (after partial treatment of wastewater) | 42 | .313 |
| 19069-15-2 | Rinses from common metals plating (after partial treatment of wastewater) | 100 | .011 |
| 21066-15-4 | Alkaline rinse from common metals plating | NA | .041 |
| 15193-21-0 | Sodium nitrate from common metals plating | NA | 1.025 |
| 12061-15-0 | Rinse water from zinc plating | 21.8 | .006 |
| 12061-15-1 | Rinse water from zinc plating | 20.9 | .007 |
| 12061-15-2 | Rinse water from zinc plating | 22.8 | .004 |
| 12061-15-0 | Rinse water from copper plating | 17.9 | .003 |
| 12061-15-1 | Rinse water from copper plating | 16.6 | .004 |
| 12061-15-2 | Rinse water from copper plating | 17.3 | .003 |
| 6960-15-0 | Acid/Alkaline rinses on common metals electroplating lines | 23 | .084 |
| 6960-15-2 | Acid/Alkaline rinses on common metals electroplating lines | 23 | .253 |
| 6960-15-4 | Acid/Alkaline rinses on common metals electroplating lines | 23 | .030 |
| 6960-15-0 | Zinc chloride plating rinse | 7 | .135 |
| 6960-15-2 | Zinc chloride plating rinse | 7 | .003 |
| 6960-15-4 | Zinc chloride plating rinse | 7 | .004 |
| 6960-15-0 | Cadmium plating rinse | 8 | .028 |
| 6960-15-2 | Cadmium plating rinse | 8 | .107 |
| 6960-15-4 | Cadmium plating rinse | 8 | .042 |

## TABLE 5-30
## TTO CONCENTRATIONS IN RAW WASTE FROM ELECTROLESS PLATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 20083-15-0 | Neutralization rinses on electroless plating line | 9 | .001 |
| 30083-15-2 | Neutralization rinses on electroless plating line | 9 | .002 |
| 20083-15-4 | Neutralization rinses on electroless plating line | 9 | .002 |
| 20083-15-0 | Rinses following catalyst application | 6 | .003 |
| 20083-15-2 | Rinses following catalyst application | 6 | .003 |
| 20083-15-4 | Rinses following catalyst application | 6 | .003 |
| 20083-15-0 | Rinses after accelerator step | 9 | .003 |
| 20083-15-2 | Rinses after accelerator step | 9 | .002 |
| 20083-15-4 | Rinses after accelerator step | 9 | .002 |
| 20083-15-0 | Electroless nickel plating rinse | 9 | .002 |
| 20083-15-2 | Electroless nickel plating rinse | 9 | .004 |
| 20083-15-4 | Electroless nickel plating rinse | 9 | .002 |
| 20083-15-0 | Electroless copper plating rinses to copper seeder | 4.6 | .003 |
| 20083-15-2 | Electroless copper plating rinses to copper seeder | NA | .003 |
| 20083-15-4 | Electroless copper plating rinses to copper seeder | 4.5 | .004 |
| 20083-15-0 | Electroless copper plating rinses not directed to copper seeder | 1.5 | .001 |
| 20083-15-2 | Electroless copper plating rinses not directed to copper seeder | 1.5 | .009 |
| 20083-15-4 | Electroless copper plating rinses not directed to copper seeder | NA | .003 |

## TABLE 5-30 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM ELECTROLESS PLATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 34051-15-0 | Electroless nickel plating line rinse water | 6.0 | .084 |
| 36048-15-0 | Alkaline rinse on electroless plating line | 1 | .040 |
| 36048-15-2 | Alkaline rinse on electroless plating line | 1 | .279 |
| 36048-15-4 | Alkaline rinse on electroless plating line | 1 | .233 |
| 36048-15-0 | Acid rinse on electroless plating line | 4 | .022 |
| 36048-15-2 | Acid rinse on electroless plating line | 4 | .011 |
| 36048-15-4 | Acid rinse on electroless plating line | 4 | .172 |
| 36048-15-0 | Descaling rinse on electroless plating line | 2 | .064 |
| 36048-15-2 | Descaling rinse on electroless plating line | 2 | .053 |
| 36048-15-4 | Descaling rinse on electroless plating line | 2 | .063 |
| 36048-15-0 | Activator rinse on electroless plating line | 1 | .087 |
| 36048-15-2 | Activator rinse on electroless plating line | 1 | .136 |
| 36048-15-4 | Activator rinse on electroless plating line | 1 | .148 |
| 36048-15-0 | Rinse after electroless nickel plating operation | 3 | .261 |
| 36048-15-2 | Rinse after electroless nickel plating operation | 3.5 | .169 |
| 36048-15-4 | Rinse after electroless nickel plating operation | 3.5 | .228 |

## TABLE 5-30 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM ELECTROLESS PLATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/l) |
|---|---|---|---|
| 2033-15-0 | Acid wastes from electroless plating line | 19.2 | .010 |
| 2033-15-2 | Acid wastes from electroless plating line | 19.2 | .007 |
| 2033-15-4 | Acid wastes from electroless plating line | 19.2 | .013 |
| 2033-15-0 | Rinse water from precious metal electroless plating | 5.05 | .035 |
| 2033-15-2 | Rinse water from precious metal electroless plating | 5.05 | .023 |
| 2033-15-4 | Rinse water from precious metal electroless plating | 5.05 | .014 |
| 12065-15-1 | Acid dip neutralizer rinse on electroless plating line | 6 | .014 |
| 12065-15-2 | Acid dip neutralizer rinse on electroless plating line | 6 | .013 |
| 12065-15-4 | Acid dip neutralizer rinse on electroless plating line | 6 | .055 |
| 12065-15-1 | Catalyst rinse from electroless plating (plastic) | 7 | .016 |
| 12065-15-2 | Catalyst rinse from electroless plating (plastic) | 7 | .030 |
| 12065-15-4 | Catalyst rinse from electroless plating (plastic) | 7 | .014 |
| 12065-15-1 | Accelerator rinse from plastic electroless plating line | 8 | .023 |
| 12065-15-2 | Accelerator rinse from plastic electroless plating line | 8 | .012 |
| 12065-15-4 | Accelerator rinse from plastic electroless plating line | 8 | .014 |

## TABLE 5-30 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM ELECTROLESS PLATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 12065-15-1 | Rinse following electroless nickel plating | 7 | .024 |
| 12065-15-2 | Rinse following electroless nickel plating | 7 | .022 |
| 12065-15-4 | Rinse following electroless nickel plating | 7 | .005 |
| 4069-15-0 | Rinse from electroless copper line | .3 | .102 |
| 4069-15-2 | Rinse from electroless copper line | .3 | .059 |

## TABLE 5-31
## TTO CONCENTRATIONS IN RAW WASTE FROM PRECIOUS METALS ELECTROPLATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 6090-14-0 | Silver-bearing raw waste | 0 | .054 |
| 19069-15-0 | Rinses from precious metals plating line | 58 | .401 |
| 19069-15-1 | Rinses from precious metals plating line | 58 | .280 |
| 2033-15-0 | DI rinses from silver electroplating | 9.2 | .035 |
| 2033-15-2 | DI rinses from silver electroplating | 9.2 | .007 |
| 2033-15-4 | DI rinses from silver electroplating | 9.2 | .006 |
| 2033-15-0 | Rinses from precious metals electroless plating | 5.05 | .035 |
| 2033-15-2 | Rinses from precious metals electroless plating | 5.05 | .023 |
| 2033-15-4 | Rinses from precious metals electroless plating | 5.05 | .014 |
| 2033-15-0 | Rinses from precious metals electroless & electroplating | 19.2 | .056 |
| 2033-15-2 | Rinses from precious metals electroless & electroplating | 19.2 | .038 |
| 2033-15-4 | Rinses from precious metals electroless & electroplating | 19.2 | .025 |
| 30054-15-0 | Rinses from gold plating | 19 | .007 |
| 30054-15-1 | Rinses from gold plating | 20 | 2.53 |
| 30054-15-2 | Rinses from gold plating | 16 | .961 |

## TABLE 5-32
## TTO CONCENTRATION IN RAW WASTE FROM ANODIZING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 20022-15-2 | Dye rinses (from anodizing plant) | 3 | .004 |
| 17050-14-0 | Raw wastes from anodizing line | 82 | .465 |
| 40060-15-1 | Alkaline cleaning rinse on anodizing line | 16 | .021 |
| 9052-15-0 | Anodizing line rinses | 55 | .009 |
| 9052-15-1 | Anodizing line rinses | 55 | .061 |
| 9052-15-2 | Anodizing line rinses | 55 | .009 |
| 41051-15-0 | Anodizing rinse water | 72 | .013 |
| 41051-15-1 | Anodizing rinse water | 72 | .018 |
| 41051-15-2 | Anodizing rinse water | 72 | .027 |

## TABLE 5-33
## TTO CONCENTRATIONS IN RAW WASTE FROM COATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 6091-15-1 | Chromating rinse | 11 | .174 |
| 34051-15-0 | Conversion coating rinse | 5 | .124 |
| 38051-15-0 | Conversion coating rinses | 78.4 | .243 |
| 38051-15-1 | Conversion coating rinses | 78.4 | .306 |
| 38051-15-2 | Conversion coating rinses | 78.4 | .084 |
| 12075-15-0 | Electrogalvanizing line rinses | 1.2 | .010 |
| 12075-15-2 | Electrogalvanizing line rinses | 1.3 | .009 |
| 12075-15-4 | Electrogalvanizing line rinses | 1.3 | .013 |
| 18538-15-3 | Appearance phosphating line rinses | 8.4 | .009 |
| 18538-15-3 | Non-appearance phosphating line rinses | 6.4 | .009 |
| 18538-14-0 | Composite of phosphating line rinses | 11.7 | .031 |
| 18538-15-5 | Composite of phosphating line rinses | 16.7 | .007 |
| 18538-15-1 | Phosphating rinse | NA | .064 |
| 18538-15-5 | Phosphating rinse | NA | .007 |
| 11103-15-1 | Rinse water from 1st rinse tank after black oxidizing process tank | 7.7 | .006 |
| 11103-15-3 | Rinse water from 1st rinse tank after light zinc phosphating process tank | 2.5 | .003 |
| 11103-15-4 | Rinse water from 1st rinse tank after zinc phosphating (auto barrel) | 2.5 | .004 |
| 11103-15-3 | Chromic acid sealer tank on zinc phosphating line | 1.0 | .007 |
| 36178 | Composite of phosphating line wastes | NA | 24.2 |

## TABLE 5-33(Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM COATING LINE RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 11103-15-0 | Conversion coating rinses | 21 | .312 |
| 11103-15-2 | Conversion coating rinses | 18 | .003 |
| 11103-15-3 | Conversion coating rinses | 18 | .006 |
| 11103-15-0 | Conversion coating rinses bypassing treatment | 38 | .022 |
| 11103-15-2 | Conversion coating rinses bypassing treatment | 33 | .018 |
| 11103-15-3 | Conversion coating rinses bypassing treatment | 33 | .021 |
| 6960-15-2 | Phosphating line cleaning rinse | 8 | .896 |
| 6960-15-4 | Phosphating line cleaning rinse | 8 | .192 |
| 6960-15-0 | Acid pickle rinse on phosphating line | 8 | .148 |
| 6960-15-2 | Acid pickle rinse on phosphating line | 8 | .031 |
| 6960-15-4 | Acid pickle rinse on phosphating line | 8 | .017 |
| 6960-15-0 | Zinc phosphating rinse | 8 | .088 |
| 6960-15-2 | Zinc phosphating rinse | 8 | .058 |
| 6960-15-4 | Zinc phosphating rinse | 8 | .049 |
| 44062-15-0 | Conversion coating line (Alodine 404) rinse water | 16 | .130 |
| 44062-15-1 | Conversion coating line (Alodine 404) rinse water | 16 | .281 |
| 44062-15-2 | Conversion coating line (Alodine 404) rinse water | 16 | .067 |
| 44062-15-0 | Conversion coating (Alodine 401) rinse water | 20 | .189 |
| 44062-15-1 | Conversion coating (Alodine 401) rinse water | 20 | .082 |
| 44062-15-2 | Conversion coating (Alodine 401) rinse water | 20 | .123 |

## TABLE 5-34
## TTO CONCENTRATIONS IN RAW WASTE FROM ETCHING AND BRIGHT DIPPING RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 6091-15-0 | Small parts caustic etch rinse | 22 | .115 |
| 6091-15-1 | Small parts caustic etch rinse | 22 | .095 |
| 6091-15-2 | Small parts caustic etch rinse | 22 | .149 |
| 20083-15-0 | Chromic acid etch rinse | 6 | .003 |
| 20083-15-2 | Chromic acid etch rinse | 6 | .001 |
| 20083-15-4 | Chromic acid etch rinse | 6 | .002 |
| 14062-21-0 | Chemical milling rinse | 27 | .496 |
| 36048-15-0 | Etching rinses | 36.5 | .027 |
| 36048-15-4 | Etching rinses | 40 | .080 |
| 2032-15-0 | Alkaline etching rinses | 9 | .003 |
| 2032-15-2 | Alkaline etching rinses | 9 | .011 |
| 2032-15-5 | Alkaline etching rinses | 8 | .006 |
| 34050-15-0 | Bright dip wastes | 18.9 | .173 |
| 34050-15-1 | Bright dip wastes | 21.1 | .032 |
| 34050-15-2 | Bright dip wastes | 21.1 | .191 |
| 4069-15-0 | Strip resist and etching rinses | 10.6 | .037 |
| 4069-15-2 | Strip resist and etching rinses | 10.6 | .270 |
| 4069-15-4 | Strip resist and etching rinses | 10.6 | .017 |
| 4282-21-0 | Rinses from chromic acid etching | 9.5 | .055 |
| 9052-15-0 | Etching rinses | 45 | .008 |
| 9052-15-1 | Etching rinses | 45 | .014 |
| 9052-15-2 | Etching rinses | 45 | .015 |

## TABLE 5-34 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM ETCHING AND BRIGHT DIPPING RINSES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 19068-15-1 | Etching rinses | 65 | .078 |
| 19068-15-2 | Etching rinses | 62 | .298 |
| 30054-15-0 | Bright dip etching rinses | 5 | .608 |
| 38052-15-0 | Bright dip chromic etching rinses | 66 | .081 |
| 38052-15-1 | Bright dip chromic etching rinses | 66 | .207 |
| 38052-15-2 | Bright dip chromic etching rinses | 66 | .248 |
| 41051-15-0 | Etching rinse waters | 24 | .016 |
| 41051-15-1 | Etching rinse waters | 24 | .022 |
| 41051-15-2 | Etching rinse waters | 24 | .010 |

## TABLE 5-35
## TTO CONCENTRATIONS IN RAW WASTE FROM CLEANING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 33617 | Small parts wash | NA | 14.5 |
| 30082 | Rinse following detergent wash of filled and sealed capacitors | .7 | .092 |
| 30082 | Detergent washing of capacitors | .002 | .86 |
| 30165-21-0 | Acid cleaning rinse | 3 | .06 |
| 30165-21-0 | Acid cleaning-muric acid concentrate | .01 | .10 |
| 44062-15-0 | Acid cleaning rinse | 34 | .062 |
| 44062-15-1 | Acid cleaning rinse | 34 | .083 |
| 44062-15-2 | Acid cleaning rinse | 34 | .117 |
| 44062-15-0 | Precleaning rinse water | 30 | .060 |
| 44062-15-1 | Precleaning rinse water | 30 | .068 |
| 44062-15-2 | Precleaning rinse water | 30 | .106 |

## TABLE 5-36
## TTO CONCENTRATIONS IN RAW WASTE FROM MACHINING, GRINDING, BARREL FINISHING, BURNISHING, AND SHEARING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 15193-21-0 | Barrel finishing rinse | 16.7 | NA |
| 15193-21-1 | Barrel finishing rinse | 16.7 | .031 |
| 30012-21-1 | Non-soluble machining oils | NA | .242 |
| 30012-21-1 | Water-soluble machining oils | NA | 4.91 |
| 3043-21-1 | Barrel finishing rinses | .07 | 1.83 |
| 31031-10-2 | Raw waste oils from tumbling | .2 | .080 |
| 31031-10-3 | Raw waste oils from grinding | .2 | .133 |
| 30166 | Raw oily wastes from machining, grinding, burnishing | NA | 2.27 |
| 30166 | Raw oily wastes from machining, grinding, burnishing | NA | 9.93 |
| 30166 | Raw oily wastes after centrifuge | NA | 1.77 |
| 30166 | Raw oily wastes after centrifuge | NA | 1.41 |
| 38217-23-0 | Machine coolants and oils, after skimmer | 88 | 1.58 |
| 38217-23-1 | Machine coolants and oils, after skimmer | 96 | 4.13 |
| 30054-15-1 | Burnishing rinses | 13 | .019 |
| 30054-15-2 | Burnishing rinses | 17 | .018 |
| 3043-21-0 | Tube shearing | 0 | 1,761 |

## TABLE 5-37
## TTO CONCENTRATIONS IN RAW WASTE FROM HEAT TREATING OPERATIONS AND QUENCH BATHS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 15193-21-0 | Hardening quench runoff | 1.7 | 1.70 |
| 15193-21-1 | Hardening quench runoff | 1.7 | .211 |
| 20005-21-0 | In-line heat treating | 0 | .020 |
| 20103-21-0 | Heat treat water and coolant quench | <.01 | .084 |
| 20103-21-1 | Heat treat water and coolant quench | <.01 | .660 |
| 14062-21-0 | Heat treating quench tank oils | 6.0 | .050 |
| 36047-23-0 | Heat treating raw wastewater | NA | .100 |
| 36119-23-0 | Heat treating quench raw wastewater | NA | .402 |
| 30012-21-1 | Alkaline bath in heat treating line | NA | .130 |
| 30012-21-1 | Dilute alkaline bath in heat treating line | NA | .130 |
| 30012-21-1 | Immunol bath in heat treating line | NA | 1.67 |
| 4282-21-0 | Heat treatment quench water | 0.4 | .319 |

## TABLE 5-38
## TTO CONCENTRATION IN WASTE FROM SOLDERING, WELDING, AND BRAZING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 36048-15-0 | Acid rinse on cleaning and solder dip line | 21.5 | .019 |
| 36048-15-3 | Acid rinse on cleaning and solder dip line | 23.5 | .046 |
| 36048-15-5 | Acid rinse on cleaning and solder dip line | 23.5 | .047 |
| 36048-15-0 | Rinses on solder wash line | 8 | .075 |
| 36048-15-3 | Rinses on solder wash line | 9 | .172 |
| 36048-15-5 | Rinses on solder wash line | 9 | .163 |
| 36048-15-0 | Solder plate line rinses | 8 | .109 |
| 18699-21-0 | Solder body rinse water | .2 | 2.63 |
| 20170-21-0 | Seam welder - roller mill collant | NA | 10.7 |
| 3043-21-0 | Curling/seam welding wastes | 12.0 | .656 |
| 30165-21-0 | Solder quench/water soluble oils | 0 | 1,043 |

# TABLE 5-39
# TTO CONCENTRATIONS IN RAW WASTE FROM PAINT STRIPPING AND SALT BATH DESCALING

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 15193-21-1 | Paint strip rinse (ethylene glycol and NaOH) | 4.2 | .428 |
| 20103-21-0 | Paint stripper concentrate | .02 | 2.20 |
| 20103-21-0 | Paint stripper rinse | <.01 | .402 |
| 28699-21-0 | Caustic paint strip rinse | NA | .140 |
| 28699-21-0 | Kolene paint strip rinse | NA | .104 |
| 28699-21-0 | Caustic paint strip concentrate | NA | 12.8 |
| 14062-21-0 | Paint stripping rinse | 1.5 | 2.00 |
| 12078-1 | Caustic rinse from paint stripping | NA | 1.61 |
| 3043-21-0 | Strip rinse | 8.0 | .318 |
| 3043-21-0 | Paint strip | 0 | .543 |
| 4892-21-0 | Salt bath descaling rinse | .20 | .107 |
| 15193-21-0 | Salt bath descaling concentrate | 0 | .502 |
| 15193-21-0 | Salt bath descaling rinse | 2.5 | .397 |
| 20103-21-0 | Kolene salt bath descaling rinse | 2.4 | .060 |
| 20103-21-1 | Kolene salt bath descaling rinse | 2.4 | .002 |
| 33617-3 | Kolene rinse | NA | .245 |
| 20005-21-0 | Kolene rinse | NA | .120 |
| 4282-21-0 | Kolene paint stripping rinse water | 47 | .214 |
| 4282-21-0 | Kolene salt bath descaling rinse | 31.6 | .460 |
| 4282-21-0 | Chromic acid and methylene chloride paint stripping rinse | 9.5 | .215 |

## TABLE 5-40
## TTO CONCENTRATIONS IN RAW WASTE FROM PAINTING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 4892-21-0 | DI rinse from EDP | 18 | .744 |
| 4892-21-0 | Influent to water curtain of water-based paint booth | .02 | .078 |
| 4892-21-0 | Discharge from solvent-based paint booth | .3 | 1.42 |
| 20005-21-0 | In-line process L-4 paint booth | .03 | .784 |
| 20005-21-0 | In-line EDP | .07 | 1.43 |
| 20005-21-0 | Final coat spray booth | .2 | 3.58 |
| 20005-21-0 | In-process V-8 paint booth | .08 | 1.62 |
| 20103-21-0 | Paint booth | .4 | 1.03 |
| 28699-21-1 | Prime spray booth | NA | 2.13 |
| 28699-21-1 | Topcoat spray | NA | 5.95 |
| 28699-21-1 | Truck prime | NA | 1.06 |
| 28699-21-1 | Truck topcoat | NA | 3.25 |
| 28699-21-1 | Electrodeposition rinse | .02 | .903 |
| 28699-21-1 | Electrodeposition permeate | .02 | 1.93 |
| 30165-21-0 | Paint booth water curtain | 0 | 2.73 |
| 18538-14-1 | Ultrafilter permeate from paint booth | NA | .935 |
| 12078-1 | Paint booth - plastic parts | NA | .728 |
| 12078-2 | Paint booth - plastic parts | NA | .096 |
| 12078-1 | Paint booth | NA | .605 |
| 12078-2 | Paint booth | NA | .105 |
| 12078-1 | Prime base coat, paint booth | NA | .769 |

## TABLE 5-40 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM PAINTING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 12078-2 | Prime base coat, paint booth | NA | .477 |
| 12078-1 | Lacquer, paint booth | NA | 4.21 |
| 12078-2 | Lacquer, paint booth | NA | 1.11 |
| 12078-1 | Urethane paint booth | NA | 5.44 |
| 15055-21-1 | EDP/DI rinse | NA | .112 |
| 15055-21-1 | Paint booth - wheels | NA | .225 |
| 15055-21-2 | Paint booth - body enamel | NA | .065 |
| 15055-21-2 | Paint booth - truck tutone | NA | .439 |
| 15055-21-2 | Paint booth - wheels | NA | .059 |
| 30012-21-1 | Paint booth water curtain | NA | 1.82 |
| 33617-2 | Painting line (2 booths) | NA | 2.69 |
| 33617-1 | Anodic EDP wastes after UF (UF perneate) | NA | .370 |
| 3043-21-1 | Paint booth | .1 | 1.50 |
| 13042-21-1 | Paint booth | 2.1 | 8.72 |
| 20170-21-0 | High solids paint booth | NA | 6.40 |
| 20170-21-1 | High solids paint booth | NA | 2.09 |
| 20170-21-0 | Powder paint booth | NA | .375 |
| 20170-21-1 | Powder paint booth | NA | .303 |
| 36178-21-0 | Paint booth, hood color | NA | 3.36 |
| 36178-21-1 | Paint booth, hood color | NA | .649 |
| 36178-21-2 | Paint booth, hood color | NA | 2.16 |
| 36178-21-0 | Paint booth, heavy chassis | NA | 4.46 |

## TABLE 5-40 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM PAINTING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 36178-21-1 | Paint booth, heavy chassis | NA | 1.62 |
| 36178-21-2 | Paint booth, heavy chassis | NA | .255 |
| 36178-21-0 | Paint booth, small parts | NA | 1.49 |
| 36178-21-1 | Paint booth, small parts | NA | .065 |
| 36178-21-2 | Paint booth, small parts | NA | .370 |
| 36178-21-0 | Paint booth, cab prime | NA | 7.11 |
| 36178-21-1 | Paint booth, cab prime | NA | 2.99 |
| 36178-21-2 | Paint booth, cab prime | NA | 3.85 |

## TABLE 5-41
## TTO CONCENTRATIONS IN RAW WASTE FROM SOLVENT DEGREASING CONDENSATES

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 15193-21-0 | Solvent degreasing condensate (water layer) | .8 | .555 |
| 15193-21-1 | Solvent degreasing condensate (water layer) | .8 | NA |
| 30012-21-1 | Condensate from carbon column on degreaser | NA | 1.85 |
| 30166 | Evaporator condensate | NA | .233 |

## TABLE 5-42
## TTO CONCENTRATIONS IN RAW WASTE FROM TESTING AND ASSEMBLY OPERATONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 20005-21-0 | Engine test water | 0 | .422 |
| 20103-21-0 | Engine test cooling water | 5 | .090 |
| 30166 | Engine test wash water | NA | .024 |
| 30166 | Engine test oily waste | NA | .525 |
| 30166 | Magna Flux wash | NA | .071 |
| 33617 | Wash testing | NA | .422 |
| 30165-21-0 | Leak testing (heating core element and radiator) | .6 | .060 |
| 6019-21-0 | Zyglo spray rinses | 2.8 | .031 |
| 6019-21-0 | Countercurrent rinse tank on Zyglo spray line | .1 | 2.48 |
| 6019-21-0 | Countercurrent rinse tank on Zyglo spray line | .1 | .236 |
| 6019-21-1 | Zyglo emulsifier rinses | 2.8 | .031 |
| 6019-21-1 | Zyglo emulsifier rinses | 2.8 | 3.11 |
| 4282-21-0 | Zyglo rinse | 2 | .484 |

## TABLE 5-43
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 13041-22-0 | Raw waste oils (spent oils) | NA | 3.0 |
| 12095-22-0 | Raw waste oils | NA | 6.14 |
| 12095-22-1 | Raw waste oils | NA | 3.15 |
| 12095-22-2 | Raw waste oils | NA | 6.50 |
| 28125-22-0 | Raw oily waste from can wash rinses | NA | .558 |
| 28125-22-1 | Raw oily waste from can wash rinses | NA | .292 |
| 40836-22-0 | Raw oily waste | NA | 21.5 |
| 41097-22-0 | Oily waste from lubricant spills | NA | .111 |
| 41097-22-1 | Oily waste from lubricant spills | NA | .200 |
| 41097-22-2 | Oily waste from lubricant spills | NA | 2.14 |
| 40070-22-0 | Raw oily waste (die cast cooling water) | NA | .538 |
| 40070-22-1 | Raw oily waste (die cast cooling water) | NA | .858 |
| 40070-22-2 | Raw oily waste (die cast cooling water) | NA | .853 |
| 41097-22-0 | Oily waste from 1st stage wash overflows | NA | .039 |
| 41097-22-1 | Oily waste from 1st stage wash overflows | NA | .015 |
| 41097-22-2 | Oily waste from 1st stage wash overflows | NA | .020 |
| 13324-21-0 | Raw oily wastes (wash water) | NA | 2.40 |

## TABLE 5-43 (Continued)
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 41115-22-0 | Raw oily wastes (car rinses) | NA | 1.14 |
| 41115-22-0 | Raw oily wastes (car rinses) | NA | 3.31 |
| 41115-22-0 | Raw oily wastes (car rinses) | NA | 1.19 |
| 1058-22-0 | Raw oily waste (spent mineral and emulsified oil) | 4.83 | 15.0 |
| 1058-22-1 | Raw oily waste (spent mineral and emulsified oil) | 4.83 | 110 |
| 1058-22-2 | Raw oily waste (spent mineral and emulsified oil) | 4.83 | 6.42 |
| 13324-22-0 | Raw oily wastes (wash water) | 9.94 | 2.40 |
| 19462-23-1 | Oily wastestream after screen and filter | NA | 1,921 |
| 30698-21-0 | Concentrated oily waste tank (prior to treatment) | NA | 7.90 |
| 6019-21-0 | Soluble cutting oils - influent totreatment | 1.1 | 24.4 |
| 30012-21-0 | Water soluble machining oils | 1.55 | 4.91 |
| 30516-23-0 | Raw oily waste (coolants and machining oils) | 0.16 | 58.1 |
| 33617-22-0 | Waste machine oil | NA | 49.8 |
| 30698-21-0 | Oily waste from drawing, welding, and shearing | NA | .289 |
| 33692-23-0 | Raw oily waste from machining, grinding, barrel finishing | NA | 1.09 |

## TABLE 5-43 (Continued)
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 33617-22-1 | Waste oil | NA | 4219 |
| 3043-21-0 | Tube shearing | 1.75 | 1761 |
| 20170-21-0 | Seam welder - roller mill coolant | NA | 10.7 |
| 30166-21-0 | Raw oily waste from machining, grinding, burning | 2.21 | 9.93 |
| 30166-21-0 | Engine test oily waste | 2.21 | .525 |
| 31031-10-3 | Raw waste oils from grinding | 0.2 | .133 |
| 15193-21-0 | Oily waste holding tank | 3.6 | 802 |
| 15193-21-1 | Machining oils | NA | 7.83 |
| 15193-21-1 | Salt bath descaling concentrate | 0 | .502 |
| 20103-21-1 | Heat treatment coolant quench | 7.42 | .659 |
| 20103-21-0 | Oily waste after cooker | 7.42 | 2.33 |
| 20103-21-0 | Heat treatment coolant quench | 7.42 | .084 |
| 38217-23-0 | Machine coolants and oils, after skimmer | 88 | 1.58 |
| 38217-23-1 | Machine coolants and oils, after skimmer | 96 | 4.13 |
| 33692-23-1 | Raw oily waste | NA | 13.5 |

## TABLE 5-43 (Continued)
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 13041-22-0 | Oily wastestream after emulsion breaking | NA | 1,037 |
| 13041-22-0 | Oily wastestream after emulsion breaking | NA | 14.3 |
| 13041-22-0 | Oily wastestream after emulsion breaking | NA | 4.84 |
| 13041-22-0 | Oily wastestream after emulsion breaking and UF | NA | 14.8 |
| 13041-22-0 | Oily wastestream after emulsion breaking and UF | NA | 13.0 |
| 13041-22-0 | Oily wastestream after emulsion breaking and UF | NA | 30.8 |
| 12095-22-0 | Oily wastestream after emulsion breaking and clarification | NA | .996 |
| 12095-22-0 | Oily wastestream after emulsion breaking and clarification | NA | .800 |
| 12095-22-0 | Oily wastestream after emulsion breaking and clarification | NA | .480 |
| 28125-22-1 | Oily wastestream after oil skimmer | NA | .767 |
| 28125-22-0 | Oily wastestream after clarification | NA | .707 |
| 28125-22-1 | Oily wastestream after clarification | NA | 1.08 |
| 28125-22-0 | Oily wastestream after filtration | NA | .635 |
| 28125-22-1 | Oily wastestream after filtration | NA | .390 |
| 30516-23-0 | Oily wastestream (ultrafilter permeate) | NA | 4.54 |
| 30516-23-1 | Oily wastestream (ultrafilter permeate) | NA | 5.51 |
| 40070-22-0 | Oily wastestream after oil skimmer | NA | .763 |
| 40070-22-0 | Oily wastestream after oil skimmer | NA | .395 |
| 40070-22-0 | Oily wastestream after oil skimmer | NA | 3.24 |

## TABLE 5-43 (Continued)
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 40836-22-0 | Oily wastestream after emulsion breaking | NA | 8.62 |
| 41097-22-0 | Oily wastestream after emulsion breaking and DAF | NA | .045 |
| 41097-22-1 | Oily wastestream after emulsion breaking and DAF | NA | .125 |
| 41097-22-2 | Oily wastestream after emulsion breaking and DAF | NA | .560 |
| 41097-22-1 | Oily wastestream after emulsion breaking, DAF, and vacuum filter | NA | 23.0 |
| 41115-22-0 | Oily wastestream after oil skimmer | NA | .655 |
| 41115-22-0 | Oily wastestream after oil skimmer | NA | 1.64 |
| 41115-22-0 | Oily wastestream after oil skimmer | NA | .905 |
| 1058-22-0 | Oily wastestream prior to emulsion breaking | NA | 2.77 |
| 1058-22-0 | Oily wastestream after emulsion breaking | NA | 1.43 |
| 1058-22-0 | Oily wastestream prior to polishing pond | NA | .364 |
| 1058-22-0 | Oily wastestream after polishing pond | NA | .323 |
| 1058-22-1 | Oily wastestream prior to polishing pond | NA | 1.34 |
| 1058-22-1 | Oily wastestream after polishing pond | NA | .278 |
| 1058-22-2 | Oily wastestream prior to polishing pond | NA | .308 |
| 1058-22-2 | Oily wastestream after polishing pond | NA | 3.79 |
| 13324-21-0 | Oily wastestream after oil/water separator | NA | 12.0 |
| 13324-21-0 | Oily wastestream after ultrafiltration and oil/water separator | NA | 1.48 |

## TABLE 5-43 (Continued)
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 19462-23-1 | Oily wastestream after screen and filter | NA | 1.92 |
| 19462-23-1 | Oily wastestream after centrifuge | NA | 1.42 |
| 19462-23-1 | Oily wastestream after ultrafiltration | NA | .234 |
| 30698-21-0 | Oily wastestream after batch treatment tank | NA | .133 |
| 31032-15-0 | Raw waste (rinses from FET and PCB) | NA | .016 |
| 31032-15-1 | Raw waste (rinses from FET and PCB) | NA | .007 |
| 31032-15-2 | Raw waste (rinses from FET and PCB) | NA | .004 |
| 31032-15-0 | Oily wastestream after UF, RO | NA | .011 |
| 31032-15-1 | Oily wastestream after UF, RO | NA | .006 |
| 31032-15-2 | Oily wastestream after UF, RO | NA | .010 |
| 33692-23-0 | Oily wastestream after clarifier | NA | .928 |
| 33692-23-0 | Oily wastestream after DAF | NA | 1.19 |
| 33692-23-0 | Oily wastestream after final settling tank | NA | .823 |
| 33692-23-1 | Oily wastestream after clarifier | NA | .720 |
| 33692-23-1 | Oily wastestream after DAF | NA | .795 |
| 33692-23-1 | Oily wastestream after final settling tank | NA | .433 |
| 38040-23-0 | Treated oily wastes (API settler, bag filter, cartridge filter, P.O., and carbon filter) | NA | .288 |
| 38040-23-1 | Treated oily wastes (API settler, bag filter, cartridge filter, P.O., and carbon filter) | NA | .377 |
| 6019-21-0 | Effluent from treatment tank | 1.1 | 9.31 |

## TABLE 5-43 (Continued)
## TTO CONCENTRATIONS IN TREATED OILY WASTESTREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 14062-21-0 | Soluble oils after centrifuge | .9 | 21.9 |
| 15193-21-0 | Permeate from UF on soluble oils | 2.75 | 80.8 |
| 15193-21-1 | Permeate from UF on soluble oils | 2.2 | 4.61 |

## TABLE 5-44
## TTO CONCENTRATIONS IN RAW WASTE FROM SEGREGATED CHROMIUM STREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 4071-15-0 | Chromium waste from PCB manufacture | .7 | .104 |
| 4071-15-1 | Chromium waste from PCB manufacture | .01 | .190 |
| 4071-15-3 | Chromium waste from PCB manufacture | .01 | .036 |
| 34050-15-0 | Chromium plating line rinse water | NA | .337 |
| 34050-15-1 | Chromium plating line rinse water | NA | .281 |
| 34050-15-2 | Chromium plating line rinse water | NA | .120 |
| 38051-15-0 | Chromium-bearing wastes | 20.3 | .151 |
| 38051-15-1 | Chromium-bearing wastes | 20.3 | .078 |
| 38051-15-2 | Chromium-bearing wastes | 20.3 | .147 |
| 12075-15-0 | Chromium-plating line rinses | 4.5 | .006 |
| 12075-15-3 | Chromium-plating line rinses | 2.8 | .014 |
| 12075-15-5 | Chromium-plating line rinses | .8 | .008 |
| 18538-15-3 | Chromium-bearing wastes | 36.2 | .006 |
| 18538-15-5 | Chromium-bearing wastes | 30.6 | .016 |
| 11103-15-0 | Acidic and chromic wastes from electroplating | 23 | .014 |
| 11103-15-2 | Acidic and chromic wastes from electroplating | 25 | .004 |
| 11103-15-4 | Acidic and chromic wastes from electroplating | 25 | .015 |
| 21066-15-0 | Chromic wastes from electroplating | 1 | .010 |
| 21066-15-1 | Chromic wastes from electroplating | 1 | .015 |
| 21066-15-3 | Chromic wastes from electroplating | 1 | .010 |
| 6960-15-0 | Mild acid rinse and chromic rinse | 15 | .053 |

## TABLE 5-44 (Continued)
## TTO CONCENTRATIONS IN RAW WASTE FROM SEGREGATED CHROMIUM STREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 6960-15-2 | Mild acid rinse and chromic rinse | 15 | .102 |
| 6960-15-4 | Mild acid rinse and chromic rinse | 15 | .008 |
| 19068-15-1 | Chromate rinses and chromic acid rinses | 35 | .199 |
| 19068-15-2 | Chromate rinses and chromic acid rinses | 38 | .046 |

## TABLE 5-45
## TTO CONCENTRATIONS IN RAW WASTE FROM SEGREGATED CYANIDE STREAMS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 11103-15-0 | Cyanide wastes from electroplating lines | 11 | .012 |
| 11103-15-2 | Cyanide wastes from electroplating lines | 18 | .010 |
| 11103-15-4 | Cyanide wastes from electroplating lines | 18 | .005 |
| 21066-15-0 | Cyanide wastes from electroplating lines | NA | .015 |
| 21066-15-1 | Cyanide wastes from electroplating lines | NA | .018 |
| 21066-15-3 | Cyanide wastes from electroplating lines | NA | .009 |

# TABLE 5-46
# TTO CONCENTRATIONS IN RAW WASTE FROM AIR SCRUBBERS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 4069-15-0 | Air scrubber discharge from all wet operations of PCB manufacture (stripping, etching, sensitizing, multilayer operations) | 10 | .017 |
| 4069-15-2 | Air scrubber discharge from all wet operations of PCB manufacture (stripping, etching, sensitizing, multilayer operations) | 10 | .053 |
| 4069-15-4 | Air scrubber discharge from all wet operations of PCB manufacture (stripping, etching, sensitizing, multilayer operations) | 10 | .032 |
| 2033-15-0 | Wet scrubber wastewater | NA | .007 |
| 2033-15-2 | Wet scrubber wastewater | NA | .012 |
| 2033-15-4 | Wet scrubber wastewater | NA | .019 |
| 11103-15-0 | Conversion coating air scrubber | 3 | .008 |
| 11103-15-0 | Electroplating air scrubber | 2 | .007 |
| 18538-15-1 | Phosphating condensate (similar to air scrubber discharge) collected from both phosphating lines process tanks. | NA | .003 |
| 18538-15-5 | Phosphating condensate (similar to air scrubber discharge) collected from both phosphating lines process tanks. | NA | .003 |
| 20022-15-0 | Air scrubber discharge from anodizing operations | 3 | .009 |
| 20022-15-1 | Air scrubber discharge from anodizing operations | 4 | .009 |
| 20022-15-1 | Air scrubber discharge from anodizing operations | 3 | .004 |
| 33617-4 | Kolene air scrubber blowdown | NA | .221 |

## TABLE 5-47
## TTO CONCENTRATIONS IN NON-METAL FINISHING OPERATIONS

| Plant ID | Description | % Total Flow | TTO Concentration (mg/ℓ) |
|---|---|---|---|
| 18538-14-0 | Composite of rinses on procelain enemaling pickle line | NA | .015 |
| 33617-7 | Plastics processing effluent | NA | 2.69 |
| 13042-21-1 | Metal impregnation rinse tank overflow | NA | .043 |
| 6097-15-0 | Rinsewater from grinding and polishing of plate glass | 70.5 | .032 |
| 6097-15-1 | Rinsewater from grinding and polishing of plate glass | 68.5 | .015 |
| 6097-15-2 | Rinsewater from grinding and polishing of plate glass | 70.5 | .181 |
| 6097-15-0 | Rinsewater from beveling and grinding of lens | 7.9 | .406 |
| 6097-15-1 | Rinsewater from beveling and grinding of lens | 8.7 | .100 |
| 6097-15-2 | Rinsewater from beveling and grinding of lens | 6.0 | .259 |

# SECTION VI
# SELECTION OF POLLUTANT PARAMETERS

## INTRODUCTION

This section presents the pollutant parameters selected for limitation in the Metal Finishing Category. These parameters were chosen from the pollutant parameters identified in Section V from:

- Laboratory analysis results of samples taken during screening and verification visits.
- Responses received from the data collection portfolios containing pollutant parameter questionnaires.
- Technical information and data received from chemical suppliers, equipment manufacturers, and previous studies.

Following are an explanation of the rationale for selection and exclusion of individual pollutant parameters and a presentation of the parameters selected for each waste type.

## SELECTION RATIONALE

The selection of pollutant parameters for regulation was based both on sampling analysis data and information received in the data collection portfolios. The sampling analysis data and a summary of the data collection portfolios are presented in Section V.

The parameters available for selection were grouped into four categories: toxic organic pollutants, toxic inorganic pollutants, non-toxic metals, and other pollutants. The selection of parameters from each of these groups is discussed below.

### TOXIC ORGANIC POLLUTANTS

The toxic organic pollutants are listed in Table 3-2. During the analysis of the wastewater samples, it was found that a variety of toxic organics could be present in both common metals and oily waste streams. It was also found that the types of toxic organics detected varied from plant to plant. Because this large variety of toxic organics is present in the Metal Finishing Category and because of the difficulty involved with regulating such a large number of pollutants, a total toxic organics (TTO) heading has been established which covers all the toxic organic pollutants.

It was recognized that some of the toxic organics should rarely be present in metal finishing wastewaters. For example, parameters either were not detected through sampling or were found upon rare occasion in low concentrations. There is no known reason why pesticide type parameters should be present within the wastewater streams generated by the Metal Finishing Category. However, the availability of the certification procedure eliminates the need to monitor for pollutants not likely to be present and focuses the identification of toxic organics even for those rarely used.

Total toxic organics are present in the total raw waste of sampled plants in concentrations ranging from zero to 13.5 mg/ℓ as shown in Table 5-28. TTO concentrations in the wastewater from various metal finishing operations is presented in Tables 5-29 through 5-47 in Section V.

Cyanide, which is commonly used within the Metal Finishing Category (as evidenced by the 298 mg/ℓ mean concentration of total cyanide in the cyanide raw waste stream), was an obvious selection as a pollutant parameter.

Of the toxic metals, cadmium, chromium, copper, lead, nickel, silver, and zinc were found at significant concentration levels in the raw waste. Table 5-16 shows the concentrations of toxic metals that were found in the raw waste discharged to end-of-pipe treatment. Consequently, cadmium, chromium, copper, lead, nickel, silver, and zinc have been selected as pollutant parameters to be regulated. Other toxic metals and asbestos were not regulated because they either were present only in insignificant concentrations, or present only at a small number of sources and effectively controlled by regulating other parameters.

## NON-TOXIC METALS

The non-toxic metals group contains those metals which were analyzed but were not listed among the 126 toxic pollutants. Table 5-18 presents the non-toxic metals, and their flow proportioned mean concentrations in the total metal finishing raw waste. Because of the priority given to the control of toxic pollutants, these non-toxic metals were not regulated. These parameters would have to be found at high concentrations with high frequency to be selected for regulations.

## OTHER POLLUTANTS

There are other pollutant parameters which are normally controlled to maintain water quality. Total suspended solids (TSS) is a traditional pollutant parameter which can serve to control the discharge of harmful pollutants. Oil and grease is a traditional pollutant parameter which can cause odor and taste problems with water and kill aquatic organisms. As evidenced by its mean concentration in the oily wastes raw waste stream (40,700 mg/ℓ), oil and grease is a significant pollutant parameter in the Metal Finishing Category.

## POLLUTANT PARAMETERS SELECTED

Table 6-1 presents the pollutant parameters selected for regulation for the Metal Finishing Category.

## TABLE 6-1

## POLLUTANT PARAMETERS SELECTED FOR REGULATION

Cadmium
Chromium, total
Copper
Lead
Nickel
Silver
Zinc
Cyanide, total (alternative - cyanide, amenable)
Total Suspended Solids
Oil and Grease
Total Toxic Organics
pH

# SECTION VII
# CONTROL AND TREATMENT TECHNOLOGY

## INTRODUCTION

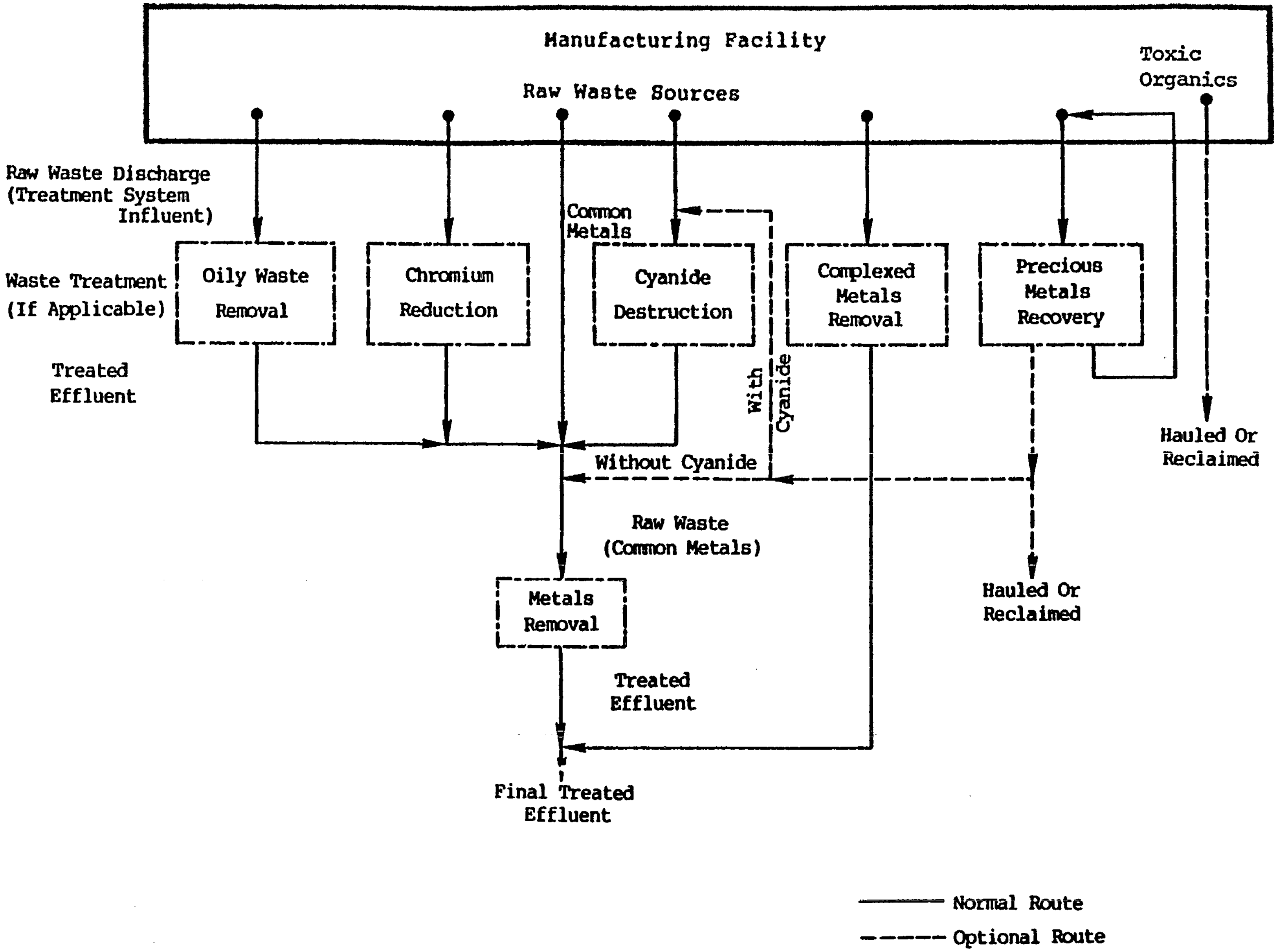
This section describes the treatment techniques currently used or available to remove or recover wastewater pollutants normally generated by the Metal Finishing Category. Included is a discussion of individual wastewater treatment technologies and in-plant control and treatment technologies. Pertinent treatment and control technology is discussed specifically for each of the seven types of raw waste that are present. The technologies presented are applicable to the metal finishing industry for both direct and indirect dischargers and reflect the entire metal finishing data base.

The raw wastes for the Metal Finishing Category were initially subdivided into two constituent types, inorganic and organic wastes. These were then further subdivided into the specific types of waste that occur in each of these two major areas and grouped into the following seven waste types:

| MAJOR SUBDIVISION | WASTE TYPE |
|---|---|
| INORGANIC WASTES | 1. Common Metals<br>2. Precious Metals<br>3. Complexed Metals<br>4. Hexavalent Chromium |
| ORGANIC WASTES | 5. Cyanide<br>6. Oils<br>7. Toxic Organics |

Treatment for each of these seven waste types is shown schematically in Figure 7-1. This schematic illustrates the types of treatment that are needed for wastes of each type. The specific treatment required for these wastes is as follows:

| WASTE TYPE | PRIMARY TREATMENT | FINAL TREATMENT |
|---|---|---|
| Common Metals | | Metals Removal |
| Precious Metals | Precious Metals Recovery | Optional (depending on other wastes present) |
| Complexed Metals | | Complexed Metals Removal |
| Hexavalent Chromium | Chromium Reduction | Metals Removal |
| Cyanide | Cyanide Destruction | Metals Removal |
| Oils | Oily Waste Removal | Metals Removal |
| Toxic Organics | | Haul or Reclaim |



Note: Discharge from precious metals recovery may be hauled in alternative ways, depending on the recovery method in use.

FIGURE 7-1

WASTE TREATMENT SCHEMATIC

The wastewater stream segregation shown in Figure 7-1 is current common practice in the Metal Finishing Category, as discussed in Section IV. This stream segregation allows the recovery of precious metals, the reduction of hexavalent chromium to trivalent chromium, the destruction of cyanide, and the removal/ recovery of oils prior to the removal of the common metals that are also present in these streams. Segregation of these streams reduces the flow rate of wastewater to be treated in each component and accordingly reduces the cost of this primary treatment. The complexed metals wastewaters require segregated treatment to preclude the complexing of other metal wastes in the treatment system.

This section is divided into subsections with the following headings: Applicability of Treatment Technologies, Treatment of Common Metals Wastes, Treatment of Precious Metals Wastes, Treatment of Complexed Metals Wastes, Treatment of Hexavalent Chromium Wastes, Treatment of Cyanide Wastes, Treatment of Oily Wastes, Treatment of Toxic Organics, Treatment of Sludges, In-Process Control Technology, and Statistical Analysis. The Applicability of Treatment Technologies Subsection defines specific applications of individual treatment technologies and references the location of their respective descriptions within this section.

The subsections that discuss treatment present three specific levels of treatment options for common metals. The organization of each of these subsections is such that the Option 1 system is described, the particular treatment components that are applicable to the first level option (Option 1) for common metals are described, and their performance is presented. Then, the Option 1 performance level is presented. The information relative to Options 2 and 3 is developed and discussed in a similar manner. The subsections that discuss treatment for other waste types present only a single option because only one level of treatment is clearly superior based on performance and demonstration status. Several alternatives to the Option 1 system are presented for the oily waste streams.

The In-Process Control Technology Subsection discusses techniques for process water usage reduction, alternative processes, integrated water treatment, and good housekeeping.

## APPLICABILITY OF TREATMENT TECHNOLOGIES

This subsection identifies the component technologies that are applicable for the treatment of raw wastes that are generated by industries that perform the metal finishing operations described in Section III. Table 7-1 lists the component technologies, shows their specific application to the Metal Finishing Category, and indicates the page on which each is described. Table 7-2 illustrates the applicability of each technology to each of the waste types.

Each treatment component is functionally described and discussions are presented of the application, performance, and the demonstration status of each component. In some instances the technique described has been demonstrated in another industry to successfully remove a particular waste constituent. Wherever the waste characteristics are similar to that for a Metal Finishing Category wastewater type, performance data have been shown to better illustrate the capabilities of the treatment techniques being described.

## TABLE 7-1
## INDEX AND SPECIFIC APPLICATION OF TREATMENT TECHNOLOGIES

| Technology | Application or Potential Application to Metal Finishing | Page |
|---|---|---|
| Aerobic Decomposition | Oil breakdown and organics removal | VII-221 |
| Carbon Adsorption | Removal of trace metals and organics | VII-209 |
| Centrifugation | Sludge dewatering, oil removal | VII-185, 238 |
| Chemical Reduction | Treatment of chromic acid and chromates | VII-115 |
| Chemical Reduction-Precipitation/ Sedimentation | Removal of Complexed Metals | VII-113 |
| Coalescing | Oil removal | VII-180 |
| Diatomaceous Earth Filtration | Metal hydroxides and suspended solids removal | VII-53 |
| Electrochemical Oxidation | Destruction of free cyanide and cyanates | VII-151 |
| Electrochemical Reduction | Reduction of chromium from metal finishing and cooling tower blowdowns | VII-120 |
| Electrochemical Regeneration | Conversion of trivalent chromium to hexavalent valence | VII-123 |
| Electrolytic Recovery | Recovery of precious and common metals | VII-102 |
| Emulsion Breaking | Breakdown of emulsified oil mixtures | VII-162 |
| Evaporation | Concentration and recovery of process chemicals | VII-76, 100<br>124, 153 |
| Ferrous Sulfate ($FeSO_4$)-Precipitation/Sedimentation | Removal of complexed metals and cyanides | VII-114, 153 |
| Flotation | Suspended solids and oil removal | VII-93, 183 |
| Granular Bed Filtration | Solids polishing of settling tank effluent | VII-48 |
| Gravity Sludge Thickening | Dewatering of clarifier underflow | VII-230 |

### TABLE 7-1 (Cont.)
### INDEX AND SPECIFIC APPLICATION OF TREATMENT TECHNOLOGIES

| Technology | Application or Potential Application to Metal Finishing | Page |
|---|---|---|
| High pH Precipitation/Sedimentation | Removal of complexed metals | VII-112 |
| Hydroxide Precipitation | Dissolved metals removal | VII-8 |
| Insoluble Starch Xanthate | Dissolved metals removal | VII-88 |
| Integrated Adsorption | Emulsified oils and paints removal | VII-186 |
| Ion Exchange | Recovery or removal of dissolved metals | VII-80, 102 114, 124 |
| Membrane Filtration | Dissolved metals and suspended solids removal | VII-98, 113 |
| Oxidation by Chlorine | Destruction of cyanides and cyanates | VII-126 |
| Oxidation by Hydrogen Peroxide | Cyanide destruction and metals removal | VII-150 |
| Oxidation by Ozone | Destruction of cyanides and cyanates | VII-144, 219 |
| Oxidation by Ozone w/UV Radiation | Destruction of cyanides and cyanates | VII-148 |
| Peat Adsorption | Dissolved metals removal | VII-86 |
| Pressure Filtration | Sludge dewatering or suspended solids removal | VII-232 |
| Resin Adsorption | Removal of organics | VII-218 |
| Reverse Osmosis | Removal of dissolved salts for water reuse | VII-178, 217 |
| Sedimentation | Suspended solids and metals removal | VII-10 |
| Skimming | Free oil removal | VII-167 |
| Sludge Bed Drying | Sludge dewatering | VII-246 |
| Sulfide Precipitation | Dissolved metals removal | VII-89, 153 |
| Ultrafiltration | Oil and suspended solids removal and paint purification | VII-241 |
| Vacuum Filtration | Sludge dewatering | VII-235 |

## TABLE 7-2
## APPLICABILITY OF TREATMENT TECHNOLOGIES TO RAW WASTE TYPES

| Technology | Common Metals | Precious Metals | Complexed Metals | Chromium Bearing | Cyanide Bearing | Oily Wastes | Toxic Organics | Sludge | In-Process |
|---|---|---|---|---|---|---|---|---|---|
| Aerobic Decomposition | | | | | | x | x | | |
| Carbon Adsorption | x | x | x | | | x | x | | |
| Centrifugation | | | | | | x | | x | |
| Chemical Reduction | | | | x | | | | | |
| Coalescing | | | | | | x | | | |
| Diatomaceous Earth Filtration | x | x | x | | | x | x | | |
| Electrochemical Oxidation | | | | | x | | | | |
| Electrochemical Reduction | | | | x | | | | | |
| Electrochemical Regeneration | | | | x | | | | | x |
| Electrodialysis | | | | x | | | | | x |
| Electrolytic Recovery | x | x | | | | | | | x |
| Emulsion Breaking | | | | | | x | | | |
| Evaporation | x | x | x | x | x | | | | x |
| Flotation | x | | x | | | x | | | |
| Granular Bed Filtration | x | x | x | | | | | | |
| Gravity Sludge Thickening | | | | | | | | x | |
| High pH Precipitation | | | x | | | | | | |
| Hydroxide Precipitation | x | x | x | | x | | | | |
| Insoluble Starch Xanthate | x | x | x | | | | | | |
| Ion Exchange | x | x | x | x | x | | | | x |
| Membrane Filtration | x | x | x | | | | | | |
| Oxidation by Chlorine | | | | | x | | | | |
| Oxidation by Hydrogen Peroxide | | | | | x | | | | |
| Oxidation by Ozone | | | | | x | | | | |
| Oxidation by Ozone with UV Radiation | | | | | x | | | | |
| Peat Adsorption | x | x | x | | | | | | |
| Pressure Filtration | x | x | x | | | | | | |
| Resin Adsorption | | | | | | x | x | | |
| Reverse Osmosis | x | x | x | | | x | x | | x |
| Sedimentation | x | x | x | | | | | | |
| Skimming | | | | | | x | | | |
| Sludge Bed Drying | | | | | | | | x | |
| Sulfide Precipitation | x | x | x | x | | | | | |
| Ultrafiltration | x | x | x | | | x | x | | x |
| Vacuum Filtration | | | | | | | | x | |

## TREATMENT OF COMMON METALS WASTES

### INTRODUCTION

Common metals wastes can be generated in the Metal Finishing Category by the unit operations that have previously been described. The methods used to treat these wastes are discussed in this section and fall into two groupings - recovery techniques and solids removal techniques. Recovery techniques are treatment methods used for the purpose of recovering or regenerating process constituents which would otherwise be lost in the wastewater or discarded. Included in this group are evaporation, ion exchange, electrolytic recovery, electrodialysis, and reverse osmosis. Solids removal techniques are employed to remove metals and other pollutants from process wastewaters to make these waters suitable for reuse or discharge. These methods include hydroxide and sulfide precipitation, sedimentation, diatomaceous earth filtration, membrane filtration, granular bed filtration, sedimentation, peat adsorption, insoluble starch xanthate treatment, and flotation.

This subsection presents the treatment systems that are applicable to common metals removal for treatment Options 1, 2, and 3; describes the treatment techniques applicable to each option; and defines the effluent performance levels for each of those options. Option 1 common metals removal incorporates hydroxide precipitation and sedimentation. Option 2 for common metals removal consists of the addition of filtration devices to the Option 1 system. The Option 3 treatment system for common metals wastes consists of the Option 1 end-of-pipe treatment system with the addition of in-plant controls for cadmium. Alternative treatment techniques that can be applied to provide Option 1, 2, or 3 system performance are described following the Option 3 discussion.

### TREATMENT OF COMMON METAL WASTES - OPTION 1

The Option 1 system for the treatment of common metals wastes consists of hydroxide precipitation followed by sedimentation, as is shown in Figure 7-2. This system accomplishes the end-of-pipe metals removal from all common metals bearing wastewater streams that are present at a facility. The recovery of precious metals, the reduction of hexavalent chromium, the removal of oily wastes, and the destruction of cyanide must be accomplished prior to common metals removal, as was shown in Figure 7-1.

Cyanide bearing wastes must undergo oxidation to destroy the cyanide in the wastewater. Cyanide, as well as being a highly toxic pollutant, will complex metals such as copper, cadmium, and zinc and prevent efficient removal of these metals in the

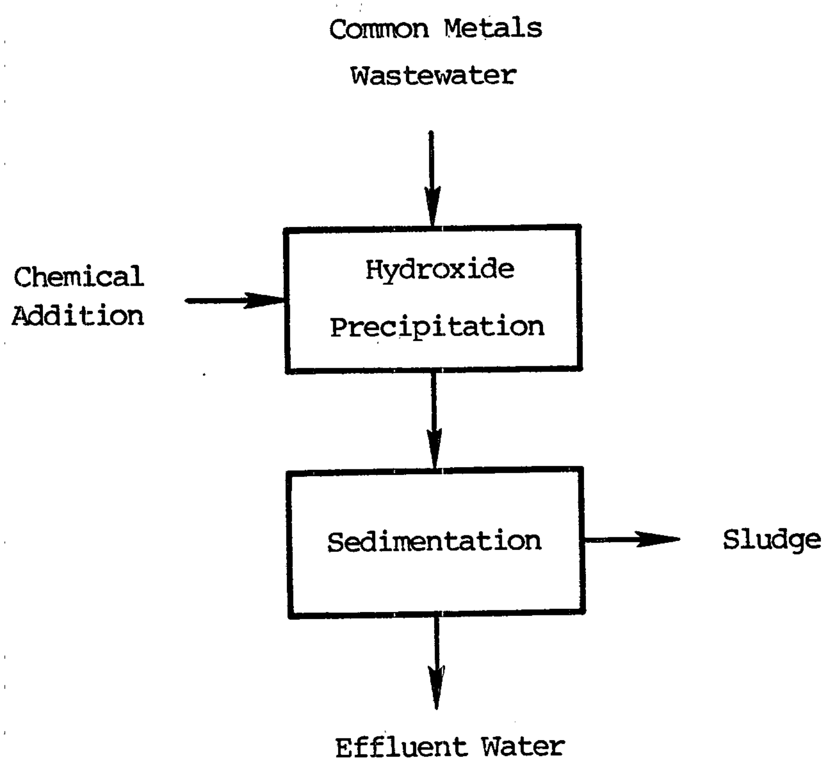


FIGURE 7-2

TREATMENT OF COMMON METALS WASTES - OPTION 1 solids removal device. Similarly, complexed metal wastes must be kept segregated and treated separately to avoid complexing metals in the primary solids removal device. Complexed metal wastes should be treated in a separate solids removal device such as a membrane filter or a high pH clarifier. The specific techniques for the treatment of all other waste types, a description of the three levels of treatment options for each waste type and the performance for all levels of these options are presented in subsequent subsections.

The treatment techniques incorporated in the Option 1 common metals waste treatment system include pH adjustment, hydroxide precipitation, flocculation, and sedimentation. Sedimentation may be carried out with equipment such as clarifiers, tube settlers, settling tanks, and sedimentation lagoons, or it may be replaced by various filtration devices preceded by hydroxide precipitation. The following paragraphs describe the hydroxide precipitation and sedimentation techniques that are employed for the Option 1 common metals treatment system.

## Hydroxide Precipitation

Dissolved heavy metal ions are often chemically precipitated as hydroxides so that they may be removed by physical means such as sedimentation, filtration, or centrifugation. Reagents commonly used to effect this precipitation include alkaline compounds such as lime and sodium hydroxide. Calcium hydroxide precipitates trivalent chromium and other metals as metal hydroxides and precipitates phosphates as insoluble calcium phosphate. These treatment chemicals may be added to a flash mixer or rapid mix tank, or directly to the sedimentation device. Because metal hydroxides tend to be colloidal in nature, coagulating agents may also be added to facilitate settling. Figure 7-3 illustrates typical chemical precipitation equipment as well as the associated sedimentation device.

After the solids have been removed, final pH adjustment may be required to reduce the high pH created by the alkaline treatment chemicals.

### Application

Hydroxide precipitation is used in metal finishing for precipitation of dissolved metals and phosphates. It can be utilized in conjunction with a solids removal device such as a clarifier or filter for removal of metal ions such as iron, lead, tin, copper, zinc, cadmium, aluminum, mercury, manganese, cobalt, antimony, arsenic, beryllium, and trivalent chromium. The process is also applicable to any substance that can be transformed into an insoluble form like soaps, phosphates, fluorides, and a variety of others.

Hydroxide precipitation has proven to be an effective technique for removing many pollutants from industrial wastewater.

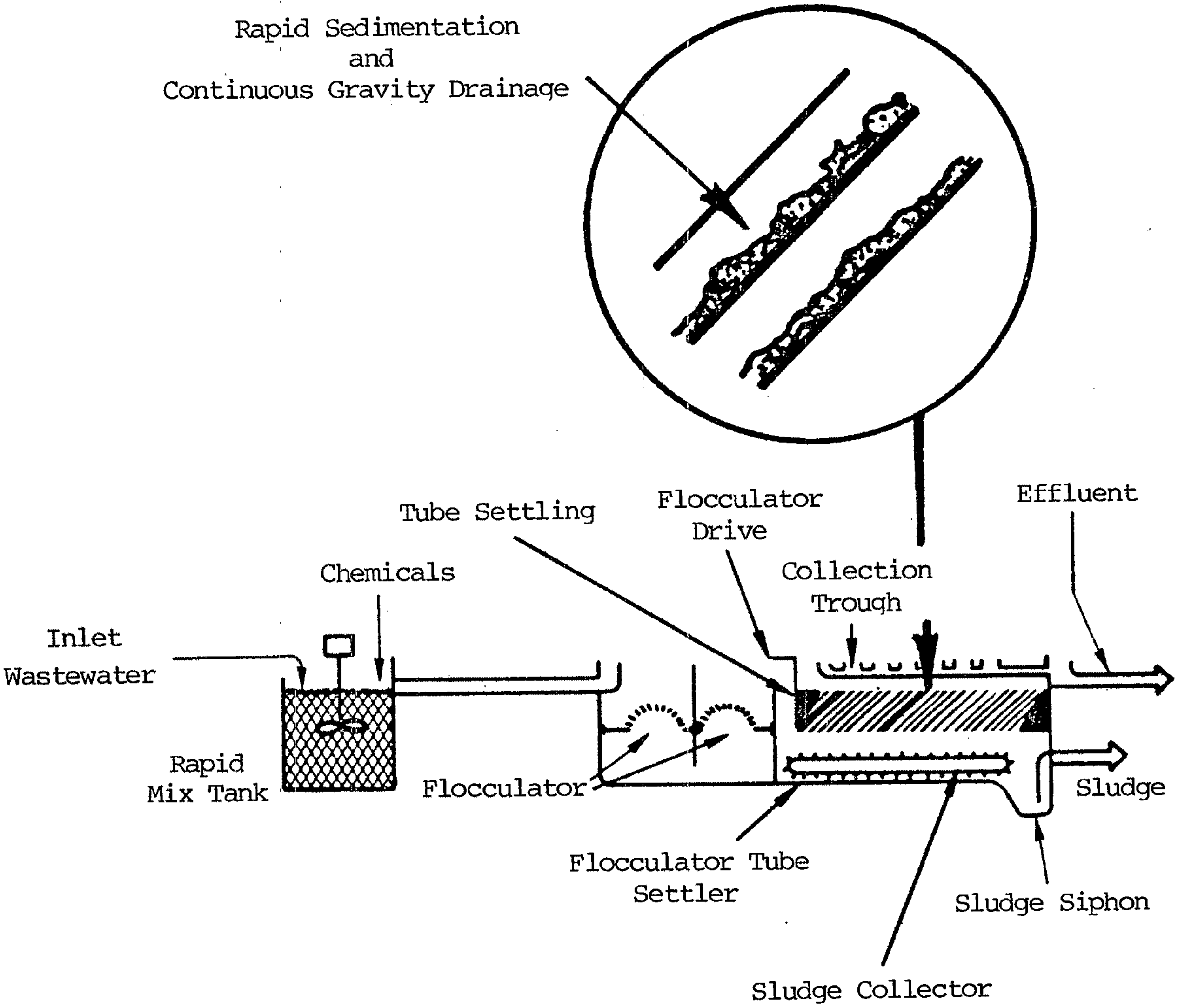


FIGURE 7-3

PRECIPITATION AND SEDIMENTATION

Hydroxide precipitation operates at ambient conditions and is well suited to automatic control. Lime is usually added as a slurry when used in hydroxide precipitation. The slurry must be kept well mixed and the addition lines periodically checked to prevent blocking, which results from a buildup of solids. The use of hydroxide precipitation does produce large quantities of sludge requiring disposal following precipitation and settling. The use of treatment chemicals requires caution because of the potentially hazardous situation involved with the storage and handling of those chemicals. Recovery of the precipitated species is sometimes difficult because of the homogeneous nature of most hydroxide sludges (where no single metal hydroxide is present in high concentrations) and because of the difficulty in smelting which results from the interference of calcium compounds.

### Performance

The performance of hydroxide precipitation depends on several variables. The most important factors affecting precipitation effectiveness are:

1. Addition of sufficient excess anions to drive the precipitation reaction to completion.
2. Maintenance of an alkaline pH throughout the precipitation reaction and subsequent settling. (Figure 7-4 details the solubilities of various metal hydroxides as a function of pH).
3. Effective removal of precipitated solids (see appropriate solids removal technologies).

### Demonstration Status

Hydroxide precipitation of metals is a classic waste treatment technology used in most industrial waste treatment systems. As noted earlier, sedimentation to remove precipitates is discussed separately; however, both techniques have been illustrated in Figure 7-3.

## Sedimentation

Sedimentation is a process which removes solid particles from a liquid waste stream by gravitational settling. The operation is effected by reducing the velocity of the feed stream in a large volume tank or lagoon so that gravitational settling can occur. Figure 7-5 shows two typical sedimentation devices.

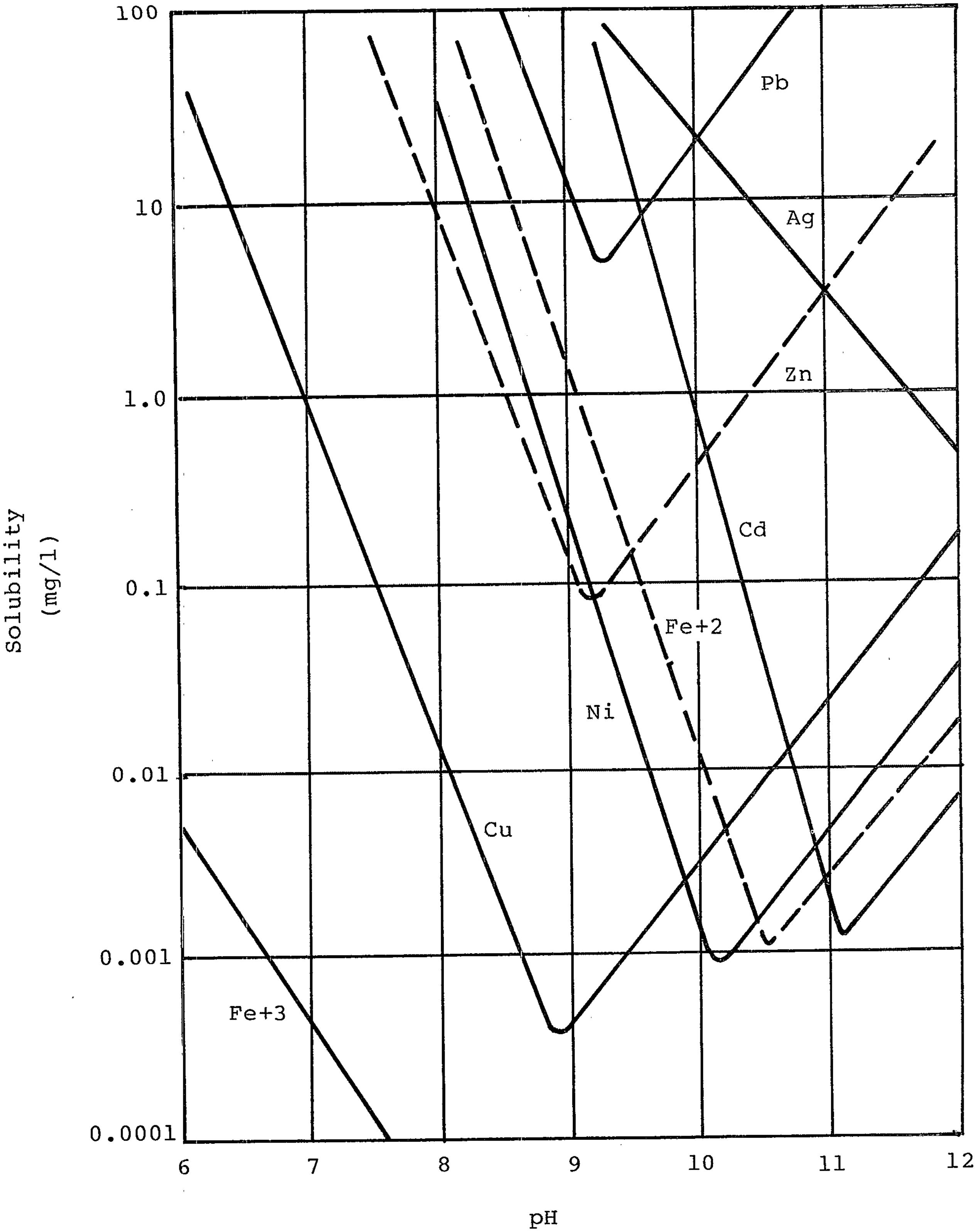
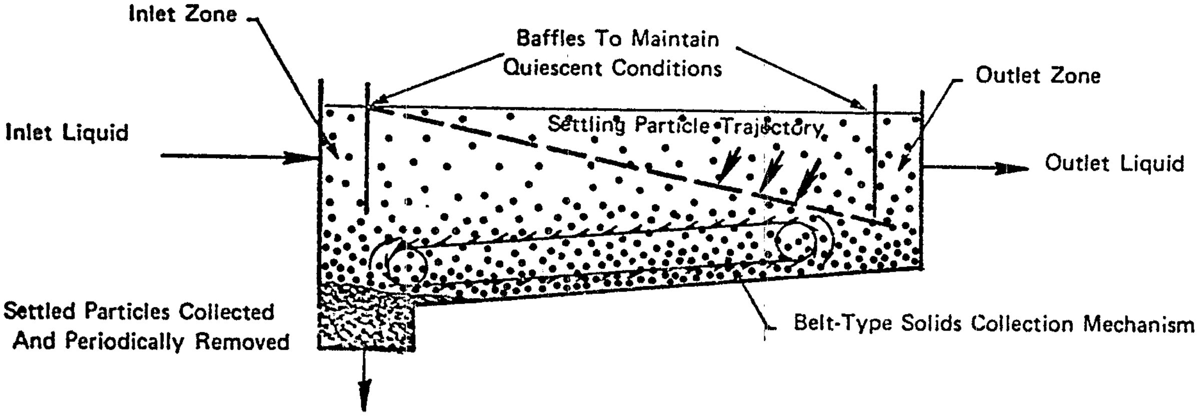


FIGURE 7-4

SOLUBILITIES OF METAL HYDROXIDES AS A FUNCTION OF pH

**Sedimentation Basin**



**Circular Clarifier**

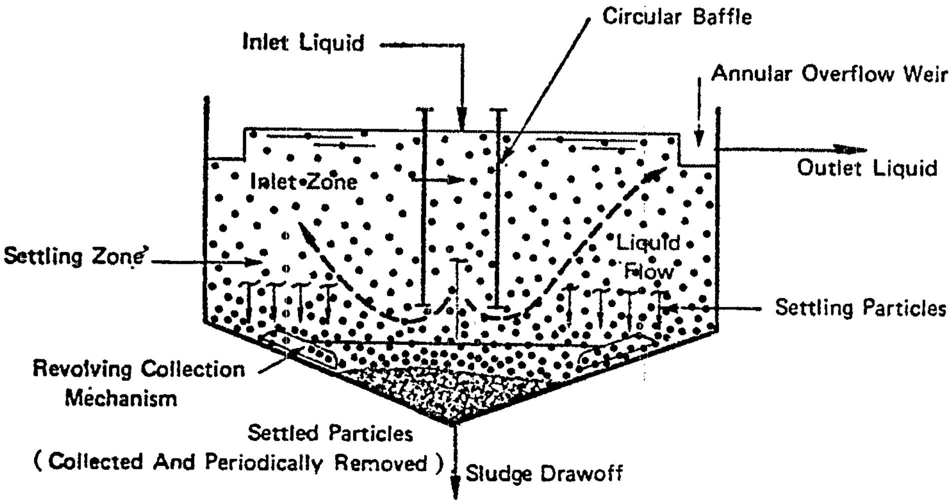


FIGURE 7-5

REPRESENTATIVE TYPES OF SEDIMENTATION

For the Option 1 system, sedimentation is preceded by hydroxide precipitation which converts dissolved metallic pollutants to solid forms and coagulates suspended precipitates into larger, faster settling particles. Wastewater is fed into a high volume tank or lagoon where it loses velocity and the suspended solids are allowed to settle. High retention times are generally required. (The plants in the data base used retention times ranging from 1 to 48 hours). Accumulated sludge can be collected and removed either periodically or continuously and either manually or mechanically.

Inorganic coagulants or polyelectrolytic flocculants are added to enhance coagulation. Common inorganic coagulants include sodium sulfate, sodium aluminate, ferrous or ferric sulfate, and ferric chloride. Organic polyelectrolytes vary in structure, but all usually form larger floccules than coagulants used alone.

The use of a clarifier for sedimentation reduces space requirements, reduces retention time, and increases solids removal efficiency. Conventional clarifiers generally consist of a circular or rectangular tank with a mechanical sludge collecting device or with a sloping funnel-shaped bottom designed for sludge collection. In advanced clarifiers, inclined plates, slanted tubes, or a lamellar network may be included within the clarifier tank in order to increase the effective settling area. A more recently developed "clarifier" utilizes centrifugal force rather than gravity to effect the separation of solids from a liquid. The precipitates are forced outward and accumulate against an outer wall, where they can later be collected. A fraction of the sludge stream is often recirculated to the clarifier inlet, promoting formation of a denser sludge.

Application

Sedimentation is used in metal finishing to remove precipitated metals, phosphates, and suspended solids. Because most metal ion pollutants are easily converted to solid metal hydroxide precipitates, sedimentation is of particular use in industries associated with metal finishing and in other industries with high concentrations of metal ions in their wastes. In addition to heavy metals, suitably precipitated materials effectively removed by sedimentation/clarification include aluminum, manganese, cobalt, arsenic, antimony, beryllium, molybdenum, fluoride, and phosphate.

The major advantage of simple sedimentation is the simplicity of the process itself - the gravitational settling of solid particulate waste in a holding tank or lagoon. The major disadvantage of sedimentation involves the long retention times necessary to achieve complete settling, especially if the specific gravity of the suspended matter is close to that of water.

A clarifier is more effective in removing slow settling suspended matter in a shorter time and in less space than a simple sedimentation system. Also, effluent quality is often better from a clarifier. The cost of installing and maintaining a clarifier is, however, substantially greater than the costs associated with sedimentation lagoons.

Inclined plate, slant tube, and lamellar clarifiers have even higher removal efficiencies than conventional clarifiers, and greater capacities per unit area are possible. Installed costs for these advanced clarification systems are claimed to be one half the cost of conventional systems of similar capacity.

### Performance

A properly operating sedimentation system is capable of efficient removal of suspended solids, precipitated metal hydroxides, and other impurities from wastewater. The performance of the process depends on a variety of factors, including the effective charge on the suspended particles (adjustments can be made in the type and dosage of flocculant or coagulant) and the types of chemicals used in prior treatment. It has been found that the site of flocculant or coagulant addition may significantly influence the effectiveness of sedimentation. If the flocculant is subjected to too much mixing before entering the settling device, the agglomerated complexes may be broken up and the settling effectiveness diminished. At the same time, the flocculant must have sufficient mixing in order for effective set-up and settling to occur. Most plant personnel select the line or trough leading into the clarifier as the most efficient site for flocculant addition. The performance of sedimentation is a function of the retention time, particle size and density, and the surface area of the sedimentation catchment.

Sampling visit data from plant 40063, a porcelain enameling facility that performs metal finishing operations, exemplify efficient operation of a chemical precipitation/settling system. The following table presents sampling data from this system, which consists of the addition of lime and caustic soda for pH adjustment and hydroxide precipitation, polyelectrolyte flocculant addition, and clarification. Samples were taken of the raw waste influent to the system and of the clarifier effluent. Flow through the system is approximately 18,900 LPH (5000 GPH). Concentrations are given in mg/l. The effluent pH shown in the table reflects readjustment with sulfuric acid after solids removal. Parameters which were not detected are listed as ND.

POLLUTANT CONCENTRATIONS (mg/l)
PLANT ID 40063

| | Day 1 | | Day 2 | | Day 3 | |
|---|---|---|---|---|---|---|
| | Inf. | Eff. | Inf. | Eff. | Inf. | Eff. |
| pH Range | 9.2-9.6 | 8.3-9.8 | 9.2 | 7.6-8.1 | 9.6 | 7.8-8.2 |
| TSS | 4390 | 9.0 | 3595 | 13 | 2805 | 13 |
| Al | 37.3 | 0.35 | 38.1 | 0.35 | 29.9 | 0.35 |
| Co | 3.92 | ND | 4.65 | ND | 4.37 | ND |
| Cu | 0.65 | 0.003 | 0.63 | 0.003 | 0.72 | 0.003 |
| Fe | 137 | 0.49 | 110 | 0.57 | 208 | 0.58 |
| Mn | 175 | 0.12 | 205 | 0.012 | 245 | 0.12 |
| Ni | 6.86 | ND | 5.84 | ND | 5.63 | ND |
| Se | 28.6 | ND | 30.2 | ND | 27.4 | ND |
| Ti | 143 | ND | 125 | ND | 115 | ND |
| Zn | 18.5 | 0.027 | 16.2 | 0.044 | 17.0 | 0.01 |

Effluent TSS levels were below 15 mg/l on each day, despite raw waste TSS concentrations in excess of 2800 mg/l. Effluent pH was maintained at approximately 8 or above, lime addition was sufficient to precipitate most of the dissolved metal ions, and the flocculant addition and clarifier retention served to effectively remove the precipitated solids.

### Demonstration Status

Sedimentation in conjunction with hydroxide precipitation (the Option 1 system) represents the typical method of solids removal and is employed extensively in industrial waste treatment. The advanced clarifiers are just beginning to appear in significant numbers in commercial applications, while the centrifugal force "clarifier" has yet to be used commercially. Sedimentation preceded by hydroxide precipitation is used in 154 plants in the Metal Finishing data base that are listed in Table 7-3.

### Common Metals Waste Treatment System Operation - Option 1

When operated properly, the Option 1 system is a highly reliable method for removing dissolved heavy metals from wastewater, although proper system monitoring, control, and preliminary treatment to remove interfering substances are required. Effective operation depends upon attention to proper chemical addition, raw waste load variations, routine maintenance, and solids removal. Control of chemical addition is required to

## TABLE 7-3
## METAL FINISHING PLANTS WITH OPTION 1 TREATMENT SYSTEMS FOR COMMON METALS
## HYDROXIDE PRECIPITATION WITH SEDIMENTATION

01003
01067
02032
02037
03049
04065
04069
04071
04105
04132
04148
04174
04211
04216
04273
05020
05021
06002
06006
06035
06037
06051
06053
06065
06073
06074
06075
06077
06079
06083
06084
06086
06087
06090
06103
06107
06110
06116
06124
06731
07001
09026
10020
11008
11098
11113
11118
11477
12002
12014
12033
12061
12071
12074
12076
12078
12087
12102
12256
12709
13042
14060
15010
15058
15070
16544
17030
17061
19050
19063
19067
19068
19098
20005
20017
20022
20070
20073
20077
20078
20079
20080
20082
20083
20086
20102
20104
20106
20116
20120
20156
20158
20160
20161
20162
20175
20249
20255
20291
20708
21078
22735
23041
23061
23062
23076
27044
28125
30022
30050
30087
30090
30150
30151
30153
31020
31037
33024
33043
33050
33065
33074
33092
33113
33120
33172
33184
33186
33199
33293
33692
34036
34037
36040
36041
36062
36112
36176
36623
38031
38050
38223
40062
40079
43052
44036
44037
44045
44050
44062
44150
45741
46036
47035

maintain the appropriate pH for precipitation of the metals present and to promote coagulation of the metals precipitated. When fluctuating levels of raw waste loading occur, constant monitoring of the system flow and pH is needed to provide chemical addition at the proper rate. Other raw waste types such as hexavalent chromium or cyanide must be appropriately treated before entering the Option 1 system. Specifically, hexavalent chromium will not be removed by the Option 1 system, and cyanide will interfere with the Option 1 system's ability to remove dissolved metals. The necessary preliminary treatment for hexavalent chromium and cyanide is discussed in detail later in Section VII.

An important factor in successful Option 1 system operation is the handling of changes in raw waste load. This is equally true for small batch systems and for large continuous systems. Most system failures, i.e. excessive discharges of pollutants, are the result of inadequate response to raw waste loading changes. Both hydraulic overloading and pollutant shock loads can be avoided by the segregation and bleed-in of concentrated batch dumps. When these practices are not employed, successful operation requires careful monitoring and quick response by the system operator. Appropriate action by the operator in the event of an upset usually involves adjusting chemical feed rate, changing residence time, recycling of treated wastewater, or shutdown for maintenance.

The major maintenance requirements involve the periodic inspection and adjustment of monitoring devices, chemical mixing and feeding equipment, feed and sludge pumps, and clarifier mixing and drive components. Removal of accumulated sludge is necessary for efficient operation of precipitation/sedimentation systems. Solids which precipitate must be continually removed and properly disposed. Proper disposal practices are discussed later in this section under Treatment of Sludges.

### Common Metals Waste Treatment System Performance - Option 1

Although the performance of many Option 1 treatment systems (as shown in Figure 7-6 with sources of wastes) is excellent, others exhibit inferior performance. The major causes of poor performance are low pH (resulting in incomplete metals precipitation) and poor sedimentation, evidenced by high suspended solids in the effluent. In analyzing the data to determine expected performance, poorly performing plants were excluded from the data base. Plants with low effluent concentrations due to dilution, low influent concentration, or similar factors were also excluded.

The performance for the Option 1 treatment system was established from a combination of visited plant sampling data and long term self-monitoring data that were submitted by industry. The following subsection describes the procedure used to establish Option 1 treatment system performance for the visited plant data set.

### Visited Plant Performance

To establish the treatment system performance characteristics, plants employing Option 1 treatment that were visited were selected from the Metal Finishing Category data base. The files for these plants were then examined to ensure that only properly operating facilities were included in the performance data base by establishing criteria to eliminate the data for improperly operating systems. The criteria for eliminating improperly operating treatment systems were as follows:

1. Data with an effluent TSS level greater than 50 mg/l were deleted. This represents a level of TSS above which no well-operated treatment plant should be discharging. Figure 7-7 shows effluent TSS concentrations vs. percentile distribution. As is shown in the graph there is an abrupt increase in slope (approximately 5.8:1) at the 50 mg/l level. Deleting data above this concentration still includes nearly seventy percent of the data base. The following presentation of TSS and metals concentrations for plants 20073 and 20083 shows that a low level of TSS is indicative of low effluent metal concentrations.

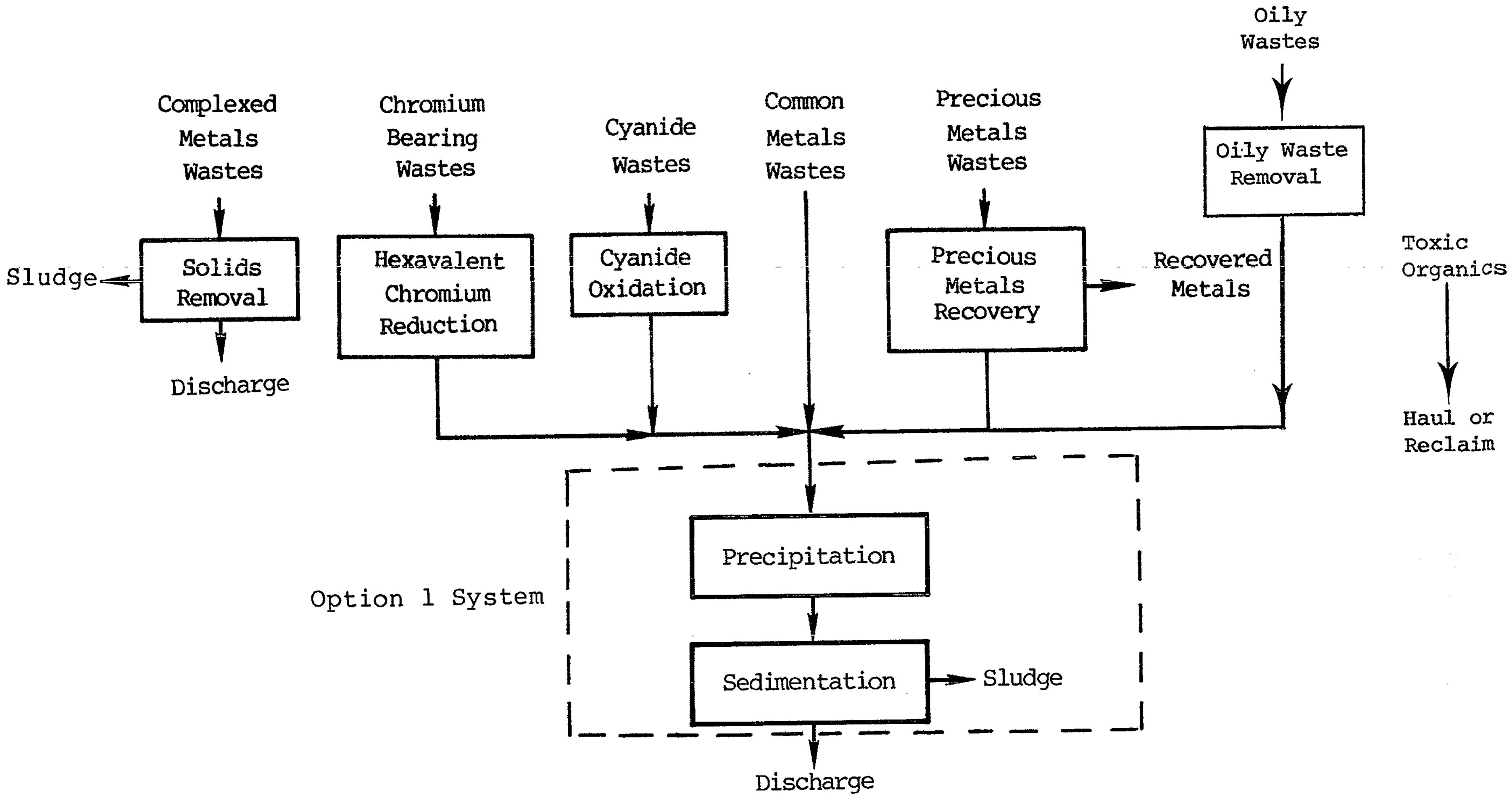


FIGURE 7-6

TREATMENT SCHEME
OPTION 1

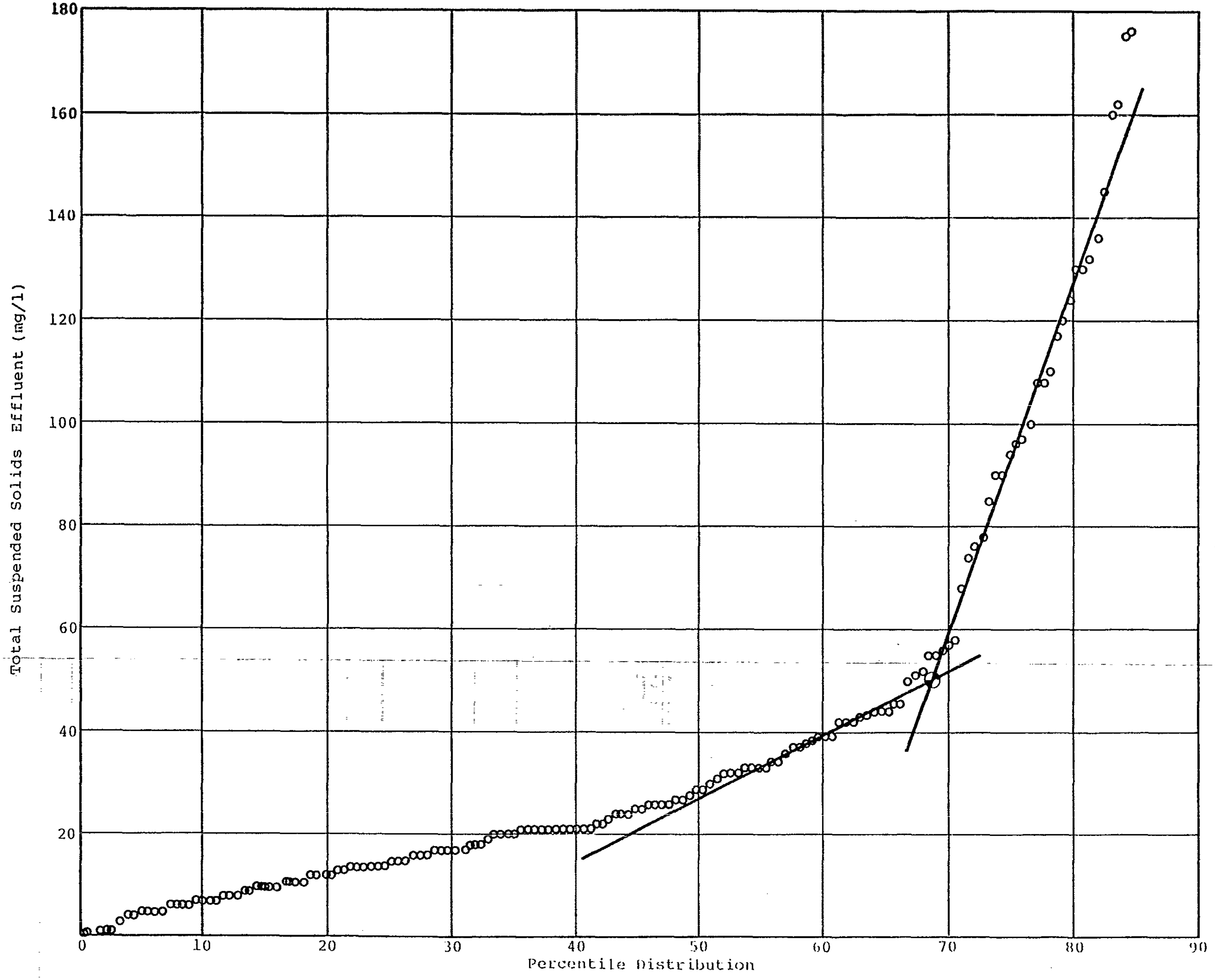


FIGURE 7-7

CLARIFIER TSS DISTRIBUTION

### POLLUTANT CONCENTRATIONS (mg/l)
### Plant ID 20073

| | Day 1 | | Day 2 | | Day 3 | |
|---|---|---|---|---|---|---|
| | Inf. | Eff. | Inf. | Eff. | Inf. | Eff. |
| TSS | 702. | 11. | 712. | 14. | 124. | 33. |
| Cu | 64.6 | .812 | 97.1 | .875 | 91.2 | 1.37 |
| Ni | 53.8 | .448 | 52.5 | .478 | 89.7 | 1.12 |
| Cr | 162. | 1.47 | 175. | 1.89 | 220. | 2.85 |

### POLLUTANT CONCENTRATIONS (mg/l)
### Plant ID 20083

| | Day 1 | | Day 2 | | Day 3 | | Day 4 | |
|---|---|---|---|---|---|---|---|---|
| | Inf. | Eff. | Inf. | Eff. | Inf. | Eff. | Inf. | Eff. |
| TSS | 24.0 | 145 | 18.0 | 23.0 | 15.0 | 27.0 | 10.0 | 97.0 |
| Cu | 56.2 | 2.75 | 57.7 | 0.38 | 39.3 | 0.21 | 50.0 | 2.44 |
| Ni | 103 | 6.13 | 153 | 0.91 | 82.8 | 0.77 | 87.1 | 4.75 |

2. Plants with alkaline precipitation systems that operated at an average effluent pH of less than 7.0 were deleted. An alkaline precipitation system will not work properly in this pH range, as is illustrated by the following data from plant 21066.

### POLLUTANT CONCENTRATIONS (mg/l)
### Plant ID 21066

| | Day 1 | | Day 2 | |
|---|---|---|---|---|
| | Inf. | Eff. | Inf. | Eff. |
| Avg. effluent pH | NA* | 5.4 | NA* | 5.1 |
| TSS | 48.0 | 448 | 61.0 | 371 |
| Cr | 5.36 | 3.74 | 8.99 | 1.28 |
| Zn | 114 | 150 | 111 | 140 |

*Not Available

Proper control of pH is absolutely essential for favorable performance of precipitation/sedimentation technologies. This is illustrated by results obtained from a sampling visit to manufacturing plant 47432 (not a metal finishing plant) as shown by the following data (concentrations are in mg/l):

## POLLUTANT CONCENTRATIONS (mg/l)
Plant ID 47432

| | Day 1 | | Day 2 | | Day 3 | |
|---|---|---|---|---|---|---|
| | In | Out | In | Out | In | Out |
| pH Range | 2.4-3.4 | 8.5-8.7 | 1.0-3.0 | 5.0-6.0 | 2.0-5.0 | 6.5-8.1 |
| TSS | 39 | 8 | 16 | 19 | 16 | 7 |
| Copper | 312 | 0.22 | 120 | 5.12 | 107 | 0.66 |
| Zinc | 250 | 0.31 | 32.5 | 25 | 43.8 | 0.66 |
| Lead | 0.16 | 0.03 | 0.16 | 0.04 | 0.15 | 0.04 |
| Nickel | 42.8 | 0.78 | 33.8 | 0.53 | 36.6 | 0.46 |

This plant utilizes lime precipitation and pH adjustment followed by flocculant addition and sedimentation. Samples were taken before and after the system. On day two effluent pH was allowed to range below 7 for the entire day and the effluent metals control was less effective than on days one and three. In general, better results will be obtained in chemical precipitation systems when pH is maintained consistently at a level between 8.5 and 9.5. It can be clearly seen that the best results were produced on day one when the effluent pH was kept within the recommended range for the entire day.

3. Plants that had complexing agents (unoxidized cyanide or nonsegregated wastes from electroless plating) present were deleted.

4. Plants which had effluent flows significantly greater than the corresponding raw waste flows were deleted. The increase in flows was assumed to be dilution by other wastewaters.

5. Pollutant parameters which had an effluent concentration greater than the raw waste concentration were deleted.

6. Plants that experienced difficulties in system operation during the sampling period were excluded. These difficulties included a few hours operation at very low pH (approximately 4.0), observed operator error,an inoperative chemical feed system, improper chemical usage, improperly maintained equipment, high flow slugs during the sampling period, and excessive surface water intrusion (heavy rains).

The following procedure was followed for each metal pollutant parameter (except for TSS which is created during precipitation) in order to eliminate spurious background metal readings. The mean effluent concentration of each parameter was calculated and when a raw waste concentration was less than the mean effluent concentration for that parameter, the corresponding effluent reading was deleted from the data set. The mean was recalculated using points not removed and the process was repeated in an iterative loop. The deletion of these points prevents the calculation of unrealistically low mean effluent concentrations from the waste treatment systems due to low raw waste pollutant loadings.

Option 1 performance data from visited plants are presented in Tables 7-4 through 7-10 for cadmium, chromium, copper, lead, nickel, zinc, and total suspended solids. The mean effluent concentrations for these parameters are summarized in Table 7-11.

## TABLE 7-4

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR CADMIUM

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.012 | 0.006 | 20083-1-5 |
| 2. | 0.012 | 0.006 | 20083-1-6 |
| 3. | 0.012 | 0.006 | 19063-1-2 |
| 4. | 0.013 | 0.005 | 6083-1-2 |
| 5. | 0.013 | 0.005 | 19063-1-3 |
| 6. | 0.013 | 0.010 | 15070-1-1 |
| 7. | 0.015 | 0.008 | 6731-1-1 |
| 8. | 0.017 | 0.006 | 6731-1-2 |
| 9. | 0.019 | 0.007 | 6731-1-3 |
| 10. | 0.021 | 0.010 | 6074-1-1 |
| 11. | 0.021 | 0.018 | 31020-1-1 |
| 12. | 0.022 | 0.013 | 6087-1-3 |
| 13. | 0.022 | 0.019 | 27044-1-0 |
| 14. | 0.024 | 0.005 | 20080-1-1 |
| 15. | 0.030 | 0.014 | 6087-1-1 |
| 16. | 0.032 | 0.005 | 4065-8-1 |
| 17. | 0.033 | 0.011 | 6074-1-1 |
| 18. | 0.037 | 0.005 | 20073-1-1 |
| 19. | 0.037 | 0.005 | 20073-1-2 |
| 20. | 0.042 | 0.006 | 36041-1-2 |
| 21. | 0.042 | 0.006 | 36041-1-3 |
| 22. | 0.053 | 0.009 | 36041-1-1 |
| 23. | 0.068 | 0.017 | 21003-15-2 |
| 24. | 0.077 | 0.005 | 33024-6-0 |
| 25. | 0.084 | 0.027 | 21003-15-0 |
| 26. | 0.087 | 0.024 | 21003-15-1 |
| 27. | 0.113 | 0.028 | 6051-6-0 |
| 28. | 0.250 | 0.008 | 15070-1-2 |
| 29. | 0.925 | 0.012 | 20086-1-1 |
| 30. | 1.00 | 0.015 | 20086-1-3 |
| 31. | 1.88 | 0.018 | 20086-1-2 |
| Mean Concentration | 0.162 (n=31) | 0.011 (n=31) | |

## TABLE 7-5

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR CHROMIUM (TOTAL)

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.65 | 0.052 | 6087-1-3 |
| 2. | 1.09 | 0.128 | 6731-1-2 |
| 3. | 1.20 | 1.12 | 15010-12-3 |
| 4. | 1.30 | 0.013 | 19068-15-1 |
| 5. | 1.31 | 0.014 | 4069-8-1 |
| 6. | 1.51 | 0.150 | 44062-15-0 |
| 7. | 1.56 | 0.255 | 6051-6-0 |
| 8. | 1.60 | 0.120 | 44062-15-1 |
| 9. | 1.70 | 1.16 | 15010-12-2 |
| 10. | 2.00 | 0.040 | 11477-22-2 |
| 11. | 2.43 | 0.070 | 33024-6-0 |
| 12. | 4.34 | 0.039 | 44062-15-2 |
| 13. | 7.00 | 0.020 | 11477-22-1 |
| 14. | 12.2 | 0.556 | 6083-1-2 |
| 15. | 12.2 | 0.611 | 36041-1-2 |
| 16. | 14.0 | 0.250 | 33065-9-1 |
| 17. | 21.6 | 0.005 | 19068-14-0 |
| 18. | 24.7 | 0.333 | 36040-1-1 |
| 19. | 25.0 | 0.333 | 36041-1-3 |
| 20. | 25.3 | 0.533 | 36040-1-1 |
| 21. | 28.6 | 0.667 | 36041-1-1 |
| 22. | 29.4 | 0.733 | 36040-1-1 |
| 23. | 32.2 | 0.0 | 19068-15-2 |
| 24. | 58.2 | 0.833 | 20086-1-2 |
| 25. | 69.3 | 1.06 | 20086-1-3 |
| 26. | 70.3 | 0.833 | 20086-1-1 |
| 27. | 76.7 | 1.64 | 20078-1-7 |
| 28. | 85.3 | 0.143 | 6074-1-1 |
| 29. | 98.0 | 0.333 | 6074-1-1 |
| 30. | 104. | 0.714 | 6074-1-1 |
| 31. | 116. | 0.018 | 31020-1-1 |
| 32. | 117. | 0.400 | 20078-1-2 |
| 33. | 117. | 0.500 | 20078-1-3 |
| 34. | 142. | 0.195 | 20080-1-1 |
| 35. | 162. | 1.47 | 20073-1-1 |
| 36. | 175. | 1.89 | 20073-1-2 |
| 37. | 190. | 2.36 | 40062-8-0 |
| 38. | 393. | 2.14 | 40062-8-0 |
| Mean Concentration | 58.6 (n=38) | 0.572 (n=38) | |

## TABLE 7-6

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR COPPER

OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.88 | 0.006 | 19068-14-0 |
| 2. | 0.94 | 0.258 | 6731-1-2 |
| 3. | 0.95 | 0.13 | 21003-15-2 |
| 4. | 1.00 | 0.044 | 6074-1-1 |
| 5. | 1.30 | 0.029 | 12061-15-2 |
| 6. | 1.39 | 0.060 | 36040-1-1 |
| 7. | 1.63 | 0.016 | 19068-15-2 |
| 8. | 1.65 | 0.588 | 6731-1-3 |
| 9. | 1.78 | 0.028 | 19068-15-1 |
| 10. | 1.90 | 0.038 | 12061-15-0 |
| 11. | 2.62 | 1.30 | 5020-1-6 |
| 12. | 2.86 | 1.85 | 5020-1-4 |
| 13. | 3.29 | 0.780 | 4071-25-3 |
| 14. | 4.35 | 0.727 | 4069-8-1 |
| 15. | 4.55 | 0.380 | 4065-8-1 |
| 16. | 6.21 | 0.076 | 36040-1-1 |
| 17. | 6.42 | 0.898 | 4065-8-1 |
| 18. | 7.53 | 0.444 | 36041-1-2 |
| 19. | 7.67 | 0.165 | 5020-1-3 |
| 20. | 7.69 | 0.247 | 20078-1-3 |
| 21. | 7.69 | 0.307 | 20078-1-2 |
| 22. | 7.79 | 0.157 | 27044-1-0 |
| 23. | 8.16 | 0.400 | 20078-1-7 |
| 24. | 8.31 | 0.372 | 20078-1-4 |
| 25. | 8.44 | 0.776 | 4069-8-1 |
| 26. | 9.56 | 1.06 | 36041-1-3 |
| 27. | 10.2 | 0.071 | 36040-1-1 |
| 28. | 11.0 | 0.160 | 33024-6-0 |
| 29. | 14.7 | 2.20 | 19063-1-2 |
| 30. | 14.9 | 4.47 | 19063-1-1 |
| 31. | 16.1 | 3.53 | 19063-1-3 |
| 32. | 19.5 | 0.900 | 5020-1-5 |
| 33. | 26.5 | 1.89 | 36041-1-1 |
| 34. | 47.5 | 1.62 | 40062-8-0 |
| 35. | 47.8 | 0.212 | 20083-1-5 |

(Continued)

## TABLE 7-6 (Continued)

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR COPPER

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 36. | 49.3 | 1.94 | 6087-1-1 |
| 37. | 51.5 | 0.163 | 20083-1-6 |
| 38. | 52.5 | 1.69 | 40062-8-0 |
| 39. | 57.7 | 0.375 | 20083-1-3 |
| 40. | 64.6 | 0.812 | 20073-1-1 |
| 41. | 80.0 | 2.63 | 6087-1-3 |
| 42. | 84.6 | 0.547 | 20086-1-2 |
| 43. | 91.7 | 0.500 | 20086-1-1 |
| 44. | 95.8 | 1.06 | 20086-1-3 |
| 45. | 96.9 | 0.533 | 33065-9-1 |
| 46. | 97.1 | 0.875 | 20073-1-2 |
| 47. | 108. | 1.00 | 31020-1-1 |
| Mean Concentration | 26.7 (n=47) | 0.815 (n=47) | |

## TABLE 7-7

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR LEAD

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.052 | 0.048 | 15070-1-3 |
| 2. | 0.054 | 0.033 | 36040-1-1 |
| 3. | 0.064 | 0.025 | 20078-1-3 |
| 4. | 0.067 | 0.013 | 6731-1-3 |
| 5. | 0.071 | 0.0 | 19068-15-1 |
| 6. | 0.072 | 0.044 | 15070-1-1 |
| 7. | 0.072 | 0.048 | 15070-1-2 |
| 8. | 0.075 | 0.010 | 20080-1-1 |
| 9. | 0.084 | 0.025 | 20078-1-2 |
| 10. | 0.102 | 0.025 | 20078-1-4 |
| 11. | 0.103 | 0.077 | 4065-8-1 |
| 12. | 0.125 | 0.050 | 20083-1-3 |
| 13. | 0.136 | 0.032 | 36041-1-2 |
| 14. | 0.136 | 0.040 | 20078-1-7 |
| 15. | 0.144 | 0.032 | 20083-1-6 |
| 16. | 0.145 | 0.038 | 20073-1-1 |
| 17. | 0.154 | 0.044 | 20086-1-3 |
| 18. | 0.160 | 0.036 | 20086-1-1 |
| 19. | 0.164 | 0.040 | 20086-1-2 |
| 20. | 0.168 | 0.032 | 20083-1-5 |
| 21. | 0.174 | 0.0 | 19068-15-2 |
| 22. | 0.182 | 0.044 | 6074-1-1 |
| 23. | 0.212 | 0.036 | 36041-1-3 |
| 24. | 0.218 | 0.044 | 6074-1-1 |
| 25. | 0.226 | 0.025 | 20073-1-2 |
| 26. | 0.233 | 0.0 | 36623-15-2 |
| 27. | 0.270 | 0.160 | 4071-15-3 |
| 28. | 0.364 | 0.067 | 27044-1-0 |
| 29. | 0.394 | 0.021 | 33065-9-1 |
| 30. | 0.474 | 0.043 | 40062-8-0 |
| 31. | 0.567 | 0.0 | 36623-15-0 |
| 32. | 0.600 | 0.036 | 40062-8-0 |
| 33. | 0.800 | 0.068 | 31020-1-1 |
| 34. | 0.909 | 0.073 | 15010-12-2 |
| 35. | 1.000 | 0.064 | 36041-1-1 |

(Continued)

TABLE 7-7 (Continued)

METAL FINISHING CATEGORY PERFORMANCE DATA FOR LEAD

OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 36. | 1.000 | 0.085 | 6087-1-1 |
| 37. | 1.000 | 0.133 | 15010-12-3 |
| 38. | 1.120 | 0.065 | 6087-1-3 |
| 39. | 2.500 | 0.160 | 6083-1-2 |
| 40. | 2.540 | 0.0 | 12061-15-2 |
| 41. | 6.928 | 0.165 | 19063-1-1 |
| 42. | 6.930 | 0.0 | 12061-15-0 |
| 43. | 8.362 | 0.098 | 19063-1-2 |
| 44. | 9.701 | 0.143 | 19063-1-3 |
| Mean Concentration | 1.11 (n=44) | 0.0505 (n=44) | |

## TABLE 7-8

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR NICKEL

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 1.07 | 0.076 | 19063-1-1 |
| 2. | 1.44 | 1.11 | 6731-1-1 |
| 3. | 1.48 | 0.150 | 21003-15-1 |
| 4. | 1.69 | 0.060 | 19063-1-2 |
| 5. | 2.14 | 0.342 | 4069-8-1 |
| 6. | 2.22 | 1.00 | 6731-1-2 |
| 7. | 2.23 | 0.190 | 19063-1-3 |
| 8. | 2.57 | 0.044 | 36041-1-2 |
| 9. | 3.20 | 0.726 | 27044-1-0 |
| 10. | 3.24 | 0.700 | 36623-15-2 |
| 11. | 3.87 | 0.122 | 4069-8-1 |
| 12. | 3.89 | 1.89 | 6731-1-3 |
| 13. | 4.49 | 0.571 | 36041-1-3 |
| 14. | 5.00 | 0.320 | 36041-1-1 |
| 15. | 5.42 | 1.20 | 36623-15-0 |
| 16. | 5.60 | 0.414 | 5020-1-6 |
| 17. | 5.80 | 1.03 | 36623-15-1 |
| 18. | 6.80 | 0.414 | 5020-1-5 |
| 19. | 7.31 | 0.759 | 5020-1-4 |
| 20. | 8.56 | 0.0 | 19068-15-2 |
| 21. | 9.33 | 2.27 | 6083-1-2 |
| 22. | 11.8 | 0.294 | 5020-1-3 |
| 23. | 27.5 | 0.120 | 31020-1-1 |
| 24. | 33.9 | 0.536 | 20086-1-2 |
| 25. | 36.7 | 0.464 | 20086-1-3 |
| 26. | 42.9 | 0.786 | 20086-1-1 |
| 27. | 50.0 | 7.30 | 6087-1-1 |
| 28. | 52.5 | 0.478 | 20073-1-2 |
| 29. | 53.8 | 0.448 | 20073-1-1 |
| 30. | 73.0 | 6.39 | 6087-1-3 |
| 31. | 76.9 | 0.381 | 20078-1-7 |
| 32. | 78.7 | 0.106 | 20078-1-3 |
| 33. | 78.7 | 0.427 | 20078-1-4 |
| 34. | 80.6 | 1.84 | 40062-8-0 |
| 35. | 85.3 | 0.144 | 20078-1-2 |

(Continued)

## TABLE 7-8 (Continued)

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR NICKEL

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 36. | 94.3 | 0.600 | 6074-1-1 |
| 37. | 94.4 | 1.52 | 40062-8-0 |
| 38. | 97.1 | 0.808 | 20083-1-5 |
| 39. | 108. | 0.778 | 36040-1-1 |
| 40. | 108 | 1.78 | 36040-1-1 |
| 41. | 111. | 0.462 | 20083-1-6 |
| 42. | 128. | 0.571 | 6074-1-1 |
| 43. | 142. | 1.56 | 36040-1-1 |
| 44. | 153. | 0.907 | 20083-1-3 |
| 45. | 167. | 0.304 | 6074-1-1 |
| Mean Concentration | 46.1 (n=45) | 0.942 (n=45) | |

## TABLE 7-9

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR ZINC

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.63 | 0.028 | 36623-15-1 |
| 2. | 0.73 | 0.024 | 36040-1-1 |
| 3. | 0.81 | 0.060 | 19068-14-0 |
| 4. | 0.87 | 0.013 | 36040-1-1 |
| 5. | 0.92 | 0.123 | 15010-12-2 |
| 6. | 1.08 | 0.020 | 19068-15-1 |
| 7. | 1.13 | 0.016 | 36040-1-1 |
| 8. | 1.25 | 0.193 | 15010-12-3 |
| 9. | 1.36 | 0.105 | 20073-1-1 |
| 10. | 1.71 | 0.070 | 20073-1-2 |
| 11. | 1.75 | 0.010 | 19068-15-2 |
| 12. | 3.71 | 0.166 | 6083-1-2 |
| 13. | 4.11 | 0.040 | 20078-1-7 |
| 14. | 4.67 | 0.029 | 20078-1-2 |
| 15. | 4.89 | 0.033 | 20078-1-3 |
| 16. | 4.89 | 0.083 | 20078-1-4 |
| 17. | 5.07 | 0.304 | 6731-1-1 |
| 18. | 9.91 | 0.889 | 6731-1-2 |
| 19. | 11.2 | 1.00 | 6087-1-1 |
| 20. | 13.4 | 0.139 | 36041-1-2 |
| 21. | 14.3 | 0.430 | 36041-1-3 |
| 22. | 17.5 | 1.12 | 6087-1-3 |
| 23. | 18.7 | 0.765 | 36041-1-1 |
| 24. | 18.8 | 0.018 | 31020-1-1 |
| 25. | 19.2 | 0.889 | 6731-1-3 |
| 26. | 42.6 | 3.00 | 15070-1-3 |
| 27. | 48.5 | 0.308 | 33065-9-1 |
| 28. | 59.4 | 0.375 | 20080-1-1 |
| 29. | 100. | 3.12 | 15070-1-2 |
| 30. | 103. | 1.33 | 15070-1-1 |
| 31. | 121. | 1.09 | 33024-6-0 |
| 32. | 169. | 0.765 | 20086-1-1 |
| 33. | 171. | 1.12 | 20086-1-2 |
| 34. | 175. | 1.00 | 20086-1-3 |
| Mean Concentration | 33.9 (n=34) | 0.549 (n=34) | |

## TABLE 7-10

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR TSS

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.0 | 0.0 | 21003-15-0 |
| 2. | 0.000 | 12.000 | 21003-15-2 |
| 3. | 1.000 | 24.000 | 33074-1-3 |
| 4. | 1.200 | 0.700 | 36623-15-2 |
| 5. | 2.000 | 38.000 | 20078-1-7 |
| 6. | 3.000 | 6.000 | 20083-1-6 |
| 7. | 3.000 | 7.000 | 27044-1-0 |
| 8. | 3.290 | 2.400 | 36623-15-1 |
| 9. | 3.610 | 2.900 | 36623-15-0 |
| 10. | 4.000 | 34.00 | 5020-1-4 |
| 11. | 6.000 | 5.000 | 21003-15-1 |
| 12. | 7.000 | 6.000 | 6731-1-1 |
| 13. | 9.000 | 24.00 | 5020-1-5 |
| 14. | 9.000 | 32.00 | 20078-1-3 |
| 15. | 10.00 | 5.000 | 20080-1-1 |
| 16. | 10.00 | 15.000 | 5020-1-6 |
| 17. | 10.00 | 11.500 | 19051-6-0 |
| 18. | 14.35 | 21.00 | 19068-15-1 |
| 19. | 15.00 | 8.000 | 6101-12-1 |
| 20. | 16.00 | 9.000 | 6101-12-1 |
| 21. | 16.00 | 9.000 | 20083-1-5 |
| 22. | 16.00 | 37.00 | 20078-1-4 |
| 23. | 16.04 | 17.00 | 19068-15-2 |
| 24. | 16.38 | 22.00 | 19068-14-0 |
| 25. | 17.00 | 1.000 | 6731-1-2 |
| 26. | 18.000 | 34.000 | 20083-1-3 |
| 27. | 21.000 | 14.000 | 20078-1-2 |
| 28. | 23.000 | 4.000 | 6731-1-3 |
| 29. | 23.000 | 27.000 | 40062-8-0 |
| 30. | 26.000 | 5.000 | 5020-1-3 |
| 31. | 33.000 | 32.000 | 40062-8-0 |
| 32. | 38.000 | 16.000 | 4065-8-1 |
| 33. | 42.518 | 28.487 | 19063-1-1 |
| 34. | 44.606 | 15.000 | 4069-8-1 |
| 35. | 45.000 | 8.0000 | 36040-1-1 |
| 36. | 46.510 | 48.000 | 4071-15-3 |
| 37. | 55.268 | 4.000 | 4069-8-1 |
| 38. | 59.000 | 27.000 | 4065-8-1 |
| 39. | 66.000 | 11.000 | 36040-1-1 |
| 40. | 67.000 | 4.000 | 23061-8-1 |

(Continued)

TABLE 7-10 (Continued)

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR TSS

OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 41. | 74.000 | 32.000 | 15010-12-2 |
| 42. | 78.000 | 5.000 | 12061-15-2 |
| 43. | 80.000 | 19.000 | 14001-12-1 |
| 44. | 88.666 | 13.238 | 19063-1-2 |
| 45. | 117.58 | 14.000 | 44062-15-1 |
| 46. | 119.00 | 3.000 | 11477-22-0 |
| 47. | 131.00 | 9.000 | 6051-6-0 |
| 48. | 139.13 | 7.9498 | 19063-1-3 |
| 49. | 162.00 | 10.900 | 33692-23-1 |
| 50. | 174.04 | 23.000 | 44062-15-2 |
| 51. | 180.00 | 42.000 | 15010-12-3 |
| 52. | 182.28 | 13.000 | 44062-15-0 |
| 53. | 194.00 | 14.000 | 36040-1-1 |
| 54. | 201.00 | 15.000 | 23061-8-2 |
| 55. | 215.00 | 12.000 | 11477-22-2 |
| 56. | 259.50 | 42.000 | 33024-6-0 |
| 57. | 344.00 | 44.000 | 6087-1-1 |
| 58. | 392.00 | 34.000 | 6087-1-3 |
| 59. | 472.00 | 22.000 | 6083-1-2 |
| 60. | 504.00 | 25.000 | 15070-1-3 |
| 61. | 524.00 | 10.000 | 36041-1-2 |
| 62. | 652.00 | 5.000 | 36041-1-3 |
| 63. | 672.00 | 0.0 | 12061-15-0 |
| 64. | 702.00 | 11.000 | 20073-1-1 |
| 65. | 712.00 | 14.000 | 20073-1-2 |
| 66. | 812.00 | 7.000 | 12061-15-1 |
| 67. | 904.00 | 21.000 | 15070-1-2 |
| 68. | 920.00 | 12.000 | 15070-1-1 |
| 69. | 1032.0 | 16.000 | 31020-1-1 |
| 70. | 1036.0 | 32.000 | 36041-1-1 |
| 71. | 1100.0 | 1.000 | 11477-22-1 |
| 72. | 2060.0 | 0.1000 | 33065-9-1 |
| 73. | 2425.0 | 17.000 | 20086-1-1 |
| 74. | 2466.8 | 25.000 | 20086-1-2 |
| 75. | 3103.8 | 22.000 | 20086-1-3 |
| 76. | 4410.0 | 21.000 | 6074-1-1 |
| 77. | 8340.0 | 26.000 | 6074-1-1 |
| 78. | 9970.0 | 46.000 | 6074-1-1 |
| Mean Concentration = | 599.558 (n=78) | 16.836 (n=78) | |

## TABLE 7-11

## TREATMENT OF COMMON METALS - VISITED PLANTS
## SUMMARY OF OPTION 1 MEAN EFFLUENT CONCENTRATIONS

| Parameter | Mean Concentration (mg/ℓ) |
|---|---|
| Cadmium | 0.011 |
| Chromium, Total | 0.572 |
| Copper | 0.815 |
| Lead | 0.051 |
| Nickel | 0.942 |
| Zinc | 0.549 |
| Total Suspended Solids | 16.8 |

## Long Term Self-Monitoring Data Performance

Long term self-monitoring data were submitted by a number of plants with Option 1 treatment systems. The total data points per parameter ranged from 485 for cadmium to 3552 for chromium. The mean concentrations, daily maximum variability factors, and 10-day variability factors were determined statistically for these data and are summarized in Tables 7-12 through 7-18. These tables also show overall values for each pollutant, specifically the total number of points, the mean value for all points, and the median of the variability factors listed in the table.

## Overall Performance

The overall Option 1 system performance is based on mean concentrations calculated from the visited plant data multiplied by variability factors calculated from the historical performance data. For cadmium and lead, the weighted mean Option 1 self-monitoring concentrations rather than the mean visit concentrations are used because of the relatively low raw waste concentrations of the visit data. The statistical procedures used to establish the Option 1 system performance are discussed in Statistical Analysis at the end of this section.

# TABLE 7-12
# EFFLUENT TSS SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 149 | 13.85 | 3.41 | 1.85 |
| 3049 | 49 | 10.08 | 7.49 | 2.55 |
| 6002 | 18 | 11.49 | 3.58 | 1.24 |
| 6035 | 12 | 4.71 | 5.33 | 1.54 |
| 6051 | 13 | 7.86 | 3.50 | 1.76 |
| 6053 | 12 | 8.41 | 4.57 | 3.27 |
| 6087 | 12 | 11.64 | 5.01 | 1.76 |
| 6103 | 13 | 21.38 | 2.52 | 1.24 |
| 6107 | 10 | 12.52 | 3.54 | -- |
| 6111 | 3 | 0.40 | 13.21 | -- |
| 11008 | 140 | 3.88 | 2.63 | 1.99 |
| 11477 | 69 | 4.29 | 3.39 | 1.36 |
| 19063 | 9 | 8.88 | 7.18 | -- |
| 20080 | 269 | 4.19 | 3.61 | 2.24 |
| 20116 | 243 | 14.05 | 2.80 | 1.48 |
| 22735 | 27 | 6.84 | 2.80 | 2.00 |
| 30050 | 292 | 4.58 | 4.42 | 2.13 |
| 30090 | 51 | 3.58 | 4.82 | 1.82 |
| 44045 | 50 | 3.50 | 3.42 | 1.85 |
| 47025 | 336 | 15.22 | 4.45 | 2.25 |
| OVERALL | 1777(Total) | 9.02(Mean) | 3.59(Median) | 1.85(Median) |

## TABLE 7-13
## EFFLUENT CADMIUM SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 222 | 0.13 | 3.08 | 2.04 |
| 6002 | 6 | 0.05 | 7.48 | -- |
| 6035 | 9 | 0.01 | -- | -- |
| 6051 | 13 | 0.04 | -- | 1.14 |
| 11008 | 185 | 0.12 | 3.14 | 2.01 |
| 47025 | 50 | 0.21 | 7.49 | 8.54 |
| OVERALL | 485(Total) | 0.13(Mean) | 5.31(Median) | 2.02(Median) |

## TABLE 7-14
## EFFLUENT TOTAL CHROMIUM SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 230 | 0.17 | 3.07 | 2.27 |
| 5020 | 228 | 0.03 | -- | 10.52 |
| 6002 | 6 | 0.74 | 13.66 | -- |
| 6035 | 12 | 0.18 | 7.52 | 1.89 |
| 6051 | 13 | 0.27 | 3.97 | 1.78 |
| 6053 | 12 | 0.14 | 8.72 | 3.02 |
| 6087 | 12 | 0.02 | -- | -- |
| 6107 | 10 | 0.10 | 5.58 | -- |
| 6111 | 3 | 0.12 | 5.57 | -- |
| 11008 | 185 | 0.09 | 5.97 | 4.08 |
| 17030 | 344 | 0.20 | 6.84 | 5.56 |
| 19063 | 238 | 0.16 | 3.51 | 4.80 |
| 20080 | 269 | 0.29 | 4.58 | 2.63 |
| 20082 | 253 | 0.60 | 5.20 | 3.70 |
| 20116 | 243 | 0.21 | 2.76 | 1.65 |
| 22735 | 35 | 0.15 | 4.64 | 1.39 |
| 23076 | 242 | 0.40 | 4.79 | 4.41 |
| 30050 | 289 | 0.01 | 3.80 | 3.07 |
| 30090 | 49 | 0.04 | 4.90 | 2.12 |
| 36040 | 224 | 0.24 | 1.67 | 1.30 |
| 44150 | 42 | 0.01 | -- | 37.26 |
| 45741 | 358 | 0.06 | 4.47 | 2.98 |
| 47025 | 255 | 0.06 | 5.57 | 2.81 |
| OVERALL | 3552(Total) | 0.19(Mean) | 4.85(Median) | 2.98(Median) |

# TABLE 7-15
# EFFLUENT COPPER SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 230 | 0.09 | 4.07 | 2.81 |
| 5020 | 232 | 0.24 | 4.56 | 2.54 |
| 6002 | 6 | 0.14 | 5.10 | -- |
| 6051 | 13 | 0.12 | 3.19 | 1.77 |
| 6087 | 12 | 1.38 | 3.56 | 2.58 |
| 6107 | 10 | 2.36 | 3.87 | -- |
| 11008 | 185 | 0.06 | 5.87 | 5.72 |
| 12002 | 59 | 0.08 | 3.65 | 2.24 |
| 19063 | 231 | 0.64 | 4.55 | 2.51 |
| 20082 | 253 | 1.38 | 4.02 | 3.37 |
| 20116 | 243 | 0.10 | 4.15 | 3.07 |
| 23076 | 241 | 0.74 | 9.29 | 6.90 |
| 30050 | 292 | 0.10 | 2.30 | 1.62 |
| 30090 | 259 | 0.18 | 2.39 | 1.62 |
| 30165 | 66 | 1.47 | 2.43 | 2.08 |
| 33050 | 112 | 0.07 | 5.06 | 2.21 |
| 34037 | 123 | 1.40 | 5.92 | 4.08 |
| 44045 | 49 | 0.16 | 4.62 | 1.72 |
| 44150 | 127 | 0.43 | 5.70 | 7.25 |
| OVERALL | 2744(Total) | 0.46(Mean) | 4.15(Median) | 2.54(Median) |

### TABLE 7-16
### EFFLUENT LEAD SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | 10-Day |
|---|---|---|---|---|
| 5020 | 229 | 0.242 | 4.50 | 2.11 |
| 19063 | 238 | 0.10 | 3.15 | 3.18 |
| 30165 | 65 | 0.45 | 2.66 | 1.93 |
| 44045 | 49 | 0.14 | 3.89 | 2.26 |
| OVERALL | 581(Total) | 0.20(Mean) | 3.52(Median) | 2.19(Median) |

# TABLE 7-17
# EFFLUENT NICKEL SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 230 | 0.21 | 4.05 | 2.39 |
| 5020 | 231 | 0.40 | 4.48 | 2.54 |
| 6002 | 6 | 0.09 | 4.72 | -- |
| 6035 | 9 | 0.06 | 5.37 | -- |
| 6051 | 13 | 0.04 | 6.55 | 6.12 |
| 6087 | 12 | 0.66 | -- | 6.30 |
| 11008 | 185 | 0.44 | 2.79 | 1.62 |
| 19063 | 10 | 0.07 | 2.90 | -- |
| 20082 | 253 | 0.32 | 3.72 | 2.77 |
| 20116 | 243 | 0.67 | 2.26 | 1.31 |
| 23076 | 241 | 0.50 | 6.38 | 4.29 |
| 30050 | 75 | 0.03 | 3.78 | 2.37 |
| 33092 | 27 | 0.25 | 4.38 | 2.51 |
| 36040 | 178 | 0.32 | 1.73 | 1.27 |
| 44045 | 49 | 0.32 | 10.13 | 2.66 |
| 44150 | 42 | 0.12 | -- | -- |
| OVERALL | 1804(Total) | 0.39(Mean) | 4.22(Median) | 2.52(Median) |

### TABLE 7-18
### EFFLUENT ZINC SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 230 | 0.61 | 3.52 | 1.96 |
| 6002 | 6 | 0.15 | 8.86 | -- |
| 6051 | 13 | 0.13 | 7.24 | 1.42 |
| 6107 | 10 | 1.50 | 5.20 | -- |
| 11008 | 184 | 0.26 | 3.93 | 2.26 |
| 12002 | 31 | 0.24 | 14.16 | 11.35 |
| 20080 | 269 | 0.41 | 2.22 | 1.41 |
| 20082 | 250 | 0.32 | 4.07 | 2.70 |
| 30165 | 66 | 1.26 | 4.34 | 3.50 |
| 33050 | 115 | 0.07 | 5.15 | 3.07 |
| 44150 | 42 | 0.02 | -- | 4.62 |
| OVERALL | 1216 (Total) | 0.41 (Mean) | 4.75 (Median) | 2.70 (Median) |

Table 7-19 summarizes the daily and 10-day variability factors calculated from the long term data and shown earlier in Tables 7-12 through 7-18.

### TABLE 7-19
### SUMMARY OF OPTION 1 DAILY MAXIMUM AND 10-DAY AVERAGE VARIABILITY FACTORS

| Pollutant | Variability Factor<br>Daily Max. | 10-Day Average |
|---|---|---|
| Total suspended solids | 3.59 | 1.85 |
| Cadmium | 5.31 | 2.02 |
| Chromium, total | 4.85 | 2.98 |
| Copper | 4.15 | 2.54 |
| Lead | 3.52 | 2.19 |
| Nickel | 4.22 | 2.52 |
| Zinc | 4.75 | 2.70 |

Table 7-20 presents the daily and monthly maximum average effluent limitations for common metals Option 1. These limitations were obtained by multiplying the visited plant mean concentrations of Table 7-11 by the respective variability factors shown in Table 7-19 (except for cadmium and lead, where the mean from the long term self-monitoring concentrations were used in place of the visited mean effluent concentrations).

### TABLE 7-20
### SUMMARY OF OPTION 1 DAILY MAXIMUM AND 10-DAY AVERAGE

| Pollutant | Daily Max. | Monthly Maximum Average | Long Term Average |
|---|---|---|---|
| Total suspended solids | 60 | 31 | 17 |
| Cadmium | 0.69 | 0.26 | 0.13 |
| Chromium, total | 2.77 | 1.71 | 0.57 |
| Copper | 3.38 | 2.07 | 0.82 |
| Lead | 0.69 | 0.43 | 0.19 |
| Nickel | 3.98 | 2.38 | 0.94 |
| Zinc | 2.61 | 1.48 | 0.55 |

Table 7-21 summarizes the percent compliance for the EPA sampled plant data presented previously in Tables 7-4 to 7-10 and for the Option 1 plants submitting long term data.

## TABLE 7-21

## PERCENTAGE OF THE MFC DATA BASE BELOW THE EFFLUENT CONCENTRATION LIMITATIONS FOR OPTION 1

| Pollutant | EPA Sampled Plants Daily Maximum | Self-Monitoring Data Daily Maximum | Self-Monitoring Data 10-day Average |
|---|---|---|---|
| Total Suspended Solids | 100.0 | 99.8 | 100.0 |
| Cadmium | 100.0 | 98.8 | 97.8 |
| Chromium, total | 100.0 | 99.7 | 99.7 |
| Copper | 95.7 | 98.5 | 96.7 |
| Lead | 100.0 | 95.9 | 92.7 |
| Nickel | 95.6 | 99.9 | 100.0 |
| Zinc | 94.1 | 99.2 | 95.8 |

## TREATMENT OF COMMON METALS WASTES - OPTION 2

The Option 2 treatment system for common metals wastes is pictured schematically in Figure 7-8. As shown in the figure, the system is identical to the Option 1 common metals treatment system with the addition of a filtration device after the primary solids removal step. The purpose of this filtration unit is to "polish" the effluent, that is, to remove suspended solids such as metal hydroxides which did not settle out in the clarifier. The filter also acts as a safeguard against pollutant discharge if an upset should occur in the sedimentation device. Filtration techniques that are applicable for Option 2 systems include granular bed filtration and diatomaceous earth filtration.

### Granular Bed Filtration

Filtration is basic to water treatment technology, and experience with the process dates back to the 1800's. Filtration occurs in nature as the surface ground waters are purified by sand. Silica sand, anthracite coal, and garnet are common filter media used in water treatment plants. These are usually supported by gravel. The media may be used singly or in combination. The multi-media filters may be arranged to maintain relatively distinct layers by virtue of balancing the forces of gravity, flow and buoyancy on the individual particles. This is accomplished by selecting appropriate filter flow rates (gpm/sq ft), media grain size, and density.

Granular bed filters may be classified in terms of filtration rate, filter media, flow pattern, or method of pressurization. Traditional rate classifications are slow sand, rapid sand, and high rate mixed media. In the slow sand filter, flux or hydraulic loading is relatively low, and removal of collected solids to clean the filter is therefore relatively infrequent. The filter is often cleaned by scraping off the inlet face (top) of the sand bed. In the higher rate filters, cleaning is frequent and is accomplished by a periodic backwash, opposite to the direction of normal flow.

A filter may use a single medium such as sand or diatomaceous earth, but dual and mixed (multiple) media filters allow higher flow rates and efficiencies. The dual media filter usually consists of a fine bed of sand under a coarser bed of anthracite coal. The coarse coal removes most of the influent solids, while the fine sand performs a polishing function. At the end of the backwash, the fine sand settles to the bottom because it is denser than the coal, and the filter is ready for normal operation. The mixed media filter operates on the same principle, with the finer, denser media at the bottom and the coarser, less dense media at the top. The usual arrangement is garnet at the bottom (outlet end) of the bed, sand in the middle, and anthracite coal at the top. Some mixing of these layers occurs and is, in fact, desirable.

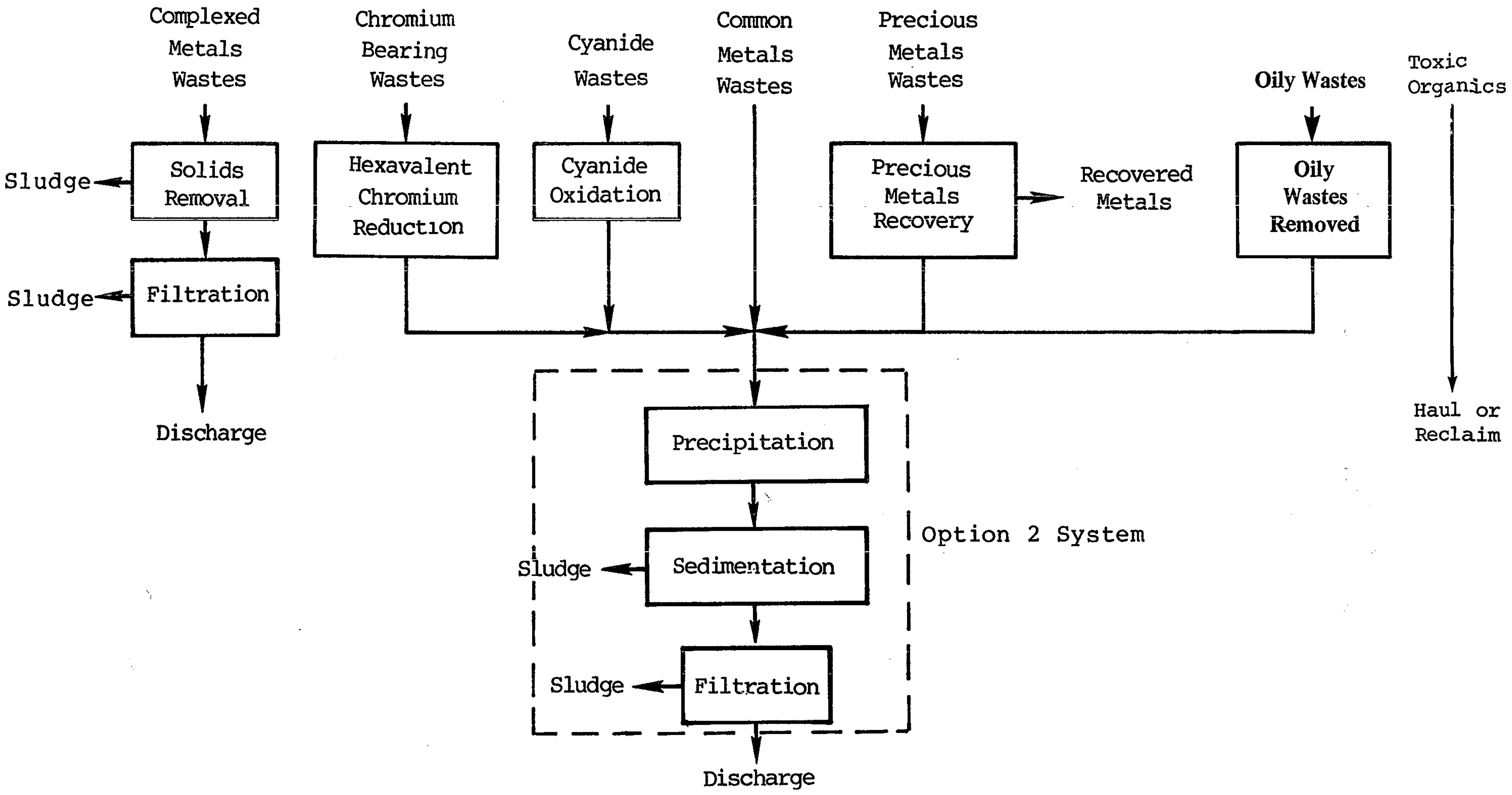


FIGURE 7-8
WASTE TREATMENT SCHEME
OPTION 2

The flow pattern is usually top-to-bottom, but other patterns are sometimes used. Upflow filters are sometimes used, and in a horizontal filter the flow is horizontal. In a biflow filter, the influent enters both the top and the bottom and exits laterally. The advantage of an upflow filter is that with an upflow backwash the particles of a single filter medium are distributed and maintained in the desired coarse-to-fine (bottom-to-top) arrangement. The disadvantage is that the bed tends to become fluidized, which ruins filtration efficiency. The biflow design is an attempt to overcome this problem.

The usual granular bed filter operates by gravity flow. However, pressure filters are also used. Pressure filters permit higher solids loadings before cleaning and are advantageous when the filter effluent must be pressurized for further downstream treatment. In addition, pressure filter systems are often less costly for low to moderate flow rates.

Figure 7-9 depicts a granular bed filter. It is a high rate, dual media, gravity downflow filter, with self-stored backwash. Both filtrate and backwash are piped around the bed in an arrangement that permits upflow of the backwash, with the stored filtrate serving as backwash. Addition of the indicated coagulant and polyelectrolyte usually results in a substantial improvement in filter performance.

Auxiliary filter cleaning is sometimes employed in the upper few inches of filter beds. This is conventionally referred to as surface wash and is accomplished by water jets just below the surface of the expanded bed during the backwash cycle. These jets enhance the scouring action in the bed by increasing the agitation.

An important feature for successful filtration and backwashing is the underdrain. This is the support structure for the bed. The underdrain provides an area for collection of the filtered water without clogging from either the filtered solids or the media grains. In addition, the underdrain prevents loss of the media with the water, and during the backwash cycle it provides even flow distribution over the bed. Failure to dissipate the velocity head during the filter or backwash cycle will result in bed upset and the need for major repairs.

Several standard approaches are employed for filter underdrains. The simplest one consists of a parallel porous pipe imbedded under a layer of coarse gravel and manifolded to a header pipe for effluent removal. Other approaches to the underdrain system are known as the Leopold and Wheeler filter bottoms. Both of these incorporate false concrete bottoms with specific porosity configurations to provide drainage and velocity head dissipation.

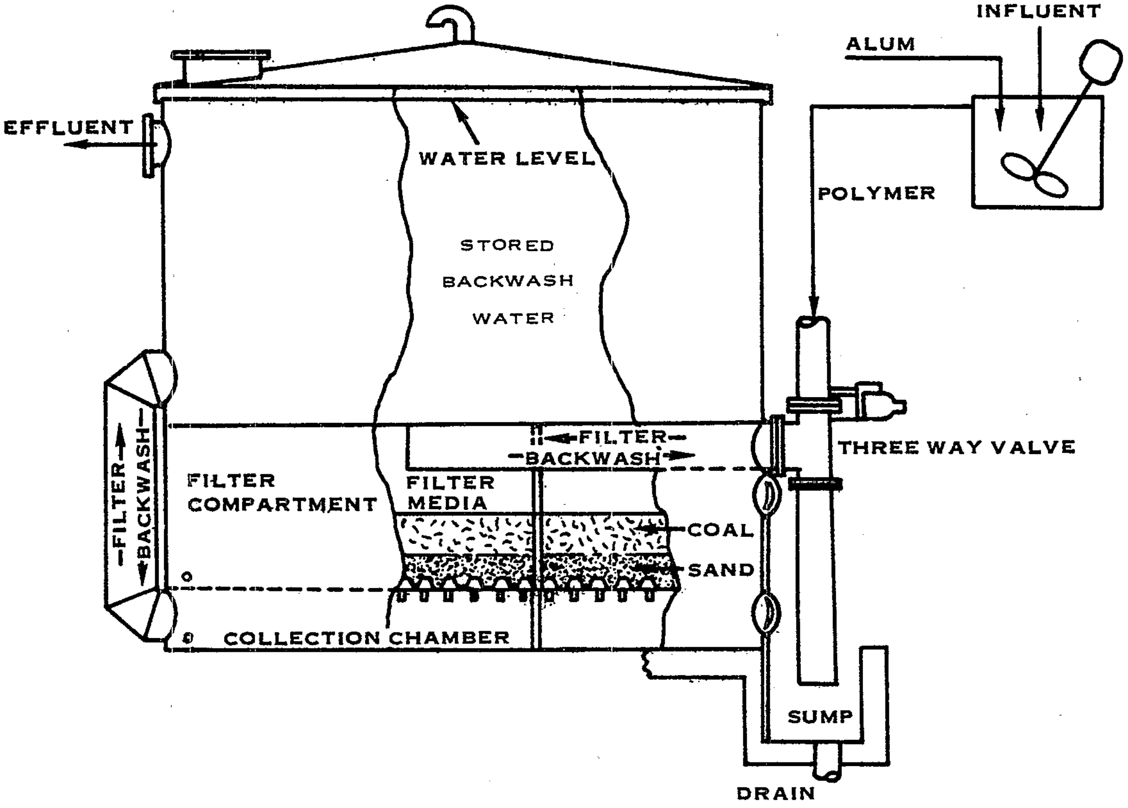


FIGURE 7-9

GRANULAR BED FILTRATION EXAMPLE

Filter system operation may be manual or automatic. The filter backwash cycle may be on a timed basis, a pressure drop basis with a terminal value which triggers backwash, or a solids carryover basis from turbidity monitoring of the outlet stream. All of these schemes have been successfully used.

## Application

Granular bed filters are used in metal finishing to remove residual solids from clarifier effluent. Filters in wastewater treatment plants are often employed for polishing following sedimentation or other similar operations. Granular bed filtration thus has potential application to nearly all industrial plants. Chemical additives which enhance the upstream treatment equipment may or may not be compatible with or enhance the filtration process. It should be borne in mind that in the overall treatment system, effectiveness and efficiency are the objectives, not the performance of any single unit. The volumetric fluxes for various types of filters are as follows:

| | |
|---|---|
| Slow Sand | 2.04 - 5.30 l/min/sq m |
| Rapid Sand | 40.74 - 51.48 l/min/sq m |
| High Rate Mixed Media | 81.48 - 122.22 l/min/sq m |

The principal advantages of granular bed filtration are its low initial and operating costs and reduced land requirements over other methods to achieve the same level of solids removal. However, the filter may require pretreatment if the solids level is high (from 100 to 150 mg/l). Operator training is fairly high due to controls and periodic backwashing, and backwash must be stored and dewatered to be disposed of economically.

The recent improvements in filter technology have significantly improved filtration reliability. Control systems, improved designs, and good operating procedures have made filtration a highly reliable method of water treatment. Deep bed filters may be operated with either manual or automatic backwash. In either case, they must be periodically inspected for media attrition, partial plugging, and leakage. Where backwashing is not used, collected solids must be removed by shoveling, and filter media must be at least partially replaced. Filter backwash is generally recycled within the wastewater treatment system, so that the solids ultimately appear in the clarifier sludge stream for subsequent dewatering. Alternatively, the backwash stream may be dewatered directly or, if there is no backwash, the collected solids may be suitably disposed. In either of these situations there is a solids disposal problem similar to that of clarifiers.

### Performance

Suspended solids are commonly removed from wastewater streams by filtering through a deep 0.3-0.9 m (1-3 feet) granular filter bed. The porous bed formed by the granular media can be designed to remove practically all suspended particles. Even colloidal suspensions (roughly 1 to 100 microns) are adsorbed on the surface of the media grains as they pass in close proximity in the narrow bed passages.

Properly operating filters following some pretreatment to reduce suspended solids should produce water averaging 12.8 mg/l TSS. Pretreatment with inorganic or polymeric coagulants can improve poor performance.

### Demonstration Status

Deep bed filters are in common use in municipal treatment plants. Their use in polishing industrial clarifier effluent is increasing, and the technology is proven and conventional.

## Diatomaceous Earth Filtration

Diatomaceous earth filtration, combined with precipitation and sedimentation, is a solids separation device which can further enhance suspended solids removal. The diatomaceous earth filter is used to remove metal hydroxides and other solids from the wastewater and provides an effluent of high quality. A diatomaceous earth filter is comprised of a filter element, a filter housing and associated pumping equipment. The filter element consists of multiple leaf screens which are coated with diatomaceous earth. The size of the filter is a function of flow rate and desired operating time between filter cleanings.

Normal operation of the system involves pumping a mixture of diatomaceous earth and water through the screen leaves. This deposits the diatomaceous earth filter media on the screens and prepares them for treatment of the wastewater. Once the screens are completely coated, the pH adjusted wastewater can be pumped through the filter. The metal hydroxides and other suspended solids are removed from the effluent in the diatomaceous earth filter. The buildup of solids in the filter increases the pressure drop across the filter. At a certain pressure, the wastewater is stopped, the filter is cleaned and the cycle is repeated.

### Application

The principal advantage of using a diatomaceous earth filter is its increased removal of suspended solids and precipitates. One additional advantage is that sludge removed from the filter is much drier than that removed from a clarifier (approximately 50% solids). This high solids content can significantly reduce the cost of hauling and landfill.

The major disadvantage to the use of a filter system is an increase in operation and maintenance costs.

## Performance

Three of the plants that were visited and sampled were operating diatomaceous earth filters. The analytical results of samples taken before and after the filters are displayed below. All of these plants were using filters in place of sedimentation, and both influent and effluent concentrations are therefore relatively high. However, the data do illustrate that removal of solids by these filters is very substantial.

POLLUTANT CONCENTRATION (mg/l)
Plant ID 09026

| | Day 1 | | Day 2 | | Day 3 | |
|---|---|---|---|---|---|---|
| Parameter | Input To Filter | Filter Effluent | Input To Filter | Filter Effluent | Input To Filter | Filter Effluent |
| TSS | 548. | 11. | 544. | 15. | 450. | 67. |
| Cu | 52.4 | 2.25 | 63.8 | 4.17 | 63.8 | 2.2 |
| Ni | .299 | .116 | .341 | .102 | .377 | .107 |
| Cr, Total | .078 | .008 | .086 | .010 | .086 | .012 |
| Zn | 22.4 | 3.06 | 27.6 | .706 | 30.6 | .882 |
| Cd | .011 | .012 | .010 | .009 | .011 | .011 |
| Sn | .086 | .086 | .086 | .086 | .086 | .086 |
| Pb | .062 | .036 | .062 | .040 | .065 | .051 |

POLLUTANT CONCENTRATION (mg/l)
Plant ID 36041

| | Day 1 | | Day 2 | | Day 3 | |
|---|---|---|---|---|---|---|
| Parameter | Input To Filter | Filter Effluent | Input To Filter | Filter Effluent | Input To Filter | Filter Effluent |
| TSS | 1036. | 32.0 | 524. | 10.0 | 652. | 5.00 |
| Cu | 26.5 | 1.89 | 7.53 | .444 | 9.56 | 1.06 |
| Ni | 5.00 | .320 | 2.57 | .044 | 4.49 | .571 |
| Cr, Total | 28.6 | .667 | 12.2 | .611 | 25.0 | .333 |
| Zn | 18.7 | .765 | 13.4 | .139 | 14.3 | .430 |
| Cd | .053 | .009 | .042 | .006 | .042 | .006 |
| Sn | 1.77 | .171 | 2.00 | .143 | 1.58 | .114 |
| Pb | 1.00 | .064 | .136 | .032 | .212 | .036 |

POLLUTANT CONCENTRATION (mg/l)
Plant ID 38217

| Parameter | Input To Filter | Filter Effluent | Input To Filter | Filter Effluent |
|---|---|---|---|---|
| TSS | 575. | 30.0 | 620. | 90.0 |
| Cu | .158 | .261 | .325 | .085 |
| Ni | .253 | .195 | .255 | .159 |
| Cr, Total | .022 | .037 | .060 | .020 |
| Zn | 1.92 | 3.79 | 5.20 | 2.31 |
| Cd | .006 | .011 | .019 | .010 |
| Sn | .028 | .034 | .054 | .003 |
| Pb | .058 | .154 | .150 | .032 |

Demonstration Status

Filters with similar operational characteristics to those described above are in common use throughout the metal finishing industry.

## Common Metals Waste Treatment System Operation - Option 2

The entire Option 1 system operation discussion applies equally to Option 2. In addition, the use of a polishing filter necessitates further precautions. Close monitoring is needed to prevent both hydraulic overloading and solids overloading. Either form of overloading may result in pollutant bypassing in a barrier filter (through element breakage or pressure relief) or pollutant reentrainment in a depth filter. Many types of filters must be shut down for solids removal. Wastewater flow must not be bypassed during this period. Bypassing can be obviated by use of a holding tank or by installation of dual filters in parallel arrangment. A further consideration concerns disposable elements for filters that use them. Because of the contained toxic metals, these elements must be treated as hazardous waste and should not be placed in the plant trash.

The following table (Table 7-22) presents a listing of 37 plants from the metal finishing data base which have an Option 2 common metals treatment system. These include both sampled plants, DCP plants, and plants which supplied long term self-monitoring data.

### TABLE 7-22
### METAL FINISHING PLANTS WITH OPTION 2 TREATMENT SYSTEMS FOR COMMON METALS

03043
04140
04151
06062
06131
11096
11125
11182
12075
12077
13031
13033
15193
19069
20483
27042
28115
28121
28699
30159
30165
30507
30519
30927
31021
31022
31033
31044
33110
36048
36082
36102
38223
40047
44150
45041

## Common Metals Waste Treatment System Performance - Option 2

Performance of a properly operating Option 2 treatment system (shown in Figure 7-8 with its sources of wastes) is demonstrated by low effluent levels of total suspended solids (TSS). Effective removal of heavy metals depends on maintaining the system pH at the level needed to form metal hydroxides.

Generally, a pH range of 8.5 to 9.5 is considered most effective for settling and filtration of precipitated hydroxides in mixed metal finishing wastes.

The performance for the Option 2 treatment system was established from a combination of visited plant sampling data and long term self-monitoring data that were submitted by industry. The following subsection describes the procedure used to establish Option 2 treatment system performance for the visited plant data set.

### Visited Plant Performance

To establish the treatment system performance characteristics, plants employing Option 2 treatment that were visited were selected from the Metal Finishing Category data base. The files for these plants were then examined to ensure that only properly operating facilities were included in the performance data base by establishing criteria to eliminate the data for improperly operating systems. The criteria for eliminating improperly operating treatment systems were as follows:

1. Data with an effluent TSS level greater than 50 mg/l were deleted. This represents a level of TSS above which no well-operated treatment plant should be discharging.

2. Plants with alkaline precipitation systems that operated at an average effluent pH of less than 7.0 were deleted. An alkaline precipitation system will not work properly in this pH range.

3. Plants that had complexing agents (unoxidized cyanide or nonsegregated wastes from electroless plating) present were deleted.

4. Plants which had effluent flows significantly greater than the corresponding raw waste flows were deleted. The increase in flows was assumed to be dilution by other wastewaters.

5. Pollutant parameters that had an effluent concentration greater than the raw waste concentration were deleted.

6. Plants that experienced difficulties in system operation during the sampling period were excluded.

The following procedure was followed for each metal pollutant parameter (except TSS which is created during precipitation) in order to eliminate spurious background metal readings. The mean effluent concentration of each parameter was calculated, and when a raw waste concentration was less than the mean effluent concentration for that parameter, the corresponding effluent reading was deleted from the data set. The mean was recalculated using points not removed and the process was repeated in an iterative loop. The deletion of these points prevents the calculation of unrealistically low mean effluent concentrations from the waste treatment systems due to low raw waste pollutant loadings.

Plots of raw waste concentration to the precipitation step vs. effluent concentration from the filter were generated for total suspended solids, cadmium, total chromium, copper, lead, nickel, and zinc. These plots are shown in Figure 7-10 through 7-16. The mean effluent concentrations for these parameters were then computed and are summarized in Table 7-23.

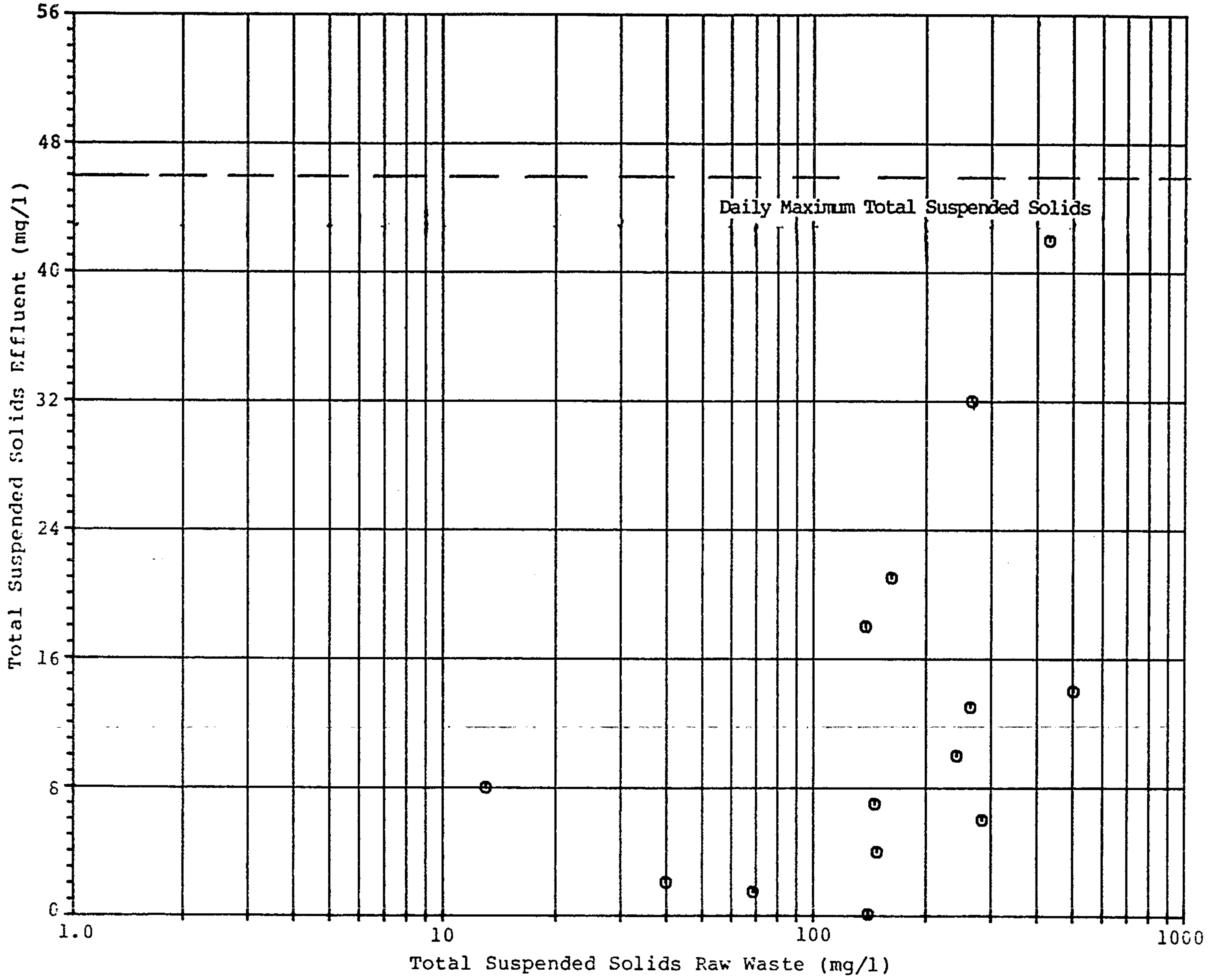
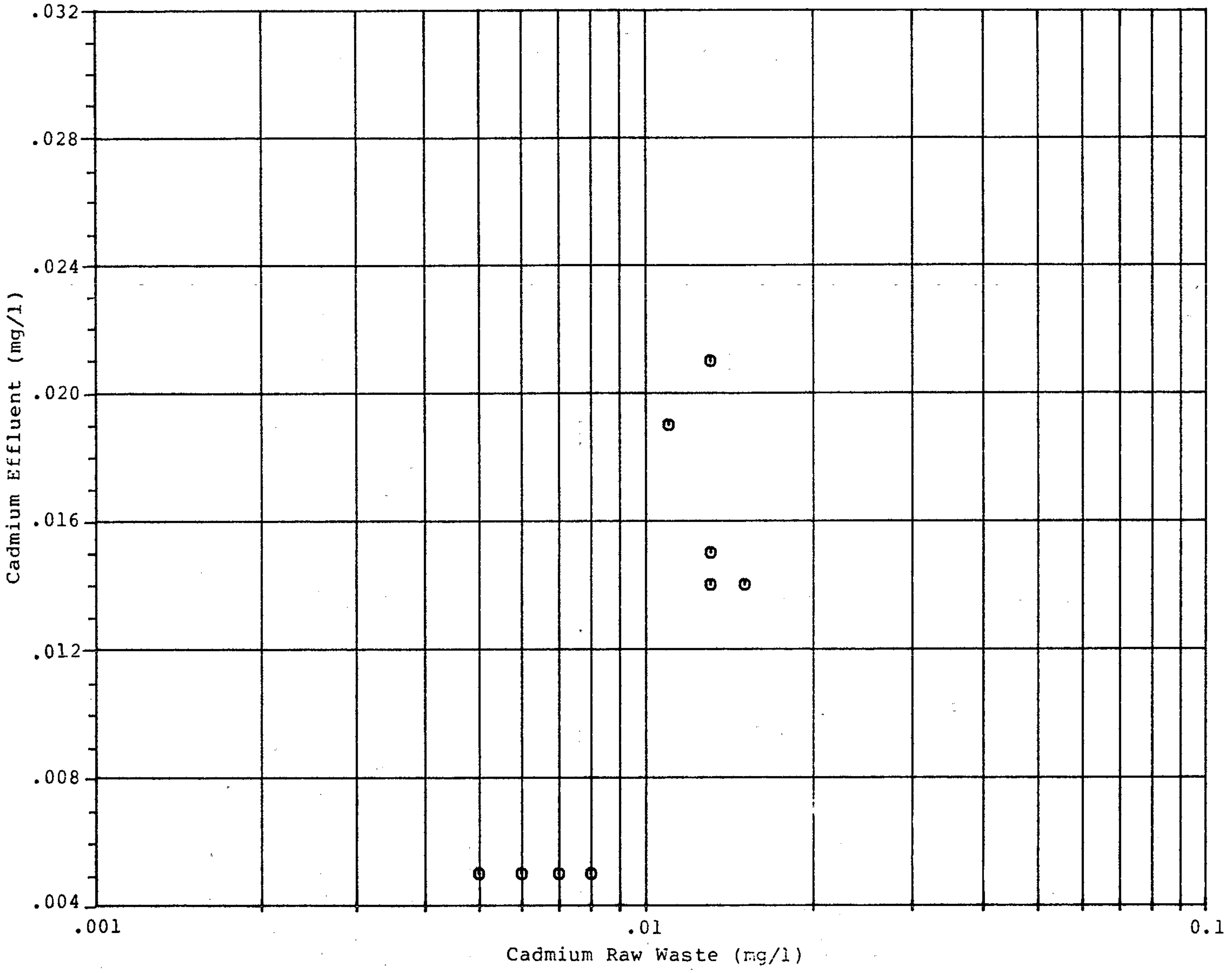


FIGURE 7-10

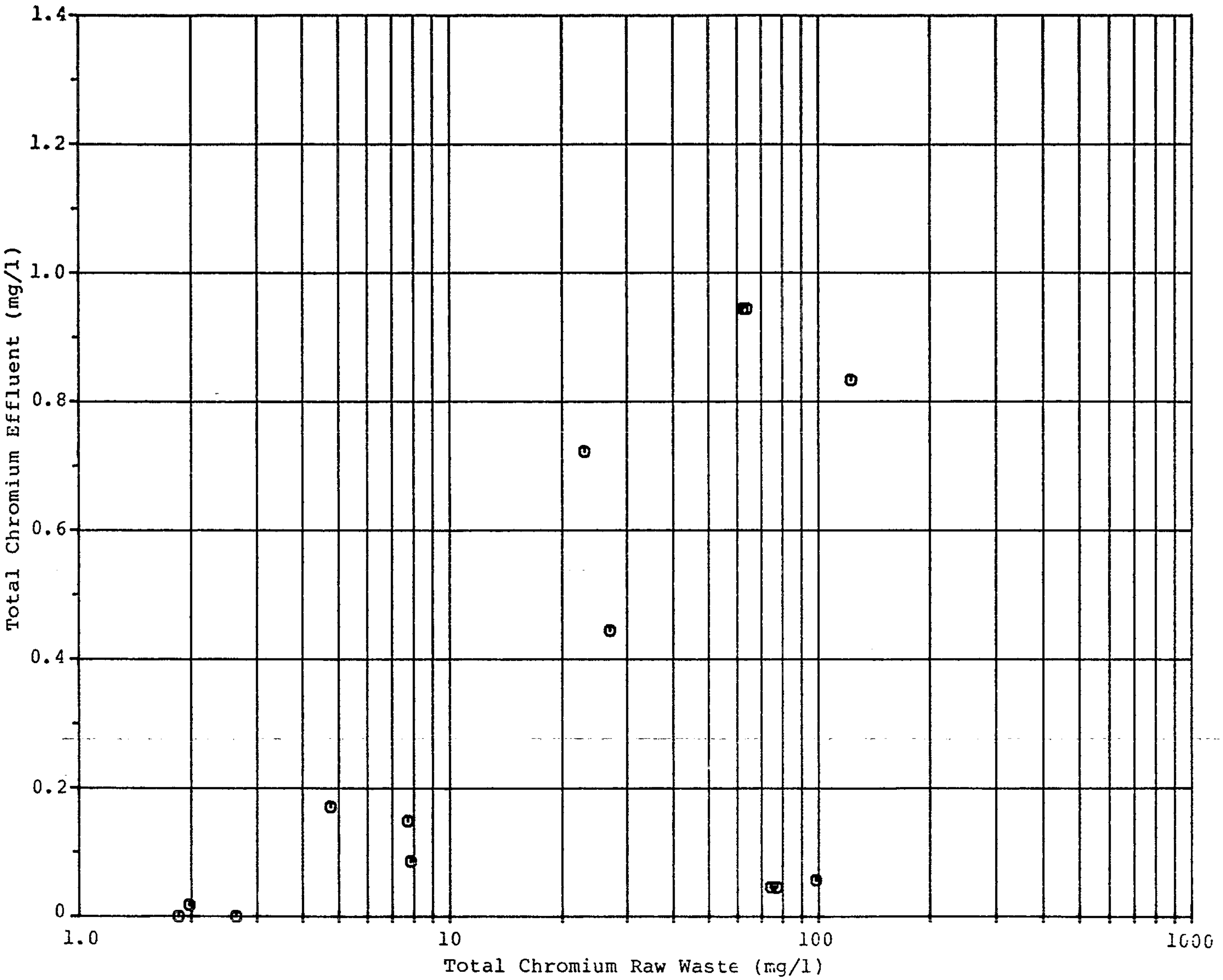
EFFLUENT TSS CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2



Daily Maximum Concentration - 0.54 mg/l

FIGURE 7-11

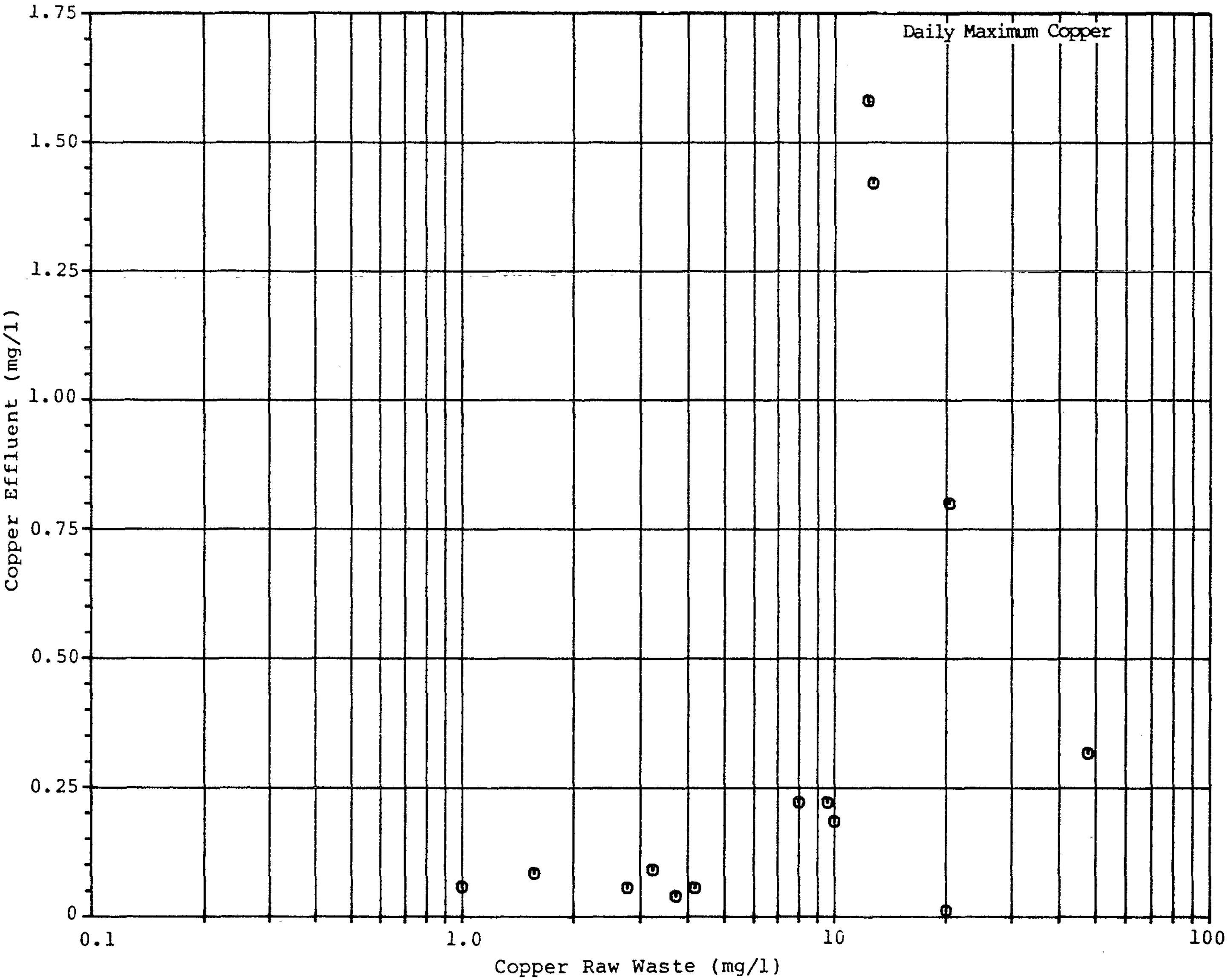
EFFLUENT CADMIUM CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2



Daily Maximum Concentration - 1.60 mg/l

FIGURE 7-12

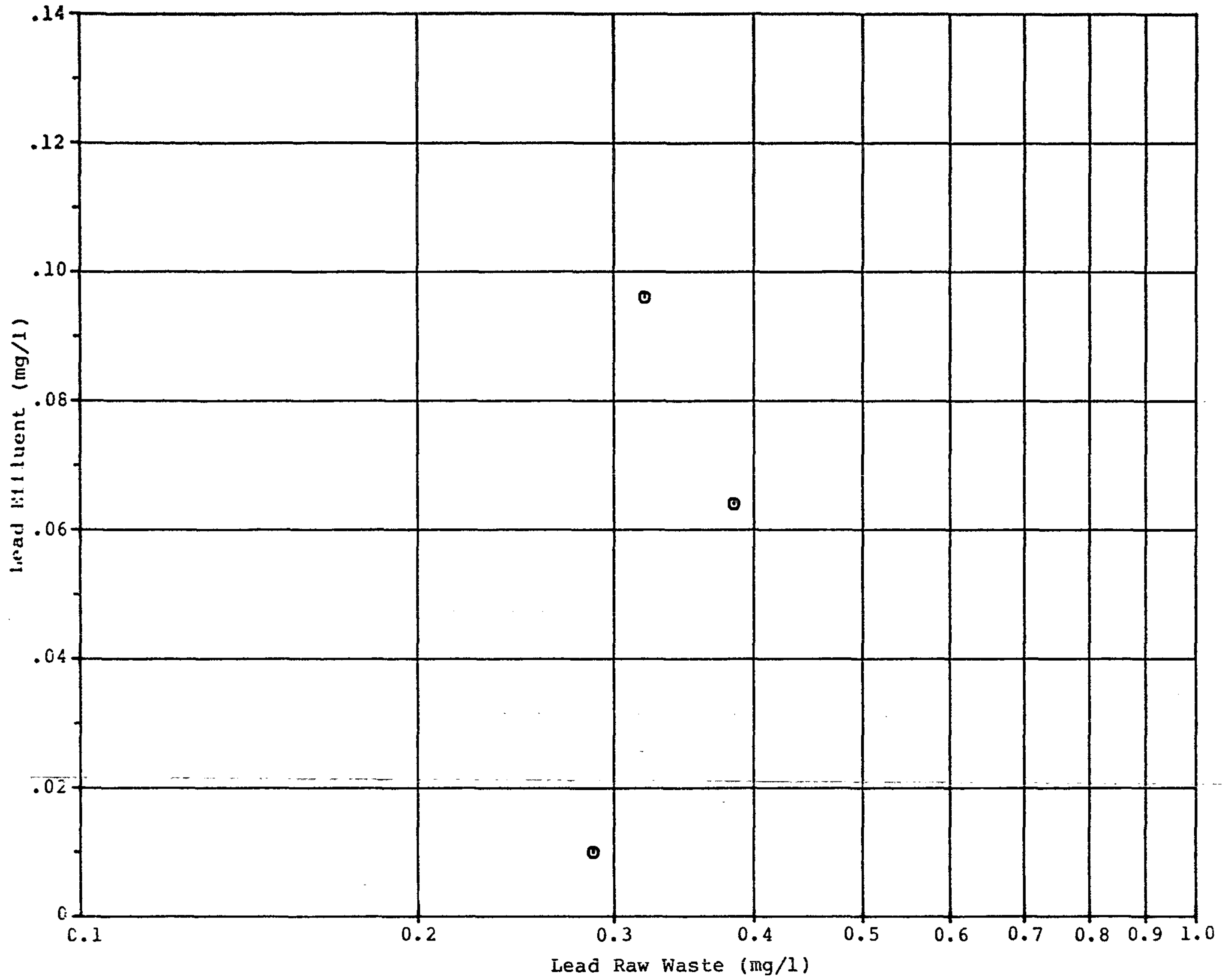
EFFLUENT CHROMIUM CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2



Daily Maximum Concentration - 1.75mg/l

FIGURE 7-13

EFFLUENT COPPER CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2



Daily Maximum Concentration - 0.48 mg/l

FIGURE 7-14

EFFLUENT LEAD CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2

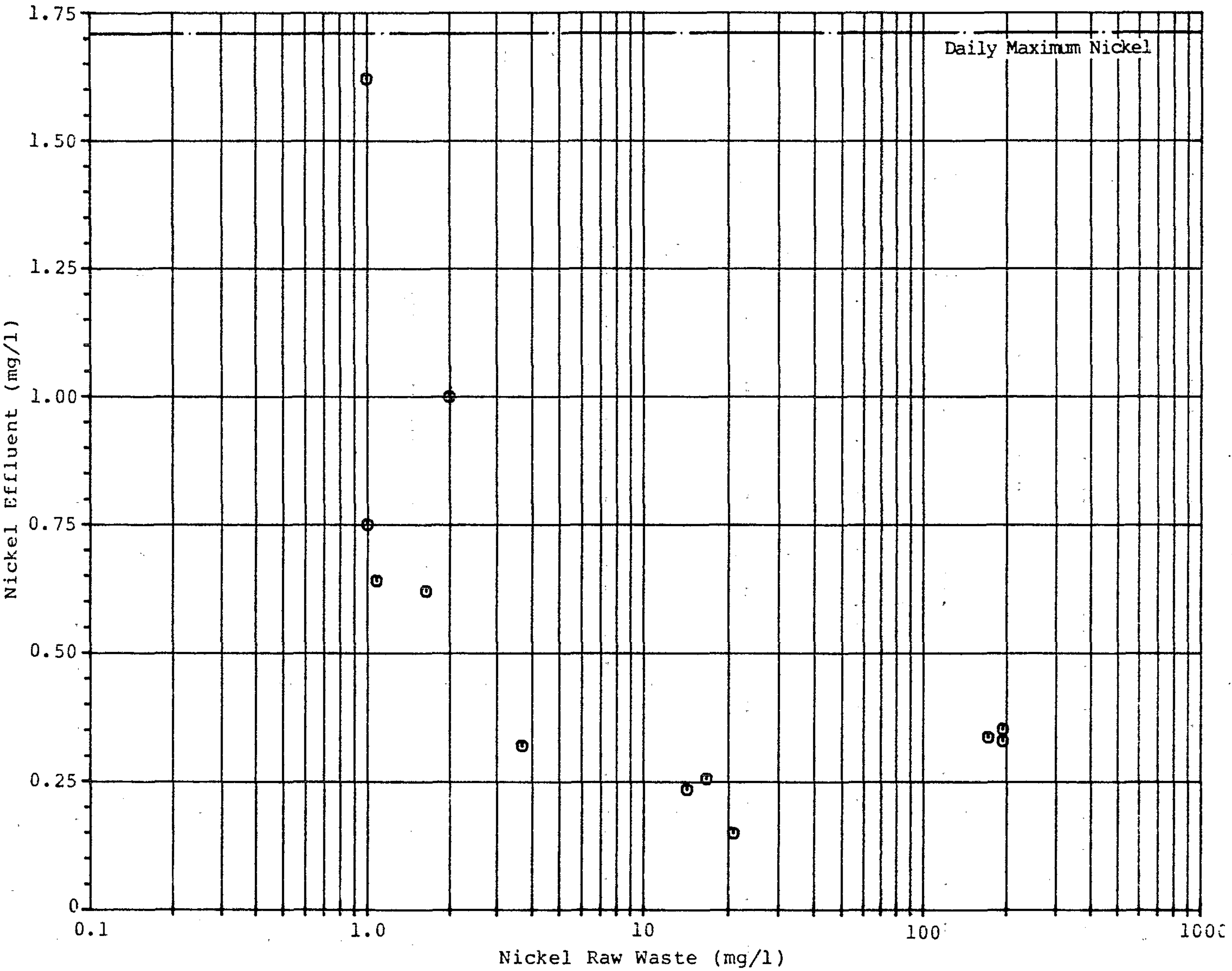


FIGURE 7-15

EFFLUENT NICKEL CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2

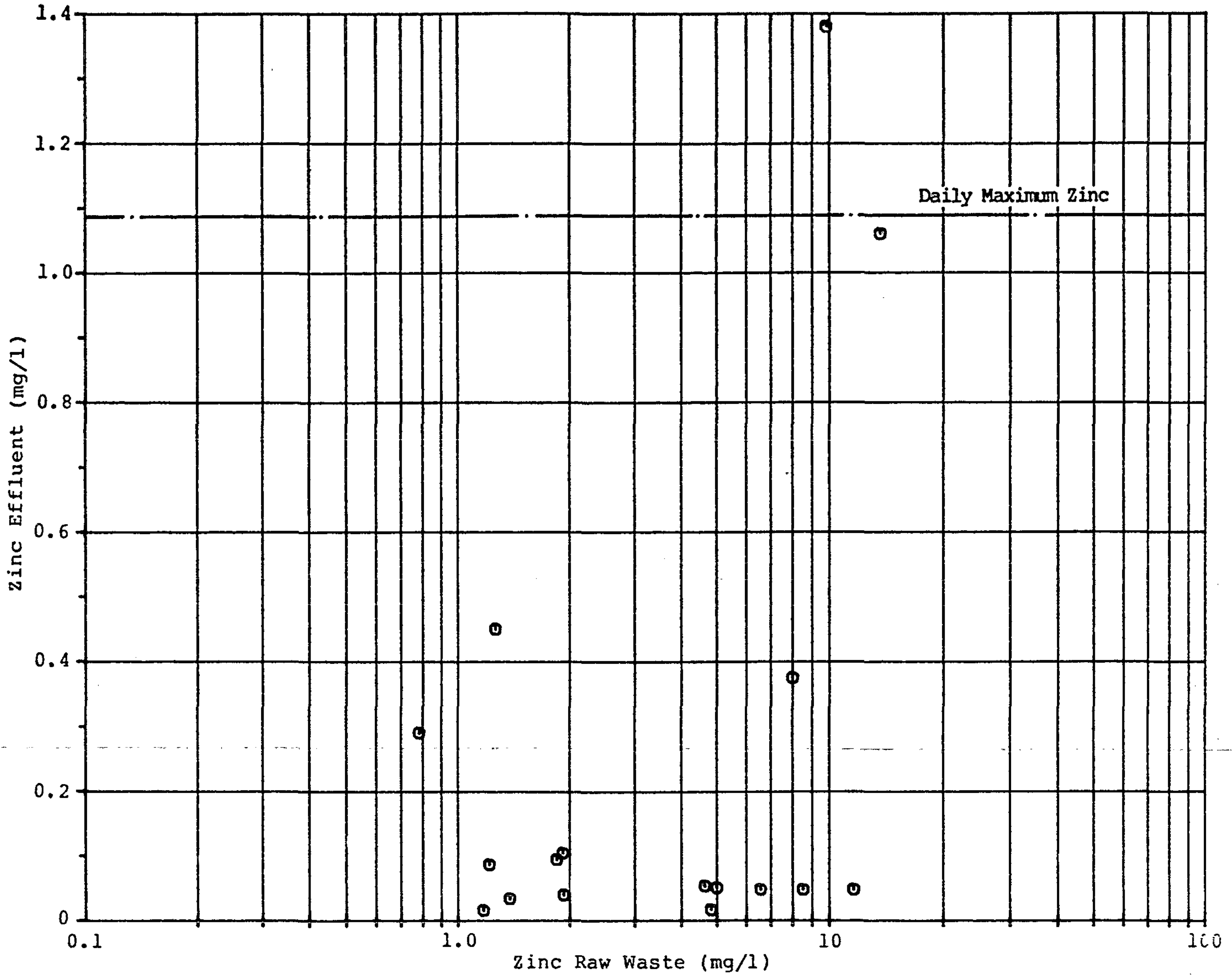


FIGURE 7-16

EFFLUENT ZINC CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2

## TABLE 7-23
## TREATMENT OF COMMON METALS
## VISITED PLANT OPTION 2 MEAN EFFLUENT CONCENTRATIONS

| Parameter | mg/l |
|---|---|
| Total Suspended Solids | 12.8 |
| Cadmium | .014 |
| Chromium, Total | .319 |
| Copper | .367 |
| Lead | .031 |
| Nickel | .459 |
| Zinc | .247 |

## Long Term Self-Monitoring Data Performance

Long term self-monitoring data were submitted by a number of plants with Option 2 treatment systems. However, the quantity of data submitted, relative to the data available for Option 1, was considered to be statistically inferior for the calculation of Option 2 variability factors. In addition, the variability for plants with Option 2 generally fell within the range of the Option 1 results. Therefore, the previously determined Option 1 variability factors were used in calculating Option 2 effluent performance. Tables 7-24 through 7-30 present overall values for each pollutant, the total number of available points, and the mean value for all points.

## Overall Performance

The overall Option 2 system performance is based on mean effluent concentrations calculated from visited plant data shown in Table 7-23 (except for cadmium and lead, where the mean from the self-monitoring data were used) multiplied by variability factors calculated from long term self-monitoring data taken at Option 1 plants. The statistical procedures used to establish Option 2 system performance are discussed in Statistical Analysis at the end of this section.

## TABLE 7-24
## EFFLUENT TSS SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 03043 | 94 | 10.07 |
| 15193 | 12 | 13.58 |
| 20483 | 357 | 5.90 |
| 38223 | 234 | 5.74 |
| OVERALL | 697 (TOTAL) | 6.54 (MEAN) |

## TABLE 7-25
## EFFLUENT CADMIUM SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 38223 | 234 | 0.08 |

## TABLE 7-26
## EFFLUENT CHROMIUM SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 03043 | 91 | 0.60 |
| 15193 | 12 | 0.11 |
| 31021 | 86 | 0.25 |
| 38223 | 234 | 0.06 |
| OVERALL | 423 (TOTAL) | 0.22 (MEAN) |

## TABLE 7-27
## EFFLUENT COPPER SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 11125 | 29 | 1.11 |
| 15193 | 12 | 0.06 |
| 31021 | 121 | 1.44 |
| OVERALL | 225 (TOTAL) | 1.32 (MEAN) |

## TABLE 7-28
## EFFLUENT LEAD SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 38223 | 234 | 0.04 |

## TABLE 7-29
## EFFLUENT NICKEL SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 03043 | 91 | 0.42 |
| 11125 | 29 | 1.75 |
| 15193 | 12 | 0.27 |
| 31021 | 120 | 0.93 |
| OVERALL | 252 (TOTAL) | 0.81 (MEAN) |

## TABLE 7-30
## EFFLUENT ZINC SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 2 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) |
|---|---|---|
| 03043 | 91 | 0.35 |
| 15193 | 12 | 0.14 |
| 31021 | 121 | 0.77 |
| 38223 | 234 | 0.11 |
| OVERALL | 252 (TOTAL) | 0.81 (MEAN) |

Table 7-31 summarizes the daily and 10-day variability factors used in determining Option 2 effluent limitations. These variability factors are a repeat of the Option 1 variability factors presented previously in Table 7-19.

### TABLE 7-31
### SUMMARY OF OPTION 2 DAILY MAXIMUM AND 10-DAY AVERAGE VARIABILITY FACTORS

| Pollutant | Variability Factor<br>Daily Max. | Variability Factor<br>10-Day Average |
|---|---|---|
| Total suspended solids | 3.59 | 1.85 |
| Cadmium | 5.31 | 2.02 |
| Chromium, total | 4.85 | 2.98 |
| Copper | 4.15 | 2.54 |
| Lead | 3.52 | 2.19 |
| Nickel | 4.22 | 2.52 |
| Zinc | 4.75 | 2.70 |

Table 7-32 presents the daily maximum, 10-day average, and long term average effluent performance for common metals Option 2. Performance was obtained by multiplying the visited plant mean concentrations of Table 7-23 by the respective variability factors shown in Table 7-31 (except for cadmium and lead, where the weighted mean Option 2 self-monitoring data concentrations were used in place of the visited plant mean effluent concentrations). The allowable daily effluent concentrations for each of the parameters have been shown on Figures 7-10 through 7-16.

### TABLE 7-32
### OPTION 2 COMMON METAL PERFORMANCE LEVELS

| Pollutant | Daily Max. | 10-Day Average | Long Term Average |
|---|---|---|---|
| Total suspended solids | 46 | 24 | 12.8 |
| Cadmium | 0.42 | 0.16 | 0.08 |
| Chromium, total | 1.55 | 0.95 | 0.32 |
| Copper | 1.52 | 0.93 | 0.37 |
| Lead | 0.14 | 0.09 | 0.04 |
| Nickel | 1.94 | 1.16 | 0.46 |
| Zinc | 1.13 | 0.67 | 0.25 |

Table 7-33 summarizes the percentage of the metal finishing data base below the Option 2 daily maximum concentration limitation for the EPA sampled plants.

### TABLE 7-33
### PERCENTAGE OF THE MFC DATA BASE BELOW THE DAILY MAXIMUM CONCENTRATIONS FOR OPTION 2

| Pollutant | EPA Sampled Plants Daily Maximum |
|---|---|
| Total suspended solids | 100.0 |
| Cadmium | 100.0 |
| Chromium, total | 100.0 |
| Copper | 100.0 |
| Lead | 100.0 |
| Nickel | 100.0 |
| Zinc | 94.1 |

Summary tables are provided to show a direct comparison of the mean, daily maximum, and 10-day average concentrations for Options 1 and 2. Table 7-34 presents a comparison of the mean concentrations and Table 7-35 lists the daily maximum and maximum monthly average concentrations for each.

### TABLE 7-34
### OPTION 1 AND OPTION 2 MEAN CONCENTRATION COMPARISON

CONCENTRATION (mg/ℓ)

| Pollutant | Option 1 | Option 2 |
|---|---|---|
| Total suspended solids | 16.8 | 12.8 |
| Cadmium | 0.19 | 0.08 |
| Chromium, total | 0.572 | 0.319 |
| Copper | 0.815 | 0.367 |
| Lead | 0.20 | 0.04 |
| Nickel | 0.942 | 0.459 |
| Zinc | 0.549 | 0.247 |

### TABLE 7-35
### OPTION 1 AND OPTION 2 PERFORMANCE COMPARISON

CONCENTRATION (mg/ℓ)

| Pollutant | Option 1 | | Option 2 | |
|---|---|---|---|---|
| | Daily Max. | Maximum Monthly Ave. | Daily Max. | Maximum Monthly Ave. |
| Total Suspended Solids | 60 | 31 | 46 | 24 |
| Cadmium | 0.69 | 0.26 | 0.42 | 0.16 |
| Chromium, total | 2.77 | 1.71 | 1.55 | 0.95 |
| Copper | 3.38 | 2.07 | 1.52 | 0.93 |
| Lead | 0.69 | 0.43 | 0.14 | 0.09 |
| Nickel | 3.98 | 2.38 | 1.94 | 1.16 |
| Zinc | 2.61 | 1.48 | 1.17 | 0.67 |

## TREATMENT OF COMMON METALS WASTES - OPTION 3

The Option 3 treatment system for metal wastes consists of the Option 1 end-of-pipe treatment system plus the addition of in-plant controls for cadmium. In-plant controls could include evaporative recovery, ion exchange, and recovery rinses. The purpose of these in-plant controls is to nearly eliminate cadmium from the raw waste stream. These additional controls will also minimize the chance of discharging this highly toxic metal due to treatment system failure.

The performance of the Option 3 treatment system, applied to cadmium plating rinse, acid stripping of cadmium plated parts, and chromating of cadmium plated parts, will be identical to the Option 1 treatment system with the exception that only background concentration levels of cadmium should be discharged. In order to establish background concentration levels for cadmium all available sampled data were studied to identify data points from plants that apply the metal. The objective was to segregate the data base into two distinct data sets: one data set for plants that apply cadmium, and one data set for plants in which cadmium is not applied. The data set for plants that do not apply cadmium is representative of background metal concentration levels.

## Cadmium Background Level

Table 7-36 presents the data set for plants that do not apply cadmium which was used to establish a background level for cadmium. A percentile distribution of these data are presented in Figure 7-17. While the average of the data is 0.013 mg/ℓ, the Agency has conservatively used the average of the two highest plants not plating cadmium - plants 36041 and 33024. These plants were determined to be statistically different from the other facilities. The resultant daily maximum is higher than all values measured. Furthermore, a new source plant which eliminates the discharge from the cadmium sources should be more than adequately able to meet the background level which was determined using raw waste values. New source performance standards are based on the in-plant cadmium controls plus precipitation/clarification. (Examination of the EPA sampled data for precipitation/clarification of cadmium in Table 7-4 showed an average of 0.011 mg/ℓ). A summary of the statistics used in deriving the new source cadmium limits is presented below.

| | |
|---|---|
| Mean Background Concentration | 0.058 mg/ℓ |
| Daily Variability Factor | 1.54 mg/ℓ |
| 10-Day Variability Factor | 0.89 mg/ℓ |
| Daily Maximum Background Concentration | 0.114 mg/ℓ |
| Maximum Monthly Average Background Concentration | 0.066 mg/ℓ |

The daily maximum and maximum monthly average background concentrations for cadmium detailed in the previous paragraphs are defined as the Option 3 effluent limitations for cadmium.

A review of the various data bases available did not identify any plants that had in-process treatment technologies specifically for the control of three cadmium sources mentioned above. This does not mean that extensive in-process treatment technologies for control of cadmium effluents are not in use within the metal finishing industrial segment; it simply means that no plants were identified which controlled all three sources based upon the available information.

## TABLE 7-36

## PERFORMANCE DATA FOR CADMIUM METAL FINISHING CATEGORY

### OPTION 3

| | Plant ID | Raw Waste Concentration (mg/ℓ) |
|---|---|---|
| 1. | 6101-12-1 | .001 |
| 2. | 6101-12-1 | .002 |
| 3. | 19068-14-0 | .002 |
| 4. | 11477-22-1 | .002 |
| 5. | 11477-22-2 | .002 |
| 6. | 15010-12-2 | .004 |
| 7. | 15010-12-3 | .005 |
| 8. | 4065-8-1 | .005 |
| 9. | 4069-8-1 | .005 |
| 10. | 4069-8-1 | .005 |
| 11. | 5020-1-4 | .005 |
| 12. | 5020-1-5 | .005 |
| 13. | 5020-1-6 | .005 |
| 14. | 19051-6-0 | .005 |
| 15. | 20078-1-2 | .005 |
| 16. | 20078-1-3 | .005 |
| 17. | 20078-1-4 | .005 |
| 18. | 20078-1-7 | .005 |
| 19. | 36040-1-1 | .005 |
| 20. | 36040-1-1 | .005 |
| 21. | 36040-1-1 | .005 |
| 22. | 31021-1-2 | .005 |
| 23. | 31021-1-3 | .005 |
| 24. | 20083-1-3 | .006 |
| 25. | 33692-23-1 | .006 |
| 26. | 31021-1-1 | .006 |
| 27. | 33070-1-1 | .007 |
| 28. | 5020-1-3 | .007 |
| 29. | 33065-9-1 | .007 |
| 30. | 33070-1-3 | .008 |
| 31. | 40062-8-0 | .008 |
| 32. | 40062-8-0 | .008 |
| 33. | 33065-9-1 | .009 |
| 34. | 15070-1-3 | .009 |
| 35. | 19063-1-1 | .011 |
| 36. | 31022-1-2 | .011 |
| 37. | 19063-1-2 | .012 |
| 38. | 20083-1-5 | .012 |
| 39. | 20083-1-6 | .012 |
| 40. | 31022-1-0 | .013 |
| 41. | 33073-1-1 | .013 |
| 42. | 33073-1-3 | .013 |
| 43. | 6083-1-2 | .013 |
| 44. | 15070-1-1 | .013 |
| 45. | 19063-1-3 | .013 |
| 46. | 15070-1-2 | .014 |
| 47. | 33073-1-2 | .015 |
| 48. | 6731-1-1 | .015 |
| 49. | 6731-1-2 | .017 |
| 50. | 6074-1-1 | .019 |
| 51. | 6731-1-3 | .019 |
| 52. | 6074-1-1 | .021 |
| 53. | 31020-1-1 | .021 |
| 54. | 27044-1-0 | .022 |
| 55. | 20080-1-1 | .024 |
| 56. | 4065-8-1 | .032 |
| 57. | 6074-1-1 | .033 |
| 58. | 36041-1-2 | .042 |
| 59. | 36041-1-3 | .042 |
| 60. | 36041-1-1 | .053 |
| 61. | 33024-6-0 | .095 |

Mean Concentration 0.0131 (n=61)

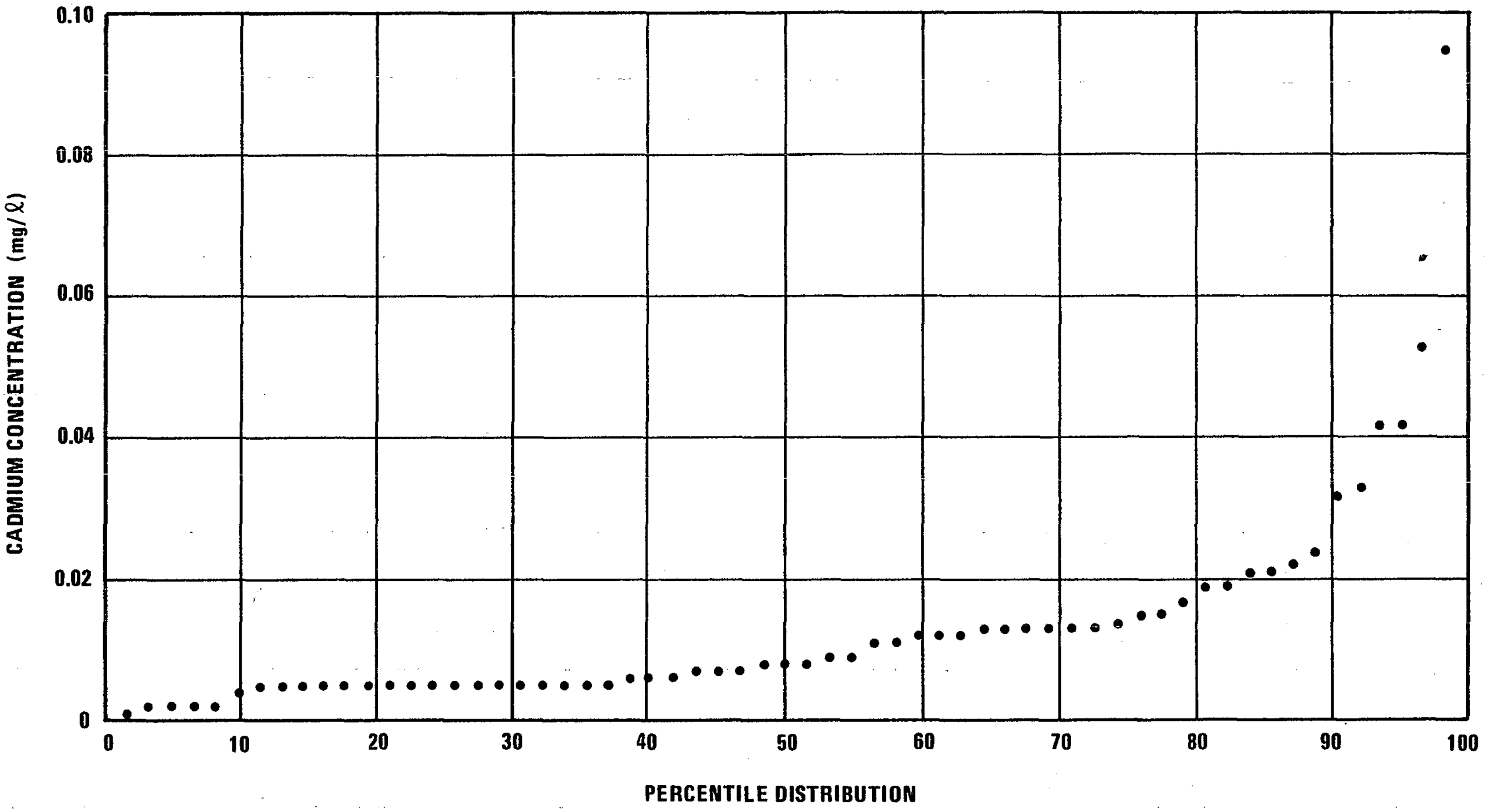


FIGURE 7-17. CADMIUM RAW WASTE CONCENTRATION DISTRIBUTION

The following paragraphs detail common metals treatment techniques that are applicable to Option 3: Evaporation and Ion Exchange.

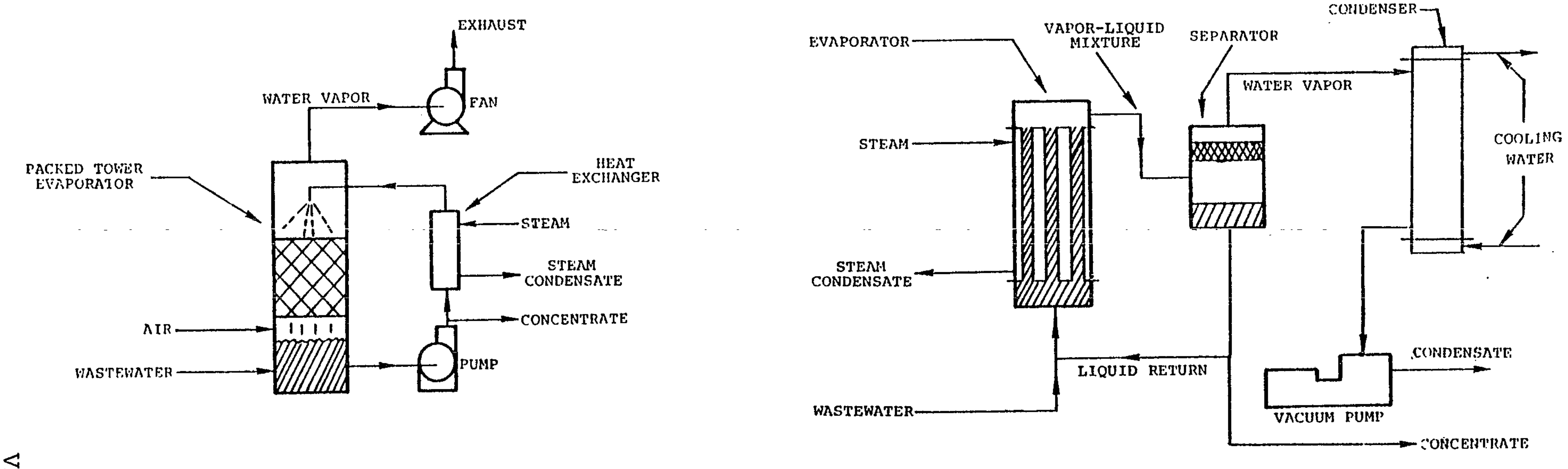
## Evaporation

Evaporation is a concentration process. Water is evaporated from a solution, increasing the concentration of solute in the remaining solution. If the resulting water vapor is condensed back to a liquid, the evaporation-condensation process is called distillation. However, to be consistent with industry terminology, evaporation is used in this report to describe both processes. Both atmospheric and vacuum evaporation are commonly used in industry today. Specific evaporation techniques are shown in Figure 7-18 and discussed below.

Atmospheric evaporation could be accomplished simply by boiling the liquid. However, to aid evaporation, heated liquid is sprayed on an evaporation surface, and air is blown over the surface and subsequently released to the atmosphere. Thus, evaporation occurs by humidification of the air stream, similar to a drying process. Equipment for carrying out atmospheric evaporation is quite similar for most applications. The major element is generally a packed column with an accumulator bottom. Accumulated wastewater is pumped from the base of the column, through a heat exchanger, and back into the top of the column, where it is sprayed into the packing. At the same time, air drawn upward through the packing by a fan is heated as it contacts the hot liquid. The liquid partially vaporizes and humidifies the air stream. The fan then blows the hot, humid air to the outside atmosphere. A scrubber is often unnecessary because the packed column itself acts as a scrubber.

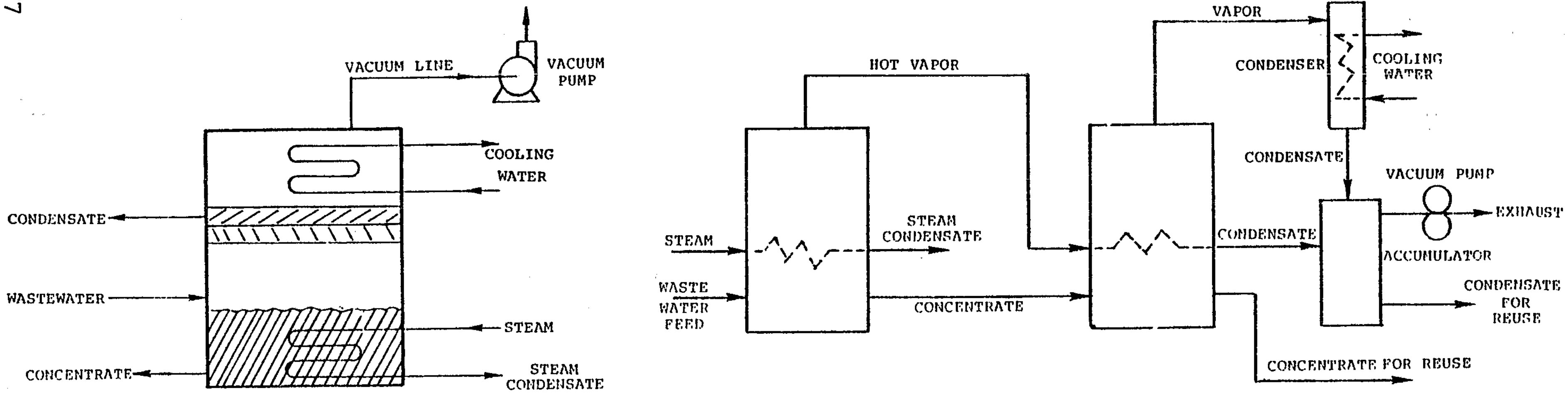
Another form of atmospheric evaporation combines evaporative recovery of plating chemicals with plating tank fume control. A third form of atmospheric evaporation also works on the air humidification principle, but the evaporated rinse water is recovered for reuse by condensation. These air humidification techniques operate well below the boiling point of water and can utilize waste process heat to supply the energy required.

In vacuum evaporation, the evaporation pressure is lowered to cause the liquid to boil at reduced temperature. All of the water vapor is condensed and, to maintain the vacuum condition, noncondensible gases (air in particular) are removed by a



ATMOSPHERIC EVAPORATOR

CLIMBING FILM EVAPORATOR



SUBMERGED TUBE EVAPORATOR

DOUBLE-EFFECT EVAPORATOR

FIGURE 7-18

TYPES OF EVAPORATION EQUIPMENT

vacuum pump. Vacuum evaporation may be either single or double effect. In double effect evaporation, two evaporators are used, and the water vapor from the first evaporator (which may be heated by steam) is used to supply heat to the second evaporator. As it supplies heat, the water vapor from the first evaporator condenses. Approximately equal quantities of wastewater are evaporated in each unit; thus, the double effect system evaporates twice the amount of water that a single effect system does, at nearly the same cost in energy but with added capital cost and complexity. The double effect technique is thermodynamically possible because the second evaporator is maintained at lower pressure (higher vacuum) and, therefore, lower evaporation temperature. Another means of increasing energy efficiency is vapor recompression (thermal or mechanical), which enables heat to be transferred from the condensing water vapor to the evaporating wastewater. Vacuum evaporation equipment may be classified as submerged tube or climbing film evaporation units.

In the most commonly used submerged tube evaporator, the heating and condensing coil are contained in a single vessel to reduce capital cost. The vacuum in the vessel is maintained by an eductor-type pump, which creates the required vacuum by the flow of the condenser cooling water through a venturi. Wastewater accumulates in the bottom of the vessel, and it is evaporated by means of submerged steam coils. The resulting water vapor condenses as it contacts the condensing coils in the top of the vessel. The condensate then drips off the condensing coils into a collection trough that carries it out of the vessel. Concentrate is removed from the bottom of the vessel. The major elements of the climbing film evaporator are the evaporator, separator, condenser, and vacuum pump. Wastewater is "drawn" into the system by the vacuum so that a constant liquid level is maintained in the separator. Liquid enters the steam-jacketed evaporator tubes, and part of it evaporates so that a mixture of vapor and liquid enters the separator. The design of the separator is such that the liquid is continuously circulated from the separator to the evaporator. The vapor entering the separator flows out through a mesh entrainment separator to the condenser, where it is condensed as it flows down through the condenser tubes. The condensate, along with any entrained air, is pumped out of the bottom of the condenser by a liquid ring vacuum pump. The liquid seal provided by the condensate keeps the vacuum in the system from being broken.

Application

Evaporation is used in the Metal Finishing Category for recovery of a variety of metals, bath concentrates, and rinse waters. Both atmospheric and vacuum evaporation are used in metal finishing plants, mainly for the concentration and recovery of plating solutions. Many of these evaporators also recover water for rinsing. Evaporation has also been applied to recovery of phosphate metal cleaning solutions. There is no fundamental limitation on the applicability of evaporation. Recent changes in construction materials used for climbing film evaporators enable them to process a wide variety of wastewaters (including cyanide-bearing solutions), as do the other types of evaporators described in this report.

Advantages of the evaporation process are that it permits recovery of a wide variety of process chemicals, and it is often applicable to removal and/or concentration of compounds which cannot be accomplished by any other means. The major disadvantage is that the evaporation process consumes relatively large amounts of energy for the evaporation of water. However, the recovery of waste heat from many industrial processes (e.g., diesel generators, incinerators, boilers and furnaces) should be considered as a source of this heat for a totally integrated evaporation system. For some applications, pretreatment may be required to remove solids and/or bacteria which tend to cause fouling in the condenser or evaporator. The buildup of scale on the evaporator surfaces reduces the heat transfer efficiency and may present a maintenance problem or increased operating cost. However, it has been demonstrated that fouling of the heat transfer surfaces can be avoided or minimized for certain dissolved solids by maintaining a seed slurry which provides preferential sites for precipitate deposition. In addition, low temperature differences in the evaporator will eliminate nucleate boiling and supersaturation effects. Steam distillable impurities in the process stream are carried over with the product water and must be handled by pre or post treatment.

## Performance

In theory, evaporation should yield a concentrate and a deionized condensate. Actually, carry-over has resulted in condensate metal concentrations as high as 10 mg/l, although the usual level is less than 3 mg/l, pure enough for most final rinses. The condensate may also contain organic brighteners and antifoaming agents. These can be removed with an activated carbon bed, if necessary. Samples from one metal finishing plant showed 1,900 mg/l zinc in the feed, 4,570 mg/l in the concentrate, and 0.4 mg/l in the condensate. Another plant had 416 mg/l copper in the feed and 21,800 mg/l in the concentrate. Chromium analysis for that plant indicated 5,060 mg/l in the feed and 27,500 mg/l in the concentrate. Evaporators are available in a range of capacities, typically from 15 to 75 gph, and may be used in parallel arrangements for processing of higher flow rates.

## Demonstration Status

Evaporation is a fully developed, commercially available wastewater treatment system. It is used extensively to recover plating chemicals, and a pilot scale unit has been used in connection with phosphate washing of aluminum coil.

Evaporation has been used in 39 of the visited plants in the present data base and these are identified in the following table (Table 7-37).

TABLE 7-37
METAL FINISHING PLANTS EMPLOYING EVAPORATION

| | | |
|---|---|---|
| 04266 | 12065 | 33033 |
| 04276 | 12075 | 33065 |
| 04284 | 13031 | 33112 |
| 06009 | 19069 | 34050 |
| 06037 | 20064 | 36062 |
| 06050 | 20069 | 36084 |
| 06072 | 20073 | 36162 |
| 06075 | 20147 | 38050 |
| 06087 | 20160 | 38052 |
| 06088 | 20162 | 40062 |
| 06090 | 23071 | 40836 |
| 06679 | 28075 | 43003 |
| 08060 | 30096 | 61001 |

## Ion Exchange

Ion exchange is a process in which ions, held by electrostatic forces to charged functional groups on the surface of the ion exchange resin, are exchanged for ions of similar charge from the solution in which the resin is immersed. This is classified as a sorption process because the exchange occurs on the surface of the resin, and the exchanging ion must undergo a phase transfer from solution phase to solid phase. Thus, ionic contaminants in a waste stream can be exchanged for the harmless ions of the resin.

Although the precise technique may vary slightly according to the application involved, a generalized process description follows. The wastewater stream being treated passes through a filter to remove any suspended solids, then flows through a cation exchanger which contains the ion exchange resin. Here, metallic impurities such as copper, iron, and trivalent chromium are retained. The stream then passes through the anion exchanger and its associated resin. Hexavalent chromium, for example, is retained in this stage. If one pass does not reduce the contaminant levels sufficiently, the stream may then enter another series of exchangers. Many ion exchange systems are equipped with more than one set of exchangers for this reason.

The other major portion of the ion exchange process concerns the regeneration of the resin, which now holds those impurities retained from the waste stream. An ion exchange unit with in-place regeneration is shown in Figure 7-19. Metal ions such as nickel are removed by an acidic cation exchange resin, which is regenerated with hydrochloric or sulfuric acid, replacing the metal ion with one or more hydrogen ions. Anions such as dichromate are removed by a basic anion exchange

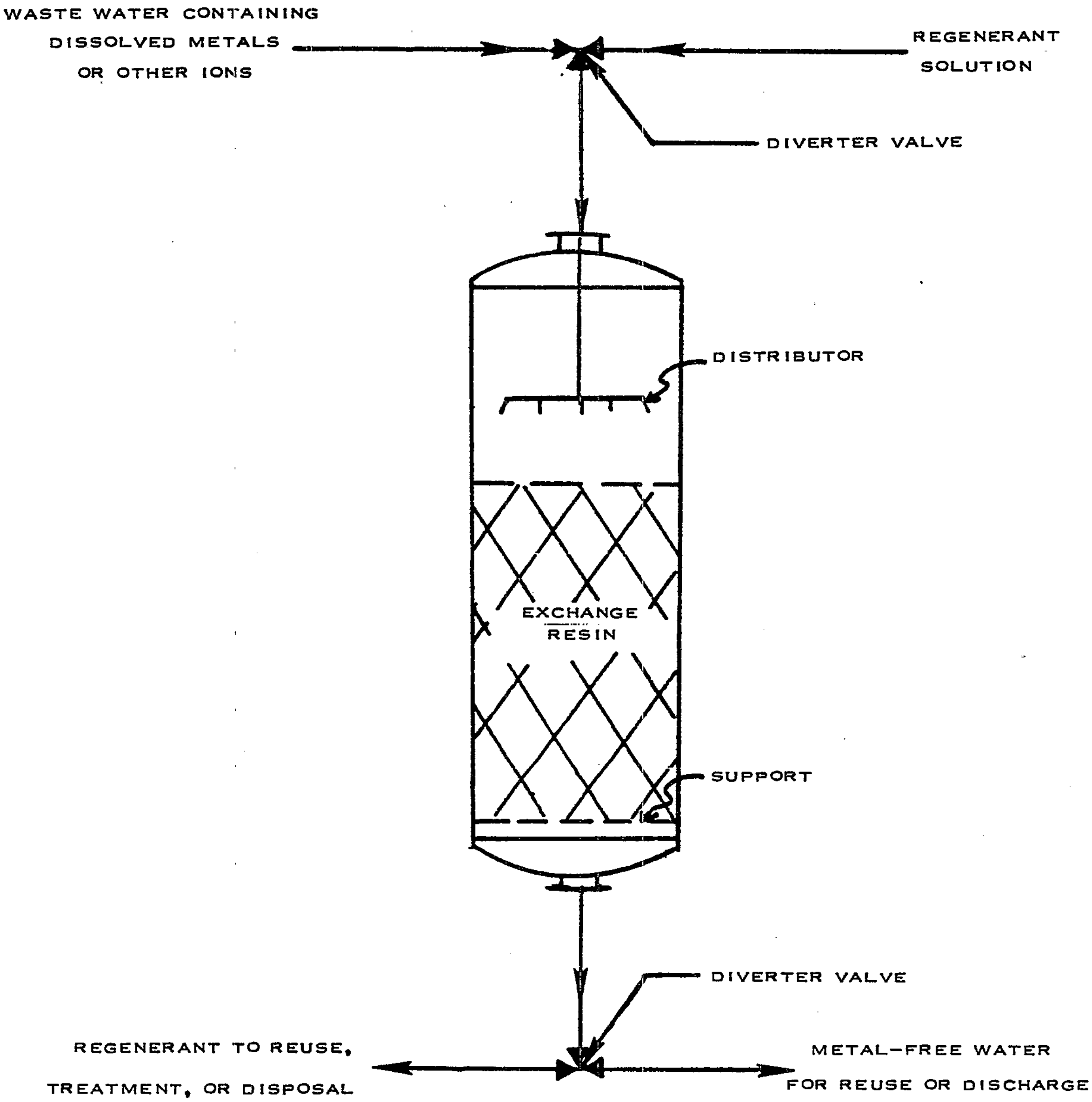


FIGURE 7-19

ION EXCHANGE WITH REGENERATION

resin, which is regenerated with sodium hydroxide, replacing the anion with one or more hydroxyl ions. The three principal methods employed by industry for regenerating the spent resin are:

A) Replacement Service - A replacement service replaces the spent resin with regenerated resin, and regenerates the spent resin at its own facility. The service then has the problem of treating and disposing of the spent regenerant.

B) In-Place Regeneration - Some establishments may find it less expensive to do their own regeneration. The spent resin column is shut down for perhaps an hour, and the spent resin is regenerated. This results in one or more waste streams which must be treated in an appropriate manner. Regeneration is performed only as the resins require it.

C) Cyclic Regeneration - In this process, the regeneration of the spent resins takes place in alternating cycles with the ion removal process. A regeneration frequency of twice an hour is typical. This very short cycle time permits operation with a very small quantity of resin and with fairly concentrated solutions, resulting in a very compact system. Again, this process varies according to application, but the regeneration cycle generally begins with caustic being pumped through the anion exchanger, carrying out hexavalent chromium, for example, as sodium dichromate. The sodium dichromate stream then passes through a cation exchanger, converting the sodium dichromate to chromic acid. After concentration by evaporation or other means, the chromic acid can be returned to the process line. Meanwhile, the cation exchanger is regenerated with sulfuric acid, resulting in a waste acid stream containing the metallic impurities removed earlier. Flushing the exchangers with water completes the cycle. Thus, the wastewater is purified and, in this example, chromic acid is recovered. The ion exchangers, with newly regenerated resin, then enter the ion removal cycle again.

### Application

Many metal finishing facilities utilize ion exchange to concentrate and purify their plating baths.

The list of pollutants for which the ion exchange system has proven effective includes aluminum, arsenic, cadmium, chromium (hexavalent and trivalent), copper, cyanide, gold, iron, lead, manganese, nickel, selenium, silver, tin, zinc, and more. Thus, it can be applied to a wide variety of industrial concerns. Because of the heavy concentrations of metals in their wastewater, the metal finishing industries utilize ion exchange in several ways. As an end-of-pipe treatment, ion exchange is certainly feasible, but its greatest value is in recovery applications. It is commonly used, however, as an integrated treatment to recover rinse water and process chemicals. In addition to metal finishing, ion exchange is finding applications in the photography industry for bath purification, in battery manufacturing for heavy metal removal, in the chemical industry, the food industry, the nuclear industry, the pharmaceutical industry, the textile industry, and others. It could also be used in the copper and copper alloys industry for recovery of copper from pickle rinses. Also, many industrial and non-industrial concerns utilize ion exchange for reducing the salt concentrations in their incoming water.

Ion exchange is a versatile technology applicable to a great many situations. This flexibility, along with its compact nature and performance, make ion exchange a very effective method of waste water treatment. However, the resins in these systems can prove to be a limiting factor. The thermal limits of the anion resins, generally placed in the vicinity of 60° C, could prevent its use in certain situations. Similarly, nitric acid, chromic acid, and hydrogen peroxide can all damage the resins as will iron, manganese, and copper when present with sufficient concentrations of dissolved oxygen. Removal of a particular trace contaminant may be uneconomical because of the presence of other ionic species that are preferentially removed. The regeneration of the resins presents its own problems. The cost of the regenerative chemicals can be high. In addition, the waste streams originating from the regeneration process are extremely high in pollutant concentrations, although low in volume. These must be further processed for proper disposal.

Performance

Ion exchange is highly efficient at recovering metal finishing chemicals. Recovery of chromium, nickel, phosphate solution, and sulfuric acid from anodizing is in commercial use. A chromic acid recovery efficiency of 99.5% has been demonstrated. Typical data for purification of rinse water in electroplating and printed circuit board plants are shown in Table 7-38.

## TABLE 7-38
## TYPICAL ION EXCHANGE PERFORMANCE DATA

| Parameter | Electroplating Plant | | Printed Circuit Board Plant | |
|---|---|---|---|---|
| All Values mg/l | Prior To Purification | After Purification | Prior To Purification | After Purification |
| Zinc (Zn) | 14.8 | 0.40 | - | - |
| Cadmium (Cd) | 5.7 | 0.00 | - | - |
| Chromium ($Cr^{+3}$) | 3.1 | 0.01 | - | - |
| Chromium ($Cr^{+6}$) | 7.1 | 0.01 | - | - |
| Copper (Cu) | 4.5 | 0.09 | 43.0 | 0.10 |
| Iron (Fe) | 7.4 | 0.01 | - | - |
| Nickel (Ni) | 6.2 | 0.00 | 1.60 | 0.01 |
| Silver (Ag) | 1.5 | 0.00 | 9.10 | 0.01 |
| Tin (Sn) | 1.7 | 0.00 | 1.10 | 0.10 |
| Cyanide (CN) | 9.8 | 0.04 | 3.40 | 0.09 |
| Manganese (Mn) | 4.4 | 0.00 | - | - |
| Aluminum (Al) | 5.6 | 0.20 | - | - |
| Sulfate (SO4) | - | - | 210.00 | 2.00 |
| Lead (Pb) | - | - | 1.70 | 0.01 |
| Gold (Au) | - | - | 2.30 | 0.10 |

Plant ID 11065, which was visited and sampled, employs an ion exchange unit to remove metals from rinsewater. The results of the sampling are displayed below:

### POLLUTANT CONCENTRATION (mg/l)
### Plant ID 11065

| Parameter | Day 1 | | Day 2 | |
|---|---|---|---|---|
| | Input To Ion Exchange | Effluent From Ion Exchange | Input To Ion Exchange | Output From Ion Exchange |
| TSS | 6.0 | 4.0 | 1.0 | 1.0 |
| Cu | 52.080 | .118 | 189.3 | .20 |
| Ni | .095 | .003 | .017 | .003 |
| Cr, Total | .043 | .051 | .026 | .006 |
| Cd | .005 | .005 | .005 | .005 |
| Sn | .06 | .06 | .06 | .06 |
| Pb | .010 | .011 | .010 | .010 |

## Demonstration Status

All of the applications mentioned in this document are available for commercial use. The research and development in ion exchange is focusing on improving the quality and efficiency of the resins, rather than new applications. Work is also being done on a continuous regeneration process whereby the resins are contained on a fluid-transfusible belt. The belt passes through a compartmented tank with ion exchange, washing, and regeneration sections. The resins are therefore continually used and regenerated. No such system, however, has been reported to be beyond the pilot stage.

Ion exchange is used in 63 plants in the present data base and these are identified in Table 7-39.

TABLE 7-39

METAL FINISHING PLANTS EMPLOYING ION EXCHANGE

02033
02034
02037
04145
04221
04223
04236
04263
04541
04676
04690
05050
06103
06679
08073
09025
11065
12065
12075
12080
13040
17030
17050
17061
18538
19081
19120
20017
20075
20120
20162
20483
21059
21065
21066
21075
23065
25033
27046
28111
28121
30153
30967
31032
31050
31070
33130
33172
33186
33187
36087
36623
37060
38036
38039
40048
40061
41086
41089
44062
46035
61001
62032

## ALTERNATIVE TREATMENT METHODS FOR COMMON METALS REMOVAL

In addition to the treatment methods described under Options 1, 2, and 3; there are several other alternative treatment technologies applicable for the treatment of common metals wastes. These technologies may be used in conjunction with or in place of the Option 1, 2, or 3 system components. The following paragraphs describe these technologies: peat adsorption, insoluble starch xanthate, sulfide precipitation, flotation, and membrane filtration.

### Peat Adsorption

Peat moss is a rather complex material with lignin and cellulose as major constituents. These constituents, particularly lignin, bear polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers, that can be involved in chemical bonding. Because of the polar nature of this material, its adsorption of dissolved solids such as transition metals and polar organic molecules is quite high. These properties have led to the use of peat as an agent for the purification of industrial wastewater.

Peat adsorption is a "polishing" process which can achieve very low effluent concentrations for several pollutants. If the concentrations of pollutants are above 10 mg/l, then peat adsorption must be preceded by pH adjustment and settling. The wastewater is then pumped into a large metal chamber (a kier) which contains a layer of peat through which the waste stream passes. The water flows to a second kier for further adsorption. The wastewater is then ready for discharge. This system may be automated or manually operated.

### Application

Peat adsorption can be used in metal finishing plants for removal of residual dissolved metals from clarifier effluent. Peat moss may be used to treat wastewaters containing heavy metals such as mercury, cadmium, zinc, copper, iron, nickel, chromium, and lead, as well as organic matter such as oil, detergents, and dyes. Peat adsorption could be used in metal finishing industries, coil coating plants, porcelain enameling, battery manufacturing plants, copper products manufacturing facilities, photographic plants, textile manufacturing, newsprint production facilities, and other industries. Peat adsorption is currently used commercially at a textile plant, a newsprint facility, and a metal reclamation operation.

### Performance

The following table contains performance figures obtained from pilot plant studies. Peat adsorption was preceded by pH adjustment for precipitation and by clarification.

| Pollutant | Before Treatment (mg/l) | After Treatment (mg/l) |
|---|---|---|
| Pb | 20.0 | 0.025 |
| Sb | 2.5 | 0.9 |
| Cu | 250.0 | 0.24 |
| Zn | 1.5 | 0.25 |
| Ni | 2.5 | 0.07 |
| $Cr^{+6}$ | 35,000.0 | <0.04 |
| CN | 36.0 | 0.7 |
| Hg | >1.0 | 0.02 |
| Ag | >1.0 | 0.05 |

In addition, pilot plant studies have shown that complexed metal wastes, as well as the complexing agents themselves, are removed by contact with peat moss. Therefore, peat adsorption could be applied to printed circuit board manufacturing, which uses complexing agents extensively.

### Demonstration Status

Only three commercial adsorption systems are currently in use in the United States. These are at a textile manufacturer, a newsprint facility, and a metal reclamation firm.

No data have been reported showing the use of peat adsorption in any metal finishing plants. Its only commercial applications are as stated above.

## Insoluble Starch Xanthate

Insoluble starch xanthate (ISX) is essentially an ion exchange medium used to remove dissolved heavy metals from wastewater. ISX is formed by reacting commercial cross-linked starch with sodium hydroxide and carbon disulfide. Magnesium sulfate is also added as a stabilizer and to improve sludge settling.

ISX acts as a cationic ion exchange material removing the heavy metal ions and replacing them with sodium and magnesium. The starch has good settling characteristics, good filtering characteristics, and is well suited for use as a filter precoat. ISX can be added as a slurry for continuous treatment operations, in solid form for batch treatments and as a precoat to a filter. The ISX process is effective for removal of all uncomplexed metals, including hexavalent chromium, and also some complexed metals such as the copper-ammonia complex. The removal of hexavalent chromium is brought about by lowering the pH to below 3 and subsequent raising of it above 7. The hexavalent chromium is reduced by the ISX at the acid pH and is removed at the alkaline pH as chromium starch xanthate or chromic hydroxide.

Presently, ISX is being used in two metal finishing establishments. One of the plants utilizes the ISX process as a polishing filter and claims to reduce levels of metals in the effluent of their clarifier from 1 mg/l to .020 mg/l. The other plant (ID 27046), which was visited and sampled, uses the ISX process to recycle rinse waters on their cleaning line and nickel, copper, and solder plating lines. The results of the sampling are listed below.

| | Solder Line | | Nickel Line | | Cleaning Line | |
|---|---|---|---|---|---|---|
| | Input To Filter | Output From Filter | Input To Filter | Output From Filter | Input To Filter | Output From Filter |
| Cu | .42 | .41 | .24 | .24 | .43 | .39 |
| Pb | .56 | .53 | - | - | - | - |
| Sn | 2.0 | 1.5 | - | - | - | - |
| Zn | .092 | .083 | .047 | .040 | .167 | .126 |
| Ni | - | - | 552. | 547. | - | - |
| Fe | - | - | - | - | .38 | .26 |

As shown by the data, the ISX was not removing a high percentage of metal. Its main purpose was to keep contaminants from building up to a point where the water would not be reusable.

## Sulfide Precipitation

### Application

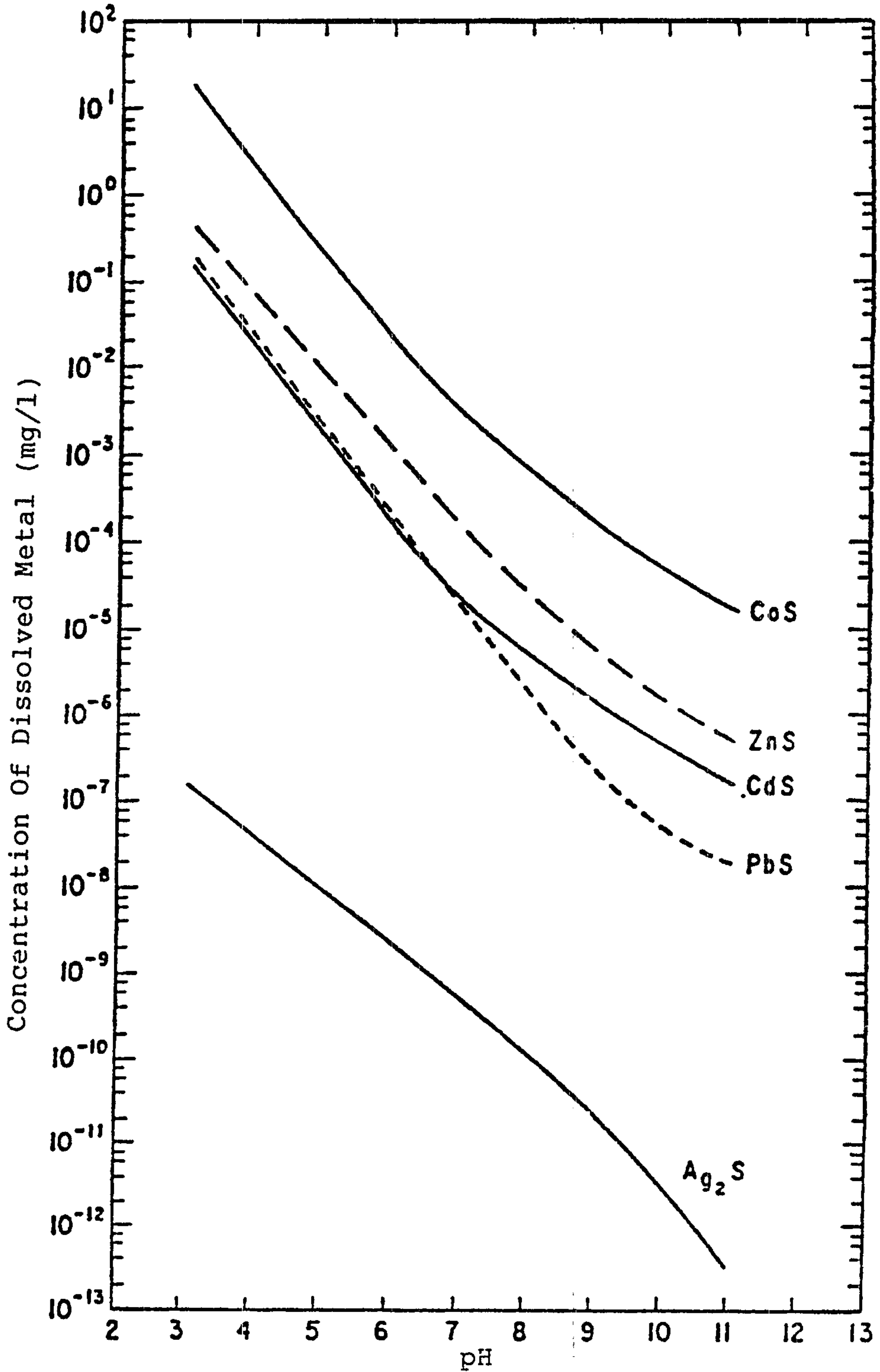
Hydrogen sulfide or soluble sulfide salts such as sodium sulfide are used to precipitate many heavy metal sulfides. Since most metal sulfides are even less soluble than metal hydroxides at alkaline pH levels, greater heavy metal removal can be accomplished through the use of sulfide rather than hydroxide as a chemical precipitant prior to sedimentation. The solubilities of metallic sulfides are pH dependent and are shown in Figure 7-20.

Of particular interest is the ability at a pH of 8 to 9 of the ferrous sulfide process to precipitate hexavalent chromium ($Cr^{+6}$) without prior reduction to the trivalent state as is required in the hydroxide process, although the chromium is still precipitated as the hydroxide. When ferrous sulfide is used as the precipitant, iron and sulfide act as reducing agents for the hexavalent chromium.

$$Cr_2O_7^{=} + 2FeS + 7H_2O = 2Fe(OH)_3 + 2Cr(OH)_3 + 2S^{\circ} + 2OH^{-}$$

In this case the sludge produced consists mainly of ferric hydroxides and chromic hydroxides. Some excess hydroxyl ions are produced in this process, possibly requiring a downward re-adjustment of pH to between 8-9 prior to discharge of the treated effluent.

In addition to the advantages listed above, the process will precipitate metals complexed with most complexing agents. However, care must be taken to maintain the pH of the solution above approximately 8 in order to prevent the generation of toxic hydrogen sulfide gas. For this reason ventilation of the treatment tanks may be a necessary precaution in some installations. The use of ferrrous sulfide virtually eliminates the problem of hydrogen sulfide evolution, however. As with hydroxide precipitation, excess sulfide must be present to drive the precipitation reaction to completion. Since sulfide itself is toxic, sulfide addition must be carefully controlled to maximize heavy metals precipitation with a minimum of excess sulfide to avoid the necessity of posttreatment. At very high excess sulfide levels and high pH, soluble mercury-sulfide compounds may also be formed. Where excess sulfide is present, aeration of the effluent stream can aid in oxidizing residual sulfide to the less harmful sodium sulfate ($Na_2SO_4$). The cost of sulfide precipitants is high in comparison with hydroxide precipitating agents, and disposal of metallic sulfide sludges may pose problems. With improper



**Note:** Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

FIGURE 7-20

COMPARATIVE SOLUBILITIES OF METAL SULFIDES AS A FUNCTION OF pH handling or disposal of sulfide precipitates, hydrogen sulfide may be released to the atmosphere creating a potential toxic hazard, toxic metals may be leached out into surface waters, and sulfide might oxidize to sulfate and release dilute sulfuric acid to surface waters. An essential element in effective sulfide precipitation is the removal of precipitated solids from the wastewater to a site where reoxidation and leaching are not likely to occur.

### Performance

Data from sampling at Plant 27045 show the effectiveness of sulfide precipitation on unreduced hexavalent chromium as well as total chromium. Mean concentrations for the only metals present in the aluminum anodizing operation were as follows:

| Parameter | Influent mg/l | Effluent mg/l |
|---|---|---|
| Chromium, hex. | 11.5 | Undetectable |
| Chromium, total | 18.4 | Undetectable |
| Aluminum | 4.18 | 0.112 |

One report (Treatment of Metal Finishing Wastes by Sulfide Precipitation, EPA-600/2-75-049, U.S. Environmental Protection Agency, 1977) concluded that (with no complexing agents present) the following effluent quality can be achieved:

| Parameter | Effluent mg/l |
|---|---|
| Cadmium | 0.01 |
| Copper | 0.01 |
| Zinc | 0.01 |
| Nickel | 0.05 |
| Chromium, Total | 0.05 |

Sampling data from three other industrial plants using sulfide precipitation are presented in Table 7-40. Concentrations are given in mg/l.

## TABLE 7-40
## SAMPLING DATA FROM SULFIDE PRECIPITATION/SEDIMENTATION SYSTEMS

| Data Source | Reference 1 | | Reference 2 | | Reference 3 | |
|---|---|---|---|---|---|---|
| Treatment | Lime, $FeS_2$, Poly-Electrolyte, Settle, Filter | | Lime, $FeS_2$, Poly-Electrolyte, Settle, Filter | | NaOH, Ferric Chloride, $Na_2S$, Clarify (1 stage) | |
| | Raw | Eff. | Raw | Eff. | Raw | Eff. |
| pH | 5.0-6.8 | 8-9 | 7.7 | 7.38 | 27 | 6.4 |
| $Cr^{+6}$ | 25.6 | <.01 | .022 | <.020 | 11.4 | <.005 |
| Cr, T | 32.3 | <.04 | 2.4 | <.1 | 18.3 | <.005 |
| Cu | - | - | - | - | .029 | .003 |
| Fe | .52 | .10 | 108 | 0.6 | - | - |
| Ni | - | - | .68 | <.1 | - | - |
| Zn | 39.5 | <.07 | 33.9 | <.1 | .060 | .009 |

Reference:

1. Treatment of Metal Finishing Wastes by Sulfide Precipitation, EPA Grant No. S804648010.
2. Industrial Finishing, Vo. 35, No. 11, Nov. 1979, p. 40 (Raw waste sample taken after chemical addition).
3. Visit Plant 27045. Concentrations are two day averages.

In all cases except iron, effluent concentrations are below 0.1 mg/l and in many cases below 0.01 mg/l for the three plants studied.

Sampling data from several chlorine/caustic inorganic chemicals manufacturing plants using sulfide precipitation reveal effluent mercury concentrations varying between 0.009 and 0.03 mg/l (Calspan Report No. ND-5782-M-72). As can be seen in Figure 7-20, the solubilities of PbS and $Ag_2S$ are lower at alkaline pH levels than either the corresponding hydroxides or other sulfide compounds. This implies that removal performance for lead and silver sulfides should be comparable to or better than shown for the metals listed in Table 7-38. Bench scale tests conducted on several types of metal finishing wastewater (Centec Corp; EPA Contract 68-03-2672) indicate that metals removal to levels of less than 0.05 mg/l and in some cases less than 0.01 mg/l are common in systems using sulfide precipitation followed by clarification. Some of the bench scale data, particularly in the case of lead, do not support such low effluent concentrations. However, no suspended solids data were provided in these studies. TSS removal is a reliable indicator of precipitation/sedimentation system performance. Lack of this data makes it difficult to fully evaluate the bench tests, and insufficient solids removal can result in high metals concentrations. Lead is consistently removed to very low levels (less than 0.02 mg/l) in systems using hydroxide precipitation and sedimentation. Therefore one would expect even lower effluent concentrations of lead resulting from properly operating sulfide precipitation systems due to the lower solubility of the lead sulfide compound.

### Demonstration Status

Full scale commercial sulfide precipitation units are in operation at numerous installations, including several plants in the Metal Finishing Category.

## Flotation

Flotation is the process of causing particles such as metal hydroxides or oil to float to the surface of a tank where they can be concentrated and removed. This is accomplished by releasing gas bubbles which attach to the solid particles, increasing their buoyancy and causing them to float. In principle, this process is the opposite of sedimentation. Figure 7-21 shows one type of flotation system. Flotation processes that are applicable to oil removal are discussed in the subsection entitled "Treatment of Oily Wastes and Organics".

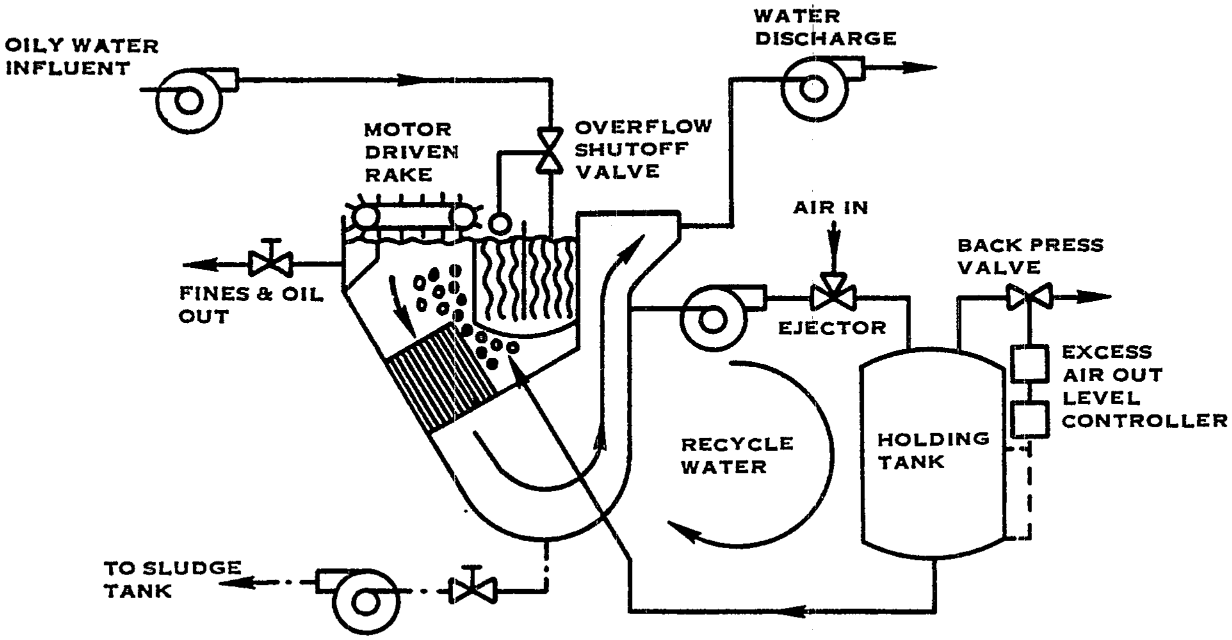


FIGURE 7-21

DISOLVED AIR FLOTATION

Flotation is used primarily in the treatment of wastewater containing large quantities of industrial wastes that carry heavy loads of finely divided suspended solids. Solids having specific gravity only slightly greater than 1.0, which would require abnormally long sedimentation times may be removed in much less time by flotation.

This process may be performed in several ways: foam, dispersed air, dissolved air, gravity, and vacuum flotation are the most commonly used techniques. Chemical additives are often used to enhance the performance of the flotation process.

The principal difference between types of flotation is the method of generation of the minute gas bubbles, usually air, in a suspension of water and small particles. Addition of chemicals to improve the efficiency may be employed with any of the basic methods. The following paragraphs describe the different flotation techniques and the method of bubble generation for each process.

Foam flotation is based on the utilization of differences in the physiochemical properties of various particles. Wettability and surface properties affect the particles' ability to attach themselves to gas bubbles in an aqueous medium. In froth flotation, air is blown through the solution containing flotation reagents. The particles with water repellant surfaces stick to air bubbles as they rise and are brought to the surface. A mineralized froth layer with mineral particles attached to air bubbles is formed. Particles of other minerals which are readily wetted by water do not stick to air bubbles and remain in suspension.

In dispersed air flotation, gas bubbles are generated by introducing the air by means of mechanical agitation with impellers or by forcing air through porous media.

In dissolved air flotation, bubbles are produced as a result of the release of air from a supersaturated solution under relatively high pressure. There are two types of contact between the gas bubbles and particles. The first type is predominant in the flotation of flocculated materials and involves the entrapment of rising gas bubbles in the flocculated particles as they increase in size. The bond between the bubble and particle is one of physical capture only. The second type of contact is one of adhesion. Adhesion results from the intermolecular attraction exerted at the interface between the solid particle and gaseous bubble.

The vacuum flotation process consists of saturating the wastewater with air either 1) directly in an aeration tank, or 2) by permitting air to enter on the suction of a wastewater pump. A partial vacuum is applied, which causes the dissolved air to come out of solution as minute bubbles. The bubbles attach to solid particles and rise to the surface to form a scum blanket, which is normally removed by a skimming mechanism. Grit and other heavy solids that settle to the bottom are generally raked to a central sludge pump for removal. A typical vacuum flotation unit consists of a covered cylindrical tank in which a partial vacuum is maintained. The tank is equipped with scum and sludge removal mechanisms. The floating material is continuously swept to the tank periphery, automatically discharged into a scum trough, and removed from the unit by a pump also under partial vacuum. Auxiliary equipment includes an aeration tank for saturating the wastewater with air, a tank with a short retention time for removal of large bubbles, vacuum pumps, and sludge and scum pumps.

## Application

Flotation applies to most situations requiring separation of suspended materials. It is most advantageous for oils and for suspended solids of low specific gravity or small particle size.

Some advantages of the flotation process are the high levels of solids separation achieved in many applications, the relatively low energy requirements, and the air flow adjustment capability to meet the requirements of treating different waste types. Limitations of flotation are that it often requires addition of chemicals to enhance process performance, and it generates large quantities of solid waste.

## Performance

Performance of a flotation unit was measured at Plant 33692, with results as follows:

| Parameter | Influent mg/l | Effluent mg/l |
|---|---|---|
| Oil & Grease | 412 | 108 |
| TSS | 416 | 210 |
| TOC | 3000 | 132 |
| BOD | 130 | 78 |

For oil removal by a variety of flotation units one literature source (Chemical Engineering Deskbook - Environmental Engineering, October 17, 1977, p. 52, McGraw-Hill) indicates effluents of 10 to 15 mg/l for influents of 61 to 100 mg/l, effluents of 15 to 62 mg/l for influents of 105 to 360 mg/l, and effluent of 60 to 128 mg/l for influents of 580 to 1930 mg/l. For suspended solids removal, another source (Process Design Manual for Suspended Solids Removal, January, 1975, U.S. Environmental Protection Agency) indicates an effluent of 70 mg/l for an influent of 2000 mg/l at one pilot plant, and an effluent of 12 to 20 mg/l for an influent of 94 to 152 mg/l at another pilot plant.

Bench scale experiments have shown foam flotation to be very effective in removing precipitated copper, lead, arsenic, zinc, and fluoride. The following table (Table 7-41) shows the results. A sodium lauryl sulfate (NLS) surfactant and a flocculant were used in each case, and pollutant concentrations were between 10 and 500 mg/l.

TABLE 7-41
FOAM FLOTATION PERFORMANCE

| Pollutant | Reagent | Optimum pH | Residual Concentration, mg/l |
|---|---|---|---|
| Copper | $Fe(OH)_3$-NLS | 7.0 | 0.1 |
| Lead | $Fe(OH)_3$-NLS | 6.5 | 0.1 |
| Arsenate | $Fe(OH)_3$-NLS | 4-5 | 0.1 |
| Zinc | $Al(OH)_3$-NLS | 8.0-8.5 | 0.2 |

Note: NLS is sodium lauryl sulfate

The primary variables for flotation design are pressure, feed solids concentration, and retention period. The effluent suspended solids decrease and the concentration of solids in the float increases with increasing retention period. When the flotation process is used primarily for clarification, a retention period of 20 to 30 minutes is adequate for separation and concentration.

Demonstration Status

Flotation is a fully developed process and is readily available for the treatment of a wide variety of industrial waste streams. It is used in 25 plants in the present data base and these are identified in Table 7-42.

TABLE 7-42
METAL FINISHING PLANTS EMPLOYING FLOTATION

01063
11704
12076
12080
12091
14062
15058
20106
20157
20165
20247
20254
30150
31051
30153
30516
31067
31068
33120
33127
33180
33692
38031
41097
41151

## Membrane Filtration

Membrane filtration is a technique for removing precipitated heavy metals from a wastewater stream. It must therefore be preceded by those treatment techniques which will properly prepare the wastewater for solids removal. Typically, a membrane filtration unit is preceded by cyanide and chromium pretreatment as well as pH adjustment for precipitation of the metals. These steps are followed by addition of a proprietary chemical reagent which causes the metal precipitate to be non-gelatinous, easily dewatered, and highly stable. The resulting mixture of pretreated wastewater is continuously recirculated through a filter module and back into a recirculation tank. The filter module contains tubular membranes. While the reagent-metal precipitates mixture flows through the inside of the tubes, the water and any dissolved salts permeate the membrane. The permeate, essentially free of precipitate, is alkaline, non-corrosive, and may be safely discharged to sewer or stream. When the recirculating slurry reaches a concentration of 10 to 15 percent solids, it is pumped out of the system as sludge.

### Application

Membrane filtration can be used in metal finishing in addition to sedimentation to remove precipitated metals and phosphates. Membrane filtration systems are being used in a number of industrial applications, particularly in the metal finishing industry and have also been used for heavy metals removal in the paper industry. They have potential application in coil coating, porcelain enameling, battery, and copper and copper alloy plants.

A major advantage of the membrane filtration system is that installation can utilize most of the conventional end-of-pipe system that may already be in place. Also, the sludge is highly stable in an alkaline state. Removal efficiencies are excellent, even with sudden variation of pollutant input rates. However, the effectiveness of the membrane filtration system can be limited by clogging of the filters. Because a change in the pH of the waste stream greatly intensifies the clogging problem, the pH must be carefully monitored and controlled. Clogging can force the shutdown of the system and may interfere with production.

The membrane filters must be regularly monitored, and cleaned or replaced as necessary. Depending on the composition of the waste stream and its flow rate, cleaning of the filters may be required quite often. Flushing with hydrochloric acid for 6-24 hours will usually suffice. In addition, the routine maintenance of pumps, valves, and other plumbing is required.

When the recirculating reagent-precipitate slurry reaches 10 to 15 percent solids, it is pumped out of the system. It can then be disposed of directly or it can undergo a dewatering process. The sludge's leaching characteristics are such that the state of South Carolina has approved the sludge for landfill, provided that an alkaline condition be maintained. Tests carried out by the state indicate that even at the slightly acidic pH of 6.5, leachate from a sludge containing 2600 mg/l of copper and 250 mg/l of zinc contained only 0.9 mg/l of copper and 0.1 mg/l of zinc.

## Performance

The permeate is guaranteed by one manufacturer to contain less than the effluent concentrations shown in the following table, regardless of the influent concentrations. These claims have been largely substantiated by the analysis of water samples at various plants including those shown for comparison in Table 7-43.

TABLE 7-43
MEMBRANE FILTER PERFORMANCE (mg/l)

| Parameter | Guarantee | Plant #19066 | | Plant #31022 | |
|---|---|---|---|---|---|
| | | Raw | Treated | Raw | Treated |
| Aluminum | 0.5 | --- | --- | --- | --- |
| Chromium, hexavalent | 0.03 | 0.46 | 0.01 | 5.25 | <.005 |
| Chromium, total | 0.02 | 4.13 | 0.018 | 98.4 | .057 |
| Copper | 0.1 | 18.8 | 0.043 | 8.00 | .222 |
| Iron | 0.1 | 288 | 0.3 | 21.1 | .263 |
| Lead | 0.05 | .652 | 0.01 | 0.288 | 0.01 |
| Cyanide | 0.02 | <.005 | <.005 | <.005 | <.005 |
| Nickel | 0.1 | 9.56 | .017 | 194. | .352 |
| Zinc | 0.1 | 2.09 | .046 | 5.00 | .051 |
| TSS | --- | 632 | 0.1 | 13.0 | 8.0 |

## Demonstration Status

There are approximately twenty membrane filtration systems presently in use by the metal finishing and other industries. Bench scale and pilot studies are being run in an attempt to expand the list of pollutants for which this system is known to be effective.

Membrane filtration is used in 7 plants in the present data base: Plant ID's 02032, 04690, 15193, 19066, 31022, 34050, and 37042.

# TREATMENT OF PRECIOUS METAL WASTES - SINGLE OPTION

## INTRODUCTION

This subsection describes the treatment for precious metal wastes which includes Option 1 common metals treatment plus precious metals recovery. Silver removal performance data for Option 1 common metals treatment systems and describes the techniques that are commonly used for the removal/recovery of precious metals from waste streams.

Precious metal wastes are produced in the Metal Finishing Category by electroplating of precious metals and subsequent finishing operations performed on the precious metals. Included among the precious metals are gold, silver, rhodium, palladium, platinum, osmium, ruthenium, iridium, and indium. Precious metal wastes can be treated using the same treatment alternatives as those described for treatment of common metal wastes. However, due to the intrinsic value of precious metals, every effort should be made to recover them. The treatment alternatives recommended for precious metal wastes are the recovery techniques: evaporation, ion exchange and electrolytic recovery.

## TREATMENT TECHNIQUES

### Option 1 Common Metals System

Included in the common metals Option 1 treatment system (precipitation/sedimentation) data base are a total of 21 sampled occurrences of silver. Performance data for properly operated Option 1 common metals treatment systems from visited plants and from plants submitting long term self-monitoring data are presented in Table 7-44. The pertinent effluent limitation data for silver are summarized as follows:

| | |
|---|---|
| Mean Silver Effluent Concentration | 0.096 mg/ℓ |
| Variability Factors (Daily/10-Day) | 4.48/2.54* mg/ℓ |
| Daily Maximum Effluent Concentration | 0.43 mg/ℓ |
| Maximum Monthly Average Effluent Concentration | 0.24 mg/ℓ |

* Median common metals variability factor was used because of insufficient silver data.

The percent compliance for the silver effluent concentrations are 100 percent for EPA sampled, 70.6 percent for the self-monitoring data daily maximum and 100 percent for the self-monitoring data 10-day averages. The lower percent compliance for the self-monitoring daily maximum can be attributed to Plant 11125 which does not segregate precious metals wastes for recovery prior to precipitation/clarification.

### Evaporation

Evaporation is used to recover precious metals by boiling off the water portion of a precious metal solution. This process is described under the "Treatment of Common Metal Wastes" heading. Solutions such as silver cyanide plating baths are now being recovered through the use of evaporation, the silver

## TABLE 7-44
## METAL FINISHING CATEGORY
## PERFORMANCE DATA FOR SILVER
## VISITED OPTION 1 PLANTS

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 0.1780 | 0.1670 | 6087-1-1 |
| 2. | 0.1780 | 0.1190 | 6087-1-3 |
| 3. | 0.2100 | 0.0610 | 21003-15-2 |
| 4. | 0.2700 | 0.0640 | 21003-15-0 |
| 5. | 0.2900 | 0.0690 | 21003-15-1 |
| Mean Concentration = | 0.2252 (n=5) | 0.0960 (n=5) | |

Effluent Silver Self-Monitoring Performance Data
for Plants with Option 1 Systems

| Plant ID | No. of Points | Concentration (mg/ℓ) |
|---|---|---|
| 6087 | 12 | 0.04 |
| 11125 | 5 | 1.66 |
| Overall | 17 | 0.52 |

cyanide portion either being returned to the process tank or held aside for subsequent sale. Figure 7-22 displays the system which was observed at Plant ID 06090. Plant personnel reported that the recovery of silver solutions paid back the capital cost of the evaporation equipment after six months.

## Ion Exchange

Ion exchange, which was described in detail under the "Treatment of Common Metal Wastes" heading, is commonly used in the recovery of precious metals, particularly gold. This recovery process can be used in an on-line or end-of-pipe capacity. Analyses of samples taken before and after ion exchange at photoprocessing plants (from Guidance Document for the Control of Water Pollution in the: Photographic Processing Industry. EPA 440/1-81/082-9 April 1981) yielded the data shown in Table 7-45:

TABLE 7-45
ION EXCHANGE PERFORMANCE

| Plant | | Silver Concentration (mg/l)<br>Influent | Effluent |
|---|---|---|---|
| 06208 | | 2.0 | 0.14 |
| 09061 | (Unit 1) | 0.74 | 0.04 |
| 09061 | (Unit 2) | 0.60 | 0.10 |

Many plants have ion exchange units hooked up to rinses immediately following precious metal plating operations to recover the metal and return the rinse water to the rinse tank. If a company does precious metal work on a large scale, it may segregate its precious metal wastes and run them through a series of ion exchangers prior to sending the water to waste treatment. In any case, the resins from the ion exchange units are saved and the precious metal recovered, normally by burning off the resin.

## Electrolytic Recovery

Although electrolytic recovery was covered under the "Treatment of Common Metal Wastes" heading, it is particularly applicable to the recovery of precious metals. This is because the more valuable precious metals offer a faster payback on the equipment and energy costs. As explained earlier, equipment normally consists of a dragout rinse located after the precious metal plating step and an off line electrolytic recovery tank with pumps and piping connecting the two. The dragout rinse solution is recirculated between the tanks while the precious metal is plated out in the electrolytic recovery tank. An electrolytic recovery system at a photoprocessing plant (Plant ID 4550; Guidance Document for the Control of Water Pollution in the: Photographic Processing Industry. EPA 440/1-81/082-9 April 1981) was able to reduce silver concentrations from 476 mg/l to 21 mg/l.

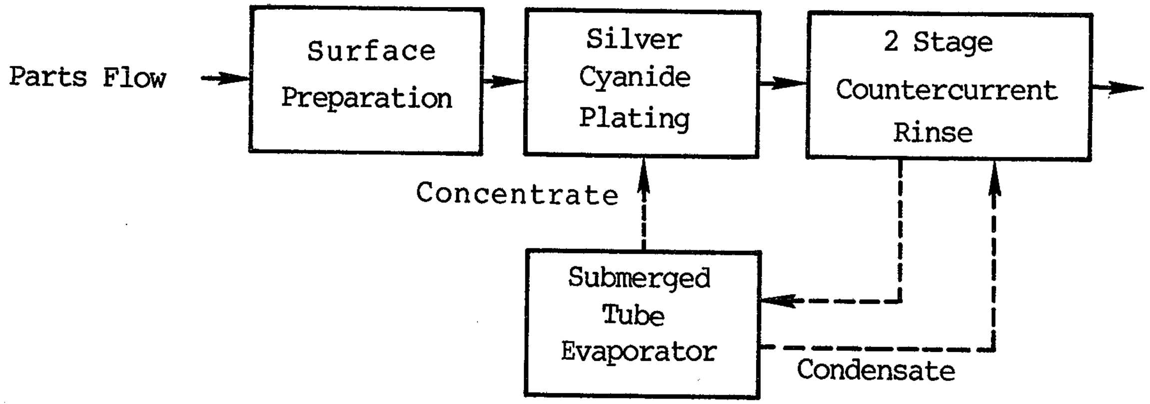


FIGURE 7-22

OBSERVED EVAPORATION SYSTEM AT PLANT ID 06090

## TREATMENT OF COMPLEXED METAL WASTES

### INTRODUCTION

This subsection describes the treatment techniques which are applicable for the removal of complexed metal wastes. The concentration limitations for the common metals wastes that remain after the complexes have been broken are identical to those tabulated in Table 7-20 for the common metals waste type.

Complexed metal wastes within the Metal Finishing Category are a product of electroless plating, immersion plating, etching, and printed circuit board manufacture. The metals in these waste streams are tied up or complexed by particular chemicals (complexing agents) whose function is to prevent metals from falling out of solution. This counteracts the precipitation techniques employed by most conventional metals removal methods, so these treatment methods are not always successful when used on complexed metal waste streams.

In order to establish the performance of waste treatment systems in which complexed metal wastes were being treated, it was necessary to establish which plants were employing complexing agents. A list of complexing agents was compiled using information contained in plant portfolios and information obtained from a literature search. Table 7-46 presents a listing of the most commonly employed complexing agents.

The complexing agents listed in Table 7-46 were then compared with the raw material information provided by visited plants. Table 7-47 presents a listing of the complexing agents used as raw materials at visited plants. It is noted that additional complexing agents, used as part of proprietary formulations may have been employed at the visited plants.

Tables 7-48 and 7-49 present a listing of the effluent concentrations for various metals sampled at visited plants which employ precipitation/clarification or precipitation/clarification/filtration respectively, and use complexing agents. The list of plants includes all visited plants for which one or more of the following are applicable: (1) a complexing agent is used as a raw material, (2) electroless plating operations are performed, (3) immersion plating operaions are performed, or (4) printed circuit board manufacturing takes place.

The plants in Table 7-48 all employ Option 1 common metals treatment. In addition, some of these plants segregate the wastestreams which contain complexed metals waste and treat these wastes separately. Plant 04069 is one plant that segregates their complexed metals

## TABLE 7-46
## COMMON COMPLEXING AGENTS

Ammonia
Ammonium Chloride
Ammonium Hydroxide
Ammonium Bifluoride
Acetylacetone
Citric Acid
Chromotropic Acid (DNS)
Cyanide*
DTPA
Dipyridyl
Disulfopyrocatechol (PDS)
Dimethylglyoxime
Disalicylaldehyde 1,2-propylenediimine
Dimercaptopropanol (BAL)
Dithizone
Diethyl Dithiophosphoric Acid
Ethylenediaminetetraacetic Acid (EDTA)
Ethylenebis (hydroxyphenylglycine) (EHPG)
Ethylenediamine
Ethylenediaminetetra(methylenephosphoric Acid) (EDTPO)
Glyceric Acid
Glycolic Acid
Gluconic Acid
Hydroxyethylethylenediaminetriacetic Acid (HEDTA)
Hydroxyethylidenediphosphonic Acid (HEDP)
HEDDA
Lactic Acid
Malic Acid
Monosodium Phosphate
Nitrilotriacetic Acid (NTA)
N-Dihydroxyethylglycine
Nitrilotrimethylenephosphonic Acid (NTPO, ATMP)
N-Hydroxyethylethylenediamine
O-phenanthroline
Oxine, 8-Hydroxyquinoline (Q)
Oxinesulphonic Acid
Phthalocyanine
Potassium Ethyl Xanthate
Phosphoric Acid
Polyethyleneimine (PEI)
Polymethacryloylacetone
Poly (p-vinylbenzyliminodiacetic Acid)
Rochelle Salts
Sodium Gluconate
Sodium Pyrophosphate
Succinic Acid
Sodium Tripolyphosphate
Sulphosalicylic Acid (SSA)
Salicylaldehyde
Salicylaldoxime
Sodium Hydroxyacetate
Sodium Citrate
Sodium Fluoride
Sodium Malate
Sodium Amino Acetate
Tartaric Acid
Trisodium Phosphate (TSP)
Trifluoroacetylacetone
Thenoyltrifluoroacetone (TTA)
Triethylenetetramine
Triaminotriethylamine
Triethanolamine (TEA)
Tetraphenylporphin
Toluene Dithiol
Thioglycolic Acid
Thiourea

* Treatment of cyanide wastes are specifically discussed within Section VII.

## TABLE 7-47
## COMPLEXING AGENTS USED IN THE VISITED PLANT DATA BASE

Ammonia
Ammonium Bifluoride
Ammonium Chloride
Ammonium Hydroxide
Citric Acid
DTPA
EDTA
Gluconic Acid
Glyceric Acid
Glycolic Acid
HEDDA
HEDTA
Lactic Acid
Malic Acid
Monosodium Phosphate
NTA
Phosphoric Acid
Rochelle Salts
Sodium Gluconate
Sodium Pyrophosphate
Succinic Acid
Tartaric Acid
Trisodium Phosphate
Uspecified Chelating Agents

wastes for separate treatment. This plant has significantly lower levels of chromium, copper, and total cyanide than plant 20083 which does not segregate and separately treat their complexed metals waste. Segregation of complexed metals wastestreams appears to be necessary to achieve compliance.

Table 7-48 and 7-49 also summarize the percentage of the metal finishing visited plant data base (that use complexing agents) that are in compliance within the daily maximum limitation concentration for the sampled plants that employ either Option 1 or Option 2 common metals waste treatment.

# TABLE 7-48
## POLLUTANT CONCENTRATIONS (mg/l) FOR SAMPLED DATA FROM PLANTS WITH COMPLEXED METAL WASTES EMPLOYING PRECIPITATION/CLARIFICATION

| PLANT ID | Cd | Cr | Cu | Pb | Ni | Ag | Zn | Fe | TSS | $CN_T$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 02032 | | | 3.87 | 0.88 | 0.049 | | | | 40 | 0.04 |
| | | | 3.07 | 2.30 | 0.034 | | | | 100 | 0.04 |
| | | | 3.30 | 2.70 | 0.075 | | | | 98 | 0.4 |
| 02033 | | | | | 1.840 | 0.040 | | | 650 | 0.2 |
| | | | | | 1.300 | 0.081 | | | 5 | 0.01 |
| 04069 | | | 0.776 | | 0.122 | | | 0.215 | 4 | 0.58 |
| | | | 0.300 | | 0.120 | | | 3.41 | 30 | 0.03 |
| | | | 0.150 | | 0.140 | | | 1.24 | 2 | 0.538 |
| | | | 0.150 | | 0.041 | | | 1.25 | 2 | 0.448 |
| 04071 | | | 1.620 | 0.0 | 1.700 | | | | 82 | 0.0 |
| | | | 0.860 | 0.200 | 1.460 | | | | 98 | 0.0 |
| | | | 0.780 | 0.160 | 2.000 | | | | 48 | 0.0 |
| 04077 | | 2.640 | 5.680 | | 24.50 | | 45.00 | | 50 | 6.3 |
| | | 3.140 | 4.170 | | 21.00 | | 37.90 | | 162 | 0.26 |
| 05020 | | 0.164 | 0.206 | | 0.400 | | | | 58 | 0.005 |
| | | 0.024 | 1.470 | | 0.300 | | | | 234 | 0.005 |
| | | 0.025 | 0.165 | | 0.294 | | | | 5 | 0.005 |
| | | 0.007 | 12.70 | | 0.150 | | | | 21 | 0.005 |
| | | 0.007 | 4.23 | | 0.160 | | | | 75 | 0.005 |
| | | 0.005 | 5.87 | | 0.065 | | | | 10 | 0.005 |
| 05021 | | | 5.060 | | 0.807 | 0.0012 | 0.045 | | 44 | 0.133 |
| | | | 0.400 | | 0.013 | 0.0012 | 0.007 | | 18 | 0.005 |
| | | | 0.116 | | 0.008 | 0.0012 | 0.005 | | 10 | 0.005 |
| | | | 7.850 | | 2.440 | 0.0012 | 0.055 | | 44 | 0.119 |
| | | | 2.780 | | 1.110 | 0.0012 | 0.020 | | 20 | 0.008 |
| | | | 2.100 | | 2.440 | 0.0012 | 0.020 | | 21 | 0.005 |
| 06036 | | | | | 0.006 | | | | 6 | 0.008 |
| | | | | | 4.154 | | | | 17 | 0.005 |
| 06074 | | 0.333 | | | 0.304 | | | 3.400 | 46 | 0.024 |
| | | 0.143 | | | 0.600 | | | 0.923 | 21 | 0.021 |
| | | 0.714 | | | 0.571 | | | 5.170 | 26 | 0.012 |
| 06091 | | 0.180 | | | 1.790 | | | 1.450 | 175 | 0.0 |
| | | 0.770 | | | 1.930 | | | 3.650 | 20 | 0.060 |
| | | 0.360 | | | 1.320 | | | 8.150 | 515 | 0.0 |
| 09025 | | 0.068 | | | | | | 0.390 | 12 | 0.005 |
| | | 0.050 | | | | | | 0.190 | 5 | 0.005 |

## TABLE 7-48 (Continued)
## POLLUTANT CONCENTRATIONS (mg/l) FOR SAMPLED DATA FROM PLANTS WITH COMPLEXED METAL WASTES EMPLOYING PRECIPITATION/CLARIFICATION

| PLANT ID | Cd | Cr | Cu | Pb | Ni | Ag | Zn | Fe | TSS | $CN_T$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 21003 | 0.027 | 0.035 | 0.160 | | 0.210 | 0.064 | 0.070 | 0.610 | 0.0 | 0.0 |
| | 0.024 | 0.035 | 0.140 | | 0.150 | 0.069 | 0.050 | 0.610 | 5.0 | 0.0 |
| | 0.017 | 0.035 | 0.130 | | 0.170 | 0.061 | 0.040 | 0.390 | 12.0 | 0.0 |
| 27044 | | | 0.157 | | 0.726 | | | | 7.0 | 0.120 |
| | | | 4.000 | | 3.280 | | | | 96.7 | 2.790 |
| | | | 1.810 | | 0.744 | | | | 57.0 | 2.050 |
| 30050 | | 0.024 | 39.61 | 0.022 | 0.312 | | 0.098 | | 0.1 | 0.006 |
| 31032 | | | 0.400 | | 0.0 | | | 0.160 | 11.8 | 0.425 |
| | | | 0.290 | | 0.0 | | | 0.120 | 5.0 | 0.450 |
| | | | 0.200 | | 0.0 | | | 0.460 | – | 0.790 |
| 35061 | 0.050 | 0.200 | 1.100 | | 0.700 | | | | 26.0 | 0.090 |
| 36623 | | 0.029 | 0.220 | 0.0 | 1.200 | 0.0 | 0.039 | | 2.9 | 0.010 |
| | | 0.0 | 0.180 | 0.0 | 1.030 | 0.0 | 0.028 | | 2.4 | 0.020 |
| | | 0.0 | 0.210 | 0.0 | 0.700 | 0.014 | 0.025 | | 0.7 | 0.033 |
| TOTAL DATA POINTS | 4 | 54 | 75 | 14 | 80 | 14 | 24 | 27 | | |
| DATA POINTS IN COMPLIANCE | 4 | 37 | 62 | 11 | 66 | 14 | 18 | 25 | | |
| % POINTS IN COMPLIANCE | 100.0 | 68.5 | 82.7 | 78.6 | 82.5 | 100.0 | 75.0 | 92.6 | | |
| TOTAL DATA POINTS WITH TSS AND CN LIMITATIONS* | 4 | 35 | 52 | 10 | 54 | 13 | 21 | 24 | | |
| DATA POINTS IN COMPLIANCE | 4 | 27 | 47 | 9 | 50 | 13 | 17 | 23 | | |
| % POINTS IN COMPLIANCE | 100.0 | 77.1 | 90.4 | 90.0 | 92.6 | 100.0 | 80.9 | 95.8 | | |

* Data points associated with TSS $\geq$ 61.0 mg/l or $CN_T \geq$ 1.30 mg/l have been deleted.

## TABLE 7-48 (Continued)

## POLLUTANT CONCENTRATIONS (mg/l) FOR SAMPLED DATA FROM PLANTS WITH COMPLEXED METAL WASTES EMPLOYING PRECIPITATION/CLARIFICATION

| PLANT ID | Cd | Cr | Cu | Pb | Ni | Ag | Zn | Fe | TSS | $CN_T$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 11065 | | | 1.273 | 0.017 | 0.017 | | | | 15 | 0.120 |
| | | | 0.455 | 0.011 | 0.023 | | | | 8 | 0.005 |
| 12061 | | | 0.038 | 0.0 | | | 26.00 | 0.290 | 0 | 0.005 |
| | | | 0.029 | 0.0 | | | 26.00 | 1.000 | 5 | 0.006 |
| 12065 | | 0.250 | 6.380 | | 9.230 | | 1.040 | 2.210 | 23 | 1.858 |
| | | 0.500 | 1.580 | | 9.230 | | 1.140 | 2.530 | 23 | 0.327 |
| | | 0.720 | 2.980 | | 11.20 | | 0.790 | 1.550 | 26.4 | 0.0 |
| | | 0.760 | 2.100 | | 6.46 | | 0.500 | 1.240 | 23.2 | 0.014 |
| 15608 | | | 0.110 | | | | 5.220 | 1.240 | 15.6 | 0.090 |
| | | | 0.100 | | | | 5.680 | 1.580 | 23.5 | 0.005 |
| | | | 0.068 | | | | 1.380 | 0.820 | 10.3 | 0.005 |
| 20064 | | 0.300 | 0.910 | | 2.386 | | | | 108 | 0.038 |
| | | 0.200 | 0.728 | | 3.216 | | | | 26.0 | 0.024 |
| 20073 | | 5.000 | 3.670 | | 2.250 | | | | 43.0 | 0.060 |
| | | 1.470 | 0.812 | | 0.448 | | | | 11.0 | 0.030 |
| | | 1.890 | 0.875 | | 0.478 | | | | 14.0 | 0.020 |
| | | 3.690 | 2.440 | | 1.380 | | | | 44.0 | 0.370 |
| | | 3.190 | 1.260 | | 1.120 | | | | 38.0 | 0.090 |
| | | 2.850 | 1.370 | | 1.120 | | | | 33.0 | 0.540 |
| 20083 | | 40.50 | 2.750 | | 6.130 | | | | 145 | 0.030 |
| | | 4.810 | 0.375 | | 0.907 | | | | 34.0 | 0.005 |
| | | 13.80 | 0.210 | | 0.767 | | | | 27.0 | 0.005 |
| | | 3.150 | 0.212 | | 0.808 | | | | 9.0 | 0.005 |
| | | 4.050 | 0.163 | | 0.462 | | | | 6.0 | 0.005 |
| | | 15.80 | 2.440 | | 4.750 | | | | 97 | 0.005 |
| | | 18.30 | 2.170 | | 5.510 | | | | 110 | 0.170 |
| | | 2.55 | 1.080 | | 0.230 | | | | 9.0 | 135.0 |
| | | 18.70 | 2.100 | | 5.990 | | | | 130 | 0.0 |
| | | 9.110 | 1.920 | | 3.580 | | | | 51.0 | 1.5 |
| | | 2.070 | 6.170 | | 1.030 | | | | 3.0 | 114 |
| | | 5.840 | 1.440 | | 2.600 | | | | 24.0 | 53 |
| | | 80.00 | 9.220 | | 30.70 | | | | 490 | 0.0 |
| | | 2.040 | 1.960 | | 0.150 | | | | 2.0 | 68 |
| | | 128.0 | 16.80 | | 38.50 | | | | 710 | 0.110 |
| 20085 | | 3.360 | 0.206 | | 1.330 | | | | 29.0 | 0.007 |
| | | 2.840 | 0.188 | | 1.330 | | | | 32.0 | 0.008 |
| | | 1.950 | 0.132 | | 0.667 | | | | 21.0 | 0.013 |

## TABLE 7-49
## POLLUTANT CONCENTRATIONS (mg/l) FOR SAMPLED DATA FROM PLANTS WITH COMPLEXED METAL WASTES EMPLOYING PRECIPITATION/CLARIFICATION/FILTRATION

| PLANT ID | Cd | Cr | Cu | Pb | Ni | Ag | Zn | Fe | TSS | $CN_T$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 06097 | | | 0.008 | | | 0.0 | | 0.078 | 0.5 | 0.0 |
| | | | 0.0 | | | 0.0 | | 0.130 | 0.0 | 0.0 |
| | | | 0.005 | | | 0.0 | | 0.062 | 0.0 | 0.0 |
| 18538 | | 0.004 | | | 0.190 | | 0.023 | 0.063 | 1.0 | 0.0 |
| 33065 | | 0.250 | 0.533 | | 9.410 | | 0.308 | | 0.1 | 0.005 |
| | | 0.125 | 0.538 | | 8.810 | | 0.065 | | 0.1 | 0.005 |
| 36048 | | | | 0.0 | 0.620 | | | 0.022 | 2.1 | 0.150 |
| | | | | 0.0 | 0.640 | | | 0.019 | 2.6 | 0.040 |
| | | | | 0.0 | 0.320 | | | 0.020 | 1.5 | 0.090 |
| 36062 | | | 0.479 | 0.070 | 0.856 | | | | 58.0 | 0.046 |
| | | | 0.101 | 0.037 | 0.305 | | | | 58.0 | 0.005 |
| 40061 | | 3.746 | 1.161 | | 6.129 | | | | 27.0 | 0.010 |
| | | 2.313 | 0.816 | | 1.618 | | | | 23.0 | 0.010 |
| TOTAL DATA POINTS | 0 | 5 | 9 | 5 | 10 | 3 | 3 | 7 | | |
| DATA POINTS IN COMPLIANCE | NA | 3 | 9 | 5 | 7 | 3 | 3 | 7 | | |
| % POINTS IN COMPLIANCE | NA | 60.0 | 100.0 | 100.0 | 70.0 | 100.0 | 100.0 | 100.0 | | |
| TOTAL DATA POINTS WITH TSS AND CN LIMITATIONS* | 0 | 5 | 7 | 3 | 8 | 3 | 3 | 7 | | |
| DATA POINTS IN COMPLIANCE | NA | 3 | 7 | 3 | 5 | 3 | 3 | 7 | | |
| % POINTS IN COMPLIANCE | NA | 60.0 | 100.0 | 100.0 | 62.5 | 100.0 | 100.0 | 100.0 | | |

* Data points associated with TSS $\geq$ 42.9 mg/l or $CN_T \geq$ 1.30 mg/l have been deleted.

A comparison (reference Tables 7-48 and 7-28) of the percent of plants that have complexed metals and meet Option 1 compliance compared to the percent of plants that do not have complexed metals and meet Option 1 compliance limitations reveals that the complexed wastes are frequently more difficult to treat. A similar comparison (reference Table 7-49 and 7-33 of the Option 2 compliance results does not necessarily reveal the same conclusion. However, the size of the Option 2 complexed metal data base is much smaller than its Option 1 counterpart, which may influence the results of the comparison. Based upon the Option 1 comparison results, segregated treatment of the complexed metal wastes is recommended.

## TREATMENT TECHNIQUES

### High pH Precipitation/Sedimentation

The wastewater treatment alternative of hydroxide precipitation was described in great detail under the heading "Treatment of Common Metal Wastes". High pH precipitation is a type of chemical precipitation which is particularly applicable to complexed metal wastes. The process involves adding chemicals to the waste solution which bring about a drastic increase in pH, thereby prompting a shift in the complex disassociation equilibrium to produce uncomplexed metal ions which then can be precipitated by available hydroxide ions.

The treatment of solutions of complexed copper with calcium hydroxide, calcium oxide (lime), calcium chloride, or calcium sulfate at a pH of 11.6 - 12.5 will effectively remove copper from the solution as a copper hydroxide. Flocculation of the copper hydroxide with an anionic polyelectrolyte accelerates the settling of sludge. This process works well with both concentrated baths and dilute rinse baths.

The process equipment required for a high pH system includes holding and treatment tanks if the operation is conducted on a batch basis. Also needed are pumps to transfer the wastewater and a settling tank to concentrate the precipitate.

Although results of lab tests have shown that the process is applicable to removing copper from complexed copper solutions with calcium ions at a high pH, the effectiveness of treatment is determined by the structure of the complexing agent in the solution. The presence of carboxyl groups within the complexing agent (ligand) increases copper removal in this procedure. Complexing agents containing no carboxyl group and only hydroxyl groups show no copper removal. Electroless nickel solutions were also prepared under laboratory conditions and the results show the calcium treatment at a high pH to be effective. The high pH precipitation process is presently in the laboratory stage of development and has been useful in the precipitation of the metals in certain copper and nickel complexes.

## Chemical Reduction - Precipitation/Sedimentation

This process involves adding chemicals to lower the pH of the waste stream (to breakup the various metal complexes) followed by the addition of a reducing agent to reduce the metals to an oxidation state which permits precipitation of the metals. Following reduction of the metals, additional chemicals are used to increase the pH of the waste solution, forming metallic precipitates which are allowed to settle out of solution.

Electroless copper wastes and solder brightener wastes generated by printed circuit board manufacturers are treated in the following manner: initially the pH of the waste stream is lowered to approximately 4.0 using a dilute sulfuric acid solution in order to break the various metallic complexes. Sodium hydrosulfite is then added to reduce the metals to their lowest oxidation state. Following reduction, lime is added to raise the pH of the waste solution to approximately 9.0 and precipitate the metals out of solution. Sedimentation is then employed to remove the precipitated metals from the waste stream.

Chemical reduction of complexed metal wastes followed by chemical precipitation and sedimentation is employed at two metal finishing plants. These are plants 17061 and 19063. Each of these plants employ the chemical reduction precipitation/sedimentation technique for the treatment of copper, tin and lead.

## Membrane Filtration

Membrane filtration is a treatment method whose primary use is as an alternative to sedimentation for solids removal. A description of this treatment process, its application and performance, advantages and limitations, operational factors and demonstration status are detailed in the "Treatment of Common Metal Wastes" segment. This process has also proven to be effective for treatment of complexed metal wastes.

Tests carried out by a printed circuit board manufacturer show that this system is also effective in the presence of strong chelating agents such as EDTA, but continuous addition of the chemical reagent is required. Also, laboratory bench scale and pilot studies have been conducted on the following waste streams:

A. Tin and lead waste containing thiourea-copper complexes were tested on a pilot unit for over 200 hours with no flux deterioration with tin, lead, and copper all less than 0.1 mg/l in the product water.

B. Cupro-ammonia complex rinse from alkaline etching was treated in the pilot unit for 400 hours with no flux deterioration and with copper in the effluent less than 0.1 mg/l.

Based on this laboratory pilot study, a 1 gpm pilot test was run in a printed circuit board manufacturing facility. Over a 200 hour period, the flux was always in excess of 1.1 gpm. The effluent copper was consistently below 0.5 mg/l and usually at 0.1 mg/l, even with a varying concentration of copper in the feed.

C. Preliminary runs of electroless copper rinse waters have yielded product water in the range of 0.1 mg/l copper.

## Ferrous Sulfate ($FeSO_4$) - Precipitation/Sedimentation

Sulfide preciptation is capable of achieving low metal solubilities is spite of the presence of certain complexing and chelating agents. The use of complexing agents such as phosphates, tartrates, EDTA and ammonia (which are common in cleaning and plating formulations) can have an adverse effect upon metal removal efficiencies when hydroxide precipitation is used. Modification of the hydroxide precipitation process can improve system performance in the removal of complexed heavy metals from the waste stream.

Improved performance is attained by the dissolution of a positively charged ion such as $Fe^{+2}$ into the waste stream followed by precipitation of the metals. The ferrous sulfate ($FeSO_4$) technique uses this principle.

## Ion Exchange

Ion exchange is applicable to the treatment of certain metal complexes. This waste treatment technology has been discussed under Treatment of Common Metals Wastes within Section VII of the document.

## TREATMENT OF HEXAVALENT CHROMIUM WASTES - SINGLE OPTION

### INTRODUCTION

This subsection describes the treatment system option for hexavalent chromium bearing wastewater, presents effluent performance, and discusses alternative treatment techniques.

Hexavalent chromium bearing wastewaters are produced in the Metal Finishing Category in several ways:

- Chromium electroplating
- Chromate conversion coatings
- Etching with chromic acid
- Metal finishing operations carried out on chromium as a basis material

The selected treatment option involves the reduction of hexavalent chromium to trivalent chromium. The reduced chromium can then be removed with a conventional precipitation-solids removal system.

### RECOMMENDED HEXAVALENT CHROMIUM TREATMENT TECHNIQUE

### Chemical Chromium Reduction

Reduction is a chemical reaction in which electrons are transferred to the chemical being reduced from the chemical initiating the transfer (the reducing agent). Sulfur dioxide, sodium bisulfite, sodium metabisulfite, and ferrous sulfate form strong reducing agents in aqueous solution and are, therefore, useful in industrial waste treatment facilities for the reduction of hexavalent chromium to the trivalent form. The reduction enables the trivalent chromium to be separated from solution in conjunction with other metallic salts by alkaline precipitation. Gaseous sulfur dioxide is a widely used reducing agent and provides a good example of the chemical reduction process. Reduction using other reagents is chemically similar. The reactions involved may be illustrated as follows:

$$3\ SO_2 + 3\ H_2O \quad = \quad 3\ H_2SO_3$$

$$3\ H_2SO_3 + H_2CrO_4 \quad = \quad Cr_2\ (SO_4)_3 + 5\ H_2O$$

The above reaction is favored by low pH. A pH of 2 to 3 is normal for situations requiring complete reduction. At pH levels above 5, the reduction rate is slow. Oxidizing agents such as dissolved oxygen and ferric iron interfere with the reduction process by consuming the reducing agent.

A typical treatment consists of two hours retention in an equalization tank followed by 45 minutes retention in each of two reaction tanks connected in series. Each reaction tank has an electronic recorder-controller device to control process conditions with respect to pH and oxidation reduction potential (ORP). Gaseous sulfur dioxide is metered to the reaction tanks to maintain the ORP within the range of 250 to 300 millivolts. Sulfuric acid is added to maintain a pH level of from 1.8 to 2.0. Each of the reaction tanks is equipped with a propeller agitator designed to provide approximately one turnover per minute. Following reduction of the hexavalent chromium, the waste is combined with other waste streams for final adjustment to an appropriate alkaline pH to remove chromium and other metals by precipitation and sedimentation. Figure 7-23 shows a continuous chromium reduction system.

Application

Chromium reduction is used in metal finishing for treating chromium bearing waste streams, including chromium plating baths, chromating baths and rinses. The main application of chemical reduction to the treatment of wastewater is in the reduction of hexavalent chromium to trivalent chromium. Rinse waters and cooling tower blowdown are two major sources of chromium in waste streams. A study of an operational waste treatment facility chemically reducing hexavalent chromium has shown that a 99.7% reduction efficiency is easily achieved. Final concentrations of 0.05 mg/l are readily attained, and concentrations down to 0.01 mg/l are documented in the literature.

The major advantage of chemical reduction of hexavalent chromium is that it is a fully proven technology based on years of experience. Operation at ambient conditions results in minimal energy consumption, and the process, especially when using sulfur dioxide, is well suited to automatic control. Furthermore, the equipment is readily obtainable from many suppliers, and operation is straightforward.

One limitation of chemical reduction of hexavalent chromium is that for high concentrations of chromium, the cost of treatment chemicals may be correspondingly high. When this situation occurs, other treatment techniques are likely to be more economical. Chemical interference by oxidizing agents is possible in the treatment of mixed wastes, and the treatment itself may introduce pollutants if not properly controlled. Storage and handling of sulfur dioxide is somewhat hazardous.

Performance

The hexavalent chromium performance data base for visited plants is presented in Figure 7-24. These data are for metal finishing plants that use chemical reduction of hexavalent chromium.

Self-monitoring performance data for plants treating hexavalent chromium by chemical reduction are shown in Table 7-47. This table shows the number of data points for each plant, the

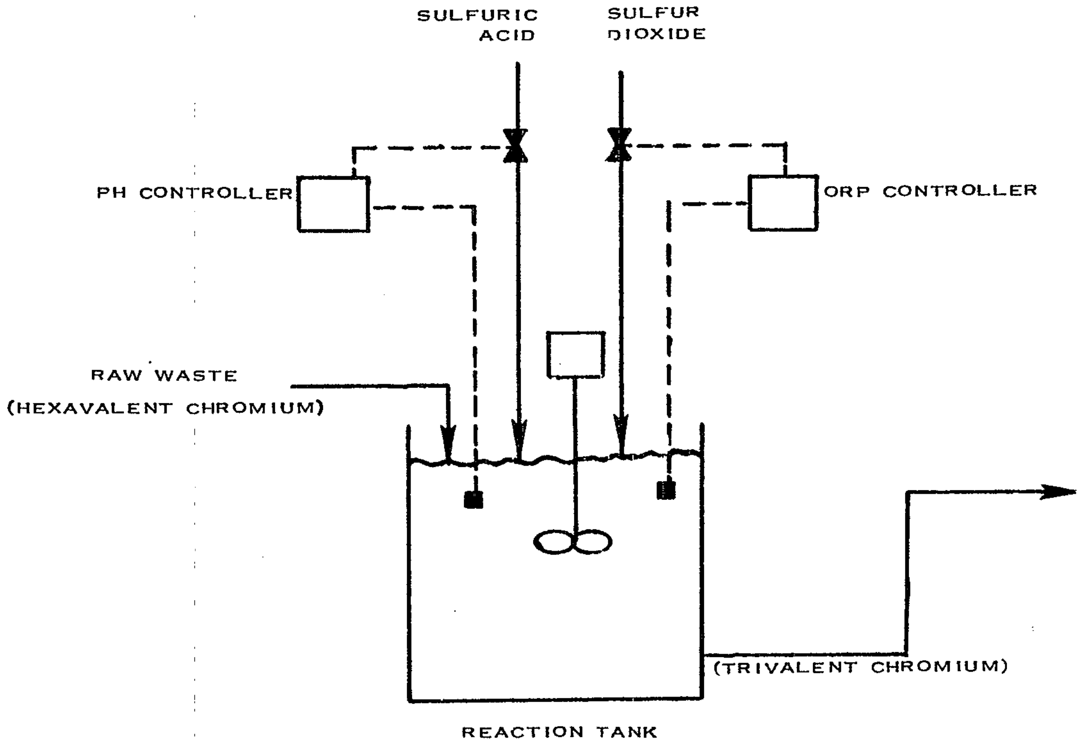
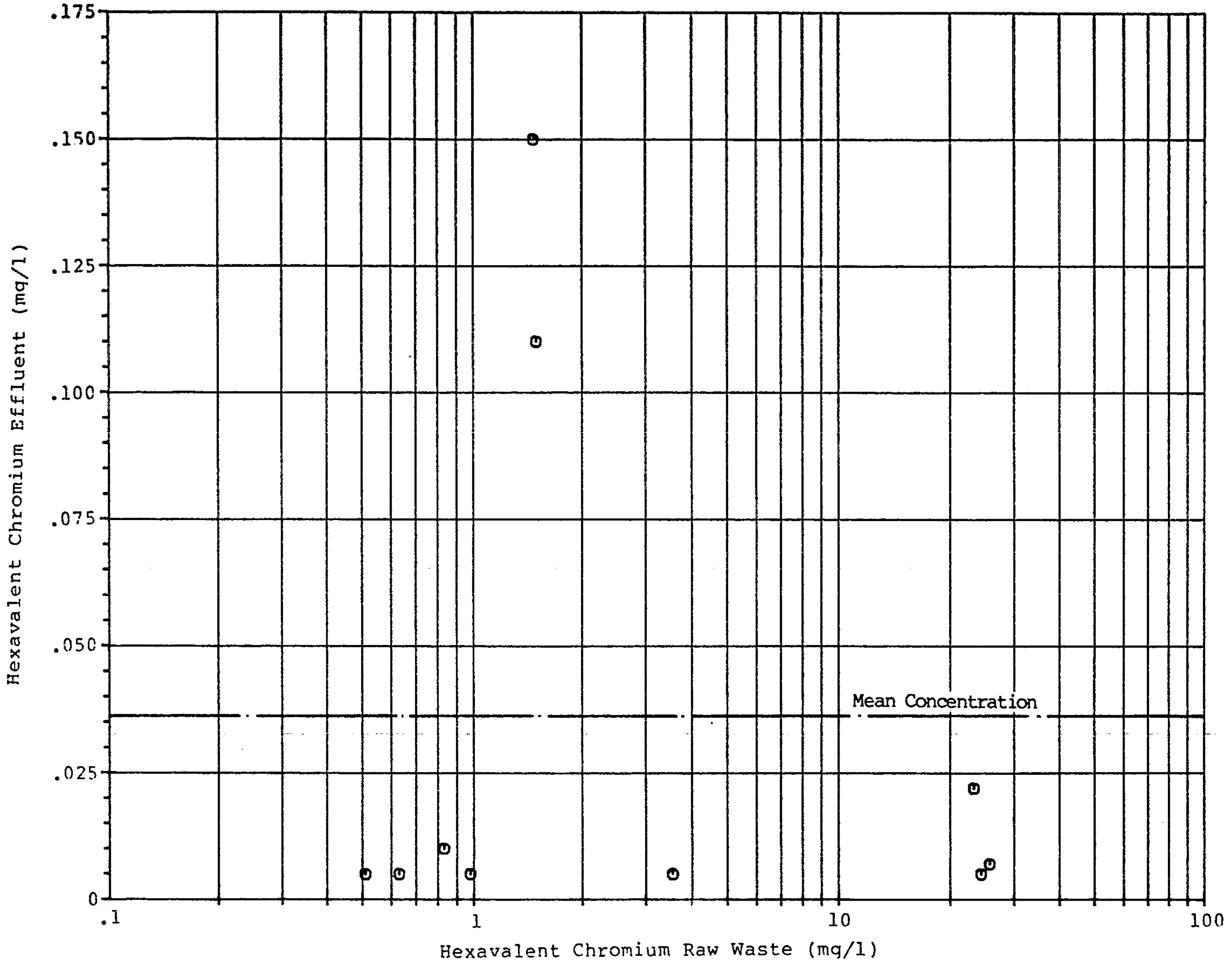


FIGURE 7-23

HEXAVALENT CHROMIUM REDUCTION WITH SULFUR DIOXIDE



Daily Maximum Concentration - 0.180 mg/l

FIGURE 7-24

EFFLUENT HEXAVALENT CHROMIUM CONCENTRATIONS vs RAW WASTE CONCENTRATIONS corresponding mean concentrations, and the calculated variability factors. Also shown are the total number of points, the overall mean concentration, and the median variability factors.

### TABLE 7-50

### EFFLUENT HEXAVALENT CHROMIUM SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number Of Points | Mean Effluent Concentration (mg/ℓ) | Variability Daily | Factor 10-Day |
|---|---|---|---|---|
| 1067 | 230 | 0.048 | 3.01 | 2.61 |
| 3043 | 94 | 0.009 | -- | 28.08 |
| 6051 | 13 | 0.020 | 8.46 | 1.95 |
| 11008 | 185 | 0.034 | 6.19 | 6.37 |
| 17030 | 282 | 0.025 | -- | 6.59 |
| 19063 | 237 | 0.011 | 2.37 | 2.12 |
| 20080 | 269 | 0.014 | 2.52 | 1.99 |
| 20116 | 243 | 0.017 | 2.88 | 1.96 |
| 30090 | 260 | 0.010 | 5.06 | 3.50 |
| 31021 | 35 | 0.096 | 5.04 | 3.05 |
| 47025 | 339 | 0.015 | 5.07 | 3.25 |
| OVERALL | 2187(Total) | 0.022(Mean) | 5.04(Median) | 3.05(Median) |

The visited plant mean performance and the self-monitoring data variability factors were used to establish the following daily and maximum monthly performance values for hexavalent chromium:

| | |
|---|---|
| Mean effluent hexavalent chromium | 0.032 mg/ℓ |
| Daily variability factor | 5.04 mg/ℓ |
| 10-Day variability factor | 3.05 mg/ℓ |
| Daily maximum effluent concentration | 0.16 mg/ℓ |
| Maximum monthly average effluent concentration | 0.10 mg/ℓ |

The percentages of hexavalent chromium effluent concentrations that are less than the daily maximum concentration limitation are 100.0 percent for the EPA sampled data base used to develop the limits.

Demonstration Status

The reduction of chromium waste by sulfur dioxide or sodium bisulfite is a classic process and is used by numerous plants employing chromium compounds in metal finishing and non-contact cooling operations.

Chemical chromium reduction is used in 343 plants in the present data base and these are identified in Table 7-51.

## ALTERNATIVE HEXAVALENT CHROMIUM TREATMENT TECHNIQUES

The following treatments are recovery techniques which can also be applied to waste streams containing hexavalent chromium. They include electrochemical chromium reduction, electrochemical chromium regeneration, evaporation and ion exchange.

### Electrochemical Chromium Reduction

This process has been developed to aid the removal of chromium from metal finishing and cooling tower blowdown wastewaters. It involves an electrochemical reaction in which consumable iron electrodes in the presence of an electrical current generate ferrous ions which react with chromate ions in solution. The reaction produces chromic hydroxides and ferric hydroxides that can be removed in a settling pond or clarifier without the need for further chemical addition. The process has also been shown effective in removing zinc and other heavy metals. The metallic hydroxides formed are gelatinous and highly adsorptive. They can therefore coprecipitate other species which might be present in a wastewater solution.

In addition to the electrochemical unit, the only equipment required is a pump and a clarifier or pond for settling. As long as the pH of the entering waste stream is between 7.0 and 8.0, no pH adjustment is necessary.

Application

Although the process was developed for removal of chromium and zinc from cooling tower discharge, electrochemical chromium reduction can also be applied to the treatment of metal finishing wastewaters such as chromating baths and rinses. Coil coating and porcelain enameling plants are other potential applications. According to manufacturers, the electrochemical reduction process performs best on low concentration, high volume wastewater streams. Conventional chemical reduction is probably more economical in treating more concentrated effluents.

## TABLE 7-51
## METAL FINISHING PLANTS EMPLOYING CHEMICAL CHROMIUM REDUCTION

01007
01067
01068
02037
02038
03043
04033
04069
04100
04114
04146
04151
04175
04199
04214
04216
04219
04221
04222
04261
04276
04277
04281

04282
04284
04690
04719
05033
05035
05050
06002
06006
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06148
06156
06358
06360
06381
06679
06371

06960
07001
08004
08008
08061
08072
08074
08081
09025
09040
09041
09046
09061
11008
11065
11096
11113
11121
11127
11129
11139
11140
11156

11165
11173
11174
11184
11477
11704
12005
12010
12014
12065
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12071
12074
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12100
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12105

13031
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14062
15010
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19051
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20241
21003
21051
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21062
21066
21074
21078
22028
22031
22735
23039
23048
23056
23059
23061
23066
23070
23076
23337
25001
25030

25031
25033
25034
25037
27042
28081
28082
28094
28096
28109
30009
30011
30050
30054
33058
30064
30074
30087
30090
30096
30097
30101
30111
30121
30127
30148

30153
30155
30157
30162
30507
30967
31020
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31037
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31069
31071
33024
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33043
33070
33071
33073
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33107
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33113

33116
33126
33129
33133
33137
33150
33172
33183
33184
33195
33197
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33281
33293
33852
34037
34039
34041
34042
34050
35040
35061
36001
36036
36040
36041

36082
36083
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36091
36102
36112
36113
36130
36149
36154
36155
36151
36161
36162
36166
36177
36179
36937
37063
38031
38035
38051
38052
38222
38223
40047

40048
40061
40062
41092
41869
43003
44037
44040
44042
44044
44050
44062
44148
44150
45035
45041
45045
46031
47005
47025
47059
47068
47074
47412
62032
62052

An advantage of the electrochemical chromium reduction process is that no pH adjustment chemicals are required with incoming pH values between 7 and 8. Retention time is unimportant when the pH is held within this range and the process is continuous and automatic. However, it is not efficient for effluents with high chromium concentrations, and species which consume hydroxide ions interfere with the precipitation of the ferric and ferrous hydroxides.

The system normally requires about thirty minutes of operator time per day. Since the iron electrodes are consumable they need to be replaced periodically. Sedimentation is part of the process and there is consequently a demand for sludge processing and removal. The precipitation of ferric and chromic hydroxides generates waste sludge which must eventually be dewatered and properly disposed. No appreciable amounts of sludge are allowed to settle in the actual electrochemical process tank.

Performance

The process is capable of removing hexavalent chromium from wastewater to less than 0.05 mg/l with input chromium concentrations up to at least 20 mg/l. Performance for one plant is as follows:

| Pollutant | Influent | Effluent |
|---|---|---|
| Hexavalent Chromium | 10 mg/l | 0.05 mg/l |
| Zinc | 3 | 0.1 |

Laboratory tests have also shown that the process is capable of removing metals other than chromium to the following levels (inlet concentrations not available):

| Metal | Concentration (mg/l) |
|---|---|
| Zinc | 0.1 |
| Nickel | 2.1 |
| Copper | 0.2 |
| Silver | 0.5 |
| Tin | <5 |

Retention time is unimportant since the reaction is instantaneous at pH values between 7.0 and 8.0, but subsequent sedimentation is needed to remove the precipitate formed in the reaction.

## Demonstration Status

There are more than 50 electrochemical reduction systems in operation in a variety of industries, mostly in organic and inorganic chemicals plants. Five are presently in service at plants in the metal finishing industry. The process has potential for applications in the photographic industry since it has been shown to successfully remove silver from wastewaters. Electrochemical chromium reduction is used in 2 plants in the present data base: 34051 and 42030.

## Electrochemical Chromium Regeneration

Chromic acid baths must be continually discarded and replenished to prevent buildup of trivalent chromium. An electrochemical system employing a lead anode and nickel cathode has been developed to recover chromium by converting the trivalent form to the hexavalent form. In this process, trivalent chromium is electro-oxidized to hexavalent chromium at the lead anode while hydrogen is released at the nickel cathode. This process is similar to the electrodialytic chromium oxidation process, but no membrane is used to separate concentrate from dilute solution. The reaction is carried out at 68°C, a cell voltage of 4.5 volts, and an anode-to-cathode area ratio of 30:1. The same process can also be used to recover chromium from chromic oxide sludges precipitated by conventional chemical chromium waste treatment. The sludges are dissolved in 200 g/l chromic acid and electro-oxidized under slightly different operating conditions than those previously described.

## Application

Electrochemical chromium regeneration can be used in metal finishing to prolong the life of chromium plating and chromating baths. Chromic acid baths are used for electroplating, anodizing, etching, chromating and sealing. The electro-oxidation process has been commercially applied to regeneration of a plastic etchant. In this particular installation, chromic acid dragged out of the etching bath into the first stage of a countercurrent rinse is concentrated by evaporation and returned to the etching bath. This closed loop system tends to cause a rapid buildup of trivalent chromium. However, when the etchant is recirculated through an electrochemical regeneration unit, the trivalent chromium is oxidized to the hexavalent form. The process has also been applied to regeneration of a chromic acid sealing bath in the coil coating industry.

Some advantages of the electrochemical chromium regeneration process are its relatively low energy consumption, its operation at normal bath temperature, eliminating need for heating or cooling, its ability for recovering and reusing valuable process chemicals, and elimination of sludges generated by conventional chromium treatment processes. Some limitations of chromium electrooxidation are low current efficiencies for baths with less than 5.0 g/l trivalent chromium, need for control of impurities which can interfere with the process, and dependence on electrical energy for oxidation to take place.

### Performance

The current efficiency for this process is 80 percent at concentrations above 5 g/l. If a trivalent chromium concentration of less than 5 g/l were treated, research has shown that the current efficiency would drop.

### Demonstration Status

One automobile plant (Plant ID 12078) is using the system experimentally to regenerate a chromic acid etching solution. In addition, one coil coater (Plant ID 01054) is using it on a full scale basis to regenerate a chromic acid sealing bath.

## Evaporation

Evaporation, which is explained in detail in the "Treatment of Common Metal Wastes" has found applicability in the treatment of chromium bearing wastes, especially the rinse waters after chromium plating. The rinse waters following the finishing operation (normally a countercurrent rinse of at least three stages) are sent to an evaporator. Here the chromium bearing solution is broken down into water and process solution (predominantly chromic acid). The water is returned to the last (cleanest) stage of the countercurrent rinse and the process solution may be returned to the process tank or put aside for sale to a scavenger. Plant 33065 has a similar arrangement on their chromium plating line. The data presented below represent the raw waste stream going to evaporation and the concentrate stream being returned to plating.

| Parameter | Input To Evaporator | (mg/l) | Concentrate |
|---|---|---|---|
| Chromium, Total | 5060 | | 27,500 |
| Chromium, Hex | 4770 | | 16,700 |
| TSS | <.1 | | 400 |
| pH | 1.6 | | 1.4 |

## Ion Exchange

Ion exchange is another possible method for recovering and regenerating chromic acid solution. As explained under the

"Treatment of Common Metal Wastes" segment, anions such as chromates or dichromates can be removed from rinse waters with an anion exchange resin. In order to regenerate the resin, caustic is pumped through the anion exchanger, carrying out sodium dichromate. The sodium dichromate stream is passed through a cation exchanger, converting the sodium dichromate to chromic acid. After some means of concentration such as evaporation, the chromic acid can be returned to the process bath.

## TREATMENT OF CYANIDE WASTES - SINGLE OPTION

### INTRODUCTION

This subsection describes the technique recommended for cyanide treatment, discusses the mean cyanide concentrations found, identifies the recommended daily maximum and monthly maximum average concentrations for cyanide and presents alternative treatments for the destruction of cyanide.

The following paragraphs describe the chlorine oxidation technique recommended for the treatment of cyanide bearing wastes.

### RECOMMENDED TREATMENT TECHNIQUE

#### Oxidation By Chlorination

Cyanides are introduced as metal salts for plating and conversion coating or are active components in plating and cleaning baths. Cyanide is generally destroyed by oxidation.

Chlorine is used primarily as an oxidizing agent in industrial waste treatment to destroy cyanide. Chlorine can be used in the elemental or hypochlorite form. This classic procedure can be illustrated by the following two step chemical reaction:

1. $Cl_2 + NaCN + 2NaOH = NaCNO + 2NaCl + H_2O$
2. $3Cl_2 + 6NaOH + 2NaCNO = 2NaHCO_3 + N_2 + 6NaCl + 2H_2O$

The reaction presented as equation(2) for the oxidation of cyanate is the final step in the oxidation of cyanide. A complete system for the alkaline chlorination of cyanide is shown in Figure 7-25.

The cyanide waste flow is treated by the alkaline chlorination process for oxidation of cyanides to carbon dioxide and nitrogen. The equipment often consists of an equalization tank followed by two reaction tanks, although the reaction can be carried out in a single tank. Each tank has an electronic recorder-controller to maintain required conditions with respect to pH and oxidation-reduction potential (ORP). In the first reaction tank, conditions are adjusted to oxidize cyanides to cyanates. To effect the reaction, chlorine is metered to the reaction tank as required to maintain the ORP in the range of 350 to 400 millivolts, and 50% aqueous caustic soda is added to maintain a pH range of 9.5 to 10. In the second reaction tank, conditions are maintained to oxidize cyanate to carbon dioxide and nitrogen. The desirable ORP and pH for this reaction are 600 millivolts and a pH of 8.0. Each of the reaction tanks is equipped with a propeller agitator designed to provide approximately one turnover per minute. Treatment by the batch process is accomplished by using two tanks, one

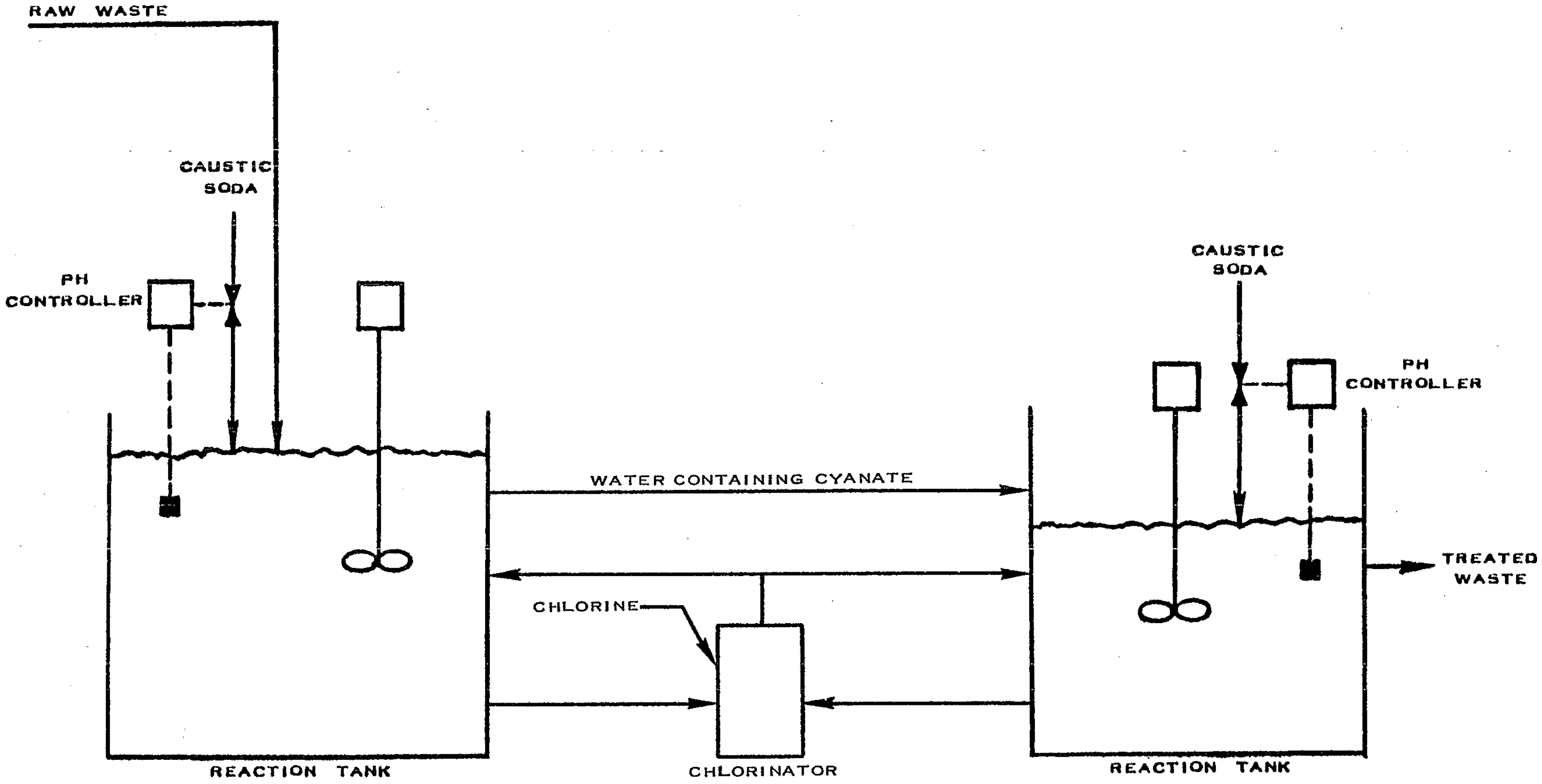

FIGURE 7-25

TREATMENT OF CYANIDE WASTE BY ALKALINE CHLORINATION for collection of waste over a specified time period, and one tank for the treatment of an accumulated batch. If dumps of concentrated wastes are frequent, another tank may be required to equalize the flow to the treatment tank. When the holding tank is full, the liquid is transferred to the reaction tank for treatment. After treatment, the supernatant is discharged and the sludges are collected for removal and ultimate disposal.

### Application

The oxidation of cyanide waste by chlorine is a classic process and is found in most plants using cyanide. This process is capable of achieving efficiencies of 99 percent or greater and effluent levels that are nondetectable. Chlorine has also been used to oxidize phenols, but use of chlorine dioxide for this purpose is much preferred because formation of toxic chlorophenols is avoided.

Some advantages of chlorine oxidation for handling process effluents are operation at ambient temperature, suitability for automatic control, and low cost. Some disadvantages of chlorine oxidation for treatment of process effluents are that toxic, volatile intermediate reaction products must be controlled by careful pH adjustment, chemical interference is possible in the treatment of mixed wastes, and a potentially hazardous situation exists when chlorine gas is stored and handled.

### Performance

Performance for cyanide oxidation was determined by evaluating the amenable cyanide effluent data from visited plants. Amenable cyanide was evaluated because treatment for cyanide is almost exclusively performed by alkaline chlorination. This form of treatment focuses upon oxidizing the cyanide which is amenable to chlorination.

Amenable cyanide data from visited plants are listed in Table 7-52. The table has the following four columns:

1. ID Number - The identification number of the visited plant. Duplicate numbers indicate different sampling days at the same plant.

2. Effluent Concentration - The measured concentration of the final effluent after treatment. At this point, cyanide wastes are mixed with other wastewaters.

3. Dilution Factor - This number represents the amount of dilution of the cyanide raw waste stream by other raw waste streams and is determined by dividing the total effluent stream flow by the cyanide stream flow.

4. Adjusted Cyanide Effluent Concentration - These concentrations are calculated by multiplying the effluent cyanide concentrations by the dilution factor applicable in each individual case.

The data contained in Table 7-52 were arranged in the following manner:

1. For each plant data set ($CN_A$) the concentrations were listed in decending order.

2. The plant data sets were listed in ascending order using the first value in each plant data set as the basis for ordering (the first value in each plant data set represents the highest concentration).

Ordering the data in this fashion facilitates identification of poorly operated treatment systems. As illustrated in the table, a break occurs between plant 20080 and 04045. The highest concentration at plant 20080 is 0.416 mg/ℓ and at plant 04045 the highest concentration is 2.2 mg/ℓ. Since alkaline chlorination is capable of reducing amenable cyanide concentrations to levels approximating zero, plants listed after plant 20080 exhibit poor control and excessive effluent concentrations. These plants have been deleted from the data base used to determine performance for cyanide oxidation.

Table 7-53 presents amenable cyanide data after deletions to remove plants with poorly operated treatment systems. The entire plant data set (both $CN_A$ and $CN_T$) was deleted if any cyanide amenable concentration for that plant exceeded the breakpoint between 0.416 mg/ℓ and 2.2 mg/ℓ. Plants which were deleted from both the amenable and total cyanide data bases are listed in Table 7-54.

Total cyanide data (after deleting the plants listed in Table 7-54) are presented in Table 7-55. These data correspond to the amenable cyanide data remaining in the data base from which performance is determined. In Table 7-55 two data points, 105.0 mg/ℓ and 5.69 mg/ℓ were deleted from the calculation of the mean effluent concentration for total cyanide. The 105.0 mg/ℓ was deleted because it was a high outlier although the corresponding cyanide amenable value did not indicate a high level. The 5.69 mg/ℓ was deleted as a high outlier and because there was no corresponding cyanide amenable value. Plant data sets which were deleted from the total cyanide data base are listed in Table 7-56.

The edited data sets (presented in Tables 7-53 and 7-55) were used to determine performance for cyanide oxidation. The adjusted mean effluent concentrations from the edited data base are presented below.

| Parameter | Adjusted Mean Effluent Concentration (mg/ℓ) |
|---|---|
| Cyanide, Total | 0.18 |
| Cyanide, Amenable | 0.06 |

## TABLE 7-52
## AMENABLE CYANIDE DATA BASE

| PLANT ID | $CN_A$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_A$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 12065 | 0 | 10.0 | 0 |
| 21051 | 0 | 1.0 | 0 |
| | 0 | 1.0 | 0 |
| | 0 | 1.0 | 0 |
| 38051 | 0 | 19.9 | 0 |
| 06075 | 0.005 | 5.0 | 0.025 |
| | 0.005 | 4.8 | 0.024 |
| 36623 | 0.005 | 5.1 | 0.025 |
| | 0.005 | 4.9 | 0.024 |
| | 0.005 | 4.3 | 0.021 |
| 19050 | 0.005 | 6.2 | 0.031 |
| 20079 | 0.005 | 7.9 | 0.039 |
| | 0.005 | 6.2 | 0.031 |
| | 0.005 | 6.1 | 0.030 |
| | 0.005 | 5.6 | 0.028 |
| | 0.005 | 5.0 | 0.025 |
| | 0.005 | 4.8 | 0.024 |
| 05021 | 0.005 | 8.0 | 0.04 |
| | 0.005 | 4.8 | 0.024 |
| | 0.005 | 4.8 | 0.024 |
| 20078 | 0.01 | 6.6 | 0.066 |
| | 0.005 | 7.4 | 0.037 |
| | 0.005 | 7.0 | 0.035 |
| | 0.005 | 6.9 | 0.034 |
| | 0.005 | 5.7 | 0.029 |
| | 0.005 | 5.6 | 0.028 |
| 15070 | 0.02 | 3.4 | 0.068 |
| | 0.005 | 2.8 | 0.014 |
| | 0.005 | 2.5 | 0.012 |
| 33073 | 0.027 | 5.5 | 0.147 |
| | 0.008 | 5.1 | 0.041 |
| 09026 | 0.06 | 2.6 | 0.156 |
| | 0.01 | 2.4 | 0.024 |
| | 0.005 | 3.8 | 0.021 |

## TABLE 7-52(CON'T)
## AMENABLE CYANIDE DATA BASE

| PLANT ID | $CN_A$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_A$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 31021 | 0.05 | 3.2 | 0.16 |
| | 0.05 | 3.2 | 0.16 |
| | 0.05 | 3.0 | 0.150 |
| 33024 | 0.04 | 5.1 | 0.204 |
| 20080 | 0.104 | 4.0 | 0.416 |
| | 0.005 | 5.8 | 0.029 |
| | 0.005 | 4.5 | 0.023 |
| | 0.005 | 4.5 | 0.023 |
| | 0.005 | 4.5 | 0.023 |
| 04045 | 2.2 | 1.0 | 2.2 |
| | 1.0 | 1.0 | 1.1 |
| | 0.25 | 1.0 | 0.25 |
| 06089 | 1.14 | 3.5 | 3.99 |
| | 0.285 | 3.0 | 0.855 |
| | 0.163 | 2.9 | 0.478 |
| 36041 | 0.4 | 10.4 | 4.16 |
| | 0.1 | 11.5 | 1.15 |
| | 0.1 | 10.1 | 1.01 |
| 06381 | 0.751 | 6.5 | 4.88 |
| | 0.089 | 8.7 | 0.733 |
| | 0.096 | 6.3 | 0.609 |
| 06085 | 1.08 | 5.0 | 5.4 |
| | 0.56 | 4.8 | 2.69 |
| | 0.06 | 5.4 | 0.323 |
| 20082 | 3.0 | 1.8 | 5.4 |
| | 1.08 | 2.1 | 2.23 |
| | 0.945 | 2.0 | 1.88 |
| | 0.625 | 2.1 | 1.32 |
| | 0.056 | 2.0 | 0.147 |
| | 0.034 | 2.0 | 0.064 |
| 06084 | 1.97 | 3.6 | 7.19 |

## TABLE 7-52(CON'T)
## AMENABLE CYANIDE DATA BASE

| PLANT ID | $CN_A$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_A$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 20081 | 0.49 | 15.6 | 7.64 |
| | 0.348 | 16.3 | 5.68 |
| | 0.075 | 17.6 | 1.32 |
| | 0.017 | 17.7 | 0.3 |
| | 0.005 | 15.9 | 0.079 |
| | 0.005 | 14.4 | 0.072 |
| 11103 | 3.37 | 3.0 | 10.0 |
| | 2.91 | 2.4 | 6.98 |
| 02033 | 4.2 | 2.6 | 11.1 |
| 20077 | 3.0 | 5.9 | 17.7 |
| | 2.1 | 7.8 | 16.4 |
| | 0.78 | 9.7 | 7.58 |
| | 0.1 | 6.5 | 0.65 |
| | 0.005 | 9.7 | 0.049 |
| | 0.005 | 7.1 | 0.036 |
| 06090 | 5.27 | 4.3 | 22.5 |
| 20086 | 5.25 | 4.5 | 23.6 |
| | 0.36 | 4.5 | 1.62 |
| | 0.005 | 4.5 | 0.023 |
| 06037 | 11.6 | 6.4 | 73.7 |
| | 0.408 | 6.4 | 2.59 |
| | 0.122 | 6.4 | 0.775 |
| 21066 | 11.75 | 7.4 | 86.9 |
| | 6.57 | 10.2 | 66.9 |
| | 8.83 | 4.7 | 41.5 |

## TABLE 7-53
## DATA USED FOR AMENABLE CYANIDE PERFORMANCE

| PLANT ID | CN$_A$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED CN$_A$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 12065 | 0 | 10.0 | 0 |
| 21051 | 0 | 1.0 | 0 |
| | 0 | 1.0 | 0 |
| | 0 | 1.0 | 0 |
| 38051 | 0 | 19.9 | 0 |
| 06075 | 0.005 | 5.0 | 0.025 |
| | 0.005 | 4.8 | 0.024 |
| 36623 | 0.005 | 5.1 | 0.025 |
| | 0.005 | 4.9 | 0.024 |
| | 0.005 | 4.3 | 0.021 |
| 19050 | 0.005 | 6.2 | 0.031 |
| 20079 | 0.005 | 7.9 | 0.039 |
| | 0.005 | 6.2 | 0.031 |
| | 0.005 | 6.1 | 0.030 |
| | 0.005 | 5.6 | 0.028 |
| | 0.005 | 5.0 | 0.025 |
| | 0.005 | 4.8 | 0.024 |
| 05021 | 0.005 | 8.0 | 0.04 |
| | 0.005 | 4.8 | 0.024 |
| | 0.005 | 4.8 | 0.024 |
| 20078 | 0.01 | 6.6 | 0.066 |
| | 0.005 | 7.4 | 0.037 |
| | 0.005 | 7.0 | 0.035 |
| | 0.005 | 6.9 | 0.034 |
| | 0.005 | 5.7 | 0.029 |
| | 0.005 | 5.6 | 0.028 |
| 15070 | 0.02 | 3.4 | 0.068 |
| | 0.005 | 2.8 | 0.014 |
| | 0.005 | 2.5 | 0.012 |
| 33073 | 0.027 | 5.5 | 0.147 |
| | 0.008 | 5.1 | 0.041 |
| 09026 | 0.06 | 2.6 | 0.156 |
| | 0.01 | 2.4 | 0.024 |
| | 0.005 | 3.8 | 0.021 |

## TABLE 7-53 (CON'T)
## DATA USED FOR AMENABLE CYANIDE PERFORMANCE

| PLANT ID | $CN_A$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_A$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 31021 | 0.05 | 3.2 | 0.16 |
| | 0.05 | 3.2 | 0.16 |
| | 0.05 | 3.0 | 0.150 |
| 33024 | 0.04 | 5.1 | 0.204 |
| 20080 | 0.104 | 4.0 | 0.416 |
| | 0.005 | 5.8 | 0.029 |
| | 0.005 | 4.5 | 0.023 |
| | 0.005 | 4.5 | 0.023 |
| | 0.005 | 4.5 | 0.023 |

## TABLE 7-54
## PLANTS DELETED FROM CYANIDE DATA BASE DUE TO POOR PERFORMANCE

04045
06089
36041
06381
06085
20082
06084
20081
11103
02033
20077
06090
20086
06037
21066

# TABLE 7-55
# DATA USED FOR TOTAL CYANIDE PERFORMANCE

| PLANT ID | $CN_T$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_T$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 12065 | 0.014 | 10 | 0.14 |
| 21051 | 0 | 1.0 | 0 |
| | 0 | 1.0 | 0 |
| | 0 | 1.0 | 0 |
| 38051 | 0 | 19.9 | 0 |
| 06075 | 0.005 | 4.8 | 0.024 |
| | 0.005 | 5.0 | 0.025 |
| | 0.014 | 4.8 | 0.067 |
| 36623 | 0.01 | 4.3 | 0.043 |
| | 0.02 | 4.9 | 0.098 |
| | 0.033 | 5.1 | 0.167 |
| 19050 | 0.005 | 6.2 | 0.031 |
| 20079 | 0.005 | 4.8 | 0.024 |
| | 0.005 | 6.1 | 0.031 |
| | 0.005 | 6.2 | 0.031 |
| | 0.005 | 7.9 | 0.039 |
| | 0.02 | 5.6 | 0.112 |
| | 21.0 | 5.0 | 105.* |
| 05021 | 0.005 | 4.8 | 0.024 |
| | 0.005 | 4.8 | 0.024 |
| | 0.007 | 8.0 | 0.056 |
| 20078 | 0.005 | 5.6 | 0.028 |
| | 0.005 | 5.7 | 0.029 |
| | 0.005 | 7.0 | 0.035 |
| | 0.005 | 7.4 | 0.037 |
| | 0.01 | 6.9 | 0.069 |
| | 0.04 | 6.6 | 0.266 |
| 20080 | 0.005 | 4.5 | 0.023 |
| | 0.005 | 4.5 | 0.023 |
| | 0.005 | 4.5 | 0.023 |
| | 0.005 | 5.8 | 0.029 |
| | 0.1 | 4.1 | 0.41 |
| | 0.111 | 4.0 | 0.444 |
| | 1.23 | 4.6 | 5.69* |

* Not used in calculation of mean effluent concentration.

## TABLE 7-55(CON'T)
## DATA USED FOR TOTAL CYANIDE PERFORMANCE

| PLANT ID | $CN_T$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_T$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 15070 | 0.02 | 2.5 | 0.05 |
|  | 0.03 | 3.4 | 0.102 |
|  | 0.29 | 2.8 | 0.818 |
| 33073 | 0.013 | 5.5 | 0.071 |
|  | 0.129 | 5.1 | 0.66 |
|  | 0.254 | 5.5 | 1.39 |
| 09026 | 0.03 | 2.4 | 0.072 |
|  | 0.02 | 3.8 | 0.076 |
|  | 0.08 | 2.6 | 0.208 |
| 31021 | 0.16 | 3.2 | 0.512 |
|  | 0.16 | 3.2 | 0.512 |
|  | 0.35 | 3.1 | 1.1 |
| 33024 | 0.04 | 5.1 | 0.204 |

## TABLE 7-56
## PLANT DATA DELETED FROM TOTAL CYANIDE DATA BASE

| PLANT ID | $CN_T$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_T$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 02033 | 10.0 | 2.6 | 26.0 |
| 04045 | 6.4 | 1.0 | 6.4 |
| | 8.7 | 1.0 | 8.7 |
| | 15.2 | 1.0 | 15.2 |
| 06037 | 0.53 | 6.3 | 3.37 |
| | 0.591 | 6.3 | 3.75 |
| | 12.6 | 6.4 | 80.6 |
| 06084 | 0.027 | 2.9 | 0.078 |
| | 0.435 | 4.3 | 1.86 |
| | 2.8 | 3.6 | 10.2 |
| 06085 | 0.96 | 4.8 | 4.61 |
| | 0.92 | 5.4 | 4.95 |
| | 1.8 | 5.0 | 9.0 |
| 06089 | 0.285 | 2.9 | 0.835 |
| | 0.428 | 3.0 | 1.28 |
| | 2.42 | 3.5 | 8.47 |
| 06090 | 2.81 | 4.3 | 12.1 |
| | 6.73 | 4.3 | 28.7 |
| | 10.8 | 4.3 | 46.1 |
| 06381 | 0.089 | 8.7 | 0.773 |
| | 0.25 | 6.3 | 1.58 |
| | 0.981 | 6.5 | 6.38 |
| 11103 | 10.0 | 2.4 | 24.0 |
| | 9.37 | 3.0 | 28.1 |
| 20077 | 0.005 | 7.1 | 0.036 |
| | 1.5 | 9.7 | 14.6 |
| | 2.5 | 6.5 | 16.2 |
| | 3.0 | 5.9 | 17.7 |
| | 2.5 | 7.8 | 19.5 |
| | 2.4 | 9.7 | 23.3 |

## TABLE 7-56(CON'T)
## PLANT DATA DELETED FROM TOTAL CYANIDE DATA BASE

| PLANT ID | $CN_T$ EFFLUENT CONCENTRATION (mg/l) | DILUTION FACTOR | ADJUSTED $CN_T$ CONCENTRATION (mg/l) |
|---|---|---|---|
| 20081 | 0.035 | 17.7 | 0.618 |
| | 0.023 | 14.4 | 0.331 |
| | 0.068 | 15.9 | 1.08 |
| | 0.911 | 17.6 | 16.0 |
| | 1.16 | 16.3 | 19.0 |
| | 3.82 | 15.6 | 59.6 |
| 20082 | 0.034 | 2.0 | 0.068 |
| | 0.635 | 2.1 | 1.34 |
| | 0.722 | 2.0 | 1.47 |
| | 0.945 | 2.0 | 1.88 |
| | 3.09 | 1.8 | 5.63 |
| | 3.31 | 2.1 | 6.85 |
| 20086 | 0.73 | 4.5 | 3.28 |
| | 1.13 | 4.5 | 5.08 |
| | 5.25 | 4.5 | 23.6 |
| 21066 | 16.38 | 4.7 | 76.9 |
| | 12.15 | 10.2 | 123.9 |
| | 20.65 | 7.4 | 152.8 |
| 36041 | 0.25 | 11.5 | 2.87 |
| | 0.4 | 10.1 | 4.04 |
| | 0.6 | 10.4 | 6.24 |

Self-monitoring data for total cyanide and amenable cyanide are shown in Table 7-57. For each plant, this table shows the number of data points, the mean effluent concentration, and the calculated variability factors plus the total number of points, the overall mean effluent concentration, and the median variability factors.

| | $CN_T$ | $CN_A$ |
|---|---|---|
| Mean Effluent Concentration (mg/ℓ) | 0.18 | 0.06 |
| Variability Factors (Daily/10-day) | 6.68/3.61 | 14.31/5.31 |
| Daily Maximum Concentration (mg/ℓ) | 1.20 | 0.86 |
| Maximum Monthly Average Concentration (mg/ℓ) | 0.65 | 0.32 |

The percent of plants with cyanide levels below the cyanide daily maximum effluent concentration limitations are as follows:

| Parameter | EPA Sampled Plants Daily Maximum | Self-Monitoring Data Daily Max. | Self-Monitoring Data 10-Day Ave. |
|---|---|---|---|
| Cyanide, Total | 97.8 | 79.2 | 62.9 |
| Cyanide, Amenable | 100.0 | 92.8 | 78 |

The percent compliance for the self-monitoring data for the cyanide total daily maximum and for the cyanide total and cyanide amenable 10-day averages is relatively low compared to the EPA samples plants. When examining the EPA sampled data, the Agency excluded numerous plants that had high cyanide levels after correcting for dilution. Apparently many plants are relying on dilution of treated cyanide wastes rather than performing alkaline chlorination to its capability. Self-monitoring data are insufficient to examine the adequacy of the treatment system because both cyanide amenable and cyanide total results are generally not available for the same plants. Two plants have both cyanide amenable and cyanide total values; however, the cyanide amenable results are indicative of inadequate treatment. This appears to indicate that there is a need for additional control of cyanide by many of the plants that submitted self-monitoring data. This is illustrated in Table 7-58 which shows the adjusted mean and maximum concentrations for cyanide total and cyanide amenable for plants with self- monitoring data for which dilution factors were available.

### Demonstration Status

The oxidation of cyanide wastes by chlorine is a widely used process in plants using cyanide in cleaning and plating baths. There has been recent attention to developing chlorine dioxide generators and bromine chloride generators. A problem that has been encountered is that the generators produce not only the bromine chloride and chlorine dioxide gas, but chlorine gas is also formed simultaneously. Both of these gases are extremely unstable, corrosive, and have low vapor pressure, which results in handling difficulties. These generators are in the development stages and as advances are made in their design, they may become competitive with chlorine.

Oxidation by chlorine is used in 206 plants in the present data base, and these are identified in Table 7-59.

## TABLE 7-57

### EFFLUENT TOTAL CYANIDE SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 1067 | 230 | 0.041 | 1.92 | 1.46 |
| 3043 | 89 | 0.154 | 10.02 | 4.75 |
| 6051 | 13 | 0.07 | -- | -- |
| 6107 | 10 | 2.20 | 25.01 | -- |
| 11008 | 179 | 0.09 | 6.10 | 4.15 |
| 11125 | 54 | 1.21 | 3.64 | 1.35 |
| 15193 | 12 | 0.053 | 3.23 | 3.68 |
| 20080 | 268 | 0.001 | -- | -- |
| 20082 | 246 | 0.132 | 7.25 | 3.55 |
| 31021 | 119 | 0.533 | 11.16 | 7.67 |
| 36082 | 121 | 0.043 | 4.23 | 3.33 |
| 44045 | 50 | 0.008 | -- | 7.68 |
| 47025 | 138 | 0.057 | 7.92 | 2.57 |
| OVERALL | 1529(Total) | 0.156(Mean) | 6.68(Median) | 3.61(Median) |

### EFFLUENT AMENABLE CYANIDE SELF-MONITORING PERFORMANCE DATA FOR PLANTS WITH OPTION 1 SYSTEMS

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 31021 | 28 | 0.196 | 14.32 | 3.18 |
| 38223 | 235 | 0.0004 | -- | 5.31 |
| 47025 | 243 | 0.007 | -- | 5.77 |
| OVERALL | 529(Total) | 0.016(Mean) | 14.31(Median) | 5.31(Median) |

# TABLE 7-58

## ADJUSTED EFFLUENT TOTAL CYANIDE SELF-MONITORING DATA

| Plant ID | Number OF Points | Adjusted CN,T Mean Concentration (mg/ℓ) | Adjusted CN,T Maximum Daily Concentration (mg/ℓ) |
|---|---|---|---|
| 3043 | 89 | 0.57 | 3.11 |
| 11008 | 179 | 0.35 | 8.40 |
| 11125 | 54 | 10.11 | 33.32 |
| 15193 | 12 | 1.75 | 5.33 |
| 20080 | 268 | 0.01 | 0.46 |
| 20082 | 246 | 0.66 | 7.0 |
| 31021 | 119 | 1.48 | 15.29 |
| 36082 | 121 | 0.21 | 5.0 |
| 44045 | 50 | 0.83 | 15.0 |
| 47025 | 138 | 2.26 | 12.32 |
| LIMITATION COMPARISON | | 0.18 (EPA Sample Data Mean) | 1.20 (Daily Max.) |

## ADJUSTED EFFLUENT AMENABLE CYANIDE SELF-MONITORING DATA

| Plant ID | Number OF Points | Adjusted CN,T Mean Concentration (mg/ℓ) | Adjusted CN,T Maximum Daily Concentration (mg/ℓ) |
|---|---|---|---|
| 31021 | 28 | 0.54 | 3.89 |
| 38223 | 235 | 0.06 | 1.43 |
| 47025 | 243 | 0.28 | 6.80 |
| LIMITATION COMPARISON | | 0.06 (EPA Sample Data Mean) | 0.86 (Daily Max.) |

## TABLE 7-59
## METAL FINISHING PLANTS EMPLOYING CYANIDE OXIDATION

01007
01067
01068
02033
02037
20240
03042
03043
04045
04076
04114
04178
04199
04124
04227
04236
04263
04277
04279
04182
05021
05029
05033
06002
06006
06037
06050
06051
06052
06053
06002
06072
06073
06075
06079
06078
06079
06081
06084
06085
06087
06089
06090
06094
06101
06107
06111
06113
06115
06119
06120
06122
06124
06129
06141
06146
06147
06152
06358
06360
06381
06679
08004
08008
08074
09026
09060
10020
11008
11096
11098
11103
11125
11118
11174
11177
11184
12005
12065
12078
12087
12709
13033
13034
13039
13040
15042
15045
15047
15048
15070
15193
16033
16035
18050
18055
18534
19050
19051
19063
19069
19084
19090
19099
19102
19104
20001
20005
20017
20073
20077
20078
20079
20080
20081
20082
20084
20086
20087
20158
20162
20172
20243
20708
21003
21062
21066
21074
21078
22028
22656
23039
23059
23061
23074
23076
23337
25001
25030
25031
27044
27046
28082
28105
30011
30022
30090
30096
30097
30109
30111
30162
30967
31021
31037
31040
31047
31070
33024
33043
33065
33070
33071
33073
33113
33120
33137
33146
33184
33187
33275
34041
34042
35061
35963
36036
36040
36041
36082
36083
36084
36090
36091
36102
36112
36113
36151
36154
36156
36623
37042
38031
38038
38051
38223
40037
40047
41116
42830
43052
44037
44040
44045
45035
47005
47025

## ALTERNATIVE CYANIDE TREATMENT TECHNIQUES

Alternative treatment techniques for the destruction of cyanide include oxidation by ozone, ozone with ultraviolet radiation (oxyphotolysis), hydrogen peroxide and electrolytic oxidation. These techniques are presented in the following paragraphs.

### Oxidation By Ozonation

Ozone may be produced by several methods, but the silent electrical discharge method is predominant in the field. The silent electrical discharge process produces ozone by passing oxygen or air between electrodes separated by an insulating material. The electrodes are usually stainless steel or aluminum. The dielectric or insulating material is usually glass. The gap or air space between electrodes or dielectrics must be uniform and is usually on the order of 0.100 to 0.125 inches. The voltage applied is 20,000 volts or more, and a single phase current is applied to the high tension electrode.

Ozone is approximately ten times more soluble than oxygen on a weight basis in water, although the amount that can be efficiently dissolved is still slight. Ozone's solubility is proportional to its partial pressure and also depends on the total pressure on the system. It should be noted, however, that it is the oxidizable contaminant in the water that determines the quantity of ozone needed to oxidize the contaminants present. A complete ozonation system is represented in Figure 7-26.

Thorough distribution of ozone in the water under treatment is extremely important for high efficiency of the process. There are four methods of mixing ozone with water; these are: (1) diffusers, (2) negative or positive pressure injection, (3) packed columns whereby ozone-containing air or oxygen is distributed throughout the water, and (4) atomizing the aqueous solution into a gaseous atmosphere containing ozone.

### Application

Ozonation has been applied commercially for oxidation of cyanides, phenolic chemicals, and organo-metal complexes. It is used commercially with good results to treat photoprocessing wastewaters. Divalent iron hexacyanato complexes (spent bleach) are oxidized to the trivalent form with ozone and reused for bleaching purposes. Ozone is used to oxidize cyanides in other industrial wastewaters and to oxidize phenols and dyes to a variety of colorless, nontoxic products.

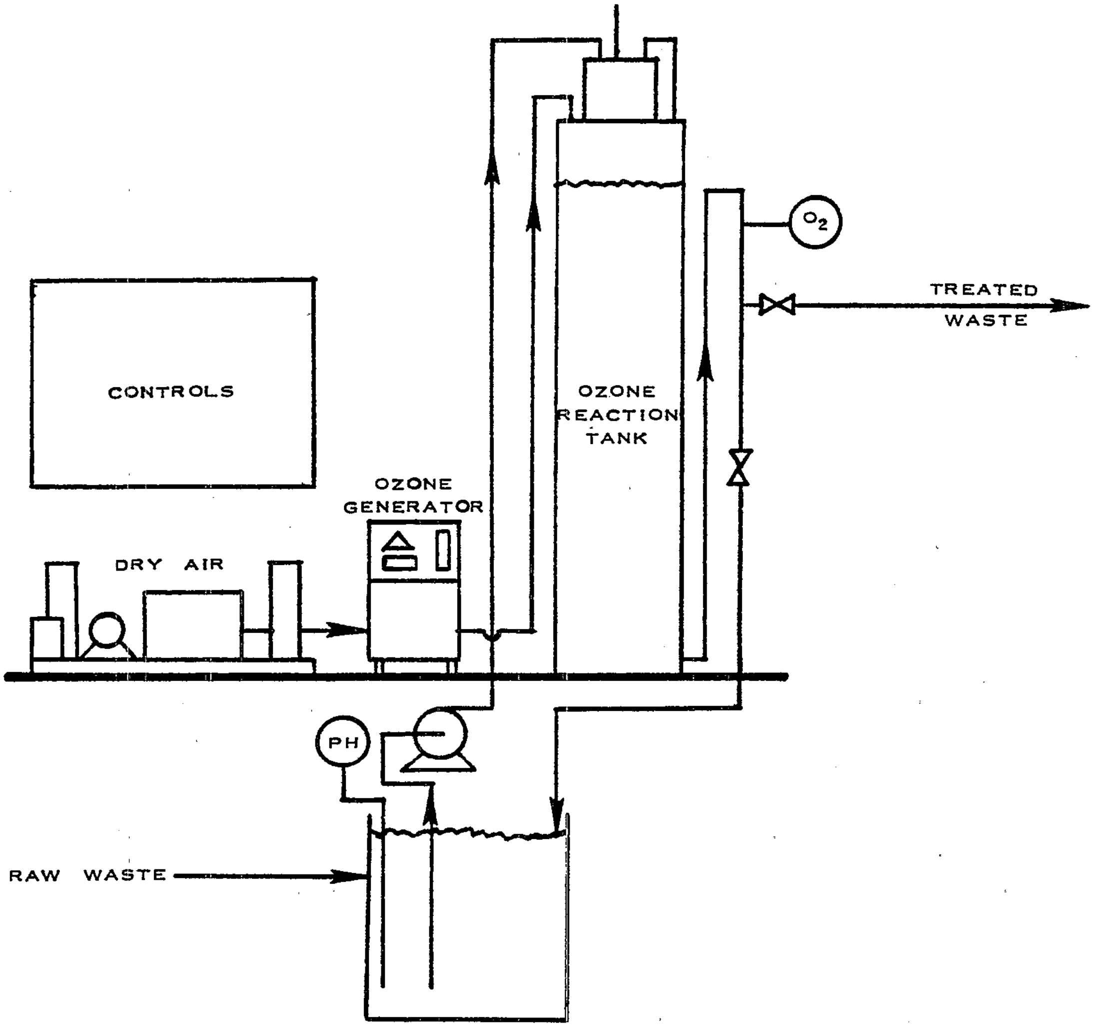

FIGURE 7-26

TYPICAL OZONATION PLANT FOR WASTE TREATMENT

Oxidation of cyanide to cyanate is illustrated below:

$$CN^{-1} + O_3 = CNO^{-1} + O_2$$

Continued exposure to ozone will convert the cyanate formed to carbon dioxide and ammonia if the reaction is allowed to proceed; however, this is not economically practical, and cyanate can be economically decomposed by biological oxidation at neutral pH.

Ozone oxidation of cyanide to cyanate requires 1.8 to 2.0 pounds of ozone per pound of $CN^-$ and complete oxidation requires 4.6 to 5.0 pounds of ozone per pound of $CN^-$. Zinc, copper, and nickel cyanides are easily destroyed to a nondetectable level, but cobalt cyanide is resistant to ozone treatment.

The first commercial plant using ozone in the treatment of cyanide waste was installed by a manufacturer of aircraft. This plant is capable of generating 54.4 Kg (120 pounds) of ozone per day. The concentration of ozone used in the treatment is approximately 20 mg/l. In this process the cyanate is hydrolyzed to $CO_2$ and $NH_3$. The final effluent from this process passes into a lagoon. Because of an increase in waste flow the original installation has been expanded to produce 162.3 Kg (360 pounds) of ozone per day.

Some advantages of ozone oxidation for handling process effluents are that it is well suited to automatic control, on-site, generation eliminates treatment chemical procurement and storage problems, reaction products are not chlorinated organics, and no dissolved solids are added in the treatment step. Ozone in the presence of ultraviolet radiation or other promoters such as hydrogen peroxide and ultrasound shows promise of reducing reaction time and improving ozone utilization. Some limitations of the process are high capital expense, possible chemical interference in the treatment of mixed wastes, and an energy requirement of 15 to 22 kwh per kilogram of ozone generated. Cyanide is not economically oxidized beyond the cyanate form.

Performance

An electroplating plant (ID 30022) that serves the electronics industry plates gold, silver, copper, and nickel. Ozone was selected for treatment of cyanide bearing waste, and the results were as follows:

A. Optimum operating conditions were determined to be 1 to 1.5 moles of ozone/mole CN at a pH of 9.0-9.5 in the ozone contactor.

B. It was established that ozone dosage is the most critical operating parameter, with 1.0 to 1.5 moles $O_3$/mole CN found to be optimum at low CN concentrations (20 mg/l) and 1.8 to 2.8 moles $O_3$/mole CN at levels greater than 40 mg/l.

C. Cost data based on plant experience were obtained. Treatment operating cost was $1.43/100 gallons of influent cyanide bearing waste water and $1.03/1000 gallons total waste water. Total capital costs were $66,613 for this installation but are estimated at $51,200 for an optimized, non-research installation.

D. The results of three days of sampling are shown below:

PLANT ID 30022 (mg/l)

| | Day 1 | | Day 2 | | Day 3 | |
|---|---|---|---|---|---|---|
| Parameter | In | Out | In | Out | In | Out |
| Cyanide, Total | 1.4 | .113 | .30 | .039 | 2.4 | .096 |
| Cyanide, Amenable | 1.4 | .110 | .30 | .039 | 2.389 | .096 |

Demonstration Status

Ozone is useful for application to cyanide destruction. There are at least two units presently in operation in the country (Plant ID's 14062 and 30022), and additional units are planned. There are numerous orders for industrial ozonation cyanide treatment systems pending.

Ozone is useful in the destruction of wastewaters containing phenolic materials, and there are several installations in operation in the United States.

Research and development activities within the photographic industry have established that ozone is capable of treating some compounds that are produced as waste products. Solutions of key ingredients in photographic products were composed and treated with ozone under laboratory conditions to determine the treatability of these solutions. It was found that some of these solutions were oxidized almost completely by ozonation and some were oxidized that were difficult to treat by conventional methods. Ozone breaks down certain developer components that biodegrade slowly, including color developing agents, pheniodone, and hydroxylamine sulfate. Developing agents, thiocyanate ions, and formate ions degrade more completely with ozone than when exposed to biological degradation. Thiosulfate, sulfite, formalin, benzyl alcohol, hydroquinone, maleic acid, and ethylene glycol can be degraded to a more or less equal degree with either biological treatment or ozone. Silver thiosulfate complexes were also treated with ozone resulting in significant recovery of the silver present in solution. Ozone for regeneration of iron cyanide photoprocessing bleach and treatment of thiosulfate, hydroquinone, and other chemicals is currently being utilized by the photoprocessing industry. There are 40 to 50 installations of this nature in use at the present time.

## Oxidation By Ozonation With UV Radiation

One of the modifications of the ozonation process is the simultaneous application of ultraviolet light and ozone for the treatment of wastewater, including treatment of halogenated organics. The combined action of these two forms produces reactions by photolysis, photosensitization, hydroxylation, oxygenation and oxidation. The process is unique because several reactions and reaction species are active simultaneously.

Ozonation is facilitated by ultraviolet absorption because both the ozone and the reactant molecules are raised to a higher energy state so that they react more rapidly. The energy and reaction intermediates created by the introduction of both ultraviolet radiation and ozone greatly reduce the amount of ozone required compared with a system that utilizes ozone alone to achieve the same level of treament. Figure 7-27 shows a three-stage UV/ozone system.

A typical process configuration employs three single stage reactors. Each reactor is a closed system which is illuminated with ultraviolet lamps placed in the reactors, and the ozone gas is sparged into the solution from the bottom of the tank. The ozone dosage rate requires 2.6 pounds of ozone per pound of chlorinated aromatic. The ultraviolet power is on the order of five watts of useful ultraviolet light per gallon of reactor volume. Operation of the system is at ambient temperature and the residence time per reaction stage is about 24 minutes. Thorough mixing is necessary and the requirement for this particular system is 20 horsepower per 1000 gallons of reactor volume in quadrant baffled reaction stages. A system to treat mixed cyanides requires pretreatment that involves chemical coagulation, sedimentation, clarification, equalization, and pH adjustment. Pretreatment is followed by a single stage reactor, where constituents with low refractory indices are oxidized. This may be followed by a second, multi-stage reactor which handles constituents with higher refractory indices. Staging in this manner reduces the ultimate reactor volume required for efficient treatment.

### Application

The ozonation/UV radiation process was developed primarily for cyanide treatment in the metal finishing and color photoprocessing areas, and it has been successfully applied to mixed cyanides and organics from organic chemicals manufacturing processes. The process is particularly useful for treatment of complexed cyanides such as ferricyanide, copper cyanide and nickel cyanide, which are resistant to ozone alone, but readily oxidized by ozone with UV radiation.

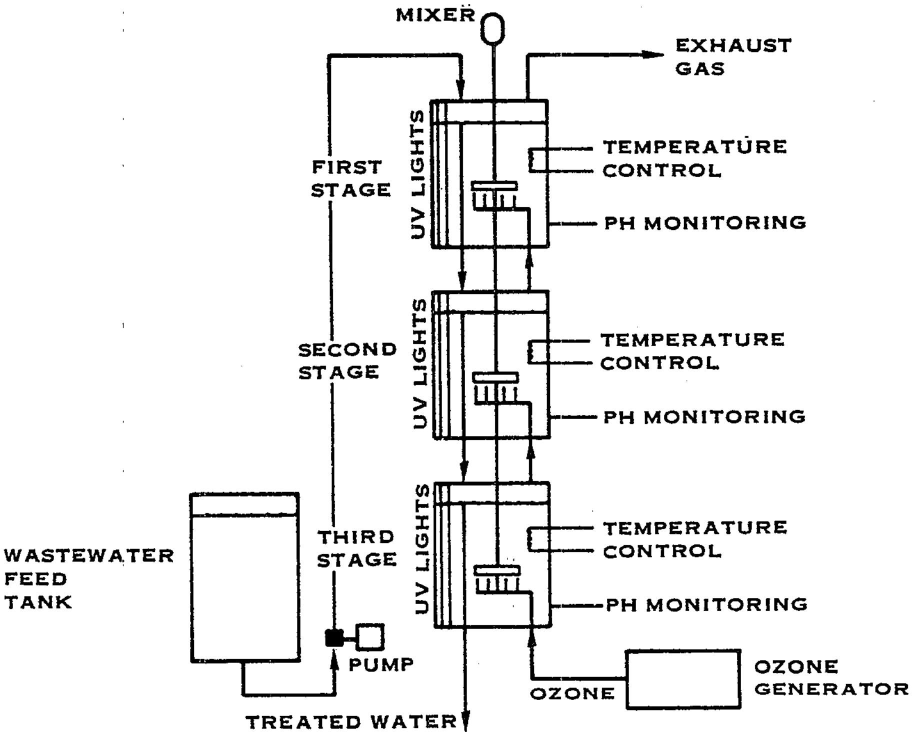

FIGURE 7-27

UV/OZONATION

## Performance

For mixed metal cyanide wastes, consistent reduction in total cyanide concentration to less than 0.1 mg/l is claimed. Metals are converted to oxides, and halogenated organics are destroyed. TOC and COD concentrations are reduced to less than 1 mg/l.

## Demonstration Status

A full scale unit to treat metal complexed cyanides has been installed in Oklahoma, while a large American chemical company in France has installed an on-line unit for the treatment of cyanides and organics and a similar design is scheduled for installation by the same company in the United States. There are also two other units known to be in service, one for treating mixed cyanides and the other for treatment of copper cyanide.

## Oxidation By Hydrogen Peroxide

The hydrogen peroxide oxidation treatment process treats both the cyanide and metals in cyanide wastewaters containing zinc or cadmium. In this process, cyanide rinse waters are heated to 49-54°C (120-130°) to break the cyanide complex, and the pH is adjusted to 10.5-11.8. Formalin (37% formaldehyde) is added, while the tank is vigorously agitated. After 2-5 minutes, a proprietary formulation (41% hydrogen peroxide with a catalyst and additives) is likewise added. After an hour of mixing, the reaction is complete. The cyanide is converted to cyanate and the metals are precipitated as oxides or hydroxides. The metals are then removed from solution by either settling or filtration.

The chemical reactions which take place are as follows:

$$CN + HCHO + H_2O = HOCH_2CN + OH^-$$

The hydrogen peroxide converts cyanide to cyanate in a single step:

$$CN + H_2O_2 = NCO + H_2O$$

The formaldehyde also acts as a reducer, combining with the cyanide ions:

$$Zn(CN)_4^{-2} + 4\ HCHO + 4H_2O = 4\ HOCH_2CN + 4\ OH^- + Zn^{+2}$$

The metals subsequently react with the hydroxyl ions formed and precipitate as hydroxides or oxides:

$$Zn^{+2} + 2\ OH^- = ZnO + H_2O$$

The main pieces of equipment required for this process are two holding tanks. These tanks must be equipped with heaters and air spargers or mechanical stirrers. These tanks may be used in a batch or continuous fashion with one tank being used for treatment while the other is being filled. A settling tank or a filter is needed to concentrate the precipitate.

### Application

The hydrogen peroxide oxidation process is applicable to cyanide bearing wastewaters, especially those from cyanide zinc and cyanide cadmium electroplating. The process has been used on photographic wastes to recover silver and oxidize toxic compounds such as cyanides, phenols and "hypo" (sodium thiosulfate pentahydrate). Additions of hydrogen peroxide are made regularly at a large wastewater treatment plant to control odors and minimize pipe corrosion by oxidizing hydrogen sulfide.

Chemical costs are similar to those for alkaline chlorination and lower than those for treatment with hypochlorite, and all free cyanide reacts and is completely oxidized to the less toxic cyanate state. In addition, metals precipitate and settle quickly, and they are recoverable in many instances. However, the process requires energy expenditures to heat the wastewater prior to treatment. Furthermore, the addition of formaldehyde results in treated wastewater having relatively high BOD values. Although cyanates are much less toxic than cyanide, there is not complete acceptance of the harmlessness of cyanates.

### Performance

In terms of waste reduction performance, this process is capable of reducing the cyanide level to less than 0.1 mg/l and the zinc or cadmium to less than 1.0 mg/l.

### Demonstration Status

This treatment process was introduced in 1971 and is being used in several facilities.

Peroxide oxidation is used in three plants in the present data base: 08061, 21058, and 30009.

## Electrochemical Cyanide Oxidation

Electrochemical cyanide oxidation is used to reduce free cyanide and cyanate levels in industrial wastewaters. In this process, wastewater is accumulated in a storage tank and then pumped to a reactor where an applied DC potential oxidizes the cyanide to nitrogen, carbon dioxide and trace amounts of ammonia. The gases generated are vented to the atmosphere. The oxidation reaction is accomplished if concentrations are not greater than 1000 mg/l. If reaction time is critical, the process can be accelerated by augmenting the system with a chemical (hypochlorite) treatment as long as the cyanide concentration level is less than 200 mg/l. The process equipment consists of a reactor, a power supply, a storage tank and a pump.

Another electrochemical oxidation system employs a low voltage anode with a metallic oxide coating. Upon application of an electrical potential several oxidation reactions occur at the anode. These reactions include the oxidation of chloride (from common salt) to chlorine or hypochlorite and the formation of ozone, as well as direct oxidation at the anode. Although untested on cyanide-bearing wastewaters, this system shows good potential in that area.

## Application

The electrochemical cyanide oxidation system has been used commercially only for heat treating applications; however, it should be equally appropriate for other cyanide bearing wastes. Its application for plating and photographic process wastewaters is still in the development stage. The process can also be applied to the electrochemical oxidation of nitrite to nitrate.

Electrochemical cyanide oxidation has the advantage of low operating costs with moderate capital investment, relative to alternative processes. There is no requirement for chemicals, thereby eliminating both their storage and control, and there is no need to dilute or pretreat the wastewater as the process is most efficient at high cyanide concentration levels. However, the process is less efficient than chemical destruction at cyanide concentrations less than 100 mg/l, and it is relatively slow when not accelerated by addition of treatment chemicals. Moreover, it will not work well in the presence of sulfates.

## Performance

Performance has been demonstrated on a commercial scale and shown to result in a reduction in the cyanide concentration level from 3500 mg/l to less than 1.0 mg/l in 160 hours. The process emits no noticeable odor with adequate ventilation.

## Demonstration Status

There is currently a unit in operation which is handling the cyanide bearing wastewater generated by a heat treating operation. The manufacturer claims that there is a potential for future use of the process in both the electroplating and photographic industries. However, despite a variety of experimental programs, industry has not been enthusiastic about the electrolytic approach to cyanide oxidation.

Electrochemical cyanide oxidation is used at plants 04224, 18534, 19002, and 30080.

## Chemical Precipitation

Chemical precipitation is a classic waste treatment process for metals removal as described under the "Treatment of Common Metal Wastes" heading. The precipitation of cyanide can be accomplished by treatment with ferrous sulfate. This precipitates the cyanide as a ferrocyanide, which can be removed in a subsequent sedimentation step. Waste streams with a total cyanide content of 2 mg/l or above have an expected waste reduction of 1.5 to 2 orders of magnitude. These expectations are substantiated by the following results from plant 01057:

CONCENTRATION OF TOTAL CYANIDE (mg/l)

| Raw Waste | Final Effluent |
|---|---|
| 2.57 | 0.024 |
| 2.42 | 0.015 |
| 3.28 | 0.032 |

## Evaporation

Evaporation is another recovery alternative applicable to cyanide process baths such as copper cyanide, zinc cyanide, and cadmium cyanide and was described in detail for common metals removal.

# TREATMENT OF OILY WASTES

## INTRODUCTION

This section presents the Option 1 treatment systems that are applicable to the treatment of oily wastes; describes the treatment techniques for Option 1 and its alternatives; and defines the effluent concentration levels for those options. Oily wastes include process coolants and lubricants, wastes from cleaning operations directly following many other unit operations, wastes from painting processes, and machinery lubricants. Oily wastes generally are of three types: free oils, emulsified or water soluble oils, and greases. Techniques commonly employed in the Metal Finishing Category to remove oil include skimming, coalescing, emulsion breaking, flotation, centrifugation, ultrafiltration, reverse osmosis, and removal by contractor hauling. Oil removal techniques may also afford additional removal of toxic organics, and the applicability and performance of these techniques for toxic organics is discussed under "Treatment of Toxic Organics."

Table 7-60 presents oily waste removal system options for free oils, combined wastewater, and segregated oily waste. The Option 1 oily waste treatment system incorporates the emulsion breaking process followed by surface skimming (gravity separation is adequate if only free oils are present). Ultrafiltration may be employed as an alternative to the Option 1 system. Polishing systems for Option 1 and its alternative are presented in the text. These may be added to further improve effluent quality. Because emulsified oils, or processes that emulsify oils, are used extensively in the Metal Finishing Category, the exclusive occurrence of free oils is nearly nonexistent. Combined wastewater (e.g., -oils in common metals wastewaters) should contain only oils that are introduced from rinsing or cleaning operations, inadvertent spills, or equipment leakage. As a result of this, these wastewaters contain low oil concentrations but have high flow rates. Because treatment system costs are proportional to the quantity of waste oil, segregation of oily waste is economically preferable. Segregated oily waste is that collected from tanks and sumps throughout a manufacturing facility for separate waste treatment or recovery.

TABLE 7-60

## OILY WASTE REMOVAL SYSTEM OPTIONS

| WASTE CHARACTERISTICS / TREATMENT OPTION | FREE OILS | COMBINED WASTEWATER | SEGREGATED OILY WASTE |
|---|---|---|---|
| | Combined or Segregated Waste | Mixture of free oils, grease, and emulsified oils | |
| | | Wastewater from rinsing or cleaning overflow, spills, and leakage | Collection from tanks and sumps |
| | | Low oil concentration, high flow rate | High oil concentration, low flow rate |
| OPTION 1 | Gravity Separator | Emulsion Breaking with Skimming | |
| ALTERNATIVE TO OPTION 1 | Ultrafiltration | | |
| POLISHING TECHNIQUES | Option 1 (or Alternative) Followed by Carbon Adsorption or Reverse Osmosis | | |

Oily waste performance data and limitations are presented herein for both combined wastewater and segregated oily wastes. The combined wastewater concentrations are applicable to the oils present in common metals wastewaters and concentration limitations are stated for both the Option 1 and Option 2 common metals treatment systems. A single option and an alternative are presented for the treatment of segregated oily wastes.

## TREATMENT OF OILY WASTES FOR COMBINED WASTEWATER

The following paragraphs present the oily waste performance data for combined wastewater in the common metals wastewater data base, identify the mean concentrations established for oil and grease, define the concentration limitations, and compare these limitations with the sampled data base and the self-monitoring data base for the Option 1 and Option 2 common metals treatment systems.

### COMBINED WASTEWATER PERFORMANCE FOR OILS - OPTION 1 COMMON METALS SYSTEM

Table 7-61 presents the oil and grease performance data for the Option 1 common metals treatment system data base for properly opreating systems. From these data a mean effluent concentration of 11.8 mg/ℓ was established for oil and grease in combined wastewater for the Option 1 common metals treatment system.

An iterative procedure was used in the calculation of the mean effluent concentration for oil and grease to prevent the calculation of an unrealistically low mean effluent concentration due to low raw waste pollutant loadings. The mean effluent concentration for oil and grease was calculated; when a raw waste concentration was less than the mean effluent concentration, the corresponding effluent value was deleted from the data set. The mean was recalculated using points not removed initially, and the process repeated in an iterative loop. This same iterative procedure was used for the toxic metals.

The variability factors for oil and grease in combined wastewater for the Option 1 common metals treatment system were established from long term self-monitoring data. The specific data set used is tabulated in Table 7-62.

## TABLE 7-61

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR OIL AND GREASE

### OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | 12.200 | 9.800 | 6101-12-1 |
| 2. | 14.200 | 11.200 | 6731-1-3 |
| 3. | 16.111 | 1.000 | 20086-1-2 |
| 4. | 16.200 | 4.000 | 19051-6-0 |
| 5. | 16.644 | 1.000 | 20086-1-3 |
| 6. | 16.900 | 11.700 | 6051-6-0 |
| 7. | 18.000 | 2.0000 | 21003-15-0 |
| 8. | 22.804 | 18.150 | 33024-6-0 |
| 9. | 23.000 | 11.000 | 15010-12-2 |
| 10. | 23.600 | 12.600 | 6101-12-1 |
| 11. | 28.000 | 19.300 | 6083-1-2 |
| 12. | 29.444 | 1.0000 | 20086-1-1 |
| 13. | 34.000 | 6.0000 | 36041-1-1 |
| 14. | 36.312 | 9.6385 | 19063-1-1 |
| 15. | 40.350 | 23.015 | 19063-1-3 |
| 16. | 41.000 | 1.0000 | 36041-1-3 |
| 17. | 43.000 | 24.000 | 15010-12-3 |
| 18. | 46.000 | 5.0000 | 36041-1-2 |
| 19. | 51.600 | 1.600 | 36040-1-1 |
| 20. | 54.000 | 7.0000 | 11477-22-2 |
| 21. | 66.000 | 14.000 | 11477-22-0 |
| 22. | 67.600 | 9.600 | 6074-1-1 |
| 23. | 72.000 | 10.000 | 11477-22-1 |
| 24. | 90.393 | 23.378 | 19063-1-2 |
| 25. | 137.15 | 12.000 | 44062-15-1 |
| 26. | 195.93 | 25.000 | 44062-15-0 |
| 27. | 224.11 | 16.000 | 44062-15-2 |
| 28. | 418.00 | 10.200 | 6074-1-1 |
| 29. | 1291.0 | 23.200 | 6074-1-1 |
| 30. | 2650.0 | 31.200 | 33692-23-1 |
| Mean Concentration = | 193.185 (n=30) | 11.819 (n=30) | |

## TABLE 7-62

## OIL AND GREASE EFFLUENT SELF-MONITORING PERFORMANCE DATA COMBINED WASTEWATER - COMMON METALS OPTION 1

| Plant ID | Number OF Points | Mean Effluent Concentration (mg/ℓ) | Variability Factor Daily | Variability Factor 10-Day |
|---|---|---|---|---|
| 3049 | 49 | 1.80 | 5.71 | 2.58 |
| 6051 | 13 | 1.75 | 6.22 | 3.09 |
| 6107 | 2 | 10.80 | 33.38 | -- |
| 11477 | 66 | 2.57 | 2.73 | 1.82 |
| 12002 | 55 | 1.95 | 5.98 | 2.65 |
| 20080 | 269 | 4.51 | 6.70 | 2.68 |
| 22735 | 45 | 4.73 | 3.01 | 1.56 |
| 30050 | 287 | 1.24 | 7.71 | 2.40 |
| 30079 | 12 | 4.88 | 1.38 | 1.41 |
| 30090 | 45 | 1.46 | 2.53 | 1.97 |
| 30165 | 20 | 3.83 | 1.63 | -- |
| 45741 | 48 | 3.48 | 3.00 | 1.42 |
| OVERALL | 893(Total) | 2.79(Mean) | 4.36(Median) | 2.18(Median) |

In a manner consistent with the development of limitations for other parameters in common metals wastewaters, the median variability factor values are used to establish the limitations presented in Table 7-63.

TABLE 7-63
OIL AND GREASE LIMITATION SUMMARY
COMBINED WASTEWATER - COMMON METALS OPTION 1

| | |
|---|---|
| Mean Effluent Concentration | 11.8 mg/ℓ |
| Daily Variability Factor | 4.36 mg/ℓ |
| 10-Day variability factor | 2.18 mg/ℓ |
| Daily Maximum Concentration | 52 mg/ℓ |
| Monthly Maximum Average Concentration | 26 mg/ℓ |

The percentage of oil and grease effluent concentrations that are less than the daily maximum concentration limitation are 100 percent for the EPA sampled data set used to establish mean effluent concentration, 100 percent for the self-monitoring data set daily values and 100 percent for the self-monitoring data set monthly averages.

### COMBINED WASTEWATER PERFORMANCE FOR OILS - OPTION 2 COMMON METALS SYSTEM

Figure 7-28 presents the oil and grease performance data for the Option 2 common metals treatment system data base. From these data, excluding the outlier at an effluent concentration of 56 mg/ℓ which exceeds the Option 1 daily maximum concentration limitation, the mean effluent oil and grease concentration was established to be 7.1 mg/ℓ.

The variability factors for oil and grease is combined wastewater for the Option 2 common metals treatment system are those used for oil and grease in the Option 1 common metals treatment system. Insufficient data are presently available to separately establish these factors for the Option 2 treatment system. Applying the Option 1 variability factors to the Option 2 oil and grease mean effluent concentration results in the performance presented in Table 7-64.

TABLE 7-64
OIL AND GREASE PERFORMANCE SUMMARY
COMBINED WASTEWATER - COMMON METALS OPTION 2

| | |
|---|---|
| Mean Effluent Concentration | 7.1 mg/ℓ |
| Daily Variability Factor | 4.36 mg/ℓ |
| 10-Day variability factor | 2.18 mg/ℓ |
| Daily Maximum Concentration | 31.0 mg/ℓ |
| Monthly Maximum Average Concentration | 15.5 mg/ℓ |

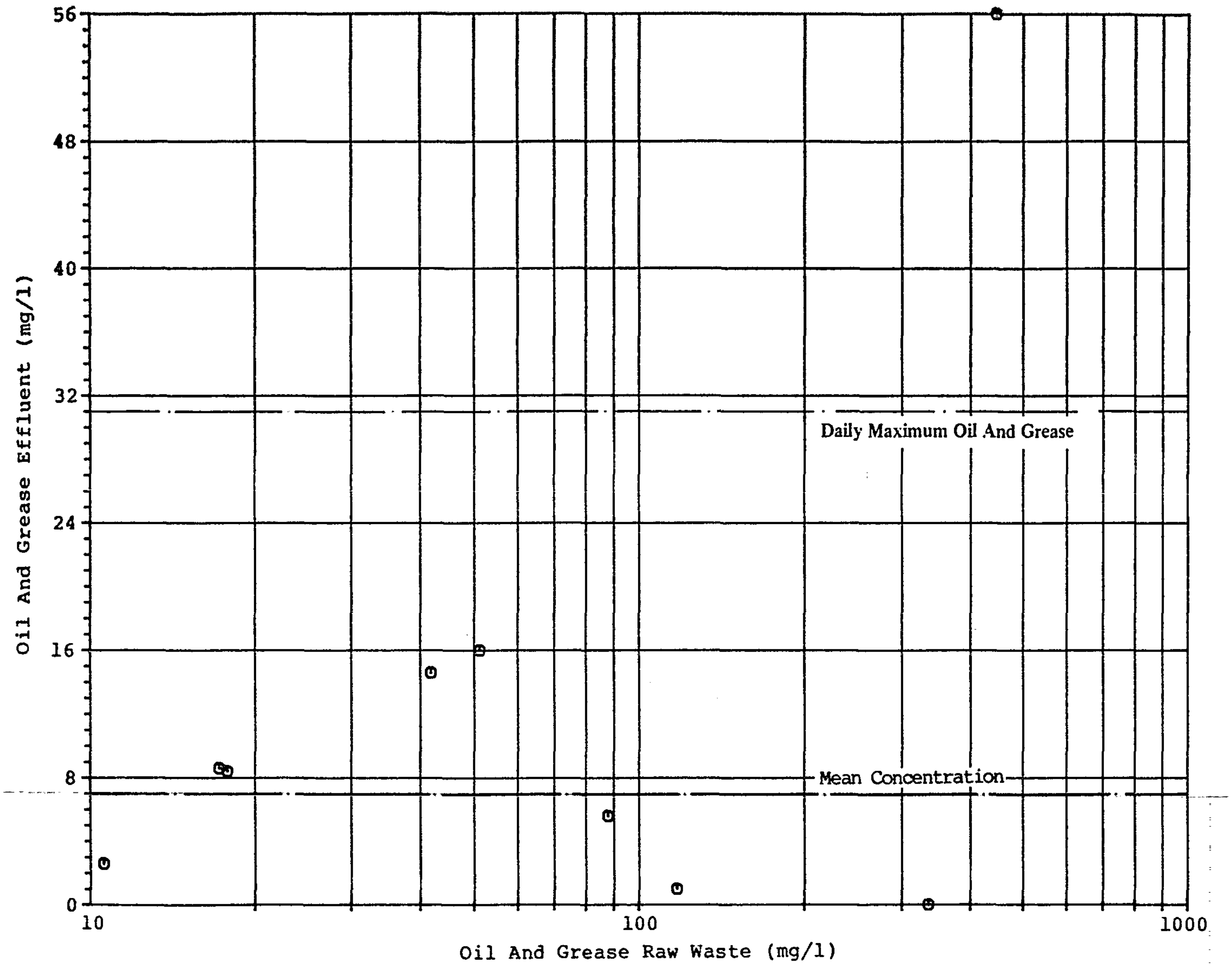

FIGURE 7-28

EFFLUENT OIL AND GREASE CONCENTRATIONS vs RAW WASTE CONCENTRATIONS
OPTION 2 COMMON METALS DATA BASE
(Combined Wastewater)

The percentage of combined wastewater oil and grease effluent concentrations that are less than the Option 2 daily maximum concentration limitation is 96.7 percent for the EPA sampled data base used in calculating the mean effluent concentration.

## TREATMENT OF SEGREGATED OILY WASTES

Treatment of oily wastes can be carried out most efficiently if oils are segregated from other wastes and treated separately. Segregated oily wastes originate in the manufacturing areas, are collected in holding tanks and sumps, and can have oil and grease concentrations as high as 400,000 mg/l. Combined oily wastes are those generated from washing or rinsing of oily parts, spills, and leakages and generally have lower oil and grease concentrations than segregated oily wastes by several orders of magnitude. Furthermore, oily wastes in combined wastewater streams, such as common metals wastewaters, require larger and thus more costly treatment systems for oils removal than do segregated oily wastewaters because the combined wastewaters have significantly greater flow rates. Performance limitations for combined wastewater oils and total priority organics are presented in the preceding subsection.

Treatment of segregated oily wastes consists of separation of the oily wastes from the water. This separation can require several different steps depending on the character of the oily wastes involved. If the oils are all of a free or floating variety, physical means such as decantation or the use of a gravity oil separator should be used to remove the oils. If the oily wastes are emulsified, techniques such as emulsion breaking or dissolved air flotation with the addition of chemicals are necessary to accomplish removal of the oils. Once the oil-water emulsion is broken, the oily waste is physically separated from the water by decantation or skimming. (Ultrafiltration is an alternative to emulsion breaking).

After the oil-water separation has been accomplished the water is sent to the precipitation/sedimentation unit described under the "Treatment of Common Metals Wastes" heading for removal of metals.

## SEGREGATED OILY WASTE TREATMENT SYSTEM - OPTION 1

The Option 1 system for the treatment of segregated oily wastewater consists of emulsion breaking followed by skimming, as is illustrated in Figure 7-29. The emulsion breaking is effected by the addition of chemicals (such as alum or polymers) to accomplish coagulation and flocculation of the oily wastes. These floating oily wastes are then removed via skimming to complete the Option 1 level of treatment.

Treatment alternatives to the Option 1 system that are presently employed in the metal finishing industry include ultrafiltration, dissolved air flotation, coalescing gravity separators, thermal emulsion breaking and the use of centrifugation. These alternative techniques, as well as contractor hauling, are described in the subsection entitled "Additional Oily Waste Treatment Techniques."

The Option 1 treatment system is employed extensively within the metal finishing data base for treatment of segregated oily waste. However, because of the increasing price of oil, metal finishing plants are tending toward the use of treatment techniques such as ultrafiltration, reverse osmosis, or centrifugation for the recovery and direct reuse of oils.

The following paragraphs describe the emulsion breaking and skimming tecniques that are applicable to the removal of oily wastes for Option 1.

### Emulsion Breaking

Emulsion breaking is a process by which emulsified oils are removed from oil/water mixtures. Emulsified oils are commonly used as coolants, lubricants, and antioxidants for many of the unit operations performed in the Metal Finishing Category. Methods of emulsion breaking include a variety of chemical processes, thermal processes, and combinations of the two processes. These techniques are discussed in the following paragraphs.

Chemical emulsion breaking can be accomplished either as a batch process or a continuous process. A typical system (with skimming incorporated) is illustrated in Figure 7-30. The mixture of emulsified oils and water is initially treated by the addition of chemicals to the wastewater. A means of agitation (either mechnical or by increasing the turbulence of the wastewater stream) is provided to ensure that the chemical added and the emulsified oils are adequately mixed to break the oil/water emulsion bond. Finally the oily residue (commonly called scum) that results rises to the surface and is separated from the remaining wastewater by a skimming or decanting process. The skimming process can be accomplished by any of the many types

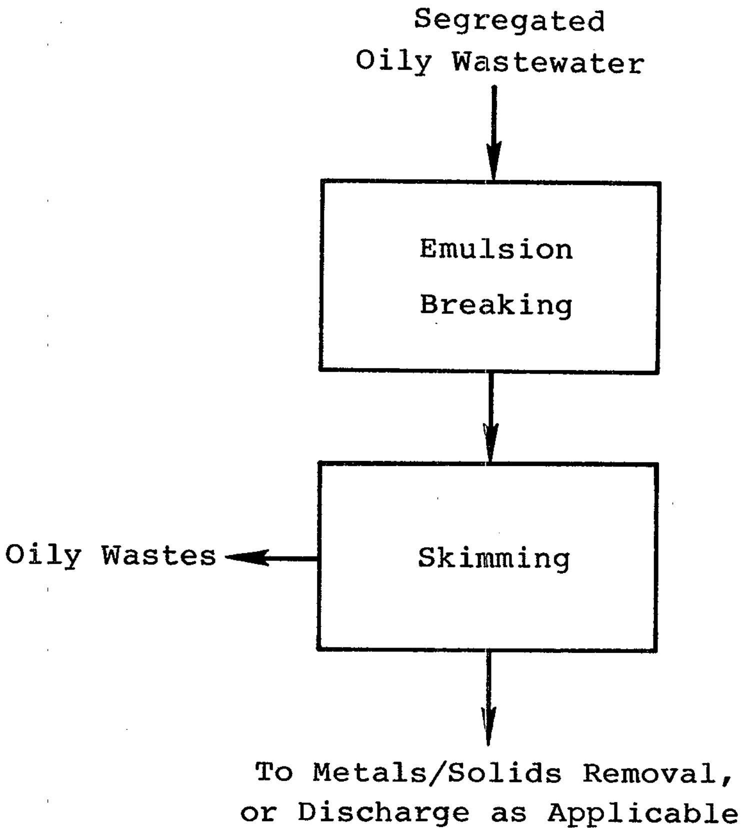

FIGURE 7-29

TREATMENT OF SEGREGATED OILY WASTES
OPTION 1

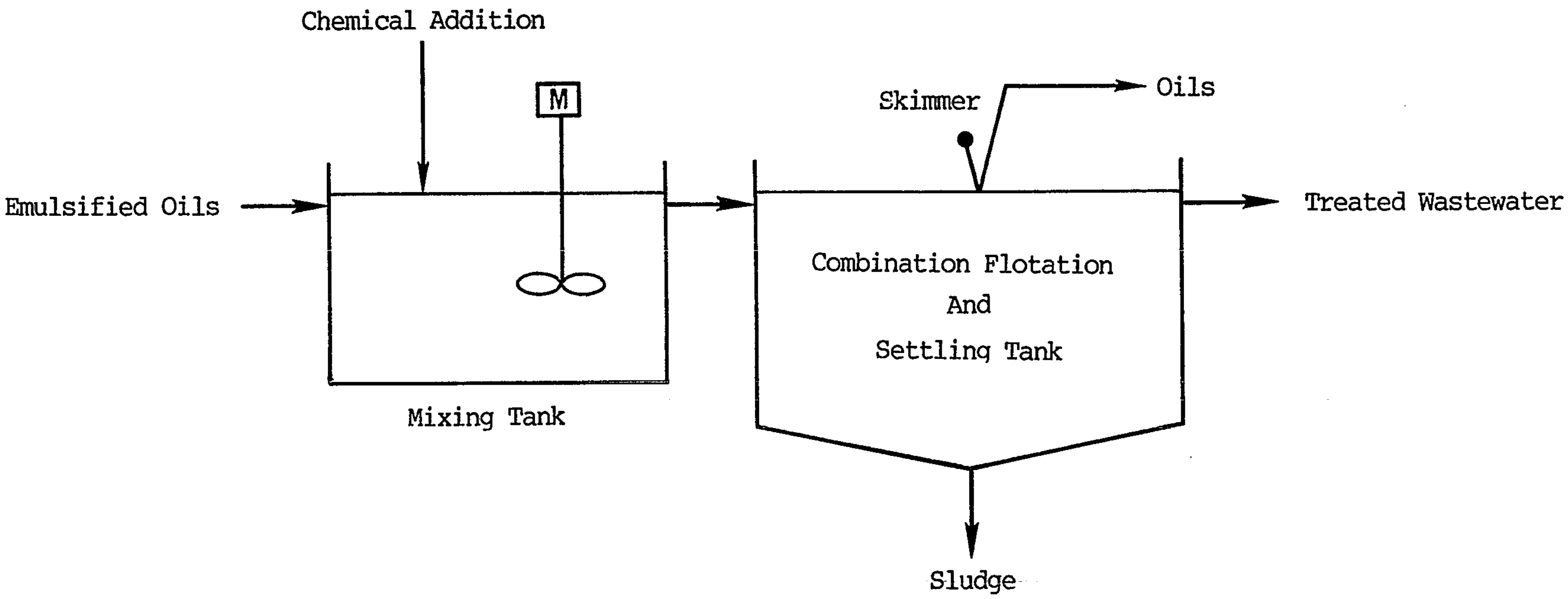

FIGURE 7-30

TYPICAL EMULSION BREAKING/SKIMMING SYSTEM of mechanical surface skimmers that are presently in use. Decanting methods include removal of the oily surface residue via a technique such as controlled tank overflow or by removal of the demulsified wastewater from the bottom of the tank. Decanting can be accomplished with a series of tap-off lines at various levels which allow the separated oils to be drawn off the top or the wastewater to be drawn off the bottom until oil appears in the wastewater line. With any of these arrangements, the oil is usually diverted to storage tanks for further processing or hauling by a licensed contractor.

Chemical emulsion breaking can be accomplished by a large variety of chemicals which include acids, salts, or polymers. These chemicals are sometimes used separately, but often are required in combination to break the various emulsions that are common in the wastewater. Acids are used to lower the pH to 3 or 4 and can cleave the ion bond between the oil and water, but can be very expensive unless acid rich wastewaters, such as pickling wastes, can be used. Acids are more commonly employed in oil recovery systems than in oily waste removal systems. Iron or aluminum salts such as ferrous sulfate, ferric chloride, or aluminum sulfate are more commonly used because they are less expensive. These salts combine with the wastewater to form acids which in turn lower the pH and break the oil/water bond (and have the additional benefit that these salts aid in agglomeration of the oil droplets), but the use of these salts produces more sludge because of the addition of iron or aluminum. Polymers, such as polyamines or polyacrylates and their copolymers, have been demonstrated to be effective emulsion breakers and generate less sludge than do metal salts. The Option 1 treatment system costing, presented in Section VIII, is based upon the use of aluminum sulfate plus a quantity of polymer as the emulsion breaking chemicals.

After chemical addition, the mixture is agitated to ensure complete contact of the emulsified oils with the demulsifying agent. With the addition of the proper amount of chemical and thorough agitation, emulsions of 5% to 10% oil can be reduced to approximately 0.01% remaining emulsified oil. The third step in the emulsion breaking process is to allow sufficient time for the oil/water mixture to separate. Differences in specific gravity will permit the oil to rise to the surface in approximately two hours. Heat can be added to decrease the separation time. After separation, the normal procedure involves skimming or decanting the oil from the tank.

## Application

Emulsion breaking technology can be applied to the treatment of emulsified oil/water mixtures in the Metal Finishing Category wherever it is necessary to separate oils, fats, soaps, etc. from wastewaters. Certain machining coolant emulsion cannot be chemically or thermally broken and must be treated by ultrafiltration.

The main advantage of the chemical emulsion breaking process is the high percentage of oil removal possible with this system. For proper and economical application of this process, the oily wastes (oil/water mixture) should be segregated from other wastewaters either by storage in a holding tank prior to treatment or be fed directly into the oily waste removal system from major collection points. Further, if a significant quantity of free oils are present, it is economically advantageous to precede the emulsion breaking with a gravity separator. Chemical and energy costs can be high, especially if heat is used to accelerate the process.

Chemical emulsion breaking can be highly reliable if adequate analysis is performed prior to the selection of chemicals and proper operator training is provided to ensure that the established procedures are followed.

For chemical emulsion breaking, routine maintenance is required on pumps, motors, and valves as well as periodic cleaning of the treatment tank to remove any sediment which may accumulate in the tank. The use of acid or acidic conditions will require a lined tank, and the lining should be checked periodically. Emulsion breaking generates sludge which requires proper disposal.

## Performance

The performance attainable by a chemical emulsion breaking process is dependent on addition of the proper amount of de-emulsifying agent, good mixing agitation and sufficient retention time for complete emulsion breaking. Since there are several types of emulsified oils, a detailed study should be conducted to determine the most effective treatment techniques and chemicals for particular application.

## Demonstration Status

Emulsion breaking is a common technique used in industry, is a proven method of effectively treating emulsified wastes, and is in use at 29 plants in the present data base. These plants are identified in Table 7-65.

TABLE 7-65
METAL FINISHING PLANTS EMPLOYING EMULSION BREAKING

| | | | | | |
|---|---|---|---|---|---|
| 01058 | 11477 | 12095 | 20173 | 30153 | 36074 |
| 01063 | 12075 | 13041 | 20247 | 33050 | 38040 |
| 03041 | 12076 | 20103 | 20249 | 33120 | 40836 |
| 06679 | 12080 | 20158 | 20254 | 33127 | 46713 |
| 11129 | 12091 | 20159 | 30135 | 33179 | |

## Skimming

Skimming is used to remove floating wastes and normally takes place in a tank designed to allow the debris (with a specific gravity less then water) to rise and remain on the surface. Skimming devices are therefore suited to the removal of oily wastes from raw waste streams after demulsification. Common skimming mechanisms include the rotating drum type, which picks up oil from the surface of the water as it rotates. A knife edge scrapes oil from the drum and collects it in a trough for disposal or reuse. The water portion is then allowed to flow under the rotating drum. Occasionally, an underflow baffle is installed after the drum; this has the advantage of retaining any floating oil which escapes the drum skimmer. The belt type skimmer is pulled vertically through the water, collecting oil from the surface which is again scraped off and collected in a tank. System design and operational controls are important in drum and belt type skimmers in order to ensure uniform flow through the system and avoid oil bypassing the skimmer mechanism.

Gravity separators, such as the API type, utilize overflow and underflow baffles to skim a floating oil layer from the surface of the wastewater. An overflow-underflow baffle allows a small amount of wastewater (the oil portion) to flow over into a trough for disposition or reuse while the majority of the water flows underneath the baffle. This is followed by an overflow baffle, which is set at a height relative to the first baffle such that only the oil bearing portion will flow over the first baffle during normal plant operation. An inlet diffusion device, such as a vertical slit baffle, aids in creating a uniform flow through the system and increasing oil removal efficiency.

### Application

Oil skimming is used in the Metal Finishing Category to remove oily wastes from many different process wastewater streams. Skimming is applicable to any waste stream containing pollutants which float to the surface. Skimming is used in conjunction with emulsion breaking, dissolved air flotation, clarifiers, and other sedimentation devices.

API or other gravity-type separators are more suitable for use where the amount of surface oil flowing through the system is consistently significant as with free oils. Drum, belt, or rotary type skimmers are applicable to waste streams which carry smaller amounts of floating oily waste and where surges of floating oil are not a problem. The use of a gravity separator system preceding emulsion breaking is a very effective method of removing free oil constituents from oily waste streams.

Skimming as a pretreatment is effective in removing naturally floating waste materials, such as free oils, and improves the performance of subsequent downstream treatments. Many pollutants, particularly dispersed or emulsified oil, will not float "naturally" but require additional treatments. Therefore, skimming alone will not remove all the pollutants capable of being removed by more sophisticated technologies.

Because of its simplicity, skimming is a very reliable technique, however, a mechanical skimming mecahnism requires periodic lubrication, adjustment, and replacement of worn parts.

The collected layer of debris (scum) must be disposed of in an approved manner. Because relatively large quantities of water are present in the collected wastes, direct combustion or incineration is not always possible.

### Performance

The performance attainable by skimming is dependent on proper mechanical operation of the skimmer and on the separation rate of the oil/water mixture which is affected by such factors as the size and specific gravity of the oil globules. Examples of performance of skimmer systems for oil and grease are presented in Table 7-66.

TABLE 7-66
SKIMMING PERFORMANCE DATA FOR OIL AND GREASE (mg/ℓ)

| Plant ID | Oil and Grease Influent (mg/ℓ) | Oil and Grease Influent (mg/ℓ) | Type of Skimmer |
|---|---|---|---|
| 6058-14-0 | 395,538 | 13.3 | API |
| 6058-15-5 | 53,800 | 16 | API |
| 6058-14-0 | 19.4 | 8.3 | Belt |
| 11477 | 61 | 14 | Belt |

### Demonstration Status

Skimming is a common operation utilized extensively in industrial waste treatment systems and is used by 94 plants in the metal finishing data base. These are identified in Table 7-67.

TABLE 7-67
METAL FINISHING PLANTS EMPLOYING SKIMMING

01063
04233
04892
06041
06051
06058
06062
06084
06086
06116
06679
07001
09047
09181
11113
12080
12091
13324
14001
14062
15010
15033
16032
17030
18091
18538
19106
20001
20064
20075
20471
20483
20708
22031
23075
25031
25339
28075
28115
28116
28125
30050
30079
30135
30150
33178
33179
33292
35001
36074
36102
36131
36155
36623
38040
38050
38217
40070
41084
41115

## TABLE 7-67 (Continued)
## METAL FINISHING PLANTS EMPLOYING SKIMMING

11129
11137
11152
11477
12007
12033
12042
12075
12076
20106
20157
20158
21059
20165
20173
20177
20249
20254
30151
30153
30516
31040
31067
33024
33050
33120
33127
44062
46025
46032
46713
47025
47048
47049
6019
20103

### Segregated Oily Waste Treatment System Performance for Oils - Option 1

Figure 7-31 presents the Option 1 system performance data base for segregated oily waste treatment systems that were sampled. From these data a mean effluent concentration of 23.8 mg/l was established for oil and grease in the Option 1 segregated oily waste treatment system. Long term self-monitoring data means are presented in Table 7-68.

Oil and grease performance for segregated oily wastewater was calculated for Option 1 using the mean effluent concentration from EPA sampled plants and the Option 1 combined oily waste variability factors. Performance is summarized below:

### OIL AND GREASE PERFORMANCE SUMMARY
### SEGREGATED OILY WASTE - OPTION 1

| | |
|---|---|
| Mean Effluent Concentration | 23.8 mg/ℓ |
| Daily Variability Factor | 4.36 mg/ℓ |
| 10-Day Variability Factor | 2.18 mg/ℓ |
| Daily Maximum Concentration | 104 mg/ℓ |
| Monthly Maximum Average Concentration | 52 mg/ℓ |

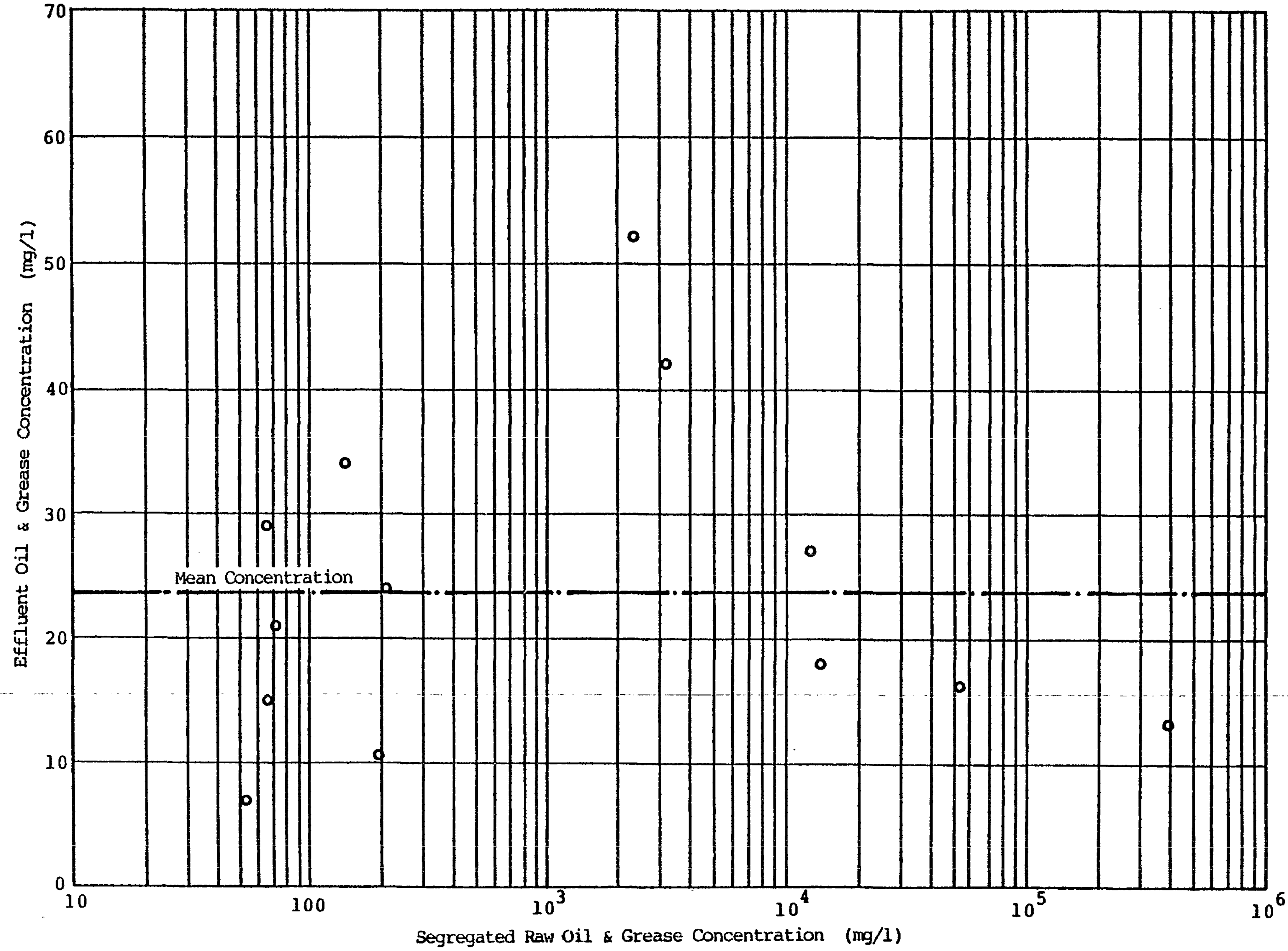

FIGURE 7-31

SEGREGATED OIL & GREASE EFFLUENT PERFORMANCE

OPTION 1

## TABLE 7-68
## EFFLUENT OIL AND GREASE SELF-MONITORING PERFORMANCE DATA
## SEGREGATED OILY WASTEWATER - OPTION 1

| Plant ID | Number of Points | Mean Effluent Concentration (mg/P) |
|---|---|---|
| 06116 | 100 | 287.4 |
| 12076 | 25 | 23.4 |
| 13042 | 142 | 52.8 |
| 20158 | 35 | 8.3 |
| 20254 | 10 | 104.8 |
| 20698 | 186 | 9.2 |
| 33692 | 55 | 26.2 |
| OVERALL | 533 (Total) | 74.70 (Mean) |

## SEGREGATED OILY WASTES TREATMENT SYSTEM - ALTERNATIVE TO OPTION 1

The alternative treatment system for segregated oily wastes is illustrated in Figure 7-32. The system consists of an ultrafiltration unit. The ultrafilter's purpose is to reclaim oils from wastewater which is to be ultimately discharged. The ultrafiltration unit removes quantities of oil and toxic organics as well as removing metals and other solids.

### Ultrafiltration

Ultrafiltration (UF) is a process using semipermeable polymeric membranes to separate emulsified or colloidal materials dissolved or suspended in a liquid phase by pressurizing the liquid so that it permeates the membrane. The membrane of an ultrafilter forms a molecular screen which separates molecular particles based on their differences in size, shape, and chemical structure. The membrane permits passage of solvents and lower molecular weight solutes while barring dissolved or dispersed molecules above a predetermined size. At present, an ultrafilter is capable of removing materials with molecular weights in the range of 1,000 to 100,000.

In the ultrafiltration process, the feed solution is pumped through a tubular membrane unit. Water and some low molecular weight materials pass through the membrane under the applied pressure of .767 kg/cm$^2$ (10 to 100 psig). Emulsified oil droplets and suspended particles are retained, concentrated, and removed continuously. In contrast to ordinary filtration, retained materials are washed off the membrane filter rather than held by the filter. Figure 7-33 illustrates the ultrafiltration process.

The pore structure of the membrane acts as a filter, passing small particles, such as salts, while blocking larger emulsified and suspended matter. The pores of ultrafiltration membranes are much smaller than the blocked particles. Therefore, these particles cannot clog the membrane structure. Clogging of the membrane by particles near the minimum removal size can be minimized by proper selection of the membrane to suit the wastewater to be treated.

Once a membrane is chosen that provides maximum attainable removal of the desired particles, the next most important design criterion is the membrane capacity. Here the term flux is used. Flux is the volume of water passed through the membrane area per unit time. The standard units are cu m/day/sq m (gpd/sq ft). The typical flux is 4.2 to 844 cu m/day/sq m (5 to 1000 gph/sq ft). Both membrane equipment and operating costs increase with the membrane area required. It is, therefore, desirable to maximize flux.

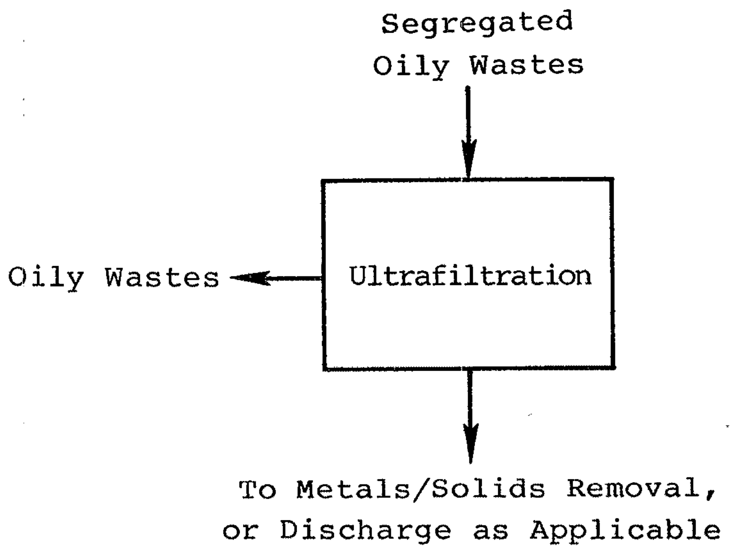

FIGURE 7-32

TREATMENT OF SEGREGATED OILY WASTES
ALTERNATIVE TO OPTION 1

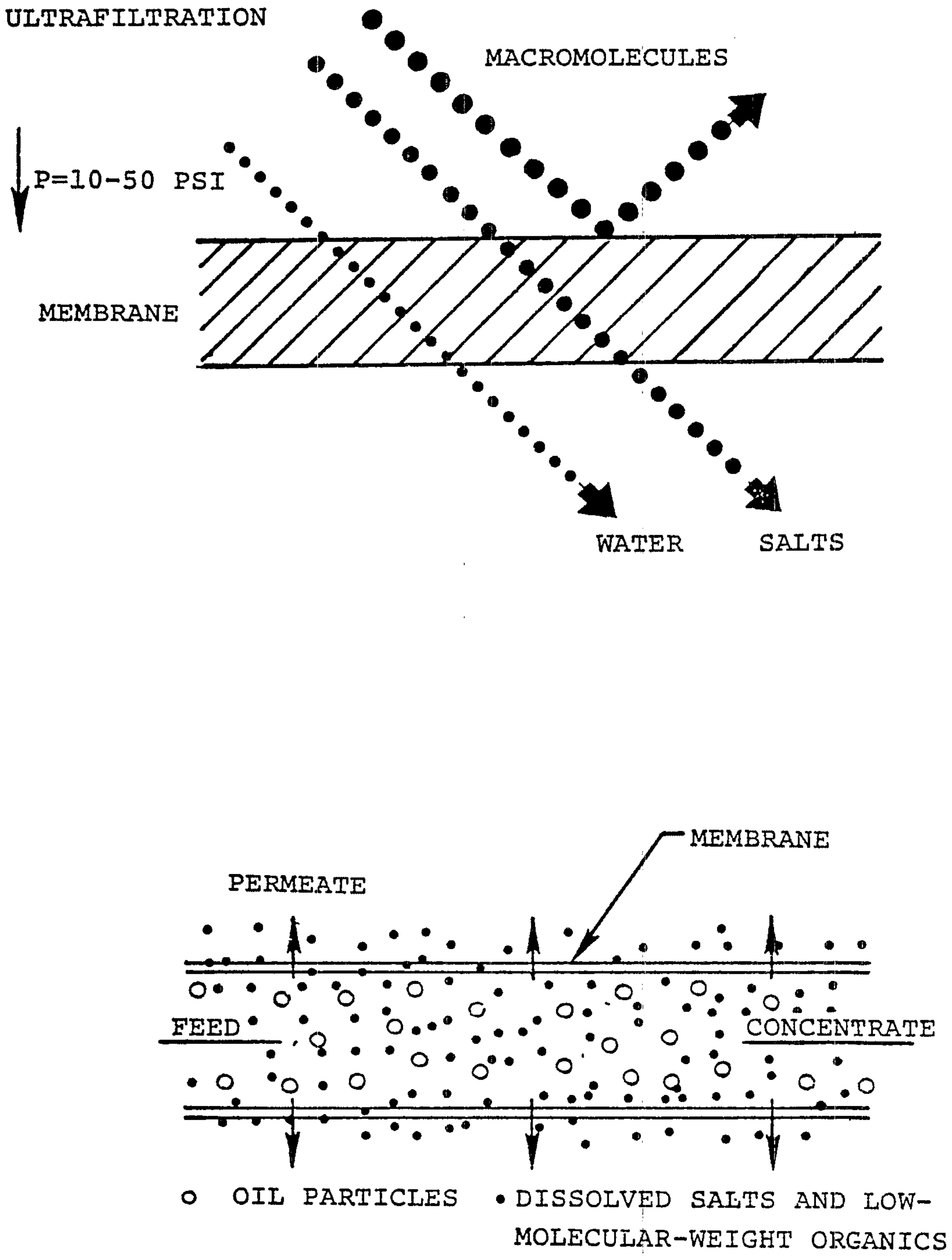

FIGURE 7-33

SIMPLIFIED ULTRAFILTRATION FLOW SCHEMATIC

Membrane flux is normally dependent on operating pressure, temperature, fluid velocity, solids concentration (both total dissolved solids and total suspended solids), membrane permeability, membrane thickness, and fluid viscosity. Membrane flux is also affected by the surface tension of the solution being processed. With a fixed geometry, membrane flux will increase as the fluid velocity is increased in the system. This increase in fluid velocity will require greater capacity and more horsepower. Less membrane area is, therefore, required per unit of effluent to be treated with higher fluid velocities; membrane replacement and initial capital costs decrease. Opposing these cost decreases is the increase in power and its resultant cost, and the fact that these operating conditions may decrease membrane life, resulting in higher maintenance costs.

### Application

Ultrafiltration is employed in metal finishing plants for the separation of oils, toxic organics, and residual solids. The major applications of ultrafiltration in the metal finishing industries have been to electropainting wastes and oily wastewaters. Successful commercial use has been proven for the removal of emulsified oils from wastewater and for recovery of rinse water and detergent solutions in phosphate washers. Recovery operations are common because of the increasing value of oils, but ultrafiltration is used for end-of-pipe treatment in industrial plants.

Ultrafiltration is a proven technique for the removal of oily or paint contaminated wastes from the process waste streams. This permits reuse of both the permeate and concentrate. With segregated oily wastes, the concentrate is essentially the recovered oils and application of ultrafiltration for this purpose is increasing. Ultrafiltration of the waste from electropainting (electrocoating) provides an excellent example of this process. Car manufacturers and many other U.S. companies use electropainting for priming purposes. In this application, the ultrafiltration unit splits the electropainting rinse water circulating through the unit into a permeate stream and paint concentrate stream. The permeate is reused for rinsing, and the concentrate is returned to the electropainting bath.

Bleeding a small amount of the ultrafiltrate, which contains low suspended solids and generally two or three percent of organic solids, to the waste system enables ionic contaminants to be removed from the paint itself. Situations where tanks of 150,000 to 190,000 liters (40,000 to 50,000 gallons) of paint were periodically dumped because of contamination have now been eliminated by using ultrafiltration, thus reducing effluent problems arising from this dumping process.

The permeate or effluent from the ultrafiltration unit is normally of a quality that can be reused in industrial applications or discharged directly.

Ultrafiltration is sometimes an attractive alternative to chemical treatment because of lower capital equipment, installation, and operating costs with a very high oil removal efficiency. Little, if any, pretreatment is required and because of its compact equipment, it utilizes only a small amount of floor space.

A limitation of ultrafiltration for treatment of process effluents is its narrow temperature range (18°C to 70°C) for satisfactory operation. Membrane life is decreased with higher temperatures, but flux increases at elevated temperatures. Therefore, surface area requirements are a function of temperature and become a tradeoff between initial costs and replacement costs for the membrane. In addition, ultrafiltration is limited in its ability to handle strong oxidizing agents, some solvents, and other organic compounds which can cause dissolution of the membrane.

The reliability of an ultrafiltration system is dependent on the application of proper filtration to incoming waste streams to prevent membrane damage. The tubular membrane configuration does not require prefiltration. A limited amount of regular maintenance is required for the pumping system. In addition, membranes must be periodically changed.

Ultrafiltration is used primarily for recovery of solids and liquids. It therefore eliminates solid waste problems when the solids (e.g., paint solids) can be recycled to the process. Otherwise, the stream containing solids must be treated by additional end-of-pipe equipment.

### Demonstration Status

The ultrafiltration process is well developed and is commercially available for the treatment of wastewater or the recovery of certain liquid and solid constituents. Ultrafiltration is used at 20 plants in the present Metal Finishing Category data base and these are identified in Table 7-69.

TABLE 7-69
METAL FINISHING PLANTS EMPLOYING ULTRAFILTRATION

| | |
|---|---|
| 06062 | 25010 |
| 06071 | 30100 |
| 06102 | 30516 |
| 12065 | 31022 |
| 12074 | 31032 |
| 13041 | 33092 |
| 13324 | 33617 |
| 15193 | 36074 |
| 19462 | 38217 |
| 23076 | 44048 |

## Segregated Oily Waste Treatment System Performance - Alternative to Option 1

The raw waste and effluent concentrations of oil and grease for streams entering into and discharged from ultrafiltration systems in the data base are displayed in Table 7-70. The performance (removal efficiency) of these ultrafiltration systems is tabulated for oil removal. Removal performance was calculated by computing the percentage of oil removal at each plant using ultrafiltration and then finding the mean of the individual performances. The removal performance was calculated by the following formula:

$$\text{Removal Efficiency} = \frac{(\text{raw waste} - \text{effluent})100}{\text{raw waste}}$$

TABLE 7-70

ULTRAFILTRATION PERFORMANCE DATA FOR OIL & GREASE REMOVAL

| Plant ID | Oil & Grease Concentration (mg/ℓ) In | Out | Removal Efficiency(%) |
|---|---|---|---|
| 13041-22-0 | 95.0 | 22.0 | 76.8 |
| 13041-22-1 | 1,540. | 52.0 | 96.6 |
| 13041-22-2 | 38,180. | 267. | 99.3 |
| 13324-21-0 | 31,000. | 21.4 | 99.9 |
| 15193-21-0 | 1,380. | 39.0 | 97.2 |
| | | Mean Removal Efficiency | 94.0% |

## SEGREGATED OILY WASTE TREATMENT SYSTEM - POLISHING TECHNIQUES

The Option 1 treatment system for oil and grease removal from segregated oily wastes with the addition of polishing techniques is illustrated in Figure 7-34. As shown, the system is comprised of the components that make up the Option 1 oily waste treatment system (or its alternative) with the addition of a final polishing component. A reverse osmosis unit has been identified as a possible polishing technique because it will remove additional oils not removed by the Option 1 system. In the case of reverse osmosis heavy loadings of oil will render the unit ineffective because oil can plug the membrane of a reverse osmosis system. As with the Option 1 system, the effluent from the polishing waste treatment components is directed to the solids removal components of the metal waste treatment system, to reuse or discharge as applicable.

The following paragraphs describe a reverse osmosis technique applicable for the treatment of segregated oily wastes for polishing.

### Reverse Osmosis

Reverse osmosis, which is explained in detail in Section XIII, "Innovative Treatment Technologies", is the process of applying a pressure to a concentrated solution and forcing a permeate through a semipermeable membrane into a dilute solution. This principle has found use in treating oily wastes. In terms of oily wastewater, reverse osmosis is used primarily as a polishing mechanism to remove oils and metals that are still remaining after treatment such as emulsion breaking or ultrafiltration. Examples of reverse osmosis performance are shown in Table 7-71.

TABLE 7-71
REVERSE OSMOSIS PERFORMANCE (mg/l)

|  | 30166 |  | 38040 Day 1 |  | 38040 Day 2 |  |
|---|---|---|---|---|---|---|
| Parameter | Influent | Effluent | Influent | Effluent | Influent | Effluent |
| Oil&Grease | 117. | 8.5 | 10.6 | 4.1 | 129. | 41. |
| TOC | 371. | 78. | 139. | 94. | 116. | 108. |
| BOD | 183. | 60. | 60. | 58. | 27. | 53. |
| TSS | 9.6 | 1.2 | 37. | 14. | 13. | 1.0 |
| Iron | - | - | 1.91 | .182 | 1.94 | .22 |

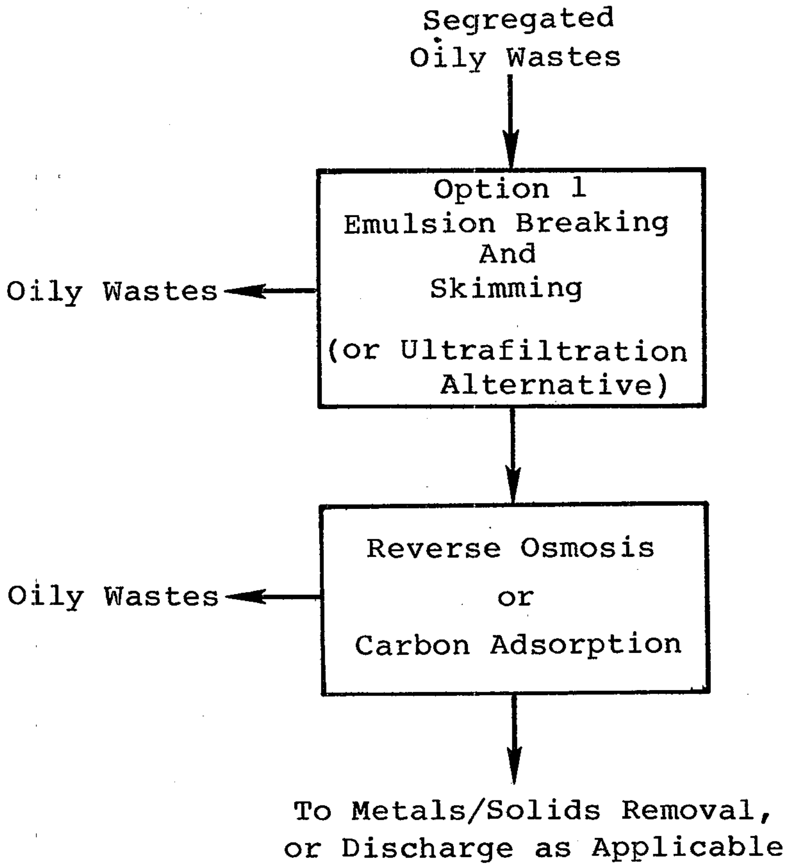

FIGURE 7-34

TREATMENT OF SEGREGATED OILY WASTES
POLISHING TECHNIQUES

## ADDITIONAL OILY WASTE TREATMENT TECHNOLOGIES

In addition to the treatment methods presented there are several other alternative technologies that are applicable for the treatment of oily wastewater. The following paragraphs describe these technologies: coalescing, flotation, centrifugation, integrated adsorption, and thermal emulsion breaking.

### Coalescing

The basic principle of coalescing involves the preferential wetting of a coalascing medium by oil droplets which accumulate on the medium, and then rise to the surface of the solution. The most important requirements for coalescing media are wettability for oil and large surface area.

Coalescing stages may be integrated with a wide variety of gravity oil separation devices, and some systems may incorporate several coalescing stages. In general, the provision of preliminary oil skimming treatment is desirable to avoid overloading the coalescer. One commercially marketed system for oily waste treatment (See Figure 7-35) combines coalescing with gravity separation. In this unit, the oily waste enters the separator where the large droplets immediately move to the top surface of the separator because of the specific gravity differential. The smaller droplets enter the corrugated plate area where laminar flow produces coalescing of the oil droplets. The oil droplets deposit on the surface of the plates and stream upward through weep holes in the plates to the surface, where adjustable skimmers remove the oil. Heavy solids are deposited in the entrance chamber before the oily wastewater enters the plate area.

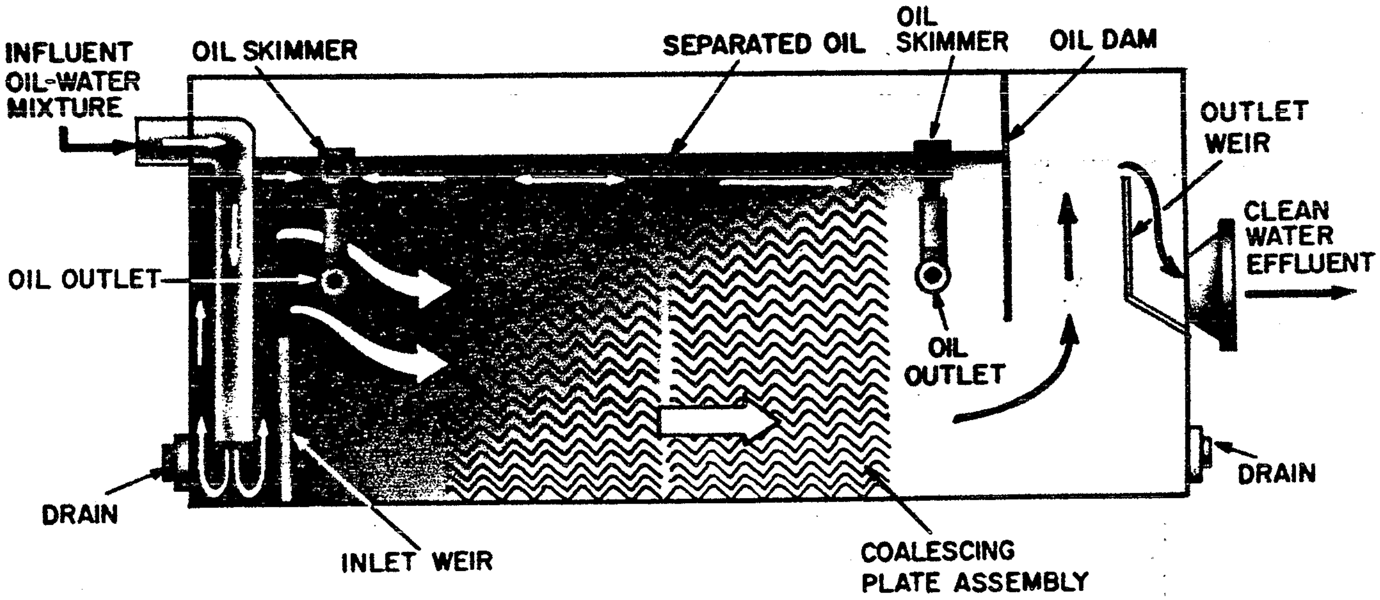

FIGURE 7-35

COALESCING GRAVITY SEPARATOR

## Application

Coalescing is used in the Metal Finishing Category for treatment of oily wastes. It allows removal of oil droplets too finely dispersed for conventional gravity separation/skimming technology. It can also significantly reduce the residence times (and therefore separator volumes) required to achieve separation of oil from some wastes. Because of their simplicity, coalescing oil separators provide generally high reliability and low capital and operating costs. Coalescing is not generally effective in removing soluble or chemically stabilized emulsified oils. To avoid plugging, coalescers must be protected by pretreatment from very high concentrations of free oil and grease and suspended solids. Frequent replacement of prefilters may be necessary when raw waste oil concentrations are high.

Coalescing is inherently highly reliable because there are no moving parts, and the coalescing substrate is inert in the process and therefore not subject to frequent regeneration or replacement requirements. Large loads or inadequate prior treatment, however, may result in plugging or bypassing of coalescing. Maintenance requirements are generally limited to replacement of the coalescing medium on an intrequent basis.

No appreciable solid waste is generated by this process, but when coalescing occurs in a gravity separator, the normal solids accumulation is experienced.

## Performance

The analysis results of samples taken before and after a coalescing gravity separator at Plant ID 38217 are shown below (Concentrations are in mg/l).

Plant ID 38217 (mg/l)

| | Day 1 | | Day 2 | |
|---|---|---|---|---|
| Parameter | Raw | Effluent | Raw | Effluent |
| Oil & Grease | 8320. | 490. | 4240. | 619. |
| TOC | 923. | 1050. | - | 535. |
| BOD | 2830. | 2950. | 1980. | 1530. |
| TSS | 637. | 575. | 1610. | 620. |

## Demonstration Status

Coalescing has been fully demonstrated in the Metal Finishing Category and in other industries that generate oily wastewater. Coalescers are used at 3 facilities in the present data base: Plant ID's 14001, 20173, and 38217.

## Flotation

Flotation, as was explained in the "Treatment of Common Metals Wastes" section, is the process of causing particles such as oil or metal hydroxides to float to the surface of a tank where they can be concentrated and removed. This is brought about by releasing gas bubbles which attach themselves to the particles, increasing their buoyancy, causing them to rise to the surface and float. Flotation units are commonly used in industrial operations to remove free and emulsified oils and grease. For these applications in the Metal Finishing Category, the flotation technique commonly referred to as dissolved air flotation (DAF) is employed. Dissolved air flotation utilizes the emulsion breaking techniques that were previously discussed and in addition uses the bubbles of dissolved air to assist in the agglomeration of the oily droplets and to provide increased buoyancy for raising the oily droplets to the surface. A typical dissolved air flotation system is shown in Figure 7-36.

### Application

The use of dissolved air for oily waste flotation subsequent to emulsion breaking can provide better performance in shorter retention times (and therefore smaller flotation tanks) than with emulsion breaking without flotation. A small reduction in the quantity of chemical for emulsion breaking is also possible. Dissolved air flotation units have been used successfully, in conjunction with further subsequent processes, to reclaim oils for direct reuse and/or use as power plant fuels in the Metal Finishing Category.

### Performance

The performance of a flotation system depends upon having sufficient air bubbles present to float essentially all of the suspended solids. An insufficient quantity of air will result in only partial flotation of the solids, and excessive air will yield no improvement. The performance of a flotation unit in terms of effluent quality and solids concentration in the float can be related to an air/ solids ratio. The shape of the curve obtained will vary with the nature of the solids in the feed.

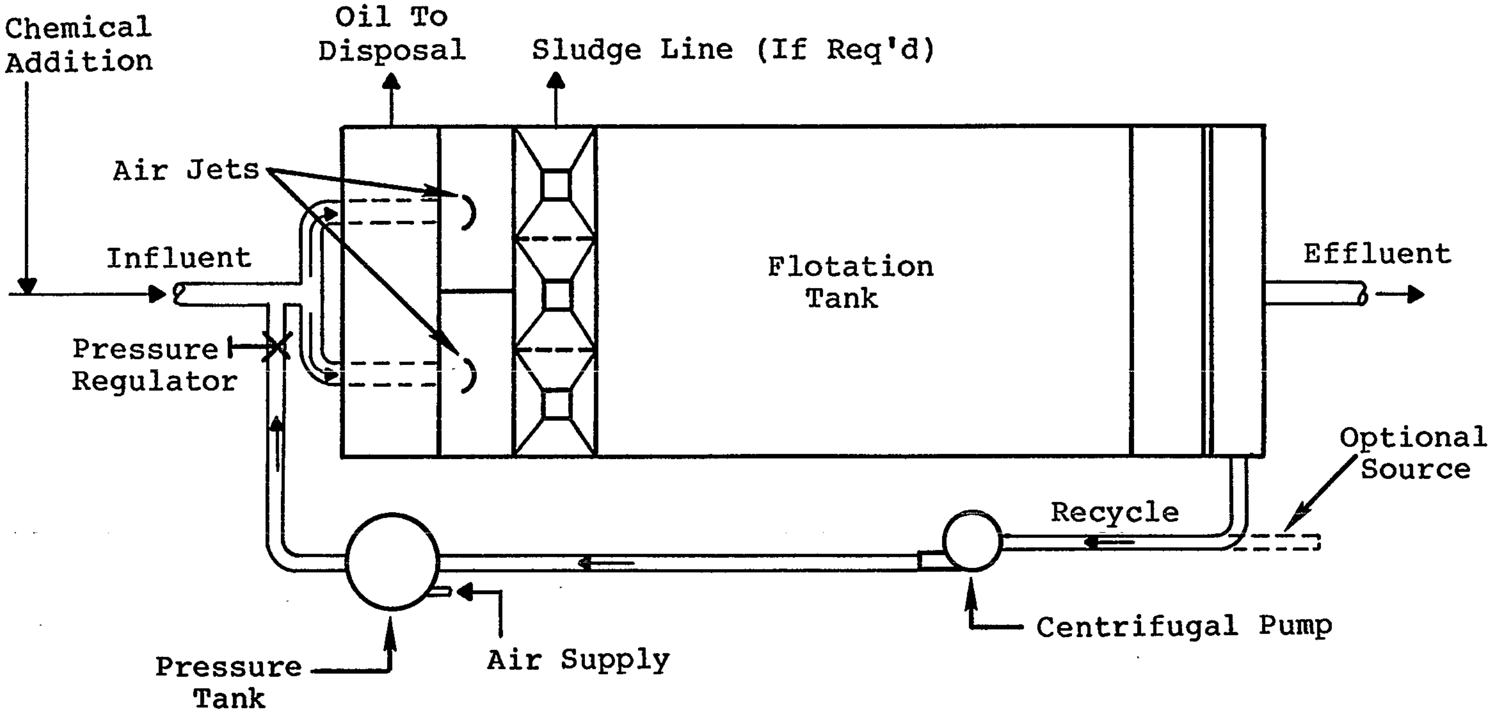

FIGURE 7-36

TYPICAL DISSOLVED AIR FLOTATION SYSTEM

The results of sampling done at Plant ID 33692 are presented below (Concentrations are in mg/l).

Plant ID 33692 (mg/l)

| | Day 1 | | Day 2 | |
|---|---|---|---|---|
| Parameter | Influent | Effluent | Influent | Effluent |
| Oil & Grease | 412. | 108. | 65.8 | 28.9 |
| TOC | 3000. | 132. | 98. | 86. |
| BOD | 130. | 78. | 31. | 24. |
| TSS | 416. | 210. | 166. | 103. |

Demonstration Status

Flotation is used in 25 facilities in the present data base and these are identified in Table 7-42.

## Centrifugation

Centrifugation is the process of applying a centrifugal force to cause the separation of materials. This force is many times the force of gravity so it allows for solids separation in a much shorter time than that required by settling. When a suspension is centrifuged, the components of the solution with the greatest specific gravity accumulate at the farthest distance from the axis of the centrifuge and those with the least specific gravity are located nearest the axis. So when oily wastes containing suspended solids are centrifuged, the solids portion collects at the outside of the centrifuge, the oil forms the innermost layer, and the water portion is sandwiched in between. The different layers that are formed can then be collected separately. Centrifuges are currently available that have been specifically designed to separate either oil/water mixtures or oil/solids/water mixtures. Centrifugation equipment is in use as a pretreatment technique to separate oil/water mixtures prior to further wastewater treatment.

The performance of the centrifuge at plant ID 19462, which employs centrifugation to lower the oil concentration of the wastewater prior to further oil removal by ultrafiltration, was established by sampling the influent and effluent streams. The results are presented below (Concentrations are in mg/l).

Plant ID 19462 (mg/l)

| | Day 1 | | Day 2 | |
|---|---|---|---|---|
| Parameter | In | Out | In | Out |
| Oil and Grease | 373,280 | 3402 | 14,639 | 1102 |
| TSS | 6866 | 1266 | 8938 | 1154 |

A detailed discussion on the various types of centrifuges is presented under the heading "Treatment of Sludges".

Centrifugation is used on oily wastes by 5 plants in the present data base: Plant ID's 06019, 11184, 14062, 19462, and 30166.

## Integrated Adsorption

### Application

The integrated adsorption process is designed for disposal of materials in dilute aqueous emulsion, such as oils and paints. The active agent is any of several aluminum silicate-based formulations in powder form. This material is added to the wastewater, and the mixture is agitated for six minutes. During this period, the powder adsorbs the emulsified materials. Next, the solid material is allowed to settle for two minutes, and the water phase is then decanted through a disposable belt filter, leaving any unsettled solids on the filter. Finally, the sludge phase is ejected on the disposable belt filter, where it is partially dewatered. Both the belt and the material retained on it feed into a disposal container. The filtered water is collected for reuse or discharge.

The integrated adsorption process is available as a commercial system. Equipment consists of a reagent feed hopper, an associated automatic feed device, a wastewater feed pump, a reaction vessel, a high-speed turbine mixer, a disposable belt, a band filter, a clean water pump, a clean water tank, and associated controls.

The integrated adsorption system does not add anything to the processed water, the pH and salinity of which are unaffected. The system is designed for automatic operation, and the sludge is leach-resistant because of the strong bonding of the adsorbed materials. The system obviates the need for other chemical treatment or physical separation, but it does entail both capital and operating expense.

### Performance

The integrated adsorption system consistently removes greater than 99 percent of the paints, detergents, and emulsified oils in the feed stream. The sludge is 20 to 40 percent solids, and is strongly resistant to leaching.

### Demonstration Status

The system is employed for treating paint booth water and emulsified oils by a leading European auto maker, among others. There are more than 100 units presently in service.

## Thermal Emulsion Breaking

Thermal emulsion breaking is usually a continuous process. In most cases, however, these systems are operated intermittently, due to the batch dump nature of most emulsified oily wastes. The emulsified raw waste is collected in a holding tank until sufficient volume has accumulated to warrant operating the thermal emulsion breaking system. One such system is an evaporation-distillation-decantation apparatus which separates the spent emulsion into distilled water, oil and other floating particles, and sludge (See Figure 7-36a). Initially, the raw waste flows from the holding tank into the main conveyorized chamber. Warm dry air is passed over a large revolving drum which is partially submerged in the emulsion. Some water evaporates from the surface of the drum and is carried upward through a filter and a condensing unit. The condensed water is discharged and can be reused as process makeup, while the air is reheated and returned to the evaporation stage. As the concentration of water in the main conveyorized chamber decreases, oil concentration increases and some gravity separation occurs. The oils and other emulsified wastes which separate flow over a weir into a decanting chamber. A rotating drum skimmer picks up oil from the surface of this chamber and discharges it for possible reprocessing or contractor removal. Meanwhile, oily water is being drawn from the bottom of the decanting chamber, reheated, and sent back into the main conveyorized chamber. This aids in increasing the concentration of oil in the main chamber and the amount of oil which floats to the top. Solids which settle out in the main chamber are removed by a conveyor belt. This conveyor, called a flight scraper, moves slowly so as not to disturb the settling action. As with the use of acids for chemical emulsion breaking, thermal emulsion breaking is more commonly used for oil recovery than for oily waste removal.

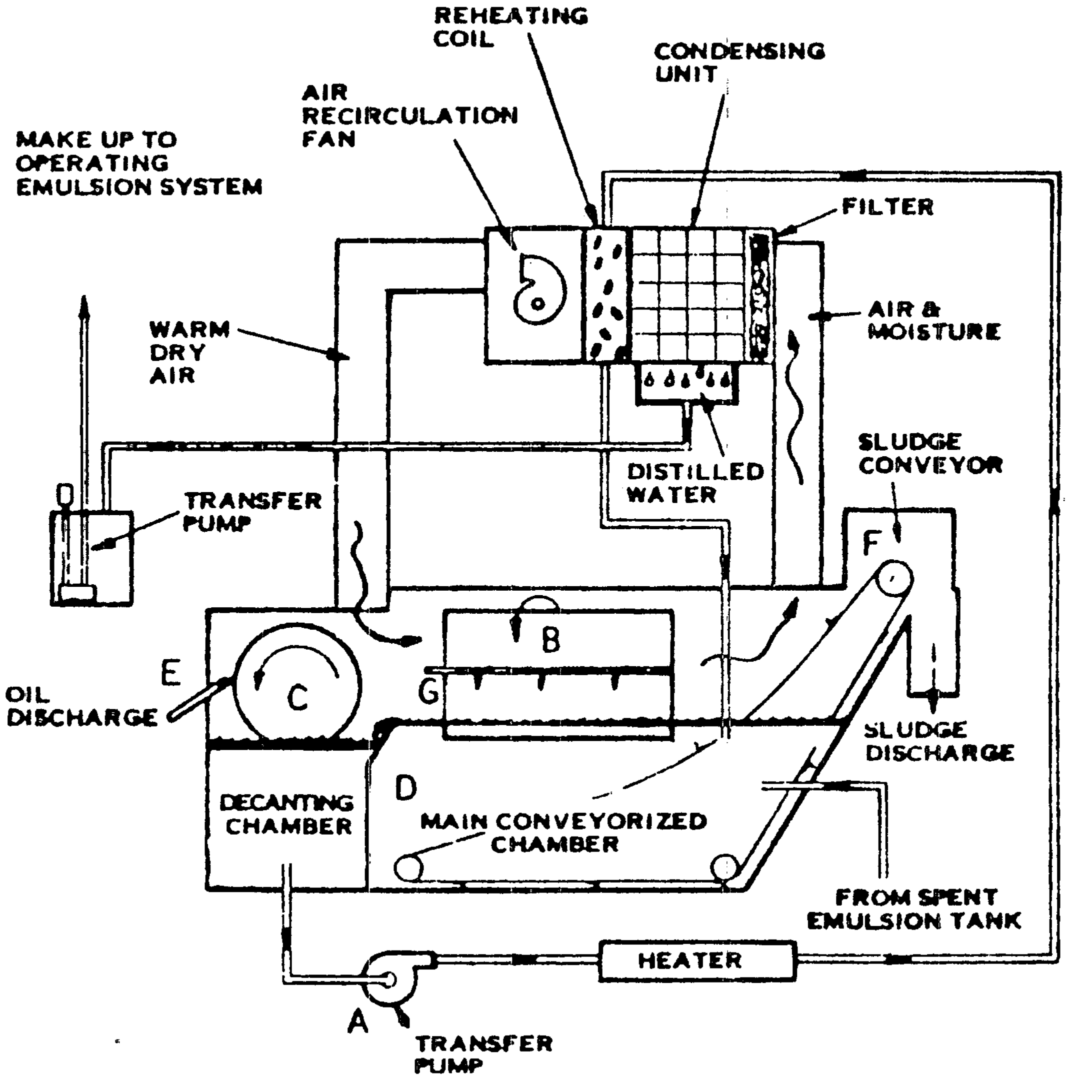

FIGURE 7-36a

THERMAL EMULSION BREAKER

## Application

Emulsion breaking technology can be applied to the treatment of emulsified oil/water mixtures in the Metal Finishing Category wherever it is necessary to separate oils, fats, soaps, etc. from wastewaters.

Advantages of thermal emulsion breaking include an extremely high percentage of oil removal, the separation of floating oil from settleable sludge, and the production of distilled water which is available for process re-use. In addition, no chemical additives are required and the operation is fully automatic, factors which reduce operating costs and maintenance requirements. Disadvantages of this system are the cost of heat to run the small boiler and the necessary installation of a large storage tank. Thermal emulsion breaking models are currently available to handle loads of 150, 300, and 600 gallons per day.

## Performance

The performance level using thermal emulsion breaking is dependent primarily on the characteristics of the raw waste and proper maintenance and functioning of the system components. Some emulsions may contain volatile compounds which could escape with the distilled water. In systems where the water is recycled back to process, however, this problem is essentially eliminated. Experience in at least two plants has shown that trace organics or other contaminants found in the effluent will not adversely affect the lubricants when this water is recycled back to process emulsions.

## Demonstration Status

Thermal emulsion breaking is known to be in regular use in at least two plants (ID 04086 and 15030) manufacturing copper wire. The process is equally applicable to oil-water emulsions used in metal finishing plants.

## CONTROL AND TREATMENT OF TOXIC ORGANICS

### INTRODUCTION

This section presents information on the control and treatment of toxic organics from spent solvents; in total plant process wastewaters; and in segregated oily waste streams. This section is organized as follows: (1) waste solvent control options; (2) treatment of toxic organics for combined wastewater; and (3) treatment of toxic organics in segregated oily wastestreams. In addition, alternative treatment methods for toxic organics control are presented.

### WASTE SOLVENT CONTROL OPTIONS

The primary control technology for toxic organics is not to dump concentrated toxic organics directly into waste streams or to combine concentrated toxic organics with any waste that will enter the waste treatment system. The major source of toxic organics in metal finishing wastewaters are waste solvents from degreasing operations that have been dumped into the waste stream. The solution to controlling toxic organics in the wastewaters, therefore, is to segregate concentrated toxic organics wastes for contract hauling or reclamation. Additionally, alternative techniques for solvent degreasing may be employed to reduce or eliminate the quantity of waste solvent generated. The following paragraphs discuss the segregation of waste solvents, contract hauling of waste solvents, and cleaning alternatives that can be substituted for solvent degreasing.

#### Waste Solvent Segregation

Spent degreasing solvents should be segregated from other process fluids to maximize the value of the solvents, to preclude the contamination of other segregated wastes (such as oily wastes), and to prevent the discharge of priority pollutants to any wastewaters. This segregation can be accomplished by providing and identifying the necessary storage container(s), establishing clear disposal procedures, training personnel in the use of these techniques, and checking periodically to ensure that proper segregation is occuring. Segregated waste solvents are appropriate for on-site solvent recovery or can be contract hauled for disposal or reclamation.

#### Contract Hauling

The DCP data identified several waste solvent haulers most of whom haul solvent in addition to their primary business of hauling waste oils. The value of waste solvents seems to be sufficient to make waste solvent hauling a viable business. Telephone interviews indicate that the number of solvent haulers is increasing and that their operations are becoming more sophisticated because of the increased value of waste solvent. In addition, a number of chemical suppliers include waste hauling costs in their new solvent price. Some of the larger solvent refiners make credit arrangements with their clientele; for example it was reported that one supplier returns 50 gallons of refined solvent for every 100 gallons hauled.

## Cleaning Alternatives to Solvent Degreasing

The substitution for solvent degreasing of cleaning techniques that use no solvents or use lesser amounts of solvents would eliminate or reduce the quantity of toxic organics that are found in wastewaters. Alternative cleaning methods for the removal of oils and grease include wiping, immersion, and spray (both liquid and vapor phase) techniques using water, alkaline or acid mixtures, and solvent emulsions. Various methods of agitation, including ultrasonic and electrolytic are helpful wherever they are applicable. Table 7-72 presents a generalized matrix of these cleaning approaches, each of which has the capability for cleaning oily metal parts.

Fundamentally, the factors required to remove oil and clean the metal surfaces of a part are:

1. A fluid to transport the cleaning agent to and the soil particles away from the surface to be cleaned.
2. A chemical in which oily residues are soluble.
3. Heat (temperatures above 150°F) to lower the viscosity of the oil and enhance the activity of the chemical agent.
4. A scrubbing or wiping mechanism to physically remove the cleaner and soil.

In the metal finishing industry, the factors that dictate the cleaning needs include:

1. Production volume
2. Product size
3. Product material (eg-ferrous, non-ferrous)
4. Product shape and complexity (eg-blind holes, internal corners)
5. Degree of cleanliness required (eg-surface purity)
6. Surface preparation required (eg-dry, oil film, oxide/scale removal, oxidation resistance)

Obviously, a single cleaning approach is not practicable for all of these diverse product and manufacturing requirements. The task of identifying feasible cleaning alternatives to solvent degreasing then becomes one of identifying areas which have similar cleaning requirements so that substitution for solvent degreasing is practicable. Typical areas that are

## TABLE 7-72
## CLEANING APPROACHES

| | | | CLEANING AGENT | | | |
|---|---|---|---|---|---|---|
| CLEANING METHOD | SORBENT | WATER | ALKALINE | ACID | EMULSION | SOLVENT |
| WIPING | | | | | | |
| A. Dry | X | | | | | |
| B. Wet | X | | X | X | X | X |
| IMMERSION | | | | | | |
| A. Cold | | | | | | |
| 1. without agitation | | | X | X | X | X |
| 2. with agitation | | | X | X | X | X |
| B. Hot | | | | | | |
| 1. without agitiation | | | X | X | | |
| 2. with agitation | | X | X | X | | |
| SPRAY | | | | | | |
| A. Liquid | | | | | | |
| 1. Cold | | | X | X | | |
| 2. Hot | | X | X | X | | |
| B. Vapor | | X | X | X | X | X |

amenable to cleaning techniques other than solvent degreasing are:

1. Low to medium volume production levels where cleaning cycle time does not impact the cost of production
2. Non-ferrous products
3. Simple product shapes
4. Small parts (adaptable to automated processes)
5. Oily film residue not objectionable
6. No exacting surface finishing required.

All of the previously described cleaning methods are applicable to some of these cleaning needs. For comparative purposes, these cleaning processes have been ranked on the relative basis of cost, quality of cleaniness, and significant environmental effects. This relative ranking is presented in Table 7-73 for the five general cleaning methods. The bases for the criteria used for relative ranking are defined as follows:

1. Cost - include equipment, facilities, chemicals, heat, power, maintenance, operation (rinsing and drying where applicble) and wastewater treatment.
2. Cleanliness Quality - surface purity.
3. Pollution - environmental effects of the process.
4. Energy - thermal and electrical energy requirement.

TABLE 7-73
CLEANING PROCESS RELATIVE RANKING
(LOWEST NUMBER IS BEST)

| CLEANING METHOD | COST | CLEANINESS QUALITY | ENVIRONMENTAL POLLUTION | ENVIRONMENTAL ENERGY | ENVIRONMENTAL COMBINED | MEAN OVERALL RANKING |
|---|---|---|---|---|---|---|
| Solvent Degreasing | 1 | 3 | 5 | 1 | 3 | 2.5 |
| Emulsion Cleaning | 3 | 4 | 4 | 2 | 3 | 3.25 |
| Alkaline Cleaning | 2 | 2 | 2 | 3 | 2.5 | 2.25 |
| Acid Cleaning | 4 | 1 | 3 | 4 | 3.5 | 3 |
| Hot Water/Steam Cleaning | 5 | 5 | 1 | 5 | 3 | 4 |

Alkaline cleaning is the most feasible substitute for solvent degreasing. This selection is based in part on the fact that the combined alkaline cleaning environmental ranking and the mean overall ranking are lowest. Further, data derived from existing cleaning processes, shows that alkaline cleaning is only 14% less cost effective than vapor degreasing. It is believed that further development of alkaline cleaners and the associated equipment should make its cost effectiveness equivalent to or better than that for solvent degreasing. The major advantage of alkaline cleaning over solvent degreasing is the elimination or reduction in the amount of priority pollutants being discharged. A major disadvantage connected with alkaline cleaning is the energy consumption. Another disadvantage is the fact that the process itself tends to dilute the oils removed and discharges these diluted oils as well as the cleaning additive, whereas in solvent degreasing, the oils are contractor hauled along with the spent solvent and not discharged. However, at least one firm produces a close-loop alkaline cleaning system oil separator that is illustrated in Figure 7-37.

This system provides in-process removal of oils and metals wastes which extends the useful alkaline cleaner life and significantly reduces treatment requirements because the spent cleaning solution is normally contract hauled. Only the alkaline solution dragout to a subsequent rinsing operation produces a waste that requires treatment. Best described as a continous-batch oil separator, the system has dual compartments holding caustic wash solution, each equipped with an oil skimmer and separated by a waste tank. Piping leads from each compartment to a series of washers and back to a pump. Automated valves control flow from the pump to one of the compartments. One compartment continuously supplies caustic solution to a group of washers as the other stands for 24 hours, allowing heavy materials to settle to the bottom as sludge and permitting the oils to float to the surface. There, surface oils are skimmed off, drained into the waste tank, and periodically drawn off for reclamation or reuse. While one wash solution in the first compartment is undergoing treatment, the clean solution in the other compartment is circulated to the washers. Four plants have these systems in operation and one installation has been in use since June 1975. At this facility they report zero discharge (via contract hauling the spent cleaning solution) and the reclamation of 25,000 gallons of oil annually from a cleaning operation prior to heat treatment. The specific advantages of applying this type of in-process oil/metal treatment are as follows:

1. The concentrated discharges of spent alkaline cleaning baths are eliminated by contract hauling the reduced volume of spent cleaner.

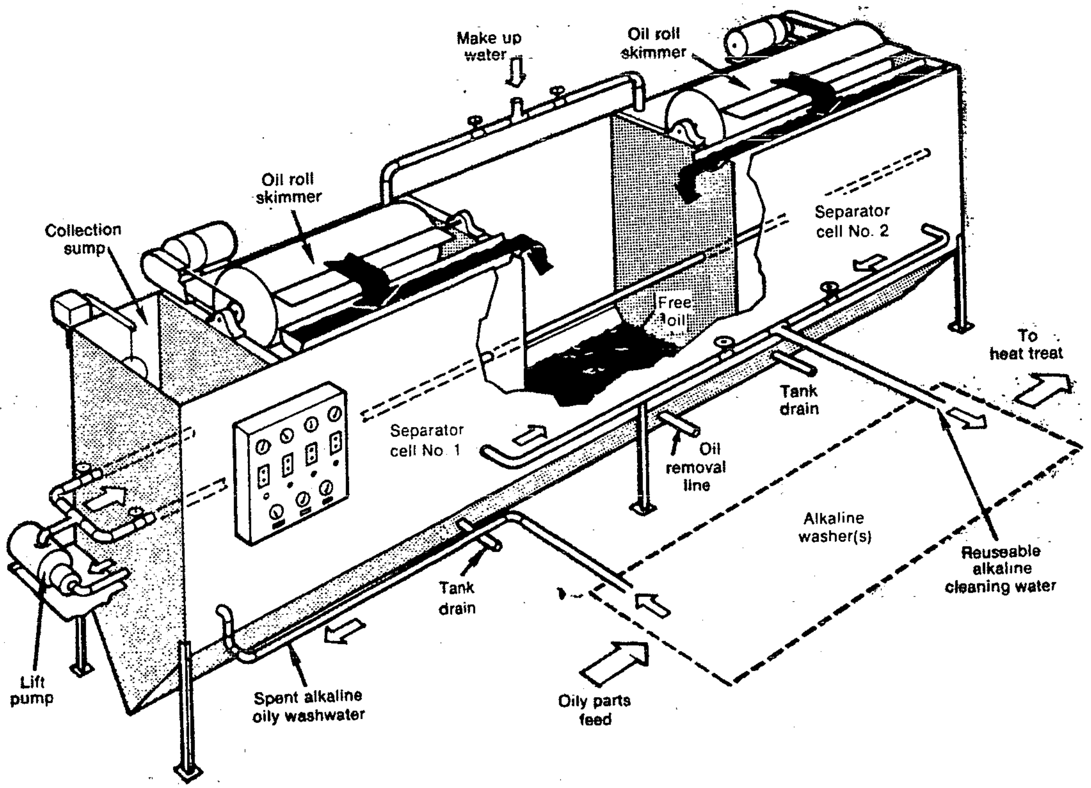

FIGURE 7-37

ALKALINE WASH OIL SEPARATOR

2. Energy requirements are lowered because of water conservation.
3. Water and air pollution resulting from alkaline cleaning are less than for the solvent degreasing operation.
4. Oil reclamation is accomplished.
5. Lower cleaning costs are available through the conservation of cleaning agent and heat; less frequent waste hauling; the use of cold cleaners; and lowered treatment requirements.

## TREATMENT OF TOXIC ORGANICS FOR COMBINED WASTEWATER

Toxic organics that enter the plant process wastewater from various sources such as rinses and paint booth water curtains are usually present at lower concentrations than toxic organics in waste solvents or in concentrated oily wastes.

The applicable treatment technologies for toxic organics removal from combined wastewater are the common metals treatment technologies. To the extent that these technologies, evaluated by the Agency for control of metals and cyanides, also remove toxic organics, the TTO limit should reflect the discharge from plants with these technologies.

The limitations for TTO are based on total plant wastewater data for EPA sampled plants. EPA sampled plants cover three technology groupings: Option 1 (precipitation/clarification), Option 2 (precipitation/clarification/filtration), and other than Option 1 or Option 2 plants. These data are presented in Tables 7-74 through 7-76. Option 1 plant data were used to derive the end-of-pipe TTO limits. The raw waste TTO limits were derived using the total plant raw waste data from all three groupings.

The TTO data were evaluated on the basis of processes, products, type of work, pre- and post-process water quality characteristics to investigate combinations of plants that generate larger amounts of TTO than other groups. The data were classified into groups, namely plants that perform painting, solvent degreasing, painting and solvent degreasing; plants with total raw waste oil and grease concentrations above and below 100 mg/ℓ; and plants with TTO concentrations in the supply water of above and below 0.1 mg/ℓ. In addition, the Agency examined job shops, captives, printed circuit board manufacturers, and automotive plants. (This classification analysis is presented in detail in Exhibit 2 at the back of the development document.)

The results of this analysis showed that plants that have both paint and solvent degreasing operations discharge the highest TTO concentrations of any other process sector of the metal finishing industry. The painting and solvent degreasing plants were used to establish an overall mean. The daily variability factor was derived using the data from plants involved in painting or degreasing. Long term self-monitoring for TTO were not available for the industry (primarily because plants typically had not been required to monitor for organics in the past). Considering the high cost of TTO monitoring, no 10-day variability factors or monthly maximum averages were developed for TTO. The results of the statistical calculations of the TTO daily maximum limitations are summarized below:

## TTO EFFLUENT LIMITATIONS - OPTION 1

| | |
|---|---|
| Mean TTO effluent concentration | 0.434 mg/ℓ |
| Daily variability factor | 4.91 mg/ℓ |
| Daily maximum effluent concentration | 2.13 mg/ℓ |

## TTO RAW WASTE LIMITATIONS

| | |
|---|---|
| Mean TTO effluent concentration | 1.08 mg/ℓ |
| Daily variability factor | 4.23 mg/ℓ |
| Daily maximum raw waste concentration | 4.57 mg/ℓ |

Percentile distribution graphs for TTO Option 1 effluent data and for TTO total raw waste data are presented in Figures 7-38 and 7-39, respectively. As is evident from these graphs, compliance with the TTO effluent limits and with the TTO raw waste limits is 100 percent when data, which are considered indicative of improper disposal of toxic organics, are excluded.

## TABLE 7-74

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR TTO

## OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | NA | 0.019 | 6091-15-0 |
| 2. | NA | 0.001 | 6091-15-1 |
| 3. | NA | 0.019 | 6091-15-2 |
| 4. | NA | 0.037 | 12061-14-0 |
| 5. | NA | 0.025 | 19068-14-0 |
| 6. | NA | 0.430 | 20005-21-0 |
| 7. | NA | 0.007 | 27046-15-2 |
| 8. | NA | 0.007 | 34050-15-0 |
| 9. | NA | 0.020 | 34050-15-1 |
| 10. | NA | 0.007 | 34050-15-2 |
| 11. | NA | 0.485 | 6019 |
| 12. | 0 | 0 | 9025-15-0 |
| 13. | 0.002 | 0.004 | 20083-15-0/1 |
| 14. | 0.003 | 0.004 | 20083-15-2/3 |
| 15. | 0.003 | 0.007 | 20083-15-4/5 |
| 16. | 0.006 | 0.005 | 12061-15-0 |
| 17. | 0.006 | 0.008 | 12061-15-2 |
| 18. | 0.007 | 0.009 | 20022-15-2 |
| 19. | 0.008 | 0.016 | 20022-15-1 |
| 20. | 0.009 | 0.005 | 6110-15-1 |
| 21. | 0.009 | 0.006 | 6110-15-2 |
| 22. | 0.009 | 0.010 | 9052-15-0 |
| 23. | 0.010 | 0.006 | 6110-15-0 |
| 24. | 0.012 | 0.007 | 9052-15-2 |
| 25. | 0.014 | 0.008 | 21003-15-2 |
| 26. | 0.014 | 0.013 | 41051-15-0 |
| 27. | 0.017 | 0.015 | 15608-15-2 |
| 28. | 0.019 | 0.004 | 15608-15-0 |
| 29. | 0.020 | 0.008 | 20022-15-0 |
| 30. | 0.020 | 0.024 | 41051-15-1 |
| 31. | 0.022 | 0.254 | 4069-15-0/1 |
| 32. | 0.023 | 0.012 | 41051-15-2 |
| 33. | 0.030 | 0.014 | 12061-15-1 |
| 34. | 0.031 | 0.207 | 2032-15-2 |
| 35. | 0.034 | 0.002 | 21003-15-0 |
| 36. | 0.036 | 0.020 | 17061-15-1 |
| 37. | 0.038 | 0.013 | 15608-15-1 |
| 38. | 0.040 | 0.002 | 9052-15-1 |
| 39. | 0.040 | 0.035 | 21003-15-1 |
| 40. | 0.043 | 0.032 | 4071-15-0 |
| 41. | 0.059 | 0.038 | 6960-15-4/5 |
| 42. | 0.091 | NA | 34051-15-0 |

(Continued)

TABLE 7-74 (Continued)

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR TTO

OPTION 1

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 43. | 0.095 | 0.016 | 34051-15-1 |
| 44. | 0.097 | 0.203 | 6090-14-0 |
| 45. | 0.097 | 0.003 | 38051-15-2 |
| 46. | 0.098 | 0.228 | 44062-15-0 |
| 47. | 0.099 | 0.180 | 38052-15-0 |
| 48. | 0.104 | 0.056 | 6960-15-0/1 |
| 49. | 0.107 | 0.081 | 44062-15-2 |
| 50. | 0.109 | 0.081 | 2032-15-5 |
| 51. | 0.110 | 0.122 | 44062-15-1 |
| 52. | 0.111 | 0.007 | 34051-15-2 |
| 53. | 0.113 | 0.131 | 4069-15-2/3 |
| 54. | 0.120 | 0.017 | 19068-15-1 |
| 55. | 0.130 | 0.093 | 4071-15-3 |
| 56. | 0.133 | 0.040 | 4071-15-1 |
| 57. | 0.140 | 0.130 | 30165-21-0 |
| 58. | 0.141 | 0.034 | 17061-15-3 |
| 59. | 0.178 | 0.322 | 4069-15-4 |
| 60. | 0.192 | 0.012 | 38052-15-1 |
| 61. | 0.200 | 0.109 | 38052-15-2 |
| 62. | 0.202 | 0.016 | 19068-15-2 |
| 63. | 0.204 | 0.144 | 6960-15-2/3 |
| 64. | 0.224 | 0.007 | 38051-15-0 |
| 65. | 0.251 | 0.008 | 9025-15-1 |
| 66. | 0.259 | 0.005 | 38051-15-1 |
| 67. | 0.283 | NA | 4282-21-0 |
| 68. | 0.289 | 18.005 | 9025-15-2 |
| 69. | 0.364 | 0.067 | 30054-15-0 |
| 70. | 0.400 | 0.002 | 27046-15-1 |
| 71. | 0.426 | 0.012 | 27046-15-0 |
| 72. | 0.473 | 0.483 | 6019 |
| 73. | 0.486 | 0.052 | 6090-15-1 |
| 74. | 0.769 | 0.140 | 30054-15-1 |
| 75. | 0.888 | 0.699 | 17061-14-1 |
| 76. | 1.161 | 0.082 | 2032-15-0 |
| 77. | 1.287 | 0.109 | 30054-15-2 |
| 78. | 1.619 | 0.643 | 28699-21-0 |
| 79. | 1.938 | 0.181 | 20103-21-0 |
| 80. | 8.466 | 37.355 | 6090-15-2 |
| 81. | 12.866 | NA | 20103-21-1 |

## TABLE 7-75
## METAL FINISHING CATEGORY PERFORMANCE DATA FOR TTO
## OPTION 2

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | NA | 0.400 | 17050-14-0 |
| 2. | NA | 0.415 | 36048-15-0/1 |
| 3. | NA | 0.103 | 36048-15-2/3 |
| 4. | NA | 0.091 | 36048-15-4/5 |
| 5. | 0.012 | 0.056 | 18538-15-3 |
| 6. | 0.021 | 0.010 | 12075-15-2/3 |
| 7. | 0.028 | 0.043 | 12075-15-0/1 |
| 8. | 0.042 | 0.007 | 12075-15-4/5 |
| 9. | 0.064 | 0.030 | 18538-14-0 |
| 10. | 0.477 | 0.037 | 17050-15-1 |
| 11. | 1.083 | 0.003 | 17050-15-0 |

# TABLE 7-76

## METAL FINISHING CATEGORY PERFORMANCE DATA FOR TTO

## OTHER THAN OPTION 1 or 2

| Data Point | Raw Waste Concentration (mg/ℓ) | Effluent Concentration (mg/ℓ) | Plant ID |
|---|---|---|---|
| 1. | NA | 2.52 | 12065-14-1 |
| 2. | NA | 0.189 | 12065-15-2 |
| 3. | NA | 0.153 | 12065-15-4 |
| 4. | NA | 0.165 | 13042-21-1 |
| 5. | NA | 0.005 | 19069-15-0 |
| 6. | NA | 0.007 | 19069-15-1 |
| 7. | NA | 0.007 | 19069-15-2 |
| 8. | NA | 0.288 | 38040-23-0 |
| 9. | NA | 0.377 | 38040-23-1 |
| 10. | NA | 0.673 | 38217-23-0 |
| 11. | 0.005 | 0.006 | 11108-15-1 |
| 12. | 0.007 | 0.001 | 11108-15-2 |
| 13. | 0.008 | 0.012 | 40060-15-0 |
| 14. | 0.009 | 0.012 | 40060-15-1 |
| 15. | 0.010 | 0.009 | 11103-15-2/3 |
| 16. | 0.011 | 0.014 | 2033-15-4/5 |
| 17. | 0.011 | 0.005 | 11108-15-0 |
| 18. | 0.011 | 0.009 | 21066-15-1 |
| 19. | 0.012 | No Data | 21066-15-0 |
| 10. | 0.013 | 0.009 | 11103-15-4 |
| 21. | 0.014 | 0.011 | 21066-15-3 |
| 22. | 0.028 | 0.014 | 2033-15-0/1 |
| 23. | 0.030 | 0.010 | 2033-15-2/3 |
| 24. | 0.084 | 0.011 | 11103-15-0 |
| 25. | 0.285 | 0.257 | 36178-21-0 |
| 26. | 0.326 | 0.140 | 36178-21-1 |
| 27. | 1.09 | 0.823 | 33692-23-0 |
| 28. | 2.005 | 0.120 | 36178-21-2 |
| 29. | 13.50 | 0.433 | 33692-23-1 |

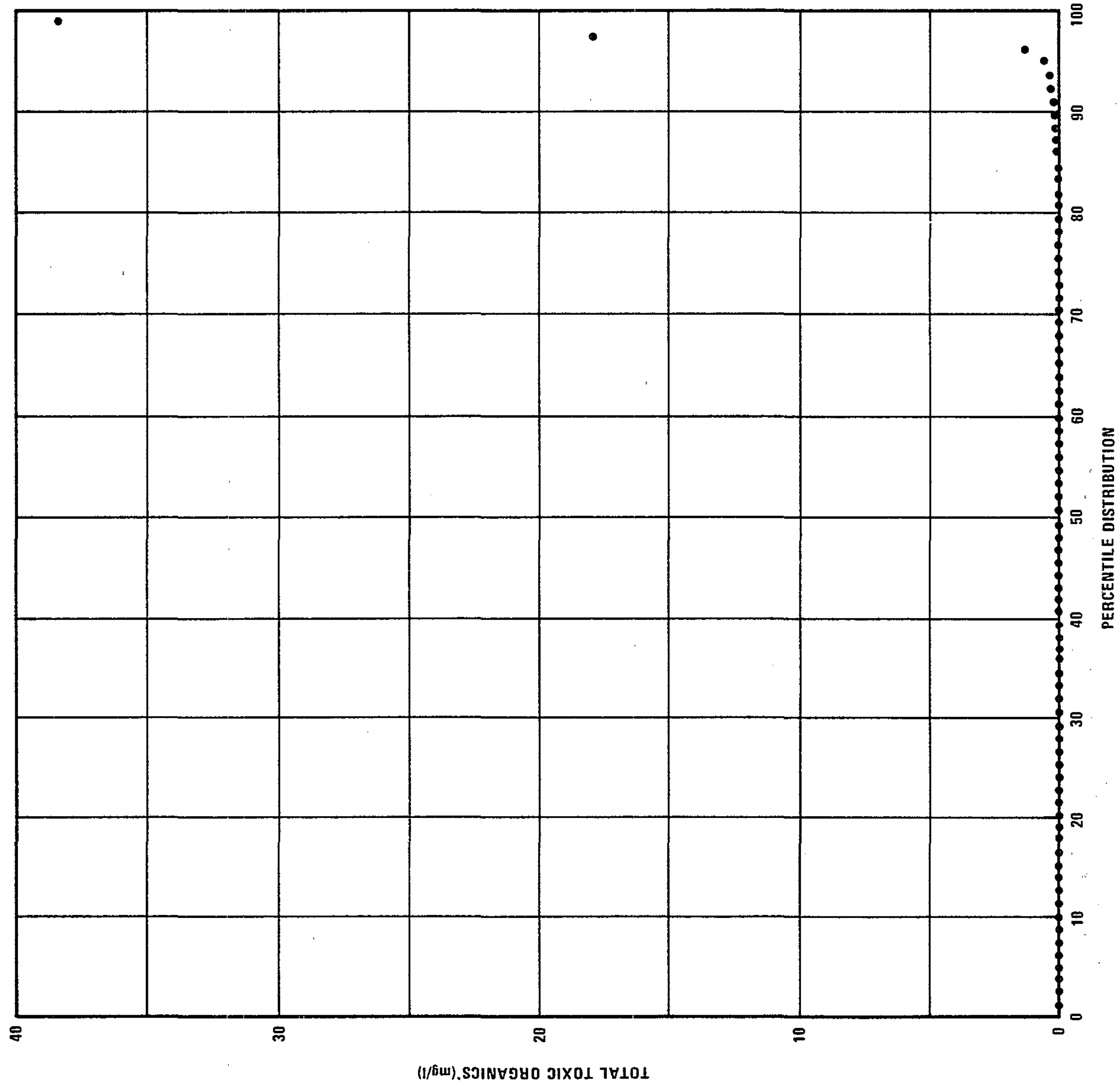

FIGURE 7-38. PERCENTILE DISTRIBUTION OF TTO IN EFFLUENT FROM OPTION 1 PLANTS

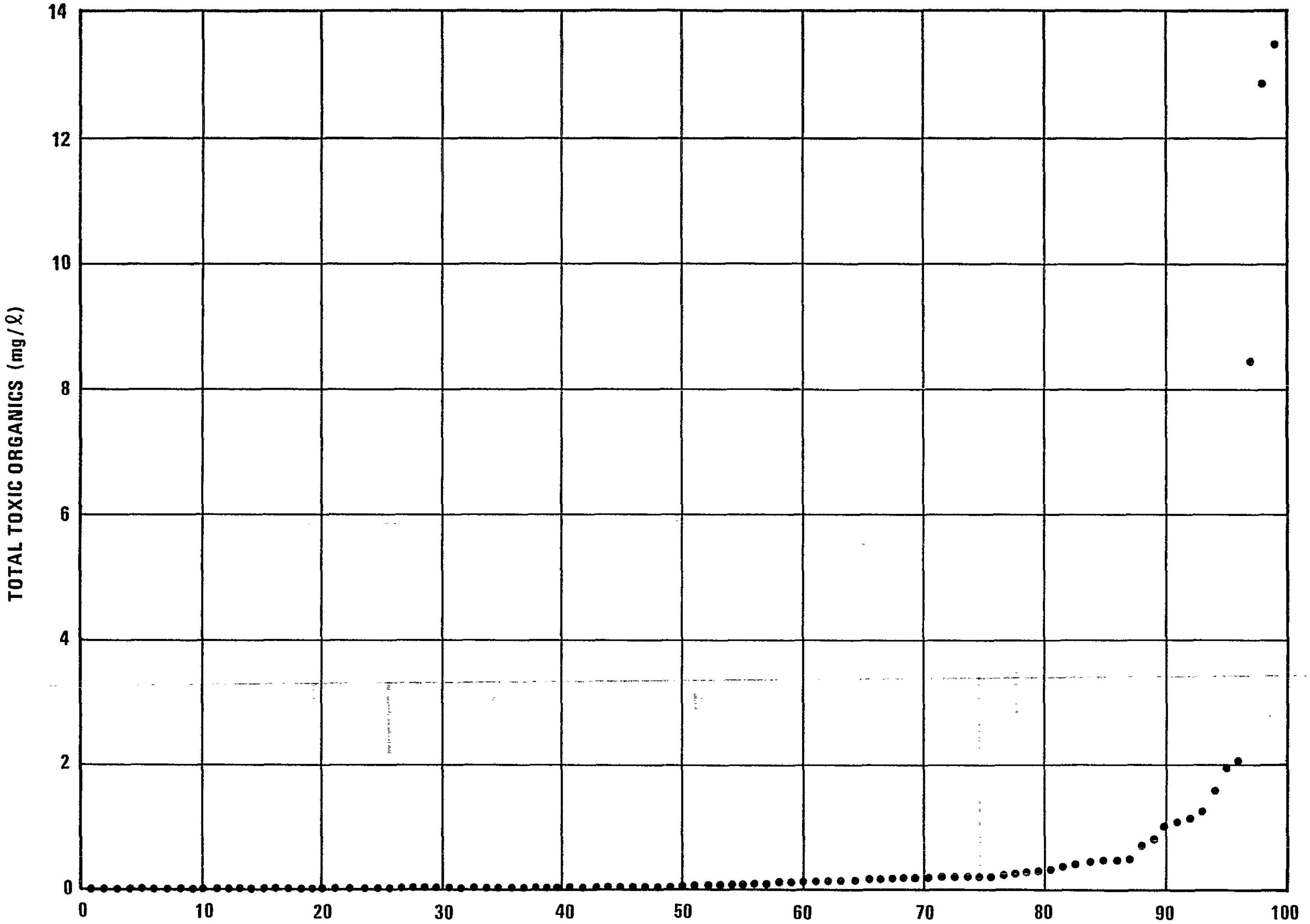

FIGURE 7-39. PERCENTILE DISTRIBUTION OF TTO IN RAW WASTE IN METAL FINISHING WASTEWATERS

## TREATMENT OF TOXIC ORGANICS IN SEGREGATED OILY WASTE

Toxic organics can be removed from wastewater streams during treatment for oil and grease because of their solubility in hydrocarbons as shown in Table 7-77. Segregated oily wastes treatment of concentrated oily wastestreams will effectively remove oil and grease, which will result in removal of toxic organics. However, as stated previously, preventing toxic organics from entering the wastewater stream can be the most effective control.

The technologies applicable to removing TTO in segregated oily waste streams include Option 1 for segregated oily wastes (emulsion breaking and skimming or ultrafiltration). A detailed description plus information on the applicability and demonstration status of these technologies is presented in "Treatment of Oily Waste."

TTO performance data for Option 1 and ultrafiltration are presented in this section in Tables 7-78 and 7-79.

## TABLE 7-77
## SOLUBILITY OF TOXIC ORGANIC PARAMETERS

| | | Solubility in | |
|---|---|---|---|
| | Parameter | Water | Hydrocarbons |
| 001 | Acenaphthene | Insoluble | Soluble |
| 006 | Carbon Tetrachloride | Very Slightly | Infinitely |
| 010 | 1,2-dichloroethane | Very Slightly | Very to Infinitely |
| 011 | 1,1,1-trichloroethane | Insoluble | Soluble |
| 013 | 1,1-dichloroethane | Very Slightly | Soluble |
| 021 | 2,4,6-trichlorophenol | Slightly | Soluble |
| 022 | Parachlorometa Cresol | Soluble | Very to Infinitely |
| 029 | 1,1-dichloroethylene | Slightly | Soluble |
| 030 | 1,2-trans-dichloroethylene | Slightly | Soluble |
| 034 | 2,4-dimethyl Phenol | Soluble | Soluble |
| 038 | Ethylbenzene | Soluble | Soluble to Infinite |
| 039 | Fluoranthene | Insoluble | Soluble |
| 044 | Methylene Chloride | Slightly | Soluble |
| 045 | Methyl Chloride | Slightly | Soluble |
| 054 | Isophorone | Slightly | Soluble |
| 055 | Naphthalene | Insoluble | Soluble |
| 059 | 2,4-dinitrophenol | Slightly | Very Soluble |
| 060 | 4,6-dinitro-o-cresol | Slightly | Infinitely |
| 062 | N-nitrosodiphenylamine | Insoluble | Soluble |
| 064 | Pentachlorophenol | Slightly | Soluble |
| 065 | Phenol | Soluble | Infinitely |
| 066 | Bis(2-ethylhexyl)phthalate | Insoluble | Soluble |
| 067 | butyl Benzyl Phthalate | Insoluble | Soluble |
| 068 | Di-n-butyl Phthalate | Insoluble | Soluble |
| 070 | Diethyl Phthalate | Insoluble | Soluble |
| 077 | Acenaphthylene | Insoluble | Very Soluble |
| 078 | Anthracene | Insoluble | Soluble |
| 081 | Phenanthrene | Insoluble | Soluble |
| 085 | Tetrachloroethylene | Insoluble | Soluble |
| 086 | Toluene | Slightly | Infinitely |
| 087 | Trichloroethylene | Insoluble | Infinitely |

## TABLE 7-78

## TTO PERFORMANCE DATA (mg/ℓ) FOR OPTION 1 SEGREGATED OILY WASTE

| Plant ID | Influent | Effluent |
|---|---|---|
| 1058-22-0 | 2.77 | 1.43 |
| 12095-22-0 | 6.14 | 0.996 |
| 12095-22-1 | 3.15 | 0.800 |
| 12095-22-2 | 6.50 | 0.480 |
| 20103-21-0 | 1.94 | 1.86 |
| 28125-22-1 | 0.767 | 1.076 |
| 40836-22-0 | 21.5 | 8.6 |

## TABLE 7-79

## TTO PERFORMANCE DATA (mg/ℓ) FOR ULTRAFILTRATION

| Plant ID | Influent | Effluent |
|---|---|---|
| 15193-21-0 | 802.05 | 80.83 |
| 30166-21-0 | 9.93 | 1.41 |
| 13041-22-0 | 1037.5 | 14.82 |
| 13041-22-1 | 14.3 | 13.0 |
| 13041-22-2 | 4.84 | 30.8 |
| 13324-21-0 | 12.02 | 1.48 |

## ADDITIONAL TREATMENT METHODS FOR TOXIC ORGANICS REMOVAL

Additional treatment technologies applicable for the treatment of TTO include carbon adsorption and reverse osmosis (polishing techniques) and resin adsorption, ozonation, chemical oxidation, and aerobic decomposition. These technologies are described in detail in this subsection.

## Carbon Adsorption

Carbon adsorption in industrial wastewater treatment involves passing the wastewater through a chamber containing activated carbon. The use of activated carbon has been proven to be applicable for removal of dissolved organics from water and wastewater. In fact, it is one of the most efficient organic removal processes available. This process is reversible, thus allowing activated carbon to be regenerated and reused by the application of heat and steam.

The term activated carbon applies to any amorphous form of carbon that has been specially treated to give high adsorption capacities. Typical raw materials include coal, wood, coconut shells, petroleum base residues and char from sewage sludge pyrolysis. A carefully controlled process of dehydration, carbonization, and oxidation yields a product which is called activated carbon. This material has a high capacity for adsorption, 500-1500 square meters/gram, resulting from a large number of internal pores. Pore sizes generally range from 10-100 angstroms in radius.

Activated carbon removes organic contaminants from water by the process of adsorption, or the attraction and accumulation of one substance on the surface of another. Activated carbon has a preference for organic compounds and, because of this selectivity, is particularly effective in removing organic compounds from aqueous solutions.

Some important but general rules based on considerations relating to carbon adsorption capacity are:

- Higher surface area will give a greater adsorption capacity.
- Larger pore sizes will give a greater adsorption capacity for large molecules.
- Adsorptivity increases as the solubility of the solute decreases. For hydrocarbons, adsorption increases with molecular weight.
- Adsorption capacity will decrease with increasing temperature.
- For solutes with ionizable groups, maximum adsorption will be achieved at a pH corresponding to the minimum ionization.

The rate of adsorption is also an important consideration. For example, while capacity is increased with the adsorption of higher molecular weight hydrocarbons, the rate of adsorption is decreased. Similarly, while temperature increases will decrease the capacity, they may increase the rate of removal of solute from solution.

Carbon adsorption requires pretreatment to remove excess suspended solids, oils, and greases. Suspended solids in the influent should be less than 50 ppm to minimize backwash requirements; a downflow carbon bed can handle much higher levels (up to 2000 ppm), but frequent backwashing is required. Backwashing more than two or three times a day is not desirable; at 50 ppm suspended solids, one backwash will suffice. Oil and grease should be less than about 10 ppm. A high level of dissolved inorganic material in the effluent may cause problems with thermal carbon reactivation (i.e., scaling and loss of activity) unless appropriate preventive steps are taken; such steps might include pH control, softening, or the use of an acid waste on the carbon prior to reactivation.

Activated carbon is available in both powdered and granular form. The equipment necessary for a granular activated carbon adsorption treatment system consists of the following: a preliminary clarification or filtration unit to remove the bulk of suspended solids; two or three adsorption columns packed with activated carbon similar to the one shown in Figure 7-40; a holding tank located between the adsorbers; and liquid transfer pumps. Unless a reactivation service is utilized, a furnace and associated quench tanks, spent carbon tank, and reactivated carbon tank are necessary for reactivation.

Powdered carbon is less expensive per unit weight than granular carbon and may have slightly higher adsorption capacity but it does have some drawbacks. For example, it is more difficult to regenerate; it is more difficult to handle (settling characteristics may be poor); and larger amounts may be required than for granular systems in order to obtain good contact. One innovative powdered carbon system uses wet oxidation for regeneration instead of fluidized bed incineration. This technique has been applied mainly to municipal treatment but can be used in industrial systems.

The necessary equipment for a two stage powdered carbon unit is as follows: four flash mixers, two sedimentation units, two surge tanks, one polyelectrolyte feed tank, one dual media filter, one filter for dewatering spent carbon, one carbon wetting tank, and a furnace for regeneration of spent carbon.

Thermal regeneration, which destroys adsorbates, is economical if carbon usage is above roughly 454 kg/day (1000 lbs/day). Reactivation is carried out in a multiple hearth furnace or a rotary kiln at temperatures from 870°C to 988°C. Required residence times are of the order of 30 minutes. With proper control, the carbon may be returned to its original activity; carbon losses will be in the range of 4-9% and must be made up with fresh carbon. Chemical regneration may be used if only one solute is present which can dissolve off the carbon. This allows material recovery. Disposal of the carbon may be required if use is less than approximately 454 kg/day (1000 lbs/day) and/or a hazardous component makes regeneration dangerous.

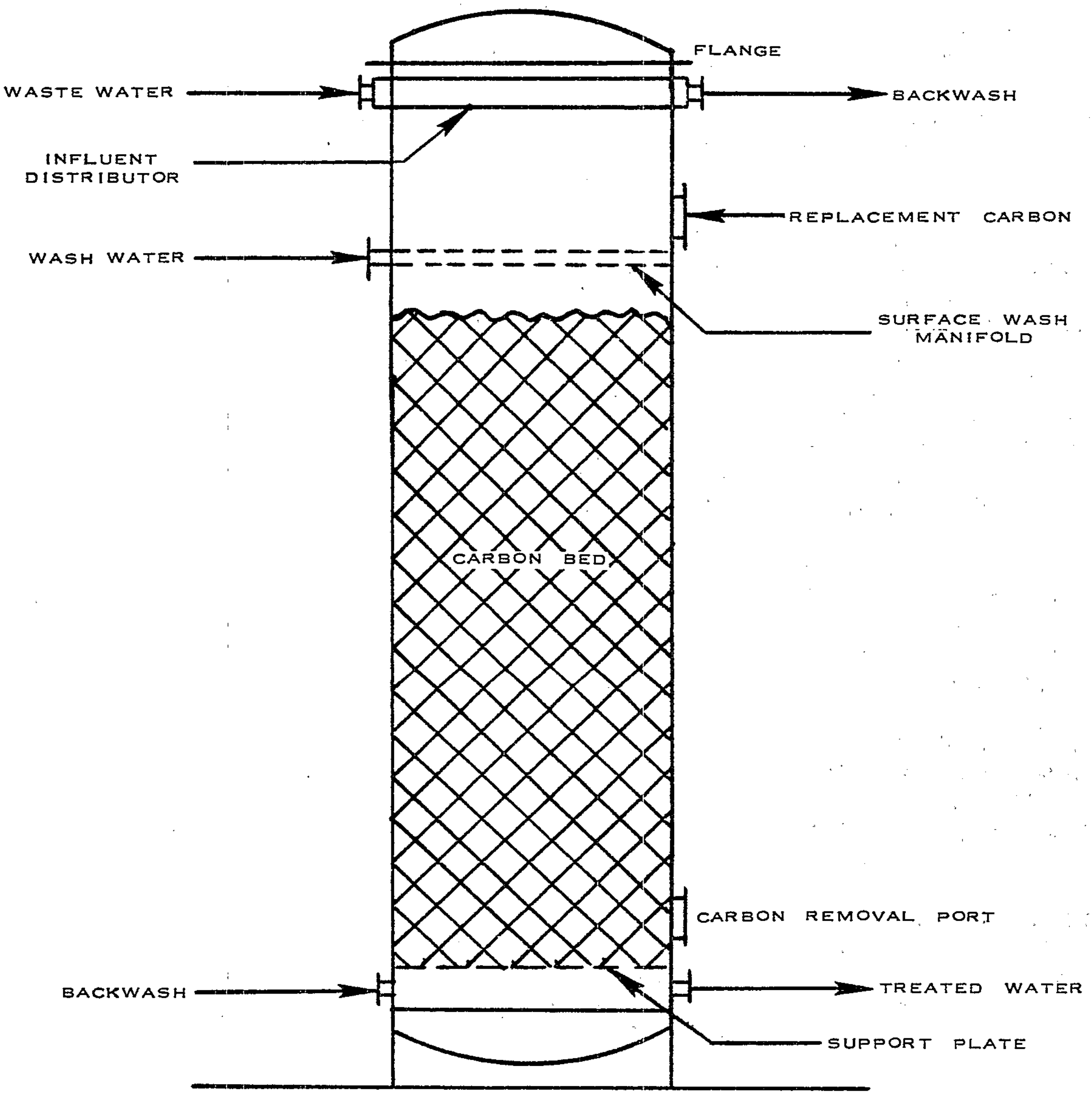

FIGURE 7-40

ACTIVATED CARBON ADSORPTION COLUMN

A new type of carbonaceous adsorbent is made by pyrolizing ion exchange resins. These spherical adsorbents appear to have the best characteristics of adsorbent resins and activated carbon. They have a greater physical strength, attrition resistance, and regeneration flexibility than either activated carbon or polymeric resins. One type is particularly suited for halogenated organics and has greater capacity than selected carbons for compounds such as 2-chloroethyl ether, bromodichloromethane, chloroform, and dieldrin. Another type (based on a different polymeric resin) is best suited for removing aromatics and unsaturated hydrocarbons. A third type has a particularly mg/l) for phenol and other relatively polar organic molecules. These adsorbents are commercially available but have not yet been proven in large scale operation.

Application

The principle liquid-phase applications of activated carbon adsorption include sugar decolorization; municipal water purification; purifications of fats, oils, foods, beverages and pharmaceuticals; and industrial/municipal wastewater treatment. Potentially, it is almost universally applicable because trace organics are found in the wastewater of almost every industrial plant.

The major benefits of carbon treatment include applicability to a wide variety of organics, with high removal efficiency. Inorganics such as cyanide, chromium, and mercury are also removed effectively. Variations in concentration and flow rate are well tolerated. The system is compact, and recovery of adsorbed materials is sometimes practical. However, destruction of adsorbed compounds often occurs during thermal regeneration. If carbon cannot be thermally desorbed, it must be disposed of along with any adsorbed pollutants. When thermal regeneration is utilized, capital and operating costs are relatively high. Cost surveys show that thermal regeneration is generally economical when carbon usage exceeds about 454 kg/day (1,000/lbday). Carbon cannot remove low molecular weight or highly soluble organics. It also has a low tolerance for suspended solids, which must be removed to at least 50 ppm in the influent water.

This system should be very reliable assuming upstream protection and proper operation and maintenance procedures. It requires periodic regeneration or replacement of spent carbon and is dependent upon raw waste load and process efficiency. Solid waste from this process is contaminated activated carbon that requires disposal. If the carbon undergoes regeneration, the solid waste problem is reduced because of much less frequent replacement.

## Performance

Carbon adsorption, when applied to well-treated secondary effluent, is capable of reducing COD to less than 10 mg/l and BOD to under 2 mg/l. Removal efficiencies may be in the range of 30% to 90% and vary with flow variations and different bed loadings. Carbon loadings in tertiary treatment plants fall within the range of 0.25 to 0.87 kg of COD removed per kg of carbon, and if the columns are operated downflow, over 90% suspended solids reduction may be achieved.

Quite frequently, segregated industrial waste streams are treated with activated carbon. The contaminants removed include BOD, TOC, phenol, color, cresol, polyesters, polynitrophenol, toluene, p-nitrophenol, p-chlorobenzene, chlorophenols, insecticides, cyanides and other chemicals, mostly organic. The flows being treated are generally small in comparison with tertiary systems (less than 75,700 liters/day (20,000 gpd)).

Thermal reactivation of the carbon does not become common until flows are above 227,100 liters/day (60,000 gpd). Some installations reactivate their carbon chemically and the adsorbate is recovered. Recoverable adsorbates are known to include phenol, acetic acid, p-nitrophenol, p-chlorobenzene, p-cresol, and ethylene diamine. Carbon loadings approach one kg COD removal per kg carbon in installations where the adsorbates are easily adsorbed and present in relatively high concentrations. In other cases, where influent concentrations are lower and where the adsorbates are not readily adsorbed, much lower loadings will result. For example, it was determined that brine wastewaters containing 150-750 ppm phenol and 1500-1800 ppm acetic acid could be reduced to about 1 ppm phenol and 100-200 ppm acetic acid with phenol loadings in the range of 0.09-0.16 kg per kg and acetic acid loadings in the range of 0.04-0.06 kg per kg.

From metal finishing, loadings for cyanide removal have been found to be on the order of 0.01 kg for influent concentrations around 100 ppm. Loadings for removal of hexavalent chromium have been shown to be as high as 0.07 kg/kg carbon at 100 ppm and 0.14 kg/kg carbon at 1000 ppm.

EPA isotherm tests have indicated that activated carbon is very effective in adsorbing 65 percent of the organic priority pollutants and reasonably effective for another 22 percent. Specifically, for the organics of particular interest, activated carbon was very effective in removing 2,4-dimethylphenol, fluoranthene, isophorone, naphthalene, all phthalates, and phenanthrene. It was reasonably effective on 1,1,1-trichloroethane, 1,1-dichloroethane, phenol, and toluene. Table 7-80 summarizes the treatability effectiveness for most of the organic priority pollutants by activated carbon as compiled by EPA. Table 7-81 summarizes classes of organic compound together with examples of organics that are readily adsorbed on carbon.

## TABLE 7-80

### TREATABILITY RATING OF PRIORITY POLLUTANTS UTILIZING CARBON ADSORPTION

| Priority Pollutant | *Removal Rating |
|---|---|
| 1. acenaphthene | H |
| 2. acrolein | L |
| 3. acrylonitrile | L |
| 4. benzene | M |
| 5. benzidine | H |
| 6. carbon tetrachloride (tetrachloromethane) | M |
| 7. chlorobenzene | H |
| 8. 1,2,4-trichlorobenzene | H |
| 9. hexachlorobenzene | H |
| 10. 1,2-dichloroethane | M |
| 11. 1,1,1-trichloroethane | M |
| 12. hexachloroethane | H |
| 13. 1,1-dichloroethane | M |
| 14. 1,1,2-trichloroethane | M |
| 15. 1,1,2,2-tetrachloroethane | H |
| 16. chloroethane | L |
| 17. bis(chloromethyl)ether | - |
| 18. bis(2-chloroethyl)ether | M |
| 19. 2-chloroethyl vinyl ether (mixed) | L |
| 20. 2-chloronaphthalene | H |
| 21. 2,4,6-trichlorophenol | H |
| 22. parachlorometa cresol | H |
| 23. chloroform (trichloromethane) | L |
| 24. 2-chlorophenol | H |
| 25. 1,2-dichlorobenzene | H |
| 26. 1,3-dichlorobenzene | H |
| 27. 1,4-dichlorobenzene | H |
| 28. 3,3'-dichlorobenzidine | H |
| 29. 1,1-dichloroethylene | L |
| 30. 1,2-trans-dichloroethylene | L |
| 31. 2,4-dichlorophenol | H |
| 32. 1,2-dichloropropane | M |
| 33. 1,2-dichloropropylene (1,3,-dichloropropene) | M |
| 34. 2,4-dimethylphenol | H |
| 35. 2,4-dinitrotoluene | H |
| 36. 2,6-dinitrotoluene | H |
| 37. 1,2-diphenylhydrazine | H |
| 38. ethylbenzene | M |
| 39. fluoranthene | H |
| 40. 4-chlorophenyl phenyl ether | H |
| 41. 4-bromophenyl phenyl ether | H |
| 42. bis(2-chloroisopropyl)ether | M |
| 43. bis(2-chloroethoxy)methane | M |
| 44. methylene chloride (dichloromethane) | L |
| 45. methyl chloride (chloromethane) | L |
| 46. methyl bromide (bromomethane) | L |
| 47. bromoform (tribromomethane) | H |
| 48. dichlorobromomethane | M |
| 49. trichlorofluoromethane | M |
| 50. dichlorodifluoromethane | L |
| 51. chlorodibromomethane | M |
| 52. hexachlorobutadiene | H |
| 53. hexachlorocyclopentadiene | H |
| 54. isophorone | H |
| 55. naphthalene | H |
| 56. nitrobenzene | H |
| 57. 2-nitrophenol | H |
| 58. 4-nitrophenol | H |
| 59. 2,4-dinitrophenol | H |
| 60. 4,6-dinitro-o-cresol | H |
| 61. N-nitrosodimethylamine | M |
| 62. N-nitrosodiphenylamine | H |
| 63. N-nitrosodi-n-propylamine | M |
| 64. pentachlorophenol | H |
| 65. phenol | M |
| 66. bis(2-ethylhexyl)phthalate | H |
| 67. butyl benzyl phthalate | H |
| 68. di-n-butyl phthalate | H |
| 69. di-n-octyl phthalate | H |
| 70. diethyl phthalate | H |
| 71. dimethyl phthalate | H |
| 72. 1,2-benzanthracene (benzo (a)anthracene) | H |
| 73. benzo(a)pyrene (3,4-benzo-pyrene) | H |
| 74. 3,4-benzofluoranthene (benzo(b)fluoranthene) | H |
| 75. 11,12-benzofluoranthene (benzo(k)fluoranthene) | H |
| 76. chrysene | H |
| 77. acenaphthylene | H |
| 78. anthracene | H |
| 79. 1,12-benzoperylene (benzo (ghi)-perylene) | H |
| 80. fluorene | H |
| 81. phenanthrene | H |
| 82. 1,2,5,6-dibenzathracene (dibenzo (a,h) anthracene) | H |
| 83. indeno (1,2,3-cd) pyrene (2,3-o-phenylene pyrene) | H |
| 84. pyrene | - |
| 85. tetrachloroethylene | M |
| 86. toluene | M |
| 87. trichloroethylene | L |
| 88. vinyl chloride (chloroethylene) | L |
| 106. PCB-1242 (Arochlor 1242) | H |
| 107. PCB-1254 (Arochlor 1254) | H |
| 108. PCB-1221 (Arochlor 1221) | H |
| 109. PCB-1332 (Arochlor 1232) | H |
| 110. PCB-1248 (Arochlor 1248) | H |
| 111. PCB-1260 (Arochlor 1260) | H |
| 112. PCB-1016 (Arochlor 1016) | H |

* NOTE: Explanation of Removal RAtings

Category H (high removal)
adsorbs at levels $\geq$ 100 mg/g carbon at $C_f$ = 10 mg/l
adsorbs at levels $\geq$ 100 mg/g carbon at $C_f$ < 1.0 mg/l

Category M (moderate removal)
adsorbs at levels $\geq$ 100 mg/g carbon at $C_f$ = 10 mg/l
adsorbs at levels $\leq$ 100 mg/g carbon at $C_f$ < 1.0 mg/l

Category L (low removal)
adsorbs at levels < 100 mg/g carbon at $C_f$ = 10 mg/l
adsorbs at levels < 10 mg/g carbon at $C_f$ < 1.0 mg/l

$C_f$ = final concentrations of priority pollutant at equilibrium

## TABLE 7-81

## CLASSES OF ORGANIC COMPOUNDS ADSORBED ON CARBON

| Organic Chemical Class | Examples of Chemical Class |
|---|---|
| Aromatic Hydrocarbons | benzene, toluene, xylene |
| Polynuclear Aromatics | naphthalene, anthracene biphenyls |
| Chlorinated Aromatics | chlorobenzene, polychlorinated biphenyls, aldrin, endrin, toxaphene, DDT |
| Phenolics | phenol, cresol, resorcenol and polyphenyls |
| Chlorinated Phenolics | trichlorophenol, pentachlorophenol |
| *High Molecular Weight Aliphatic and Branch Chain Hydrocarbons | gasoline, kerosine |
| Chlorinated Aliphatic Hydrocarbons | 1,1,1-Trichloroethane, trichloroethylene, carbon tetrachloride, perchloroethylene |
| *High Molecular Weight Aliphatic Acids and Aromatic Acids | tar acids, benzoic acid |
| *High Molecular Weight Aliphatic Amines and Aromatic Amines | aniline, toluene diamine |
| *High Molecular Weight Ketones, Esters, Ethers & Alcohols | hydroquinone, polyethylene glycol |
| Surfactants | alkyl benzene sulfonates |
| Soluble Organic Dyes | methylene blue, Indigo carmine |

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* High Molecular Weight includes compounds in the range of 4 to 20 carbon atoms

Samples were taken of influent and effluent streams around the carbon adsorption unit at Plant ID 38040. The results of this sampling are presented in Table 7-82.

TABLE 7-82
PERFORMANCE OF CARBON ADSORPTION AT PLANT 38040
(mg/l)

| | Day 1 | | Day 2 | |
|---|---|---|---|---|
| Parameter | Influent | Effluent | Influent | Effluent |
| oil and Grease | 4.1 | 3.3 | 41.0 | 2.0 |
| BOD | 58.0 | * | 53.0 | 8.0 |
| TOC | 93.9 | 87.7 | 108.0 | 77.5 |
| TSS | 14.0 | 11.0 | 1.0 | 9.0 |
| TTO | 1.02 | 0.29 | 1.40 | 0.38 |

* Lab analysis experienced interference

Demonstration Status

Carbon adsorption systems have been demonstrated to be practical and economical for the reduction of COD, BOD and related parameters in secondary municipal and industrial wastewaters; for the removal of toxic or refractory organics from isolated industrial wastewaters; for the removal and recovery of certain organics from wastewaters; and for the removal, at times with recovery, of selected inorganic chemicals from aqueous wastes. Carbon adsorption must be considered a viable and economic process for organic waste streams containing up to 1-5% of refractory or toxic organics; its applicability for removal of inorganics such as metals, although demonstrated in a few cases, is probably much more limited.

Carbon adsorption is being used in 10 plants in the present Metal Finishing Category data base. These plants are identified in Table 7-83.

TABLE 7-83
METAL FINISHING PLANTS EMPLOYING CARBON ADSORPTION

04236
04690
12065
14062
17061
18538
19120
25033
31044
38040

## Reverse Osmosis

A detailed description of reverse osmosis along with information on general applicability and demonstration status are presented in "Treatment of Oily Waste." Reverse osmosis or carbon adsorption are considered effective polishing techniques for wastewaters containing toxic organics.

### Performance Data

Table 7-84 presents the performance data for TTO for reverse osmosis.

TABLE 7-84

TTO PERFORMANCE DATA (mg/ℓ) FOR REVERSE OSMOSIS

| Plant ID | Influent | Effluent |
|---|---|---|
| 38040-23-0 | 4.301 | 1.018 |
| 38040-23-1 | 0.887 | 1.401 |
| 30166-21-0 | 1.413 | 0.774 |

## Resin Adsorption

Adsorption of trace organics on synthetic resins is similar to adsorption on activated carbon. The basic materials are different and the means of regeneration are different. A potential advantage is that resins are more easily tailored for removal of specific pollutants.

The resins are generally microporous styrene-divinylbenzenes, acrylic esters, or phenol-formaldehydes. Each type may be produced in a range of densities, void volumes, bulk densities, surface areas, and pore sizes. The formaldehyde resins are granular, and the others are in the form of beads.

Adsorptive resins are in limited commercial use for removal of priority and other organics. There are existing operations for removal of phenols in two plants (one in Indiana and the other at a coal liquefaction plant in West Virginia), for removal of fats at a food processing plant, and for removal of organic dyes at several plants. Pilot plant operations have been designed for removal of trinitrotoluene, 2,4-dinitrotoluene, cyclomethylene-trinitramine, cyclotetramethylenetetranitramine, Endrin, other pesticides, laboratory carcinogens (unspecified), 2,4-dichlorophenol, ethylene dichloride, and vinyl chloride. In a non-industrial application, organic carbon removal efficiency decreased from 58 percent to 40 percent during a through-put of 5,000 bed volumes, with an input concentration of about 6 mg/ℓ.

Regeneration of the resins is done chemically, while regeneration of activated carbon is thermal. The chemical may be an inorganic acid, base, or salt, or an organic solvent such as acetone.

## Ozonation

Ozone is effective in the treatment of phenols. It is about twice as powerful as hydrogen peroxide and is not as selective; thus it oxidizes a wider range of material. For low concentration phenolic wastes, the usual practice is to oxidize the phenolic compound to intermediate organic compounds that are toxic but readily biodegrdable. For this application, ozone requirements are in the range of 1.5 to 2.5 parts of ozone per part of phenol. As the concentration decreases, the relative amount of ozone needed increases. If other material with COD is present, the ozone requirement will be still greater. When pH values of 11.5 to 11.8 are maintained, this range appears to result in selective or preferential oxidation of phenol over other substances.

For concentrated or intermediate level phenolic wastes chemical oxidation by ozone may not be economical as a primary treatment system; however, it is useful as a polishing process following a biological system. In treating phenolic refinery wastes, ozone is used as tertiary treatment to produce final effluents as low as 3 ug/l phenol.

Several manufacturers have begun using ozone for the treatment of phenolic industrial wastewaters. They are listed and briefly described below:

A. An oil refinery in Canada treats waste effluent of 1,514,000 liters/day (400,000 gallons/day) with the phenol concentration averaging 50 mg/l.

   Pretreatment consists of pre-aeration and a biological trickling filter. Ozonation is the final treatment step and utilization is 86 kg/day (190 pounds/day). This treatment results in an effluent of less than 0.012 mg/l residual phenol.

B. A manufacturer of a thermoplastic resin in New York treats a phenolic effluent by biological oxidation. Further treatment was necessary to meet state standards. The effluent had a high COD of about 1500 mg/l which competed with the phenol for ozone; therefore a large ozone dosage level, 300 ppm, was required to reach the desired phenol effluent concentration. At a flow rate of 946,250 liters/day (0.25 MGD), a total of 283.5 kg (625 pounds) of ozone was required daily. The air feed generating equipment represents a capital investment of $220,000 and requires daily operating expenditures of $98.43 including electrical costs of 1.5¢/kwh. Concurrent with phenol removal, 30 percent of the color, 29 percent of the turbidity and 17 percent of the COD were removed.

C. Study of various coke plant wastes shows that various ozone requirements are necessary to oxidize the phenol. The results are displayed in Table 7-85. The great variation in the ozone-to-phenol ratios of samples from different sources illustrates the differences in the composition of the wastes.

TABLE 7-85
OZONE REQUIREMENTS FOR PHENOL OXIDATION

| Source | Initial Phenols mg/l | Ozone Demand mg/l | Ozone/ Phenol ratio | Residual Phenols mg/l |
|---|---|---|---|---|
| Coke Plant A | 1240 | 2500 | 2.0 | 1.2 |
| " " B | 800 | 1200 | 1.5 | 0.6 |
| " " C | 330 | 1700 | 5.2 | 1.0 |
| " " D | 140 | 950 | 6.8 | 1.0 |
| " " E | 127 | 550 | 4.3 | 0.2 |
| " " F | 102 | 900 | 8.8 | 0.0 |
| " " G | 51 | 1000 | 20 | 0.4 |
| " " H | 38 | 700 | 18 | 0.1 |
| Chemical " A* | 290 | 400 | 1.4 | 0.3 |
| Refinery A | 605 | 11,000 | 18.0 | 2.5 |

*This plant effluent contained 2,4-dichlorophenol and the results are expressed as such.

There are 40 to 50 commercial installations utilizing ozone for bleach regeneration and photoprocessing wastewater treatment. Ozone is also effective in treating wastewaters containing other organics and organo-metal complexes. In organo-metal complexes the metals can be released and then precipitated. One kilogram of COD should consume three kilograms of ozone and yield two kilograms of molecular oxygen.

## Chemical Oxidation

Chemical oxidation can be effective in destroying some of the priority organic compounds. Oxidation can be accomplished by ozone, by ozone with ultraviolet radiation, by hydrogen peroxide, and possibly by electrolytic oxidation. Oxidation by chlorine is more likely to generate priority organics than to destroy them.

These oxidation techniques are used industrially primarily for cyanide destruction. They are therefore discussed in detail under the general heading of "Treatment of Cyanide Wastes", earlier in this section. Where information is available, these discussions include consideration of ability to destroy priority organics.

## Aerobic Decomposition

Aerobic decomposition is the biochemically actuated decomposition or digestion of organic materials in the presence of oxygen. The chemical agents effecting the decomposition are microorganism secretions termed enzymes. The principal products in a properly controlled aerobic decomposition are carbon dioxide and water. Aerobic decomposition is used mainly in the treatment of organic chemicals and lubricants used in the film industry and such other industries that use organic lubricants.

As a waste treatment aid, aerobic decomposition plays an important role in the following organic waste treatment processes:

1. Activated Sludge Process
2. Trickling Filter Process
3. Aerated Lagoon

The activated sludge process consists of the aeration of a biodegradable waste for a sufficient time to allow the formation of a large mass of settleable solids. These settleable solids are masses of living microorganisms and are termed activated sludge.

A schematic diagram of the basic process is shown as Figure 7-41. The wastes enter the aeration tank after being mixed with return sludge. The microorganisms from the returned sludge aerobically stabilize the organic mixture which then flows to a sedimentation tank. Sedimentation allows the activated sludge to flocculate and to settle out, producing a clear effluent of low organic content. A portion of the waste sludge is returned to the aeration tank, thereby repeating the process. Excess sludge is discharged from the process for further treatment or disposal.

The trickling filter is basically a bed of stones or other suitable material covered with slime over which organic wastes slowly flow. A schematic cross section of a trickling filter is shown as Figure 7-42. As wastewater passes through the filter, it diffuses into the slimes where aerobic and anaerobic decomposition occurs. After primary sedimentation, the wastewater is introduced onto the filter by a rotary distributor so designed that the wastes are discharged at a uniform volume per unit of filter surface. The waste flows by gravity over the filter bed into an underdrain system. The liquid is collected into a main effluent channel which flows to a final sedimentation tank. A schematic diagram of a single stage trickling

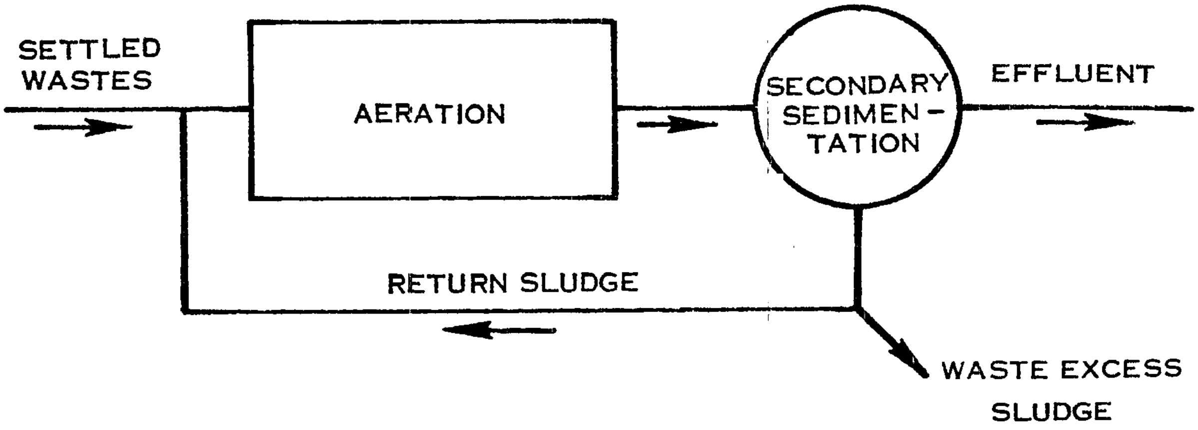

FIGURE 7-41

SCHEMATIC DIAGRAM OF A CONVENTIONAL ACTIVATED SLUDGE SYSTEM

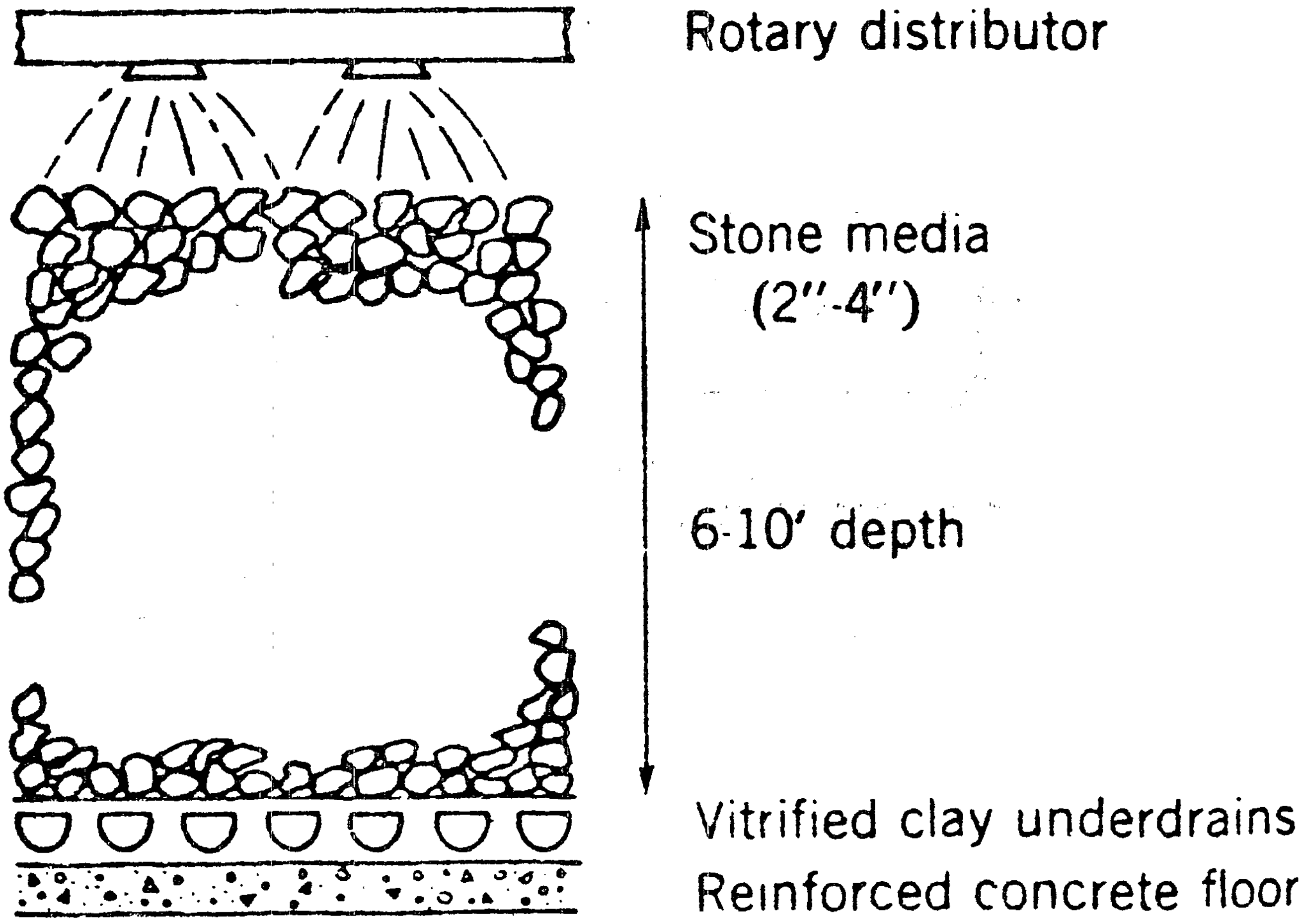

FIGURE 7-42

SCHEMATIC CROSS SECTION OF A TRICKLING FILTER

filter is shown as Figure 7-43.

An aerated lagoon is a large shallow pond to which raw waste is added at one end or in the center and the treated effluent discharged at the other end. Aeration is accomplished by mechanical aerators or diffusers in the wastewater. Aerobic decomposition is one of the factors involved in degradation of the organic matter and is carried out by bacteria in a manner similar to activated sludge. It is necessary to periodically dredge the oxidation pond in order to maintain the proper ecological balance.

### Application

Aerobic decomposition can be applied to the treatment of oily wastes from the Metal Finishing Category.

Advantages of aerobic decomposition include 1) low BOD concentrations in supernatant liquor, 2) production of an odorless, humuslike, biologically stable end product with excellent dewatering characteristics that can be easily disposed, 3) recovery of more of the basic fertilizer values in the sludge, and 4) few operational problems and low initial cost. The major disadvantages of the aerobic decomposition process are 1) high operational cost associated with supplying the required oxygen, and 2) sensitivity of the bacterial population to small changes in the characteristics of their environment.

Reliability can be high, assuming adequate temperature, pH, detention time, and oxygen content control. Prior treatment to eliminate substances toxic to the microorganisms affecting decomposition may be necessary. (In some cases, adaptation will increase the tolerance level of the microorganisms for toxic substances).

Maintenance of the three main waste treatment techniques employing aerobic decomposition is detailed in the following Table 7-86.

TABLE 7-86
Maintenance Techniques for Aerobic Decomposition

| Process | Maintenance |
|---|---|
| Activated Sludge | Periodic removal of excess sludge and skimming of scum layer. |
| Trickling Filter | Periodic application of insecticides to reduce the insect population and periodic chlorination to reduce excess bacterial population. |
| Aerated Lagoon | Periodic dredging to remove excess sludge, and periodic aeration to maintain the pond's aerobic character. |

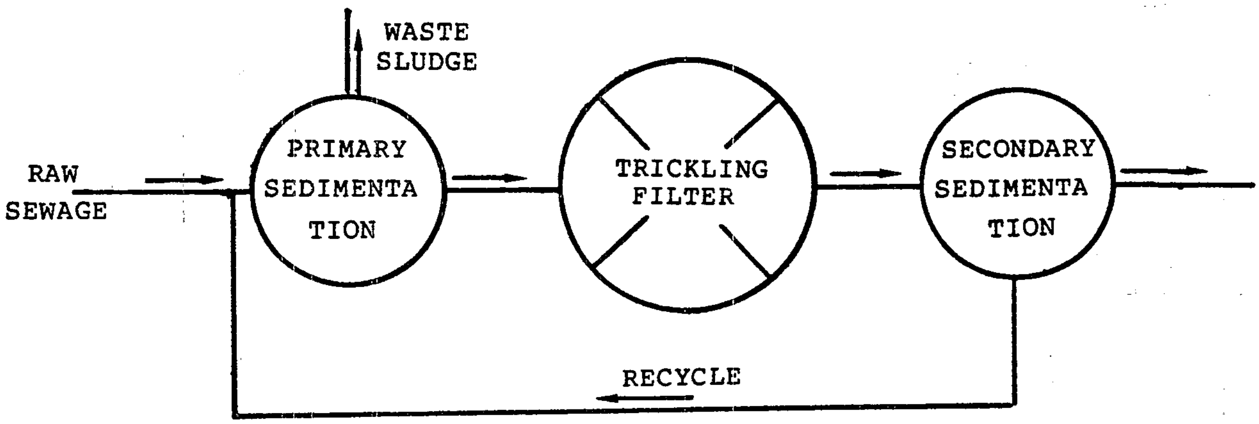

FIGURE 7-43

SCHEMATIC DIAGRAM OF A SINGLE-STAGE TRICKLING FILTER

## Performance

Aerobic decomposition is very effective for organic constituents that are readily biodegradeable. The toxic organics, however, represent a range of biodegradability. Performance of a pilot scale activated sludge system is reported in "Removal of Organic Constituents in a Coal Gasification Process Wastewater by Activated Sludge Treatment," Argonne National La;oratory, 1979. In this system, phenol was reduced from 250 mg/ℓ to an undetectable level, naphthalene was reduced from 0.405 to 0.009 mg/ℓ, and ethylbenzene at 0.015 mg/ℓ concentration was not reduced.

Another source of information on organics (Handbook of Environmental Data on Organic Chemicals, Verschueren, 1977) indicates treatability for a number of priority organics. These data are summarized in Table 7-87.

An additional source of toxic organics performance information are the BAT limitations for the organic chemicals industry developed using data from plants using biological treatment. These limits, proposed by EPA in March 21, 1983, are presented in Table 7-88.

The activated sludge process also reduces concentrations of toxic metals, by agglomeration of precipitates and by adsorption of dissolved metals. However, effectiveness ;is highly variable and unpredictable.

TABLE 7-87
ACTIVATED SLUDGE REMOVAL OF SOME PRIORITY ORGANIC COMPOUNDS

| Compound | Influent Concentration (mg/ℓ) | Reported Removal Efficiency, Percent |
|---|---|---|
| Benzene | 500 | 33 |
| 1,2-Dichloroethane | 200 | 45 |
| " " | 400 | 30 |
| " " | 1000 | 9 |
| 2,4-Dimethylphenol | --- | 94.5 |
| Ethylbenzene | 500 | 27 |
| " " | 50-100 | 8 |
| Phenol | 500 | 33 |

## TABLE 7-88
## PROPOSED BAT EFFLUENT LIMITATIONS FOR THE ORGANIC CHEMICALS INDUSTRY

| Toxic Organic | BAT Effluent Limitations (mg/ℓ)<br>Maximum For Any 1 Day | Average of Daily Values for 4 Consecutive Monitoring Days |
|---|---|---|
| 2,4,6-trichlorophenol | 175 | 100 |
| 2-chlorophenol | 75 | 50 |
| 2,4-dichlorophenol | 200 | 100 |
| 2,4-dimethylphenol | 50 | -- |
| 2-nitrophenol | 100 | 75 |
| 4-nitrophenol | 500 | 325 |
| 2,4-dinitrophenol | 150 | 100 |
| pentachlorophenol | 100 | 50 |
| phenol | 50 | -- |
| acenaphthene | 50 | -- |
| 1,2,4-trichlorobenzene | 225 | 125 |
| 1,2-dichlorobenzene | 250 | 125 |
| isophorone | 50 | -- |
| bis(2-ethylhexyl) phthalate | 350 | 150 |
| di-n-butyl phthalate | 300 | 150 |
| diethyl phthalate | 275 | 125 |
| dimethyl phthalate | 375 | 175 |
| acenaphthylene | 50 | -- |
| fluorene | 50 | -- |
| phenanthrene | 50 | -- |
| benzene | 125 | 75 |
| carbon tetrachloride | 50 | -- |
| 1,2-dichloroethane | 150 | 100 |
| 1,1,1-trichloroethane | 50 | -- |
| 1,1-dichloroethane | 225 | 125 |
| 1,1,2-trichloroethane | 75 | 50 |
| chloroethane | 50 | -- |
| chloroform | 75 | 50 |
| 1,1-dichloroethylene | 125 | 75 |
| ethylbenzene | 275 | 150 |
| methylene chloride | 50 | -- |
| methyl chloride | 50 | -- |
| methyl bromide | 50 | -- |
| dichlorobromomethane | 50 | -- |
| toluene | 225 | 125 |
| trichloroethylene | 75 | 50 |

## Demonstration Status

Aerobic digestion is a widely used unit process to reduce organic content of wastewaters. It is currently employed at 14 of the plants in the data base. These plants are identified in Table 7-89.

TABLE 7-89
METAL FINISHING PLANTS EMPLOYING AEROBIC DECOMPOSITION

05050
06067
08172
11050
11560
11179
13031
14062
23041
30927
31050
33050
33263
44050

## TREATMENT OF SLUDGES

### INTRODUCTION

Sludges are created by waste treatment alternatives which remove solids from wastewater. Removal of sludges from the treatment system as soon as possible in the treatment process minimizes returning pollutants to the waste stream through re-solubilization. One plant visited during this program (ID# 23061) utilized a settling tank in their treatment system that required periodic cleaning. Such cleaning had not been done for some time, and analysis of both their raw and treated wastes showed little difference. The accumulation of sludge apparently decreased the effective residence time to a point where the sedimentation process was unsuccessful. Subsequent pumping out of this settling tank resulted in an improved effluent (Reference Table 7-90).

Once removed from the primary effluent stream, waste sludges must be disposed of properly. If landfills are used for sludge disposal, the landfill must be designed to prevent material from leaching back into the water supply. Mixing of waste sludges which might form soluble compounds should be prevented. If sludge is disposed of by incineration, the burning must be carefully controlled to prevent air pollution. A licensed scavenger may be substituted for plant personnel to oversee disposal of the removed sludge.

TABLE 7-90
COMPARISON OF WASTEWATER AT PLANT ID 23061
BEFORE AND AFTER PUMPING OF SETTLING TANK

| Parameter | Concentration (mg/l) Before Sludge Removal | | Concentration (mg/l) After Sludge Removal | |
|---|---|---|---|---|
| | Total Raw Waste | Treated Effluent | Total Raw Waste | Treated Effluent |
| Cyanide, Amen. to Chlorination | 0.007 | 0.001 | 0.005 | 0.005 |
| Cyanide, Total | 0.025 | 0.035 | 0.005 | 0.005 |
| Phosphorus | 2.413 | 2.675 | 14.35 | 13.89 |
| Silver | 0.001 | 0.001 | 0.002 | 0.003 |
| Gold | 0.007 | 0.010 | 0.005 | 0.005 |
| Cadmium | 0.001 | 0.006 | 0.005 | 0.002 |
| Chromium, Hexavalent | 0.005 | 0.105 | 0.005 | 0.005 |
| Chromium, Total | 0.023 | 0.394 | 0.010 | 0.006 |
| Copper | 0.028 | 0.500 | 0.127 | 0.034 |
| Iron | 0.885 | 3.667 | 2.883 | 1.718 |
| Fluoride | 0.16 | 0.62 | 0.94 | 0.520 |
| Nickel | 0.971 | 1.445 | 0.378 | 0.312 |
| Lead | 0.023 | 0.034 | 0.007 | 0.014 |
| Tin | 0.025 | 0.040 | 0.121 | 0.134 |
| Zinc | 0.057 | 0.185 | 0.040 | 0.034 |
| Total Suspended Solids | 17.0 | 36.00 | 67.00 | 4.00 |

## TREATMENT TECHNIQUES

Sludges can typically vary between one and five percent solids. The sludge should be dewatered to lessen space requirements if sludges are landfilled on the plant site and to decrease shipping costs if sludges are hauled away by a contractor. Applicable sludge dewatering techniques include gravity sludge thickening, pressure filtration, vacuum filtration, centrifugation and sludge bed drying. These techniques are discussed in the following subsections.

### Gravity Sludge Thickening

In the gravity thickening process, dilute sludge is fed from a primary settling tank or clarifier to a thickening tank. Rakes stir the sludge gently to densify the sludge and to push it to a central collection well. The supernatant is returned to the primary settling tank. The thickened sludge that collects on the bottom of the tank is pumped to dewatering equipment or hauled away. Figure 7-44 shows the construction of a gravity thickener.

### Application

Thickeners are generally used in facilities where the sludge is to be further dewatered by a compact mechanical device such as a vacuum filter or centrifuge. Doubling the solids content in the thickener substantially reduces capital and operating cost of the subsequent dewatering device and also reduces cost for hauling. The process is potentially applicable to almost any industrial plant.

The principal advantage of a gravity sludge thickening process is that it facilitates further sludge dewatering. Other advantages are high reliability and minimum maintenance requirements. Limitations of the sludge thickening process are its sensitivity to the flow rate through the thickener and the sludge removal rate. These rates must be low enough not to disturb the thickened sludge.

Reliability is high assuming proper design and operation. A gravity thickener is designed on the basis of square feet per pound of solids per day, entering and leaving the unit. Thickener area requirements are also expressed in terms of mass loading, grams of solids per square meter per day (pounds per square foot per day).

Twice a year, a thickener must be shut down for lubrication of the drive mechanisms. Occasionally, water must be pumped back through the system in order to clear sludge pipes. Thickened sludge from a gravity thickening process will usually require further dewatering prior to disposal, incineration, or drying. The clear effluent may be recirculated in part, or it may be subjected to further treatment prior to discharge.

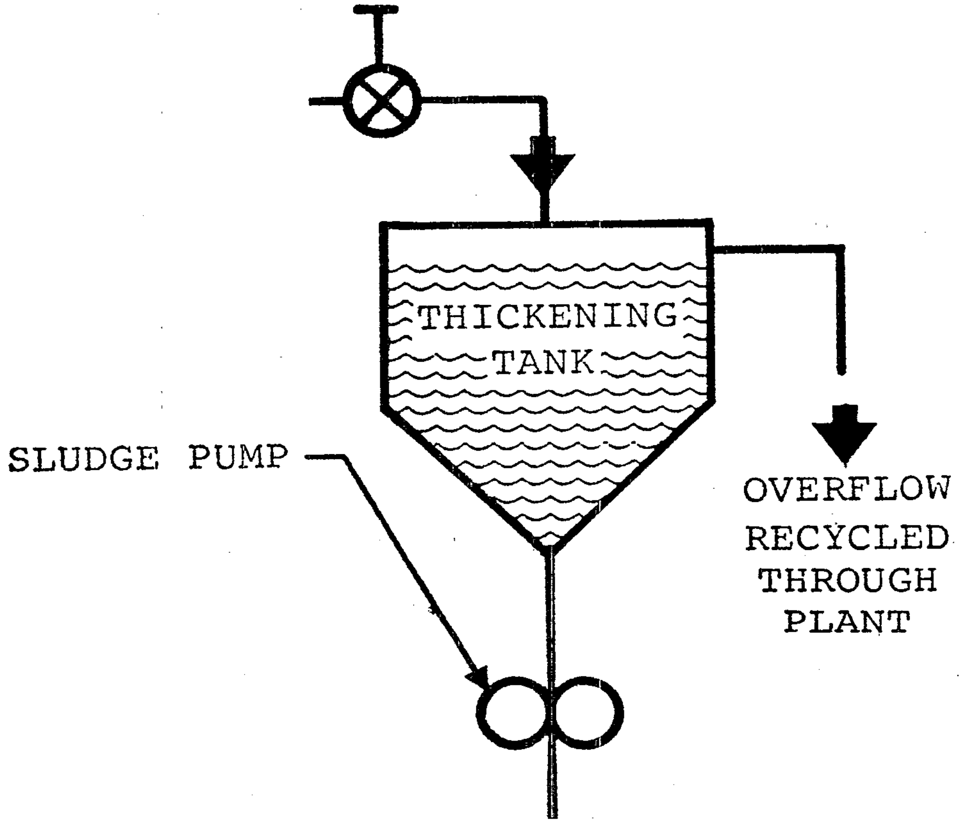

FIGURE 7-44
MECHANICAL GRAVITY THICKENING

## Performance

Organic sludges from sedimentation units of one to two percent solids concentration can usually be gravity thickened to six to ten percent; chemical sludges can be thickened to four to six percent.

## Demonstration Status

Gravity sludge thickeners are used throughout industry to reduce water content to a level where the sludge may be efficiently handled. Further dewatering is usually practiced to minimize costs of hauling the sludge to approved landfill areas.

Sludge thickening is used in 78 plants in the present data base. These are identified in Table 7-91.

TABLE 7-91
METAL FINISHING PLANTS EMPLOYING GRAVITY/SLUDGE THICKENING

03043
04069
04071
04263
04719
04981
05021
05035
06052
08004
11156
11177
11182
11704
12033
12074
12075
12078
12091
12100
12102
12709
13031
13040
14061
15042
15044
17061
18050
18091
19063
20005
20010
20064
20073
20075
20078
20082
20085
20116
20120
20157
20165
20248
20291
21078
23062
23337
25001
27044
28082
28115
30079
30087
30090
30151
30153
30927
30967
33065
33070
33113
33120
36085
36090
36091
36092
36112
36130
36180
36623
40061
40063
41151
43003
43052
44044
62032

## Pressure Filtration

Pressure filtration is achieved by pumping the liquid through a filter material which is impenetrable to the solid phase. The positive pressure exerted by the feed pumps or other mechanical means provides the pressure differential which is the principal driving force. Figure 7-45 represents the operation of one type of pressure filter.

A typical pressure filtration unit consists of a number of plates or trays which are held rigidly in a frame to ensure alignment and are pressed together between a fixed end and a

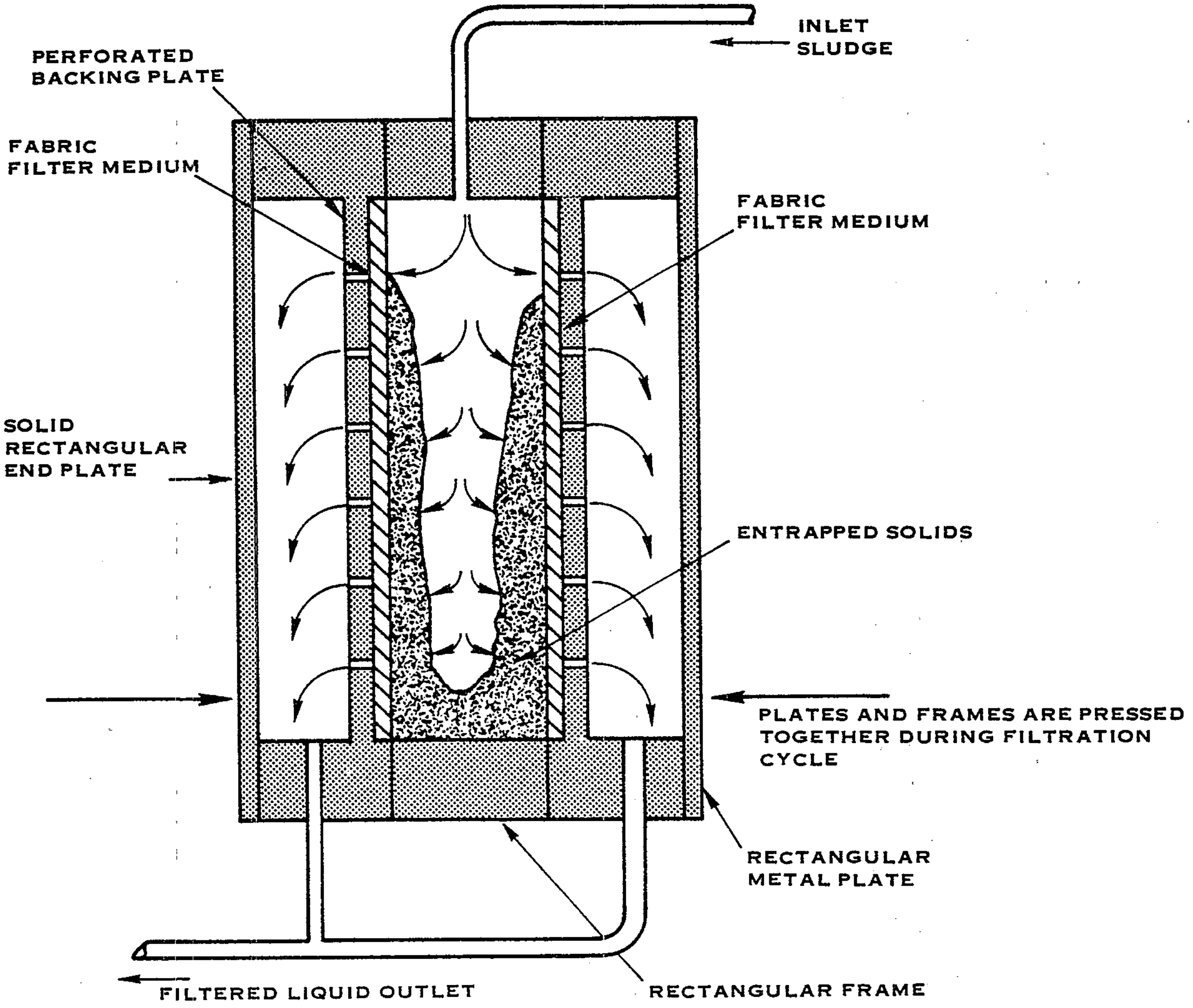

FIGURE 7-45

PRESSURE FILTRATION

traveling end. On the surface of each plate is mounted a filter made of cloth or a synthetic fiber. The sludge is pumped into the unit and passes through feed holes in the trays along the length of the press until the cavities or chambers between the trays are completely filled. The solids in the sludge are then entrapped, and a cake begins to form on the surface of the filter material. The water passes through the fibers, and the solids are retained.

At the bottom of the trays are drainage ports. The filtrate is collected and discharged to a common drain. As the filter medium becomes coated with sludge, the flow of filtrate through the filter drops sharply, indicating that the capacity of the filter has been exhausted. The unit must then be cleaned of the sludge. After the cleaning or replacement of the filter media, the unit is again ready for operation.

## Application

Because dewatering is such a common operation in treatment systems, pressure filtration is a technique which can be found in many industry applications concerned with removing solids from their waste stream.

The pressures which may be applied to a sludge for removal of water by filter presses that are currently available range from 5 to 13 atmospheres. Pressure filtration may also reduce the amount of chemical pretreatment required. The sludge, retained in the form of the filter cake, has a higher percentage of solids than either a centrifuge or vacuum filter yield. Thus, the sludge can be easily accommodated by materials handling systems.

Two disadvantages associated with pressure filtration in the past have been the short life of the filter cloths and lack of automation. New synthetic fibers have largely offset the first of these problems. Also, units with automatic feeding and pressing cycles are now available.

Assuming proper pretreatment, design, and control, pressure filtration is a highly dependable system. Maintenance consists of periodic cleaning or replacement of the filter media, drainage grids, drainage piping, filter pans, and other parts of the system. If the removal of the sludge cake is not automated, additional time is required for this operation. Because it is generally drier than other types of sludges, the filter sludge cake can be handled with relative ease. Disposal of the accumulated sludge may be accomplished by any of the accepted procedures.

## Performance

In a typical pressure filter, chemically preconditioned sludge detained in the unit for one to three hours under pressures varying from 5 to 13 atmospheres exhibited final moisture content between 50 and 75 percent.

### Demonstration Status

Pressure filtration is a commonly used technology that is currently utilized in a great many commercial applications.

Pressure filtration is used in 66 plants in the present data base and these are identified in Table 7-92.

TABLE 7-92
METAL FINISHING PLANTS EMPLOYING PRESSURE FILTRATION

01002
01003
10007
03043
04069
04146
04276
04284
05050
06050
06077
06107
06153
06960
08060
09046
11096
11103
11115
12005
12065
12071
12074
13031
14060
19066
19083
20022
20070
20083
20115
20255
20483
23039
23076
27042
27044
27045
28043
28121
30087
30927
30967
31021
31033
31035
31068
31070
33110
33113
33148
33172
33195
33293
34050
35041
36102
36176
38223
40047
41051
41068
42030
44044
47025
47074

### Vacuum Filtration

In wastewater treatment plants, sludge dewatering by vacuum filtration is an operation that is generally accomplished on cylindrical drum filters. These drums have a filter medium which may be cloth made of natural or synthetic fibers, coil springs, or a wire-mesh fabric. The drum is suspended above and dips into a vat of sludge. As the drum rotates slowly, part of its circumference is subject to an internal vacuum that draws sludge to the filter medium. Water is drawn through the porous filter cake to a discharge port, and the dewatered sludge, loosened by compressed air, is scraped from the filter mesh. Because the dewatering of sludge on vacuum filters is relativley expensive per kilogram of water removed, the liquid sludge is frequently thickened prior to processing. A vacuum filter is shown in Figure 7-46.

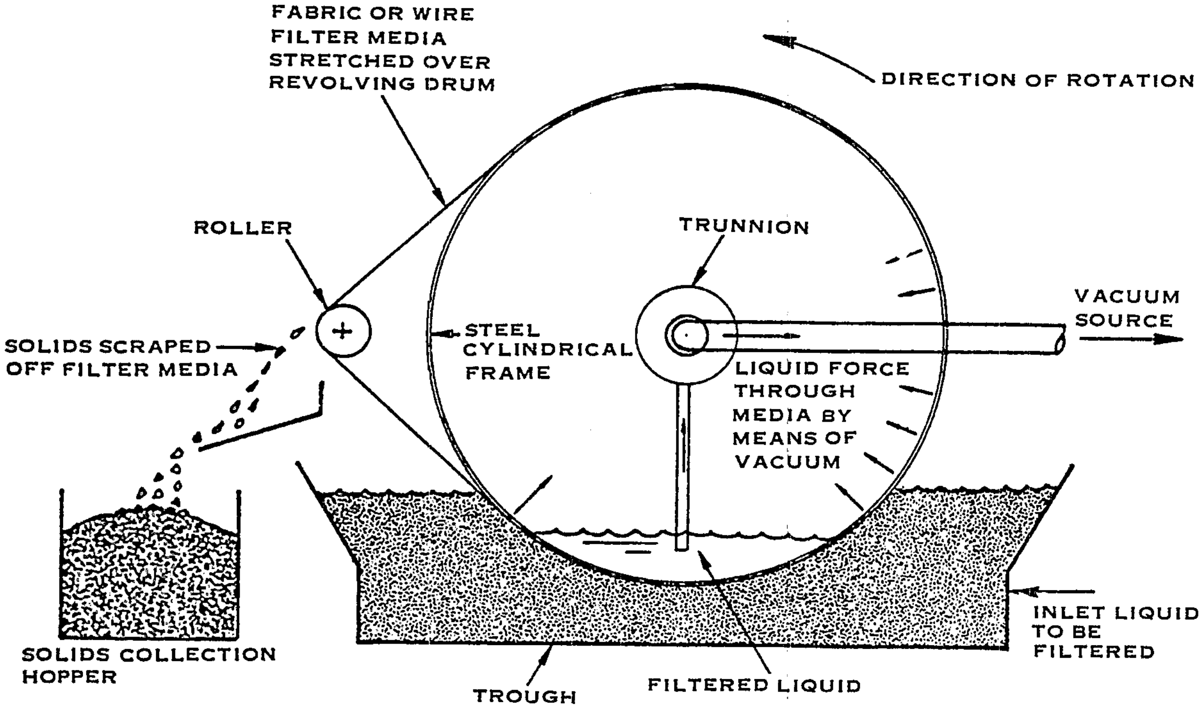

FIGURE 7-46

VACUUM FILTRATION

## Application

Vacuum filters are frequently used both in municipal treatment plants and in a wide variety of industries for dewatering sludge. They are most commonly used in larger facilities, which have a thickener to double the solids content of clarifier sludge before vacuum filtering.

Although the initial cost and area requirement of the vacuum filtration system are higher than those of a centrifuge, the operating cost is lower, and no special provisions for sound and vibration protection need be made. The dewatered sludge from this process is in the form of a moist cake and can be conveniently handled.

Vacuum filter systems have been proven reliable at many industrial and municipal facilities. At present, the largest municipal installation is at the West Southwest wastewater treatment plant of Chicago, Illinois, where 96 large filters were installed in 1925, functioned approximately 25 years, and then were replaced with larger units. Original vacuum filters at Minneapolis-St. Paul, Minnesota now have over 28 years of continuous service, and Chicago has some units with similar or greater service life.

Maintenance consists of the cleaning or replacement of the filter media, drainage grids, drainage piping, filter pans, and other parts of the equipment. Experience in a number of vacuum filter plants indicates that maintenance consumes approximately 5 to 15 percent of the total time. If carbonate buildup or other problems are unusually severe, maintenance time may be as high as 20 percent. If intermittent operation is to be employed, the filter equipment should be drained and washed each time it is taken out of service and an allowance for wash time should be made in the selection of sludge filtering schedules.

Vacuum filters generate a solid cake. All of the metals extracted from the plant wastewater are concentrated in the filter cake as hydroxides, oxides, sulfides, or other salts. These metals are subject to leaching into ground water, especially under acid conditions.

## Performance

The function of vacuum filtration is to reduce the water content of sludge, so that the proportion of solids increases from about 5 percent to about 30 percent.

## Demonstration Status

Vacuum filtration has been widely used for many years. It is a fully proven, conventional technology for sludge dewatering.

Vacuum filtration is used in 67 plants in the present data base and these are identified in Table 7-93.

### TABLE 7-93
### METAL FINISHING PLANTS EMPLOYING VACUUM FILTRATION

02062
03041
03042
06037
06074
06087
06088
06152
09052
09060
11182
11704
12002
12014
12042
12075
12078
12091
12709
15058
15070
16544
17030
18050
19084
19090
20005
20010
20073
20077
20080
20100
20161
20175
20248
20249
20291
21078
28115
30079
30090
30153
30927
31044
31047
33092
33110
33120
33124
33195
33263
34036
36040
36092
36113
36130
36623
38217
40037
40063
40067
40079
41097
41151
42030
43003
44036

## Centrifugation

Centrifugation is the application of centrifugal force to separate solids and liquids in a liquid/solid mixture or to effect concentration of the solids. The application of centrifugal force is effective because of the density differential normally found between the insoluble solids and the liquid in which they are contained. As a waste treatment procedure, centrifugation is applied to dewatering of sludges. One type of centrifuge is shown in Figure 7-47.

There are three common types of centrifuges: the disc, basket, and conveyor type. All three operate by removing solids under the influence of centrifugal force. The fundamental difference between the three types is the method by which solids are collected and discharged.

In the disc centrifuge, the sludge feed is distributed between narrow channels that are present as spaces between stacked conical discs. Suspended particles are collected and discharged continuously through small orifices in the bowl wall. The clarified effluent is discharged through an overflow weir.

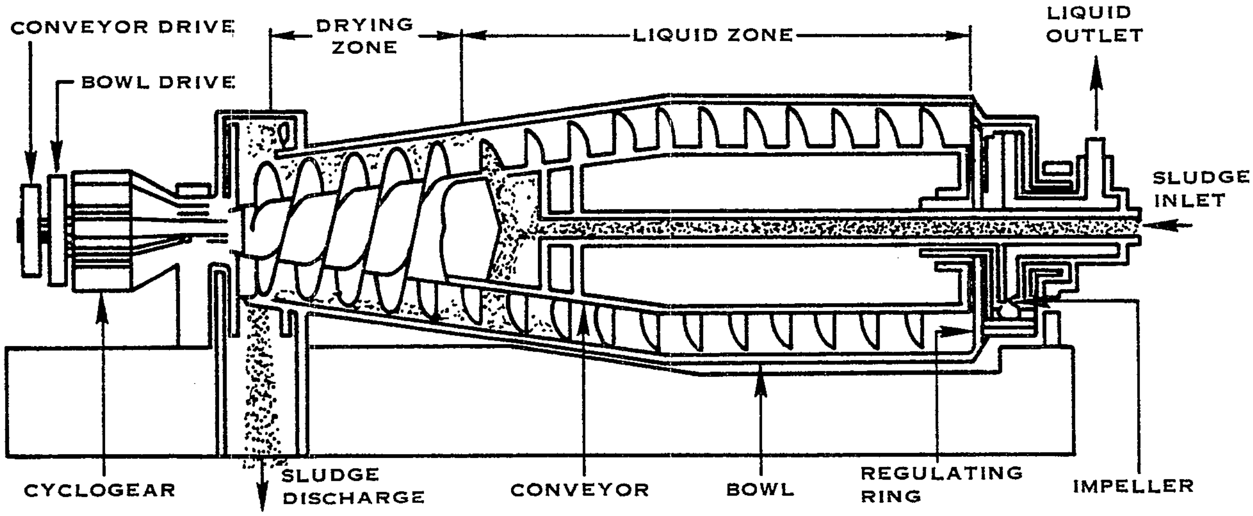

FIGURE 7-47

CENTRIFUGATION

A second type of centrifuge which is useful in dewatering sludges is the basket centrifuge. In this type of centrifuge, sludge feed is introduced at the bottom of the basket, and solids collect at the bowl wall while clarified effluent overflows the lip ring at the top. Since the basket centrifuge does not have provision for continuous discharge of collected cake, operation requires interruption of the feed for cake discharge for a minute or two in a 10 to 30 minute overall cycle.

The third type of centrifuge commonly used in sludge dewatering is the conveyor type. Sludge is fed through a stationary feed pipe into a rotating bowl in which the solids are settled out against the bowl wall by centrifugal force. From the bowl wall, they are moved by a screw to the end of the machine, at which point they are discharged. The liquid effluent is discharged through ports after passing the length of the bowl.

### Application

Virtually all of those industrial waste treatment systems producing sludge can utilize centrifugation to dewater it. Centrifugation is currently being used by a wide range of industrial concerns.

Sludge dewatering centrifuges have minimal space requirements and show a high degree of effluent clarification. The operation is simple, clean, and relatively inexpensive. The area required for a centrifuge system installation is less than that required for a filter system or sludge drying bed of equal capacity, and the initial cost is lower.

Centrifuges have a high power cost that partially offsets the low initial cost. Special consideration must also be given to providing sturdy foundations and soundproofing because of the vibration and noise that result from centrifuge operation. Adequate electrical power must also be provided since large motors are required. The major difficulty encountered in the operation of centrifuges has been the disposal of the concentrate which is relatively high in suspended, non-settling solids.

Reliability is high, assuming proper control of factors such as sludge feed, consistency, and temperature. Pretreatment such as grit removal and coagulant addition may be necessary. Pretreatment requirements will vary depending on the composition of the sludge and on the type of centrifuge employed.

Maintenance consists of periodic lubrication, cleaning, and inspection. The frequency and degree of inspection required varies depending on the type of sludge solids being dewatered and the maintenance service conditions. If the sludge is abrasive, it is recommended that the first inspection of the rotating assembly be made after approximately 1,000 hours of operation. If the sludge is not abrasive or corrosive, then the initial inspection might be delayed. Centrifuges not equipped with a continuous sludge discharge system require periodic shutdowns for manual sludge cake removal.

Performance

The performance of sludge dewatering by centrifugation depends on the feed rate, the rotational velocity of the drum, and the sludge composition and concentration. Assuming proper design and operation, the solids content of the sludge can be increased to 20-35 percent.

Demonstration Status

Centrifugation is currently used in a great many commercial applications to dewater sludge. Work is underway to improve the efficiency, increase the capacity, and lower the costs associated with centrifugation.

Centrifugation is used in 55 plants in the present data base and these are identified in Table 7-94.

TABLE 7-94
METAL FINISHING PLANTS EMPLOYING CENTRIFUGATION

02032
04151
04153
06006
06071
06075
06086
06148
11050
11125
11127
12005
12033
12061
12075
12077
14062
15044
17050
19067
19068
19104
19107
19462
20070
20079
20106
20140
20149
20241
20708
21062
21065
21074
23048
27044
30097
30111
30155
30927
31022
33024
33071
34051
36091
36937
38052
41086
41116
41629
41869
44040
44150
45041
47041

## Sludge Bed Drying

As a waste treatment procedure, sludge bed drying is employed to reduce the water content of a variety of sludges to the point where they are amenable to mechanical collection and removal. These beds usually consist of 15.24 to 45.72 cm (6 to 18 inches) of sand over a 30.48 cm (12 inch) deep gravel drain system made up of 3.175 to 6.35 mm (1/8 to 1/4 inch) graded gravel overlying drain tiles.

Drying beds are usually divided into sectional areas approximately 7.62 meters (25 feet) wide x 30.48 to 60.96 meters (100 to 200 feet) long. The partitions may be earth embankments, but more often are made of planks and supporting grooved posts.

To apply liquid sludge to the sand bed, a closed conduit or a pressure pipeline with valved outlets at each sand bed section is often employed. Another method of application is by means of an open channel with appropriately placed side openings which are controlled by slide gates. With either type of delivery system, a concrete splash slab should be provided to receive the falling sludge and prevent erosion of the sand surface.

Where it is necessary to dewater sludge continuously throughout the year regardless of the weather, sludge beds may be covered with a fiberglass reinforced plastic roof. Covered drying beds permit a greater volume of sludge drying per year in most climates because of the protection afforded from rain or snow and because of more efficient control of temperature. Depending on the climate, a combination of open and enclosed beds will provide maximum utilization of the sludge bed drying facilities.

## Application

Sludge drying beds are a common means of dewatering sludge from clarifiers and thickeners. They are widely used both in municipal and industrial treatment facilities.

The main advantage of sand drying beds over other types of sludge dewatering is the relatively low cost of construction, operation, and maintenance. Its disadvantages are the large area of land required and long drying times that depend, to a great extent, on climate and weather.

Maintenance consists of periodic removal of the dried sludge. Sand removed from the drying bed with the sludge must be replaced and the sand layer resurfaced. The resurfacing of sludge beds is the major expense item in sludge bed maintenance, but there are other areas which may require attention. Underdrains occasionally become clogged and have to be cleaned. Valves or sludge gates that control the flow of sludge to the beds must be kept watertight. Provision for drainage of lines in winter should be made to prevent damage from freezing. The partitions between beds should be tight so that sludge will not flow from one compartment to another. The outer walls or banks around the beds should also be watertight.

The full sludge drying bed must either be abandoned or the collected solids must be removed. These solids contain whatever metals or other materials were settled in the clarifier. Metals will be present as hydroxides, oxides, sulfides, or other salts. They have the potential for leaching and contaminating ground water, whatever the location of the semidried solids. Thus an abandoned bed should include provision for runoff control and leachate monitoring.

### Performance

Dewatering of sludge on sand beds occurs by two mechanisms: filtration of water through the bed and evaporation of water as a result of radiation and convection. Filtration is generally complete in one to two days and may result in solids concentrations as high as 15 to 20 percent. The rate of filtration depends on the drainability of the sludge.

The rate of air drying of sludge is related to temperature, relative humidity, and air velocity. Evaporation will proceed at a constant rate to a critical moisture content, then at a falling rate to an equilibrium moisture content. The average evaporation rate for a sludge is about 75 percent of that from a free water surface.

### Demonstration Status

Sludge beds have been in common use in both municipal and industrial facilities for many years. However, protection of ground water from contamination is not always adequate. Sludge bed drying is used in 77 plants in the present data base and these are identified in Table 7-95.

## Sludge Disposal

There are several methods of disposal of sludges from industrial wastewater treatment. The two most common techniques are landfilling by the company on its own property and removal by licensed contractor to an outside landfill or reclamation point. Other disposal techniques proposed for industrial waste sludges include chemical containment, encapsulation, fixation, and thermal conversion. All of these techniques require landfilling, but they reduce the probability of groundwater contamination.

The chemical containment approach has been demonstrated commercially. The heavy metal sludge is placed in pits lined with powdered limestone. This keeps the pit-soil interface at an alkaline pH, reducing the solubility of metals at the interface to a very low value. This minimizes heavy metal leaching, even by acid rainfall.

Encapsulation consists of two approaches. One is to seal the sludge in a heavy concrete container. The other is to coat the material with a nondegradable, waterproof polymer.

## TABLE 7-95
## METAL FINISHING PLANTS EMPLOYING SLUDGE DRYING BEDS

01067
01068
04076
04262
05050
06002
06035
06051
06067
06073
06076
06081
06083
06084
06091
06094
06101
06113
06117
06119
06124
06128
06138
06360
08061
08072
09025
09047
11008
11113
11152
11173
12075
13041
14061
14062
15048
17061
18050
19050
20003
20064
20082
20085
20247
21003
22735
23039
23070
23072
25001
30009
30031
30064
30519
31032
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## IN-PROCESS CONTROL TECHNOLOGY

### INTRODUCTION

This section presents flow guidance and process controls in the form of available methods and practices which can help reduce the water usage and pollution discharge at metal finishing facilities.

### CONTROL TECHNIQUES

The in-process control techniques described below include techniques for:

- Flow reduction through efficient rinsing
- Process bath conservation
- Waste oil segregation
- Process bath segregation
- Process modification
- Cutting fluid cleaning
- Integrated waste treatment
- Good housekeeping

These techniques deal with reducing water usage and with efficient handling of process wastes. All of the areas of in-process control are presented in the following sections.

### Flow Reduction Through Efficient Rinsing

Reductions in the amount of water used in metal finishing can be realized through installation and use of efficient rinse techniques. Cost savings associated with water use reduction result from lower cost for rinse water and reduced chemical costs for wastewater treatment. An added benefit is that the waste treatment efficiency is also improved. It is estimated that rinse steps may consume over 90 percent of the water used by a typical metal finishing facility. Consequently, the greatest water use reductions can be anticipated to come from modifications of rinse techniques.

Rinsing is essentially a dilution step which reduces the concentration of contaminants on the work piece. The design of rinse systems for minimum water use depends on the maximum level of contamination allowed to remain on the work piece (without reducing acceptable product quality or causing poisoning of a subsequent bath) as well as on the efficiency or effectiveness of each rinse stage.

A rinse system should be considered efficient if the dissolved solids concentration is reduced just to the point where no noticeable effects occur either as a quality problem or as excessive drag-in to the next process step. Operation of a rinse tank or tanks which achieve a 10,000 to 1 reduction in concentration where only a 1,000 to 1 reduction is required represents inefficient use of water. Operating rinse tanks at or near their maximum acceptable level of contamination provides the most efficient and economical form of rinsing. Insufficient operation manifests itself in higher operating costs not only from the purchase cost of water, but also from the treatment of it.

## Dragout Control

Since the purpose of rinsing is to remove process solution dragout from the surface of the workpiece, the best way to reduce the amount of rinsing required is to reduce the dragout. A reduction in dragout results in a reduction of waste that has to be treated. Dragout is a function of several factors including workpiece geometry, viscosity and surface tension of the process solution, withdrawal and drainage time and racking. These factors affecting dragout are described below.

Geometry of the Part - This partly determines the amount of dragout contributed by a part and is one of the principal determinants for the type of rinsing arrangement selected. A flat sheet with holes is well suited for an impact spray rinse rather than an immersion rinse, but for parts with cups or recesses such as a jet fuel control, a spray rinse is totally ineffective.

Kinematic Viscosity of the Process Solution - The kinematic viscosity is an important factor in determining process bath dragout. The effect of increasing kinematic viscosity is that it increases the dragout volume in the withdrawal phase and decreases the rate of draining during the drainage phase. It is advantageous to decrease the dragout and increase the drainage rate. Consequently, the process solution kinematic viscosity should be as low as possible. Increasing the temperature of the solution decreases its viscosity, thereby reducing the volume of process solution going to the rinse tank. Care must be exercised in increasing bath temperature, particularly with electroless plating baths, because the rate of bath decomposition may increase significantly with temperature increases.

Surface Tension of the Process Solution - Surface tension is a major factor that controls the removal of dragout during the drainage phase. To remove a liquid film from a solid surface, the gravitation force must overcome the adhesive force between the liquid and the surface. The amount of work required to remove the film is a function of the surface tension of the liquid and the contact angle. Lowering the surface tension reduces the amount of work required to remove the liquid and reduces the edge effect (the bead of liquid adhering to the edges of the part). Surface tension is reduced by increasing the temperature of the process solution or more effectively, by use of a wetting agent.

Time of Withdrawal and Drainage - The withdrawal velocity of a part from a solution has an effect similar to that of kinematic viscosity. Increasing the velocity or decreasing the time of withdrawal increases the volume of solution that is retained by the part. Since time is directly related to production rate, it is more advantageous to reduce the dragout volume initially adhering to the part rather than attempt to drain a large volume from the part.

Racking - Proper racking of parts is the most effective way to reduce dragout. Parts should be arranged so that no cup-like recesses are formed, the longest dimension should be horizontal, the major surface vertical, and each part should drain freely without dripping onto another part. The racks themselves should be periodically inspected to insure the integrity of the rack coating. Loose coatings can contribute significantly to dragout. Physical or geometrical design of racks is of primary concern for the control of dragout both from the racks and the parts themselves. Dragout from the rack itself can be minimized by designing it to drain freely such that no pockets of process solution can be retained.

### Rinsing Techniques

The different types of rinsing commonly used within the metal finishing industry are described below.

Single Running Rinse - This arrangement requires a large volume of water to effect a large degree of contaminant removal. Although in widespread use, single running rinse tanks should be modified or replaced by a more effective rinsing arrangement to reduce water use.

Countercurrent Rinse - The countercurrent rinse provides for the most efficient water usage and thus, where possible, the countercurrent rinse should be used. There is only one fresh water feed for the entire set of tanks, and it is introduced in the last tank of the arrangement. The overflow from each tank becomes the feed for the tank preceding it. Thus, the concentration of dissolved salts decreases rapidly from the first to the last tank.

In a situation requiring a 1,000 to 1 concentration reduction, the addition of a second rinse tank (with a countercurrent flow arrangement) will reduce the theoretical water demand by 97 percent.

Series Rinse - The major advantage of the series rinse over the countercurrent system is that the tanks of the series can be individually heated or level controlled since each has a separate feed. Each tank reaches its own equilibrium condition; the first rinse having the highest concentration, and the last rinse having the lowest concentration. This system uses water more efficiently than the single running rinse, and the concentration of dissolved salts decreases in each successive tank.

Spray Rinse - Spray rinsing is considered the most efficient of the various rinse techniques in continuous dilution rinsing. The main concern encountered in use of this mode is the efficiency of the spray (i.e., the volume of water contacting the part and removing contamination compared to the volume of water discharged). Spray rinsing is well suited for flat sheets. The impact of the spray also provides an effective mechanism for removing dragout from recesses with a large width to depth ratio.

Dead, Still, or Reclaim Rinses - This form of rinsing is particularly applicable for initial rinsing after metal plating because the dead rinse allows for easier recovery of the metal and lower water usage. The rinse water can often be periodically transferred to the plating tank that precedes it. The dead rinse is followed by spray or other running rinses.

Effect on Water Use - The use of different rinse types will result in wide variations in water use. Table 7-96 shows the theoretical flow arrangements for several different rinse types to maintain a 1,000 to 1 reduction in concentration. Table 7-97 shows the mean flows ($1/m^2$) found at sampled plants for three rinse water-intensive operations.

TABLE 7-96
THEORETICAL RINSE WATER FLOWS REQUIRED TO MAINTAIN A 1,000 TO 1 CONCENTRATION REDUCTION

| Type of Rinse | Single | Series | | Countercurrent | |
|---|---|---|---|---|---|
| Number of Rinses | 1 | 2 | 3 | 2 | 3 |
| Required Flow (gpm) | 10 | 0.61 | 0.27 | 0.31 | 0.1 |

TABLE 7-97
COMPARISON OF RINSE TYPE FLOW RATES FOR SAMPLED PLANTS

| | Rinse Type and Mean Flow ($1/m^2$) | | | |
|---|---|---|---|---|
| Operation | Single Stage | 2 Stage Series | 2 Stage Countercurrent | 3 Stage Countercurrent |
| Alkaline Cleaning | 1504. | 235.6 | 67.36 | 28.76 |
| Nickel Electroplate | 322.9 | 88.96 | 26.54 | 7.44 |
| Zinc Electroplate | 236.8 | 33.78 | 21.79 | 7.84 |

## Rinsing Systems

By combining different rinse techniques, a plant can greatly reduce water consumption and in some cases form a closed loop rinsing arrangement. Some examples of primary rinse types and specialized rinsing arrangements applicable to metal finishing are discussed below.

Closing The Loop With A Countercurrent Rinse - This particular arrangement is well suited for use with heated process baths. The overflow from the countercurrent rinse becomes the evaporative makeup for the process bath. By installing the proper number of countercurrent tanks, the fresh feed rate for a given dilution ratio is sized to equal the bath's evaporative rate. This arrangement is easily controlled by using liquid level controllers in both the process bath and rinse tank, a pump to transfer rinse solution to the process bath, and a solenoid valve on the fresh feed line for the rinse tanks. Plant ID's 06037, 06072, and 20064 use this arrangement.

Closing The Loop With Spray Followed By Countercurrent Rinse - The spray followed by countercurrent rinse is well suited for flat sheets and parts without complex geometry. The spray is mounted over the process bath, and the work is fogged before moving to the countercurrent rinse. A major advantage of this arrangement is that the spray reduces concentration of the dragout on the part, returning the removed portion to the process tank. This provides for evaporative makeup of the process bath and a lower water usage and/or a smaller number of tanks necessary for the countercurrent rinse. Plant ID 40062 utilizes this rinse technique.

Closing The Loop With Countercurrent Rinsing Followed By Spray Rinsing - The countercurrent followed by spray rinsing approach can be used when a very clean workpiece (and, therefore, final rinse) is required. The spray is mounted above the last countercurrent rinse. Depending on the evaporation rate of the process solution, the evaporative makeup can come from the first countercurrent tank.

Closing The Loop With Dead Rinse Followed By Countercurrent - The dead rinse followed by countercurrent rinse arrangement is particularly useful with parts of a complex geometry. Evaporative losses from the original solution tank can be made up from the dead rinse tank and the required flow for the countercurrent system can be greatly reduced. The following plants make use of this rinsing arrangement: 04045, 06036, 06072, 06081, 06088, 20064, 20073, 20080, 21003, 21651, 30022, 31022, 33065, 33070, 33073, 36041, 41069, 61001.

Closing The Loop With Recirculatory Spray - When the geometry of the work permits, the recirculating spray offers an improved alternative to the dead rinse. Operating with a captive supply of rinse solution, the solution is sprayed onto the work. The advantage of this system is that the impact of the spray is used to remove dragout, particularly for work with holes in it. The basic equations for concentration buildup hold but are modified by the removal efficiency of the spray. The required flow rate of the spray is dependent on the geometry of the parts, the production rate and the solution evaporation rate. Plant ID's 15608 and 27046 have this rinsing system.

### Rinse Water Control

Another method of conserving water through efficient rinsing is by controlling the flow of the feed water entering the rinse tanks. Some flow control methods are listed below.

Conductivity Controllers - Conductivity controllers provide for efficient use and good control of the rinse process. This controller utilizes a conductivity cell to measure the conductance of the solution which, for an electrolyte, is dependent upon the ionic concentration. The conductivity cell is tied to a controller which will open or close a solenoid on the makeup line. As the rinse becomes more contaminated, its conductance increases until the set point of the controller is reached, causing the solenoid to open and allowing makeup to enter. Makeup will continue until the conductance drops below the set point. The advantage of this method of control is that water is flowing only when required. A major manufacturer of conductivity controllers supplied to plants in the Metal Finishing Category claims that water usage can be reduced by as much as 50-85% when the controllers are used.

Liquid Level Controllers - These controllers find their greatest use on closed loop rinsing systems. A typical arrangement uses a liquid level sensor in both the process solution tank and in the first rinse tank, and a solenoid on the rinse tank makeup water line. When the process solution evaporates to below the level of the level controller, the pump is activated, and solution is transferred from the first tank to the process tank. The pump will remain active until the process tank level controller is satisfied. As the liquid level of the rinse tank drops due to the pumpout, the rinse tank controller will open the solenoid allowing fresh feed to enter.

Manually Operated Valves - Manually operated valves are susceptible to misuse and should, therefore, be installed in conjunction only with other devices. Orifices should be installed in addition to the valve to limit the flow rate of rinse water. For rinse stations that require manual movement of work and require control of the rinse (possibly due to low utilization), dead man valves should be installed in addition to the orifice to limit the flow rate of rinse water. They should be located so as to discourage jamming them open.

Orifices or Flow Restrictors - These devices are usually installed for rinse tanks that have a constant production rate. The newer restrictors can maintain a constant flow even if the water supply pressure fluctuates. Orifices are not as efficient as conductivity or liquid level controllers, but are far superior to manual valves.

## Process Bath Conservation

There are a number of techniques that are utilized to recover or reuse process solutions in the Metal Finishing Category. The costs and reduced availability of certain process solutions have encouraged finishers to recognize process solutions as a valuable resource rather than a disposal problem. Some examples of chemical recovery and reuse are: reprocessing of oil, reclamation of oil, recycling of oil, reuse of spent etchants, recovery of metal from spent process baths, regeneration of etchants and dragout recovery. These techniques are described below.

### Oil Recovery

Reprocessing of Oil - Reprocessing consists of contaminant removal by physical separation, filtering, centrifuging, or magnetic separation, as previously discussed. Reprocessing also includes the preparation of waste oils for burning as a fuel supplement.

Reclamation of Oil - Oil reclamation combines the elements of reprocessing along with mechanical or chemical steps. Reclamation is used to remove solids and water, fuel or solvents, and degradation products such as acid. Two common processes are flash distillation and chemical adsorption. The addition of heat with a partial vacuum and filtration are employed to remove degradation products in used oil.

Reclamation is used with synthethic fluids or highly refined mineral oils. Reclamation systems are available for either fixed or portable operation, and outside reclamation services are available.

Recycling of Oil - Recycling is the most comprehensive treatment. The waste oil is prefiltered to remove most of the solids, solvents/ fuel, and water, leaving essentially base oil and additives. Removing the additives leaves a high quality basestock. The basestock is then formulated with conventional additives and can be used in the same application as the virgin basestock. Re-refining provides the best economics when large volumes of waste oil are available. Re-refiners may accept industrial oil wastes when a large source or many smaller sources of waste oils are available for collection in a region.

Other Recovery Operations

Reuse of Spent Etchant - If a facility maintains both an additive and a conventional subtractive line for the manufacturing of printed boards, a two-fold incentive exists for reuse of spent copper etchant. The copper etchant used in a conventional subtractive process is normally dumped when the copper concentration reaches approximately 45,000 mg/l. However, by removing the iron and chromium from the etchant, it can become an inexpensive source of copper for the additive plating baths. This technique can be extended to recover the copper bearing waters from copper etchant rinse tanks as well as from the etch tank and is practiced at Plant ID 11065. Some concentrating devices, such as vacuum distillation, may be required to reduce the volume of the rinse.

Recovery of Metal from Spent Plating Baths - Spent plating baths contain a significant percentage of metal in solution. Recovery can be effected by electrolizing the solution at low voltage or by decomposing a hot bath with seed nuclei. The resultant material, while pure, can be refined or sold to recover some of its original value. The advantage of this type of treatment is that a large percentage of the metal is recovered and does not require treatment. This type of metal recovery is performed by Plant ID's 17061 and 11065.

Regeneration of Etchants - Regeneration of etchants from a copper etchant solution can be achieved by partially dumping the bath and then adding fresh make-up acid and water. If this is done, the etchant life can be extended indefinitely. Another method practiced for the regeneration of etchants used in the electroless plating of plastics is to oxidize the trivalent chromium back to the active hexavalent chromium. The oxidization is done by an electrolytic cell. Plant 20064 regenerates its preplate etchants in this manner. Use of this method reduces the amount of material requiring waste treatment.

Reclamation of Paint Powders - A plant which uses powder coating does not need water wash spray booths to catch overspray. The oversprayed particles can be collected with a vacuum arrangement in a dry booth, filtered, and reused on the production line.

Dragout Recovery - If the overflow water from a rinse tank can be reused, it does not have to be treated, and additional water does not have to be purchased. One approach currently in use is to replace the evaporative losses from the process bath with overflow from the rinse station. This way a large percentage of process solution normally lost by dragout can be returned and reused.

The usefulness of this method depends on the rate of evaporation from the process tank. The evaporation from a bath is a function of its temperature, surface area, and ventillation rate, while the overflow rate is dependent on the dilution ratio, the geometry of the part, and the dragout rates. If the rinse is noncritical, i.e., where the part is going to another finishing operation, closing the loop (returning rinse overflow to the process tank) can be accomplished with far fewer rinse tanks than a critical rinse (following the last process operation). For example, if a particular line is always used to plate base metals only, and afterwards the work always goes to another process, then this permits a lower flow rate with consequently higher buildup of pollutants in the rinse. Under these conditions, an external concentrator, such as an evaporator, is not required, and the rinse overflow can be used directly for process bath makeup. The reverse is often true with the rinse following the final finishing step. The flow rate in this instance may be high enough that it exceeds the bath evaporation rate and some form of concentrator is required.

When using any rinse arrangement for makeup of evaporative losses from a process solution, the quality of the rinse water must be known and carefully monitored. Naturally occurring dissolved solids such as calcium and magnesium salts can slowly build up and cause the process to go out of control. Even using softened water can cause process control problems. For this reason, deionized water is often used as a feed for rinsing arrangements which will be used for evaporative makeup of process solutions.

### Oily Waste Segregation

Many different types (or compounds) of oils and related fluids are common in oily wastes and include cutting oils, fluids, lubricants, greases, solvents, and hydraulic fluids. Segregation of these oily wastes from other wastewaters reduces the expense of both the wastewater treatment and the oil recovery process by minimizing the quantity and number of constituents involved. In addition, segregated oily wastes are appropriate for hauling to disposal/reclamation by a contractor in lieu of on-site treatment. Additional segregation of oily wastes by type or compound can further reduce treatment or hauling costs. Some oils have high reclaimer values and are more desirable if they are not contaminated by other oils.

Properly segregated spent oils containing common base oils and additives will retain much more of their original value and can be efficiently processed. Spent oils, properly segregated, can be reprocessed in-house or sold to an outside contractor. Some plants purchase reprocessed oils which results in substantial savings.

The true value of oils and cutting fluids should be realized during its entire use cycle, from purchase to disposal and reuse. This is particularly true during used oil collection and storage.

## Process Bath Segregation

Process baths which are to be sent to waste treatment rather than being shipped out should be segregated from one another. The purpose of this is the same as for segregating raw waste streams. Mixing together of process solutions may form compounds which are very difficult to treat or create unnecessarily larger volumes of water requiring specialized treatment such as chromium reduction or cyanide oxidation.

## Process Modification

Process modifications can reduce the amount of water required for rinsing or reduce the load of certain pollutants on a waste treatment facility. For example, a rinse step can be eliminated in electroless plating by using a combined sensitization and activation solution followed by a rinse in place of a process sequence of sensitization-rinse-activation-rinse. Another potential process modification would be to change from a high concentration plating bath to one with a lower concentration. Parts plated in the lower concentration bath require less rinsing (a dilution operation) and, thus, decrease the water usage relative to high concentration baths.

There are also constantly increasing numbers of substitute bath solutions and plating processes becoming commercially available. A number of these are listed below:

Non-chromic acid pickling solutions
Non-cyanide zinc and copper plating
Non-aqueous plating processes
Trivalent chromium plating
Etch recovery and recirculating systems
Non-chromium decorative plating
Substitutions for cadmium where applicable
Phosphate-free and biodegradable cleaners

These options have been formulated in an effort to reduce the level of critical pollutants generated.

For plants which are currently using spraying as their painting application method, there are several alternative methods of application which could reduce the amount of wastewater generated by the painting operation. Among these methods are electrostatic spraying, powder coating, flow coating and dip coating. Electrostatic spraying has a smaller percent of overspray so less paint enters into the wastewater stream. Powder coating, flow coating and dip coating generate no wastewater and the powders or paints used can be recycled.

The selection of an application method is highly dependent upon the geometry of the part being painted so not all of the methods mentioned above will work for a specific work piece.

A plant which has a painting operation and employs water wash spray booths to capture overspray may reduce its pollutant generation by modifications to the spray booths. One possibility is switching over to dry filter booths or oil wash booths. Neither of these produces any wastewater. Another alternative is improving the existing booths by adding automatic screening or electrostatic treatment. Both of these features continuously remove paint solids from the water and allow for less frequent dumps of the booth water, thereby reducing wastewater generation.

Another process modification applicable to metal finishing plants is the replacement of solvent degreasing, where possible, with an alternative cleaning method such as alkaline cleaning. Typical areas that are amenable to cleaning techniques other than solvent degreasing are:

1. Low to medium volume production levels when cleaning cycle time does not impact the cost of production.
2. Non-ferrous products.
3. Simple product shapes
4. Small parts (adaptable to automated processes)
5. Situations where an oily film residue is not objectionable.
6. Situations where no exacting surface finishing is required.

## Cutting Fluid Cleaning

Essential to efficient machining operations is a clean and efficient cutting fluid cleaning system. An efficient cleaning system allows for recycling and reuse of oils. In maintaining clean fluid, the operation, the metal, and the fluid must be considered. Settling and skimming is only efficient when large volumes of fluid and long retention times are available. When fine particles or micro-debris are involved, the cleaning or maintenance of a cutting fluid also depends on whether it is a straight oil or an aqueous emulsion. Many operations and metals will produce coarse debris while brittle metals produce fine debris requiring a more sophisticated type of treatment. Filtration, centrifuging, or magnetic separation may be necessary.

## Straining

Oil or water solutions require straining to ensure pump protection. Double strainers should be inserted and kept free of rags, lint, or other clogging elements. Stainless mesh strainers are recommended for aqueous systems to minimize corrosion.

## Settling

Large sumps or central systems permit settling. Particle size and retention time are important considerations to ensure debris or sediment removal. Settling is essential to other methods of fluid cleaning by helping reduce sediment loads on filters and centrifuges.

Baffles above and below the surface of the fluid level will improve settling and deposition. Tramp oils, scums, and soaps may be skimmed either continuously or intermittently. Dense debris and sediment can be removed by drag chains, periodic sump cleanout, scum gutters, or surface paddles and sweeps.

## Centrifuging

As an accelerated settling process, the centrifuge is largely limited to low solids content removal. It may be used to enhance the efficiency of low volume systems and will remove fine particles.

## Magnetic Separators

Magnetic separators are an effective means of removing ferrous or magnetic metals and are most efficiently used with low viscosity fluids or aqueous systems.

## Filtration

The pore size or opening of a filter medium will determine the particle size which may be removed. The most common filtering systems consist of self-advancing rolled fabric. Filtration may be enhanced by vacuum or negative pressure. Supplemental coatings on filter media, such as diatomaceous earth, add depth to barrier filtration.

## Flotation

The cleaning of cutting fluids can utilize the aeration process, which causes fine particles to attach themselves to air bubbles, producing an efficient flotation system. Floating matter, foam, and scum are then removed by continuous skimmers or froth paddles. Flotation by aeration has the advantage of high solids removal in relation to liquid losses and effectively conserves coolant. In general, the flotation-type system works best with emulsifiable coolants, but foam must be controlled. This system cannot be used with water miscible fluids of high wettability.

## Integrated Waste Treatment

Waste treatment can be accomplished in the production area with constant recycling of the effluent. This process is generally known as integrated waste treatment. Integrated waste treatment can be applied to oily wash waters and electroplating rinse waters.

The washing of oily metal parts, rinses following oil quenches, machine system leaks, and some testing washes or rinses produce the largest majority of oily wastewater. Steps should be taken in-plant to segregate cutting fluids, hydraulic oils, crankcase oil, quench oils, and solvents from these waste streams.

Closed loop systems are available for removing oils, metal fines, and other residues from wash water through a combination of settling and skimming. A typical closed loop system consists of two compartments holding caustic wash solution, each equipped with an oil roll skimmer. While one compartment supplies wash solution to a series of washers, the other remains dormant, allowing heavy material to settle and oils float to the surface. The solids are collected as sludge and the oils are skimmed off. An alternative system would be an ultrafiltration system which can recycle water back to rinse and wash make-up stations.

Integrated treatment for plating processes uses a treatment rinse tank in the process line immediately following a process tank (plating, chromating, etc). Treatment solution (usually caustic soda in excess) circulating through the rinse tank reacts with the dragout to form a precipitate and removes it to a clarifier. This clarifier is a small reservoir usually designed to fit near the treatment rinse tank and is an integral part of water use in the production process. Further treatment may take place in the clarifier (cyanide oxidation, chromium reduction) or settling alone may be used to separate the solids. Sludge is removed near the spillover plate on the effluent side of the clarifier, and the effluent is returned to the treatment rinse tank. Consequently, no pollutants are directly discharged by the waste treatment process. Although further rinsing of the parts is required to remove treatment chemicals, this rinse will not contain pollutants from the original process tank, and no further treatment is needed.

## Good Housekeeping

Good housekeeping, proper selection and handling of process solutions, and proper maintenance of metal finishing equipment are required to reduce wastewater loads to the treatment system. Good housekeeping techniques prevent premature or unnecessary dumps of process solutions and cooling oils. Examples of good housekeeping are discussed below.

- Frequent inspection of plating racks for loose insulation prevents excessive dragout of process solutions. Also, periodic inspection of the condition of tank liners and the tanks themselves reduces the chance of a catastrophic failure which would overload the treatment system.

- Steps should be taken to prevent the formation of hard-to-treat wastes. Separation of cyanide wastes from nickel or iron wastes is advisable to avoid formation of cyanide complexes. Proper tank linings in steel tanks prevent the formation of ferrocyanides.

- Periodic inspection should be performed on all auxiliary metal finishing equipment. This includes inspection of sumps, filters, process piping, and immersion steam heating coils for leaks. Filter replacement should be done in curbed areas or in a manner such that solution retained by the filter is dumped to the appropriate waste stream.

- Chemical storage areas should be isolated from high hazard fire areas and arranged such that if a fire or explosion occurs in the storage area, loss of the stored chemicals due to deluge quantities of water would not overwhelm the treatment facilities.

- To prevent bacterial buildup on machines, sump walls and circulatory systems should be sterilized at regular intervals. Centralized cooling systems are self-cleaning to some extent, but physical and biological cleaning are required. The physical cleaning entails the removal of metallic fines, oxidized oil and other sludge forming matter. Biological cleaning involves the use of antiseptic agents, detergents and germicides.

- Chip removal from machining operations should include oil recovery and salvage provisions.

- A lubrication program schedule keeps track of leakage and contamination. By analyzing records of consumption, it is possible to identify high consumption equipment. Premature drain intervals may indicate abnormal system contamination which should be corrected.

- A general accounting of oils and fluids throughout their life cycle (purchasing, storage, application, cleaning and disposal) will lead to oil and fluid conservation.

- It is important that proper lubricants should be employed in a particular piece of machinery. Marking each piece of equipment with the product type required is practiced throughout the industry. This helps prevent the use of an improper oil and the subsequent premature dumping of that oil.

- Training and educating the operators of production equipment and waste treatment equipment can prevent unnecessary waste.

# STATISTICAL ANALYSIS

## INTRODUCTION

To establish effluent guideline limitations for the Metal Finishing Category, the available toxic pollutant data were examined statistically to determine the performance levels that were attained by properly operated metal finishing treatment systems.

Details regarding the statistical analysis of toxic pollutants are described in exhibits: total toxic organics in Exhibit 2, new source Cd in Exhibit 3, and all other pollutants in Exhibit 1. The statistical analysis followed three approaches with fundamentally similar methodology. Differences in approach are due mainly to differences in quantity and structure of the data.

## DATA

The types of data usable for TTO and new source Cd were similar and are therefore discussed together. That data consisted of one set of EPA sampling data resulting from samples taken daily over a 1 to 4 day period. The data sets were subdivided (the resulting set of data is refered to as a "subgroup") based on industrial process (for TTO) or statistical properties (for new source Cd). For each pollutant the "subgroup" provided all the numerical information used for the estimation of variability, and a "subset" of the "subgroup" provided estimation of the long term average.

The limitations on all other pollutants were based on two distinct sets of sampling data. The first set consists of raw and effluent concentration data that were collected during EPA conducted sampling visits. Typically, these data cover a period of 3 days of sampling, although as many as 6 days were occassionally recorded. The other data consisted of sets of long term self monitoring effluent data (usually without parallel raw waste data) that were submitted by plants in the Metal Finishing Category. These self monitoring data cover periods of continuous effluent monitoring up to a year, with much of the data collected on a daily basis. The self monitoring data were used to estimate variability and the EPA data were used to estimate the long term average concentration. There are only a few exceptions to the above. For Cd and Pb self monitoring data were used to estimate the long term average and variability; EPA sampling data were not used. This was because the EPA sampled data indicated very low raw waste Pb and Cd levels and it was not certain that they adequately represented the range of Pb or Cd in actual use. For Ag no usable self monitoring data were available so variability was estimated using the variability estimates of other toxic metals.

# STATISTICAL CALCULATIONS

## DAILY VARIABILITY

For all pollutants a measure of variability (referred to as a variability factor) is calculated. In all cases the variability factor is the ratio of the 99th percentile estimated using a lognomal distribution to the arithmetic mean of the same data that was used to estimate the 99th percentile. Variability factors are used to account for fluctuations in effluent levels expected in well operated treatment systems.

Variability factors for TTO and new source Cd, because of the data similiarities, have been calculated in a similar manner and are described together. The data were assumed to follow a lognormal distribution by plant although the new source Cd and TTO data sets have no single plants with data sets sufficient to test lognormality. This assumption has been found to be satisfactory for the discharge of other pollutants in this industry as well as other industries. Although not tested formally, these data do not display significant departures from lognormality. The 99th percentiles in these cases were estimated using a pooled within plant variance. The pooled within plant variance uses only those plants with multiple observations. The 99th percentile of the "subgroup" is then divided by the arithmetic mean of the entire "subgroup" to arrive at the variability factor for the pollutant.

The variability factors for all the remaining toxic pollutants have been calculated in a similar manner and are discused below. Because the self monitoring data base contained large within plant data sets, lognormality of the toxic pollutant data was graphically and statistically verified by plant. In cases where detection limit observations were present in the data, a generalized form of the lognormal, known as the delta lognormal distribution was used. The variability factor used to calculate the limitations was determined by taking the median of the variability factors for each pollutant. Any datum reported as below a detection limit was assigned a value of zero. If more than 50 percent of the data were reported below the detection limit the plant was not used to estimate variability.

## MONTHLY AVERAGE VARIABILITY

The monthly average variability calculations for new source Cd were based upon the average of ten daily samples. The assumption is made that the distribution of means of small samples of lognormally distributed values are also lognormally distributed.* This assumption provides the basis for the parameter estimates used to determine the 10-day (monthly average) 99th percentile estimate. Details regarding the methodology behind this approach to 10-day 99th percentiles are described in Exhibit 3. The 10-day (monthly average) variability factor is calculated in an identical manner to the daily variability factor; the 99th percentile estimate is divided by the arithmetic mean of the same data used to estimate the 99th percentile. No monthly average limitations were calculated for TTO.

The monthly average variability calculations for all other toxic pollutants was also based on the assumption that averages of 10 daily samples are approximately lognormally distributed. In these cases, however, with large quantities of self monitoring data, the 10 day average limitations

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* This lognormal characteristic of small sample averages from lognormal distributions has been observed in many industry categories for a wide variety of pollutants and was used as the basis of four (4) sample monthly average limitations in Pretreatment Standards for the Electroplating industry.

were based on empiricial distributions of the logs of 10 day averages. That is, averages of 10 sequential daily values were constructed from each plants' self monitoring data and fit to a lognormal distribution. The estimated 99th percentiles of these fitted distributions were then used as the numerator of the variability factor. The arithmetic mean of the 10 day averages was used as the denominator. The median plant 10 day average variability factor for each pollutant was then used to determine 10 day average monthly limitations.

## LONG TERM AVERAGES

Long term averages were calculated for TTO, and new source Cd in a similar manner. A "subgroup" was used to estimate variability and a "subset" of the "subgroup" was used to estimate the long term average. The "subsets" for both pollutants contained plants that were exceptional either because of the statistical properties (eg. extremely large average) and/or because of a special industrial process (eg. painting and solvent degreasing). An arithmetic average was calculated from the "subset" and was used as the long term average.

The long term averages for all the other toxic pollutants (except Pb and Cd) were calculated from the EPA sampling data described above. Arithmetic means of all values for each pollutant were used as the long term average. The arithmetic averages of the previously described self monitoring data were used for Cd and Pb.

## EFFLUENT LIMITS

The effluent limitations are based on a plant's treatment system being operated to maintain an average effluent concentrations equal to the long term averages. The day-to-day concentrations are expected to fluctuate about these average concentrations.

The variability factors estimated from the long term self monitoring data account for these fluctuations. Daily and monthly average limitations were determined by multiplying the appropriate variability factors and averages. Details of the data and analysis used to determine the limitations are provided in exhibits attached to this document and supplemental computer printouts and worksheets contained in the administrative record supporting this rulemaking.

# SECTION VIII
# COST OF WASTE WATER CONTROL AND TREATMENT

## INTRODUCTION

This section presents estimates of the cost of implementation of wastewater treatment and control options for each of the subcategories included in the Metal Finishing Category. These costs estimates, together with the pollutant reduction performance for each treatment and control option presented in Section VII provide a basis for evaluation of the options presented. The cost estimates also provide the basis for the determination of the probable economic impact of regulation at different pollutant discharge levels on the Metal Finishing Category. In addition, this section addresses non-water quality environmental impacts of wastewater treatment and control alternatives including air pollution, noise pollution, solid wastes, and energy requirements.

To arrive at the cost estimates presented in this section, specific wastewater treatment technologies and in-process control techniques from among those discussed in Section VII were selected and combined in wastewater treatment and control systems appropriate for each waste type. The different waste treatment systems were combined for cost estimation in six different plant treatment systems corresponding to the most common types of facilities operating within the Metal Finishing Category. As described in more detail below, investment and annual costs for each system were estimated based on wastewater flows and raw wastewater characteristics for each waste type as presented in Section V. Cost estimates are also presented for individual treatment technologies included in the waste treatment systems.

## COST ESTIMATION METHODOLOGY

Cost estimation is accomplished using a computer program which accepts inputs specifying the treatment system to be estimated, chemical characteristics of the raw wastewater streams treated, flow rates and operating schedules. The program accesses models for specific treatment components which relate component investment and operating costs, materials and energy requirements, and effluent stream characteristics to influent flow rates and stream characteristics. Component models are exercised sequentially as the components are encountered in the system to determine chemical characteristics and flow rates at each point. Component investment and annual costs are also determined and used in the computation of total system costs. Mass balance calculations are used to determine the characteristics of combined streams resulting from mixing two or more streams and to determine the volume of sludges or liquid wastes resulting from treatment operations such as chemical precipitation and settling, filtration, and oil separation.

Cost estimates are broken down into several distinct elements in addition to total investment and annual costs: operation and maintenance costs, energy costs, depreciation, and annual costs of capital. The cost estimation program incorporates provisions for adjustment of all costs to a common dollar base on the basis of economic indices appropriate to capital equipment and operating supplies. Labor and electrical power costs are input variables appropriate to the dollar base year for cost estimates. These cost breakdown and adjustment factors as well as other aspects of the cost estimation process are discussed in greater detail in the following paragraphs.

## Cost Estimation Input Data

The wastewater treatment system descriptions input to the computer cost estimation program include both a specification of the wastewater treatment components included and a definition of their interconnections. For some components, retention times or other operating parameters are specified in the input, while for others, such as reagent mix tanks and clarifiers, these parameters are specified within the program based on prevailing design practice in industrial wastewater treatment. The wastewater treatment system descriptions may include multiple raw wastewater stream inputs and multiple treatment trains. For example, cyanide bearing waste streams are segregated and treated for cyanide oxidation and chromium bearing wastes are segregated for chromium reduction prior to subsequent chemical precipitation treatment with the remaining process wastewater.

The specific treatment systems selected for cost estimation for each subcategory were based on an examination of raw waste characteristics, consideration of manufacturing processes, and an evaluation of available treatment technologies discussed in Section VII. The rationale for selection of these systems and their pollutant removal effectiveness are also addressed in Section VII.

The input data set also includes chemical characteristics for each raw wastewater stream specified as input to the treatment systems for which costs are to be estimated. These characteristics are derived from the raw wastewater sampling data presented in Section V. The pollutant parameters which are presently accepted as input by the cost estimation program are shown in Table 8-1. The values of these parameters are used in determining materials consumption, sludge volumes, treatment component sizes, and effluent characteristics. The list of input parameters is expanded periodically as additonal pollutants are found to be significant in wastewater streams from industries under study and as additional treatment technology cost and performance data become available. Within the Metal Finishing Category, individual waste types commonly encompass a number of different wastewater streams which are present to varying degrees at different facilities. The raw wastewater characteristics shown as input to wastewater treatment represent a mix of these streams including all significant pollutants found and will not in general correspond precisely to process wastewater at any existing facility. The process by which these raw wastewaters were defined is explained in Section V.

TABLE 8-1

COST PROGRAM POLLUTANT PARAMETERS

| Parameter, Units |
|---|
| Flow, MGD |
| pH, pH units |
| Turbidity, Jackson Units |
| Temperature, degrees C |
| Dissolved oxygen, mg/l |
| Residual Chlorine, mg/l |
| Acidity, mg/l CaCO3 |
| Alkalinity, mg/l CaCO3 |
| Ammonia, mg/l |
| Biochemical Oxygen Demand mg/l |
| Color, Chloroplatinate units |
| Sulfide, mg/l |
| Cyanides, mg/l |
| Kjeldahl Nitrogen, mg/l |
| Phenols, mg/l |
| Conductance, micromhos/cm |
| Total Solids, mg/l |
| Total Suspended Solids, mg/l |
| Settleable Solids, mg/l |
| Aluminum, mg/l |
| Barium, mg/l |
| Cadmium, mg/l |
| Calcium, mg/l |
| Chromium, Total, mg/l |
| Copper, mg/l |
| Fluoride, mg/l |
| Iron, Total, mg/l |
| Lead, mg/l |
| Magnesium, mg/l |
| Molybdenum, mg/l |
| Total Volatile Solids, mg/l |

| Parameter, Units |
|---|
| Oil, Grease, mg/l |
| Hardness, mg/l CaCO3 |
| Chemical Oxygen Demand, mg/l |
| Algicides, mg/l |
| Total Phosphates, mg/l |
| Polychlorobiphenyls, mg/l |
| Potassium, mg/l |
| Silica, mg/l |
| Sodium, mg/l |
| Sulfate, mg/l |
| Sulfite, mg/l |
| Titanium, mg/l |
| Zinc, mg/l |
| Arsenic, mg/l |
| Boron, mg/l |
| Iron, Dissolved, mg/l |
| Mercury, mg/l |
| Nickel, mg/l |
| Nitrate, mg/l |
| Selenium, mg/l |
| Silver, mg/l |
| Strontium, mg/l |
| Surfactants, mg/l |
| Beryllium, mg/l |
| Plasticizers, mg/l |
| Antimony, mg/l |
| Bromide, mg/l |
| Cobalt, mg/l |
| Thallium, mg/l |
| Tin, mg/l |
| Chromium, Hexavalent, mg/l |

The final input data set comprises raw wastewater flow rates for each subcategory input stream addressed. Six treatment scenarios corresponding to different types of manufacturing facilities within the Metal Finishing Category are addressed in the cost estimates. Each scenario entails a different combination of individual subcategory wastewater streams. For each, costs are estimated for five total plant wastewater flow rates spanning the range of flows generally encountered within the Metal Finishing Category (1,000 - 10,000,000 l/day). From these data, graphs have been prepared showing total treatment system investment costs and total annual costs as a function of flow rate for each scenario.

In establishing costs for the Metal Finishing Category, the Agency used the total plant process flow which could include wastewaters from other categories, e.g., porcelain enameling. This analysis provides conservative cost estimates for metal finishing in that other categorical regulations have costed and examined the impact of pollution control for non-metal finishing wastewater streams.

## System Cost Computation

A simplified flow chart for the estimation of wastewater treatment and control costs from the input data described above is presented in Figure 8-1. In the computation, raw wastewater characteristics and flow rates are used as input to the model for the first treatment technology specified in the system definition. This model is used to determine the size and cost of the component, materials and energy consumed in its operation, and the volume and characteristics of the stream(s) discharged from it. These stream characteristics are then used as input to the next component(s) encountered in the system definition. This procedure is continued until the complete system costs and the volume and characteristics of the final effluent stream(s) and sludge wastes have been determined. In addition to treatment components, the system may include mixers in which two streams are combined, and splitters in which part of a stream is directed to another destination. These elements are handled by mass balance calculations and allow cost estimation for specific treatment of segregated process wastewaters prior to combination with other process wastewaters for further treatment, and representation of partial recycle of wastewater.

As an example of this computation process, the sequence of calculations involved in the development of cost estimates for the simple treatment system shown in Figure 8-2 may be described. Initially, input specifications for the treatment system are read to set up the sequence of computations. The subroutine addressing chemical precipitation and clarification is then accessed. The sizes of the mixing tank and clarification basin are calculated based on the raw wastewater flow rate to provide 45 minute retention in the mix tank and 4 hour retention with a 33.3 gal/hr/sq ft surface loading in the clarifier. Based on these sizes, investment and annual costs for labor, supplies for

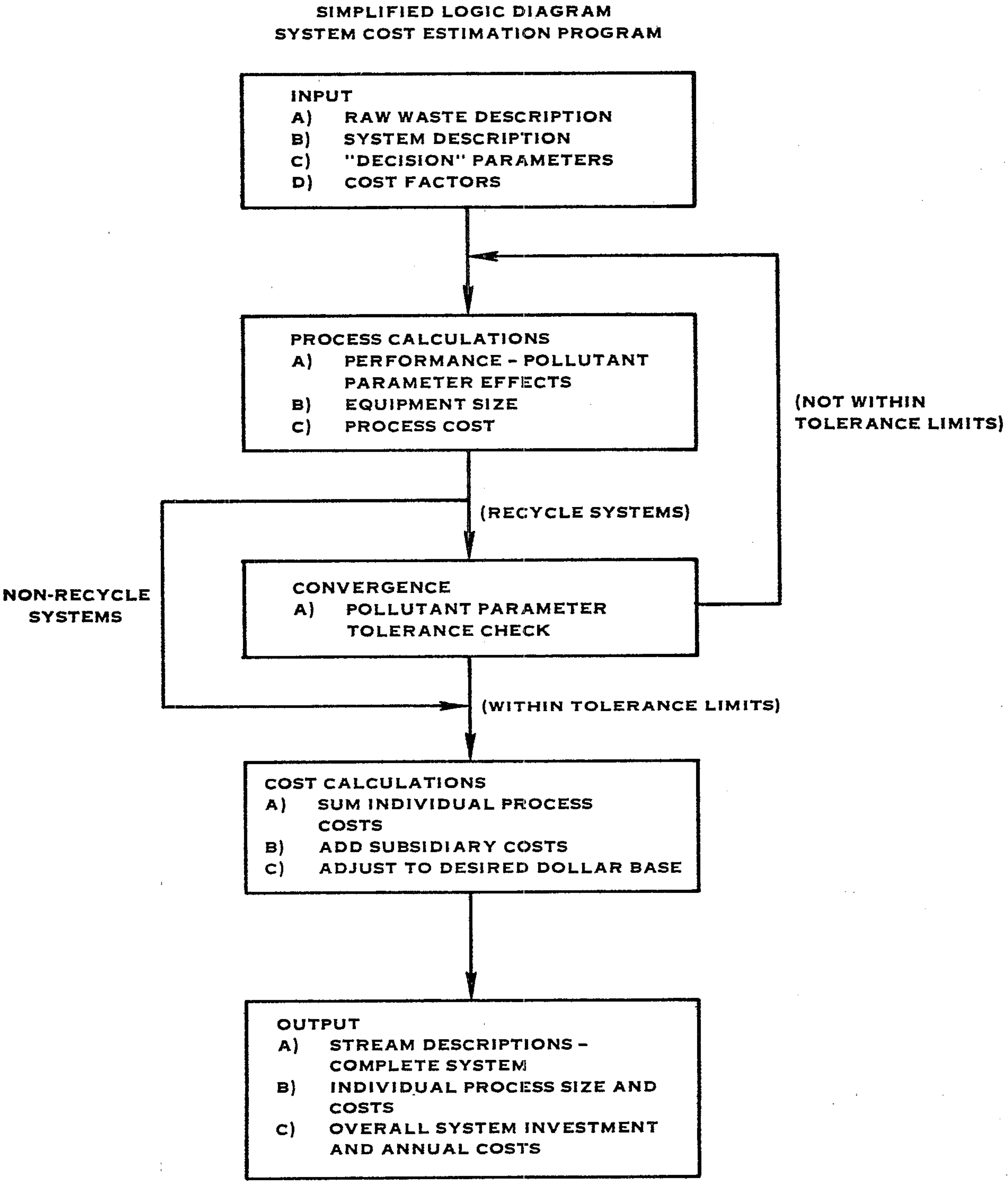


FIGURE 8–1

COST ESTIMATION PROGRAM

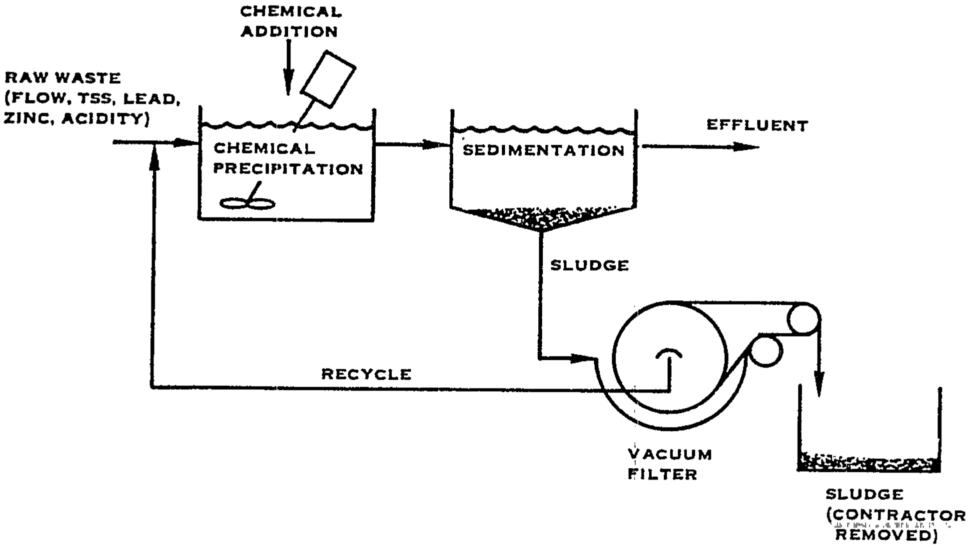


FIGURE 8–2

SIMPLE WASTE TREATMENT SYSTEM

the mixing tank and clarifier including mixers, clarifier rakes and other directly related equipment are determined. Fixed investment costs are then added to account for sludge pumps, controls, piping, and reagent feed systems.

Based on the input raw wastewater concentrations and flow rates, the reagent additions (lime, alum and polyelectrolyte) are calculated to provide fixed concentrations of alum and polyelectrolyte and 10% excess lime over that required for stoichiometric reaction with the acidity and metals present in the wastewater stream. Costs are calculated for these materials, and the suspended solids and flow leaving the mixing tank and entering the clarifier are increased to reflect the lime solids added and precipitates formed. These modified stream characteristics are then used with performance algorithms for the clarifier (as discussed in Section VII) to determine concentrations of each pollutant in the clarifier effluent stream. By mass balance, the amount of each pollutant in the clarifier sludge may be determined. The volume of the sludge stream is determined by the concentration of TSS which is fixed at 4.5% based on general operating experience, and concentrations of other pollutants in the sludge stream are determined from their masses and the volume of the stream.

The subroutine describing vacuum filtration is then called, and the mass of suspended solids in the clarifier sludge stream is used to determine the size and investment cost of the vacuum filtration unit. To determine manhours required for operation, operating hours for the filter are calculated from the flow rate and TSS concentration. Maintenance labor requirements are added as a fixed additional cost.

The sludge flow rate and TSS content are then used to determine costs of materials and supplies for vacuum filter operation including iron and alum added as filter aids, and the electrical power costs for operation. Finally, the vacuum filter performance algorithms are used to determine the volume and characteristics of the vacuum filter sludge and filtrate, and the costs of contract disposal of the sludge are calculated. The recycle of vacuum filter filtrate to the chemical precipitation and settling system is not reflected in the calculations due to the difficulty of iterative solution of such loops and the general observation that the contributions of such streams to the total flow and pollutant levels are, in practice, negligibly small. Allowance for such minor contributions is made in the 20% excess capacity provided in most components.

The costs determined for all components of the system are summed and subsidiary costs are added to provide output specifying total investment and annual costs for the system and annual costs for capital, depreciation, operation and maintenance, and energy. Costs for specific system components and the characteristics of all streams in the system may also be specified as output from the program.

## Treatment Component Models

The cost estimation program presently incorporates subroutines providing cost and performance calculations for the treatment technologies identified in Table 8-2. These subroutines have been developed over a period of years from the best available information including on-site observations of treatment system performance, costs, and construction practices at a large number of industrial facilities, published data, and information obtained from suppliers of wastewater treatment equipment. The subroutines are modified and new subroutines added as additional data allow improvements in models for treatment technologies presently available, and as additional treatment technologies are required for the industrial wastewater streams under study. Specific discussions of each of the treatment component models used in costing wastewater treatment and control systems for the Metal Finishing Category is presented later in this section where cost estimation is addressed, and in Section VII where performance aspects were developed.

## TABLE 8-2

## TREATMENT TECHNOLOGY SUBROUTINES

### Treatment Process Subroutines

Spray/Fog Rinse
Countercurrent Rinse
Vacuum Filtration
Gravity Thickening
Sludge Drying Beds
Holding Tanks
Centrifugation
Equalization
Contractor Removal
Reverse Osmosis
Landfill
Chemical Reduction of Chromium
Chemical Oxidation of Cyanide
Neutralization
Clarification (Settling Tank/Tube Settler)
API Oil Skimming
Emulsion Breaking (Chem/Thermal)
Membrane Filtration
Filtration (Diatomaceous Earth)
Ion Exchange - w/Plant Regeneration
Ion Exchange - Service Regeneration
Flash Evaporation
Climbing Film Evaporation
Atmospheric Evaporation
Cyclic Ion Exchange
Post Aeration
Sludge Pumping
Copper Cementation

Sanitary Sewer Discharge Fee
Ultrafiltration
Submerged Tube Evaporation
Flotation/Separation
Wiped Film Evaporation
Trickling Filter
Activated Carbon Adsorption
Nickel Filter
Sulfide Precipitation
Sand Filter
Chromium Regeneration
Pressure Filter
Multimedia Granular Filter
Sump

Cooling Tower
Ozonation
Activated Sludge
Coalescing Oil Separator
Non Contact Cooling Basin

Raw Wastewater Pumping
Preliminary Treatment
Preliminary Sedimentation
Aerator - Final Settler
Chlorination
Flotation Thickening
Multiple Hearth Incineration
Aerobic Digestion

In general terms, cost estimation is provided by mathematical relationships in each subroutine approximating observed correlations between component costs and the most significant operational parameters such as water flow rates, retention times, and pollutant concentrations. In general, flow rate is the primary determinant of investment costs and of most annual costs with the exception of material costs. In some cases, however, as discussed for the vacuum filter, pollutant concentrations may also significantly influence costs.

## Cost Factors and Adjustments

As previously indicated, costs are adjusted to a common dollar base and are generally influenced by a number of factors including: Cost of Labor, Cost of Energy, Capital Recovery Costs and Debt-Equity Ratio. These cost adjustments and factors are discussed below.

Dollar Base - A dollar base of August 1979 was used for all costs.

Investment Cost Adjustment - Investment costs were adjusted to the aforementioned dollar base by use of Sewage Treatment Plant Construction Cost Index. This cost is published monthly by the EPA Division of Facilities Construction and Operation. The national average of the Construction Cost Index for August 1979 was 337.8.

Supply Cost Adjustment - Costs of supplies such as chemicals were related to the dollar base by use of the Producer Price Index (formerly known as the Wholesale Price Index). This figure was obtained from the U.S. Department of Labor, Bureau of Labor Statistics, "Monthly Labor Review". For August 1979 the "Industrial Commodities" Producer Price Index was 240.3. Process supply and replacement costs were included in the estimate of the total process operating and maintenance cost.

Cost of Labor - To relate the operating and maintenance labor costs, the hourly wage rate for non-supervisory workers in sanitary services was used from the U.S. Department of Labor, Bureau of Labor Statistics October, 1979, publication, "Employment and Earnings". For August 1979, this wage rate was $6.71 per hour. This wage rate was then applied to estimates of operation and maintenance man-hours within each process to obtain process direct labor charges. To account for indirect labor charges, 15 percent of the direct labor costs was added to the direct labor charge to yield estimated total labor costs. Such items as Social Security, employer contributions to pension or retirement funds, and employer-paid premiums to various forms of insurance programs were considered indirect labor costs.

Cost of Energy - Energy requirements were calculated directly within each process. Estimated costs were than determined by applying an electrical rate of 4.5 cents per kilowatt hour.

This electrical charge was determined by assuming that any electrical needs of a waste treatment facility or in-process technology would be satisfied by an existing electrical distribution system, i.e., no new meter would be required. This eliminated the formation of any new demand load base for the electrical charge.

Capital Recovery Costs - Capital recovery costs were divided into straight line five-year depreciation and cost of capital at a thirteen percent annual interest rate for a period of five years. The five year depreciation period was consistent with the faster write-off (financial life) allowed for these facilities even though the equipment life is in the range of 20 to 25 years.

The annual cost of capital was calculated by using the capital recovery factor approach.

The capital recovery factor is normally used in industry to help allocate the initial investment and the interest to the total operating cost of the facility. It is equal to:

$$i + \frac{i}{(1+i)^{N-1}}$$

where i is the annual interest rate and N is the number of years over which the capital is to be recovered. The annual capital recovery was obtained by multiplying the initial investment by the capital recovery factor. The annual depreciation of the capital investment was calculated by dividing the initial investment by the depreciation period N, which was assumed to be five years. The annual cost of capital was then equal to the annual capital recovery minus the depreciation.

Debt-Equity Ratio - Limitations on new borrowings assume that debt may not exceed a set percentage of the shareholders' equity. This defines the breakdown of the capital investment between debt and equity charges. However, due to the lack of information about the financial status of various plants, it was not feasible to estimate typical shareholders equity to obtain debt financing limitations. For these reasons, capital cost was not broken into debt and equity charges. Rather, the annual cost of capital was calculated via the procedure outlined in the Capital Recovery Costs section above.

## Subsidiary Costs

The waste treatment and control system costs presented in Figures 8-34 through 8-65 for end-of-pipe and in-process wastewater control and treatment systems include subsidiary costs associated with system construction and operation. These subsidiary costs include:

- administration and laboratory facilities
- garage and shop facilities
- line segregation
- yardwork
- piping
- instrumentation
- land
- engineering
- legal, fiscal, and administrative
- interest during construction
- contingency

Administrative and laboratory facility treatment investment is the cost of constructing space for administration and laboratory functions for the wastewater treatment system. For these cost computations, it was assumed that there was already an existing building and space for administration and laboratory functions. Therefore, there was no investment cost for this item.

**For laboratory operations, an analytical fee of $105 (August 1979 dollars) was charged for metals and cyanide and $635 for toxic organics for each wastewater sample, regardless of whether the laboratory work was done on or off site. This analytical fee is typical of the charges experienced by the EPA contractor during the past several years of sampling programs. The frequency of wastewater sampling is a function of wastewater discharge flow and is presented in Table 8-3. This frequency was suggested by** the Water Compliance Division of the USEPA. However, for the economic **impact analysis, the Agency costed 10 samples per month for metals and cyanide which is consistent with the statistical basis for the monthly limit.**

For industrial waste treatment facilities being costed, no garage and shop investment cost was included. This cost item was assumed to be part of the normal plant costs and was not allocated to the wastewater treatment system.

Line segregation investment costs account for plant modifications to segregate wastewater streams. The investment costs for line segregation included placing a trench in the existing plant floor and installing the lines in this trench. The same trench was used for all pipes. The pipes were assumed to run from the center of the floor to a corner. A rate of 2.04 liters per hour of wastewater discharge per square meter of area (0.05 gallons per hour per square foot) was used to determine floor and trench dimensions from wastewater flow rates for use in this cost estimation process. It was assumed that a transfer pump would be required for each segregated process line in order to transfer the wastes to the treatment system.

TABLE 8-3

WASTEWATER SAMPLING FREQUENCY

| Waste Water Discharge (liters per day) | Sampling Freqency |
|---|---|
| 0 - 37,850 | once per month |
| 37,850 - 189,250 | twice per month |
| 189,250 - 378,500 | once per week |
| 378,500 - 946,250 | twice per week |
| 946,250+ | thrice per week |

The yardwork investment cost item includes the cost of general site clearing, lighting, manholes, tunnels, conduits, and general site items outside the structural confines of particular individual plant components. This cost is typically 9 to 18 percent of the installed components investment costs. For these cost estimates, an average of 14 percent was utilized. Annual yardwork operation and maintenance costs are considered a part of normal plant maintenance and were not included in these cost estimates.

The piping investment cost item includes the cost of intercomponent piping, valves, and piping required to transfer the wastes to the waste treatment system. This cost is estimated to be equal to 20 percent of installed component investment costs.

The instrumentation investment cost item includes the cost of metering equipment, electrical wiring and cable, treatment component operational controls, and motor control centers as required for each of the waste treatment systems described in Section VII of the document. The instrumentation investment cost is estimated based upon the requirements of each waste treatment system. For continuous operations a base cost of $25,000 was used for instrumentation and was adjusted upward by a variable factor that depended on the complexity of the treatment system.

No new land purchases were required. It was assumed that the land required for the end-of-pipe treatment system was already available at the plant.

Engineering costs include both basic and special services. Basic services include preliminary design reports, detailed design, and certain office and field engineering services during construction of projects. Special services include improvement studies, resident engineering, soils investigations, land surveys, operation and maintenance manuals, and other miscellaneous services. Engineering cost is a function of process installed and yardwork investment costs. The engineering cost ranges from approximately one percent for investment costs of about $1.2 million to 37 percent for investment costs of about $12,000.

Legal, fiscal and administrative costs relate to planning and construction of waste water treatment facilities and include such items as preparation of legal documents, preparation of construction contracts, acquisition of land, etc. These costs are a function of process installed, yardwork, engineering, and land investment costs, ranging between approximately 0.5 and 5.3 percent of the total of these costs.

Interest cost during construction is the interest cost accrued on funds from the time payment is made to the contractor to the end of the construction period. The total of all other project investment costs (process installed; yardwork; land; engineering; and legal, fiscal, and administrative) and the applied interest affect this cost. An interest rate of 13 percent was used to determine the interest cost for these estimates.

A contingency allowance was included equal to ten percent of the sum of the cost of individual treatment technologies plus piping, line segregation, and yard work.

## COST ESTIMATES FOR INDIVIDUAL TREATMENT TECHNOLOGIES

Table 8-4 lists those technologies which are incorporated in the wastewater treatment and control options offered for the metal finishing category and for which cost estimates have been developed. These treatment technologies have been selected from among the larger set of available alternatives discussed in Section VII on the basis of an evaluation of raw waste characteristics, typical plant characteristics (e.g. location, production schedules, product mix, and land availability), and present treatment practices within the subcategory addressed. Specific rationale for selection is addressed in Section IX, X XI and XII. Cost estimates for each technology addressed in this section include investment costs and annual costs for depreciation, capital, operation and maintenance, and energy.

Investment - Investment is the capital expenditure required to bring the technology into operation. If the installation is a package contract, the investment is the purchase price of the installed equipment. Otherwise, it includes the equipment cost, cost of freight, insurance and taxes, and installation costs.

Total Annual Cost - Total annual cost is the sum of annual costs for depreciation, capital, operation and maintenance (less energy), and energy (as a separate function).

Depreciation - Depreciation is an allowance, based on tax regulations, for the recovery of fixed capital from an investment to be considered as a non-cash annual expense.

It may be regarded as the decline in value of a capital asset due to wearout and obsolescence.

Capital - The annual cost of capital is the cost, to the plant, of obtaining capital expressed as an interest rate. It is equal to the capital recovery cost (as previously discussed on cost factors) less depreciation.

Operation and Maintenance - Operation and maintenance cost is the annual cost of running the wastewater treatment equipment. It includes labor and materials such as waste treatment chemicals. As presented in the tables, operation and maintenance cost does not include energy (power or fuel) costs because these costs are shown separately.

Energy - The annual cost of energy is shown separately, although it is commonly included as part of operation and maintenance cost. Energy cost has been shown separately because of its importance to the nation's economy and natural resources.

TABLE 8-4
INDEX TO TECHNOLOGY COSTS

| Technology | Figure or Table |
|---|---|
| CN Oxidation | Figures 8-3 to 8-5 |
| Chromium Reduction | Figures 8-6 & 8-7 |
| Clarification | Figures 8-8 to 8-10 |
| Emulsion Breaking | Figures 8-11 to 8-13 |
| Holding Tanks | Figures 8-14 to 8-16 |
| Multimedia Filtration | Figures 8-17 & 8-18 |
| Ultrafiltration | Figures 8-19 to 8-21 |
| Carbon Adsorption | Figures 8-22 to 8-24 |
| Sludge Drying Beds | Figures 8-25 & 8-26 |
| Vacuum Filtration | Figures 8-27 to 8-29 |
| Contract Removal | |
| Countercurrent Rinse | Tables 8-6 & 8-7 |
| Evaporation | Figures 8-30 to 8-32 |

## Cyanide Oxidation

In this technology, cyanide is destroyed by reaction with sodium hypochlorite under alkaline conditions. A complete system for accomplishing this operation includes reactors, sensors, controls, mixers, and chemical feed equipment. Control of both pH and chlorine concentration (through oxidation-reduction potential) is important for effective treatment.

Investment Costs - Investment costs for cyanide oxidation as shown in Figure 8-3 include reaction tanks, reagent storage, mixers, sensors and controls necessary for operation. Costs are estimated for both batch and continuous systems with the operating mode selected on a least cost basis. Specific costing assumptions are as follows:

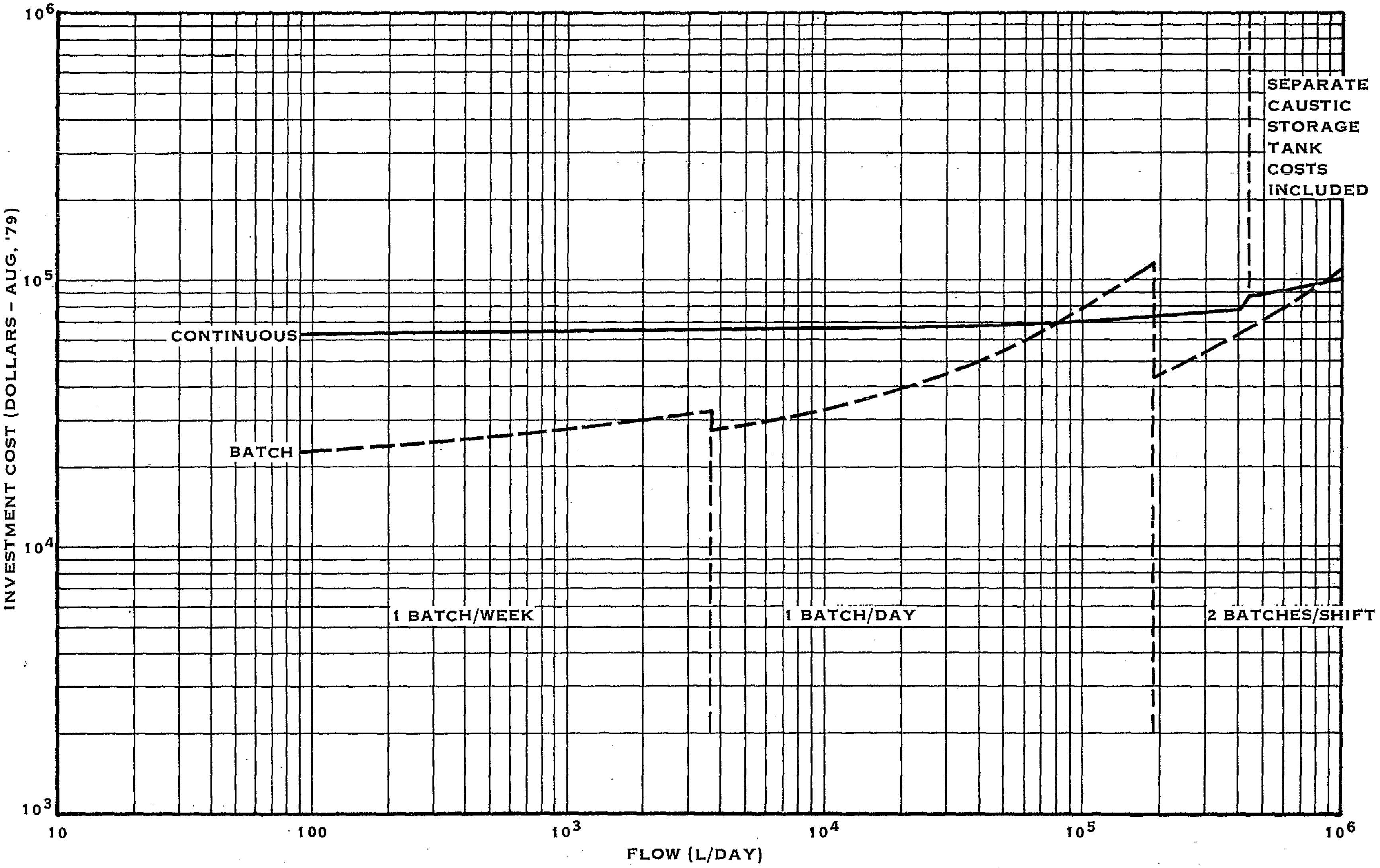


FIGURE 8-3
CYANIDE OXIDATION INVESTMENT COSTS

For batch teatment, oxidation is accomplished by the addition of sodium hypochlorite. Sodium hydroxide and sulfuric acid are added to maintain the proper pH level. A manually controlled feed pump is included for each treatment chemical. Chemical storage for the limited quantities generally involved in batch treatment is assumed to be in shipping containers, and no investment costs for storage facilities are calculated. Reaction tank costs are based on two fiberglass tanks, each of which is sized to provide four hours retention based on process flow rates. Mixers, based on one horsepower per 1000 gallons of reaction tank volume (0.5 HP minimum) are also provided. Investment costs also include a transfer pump and a manual instrumentation set including:

2 pH probes
1 pH probe maintenance kit
1 pH meter
3 ORP probes
1 ORP meter

Installation is included as 60% of the sum of the component costs.

For continuous treatment, oxidation is accomplished using chlorine obtained as a gas. Sodium hydroxide and sulfuric acid are used for pH control. Investment costs include a chlorination system and automatically controlled pH control systems for two treatment tanks (for the two-stage cyanide destruction process). These systems include:

pH Control and Instrumentation

2 Pump stands
2 Feed pumps
2 Liquid Level detectors
15 days storage for acid and sodium hydroxide
2 pH probes
2 pH meters
1 pH probe maintenance kit
2 pH controllers
3 ORP probes
2 ORP meters
2 ORP controllers
2 Recorders

Chlorination System

Chlorinator
Pressure Reducing valves
Venturi ejector
Diffuser
Piping and fittings
Evaporator

Weighing scale
Gas detector
Emergency vent system
Hoisting equipment
Installation and start-up service

Costs are estimated for fiberglass reaction tanks providing 0.5 hours retention for the first stage of treatment and 1 hour retention for the second stage. Mixers based on 1 horsepower per 1000 gallons with a minimum of 1 horsepower are costed for each tank. Cost estimates also include 2 emergency vent fans, 3 circulation pumps, and 2 transfer pumps.

Operation and Maintenance Costs - Costs for operating and maintaining cyanide oxidation systems include labor and chemical expenses. Annual operation and maintenance expenses for batch and continuous cyanide oxidation systems are shown in Figure 8-4 as a function of waste stream flow rate.

Labor expenses for the batch treatment system are estimated based on 1.5 hours of labor per batch of waste treated plus 2 hours of maintenance labor per week plus additional labor for chemical handling based on the amounts of treatment chemicals consumed. For continuous treatment, maintenance labor is estimated at 4 hours per week, and operating labor at 1 hour per shift plus an additional 0.5 hours per cylinder (1 ton) of chlorine consumed.

Chlorine or sodium hypochlorite addition is calculated based on a 10% excess over stoichiometric requirements calculated from measured cyanide concentrations plus concentrations of some metals, (copper, iron, and nickel) which form cyanide complexes. Sodium hydroxide requirements to maintain pH are calculated based on the flow and the amount of cyanide being treated, and sulfuric acid consumption is based on flow and sodium hydroxide consumption.

Chemical costs have been based on the following unit prices:

| | |
|---|---|
| \$ 600 | Per ton of chlorine (August, 1979 price) |
| \$1462 | Per ton of sodium hypochlorite (August, 1979 price) |
| \$ 699 | Per ton of sodium hydroxide (August, 1979 price) |
| \$ 113 | Per ton of sulfuric acid (August, 1979 price) |

The assumption has been made that the plants operate 24 hours per day, 260 days per year. This assumption overestimates the costs for facilities which operate less than 24 hours per day.

Energy Costs - Motor horsepower requirements for chemical mixing have been described above. Mixing equipment is assumed to operate continuously over the operation time of the treatment system for both the continuous and batch modes. Pump motor

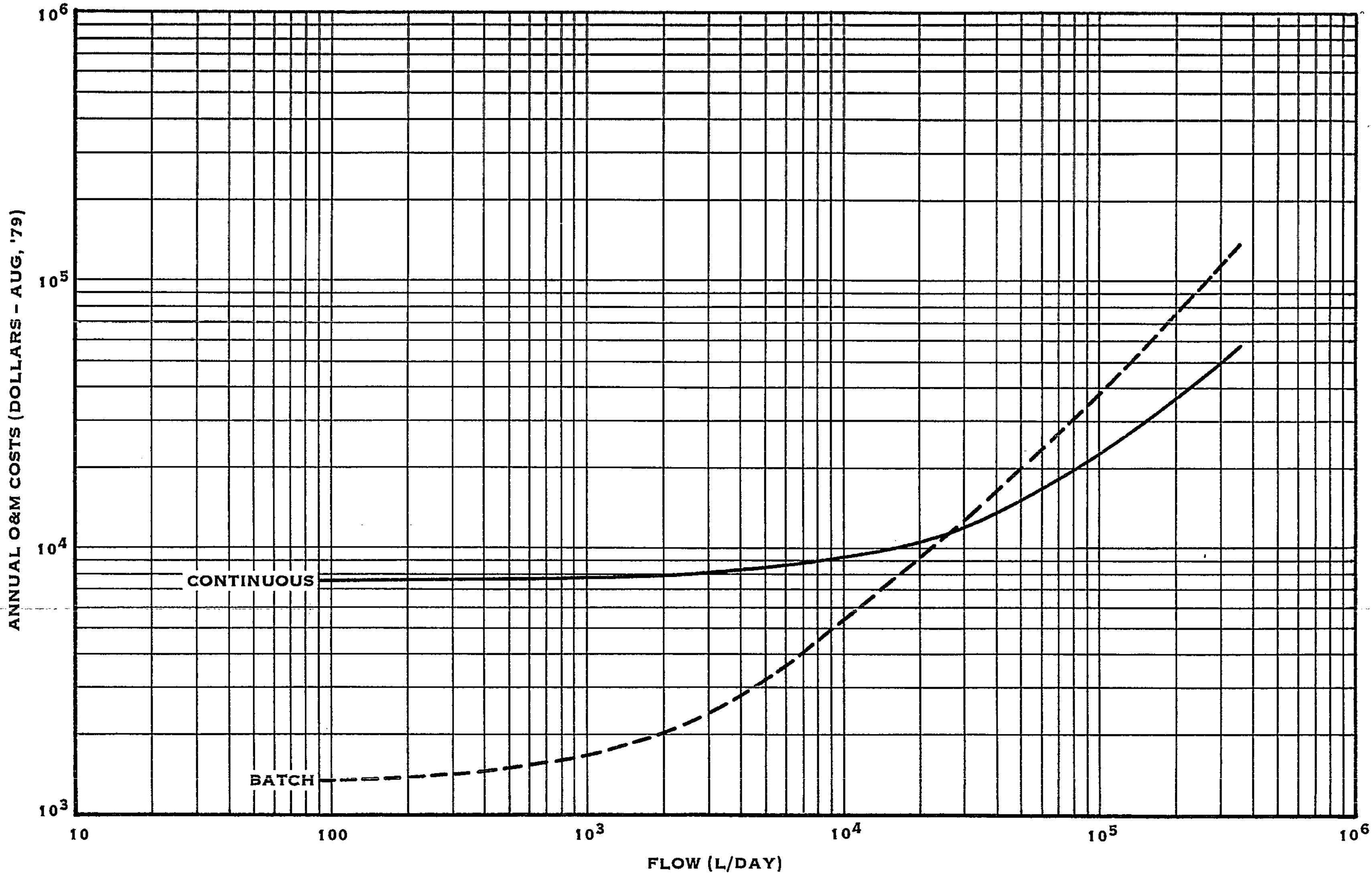


FIGURE 8-4
ANNUAL O&M COSTS VS. FLOW RATE FOR CYANIDE OXIDATION

horsepower requirements are calculated based on several variables. These include system flow, pump head and system operating time.

Annual energy expenses for batch and continuous cyanide oxidation systems are shown in Figure 8-5 as a function of waste stream flow rate. Energy expenses have been estimated based upon a rate of $0.045/kilowatt hour of required electricity. Plant operation was assumed to be for 24 hours/day, 260 days/year. For continuous treatment, the treatment system operates during plant operation. Batch treatment operation schedules vary with flow rate as discussed above.

## Chromium Reduction

This technology provides chemical reduction of hexavalent chromium under acidic conditions to allow subsequent removal of the trivalent form by precipitation as the hydroxide. Treatment may be provided in either continuous or batch mode; cost estimates are developed for each. Operating mode for system cost estimates is selected on a least cost basis.

Investment Cost - Cost estimates include all required equipment for performing this treatment technology including reagent dosage, reaction tanks, mixers and controls. Different reagents are provided for batch and continuous treatment resulting in different system design considerations as discussed below.

For both continuous and batch treatment, sulfuric acid is added for pH control. The acid is purchased at 93% concentration and stored in the cylindrical drums in which it is purchased.

For continuous chromium reduction a single chromium reduction tank is used. Costs are estimated for an above-ground cylindrical rubber lined tank with a one hour retention time, and an excess capacity factor of 1.2. Sulfur dioxide is added to convert the influent hexavalent chromium to the trivalent form. The control system for continuous chromium reduction consists of:

| | |
|---|---|
| 1 | immersion pH probe and transmitter |
| 2 | immersion ORP probes and transmitter |
| 1 | pH monitor and controller |
| 1 | ORP monitor and controller |
| 1 | sulfonator and associated controls, diffuser, evaporator, and pressure regulator |
| 1 | sulfuric acid pump |
| 2 | dilute acid pumps and pump stands |
| 1 | transfer pump for sulfur dioxide ejector with pump stand |
| 1 | pH probe maintenance kit |
| 1 | pen recorder |
| 2 | mixers |

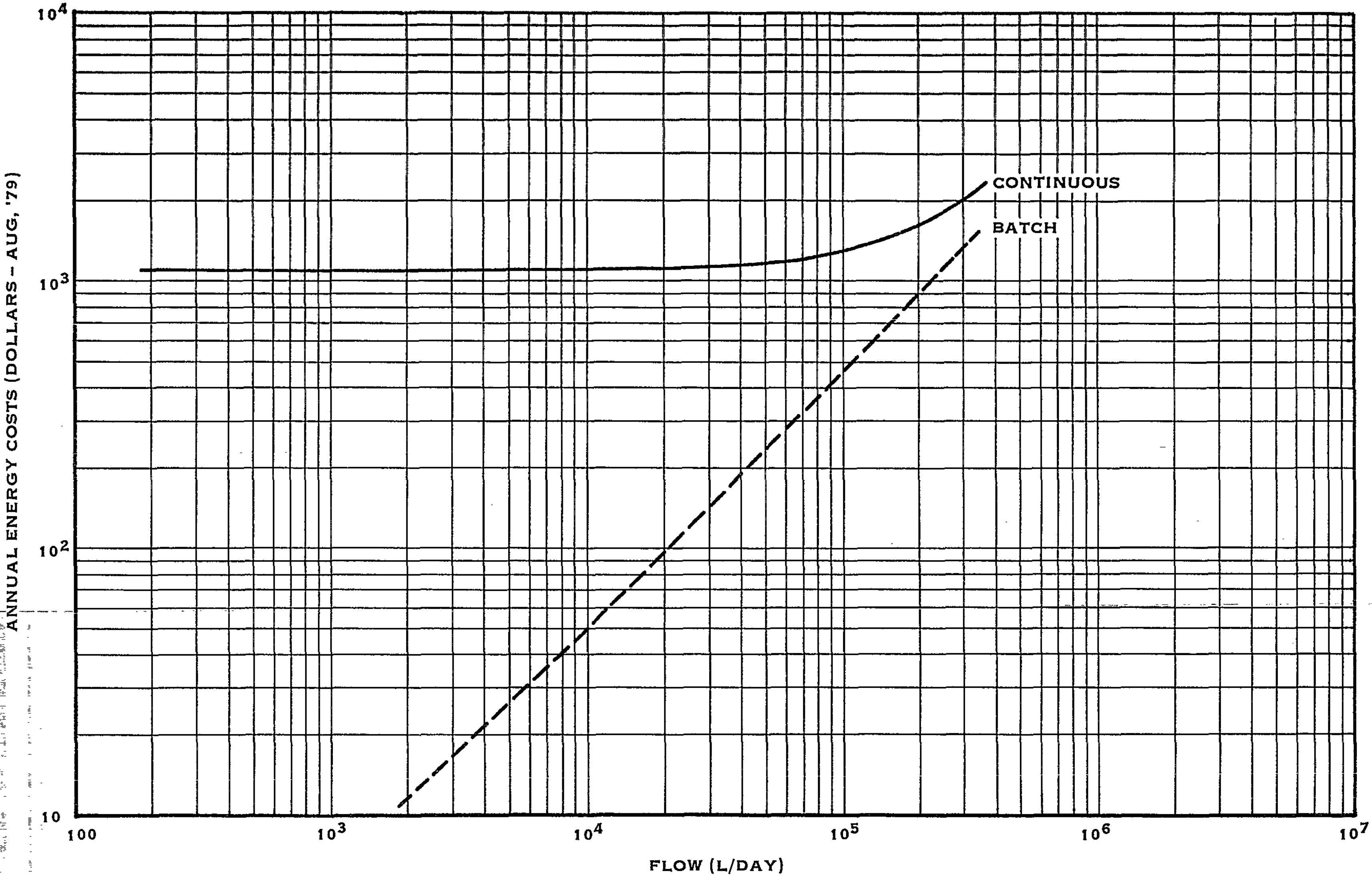


FIGURE 8-5

ANNUAL ENERGY COSTS VS. FLOW RATE FOR CYANIDE OXIDATION

For batch chromium reduction, the dual chromium reduction tanks are sized as above-ground cylindrical rubber-lined tanks, with a variable retention time, depending on flow rates. Up to a flow of 400 l/day to chromium reduction, one batch is treated per 5 days of operation, and treatment tanks are sized to contain 5 days' flow. Above this flow rate, one batch is treated each day. Sodium bisulfite is added to reduce the hexavalent chromium.

A completely manual system is provided for batch operation. Subsidiary equipment includes:

| | |
|---|---|
| 2 | immersion pH probes |
| 1 | pH probe maintenance kit |
| 1 | pH meter |
| 3 | immersion ORP probes (one stand by) |
| 1 | ORP meter |
| 1 | sulfuric acid transfer pump and stand |
| 1 | sulfuric acid dilution tank |
| 1 | sulfuric acid feed pump and stand |
| 1 | reduction tank drain transfer pump |

Investment costs for batch and continuous treatment systems are presented in Figure 8-6.

Operation and Maintenance - Costs for operating and maintaining chromium reduction systems include labor and chemical expenses. Annual operation and maintenance expenses for batch and continuous chromium reduction systems are shown in Figure 8-7 as a function of waste stream flow rate.

Labor requirements for batch treatment include 2 hours/week maintenance, 45 minutes/batch treated and additional labor for chemical handling depending on the amount of sulfuric acid consumed. For continuous treatment, labor requirements are 4 hours/week maintenance, 1 hour/day operation and additional labor for chemical handling depending on the amount of sulfuric acid consumed.

For the continuous system, sulfur dioxide is added according to the following:

(lbs $SO_2$/day) - (8.34)(flow to unit-MGD)(1.85xmg/lCr$^{+6}$+4 x mg/l dissolved $O_2$) (1.1 excess capacity factor)

In the batch mode, sodium bisulfite is added in place of sulfur dioxide according to the following:

(lbs $NaHSO_3$/day) = (8.34)(flow to unit-MGD)(2.74 x mg/lCr$^{+6}$ + 5.94 x mg/l dissolved $O_2$)(1.1 excess capacity factor)

Costs for these labor and chemical requirements are estimated based on the following:

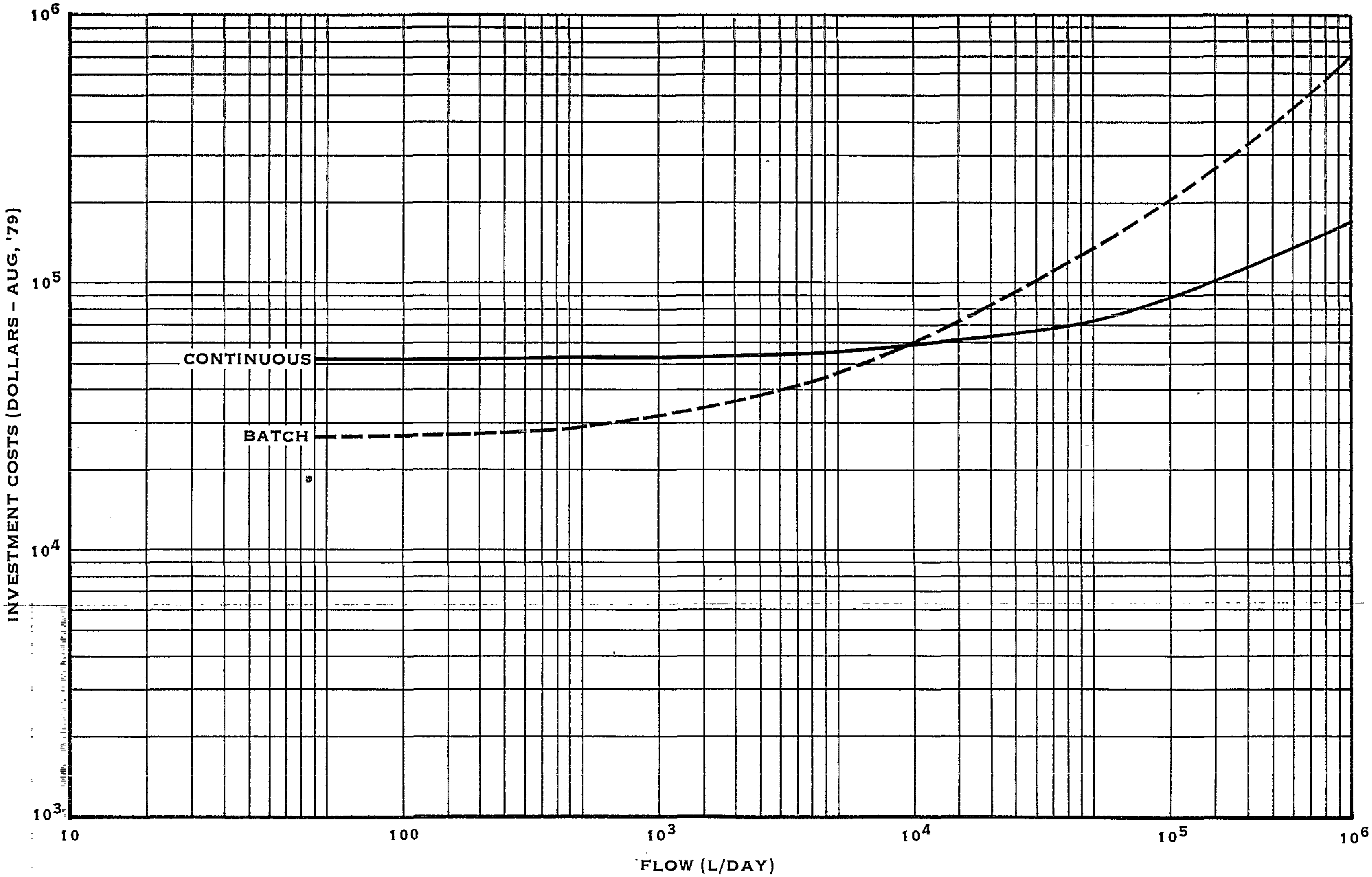


FIGURE 8-6
CHROMIUM REDUCTION INVESTMENT COSTS

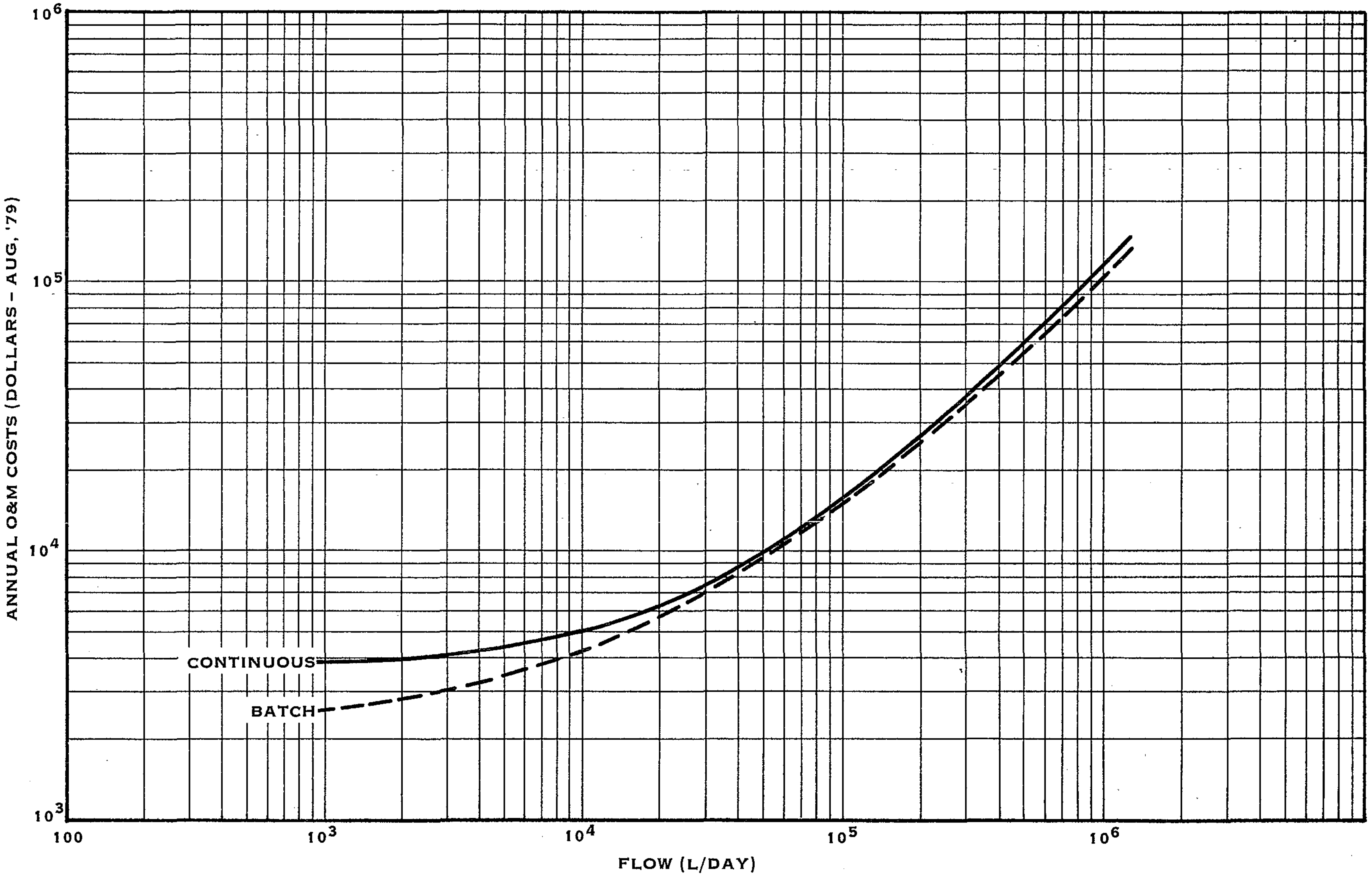


FIGURE 8-7

ANNUAL O&M COSTS VS. FLOW RATE FOR CHROMIUM REDUCTION

$6.71 per manhour +15% indirect labor charge
$760. per ton of sulfur dioxide
$280. per ton of sodium metabisulfite (1978 dollars)

Energy Costs - The horsepower required for chemical mixing is estimated based on tank volumes at 1 hp per 1,000 gallons. The mixers are assumed to operate continuously over the operation time of the treatment system. Pump motor horsepower requirements are calculated based on system flow, pump head, and operating time. Energy expenses are estimated based on a rate of $0.045/kilowatt hour of required electricity.

## Chemical Precipitation and Settling

This technology removes dissolved pollutants by the formation of precipitates by reaction with added lime and subsequent removal of the precipitated solids by gravity settling in a clarifier. Several distinct operating modes and construction techniques are costed to provide least cost treatment over a broad range of flow rates. Because of their interrelationships and integration in common equipment in some installations, both the chemical addition and solids removal equipment are addressed in a single subroutine. The chemical precipitation/sedimentation subroutine also incorporates an oil skimming device on the clarifier for removal of floating oils.

Investment Costs - Investment costs are determined for this technology for both batch and continuous treatment systems using steel tank or concrete tank construction. The system selected is based upon least cost on an annual basis as discussed previously in this section of the development document. Continuous treatment systems include a mix tank for reagent feed addition (flocculation basin) and a clarification basin with associated sludge rakes and pumps. Batch treatment systems include only reaction settling tanks and sludge pumps.

The flocculator included in the continuous chemical precipitation and sedimentation system can be either a steel tank or concrete tank unit. The concrete unit is based on a 45 minute retention time, a length to width ratio of 5, a depth of 8 feet, a wall thickness of 1 foot, and a 20 percent excess capacity factor. The steel unit size is based on a 45 minute retention time, and a 20 percent excess capacity factor. Capital costs for the concrete units include excavation (as required). A mixer is included in flocculators of both constructions.

The concrete settling tank included in the continuous chemical precipitation and clarification system is an in-ground unit sized for a hydraulic loading of 33.3 gph/square foot, a wall thickness of 1 foot, and an excess capacity factor of 20 percent. The steel settling tank included in the continuous chemical precipitation and sedimentation system is a circular above-ground unit sized for a hydraulic loading of 33.3 gph/square foot, and an excess capacity factor of 20 percent. The depth of the circular steel tank is assumed to increase linearly between six and fifteen feet for tanks with diameters between eight and twenty-four feet respectively. For tanks greater than twenty-four feet in diameter, the depth is assumed to be a constant fifteen feet. An allowance for field fabrication for the larger volume steel settling tanks is included in the capital cost estimation.

For batch treatment systems, dual above ground cylindrical steel tanks sized for an eight hour retention period and a 20 percent excess capacity factor are employed. The batch treatment system does not include a flocculation unit.

A fixed cost of $3,349 is included in the clarifier investment cost estimates for sludge pumps regardless of whether above-ground steel tanks (in the batch or continuous operation modes) or the in-ground concrete settling tank are used. This cost covers the expense of two centrifugal sludge pumps. Fixed costs of $2,346 and $12,902 are included to cover the expense of polymer feed systems for the batch and continuous operation modes respectively. The $12,902 figure is included regardless of whether concrete or steel tank construction is employed for the continuous operation mode.

Lime addition for chemical precipitation in the batch mode is assumed to be performed manually. A variable cost allowance for lime addition equipment is included in the continuous operation mode. This cost allowance covers the expense associated with a lime storage hopper, feeding equipment, slurry formation and mixing and slurry feed pumps. The cost allowance increases as clarifier tank size increases.

Figure 8-8 shows a comparison of investment cost curves for batch and continuous chemical precipitation and sedimentation systems. The continuous treatment system investment cost is based on a steel flocculation unit followed by a steel clarification basin. This combination of treatment components was found to be less expensive than the concrete flocculation basin, concrete clarification basin combination, or any combination of steel and concrete flocculation and clarification units. The batch treatment investment curve is based upon two above-ground cylindrical steel tank clarifier units. Both the continuous and batch system investment curves include allowances for the sludge pump, polymer feed systems, and lime addition equipment (continuous system only).

All costs presented above include motors, controls, pump stands, and piping specifically associated with each treatment component.

Operation and Maintenance Costs - The operation and maintenance costs for the clarifier routine include the cost of chemicals

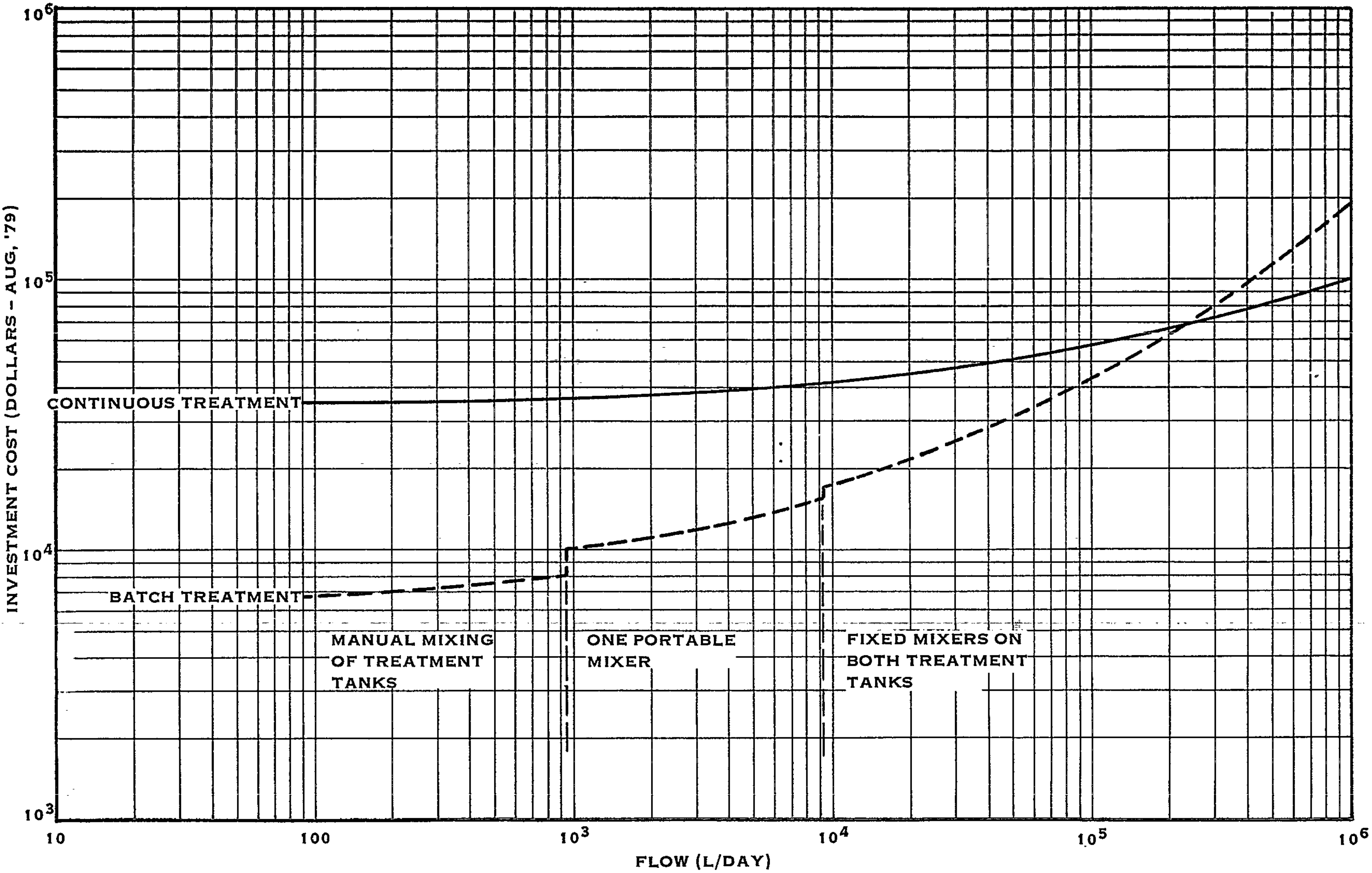


FIGURE 8-8
CHEMICAL PRECIPITATION AND CLARIFICATION INVESTMENT COSTS

added (lime, flocculants), and of labor for operation and maintenance. Each of these contributing factors is discussed below.

Figure 8-9 presents the annual manhour requirements for the continuously operating chemical precipitation and settling system. For the batch system, maintenance labor is calculated from the following equation:

Annual manhours for maintenance = 0.75 x (Days of operation per year)

Operational labor for the batch system is calculated from the following equation:

Annual manhours for operation = 780 + (1.3) (lbs of lime added per day)

Labor expenses have been estimated using a labor rate of $6.71 per manhour plus an additional 15% to cover indirect labor expenses.

Lime is added to the waste solution in order to precipitate dissolved metals so that the metal may be removed from the waste stream as settleable particulates. The amount of lime required for addition is based on equivalent amounts of various pollutant parameters present in the waste stream entering the unit. The coefficients used for calculating lime requirements are shown in Table 8-5.

The cost of lime required has been determined using a rate of:

$44.61 per ton of lime (August, 1979 price)

Figure 8-10 presents annual operation and maintenance cost curves for the continuous and batch operation modes of the chemical precipitation and settling system as a function of waste stream flow rate. The cost curves have been based on the assumption that the waste treatment system will operate 24 hours per day, 5 days per week, 260 days per year.

Energy Costs - The energy costs are calculated from the clarifier and sludge pump horsepower requirements.

Continous Mode - The clarifier horsepower requirement is assumed constant over the hours of operation of the treatment system at a level of 0.0000265 horsepower per 3.8 l/hour (1 gph) of flow influent to the clarifier. The sludge pumps are assumed operational for 5 minutes of each operational hour at a level of 0.00212 horsepower per 3.8 l/hour (1 gph) of sludge stream flow.

Batch Mode - The clarifier horsepower requirement is assumed to occur for 7.5 minutes per operational hour at the following level:

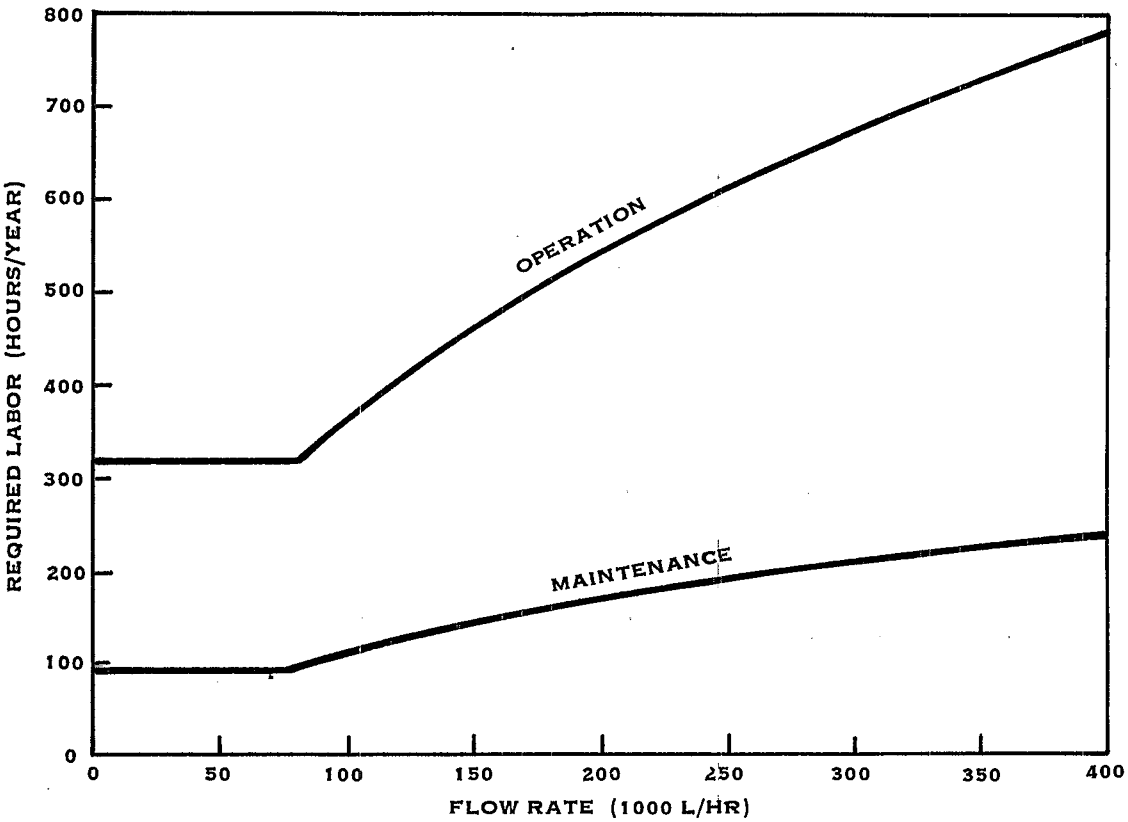


FIGURE 8-9
CHEMICAL PRECIPITATION AND SETTLING
ANNUAL OPERATION AND MAINTENANCE LABOR REQUIREMENTS

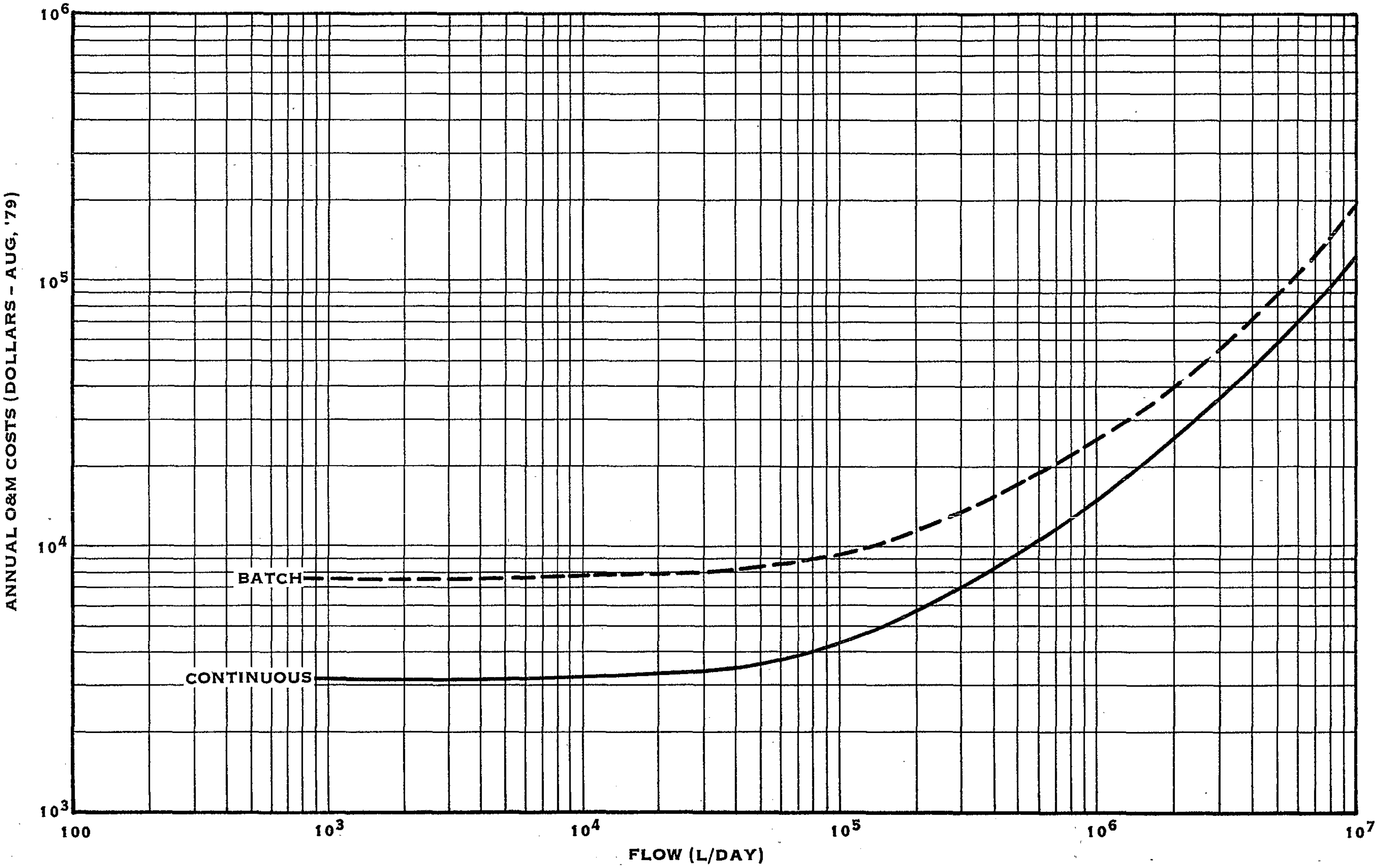


FIGURE 8-10
ANNUAL O&M COSTS VS. FLOW RATE FOR CLARIFIER

influent flow < 3944 l/hour; 0.0048 hp/gph

influent flow > 3944 l/hour; 0.0096 hp/gph

The power required for the sludge pumps in the batch system is the same as that required for the sludge pumps in the continuous system. Energy costs for these requirements are estimated based on a unit cost of $0.045/kilowatt hour of required electricity.

TABLE 8-5

LIME ADDITIONS FOR LIME PRECIPITATION

| Stream Parameter | Lime Addition kg/kg (lbs/lb) |
|---|---|
| Aluminum | 0.81 |
| Antimony | 4.53 |
| Arsenic | 1.75 |
| Cadmium | 2.84 |
| Chromium | 2.73 |
| Cobalt | 2.35 |
| Copper | 1.38 |
| Iron (Dissolved) | 1.28 |
| Lead | 2.19 |
| Magnesium | 0.205 |
| Manganese | 3.50 |
| Mercury | 1.48 |
| Nickel | 0.42 |
| Selenium | 1.45 |
| Silver | 3.23 |
| Zinc | 1.25 |

## Chemical Emulsion Breaking

Chemical emulsion breaking removes emulsified oil droplets from suspension through chemical destabilization. Destabilization allows the oil droplets to agglomerate, rise to the surface of the separation tank, and be removed from the wastewater by surface skimming mechanisms. This technology assumes that the waste oil emulsion is capable of being broken through chemical addition only, and that addition of heat will not be required.

In this waste treatment system, emulsified oil wastes are mixed with alum and chemical polymers, then allowed to separate via gravity separation in a settling tank. Once separation has occurred, the waste oils can be skimmed from the tank surface and disposed. The remaining wastewater is either passed on to further treatment or discharged depending on the waste treatment system.

Chemical emulsion breaking can be performed in either a continuous or a batch mode. Each operating mode, the equipment associated with each mode, and the design and operating assumptions incorporated are discussed in the following paragraphs.

Investment Costs - The investment costs associated with the continuous and batch operating modes for chemical emulsion breaking are shown in Figure 8-11 as a function of waste stream flow rate. For the continuous operating mode, the cost curve is based upon the purchase and installation of the following equipment:

| | |
|---|---|
| 2 | 946 liter (250 gallon) alum dilution tanks |
| 2 | Alum dilution tank mixers |
| 2 | Variable speed alum feed pumps (with pump stands and associated automatic control equipment) |
| 2 | 946 liter (250 gallon) polymer dilution tanks |
| 2 | Polymer dilution tank mixers |
| 2 | Variable speed polymer feed pumps (with pump stands and associated automatic control equipment) |
| 1 | Steel mixing tank with liner for chemical addition (sized for 15 minute retention time) |
| 1 | Mixing tank mixer (motor horsepower variable with mixing tank volume) |
| 1 | Steel gravity separation tank with liner, weirs, and baffles (sized for 1 hour retention time) |
| 1 | Separation tank surface oil skimming mechanism |
| 1 | Skimmed oil transfer pump |
| 1 | Waste oil storage tank (steel tank with liner, sized for 20 day retention) |
| 1 | Separation tank effluent transfer pump |

For the chemical emulsion breaking unit operated in the batch mode, the cost curve is based upon the purchase and installation of the following equipment:

| | |
|---|---|
| 1 | 946 liter (250 gallon) alum dilution tank |
| 1 | Alum dilution tank mixer |
| 1 | Alum feed pump with pump stand |
| 1 | 946 liter (250 gallon) polymer dilution tank |
| 1 | Polymer dilution tank mixer |
| 1 | Polymer feed pump with pump stand |
| 2 | Steel gravity separation tanks with liners (sized for variable retention depending on least cost mode) |
| 2 | Tank mixers (motor hp variable with separation tank volume) |
| 1 | Separation tank effluent transfer pump |

The chemical emulsion breaking system (both batch and continuous operating modes) have been sized for a 20% excess capacity factor. Selection of the operating mode is based on a least cost basis as discussed previously in the Section VIII text.

Operation and Maintenance Costs - The operation and maintenance costs associated with the chemical emulsion breaking unit consist of labor and material expenses.

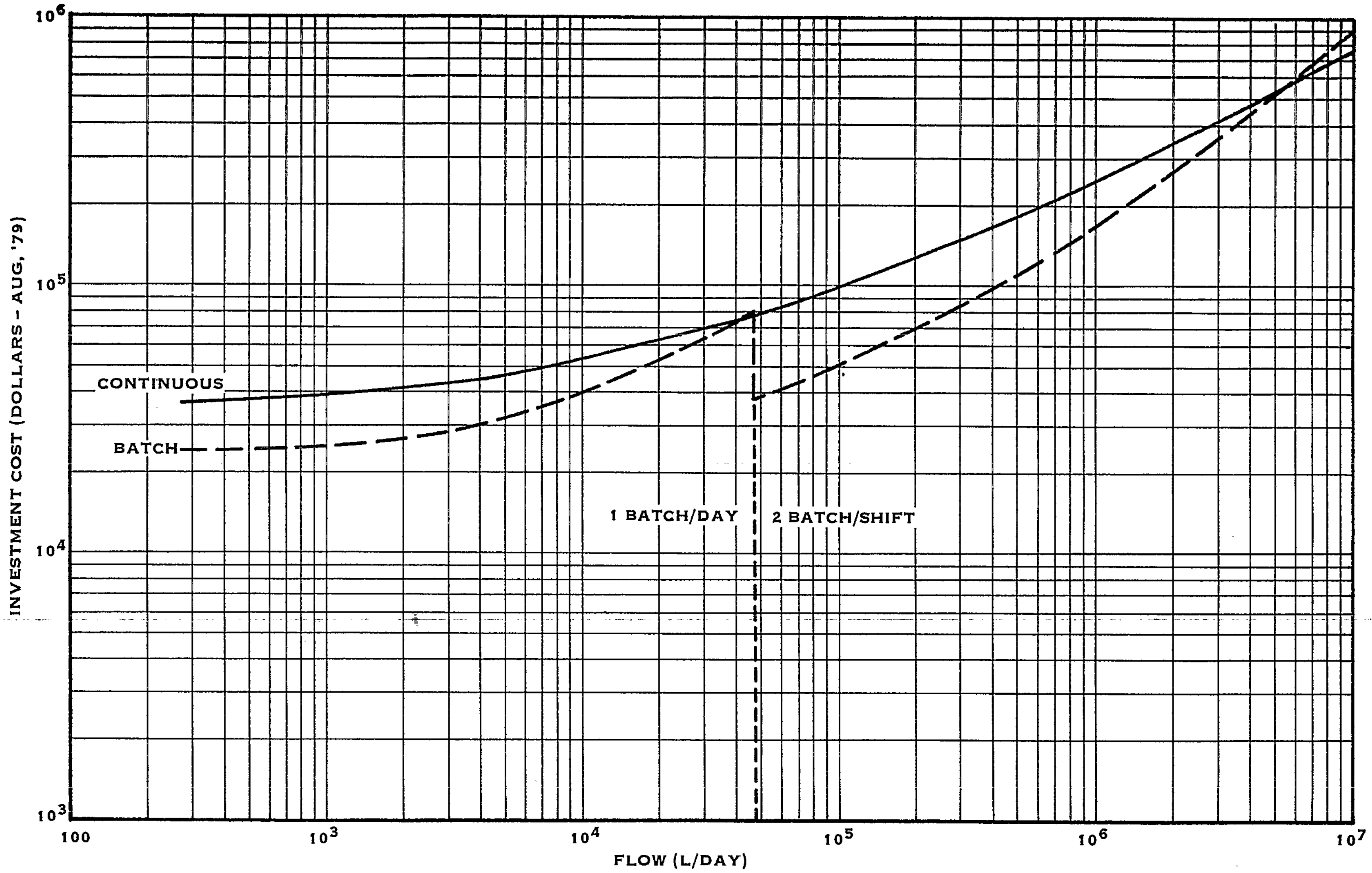


FIGURE 8-11
EMULSION BREAKING INVESTMENT COSTS

Annual labor expenses for both the continuous and batch operating modes for the chemical emulsion breaking unit are shown in Figure 8-12 as a function of waste stream flow rate. For the continuous operating mode, labor requirements are based on estimated manhours required for diluting and mixing the polymer and alum solutions and operating the unit. General operation labor has been estimated at 0.75 manhours per 8 hour shift. General maintenance of the entire system has been estimated at 2 manhours per week.

For the batch operating mode, labor requirements are based on estimated manhours required for diluting and mixing the polymer and alum solutions and operating the unit. General operation labor has been estimated at 0.75 manhours required per batch. General maintenance of the entire system has been estimated at 1 manhour per week.

Labor expenses have been calculated using a labor rate of $6.71 per manhour plus an additional 15% to cover indirect labor costs.

Material costs are associated with the alum and polymer chemical addition requirements. Polymer is added to the wastewater until a concentration of 150 mg/l is attained. Alum is added to the wastewater until a concentration of 25 mg/l is attained. Chemical costs have been based upon the following unit prices:

$0.38 per kg of alum
$1.55 per kg of polymer

The assumption has been made that the unit operates 24 hours per day, 5 days per week, 52 weeks per year.

Energy Costs - Annual energy expenses for the chemical emulsion breaking system (both batch and continuous operating modes) are shown in Figure 8-13 as a function of waste stream flow rate. These costs are based on operation of the dilution tank mixers, chemical feed pumps, mixing and separation tank mixers (as applicable), oil skimmer (as applicable), and solution transfer pumps (oil and separation tank transfer pumps, as applicable). Energy expenses have been estimated based upon a rate of $0.045/kilowatt-hour of required electricity. It has been assumed that the unit operates 24 hours per day, 5 days per week, 52 weeks per year.

### Holding Tanks

Tanks serving a variety of purposes in wastewater treatment and control systems are fundamentally similar in design and construction and in cost. They may include equalization tanks, solution holding tanks, slurry or sludge holding tanks, mixing tanks, and settling tanks from which sludge is intermittently removed manually or by sludge pumps. Tanks for all of these purposes are addressed in a single cost estimation subroutine with additional costs for auxilliary equipment such as sludge pumps added as appropriate.

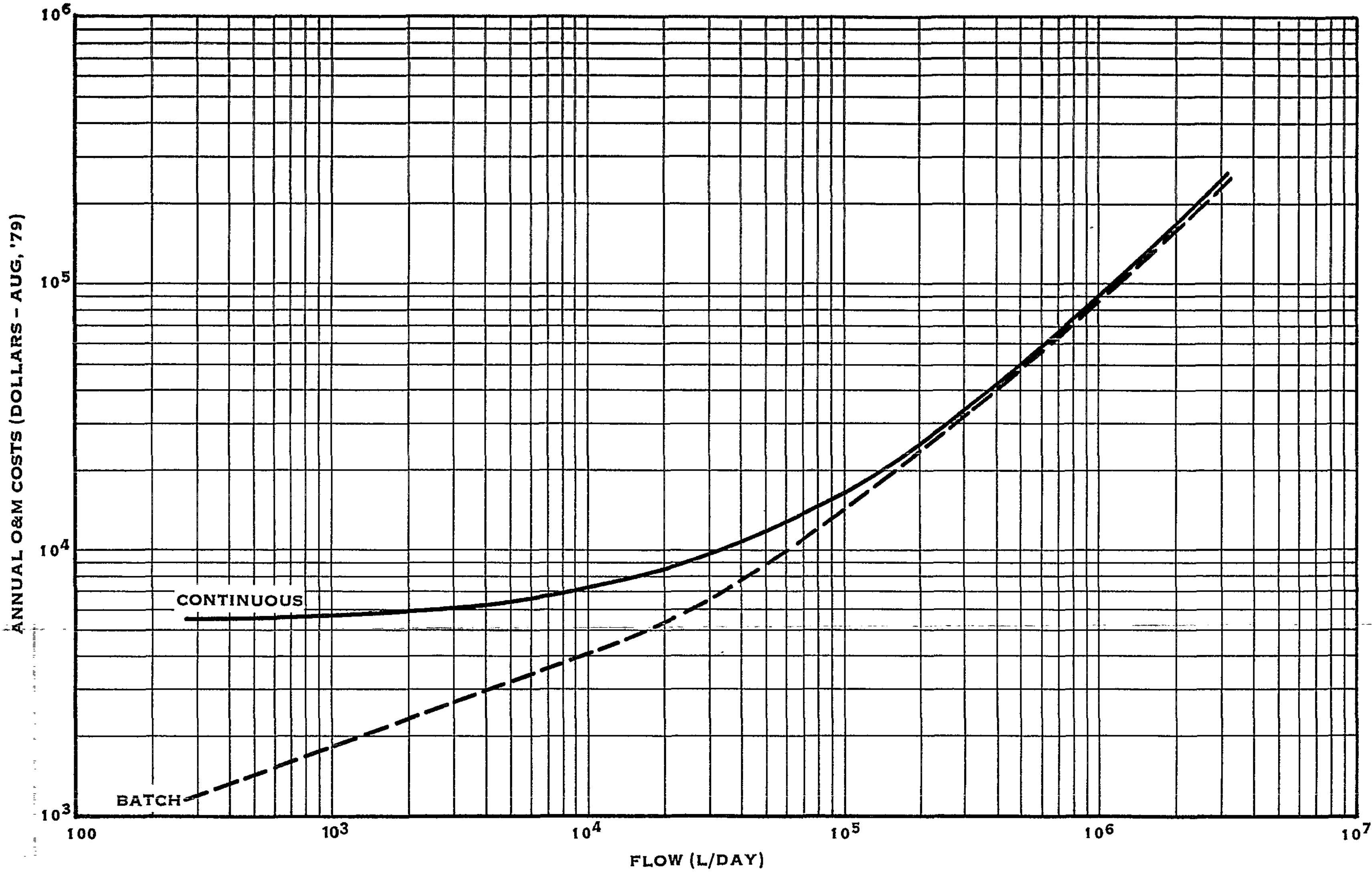


FIGURE 8-12

ANNUAL O&M COSTS VS. FLOW RATE FOR CHEMICAL EMULSION BREAKING

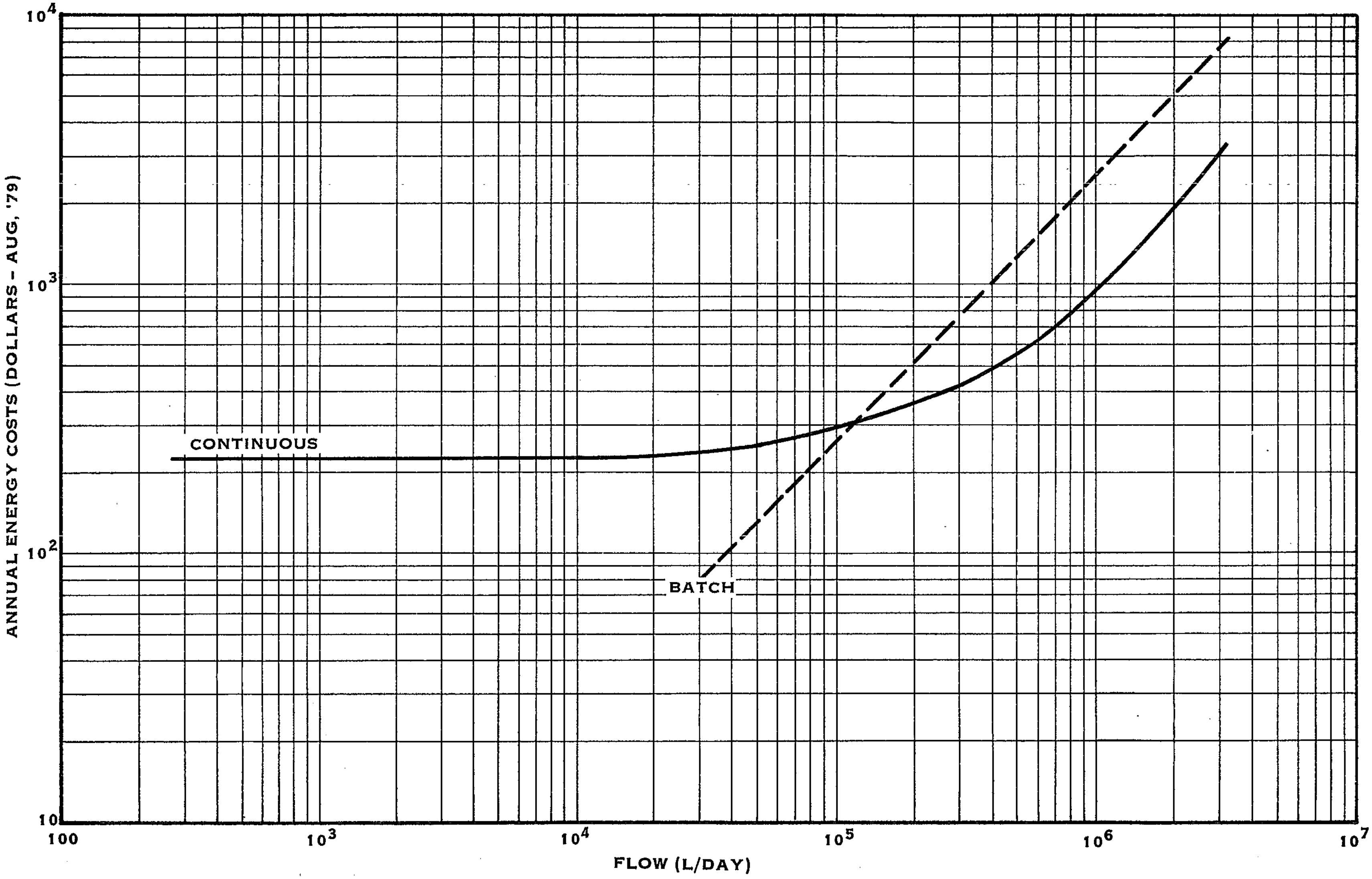


FIGURE 8-13

ANNUAL ENERGY COSTS VS. FLOW RATE FOR CHEMICAL EMULSION BREAKING

Investment Costs - Costs are estimated for steel tanks. Tank construction may be specified as input data, or determined on a least cost basis. Retention time is specified as input data and, together with stream flow rate, determines tank size. Investment costs for steel tanks sized for 0.5 days retention and 20% excess capacity are shown as functions of stream flow rate in Figure 8-14. These costs include mixers, pumps and installation.

Operation and Maintenance Costs - For all holding tanks except sludge holding tanks, operation and maintenance costs are minimal in comparison to other system O&M costs. Therefore only energy costs for pump and mixer operation are determined. These energy costs are presented in Figure 8-15.

For sludge holding tanks, additional operation and maintenance labor requirements are reflected in increased O&M costs. The required manhours used in cost estimation are prsented in Figure 8-16. Labor costs are determined using a labor rate of $6.71 per manhour plus 15% indirect labor charge.

Where tanks are used for settling as in lime precipitation and clarification batch treatment, additional operation and maintenance costs are calculated as discussed specifically for each technology.

## Multimedia Filtration

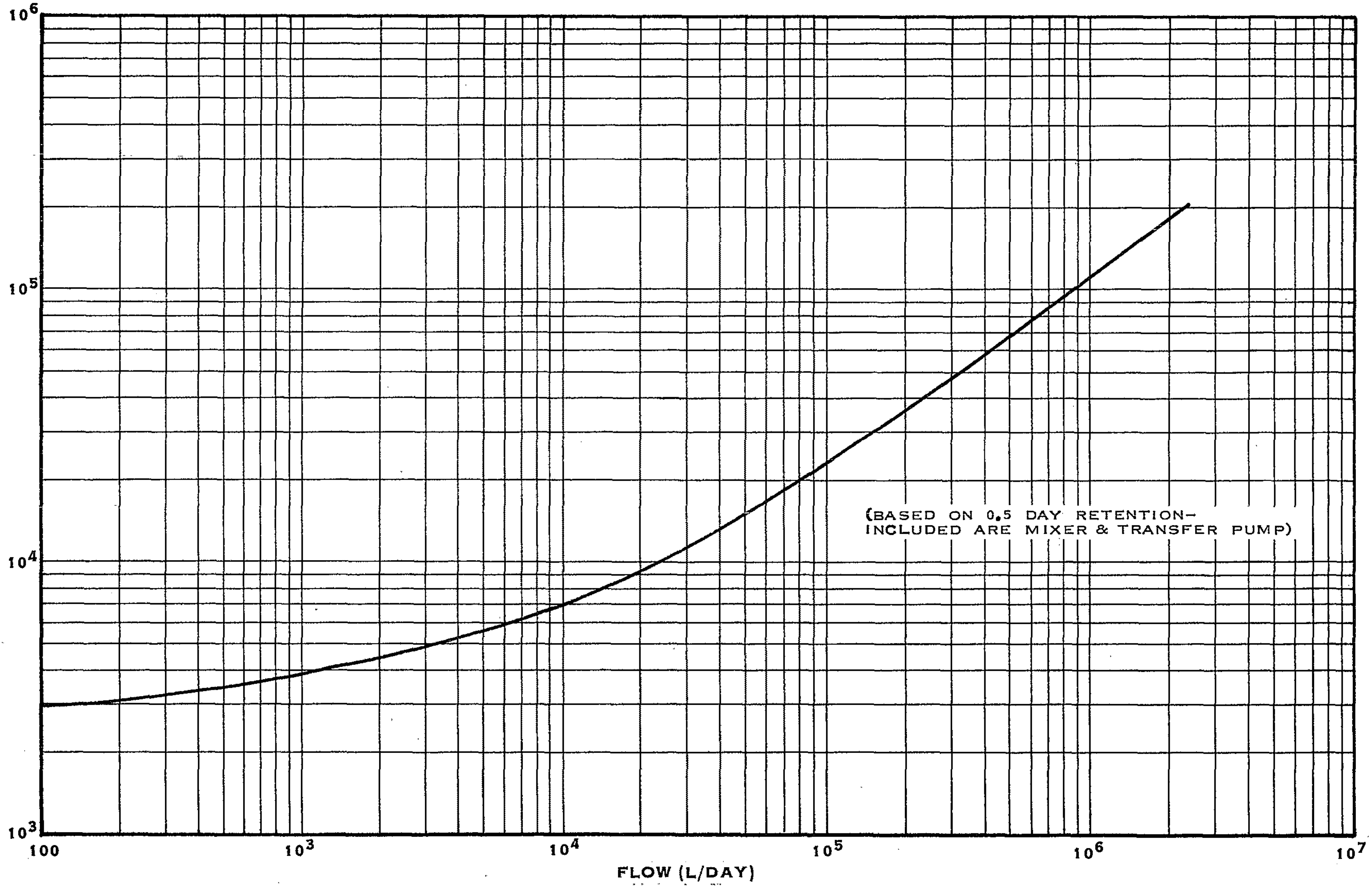
This technology provides removal of suspended solids by filtration through a bed of particles of several distinct size ranges. As a polishing treatment after chemical precipitation and clarification processes, multimedia filtration provides improved removal of precipitates and thereby improved removal of the original dissolved pollutants.

Investment Costs - The size of the granular bed multimedia filtration unit is based on 20% excess flow capacity and a hydraulic loading of 81.5 $lpm/m^2$. Investment cost is presented in Figure 8-17 as a function of flow installation.

Operation and Maintenance - The costs shown in Figure 8-18 for operation and maintenance include contributions of materials, electricity and labor. These curves result from correlations made with data obtained by a major manufacturer. Energy costs are estimated to be 3% of total O&M.

## Ultrafiltration

Ultrafiltration is a separation process involving the use of a semipermeable polymeric membrane. The porous membrane acts as a barrier, separating molecular sized particulates from the waste stream. Membrane permeation by particulates is dependent upon particulate size, shape and chemical structure. Solvents and lower molecular weight solutes are typically passed through the



(BASED ON 0.5 DAY RETENTION–INCLUDED ARE MIXER & TRANSFER PUMP)

FIGURE 8-14
HOLDING TANK INVESTMENT COSTS

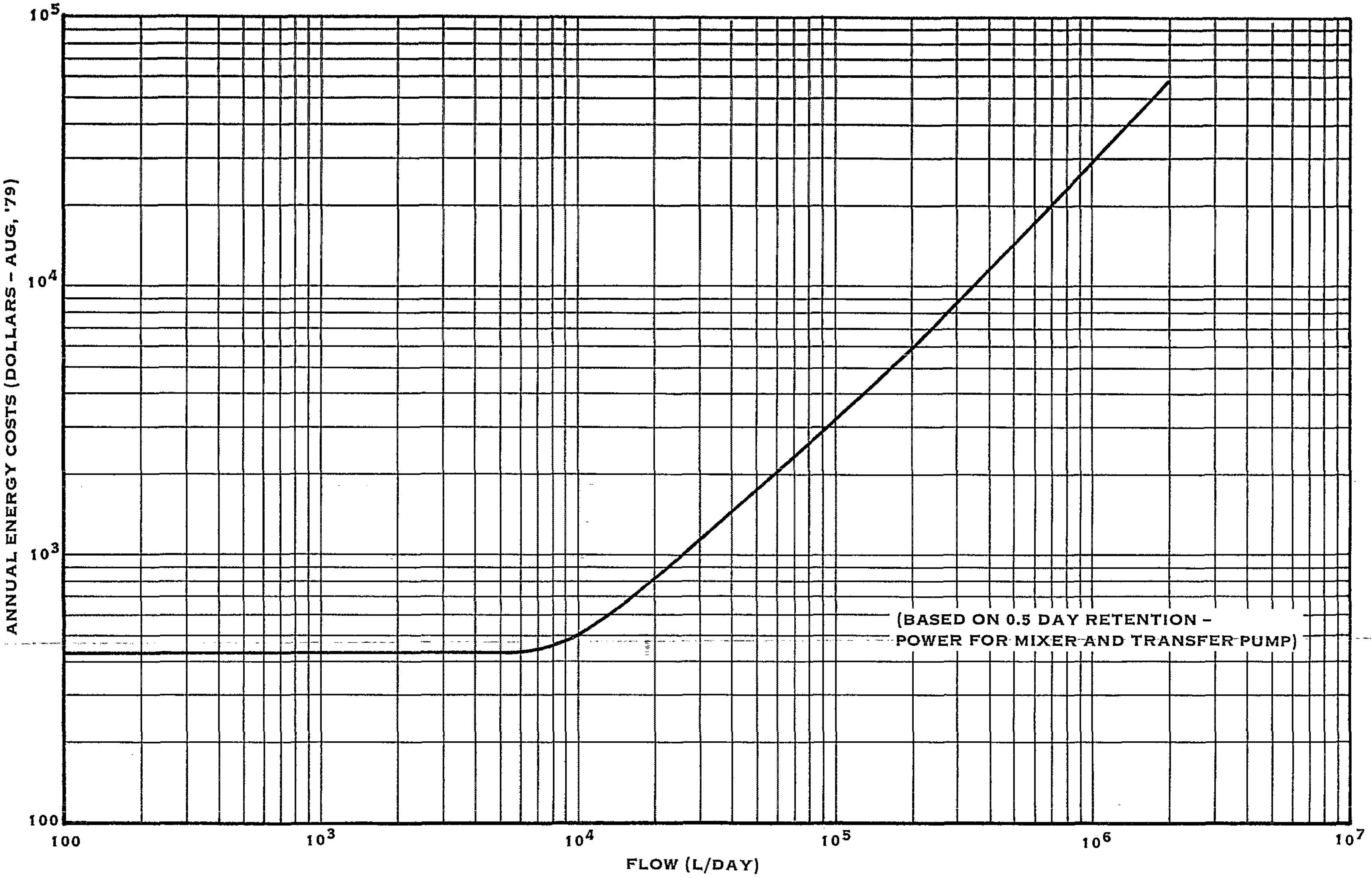


FIGURE 8-15
ANNUAL ENERGY COSTS VS. FLOW FOR HOLDING TANKS

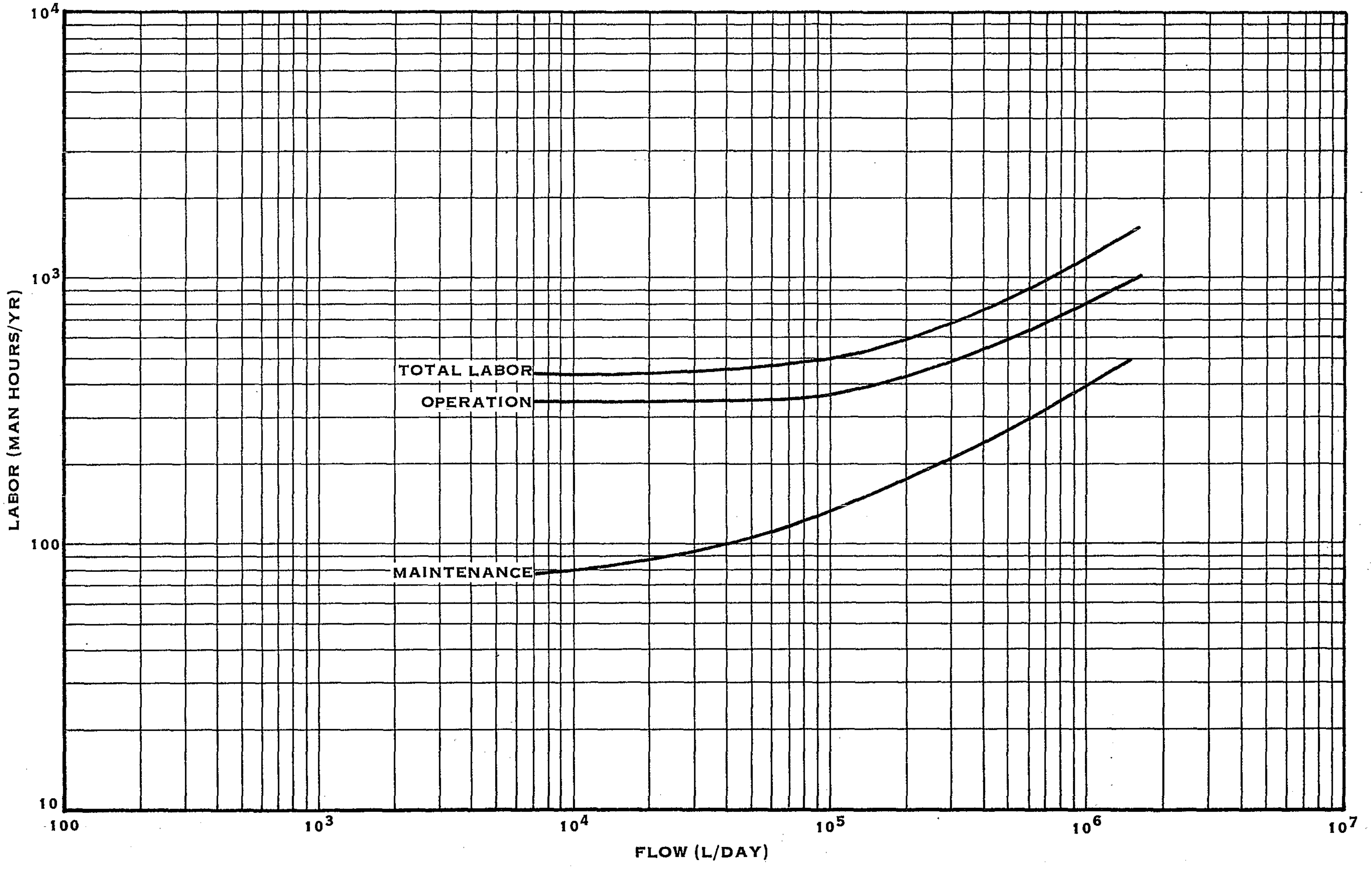


FIGURE 8-16
LABOR REQUIREMENTS VS. FLOW FOR SLUDGE HOLDING TANKS

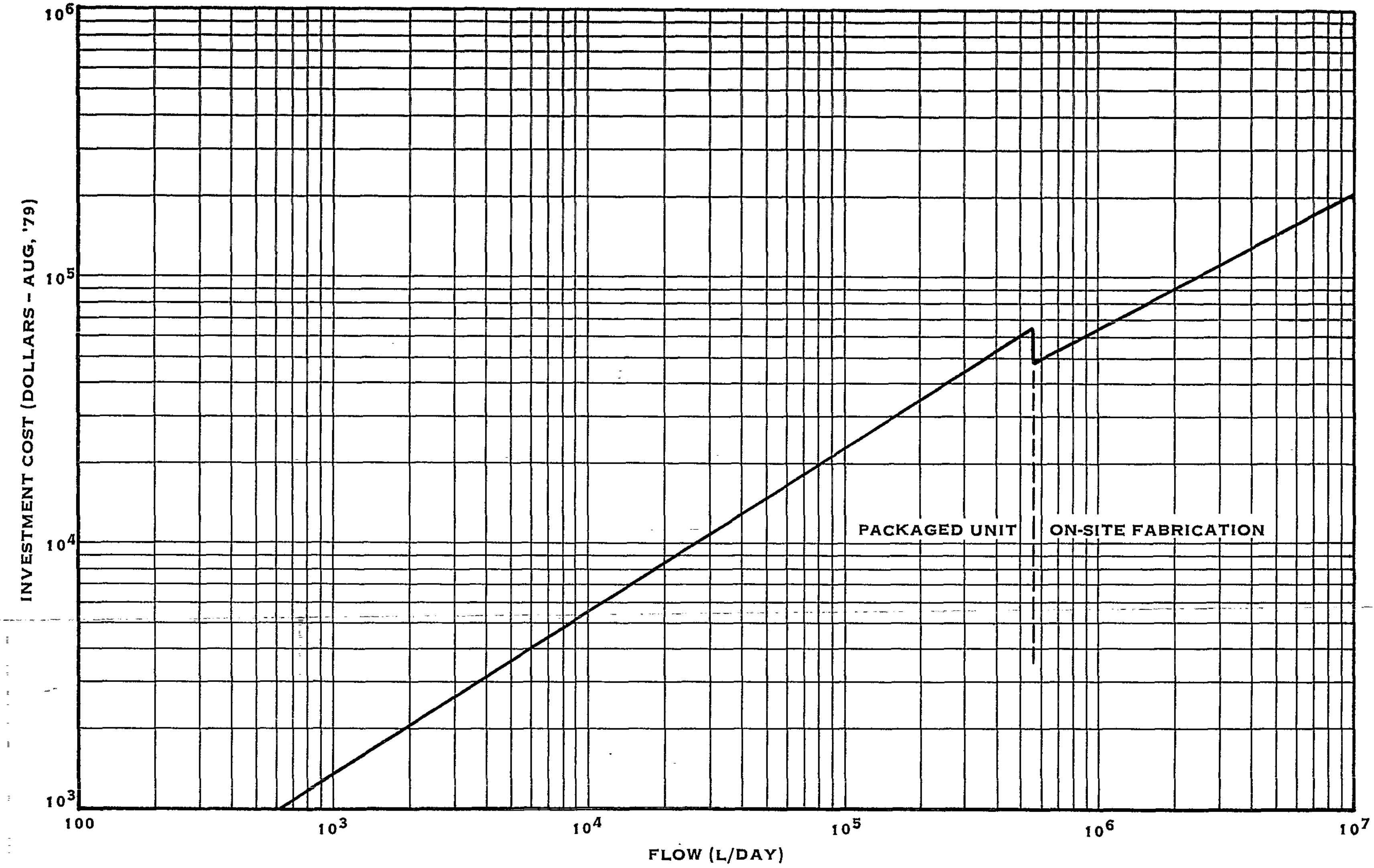


FIGURE 8-17
MULTIMEDIA FILTRATION INVESTMENT COSTS

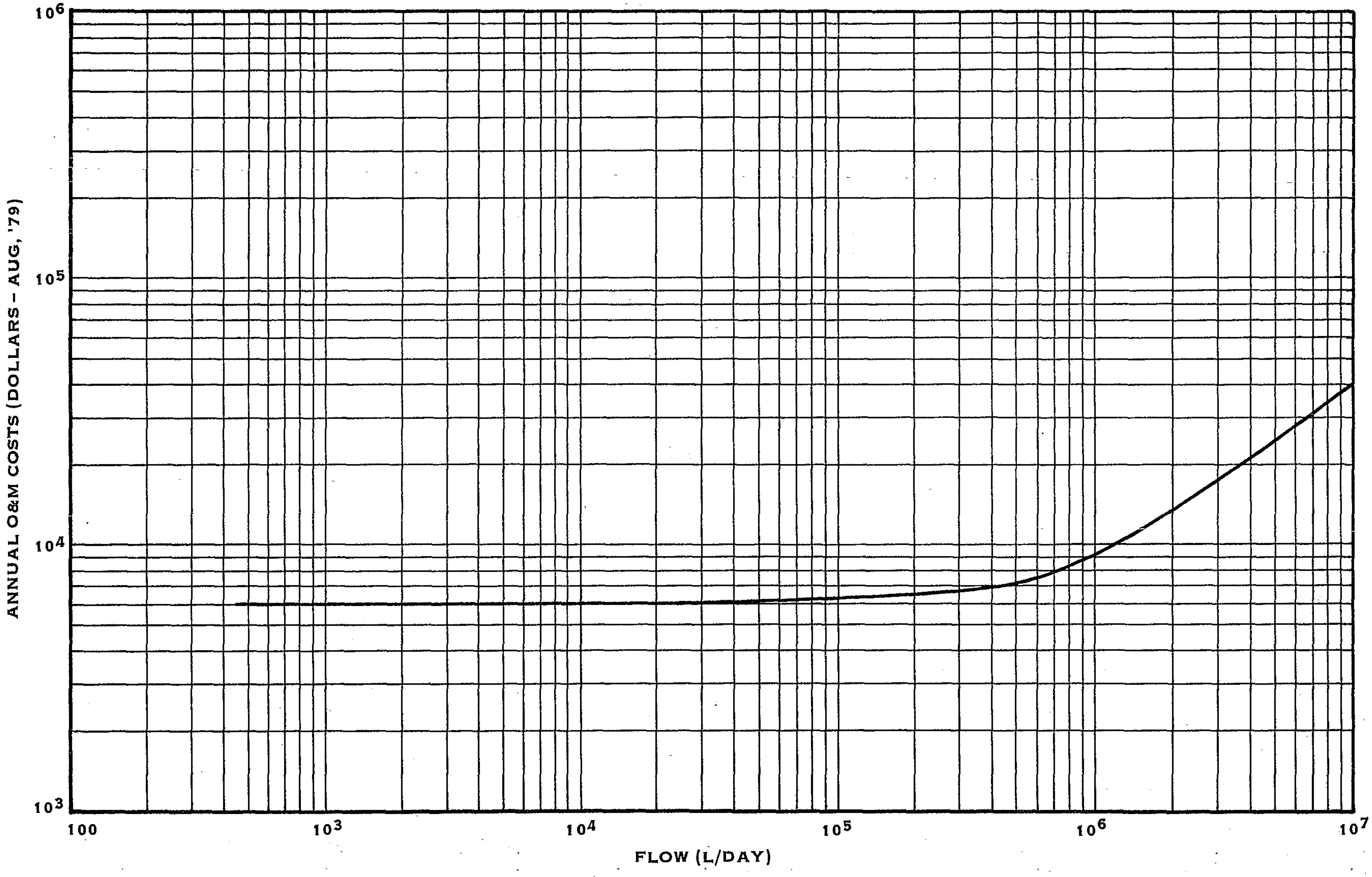


FIGURE 8-18

ANNUAL O&M COSTS VS. FLOW RATE FOR MULTIMEDIA FILTRATION membrane, while dissolved or dispersed materials with molecular weights in the range of 1,000 to 100,000 are removed from solution.

The ultrafiltration process occurs when a waste solution is pumped under a fixed head (10 to 100 psig) through a tubular membrane unit. Water and low molecular weight materials pass through the membrane and are recycled, passed on to further treatment or are discharged. Emulsified oils and larger sized suspended particulates are blocked by the membrane and are thus concentrated in a continuously discharged waste stream. The concentrated waste solution can then be passed on to further treatment or disposal.

Investment Costs - The investment cost curve for the ultrafiltration unit has been calculated using information supplied by leading manufacturers in the industry. Figure 8-19 presents investment cost information for ultrafiltration systems as a function of waste stream flow rate. This cost curve has been generated based upon purchase and installation of a complete package ultrafiltration system. This system includes the following equipment:

| | |
|---|---|
| 1 | wastewater flow equalization tank |
| 1 | wastewater process tank |
| 1 | set of ultrafiltration membrane modules (quantity variable with wastewater flow rate) |
| 1 | set of transfer and circulation pumps |
| 1 | acid feed system (includes storage and pumps as required for membrane cleaning) |
| 1 | set of process controls and instrumentation |

Operation and Maintenance Costs - Annual operation and maintenance costs for the ultrafiltration system are shown in Figure 8-20 as a function of waste stream flow rate. This cost curve includes labor and materials required for system operation. The operation and maintenance cost curve has been estimated based upon information supplied by a leading ultrafiltration system manufacturer. The curve is based on the assumption that the system operates 24 hours per day, 5 days per week, 52 weeks per year.

Energy Costs - Annual energy costs for the ultrafiltration system are shown in Figure 8-21 as a function of waste stream flow rate. This cost curve has been generated based upon information supplied by a leading ultrafiltration system manufacturer. The curve is based on the assumption that the system operates 24 hours per day, 5 days per week, 52 week per year.

## Carbon Adsorption

This technology removes organic pollutants and suspended solids by pore adsorption, surface reactions, and physical filtering by the carbon grains. It typically follows other types of treat-

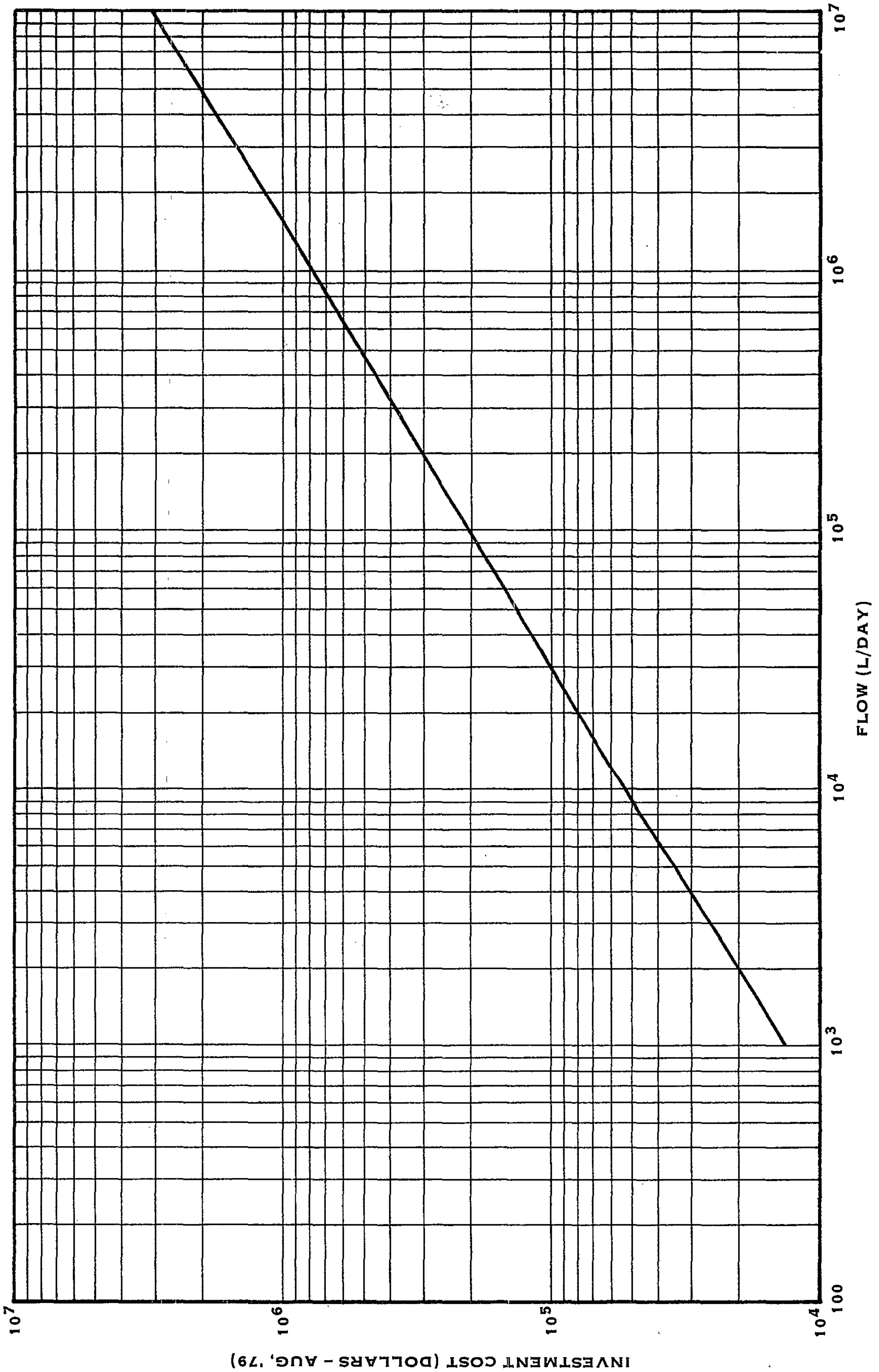


FIGURE 8-19
ULTRAFILTRATION INVESTMENT COSTS

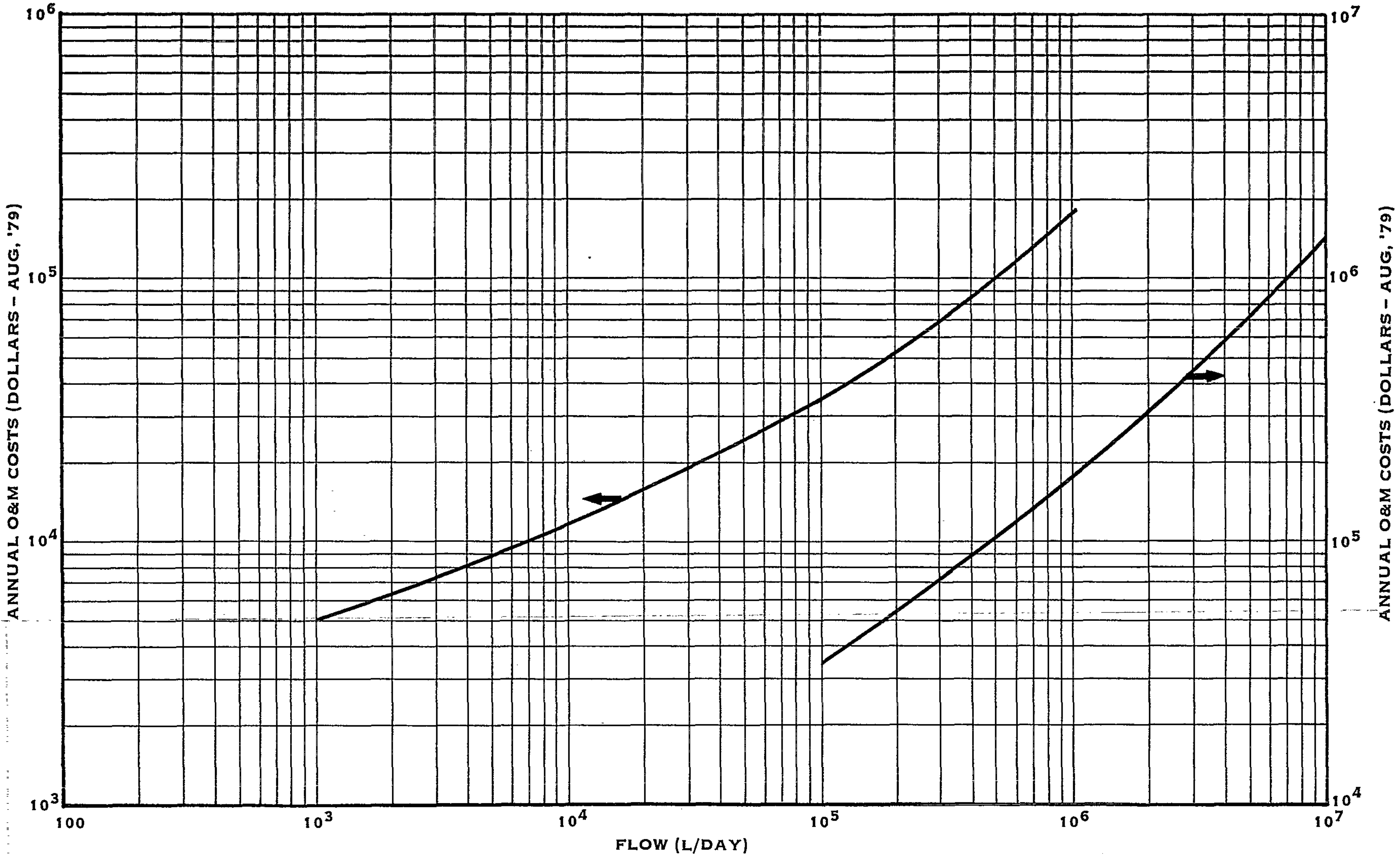


FIGURE 8-20
ANNUAL O&M COSTS VS. FLOW RATE FOR ULTRAFILTRATION

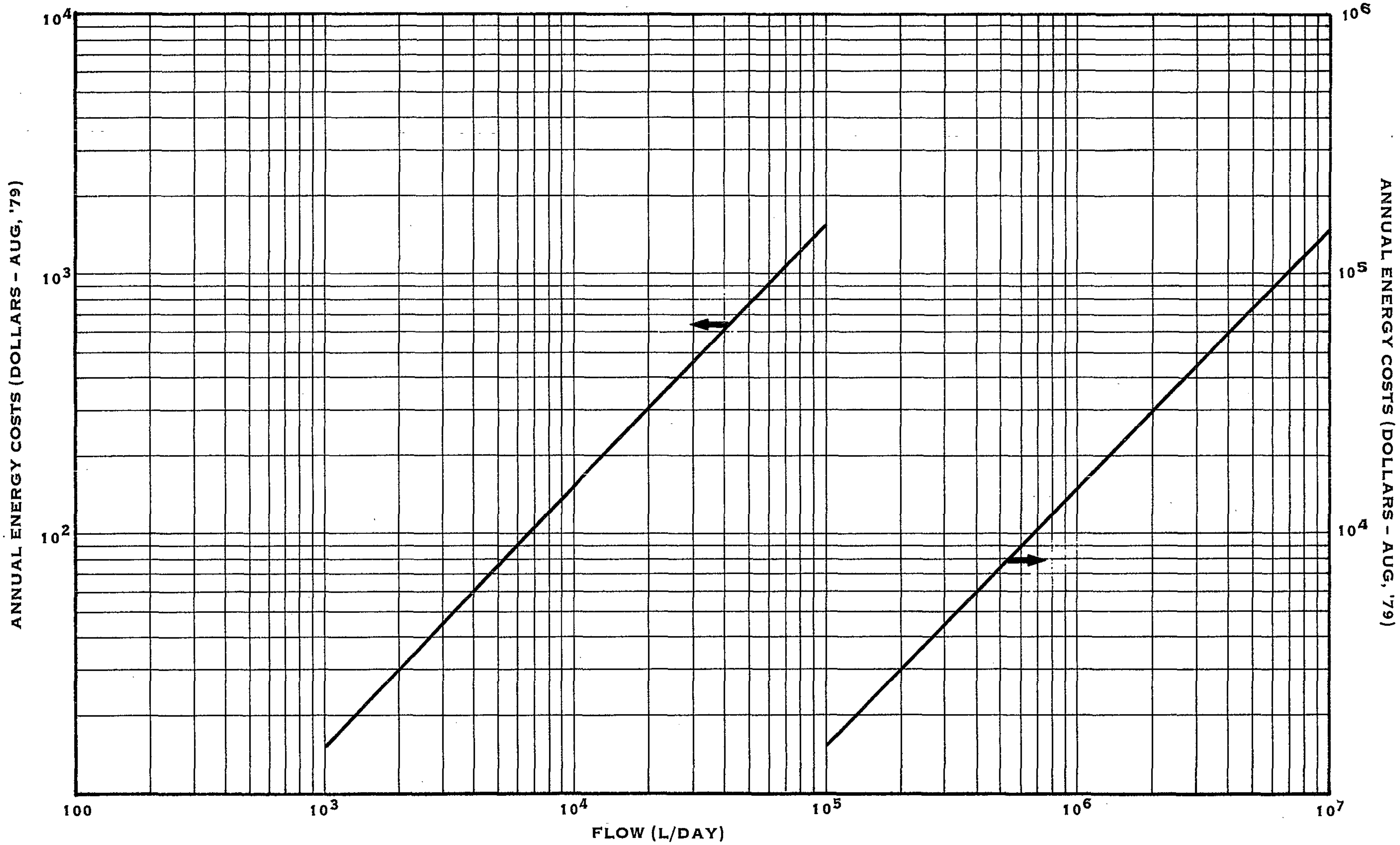


FIGURE 8-21
ANNUAL ENERGY COSTS VS. FLOW RATE FOR ULTRAFILTRATION

ment as a means of polishing the effluent. A variety of carbon adsorption systems exist: upflow, downflow, packed bed, expanding bed, regenerative, and throwaway. Regeneration of carbon requires an expensive furnace and fuel for regeneration that are not required for a throwaway system. Large systems may find that the high cost of replacement carbon makes a regenerative system economically attractive.

Investment Costs - The investment costs presented in Figure 8-22 are for a packed-bed throwaway system as based on the EPA Technology Transfer Process Design Manual for Carbon Adsorption. They include a contactor system, a pump station, and initial carbon. The design assumes a contact time of 30 minutes, a hydraulic loading of 1.41 liters/minute/ft$^2$ (4 gpm/ft$^2$,) and 20% excess capacity.

Operation and Maintenance Costs - The chief operation and maintenance costs are labor and replacement carbon. The labor hours required are computed using Figure 8-23 which is taken from an EPA Technology Transfer. The labor unit cost used is $6.71/hr plus 15% indirect charges. The replacement carbon cost was calculated by assuming:

1) One pound of replacement carbon is required per pound of organics removed.

2) The influent organic concentration (materials effectively adsorbed) is 0.42 mg/l.

3) Activated carbon costs $2.62/kg. ($1.19 lb).

Energy Costs - Energy is required for carbon adsorption operated in the throwaway mode for the operation of pumps. Costs for this electrical energy requirement based on a unit cost of $0.045/kilowatt hour of required electricity are shown as a function of wastewater flow rate in Figure 8-24.

## Sludge Drying Beds

This technology provides for the dewatering of sludge by means of gravity drainage and natural evaporation. Beds of highly permeable gravel and sand underlain by drain pipes allow the water to drain easily from the sludge. This is a non energy-intensive alternative to sludge dewatering.

Investment Costs - The curve shown in Figure 8-25 illustrates the correlation used to estimate the cost of sludge drying beds. The investment cost is a function of both the flow rate to the beds and the settleable solids concentration in the stream influent to the sludge beds; however, the effect of solids concentration is very small in comparison to the dependence on flow rate. The cost estimates presented include excavation, fill, drain and feed pipes, and concrete splash boxes.

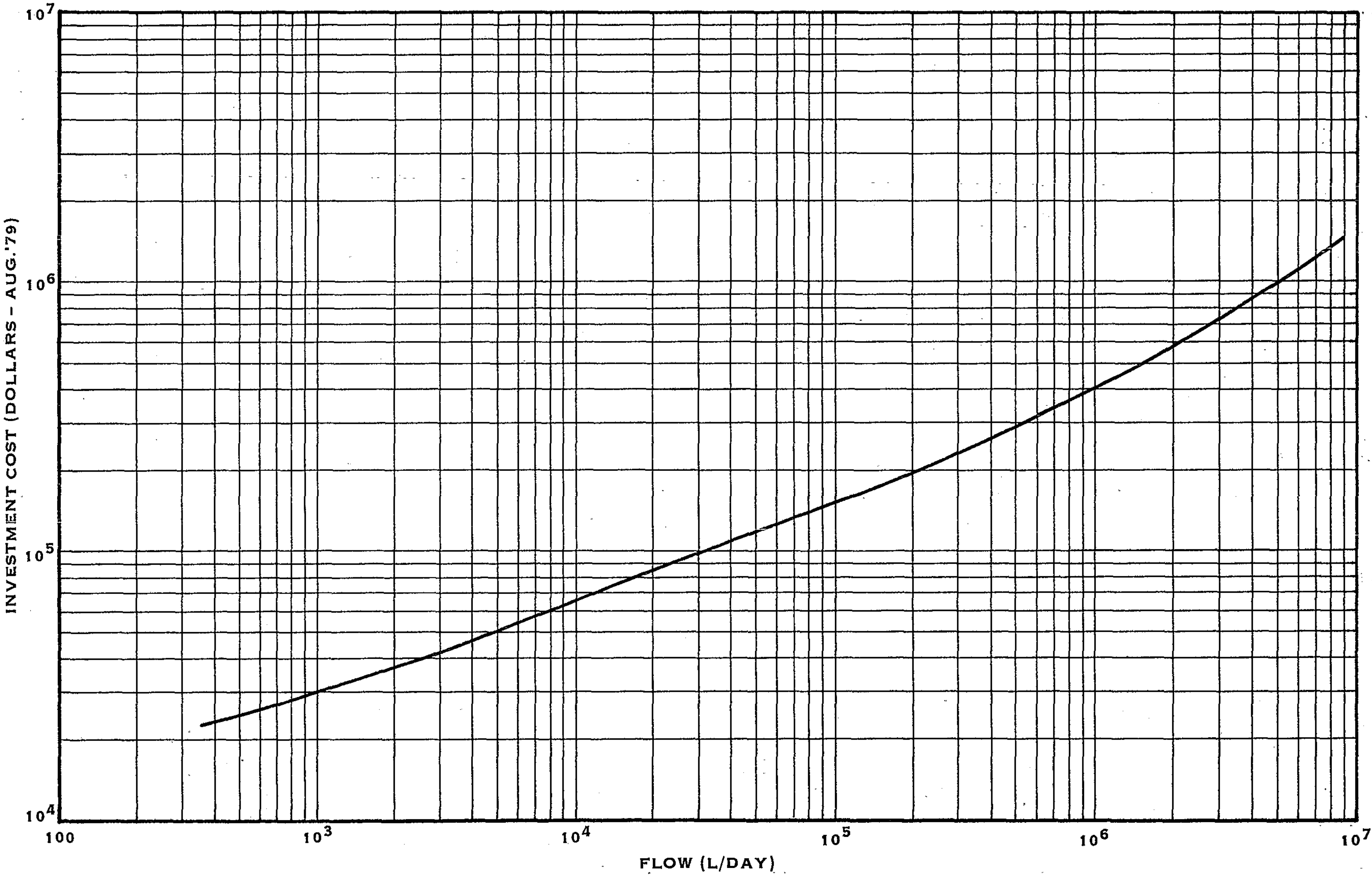


FIGURE 8-22
CARBON ADSORPTION INVESTMENT COSTS

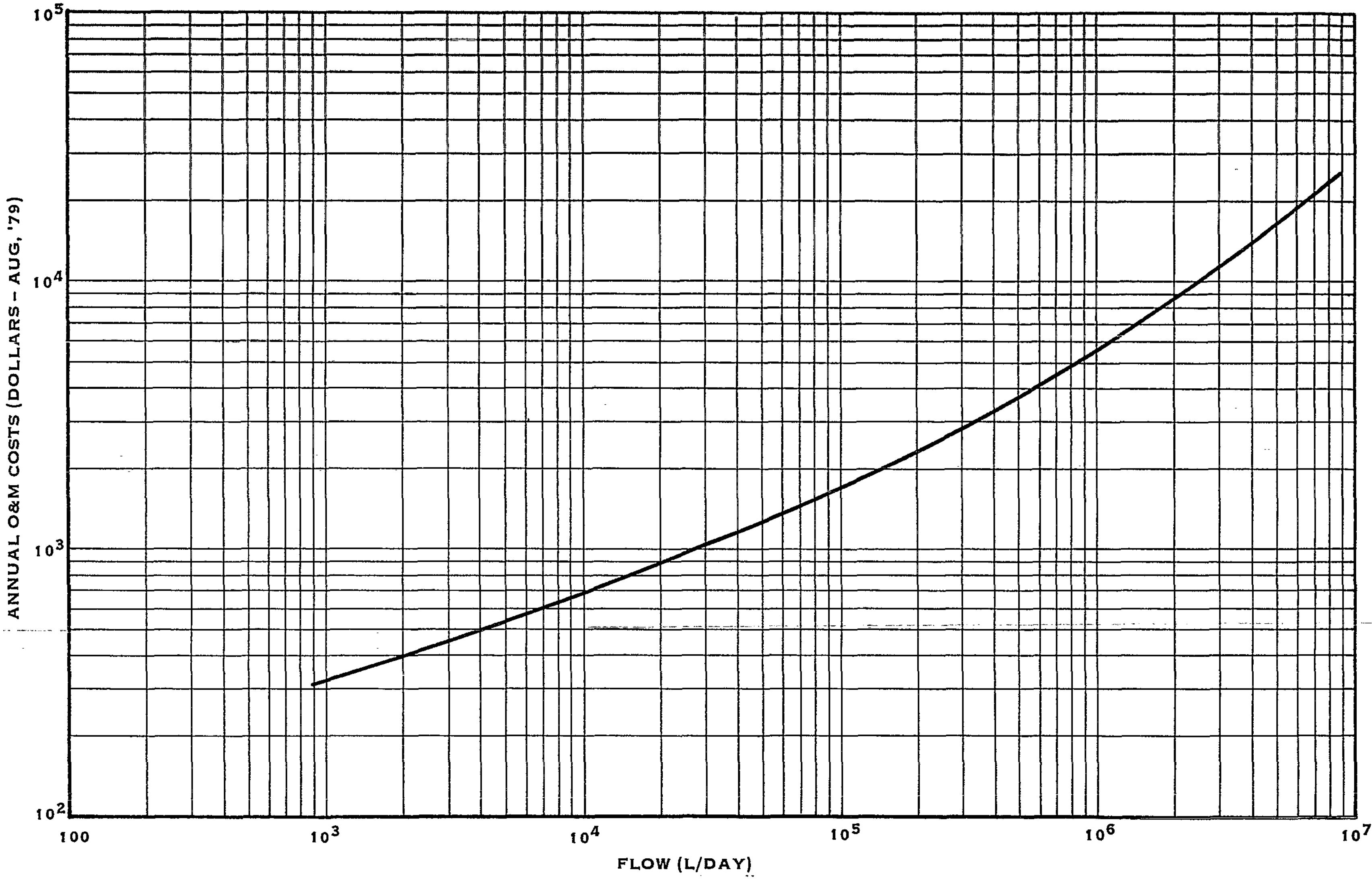


FIGURE 8-23

ANNUAL O&M COSTS VS. FLOW RATE FOR CARBON ADSORPTION

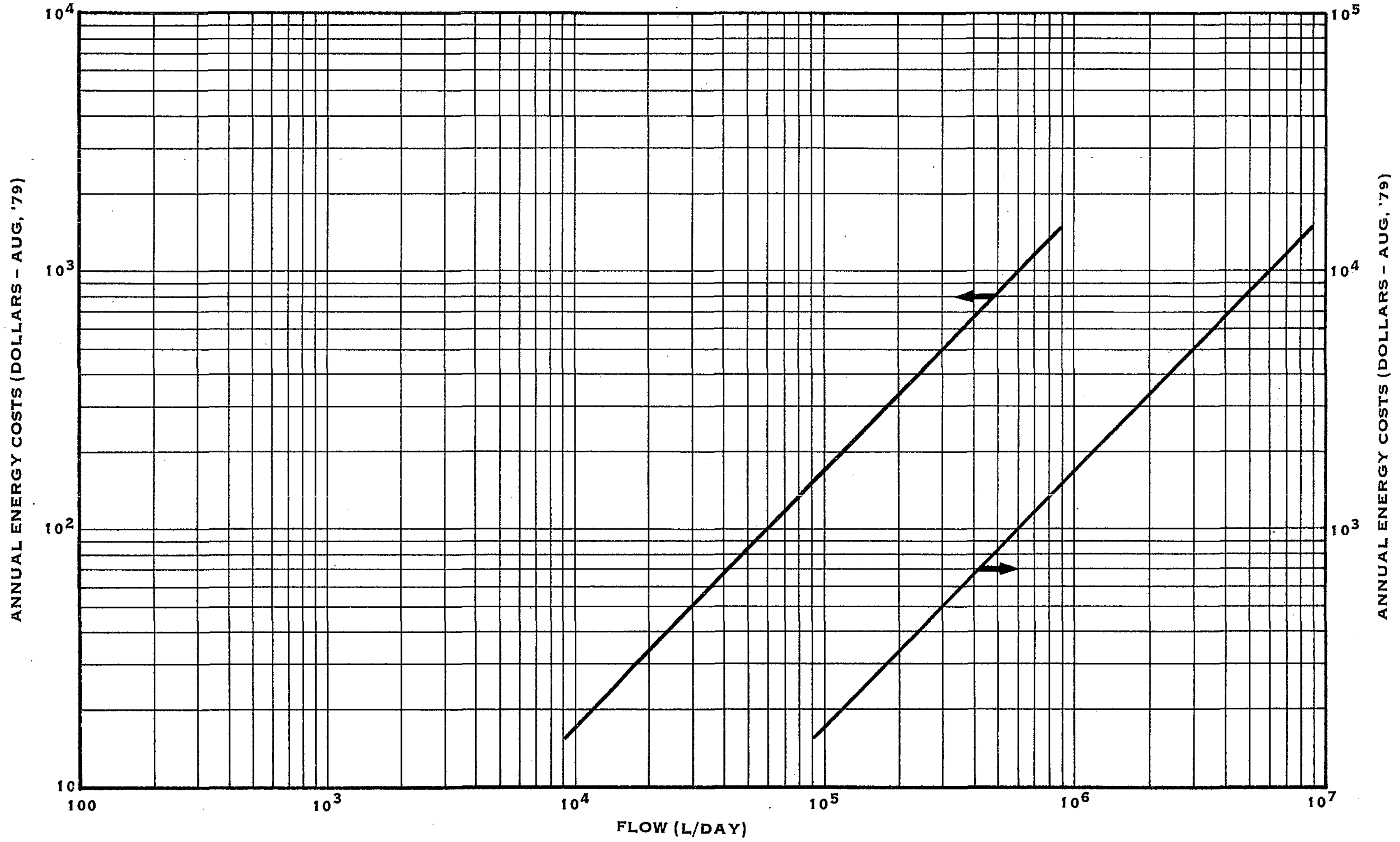


FIGURE 8-24

ANNUAL ENERGY COSTS VS. FLOW RATE FOR CARBON ADSORPTION

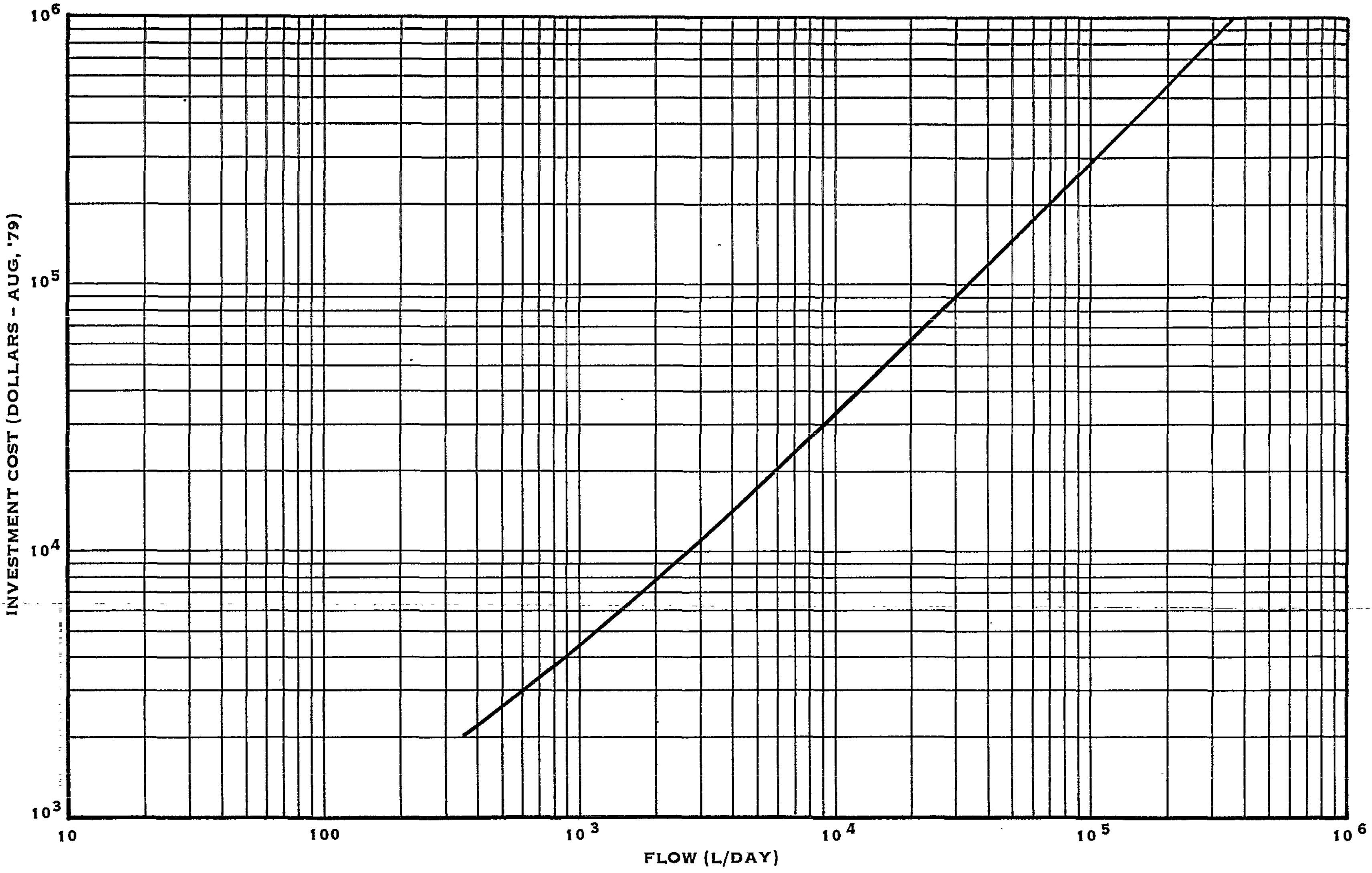


FIGURE 8-25
SLUDGE DRYING BEDS INVESTMENT COSTS

Operation and Maintenance - Operation and maintenance costs for sludge drying beds include labor and materials. Labor requirements include routine operation and maintenance and periodic removal of sludge from the beds. Material costs include the replacement of sand and gravel removed with the sludge.

The cost of labor and material required to maintain and operate the sludge beds is shown as a function of flow rate to the beds in Figure 8-26.

## Vacuum Filtration

Vacuum filtration is widely used to reduce the water content of high solids streams. In the metal finishing category, this technology is applied to dewatering sludge from clarifiers, where the volume of sludge is too large for economical dewatering in sludge drying beds.

Investment Costs - The vacuum filter is sized based on a typical loading of 14.6 kilograms of influent solids per hour per square meter of filter area (3 lbs/ft$^2$/hr). The investment costs are shown as a function of sludge flow rate to the filter in Figure 8-27. The investment costs shown on this curve include installation costs and correspond to a solids content of 4.5% in the influent to the filter, typical of the sludge stream from a clarifier.

Operation and Maintenance Costs - Annual costs for operation and maintenance for vacuum filtration include both operation and maintenance labor and the cost of materials and supplies. These costs are presented as a function of sludge flow rate to the filter in Figure 8-28.

The vacuum filtration subroutine calculates operating hours per year based on flow rate and the total suspended solids concentration in the influent stream. Maintenance labor for vacuum filtration is fixed at 24 manhours per year.

The cost of materials and supplies needed for operation and maintenance includes belts, oil, grease, seals, and chemicals required to raise the total suspended solids to the vacuum filter. The amount of chemicals required (iron and alum) is based on raising the TSS concentration to the filter by 1 mg/l.

Energy Costs - Electrical costs needed to supply power for pumps and controls are presented in Figure 8-29. The required horsepower of the pumps is dependent on the influent TSS level. The costs shown are based on a unit cost of $0.045/kilowatt hour of required electricity.

## Countercurrent Rinsing

This technology is applied in rinsing operations to substantially improve the efficiency of rinse water use and decrease

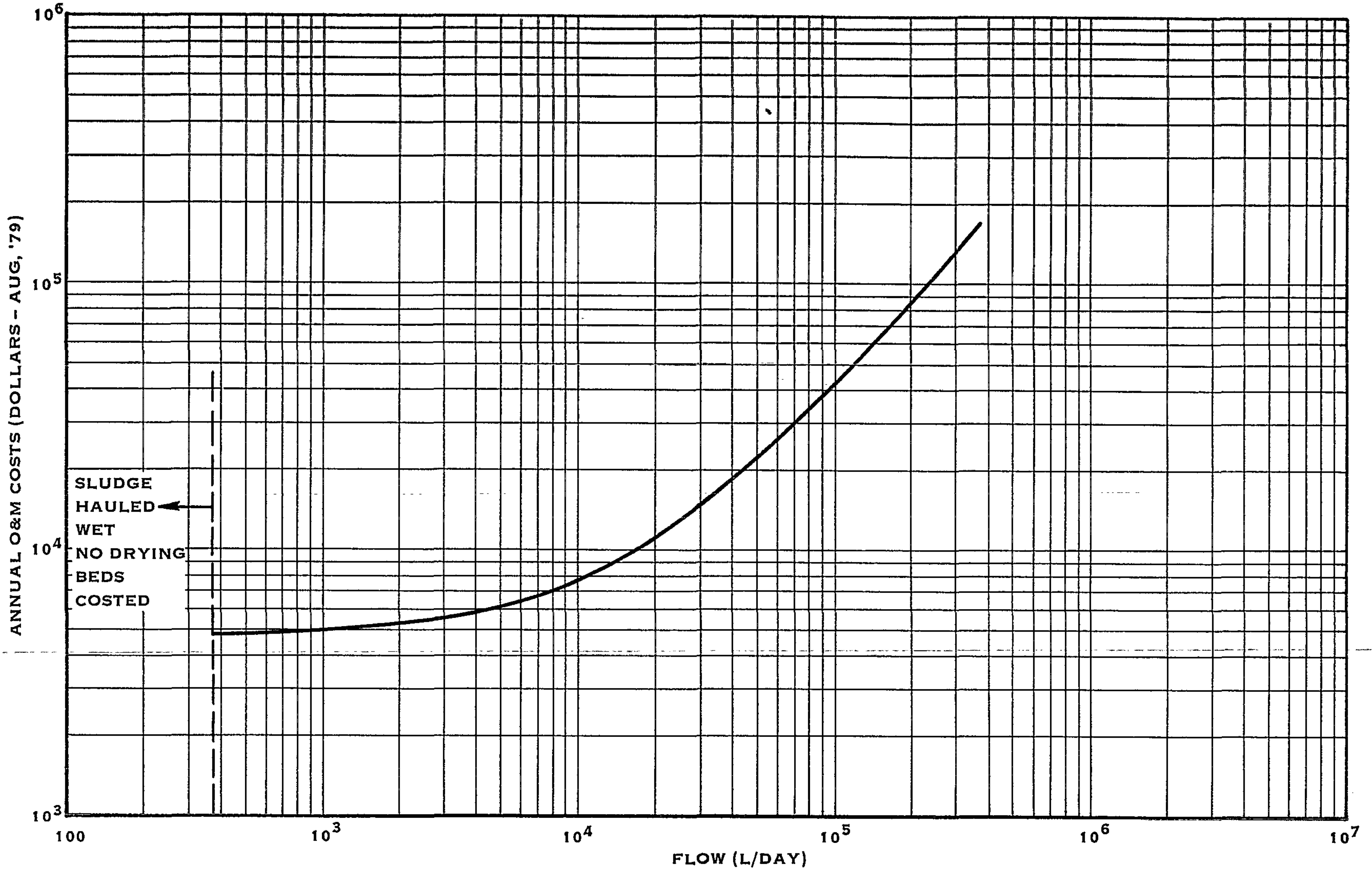


FIGURE 8-26
ANNUAL O&M COSTS VS. FLOW RATE FOR SLUDGE BEDS

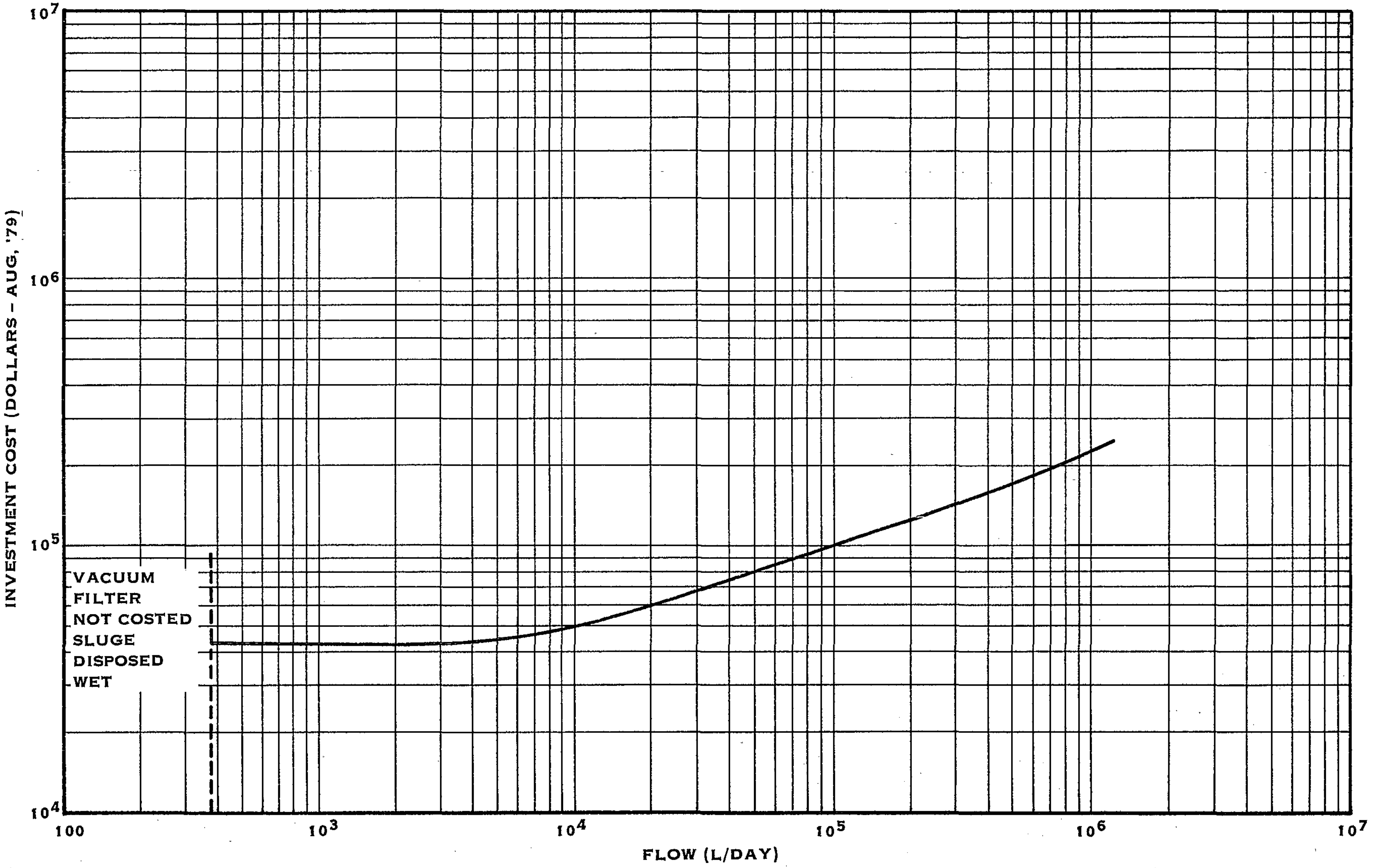


FIGURE 8-27
VACUUM FILTRATION INVESTMENT COSTS

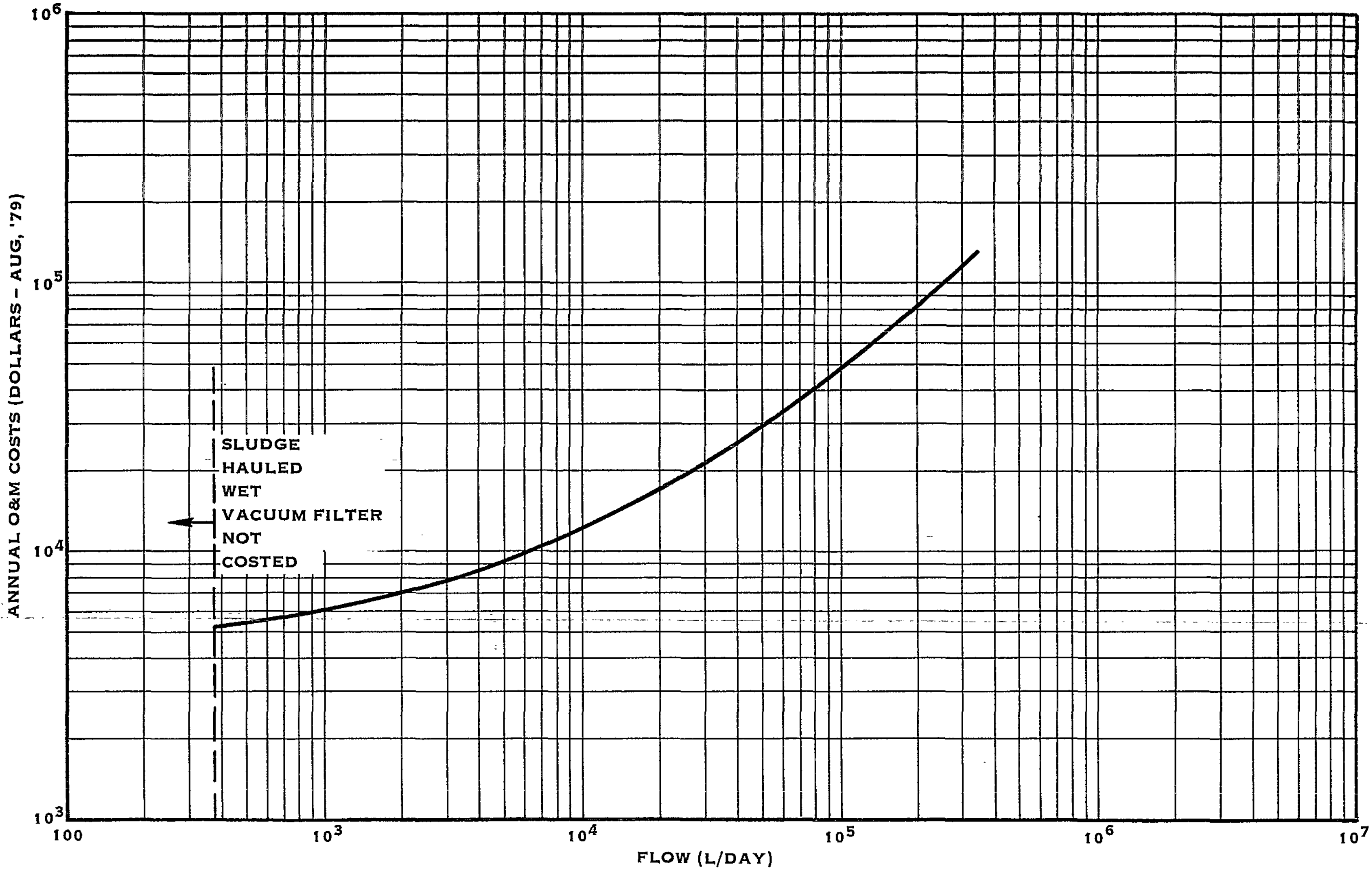


FIGURE 8-28
ANNUAL O&M COSTS VS. FLOW RATE FOR VACUUM FILTRATION

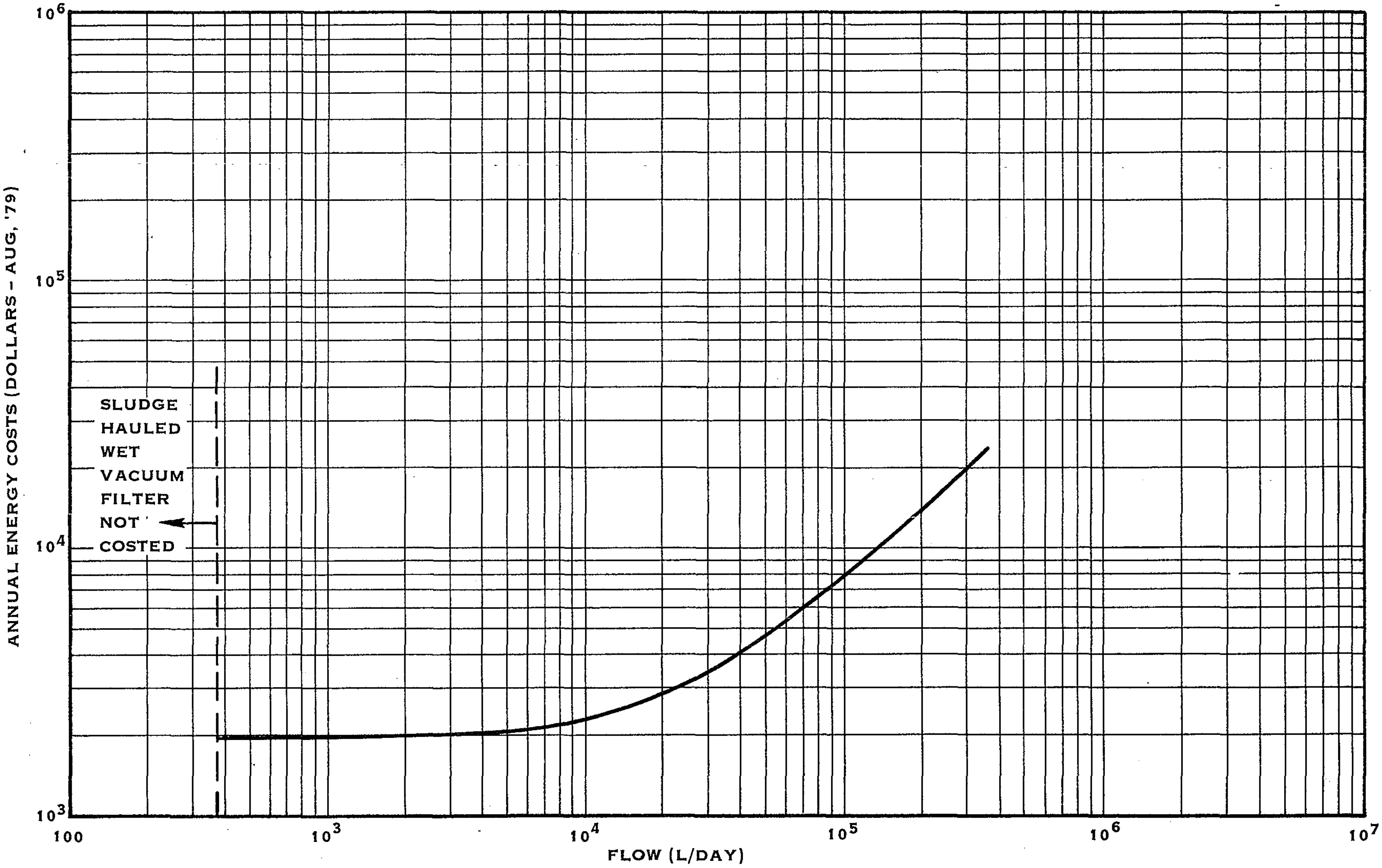


FIGURE 8-29

ANNUAL ENERGY COSTS VS. FLOW RATE FOR VACUUM FILTRATION the volume of wastewater generated. In countercurrent rinsing the product is rinsed in several tanks in series. Water flows counter to the movement of product so that clean water enters the last rinse tank from which clean product is removed, and wastewater is discharged from the first rinse tank which receives the contaminated product to be rinsed. Two different countercurrent rinsing modes are addressed in costing depending on whether wastewater is discharged from the rinse or is used as make-up for evaporative losses from a process bath. The costs of countercurrent rinsing without using the first stage for evaporative loss recovery are presented in Table 8-6 as a function of the number of rinse tanks utilized. Costing assumptions are:

Investment Costs - Unit cost is based on open top stainless steel tanks with a depth of 1.22 meters (4 feet), length of 1.22 meters (4 feet), and width of 0.91 meters (3 feet). Investment cost includes all water and air piping, a blower on each rinse tank for agitation, and programmed hoist line conversions.

Operation and Maintenance Costs - Operation and maintenance costs include a cost for electricity for the blowers based on a capacity of 1,219 liters/min./sq. meter of tank surface area (4 cfm/sq. ft.) at a discharge pressure of 1,538 kg/meter$^2$/meter of tank depth (1 psi/18 in.). Fan efficiency is assumed to be 60 percent. A water charge based on a rinse ratio of 8,180 is also included. Rinse maintenance charges are assumed to be negligible when compared to normal plating line maintenance and are ignored.

## TABLE 8-6
## COUNTERCURRENT RINSE (FOR OTHER THAN RECOVERY OF EVAPORATIVE PLATING LOSS)

| Number of Rinse Tanks: | 3 | 4 | 5 |
|---|---|---|---|
| Investment: | 10,794 | 13,885 | 16,978 |
| Annual Costs: | | | |
| Capital Cost | 909 | 1,170 | 1,430 |
| Depreciation | 2,158 | 2,777 | 3,396 |
| Operation & Maintenance Costs (Excluding Energy & Power Costs) | 27 | 12 | 8 |
| Energy & Power Costs | 511 | 682 | 851 |
| Total Annual Costs | $3,605 | $4,641 | $5,685 |

The costs of countercurrent rinsing with a rinse flow rate sufficient to replace plating tank evaporative losses are presented in Table 8-7. The results are tabulated for various evaporative rates which are equal to the rinse water flow rates. Costing assumptions are:

TABLE 8-7

COUNTERCURRENT RINSE USED FOR RECOVERY OF EVAPORATIVE PLATING LOSS

| | | | |
|---|---|---|---|
| Evaporative Rate (Liters/Hr): | 15.3 | 24.0 | 50.8 |
| Investment: | $15,430 | $12,736 | $10,042 |
| Annual Costs: | | | |
| Capital Costs | 1,301 | 1,074 | 847 |
| Depreciation | 3,086 | 2,547 | 2,008 |
| Operation & Maintenance Costs (Excluding Energy & Power Costs) | 5 | 7 | 16 |
| Energy & Power Costs | 714 | 572 | 428 |
| Total Annual Cost | $ 5,105 | $ 4,200 | $ 3,300 |

Note: Savings due to recovery of plating solution are not presented in this table.

Investment Costs - Unit cost is based on a sufficient number of rinse stages to replace the evaporative loss from a plating bath at approximately 43 degrees C while also maintaining a rinse ratio of 8,180.

Investment costs include open top stainless steel tanks with a depth of 0.91 meters (3 feet), length of 1.22 meters (4 feet), and width of 1.22 meters (4 feet). All water and air piping, a blower on each rinse tank for agitation, a liquid level controller, solenoid, and pump are also included in the investment cost. Operation is assumed to be programmed. Hoist and line conversion costs are included.

Operation and Maintenance Costs - Operation and maintenance costs include a cost for electricity for the blowers based on a capacity of 1.219 liters/min/sq. meter of tank surface area (4 cfm/sq. ft.) at a discharge pressure of 1,538 kg/sq. meter/meter of tank depth (1 psi/18 in.). A fan efficiency of 60 percent is assumed. A water charge is also included. Rinse maintenance charges are assumed to be neglible when compared to normal plating line maintenance and are ignored.

## Submerged Tube Evaporation

In this technology, contaminants present in process wastewater are concentrated by removing the water as vapor. Evaporation is accomplished by applying heat, and the evaporated water is condensed using non-contact cooling water, and reclaimed for process use. Costs generated in this subroutine are based on double effect evaporation in which heat contained in vapor from the first stage (effect) is used to evaporate water from the second.

Investment Costs - Investment costs for this technology are estimated based on data supplied by a manufacturer of submerged tube evaporation equipment. As shown by the plot of costs versus wastewater flow rate in Figure 8-30, costs were supplied for units of specified capacities which are available from the manufacturer. Cost estimates are based on the smallest available unit which is adequate for the specified wastewater flow rate. The investment costs shown include the evaporation unit and purification devices required for the return of the evaporation concentrate to a process bath. Costs for installation of a non-contact cooling loop are not included. The availability of this service on-site is assumed.

Operation and Maintenance Costs - Estimates for operation and maintenance costs are based on manufacturer supplied data. These costs are shown as a function of wastewater flow rate in Figure 8-31.

Energy Costs - Energy is required in this technology primarily to supply the heat of vaporization for the evaporated water. The use of a double effect evaporator significantly reduces the total amount of heat consumed per unit of water evaporated.

Energy requirements are based on an evaporative heat of 583 cal/gram of water which is reduced to an effective value of 292 cal/gram in the double effect unit. Fuel consumption is based on a lower heat value of 10,140 cal/gram with an 85% heat recovery efficiency. Energy costs based on these factors are shown in Figure 8-32 as a function of wastewater flow rate to the evaporator.

## Contract Removal

Sludge, waste oils, and in some cases concentrated waste solutions frequently result from wastewaster treatment processes. These may be disposed of on-site by incineration, landfill or reclamation, but are most often removed on a contract basis for off-site disposal. System cost estimates presented in this report are based on contract removal of sludges. In addition, where only small volumes of concentrated wastewater are produced, contract-removal or off-site treatment may represent the most cost effective approach to water pollution abatement. Estimates of solution contract haul costs are also provided by

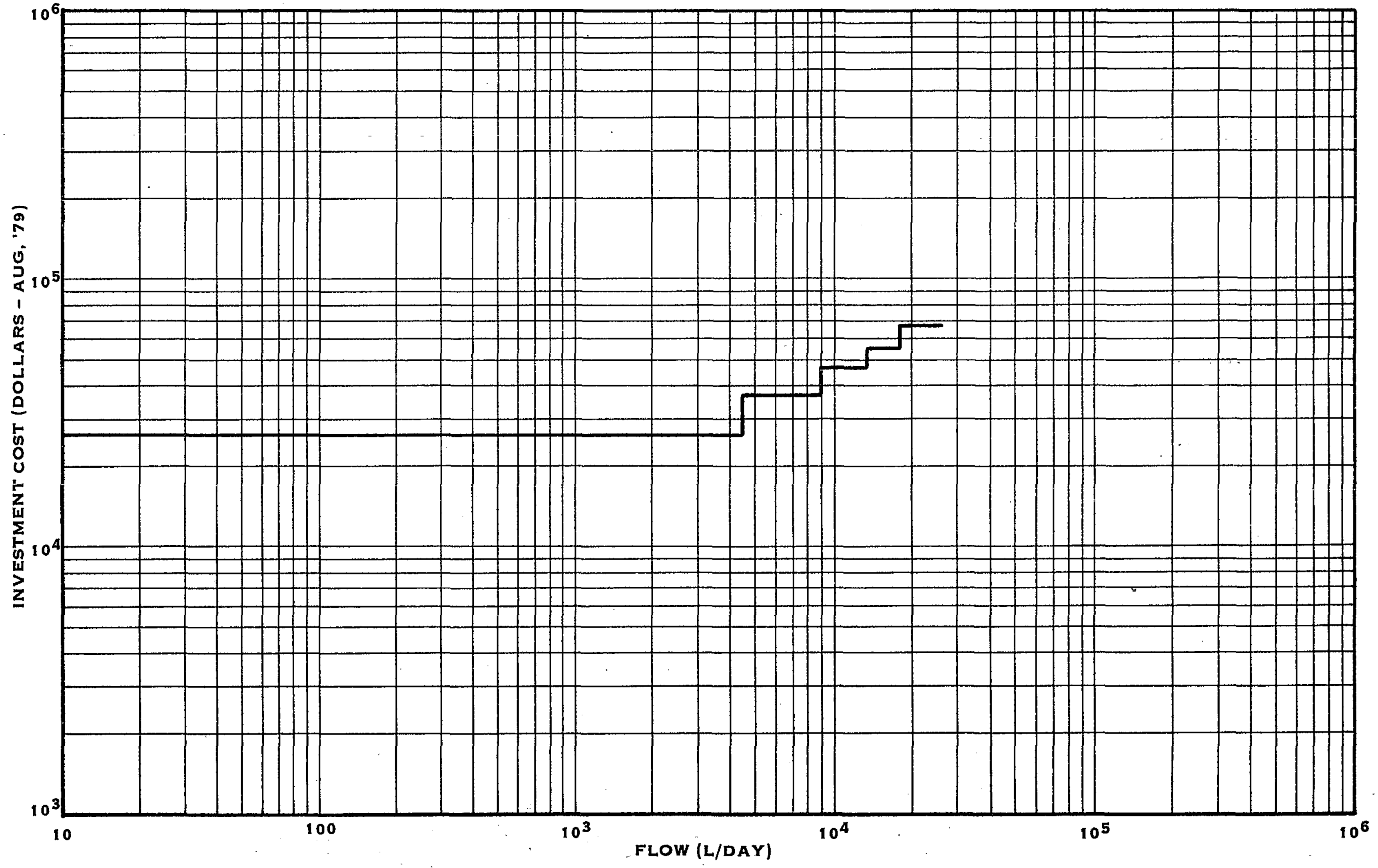


FIGURE 8-30
SUBMERGED TUBE EVAPORATION (DOUBLE EFFECT) INVESTMENT COSTS

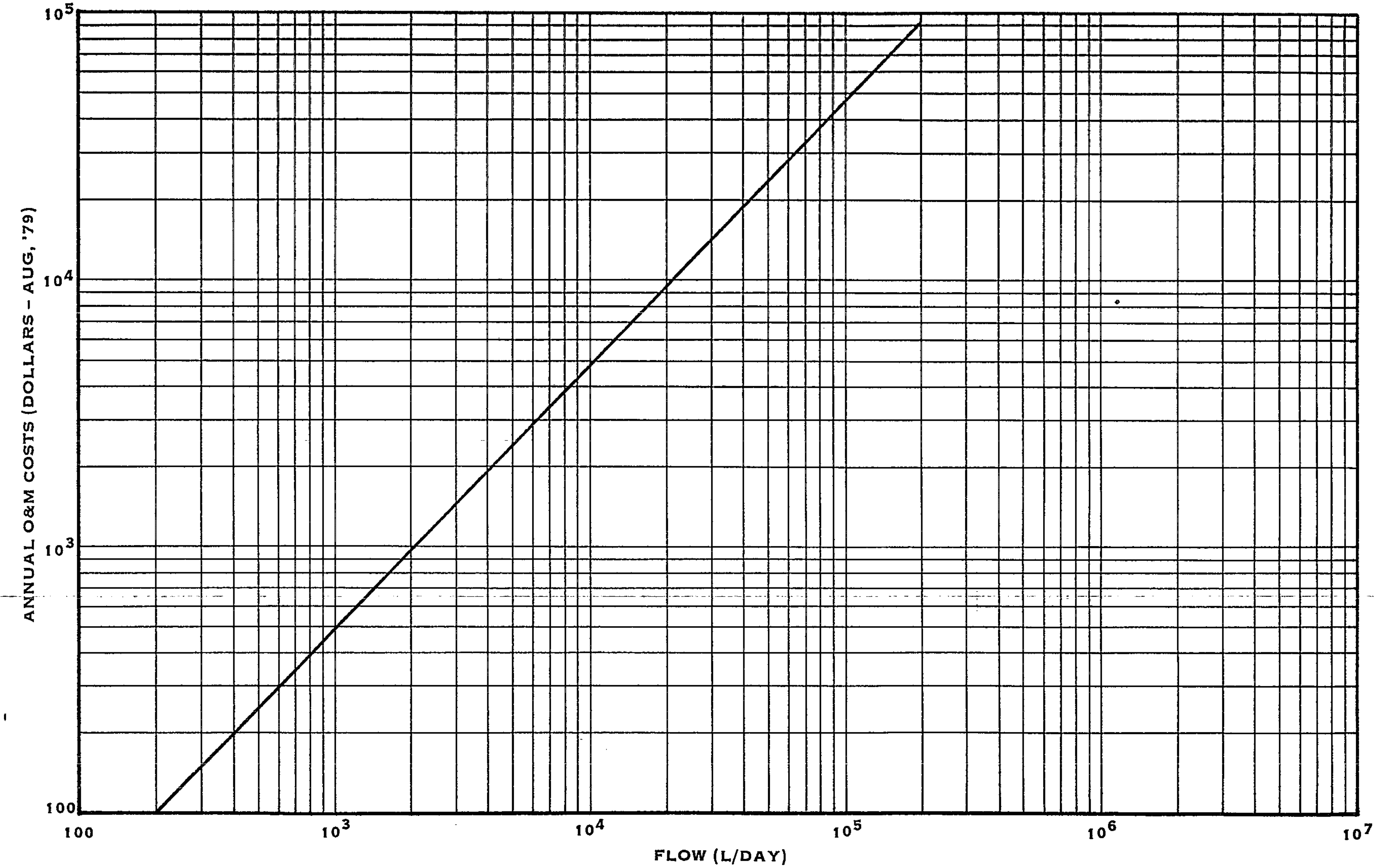


FIGURE 8-31
ANNUAL O&M COSTS VS. FLOW RATE FOR SUBMERGED TUBE EVAPORATION

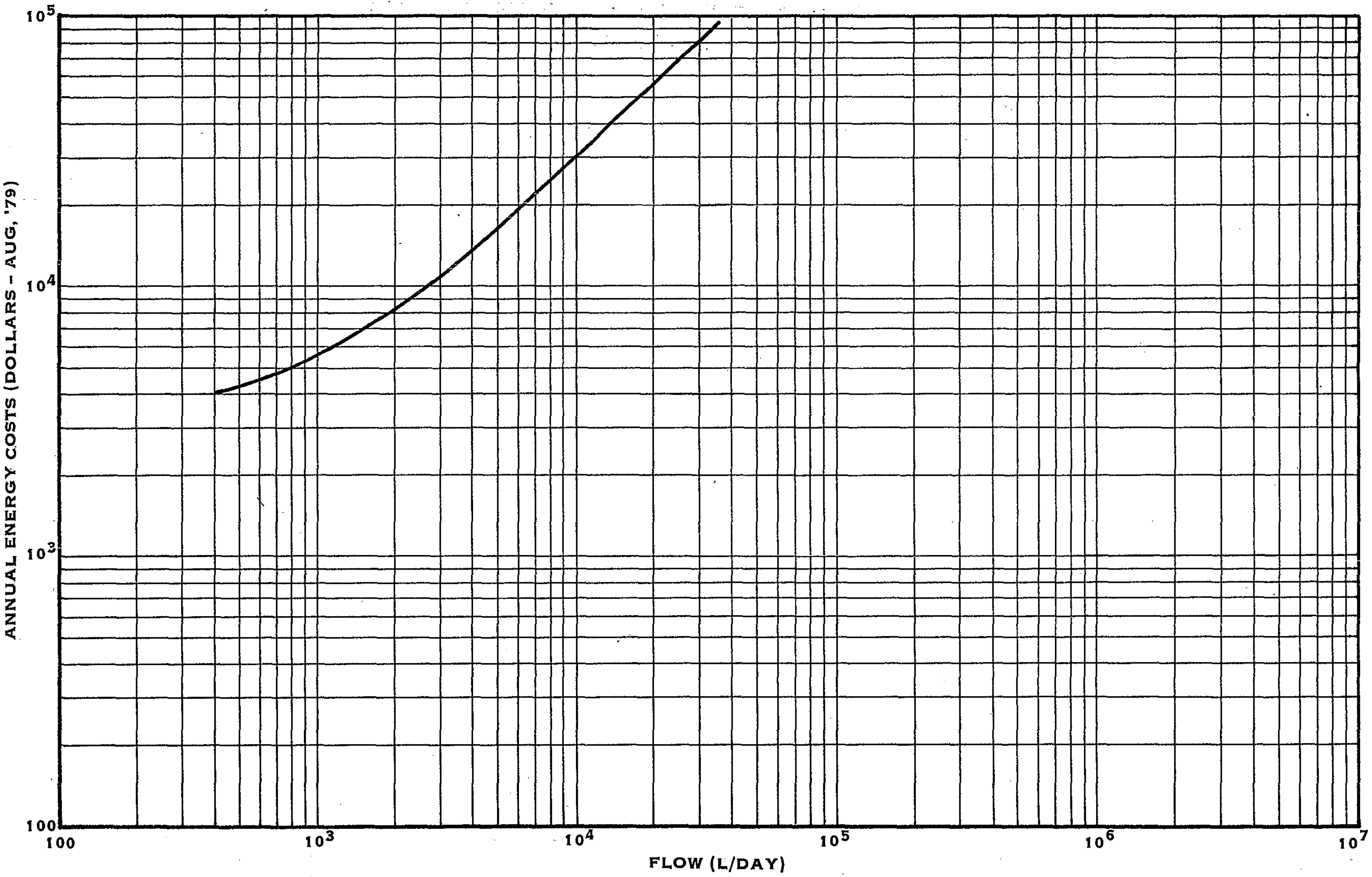


FIGURE 8-32
ANNUAL ENERGY COSTS VS. FLOW RATE FOR SUBMERGED TUBE EVAPORATION

this subroutine and may be selected in place of on-site treatment on a least-cost basis.

Investment Costs - Investment for contract removal is zero.

Operating Costs - Annual costs are estimated for contract removal of total waste streams of sludge and oil streams as specified in input data. Sludge and oil removal costs are further divided into wet and dry haulage depending upon whether or not upstream sludge dewatering is provided. The use of wet haulage or of sludge dewatering and dry haulage is based on least cost as determined by annualized system costs over a ten year period. Wet haulage costs are always used when the volume of the sludge stream is less than 100 gallons per day.

Both wet sludge haulage and total waste haulage differ in cost depending on the chemical composition of the waste removed. Wastes are classified as cyanide bearing, hexavalent chromium bearing, or oily and assigned different haulage costs as shown below.

| Waste Composition | Haulage Cost |
|---|---|
| >0.05 mg/l CN- | $0.16/liter ($0.60/gallon) |
| ≥0.1 mg/l Cr+6 | $0.18/liter ($0.56/gallon) |
| Oil & grease-TSS | $0.08/liter (0.30/gallon) |
| All others | $0.06/liter (0.24/gallon) |

Dry sludge haul costs are estimated at $0.07/liter ($0.27/gallon).

## RCRA COST ANALYSIS

RCRA costs were originally developed for sludge disposal from electroplating plants using data from 48 surveyed plants and from contacting haulers. Of the 48 plants surveyed, 38 plants had their waste hauled to a commercial or municipal site for disposal while 10 plants disposed of the sludge at company owned sites. The cost for transport and disposal of these sludges reported by the plants varied from zero to $2.04 per gallon. Haulers quoted costs for transport and disposal ranging from $0.06 per gallon to $2.80 per gallon, dependent on the quantity and type of sludge.

The detailed results of the RCRA analyses are presented in: "Electroplating RCRA Review - Technical Contractor's Final Report," and "RCRA Impact Analysis for Sludge Disposal for the Machinery and Mechanical Products Category." These reports along with the supporting data are available in the metal finishing record.

RCRA sludge disposal was recosted to reflect costs for the entire Metal Finishing Category. RCRA related costs were generated for 39 job shops, 100 captive indirects, and 103 captive directs. For each plant RCRA related annual costs, initial costs, and capital costs were developed using the methods and equations presented in "Guidance for RCRA ISS Costs," Office of Analysis and Evaluation, December 1980.

## TREATMENT SYSTEM COST ESTIMATES

This section presents estimates of the total cost of wastewater treatment and control systems for metal finishing process wastewater incorporating the treatment and control components discussed above. Flows in the Metal Finishing Category vary from approximately 378 to 3,785,000 liters/day (100 gpd to 1,000,000 gpd). This wide variation in flow rate necessitates the presentation of treatment system total annual cost curves for each option. Total annual costs have been plotted against flow in units enabling the determination of cost for any flow rate. All available flow data from industry data collection portfolios were used in defining the raw waste flows. Raw waste characteristics were determined based on sampling data as discussed in Section V.

Cost curves for each option are presented for six different cases for Option 1 and five different cases for Options 2 and 3. Each case corresponds to different types of plants encountered in the Metal Finishing Category. Cases one and two represent facilities primarily engaged in electroplating. In case two electroless plating is performed resulting in the presence of complexed metal wastes. Cases three and five represent integrated facilities combining electroplating with other metal finishing operations. In case five electroless plating is practiced. Case four represents plants performing a variety of metal finishing operations including heat treating, but without on-site electroplating, while case six represents plants generating only oily wastewater. The flow splits for those cases as shown in Table 8-8 are based on the ratios of the average wastewater flow rates from all subcategories included in each case. These flow splits are presented to show examples of a broad range of cases which occur within the Metal Finishing Category.

TABLE 8-8
FLOW SPLIT CASES FOR OPTIONS 1, 2, AND 3

| Case | Waste Type Flows (% of total plant flow) | | | | |
|---|---|---|---|---|---|
| | Oily | Cyanide | Chromium | Metals | Complexed Metals |
| 1 | | 7 | 13 | 80 | |
| 2 | | 6 | 12.5 | 75.5 | 6 |
| 3 | 31.5 | 4.5 | 9 | 55 | |
| 4 | 30 | | | 70 | |
| 5 | 30 | 4 | 9 | 52.5 | 4.5 |
| 6 | 100 | | | | |

Five examples of varying total daily waste volumes (gallons per day) have been presented for each of the six cases in order to provide a range of estimated system costs. The system costs presented include component costs as discussed above and subsidiary costs including engineering, line segregation, administration, and interest expenses during construction. In developing cost estimates for these option systems, it is assumed that none of the specified treatment and control measures is in place so that the presented costs represent total costs for the systems.

Several of these system cost curves show discontinuities. Some of these result from transitions occurring in specific component cost subroutines, and others result from changes in system cost factors. Sludge dewatering costs are of particular significance. For flows below $10^6$ l/day sludge dewatering is accomplished using sludge drying beds, and cost estimates reflect this technology. Above this flow sludge dewatering is accomplished using a vacuum filter. Since the degree of dewatering achieved (typically 40% solids from a sludge drying bed and 20% solids from a vacuum filter) is influenced by this change, system costs are influenced not only by the dewatering costs themselves, but also through an effect on the volume of sludge requiring contract removal. At very high flow rates, the cost of removing sludge at 20% solids may become substantial, and the most economical system design would incorporate further dewatering of the vacuum filter product. This refinement, however, has not been included in these cost estimates.

## System Cost Estimates (Option 1)

This section presents the system cost estimates for the Option 1 end-of-pipe treatment systems. The representative flow rates used in these system cost estimates were determined based upon actually sampled flows and flow information received in the data collection portfolios. The complete system block diagram applicable to cases 1-5 is shown in Figure 8-33. Option 1 treatment for the isolated oily waste stream addressed in case 6 is shown in Figure 8-34.

The costing assumptions for each component of the Option 1 system were discussed above under Technology Costs and Assumptions. In addition to these components, contract sludge removal was included in all cost estimates.

Table 8-9 presents costs for each of the six cases discussed above for various treatment system influent flow rates. The basic cost elements used in preparing these tables are the same as those presented for the individual technologies: investment, annual capital costs, annual depreciation, annual operations and maintenance cost (less energy cost), energy cost, and total annual cost. These elements were discussed in detail earlier in this section.

For the cost computations, a least cost treatment system selection was performed. This procedure calculated the costs for a batch treatment system and a continuous treatment system over a 5 year comparison period. Figures 8-35 through 8-46 show the investment and total annual costs for each case shown in Table 8-9.

# TABLE 8-9

## Option 1 Costs

| Case Number | | Flow gpd | Flow 1/day | Investment (Dollars) | Capital Costs (Dollars) | Depreciation (Dollars) | Operation & Maintenance (Dollars) | Energy (Dollars) | Total Annual (Dollars) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Batch | 264. | 1,000. | 129466.937 | 10916.160 | 25893.387 | 12446.344 | 35.090 | 49290.977 |
| 1 | Batch | 2638. | 10,000. | 156768.312 | 13217.984 | 31353.660 | 22896.891 | 53.571 | 67522.062 |
| 1 | Batch | 26380. | 100,000. | 271783.812 | 22915.613 | 54356.762 | 32761.973 | 396.887 | 110431.187 |
| 1 | Continuous | 263800. | 1,000,000. | 658308.687 | 55505.562 | 131661.687 | 182141.437 | 5877.852 | 375186.500 |
| 1 | Continuous | 2637999. | 10,000,000. | 1389210.00 | 117132.437 | 277842.000 | 1433646.00 | 36224.941 | 1864844.00 |
| 2 | Batch | 264. | 1,000. | 141021.000 | 11890.398 | 28204.199 | 19893.262 | 63.154 | 60051.012 |
| 2 | Batch | 2662. | 10,000. | 169637.562 | 14303.066 | 33927.512 | 24395.422 | 81.395 | 72707.375 |
| 2 | Batch | 26350. | 100,000. | 295868.875 | 24946.352 | 59173.773 | 39586.777 | 271.490 | 123978.312 |
| 2 | Continuous | 263600. | 1,000,000. | 754696.125 | 63632.437 | 150939.187 | 178190.812 | 5740.566 | 398503.000 |
| 2 | Continuous | 2637998. | 10,000,000. | 1547783.00 | 130502.937 | 309556.562 | 1368158.00 | 34512.113 | 1842729.00 |
| 3 | Batch | 264. | 1,000. | 177289.500 | 14948.301 | 35457.898 | 14035.863 | 36.611 | 64478.672 |
| 3 | Batch | 2660. | 10,000. | 207743.000 | 17516.000 | 41548.598 | 21761.270 | 61.020 | 80886.812 |
| 3 | Batch | 26410. | 100,000. | 386569.187 | 32593.875 | 77313.812 | 40553.965 | 463.474 | 150925.062 |
| 3 | Continuous | 266330. | 1,000,000. | 947278.312 | 79870.062 | 189455.625 | 268203.125 | 6650.617 | 544179.375 |
| 3 | Continuous | 2638998. | 10,000,000. | 2148885.00 | 181185.187 | 429777.000 | 2172029.00 | 41918.371 | 2824909.00 |
| 4 | Batch | 264. | 1,000. | 76337.000 | 6436.414 | 15267.398 | 10597.324 | 31.078 | 32332.215 |
| 4 | Batch | 2642. | 10,000. | 98451.000 | 8300.969 | 19690.199 | 17826.531 | 51.313 | 45869.012 |
| 4 | Batch | 26420. | 100,000. | 239445.562 | 20188.953 | 47889.109 | 31906.484 | 405.359 | 100389.812 |
| 4 | Continuous | 264300. | 1,000,000. | 674088.500 | 56836.125 | 134817.687 | 242074.375 | 4442.797 | 438170.937 |
| 4 | Continuous | 2642999. | 10,000,000. | 1638202.00 | 138126.312 | 327640.375 | 2034457.00 | 28883.500 | 2529106.00 |
| 5 | Batch | 264. | 1,000. | 144796.750 | 12208.711 | 28959.348 | 19384.918 | 59.962 | 60612.937 |
| 5 | Batch | 2638. | 10,000. | 223017.687 | 18803.766 | 44603.535 | 28946.770 | 88.451 | 92442.500 |
| 5 | Batch | 26460. | 100,000. | 408999.937 | 34485.125 | 81799.937 | 47390.582 | 479.039 | 164154.625 |
| 5 | Continuous | 264600. | 1,000,000. | 1035760.50 | 87330.375 | 207152.062 | 261455.187 | 6539.930 | 562477.500 |
| 5 | Continuous | 2645998. | 10,000,000. | 2291527.00 | 193212.625 | 458305.375 | 2095432.00 | 40662.414 | 2787612.00 |
| 6 | Batch | 264. | 1,000. | 48120.527 | 4057.312 | 9624.105 | 3676.566 | 7.431 | 17365.414 |
| 6 | Batch | 2640. | 10,000. | 79619.937 | 6713.219 | 15923.984 | 5396.180 | 26.372 | 28059.754 |
| 6 | Batch | 26400. | 100,000. | 95708.812 | 8069.754 | 19141.762 | 21783.789 | 263.722 | 49259.023 |
| 6 | Batch | 264000. | 1,000,000. | 306961.562 | 25881.625 | 61392.312 | 108626.562 | 2637.227 | 198537.687 |
| 6 | Continuous | 2640000. | 10,000,000. | 1412968.00 | 119135.750 | 282593.562 | 818738.375 | 10542.426 | 1231010.00 |

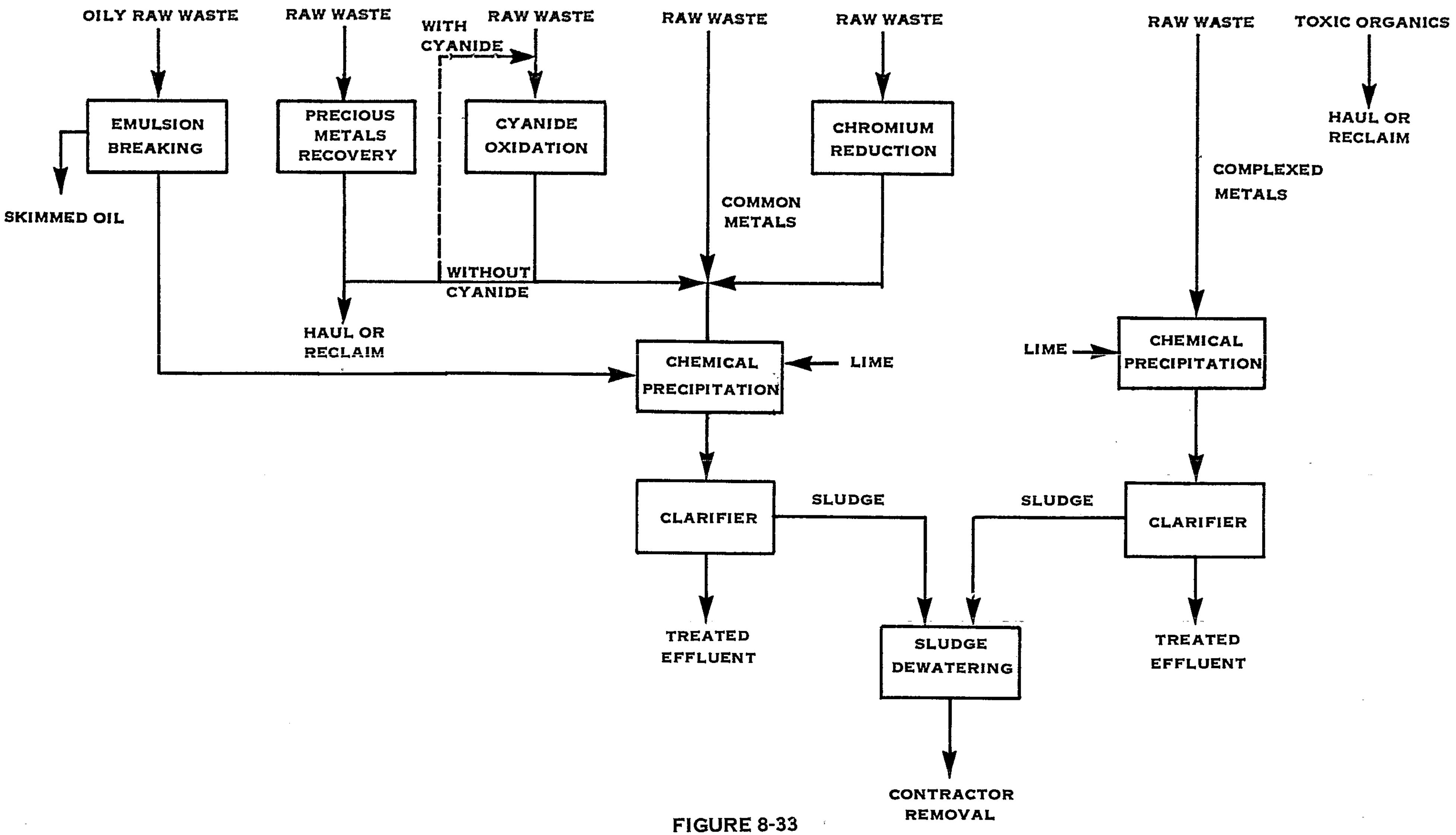


FIGURE 8-33
OPTION 1 SYSTEM

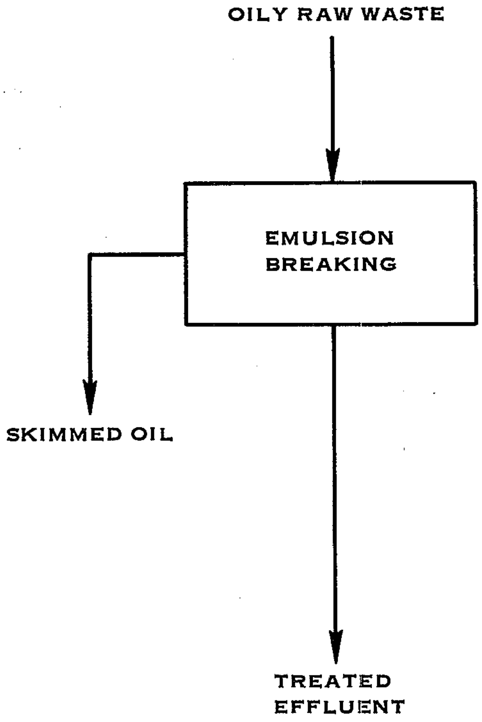


FIGURE 8-34
OPTION 1 TREATMENT SYSTEM
FOR SEGREGATED OILY WASTE STREAMS

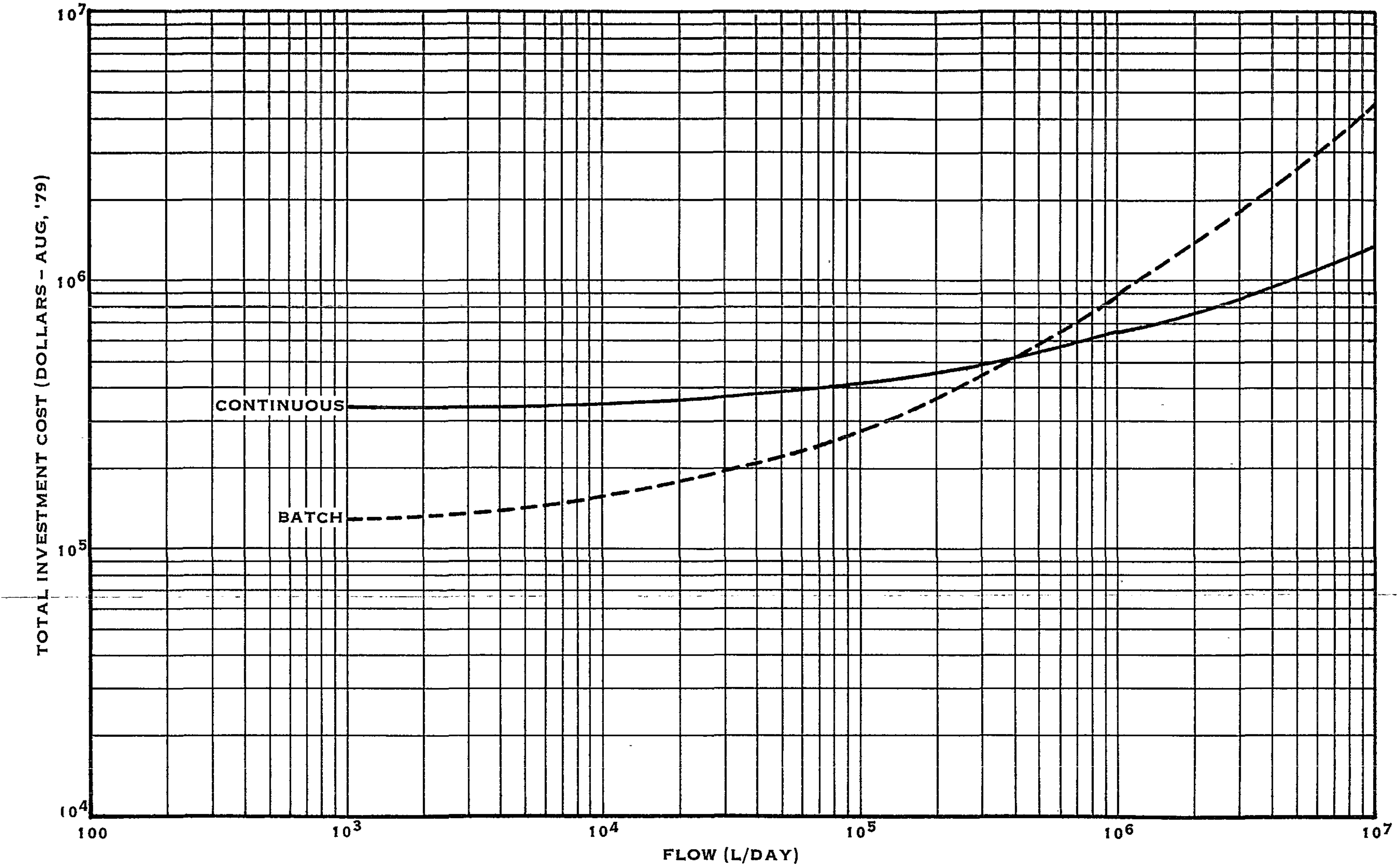


FIGURE 8-35
TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 1

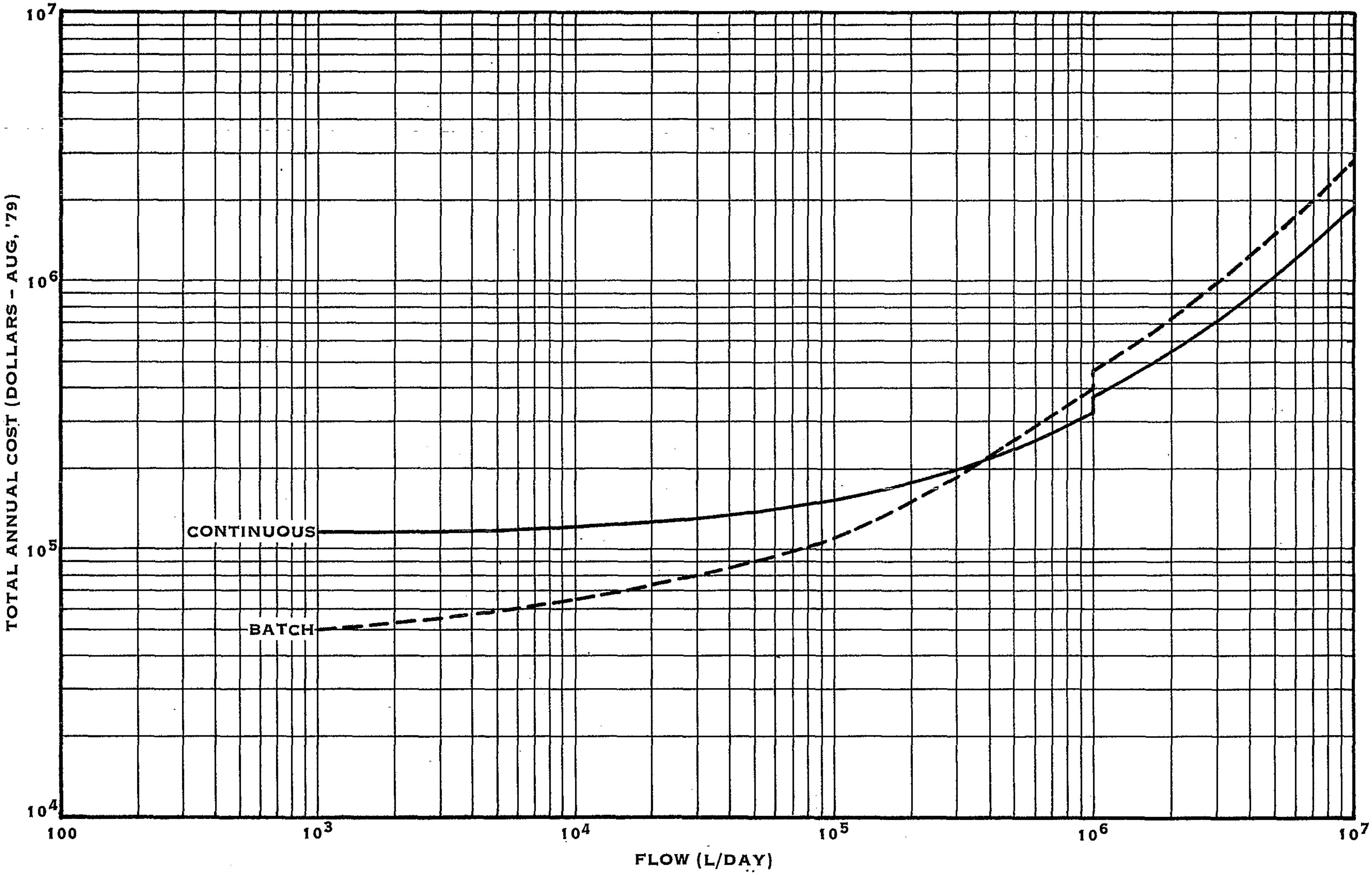


FIGURE 8-36

TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 1

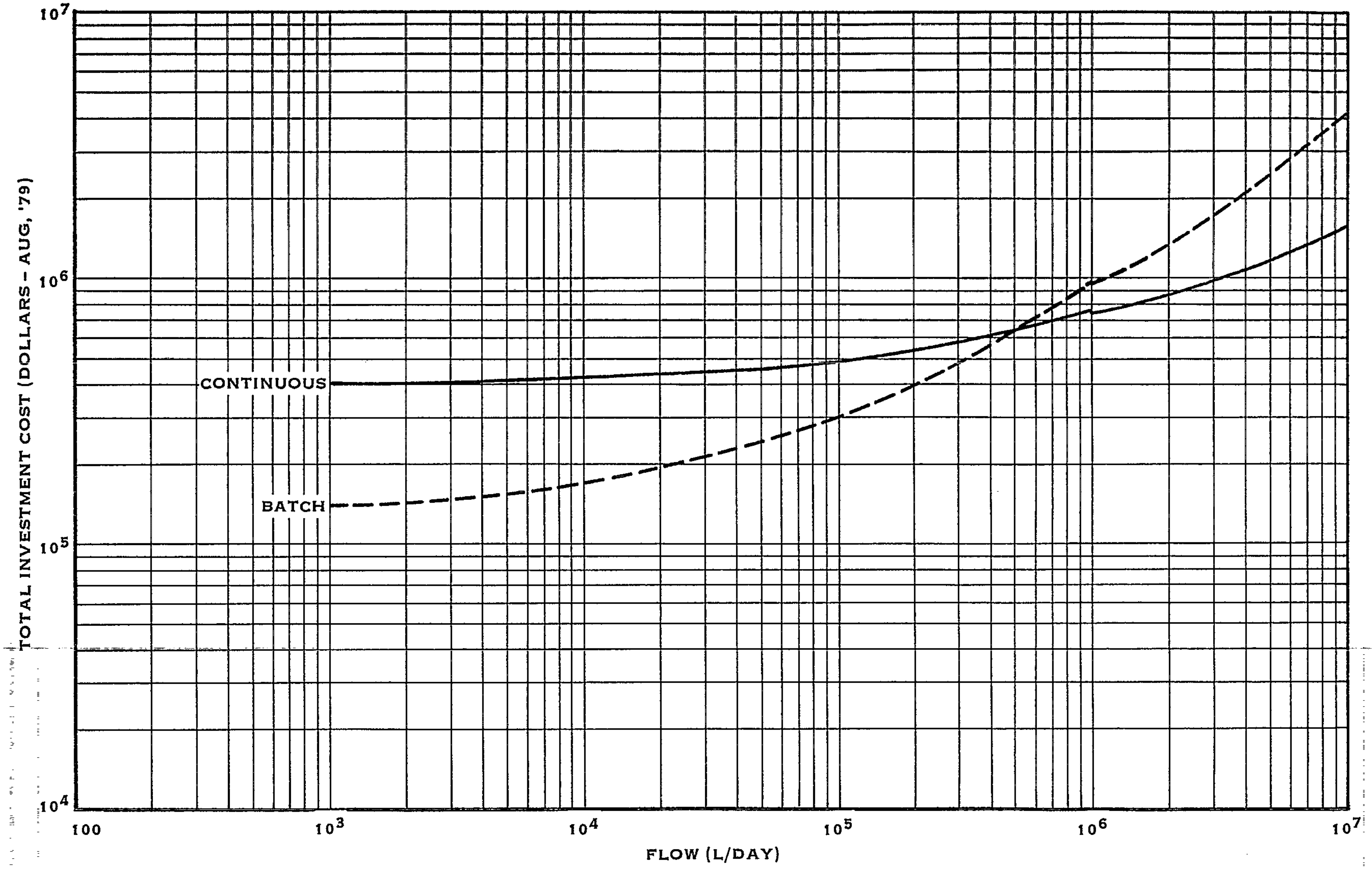


FIGURE 8-37

TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 2

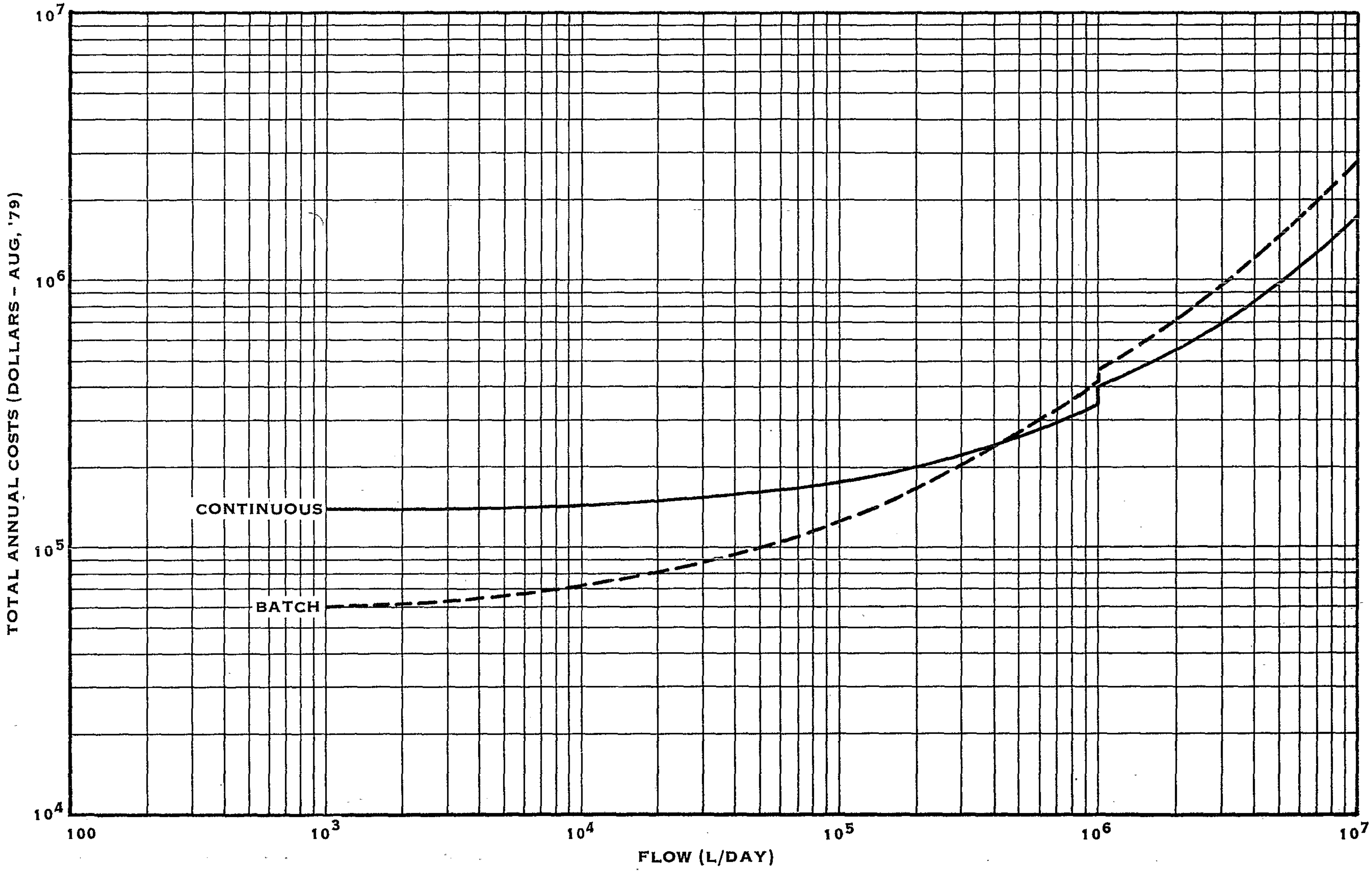


FIGURE 8-38

TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 2

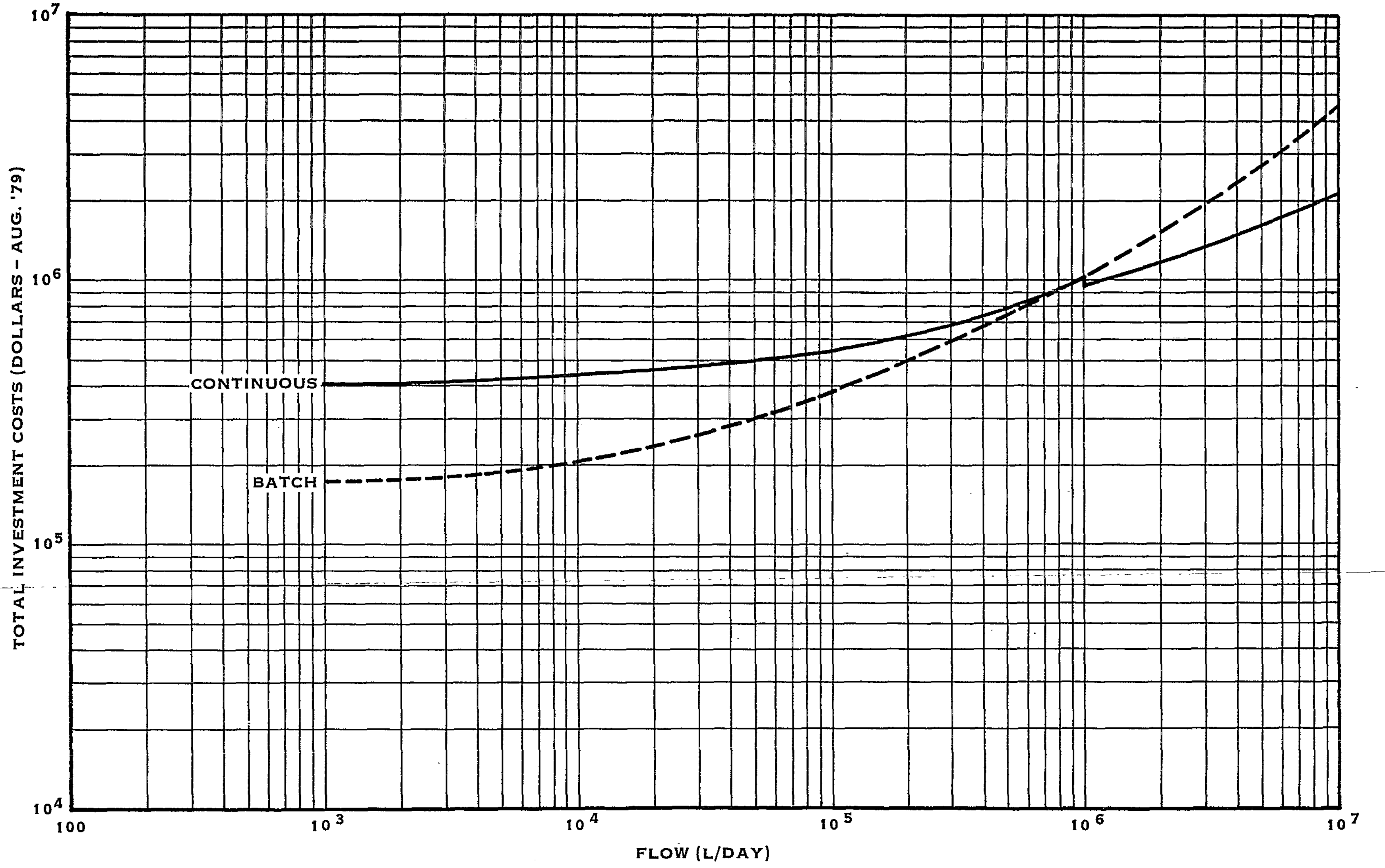


FIGURE 8-39

TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 3

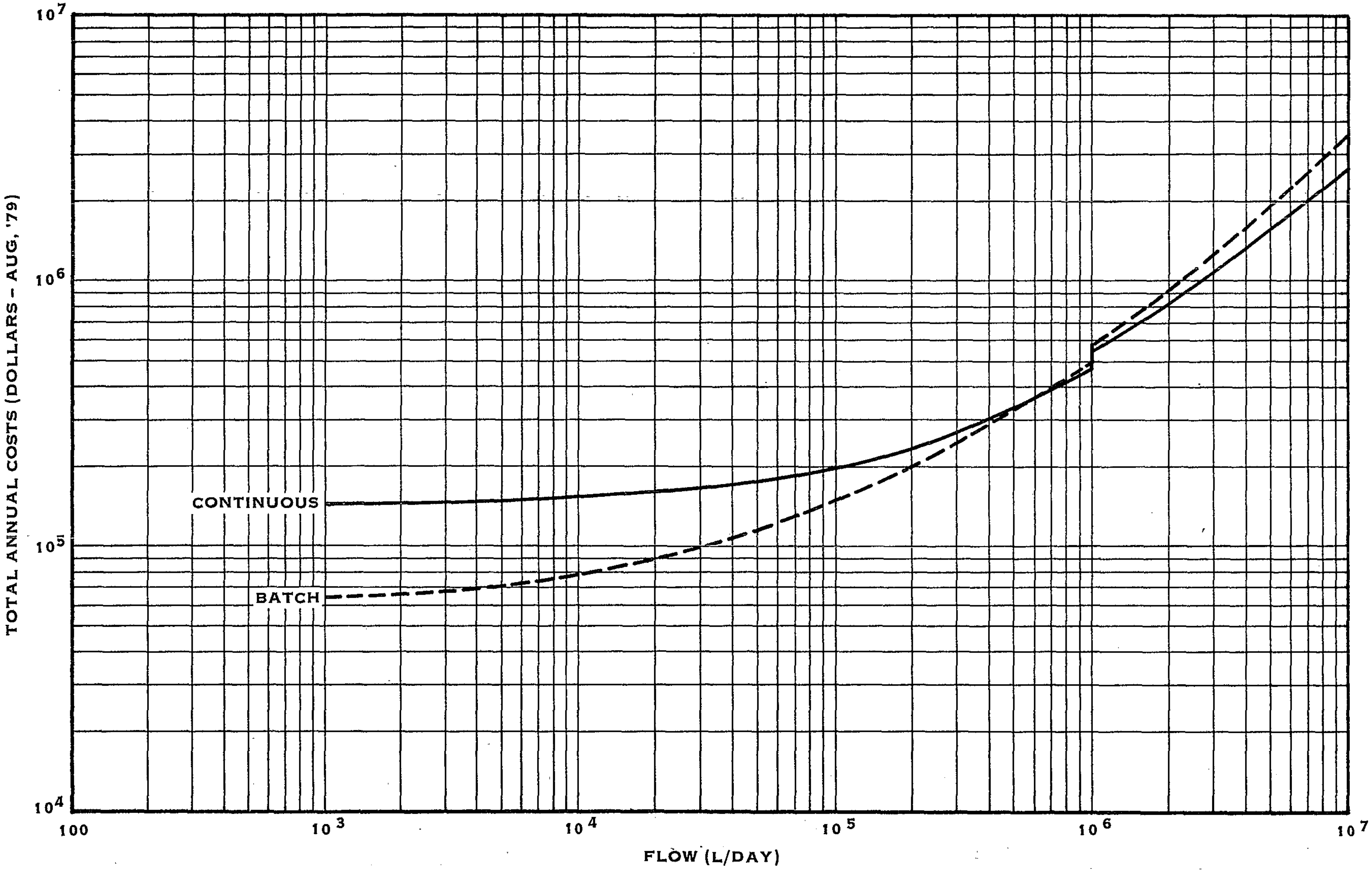


FIGURE 8-40

TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 3

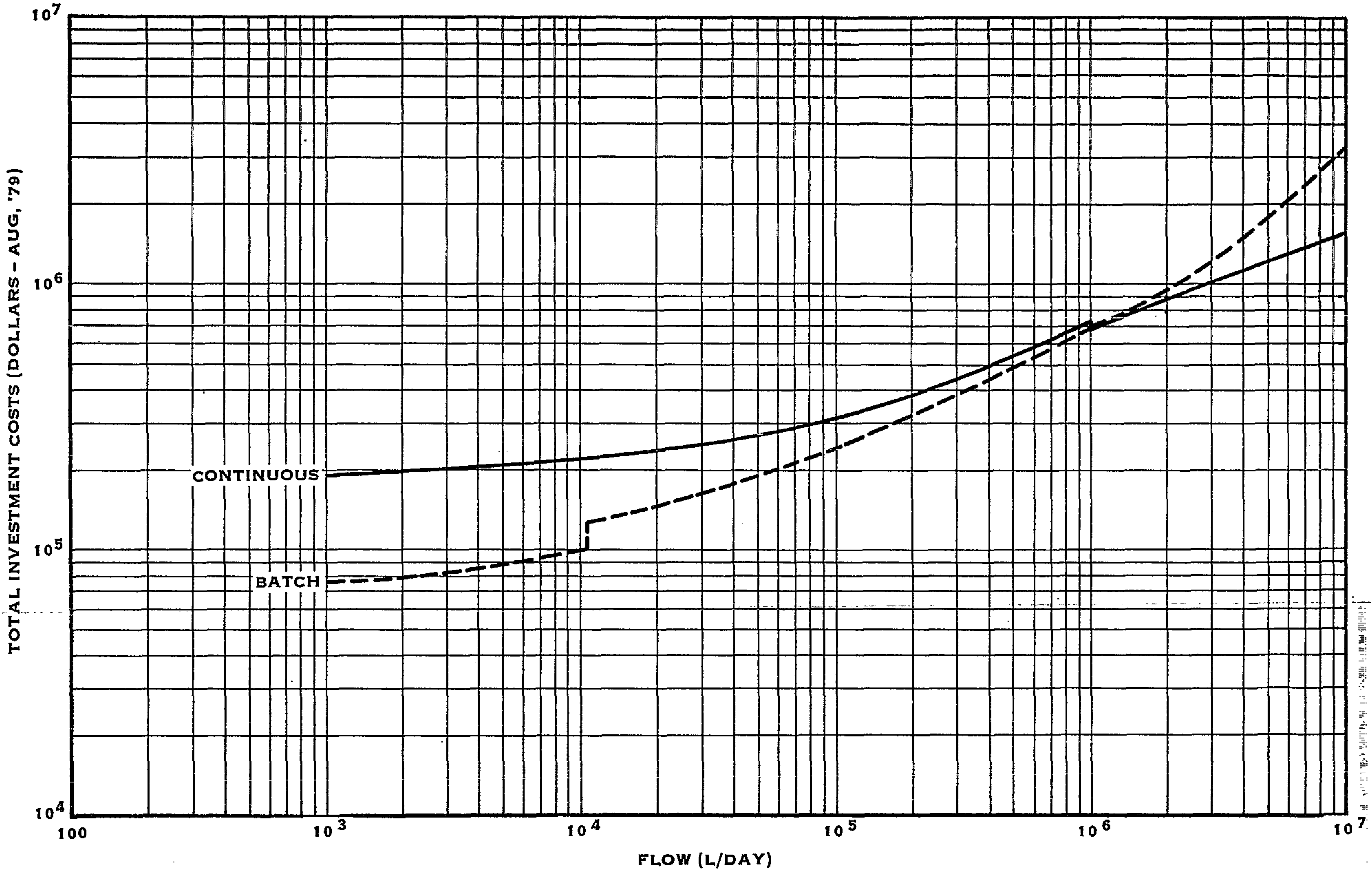


FIGURE 8-41

TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 4

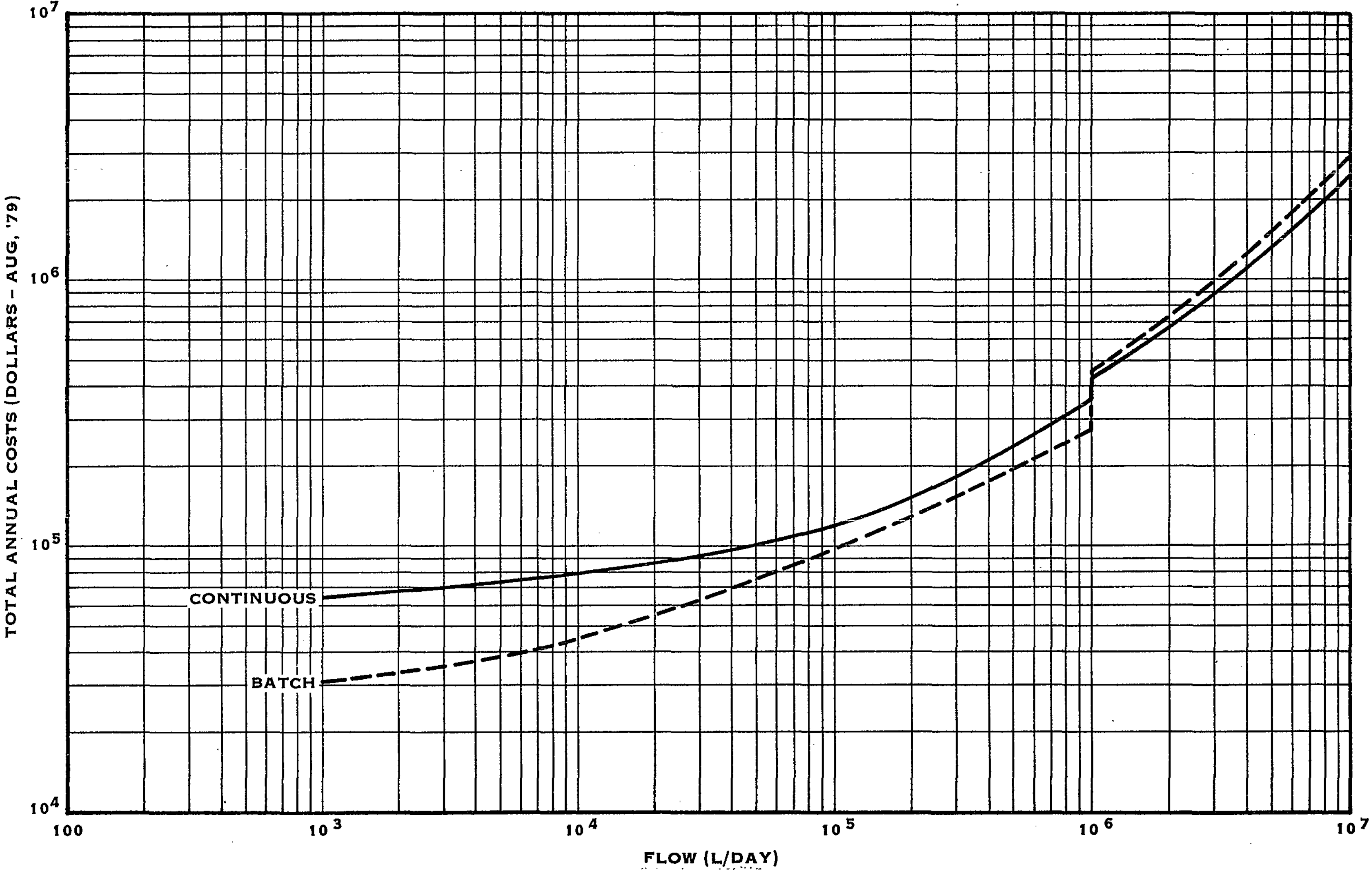


FIGURE 8-42
TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 4

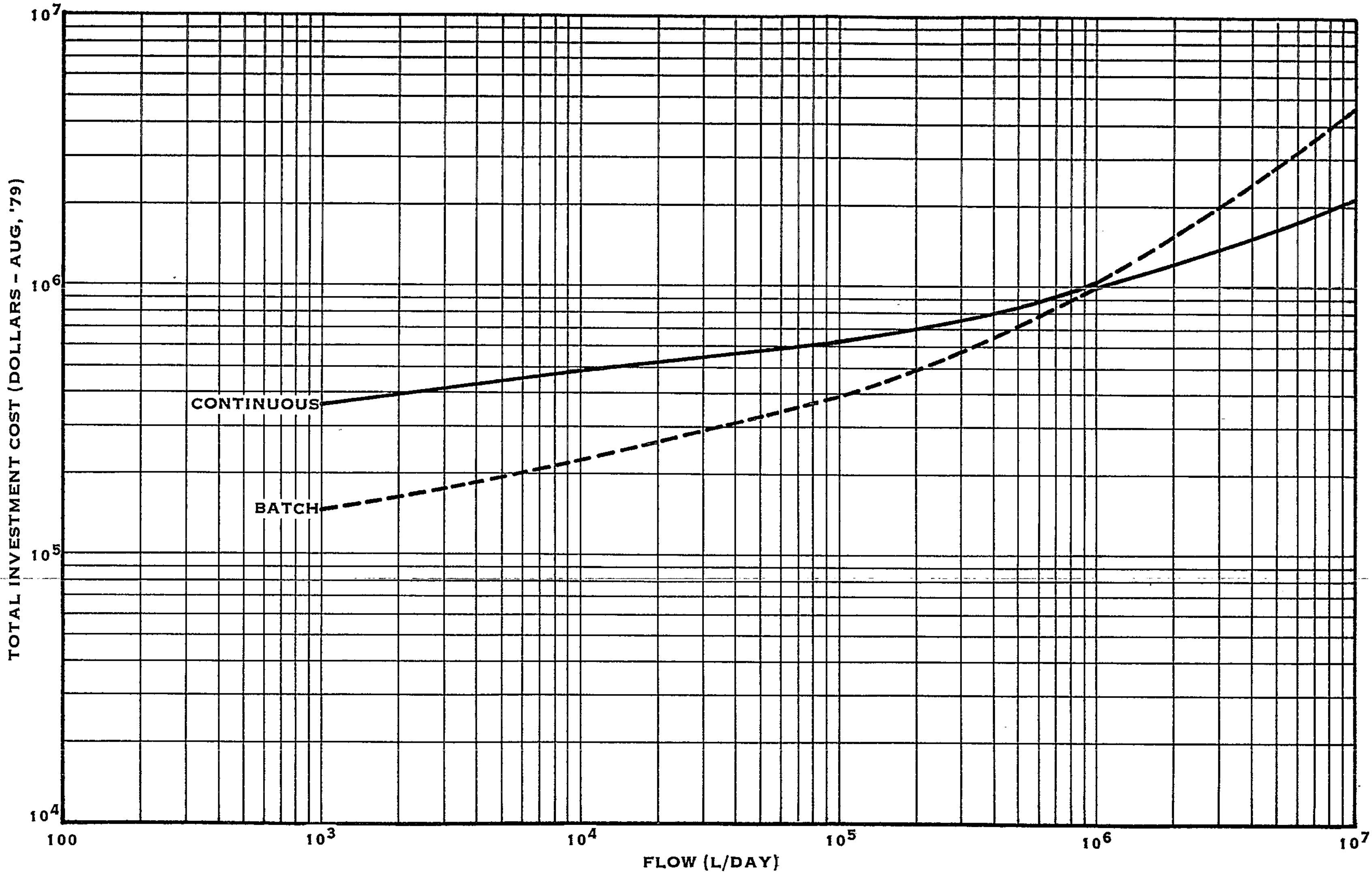


FIGURE 8-43

TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 5

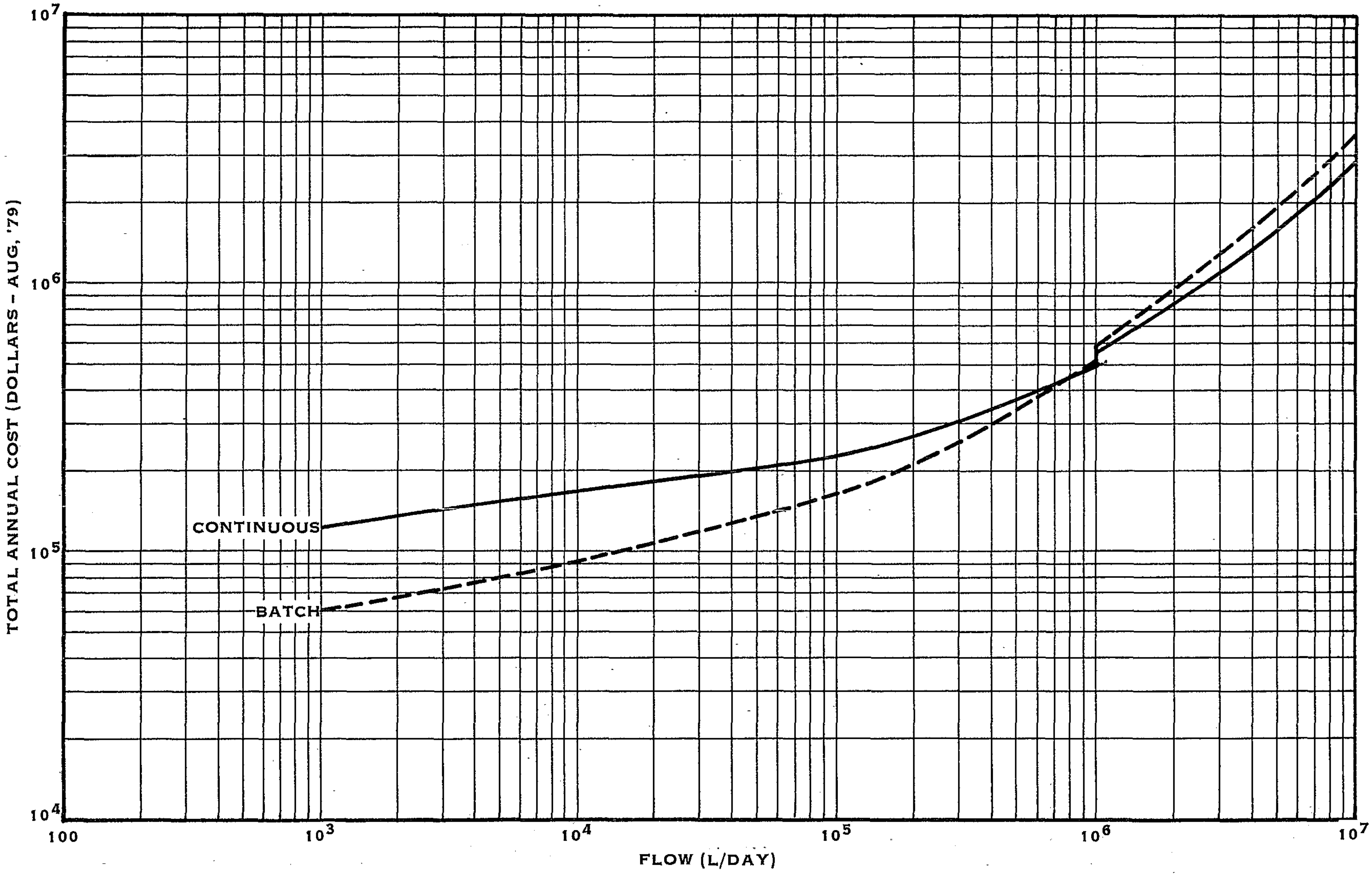


FIGURE 8-44

TOTAL ANNUAL COST VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 5

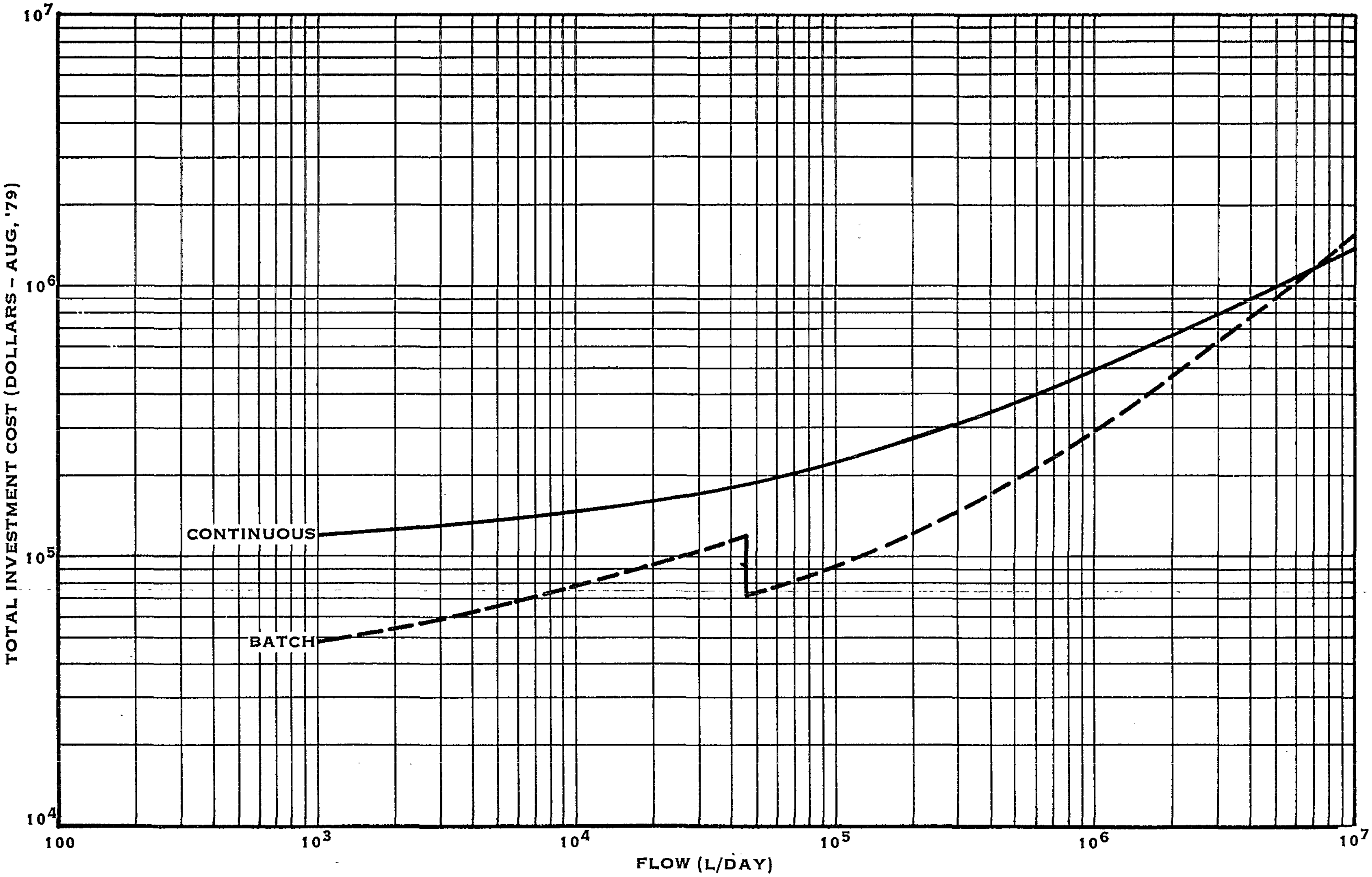


FIGURE 8-45

TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM, CASE 6

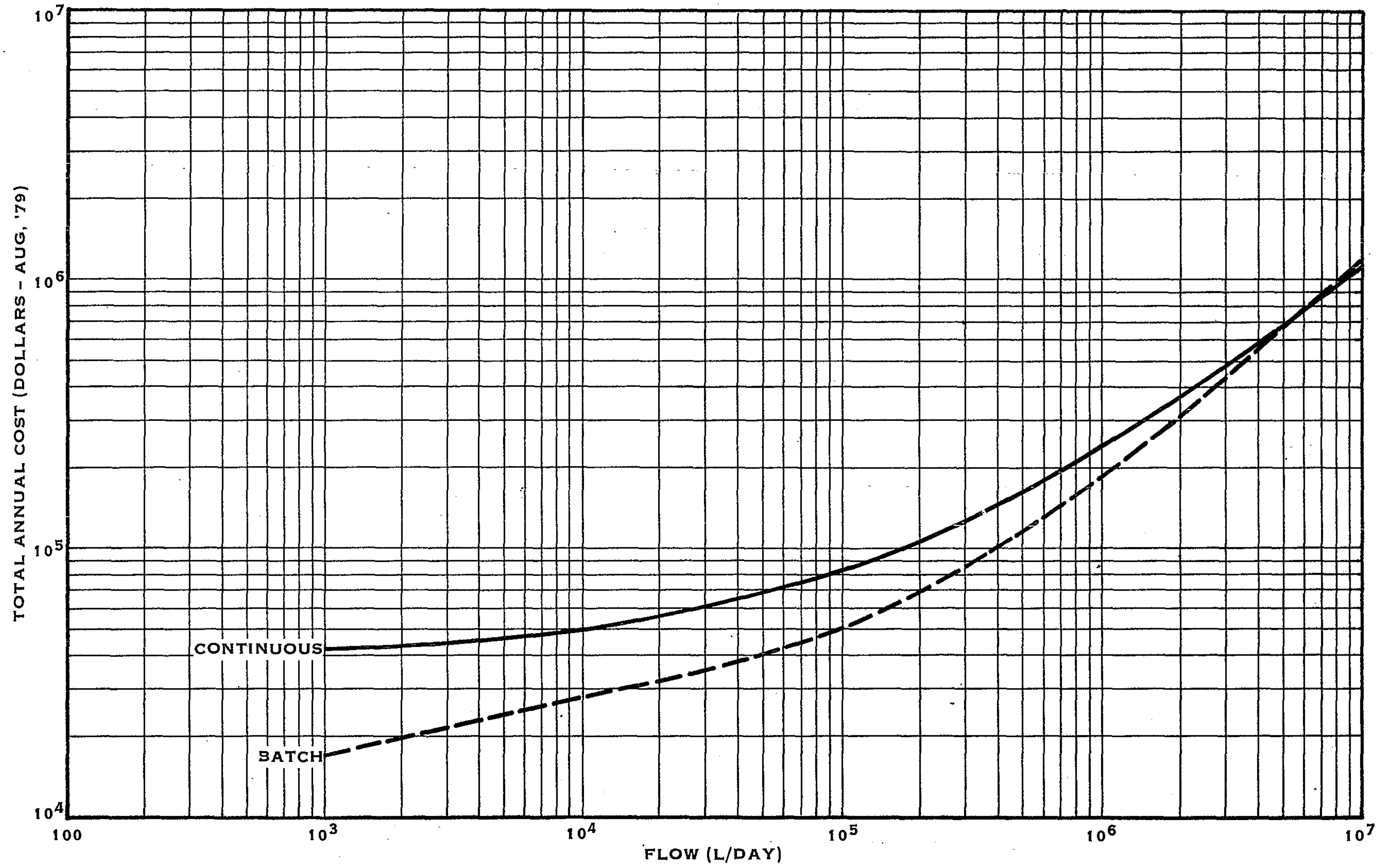


FIGURE 8-46

TOTAL ANNUAL COST VS. FLOW RATE FOR OPTION 1 TREATMENT SYSTEM , CASE 6

The investment costs shown assume that the treatment system must be specially constructed and include all subsidiary costs discussed under the Cost Breakdown Factors segment of this section. It is also assumed all plants operate 24 hours a day, 5 days per week, for 52 weeks per year (260 total days). This assumption overestimates the costs for facilities which operate less than 24 hours per day.

## System Cost Estimates (Option 2)

System cost estimates of the effects of adding a multimedia filter to the previously discussed end-of-pipe systems were developed to provide Option 2 Treatment Cost Estimates. A schematic of the system for cases 1-5 is shown in Figure 8-47. The cases used are the same as those for Option 1 and are shown in Table 8-8. The costing assumptions for the multimedia filter were discussed above under the technology costs and assumptions subsection.

Several flow rates were used for each case to effectively model a wide spectrum of plant sites. Figures 8-48 through 8-57 present the investment and total annual costs for each case in Option 2.

Table 8-10 presents Option 2 treatment costs for construction of the entire end-of-pipe system. These costs would be representative of expenditures to be expected to attain Option 2 for a plant with no treatment in place.

## System Cost Estimates (Option 3)

The Option 3 system takes the Option 1 system and makes one significant change. The one change requires the closed loop operation (zero discharge) of any processes using cadmium. For costing purposes, an evaporative system has been used with the condensate reused for rinsing and the concentrate hauled for disposal. This may also be accomplished by other means selected by the individual plants. Closed loop precipitation with reuse of the treated water and licensed hauling of the sludge, or ion exchange with reuse of the water and treatment and hauling of the regenerant solution are two possible options. The schematic for the complete Option 3 system for cases 1-5 is shown in Figure 8-58. The investment and total annual cost curves for each case are shown in Figures 8-59 through 8-68. Table 8-11 presents a summary of the Option 3 costs.

## Use of Cost Estimation Results

Cost estimates presented in the tables and figures in this section are representative of costs typically incurred in implementing treatment and control equivalent to the specified options. They will not, in general, correspond precisely to cost experience at any individual plant. Specific plant conditions such as age, location, plant layout, or present production and treatment practices may yield costs which are either higher or lower than the presented costs. Because the costs shown are

## TABLE 8-10

### Option 2 Costs

| Case Number | | Flow gpd | Flow 1/day | Investment (Dollars) | Capital Costs (Dollars) | Depreciation (Dollars) | Operation & Maintenance (Dollars) | Energy (Dollars) | Total Annual (Dollars) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Batch | 264. | 1,000. | 131895.812 | 11120.953 | 26379.160 | 18059.805 | 41.582 | 55601.496 |
| 1 | Batch | 2638. | 10,000. | 166617.562 | 14048.422 | 33323.512 | 24661.469 | 80.944 | 72114.312 |
| 1 | Batch | 26380. | 100,000. | 317501.875 | 26770.312 | 63500.375 | 39294.414 | 512.365 | 130077.375 |
| 1 | Continuous | 263800. | 1,000,000. | 775782.562 | 65410.125 | 155156.500 | 191502.062 | 6365.043 | 418433.687 |
| 1 | Continuous | 2637999. | 10,000,000. | 1759412.00 | 148346.250 | 351882.375 | 1473137.00 | 38280.355 | 2011645.00 |
| 2 | Batch | 264. | 1,000. | 143877.062 | 12131.211 | 28775.410 | 31575.918 | 70.738 | 72553.187 |
| 2 | Batch | 2662. | 10,000. | 180996.687 | 15260.781 | 36199.336 | 38055.617 | 112.773 | 89628.437 |
| 2 | Batch | 26350. | 100,000. | 347292.000 | 29282.125 | 69458.375 | 52200.605 | 402.604 | 151343.625 |
| 2 | Continuous | 263600. | 1,000,000. | 897996.562 | 75714.625 | 179599.312 | 193548.937 | 6294.062 | 455156.937 |
| 2 | Continuous | 2637998. | 10,000,000. | 1999361.00 | 168577.750 | 399872.187 | 1413598.00 | 36848.262 | 2018895.00 |
| 3 | Batch | 264. | 1,000. | 179689.062 | 15150.605 | 35937.812 | 19417.297 | 43.060 | 70548.687 |
| 3 | Batch | 2660. | 10,000. | 222102.125 | 18726.656 | 44420.422 | 28194.559 | 88.314 | 91429.937 |
| 3 | Batch | 26410. | 100,000. | 433213.250 | 36526.687 | 86642.625 | 47096.309 | 578.113 | 170843.625 |
| 3 | Continuous | 266300. | 1,000,000. | 1064609.00 | 89762.937 | 212921.750 | 277545.437 | 7136.859 | 587366.937 |
| 3 | Continuous | 2638998. | 10,000,000. | 2517744.00 | 212285.625 | 503548.750 | 2211218.00 | 43957.875 | 2971009.00 |
| 4 | Batch | 264. | 1,000. | 78779.750 | 6642.379 | 15755.949 | 16829.016 | 37.520 | 39264.863 |
| 4 | Batch | 2642. | 10,000. | 112982.875 | 9526.258 | 22596.574 | 24253.570 | 78.484 | 56454.887 |
| 4 | Batch | 26420. | 100,000. | 286488.000 | 24155.402 | 57297.598 | 38450.984 | 519.993 | 120423.875 |
| 4 | Continuous | 264300. | 1,000,000. | 790898.375 | 66684.812 | 158179.750 | 251368.750 | 4926.543 | 481159.812 |
| 4 | Continuous | 2642999. | 10,000,000. | 2006627.00 | 169190.500 | 401325.375 | 2073672.00 | 30924.371 | 2675111.00 |
| 5 | Batch | 264. | 1,000. | 147632.500 | 12447.863 | 29526.500 | 31636.180 | 67.495 | 73677.937 |
| 5 | Batch | 2638. | 10,000. | 238419.312 | 20102.391 | 47683.859 | 41643.074 | 118.835 | 109548.125 |
| 5 | Batch | 26460. | 100,000. | 460628.062 | 38838.125 | 92125.562 | 60006.383 | 607.457 | 191577.500 |
| 5 | Continuous | 264600. | 1,000,000. | 1174778.00 | 99051.750 | 234955.562 | 276797.875 | 7081.457 | 617886.625 |
| 5 | Continuous | 2645998. | 10,000,000. | 2753802.00 | 232189.375 | 550760.375 | 2140789.00 | 42947.062 | 2966685.00 |

# TABLE 8-11

## Option 3 Costs

| Case Number | | Flow gpd | Flow 1/day | Investment (Dollars) | Capital Costs (Dollars) | Depreciation (Dollars) | Operation & Maintenance (Dollars) | Energy (Dollars) | Total Annual (Dollars) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Batch | 264. | 1,000. | 192780.875 | 16254.516 | 38556.172 | 12600.187 | 4827.246 | 72238.062 |
| 1 | Batch | 2476. | 10,000. | 215883.312 | 18202.301 | 43176.660 | 16988.187 | 4843.324 | 83210.437 |
| 1 | Batch | 24490. | 100,000. | 348419.812 | 29377.250 | 69683.937 | 29551.547 | 5002.102 | 133614.750 |
| 1 | Continuous | 244684. | 1,000,000. | 715315.000 | 60312.000 | 143063.000 | 166658.062 | 16672.348 | 386705.375 |
| 1 | Continuous | 2446819. | 10,000,000. | 1472822.00 | 124182.125 | 294564.375 | 1334110.00 | 107447.812 | 1860303.00 |
| 2 | Batch | 264. | 1,000. | 208025.375 | 17539.859 | 41605.074 | 20047.117 | 4855.309 | 84047.250 |
| 2 | Batch | 2500. | 10,000. | 232406.812 | 19595.391 | 46481.359 | 24332.359 | 4871.309 | 95280.312 |
| 2 | Batch | 24686. | 100,000. | 371089.625 | 31288.687 | 74217.875 | 36565.973 | 5028.004 | 147100.500 |
| 2 | Continuous | 246740. | 1,000,000. | 812359.375 | 68494.250 | 162471.875 | 163858.187 | 15326.258 | 410150.562 |
| 2 | Continuous | 2459499. | 10,000,000. | 1634327.00 | 137799.500 | 326865.375 | 1276480.00 | 99898.000 | 1841042.00 |
| 3 | Batch | 264. | 1,000. | 240344.062 | 20264.812 | 48068.812 | 14189.594 | 4828.766 | 87351.937 |
| 3 | Batch | 2542. | 10,000. | 271247.562 | 22870.301 | 54249.512 | 21771.258 | 4851.891 | 103742.937 |
| 3 | Batch | 25134. | 100,000. | 460278.000 | 38808.687 | 92055.562 | 37829.395 | 5217.797 | 173911.375 |
| 3 | Continuous | 251046. | 1,000,000. | 1005995.31 | 84820.250 | 201199.062 | 259804.250 | 15027.391 | 560850.937 |
| 3 | Continuous | 2510287. | 10,000,000. | 2223688.00 | 187492.875 | 444737.562 | 2105460.00 | 91024.125 | 2828714.00 |
| 4 | Batch | 264. | 1,000. | 140197.937 | 11820.918 | 28039.586 | 10807.941 | 4823.234 | 55491.680 |
| 4 | Batch | 2566. | 10,000. | 165645.187 | 13966.504 | 33129.035 | 17912.301 | 4843.039 | 69850.875 |
| 4 | Batch | 25544. | 100,000. | 304231.000 | 25651.426 | 60846.199 | 31900.461 | 5187.508 | 123585.562 |
| 4 | Continuous | 255372. | 1,000,000. | 737350.312 | 62170.000 | 147470.062 | 238480.000 | 11617.648 | 459737.687 |
| 4 | Continuous | 2553623. | 10,000,000. | 1732473.00 | 146075.062 | 346494.562 | 1998380.00 | 65666.812 | 2556615.00 |
| 5 | Batch | 288. | 1,000. | 255809.187 | 21568.664 | 51161.836 | 21734.387 | 4856.965 | 99321.812 |
| 5 | Batch | 2544. | 10,000. | 283810.000 | 23929.562 | 56762.000 | 28998.359 | 4879.828 | 114569.687 |
| 5 | Batch | 25252. | 100,000. | 481832.250 | 40625.937 | 96366.437 | 44753.180 | 5100.312 | 186845.812 |
| 5 | Continuous | 252328. | 1,000,000. | 1095964.00 | 92406.125 | 219192.750 | 254738.937 | 12488.359 | 578826.125 |
| 5 | Continuous | 2523349. | 10,000,000. | 2353792.00 | 198462.500 | 470758.375 | 2029948.00 | 72823.687 | 2771991.00 |

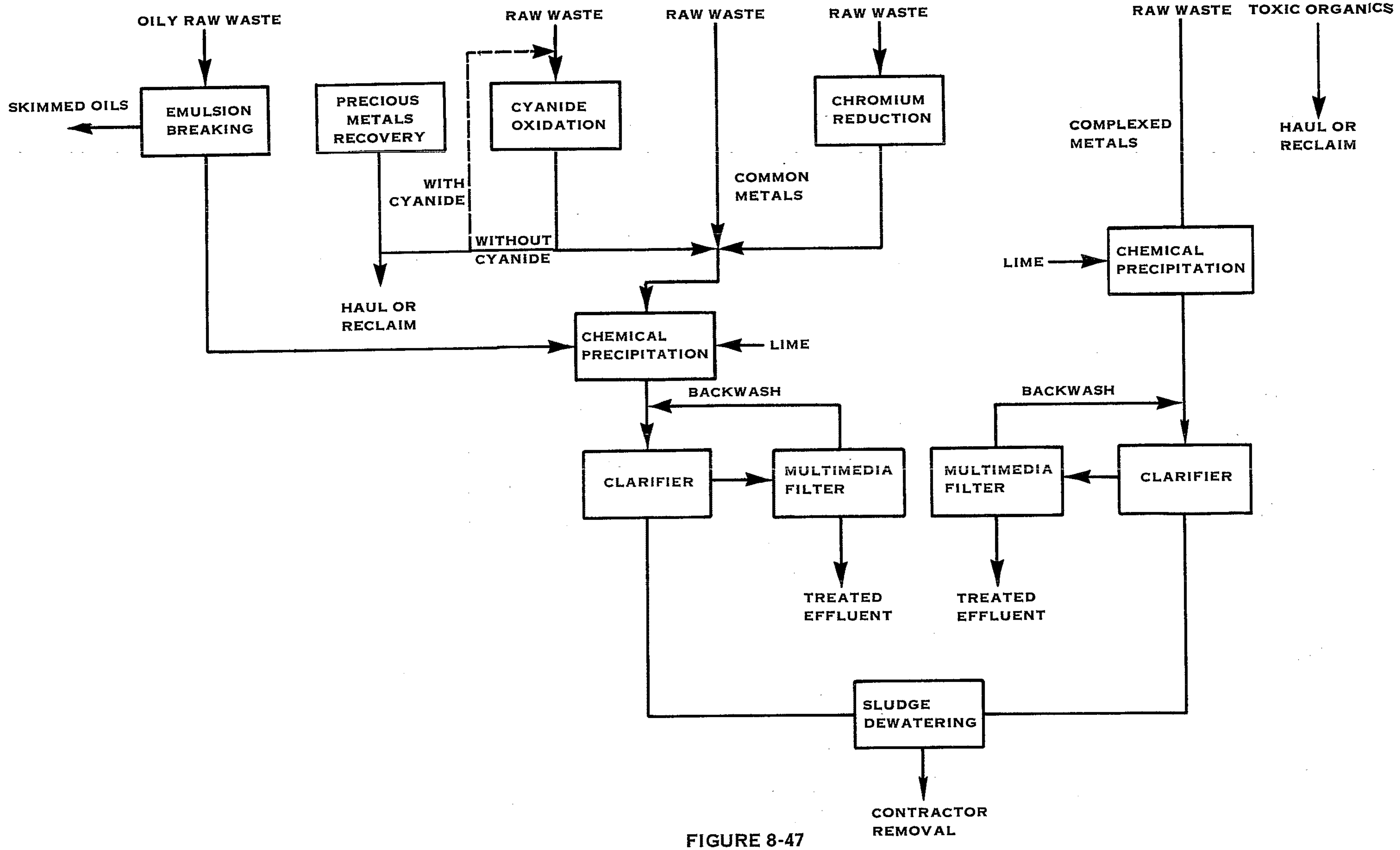


FIGURE 8-47
OPTION 2 SYSTEM

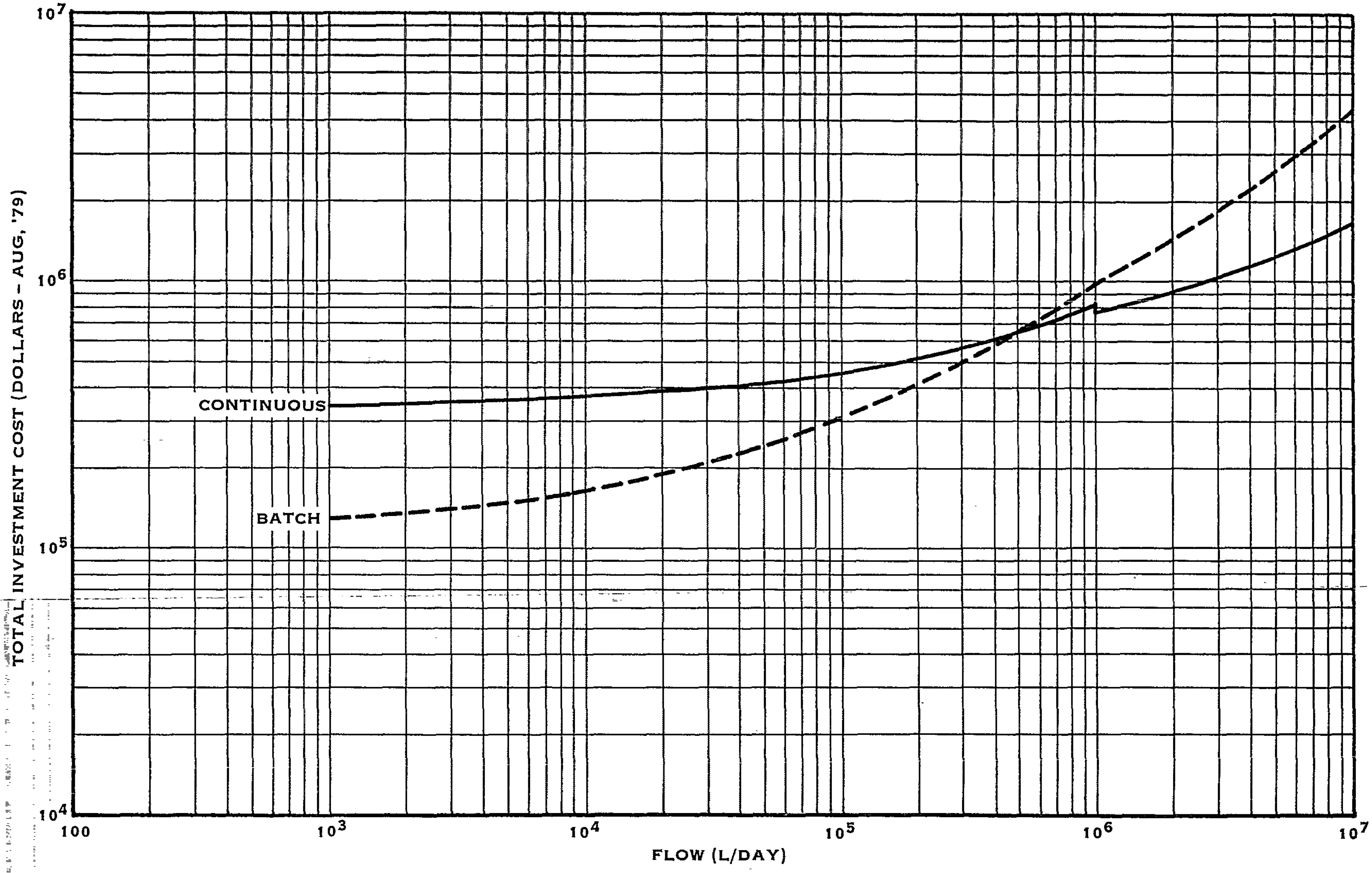


FIGURE 8-48

TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 1

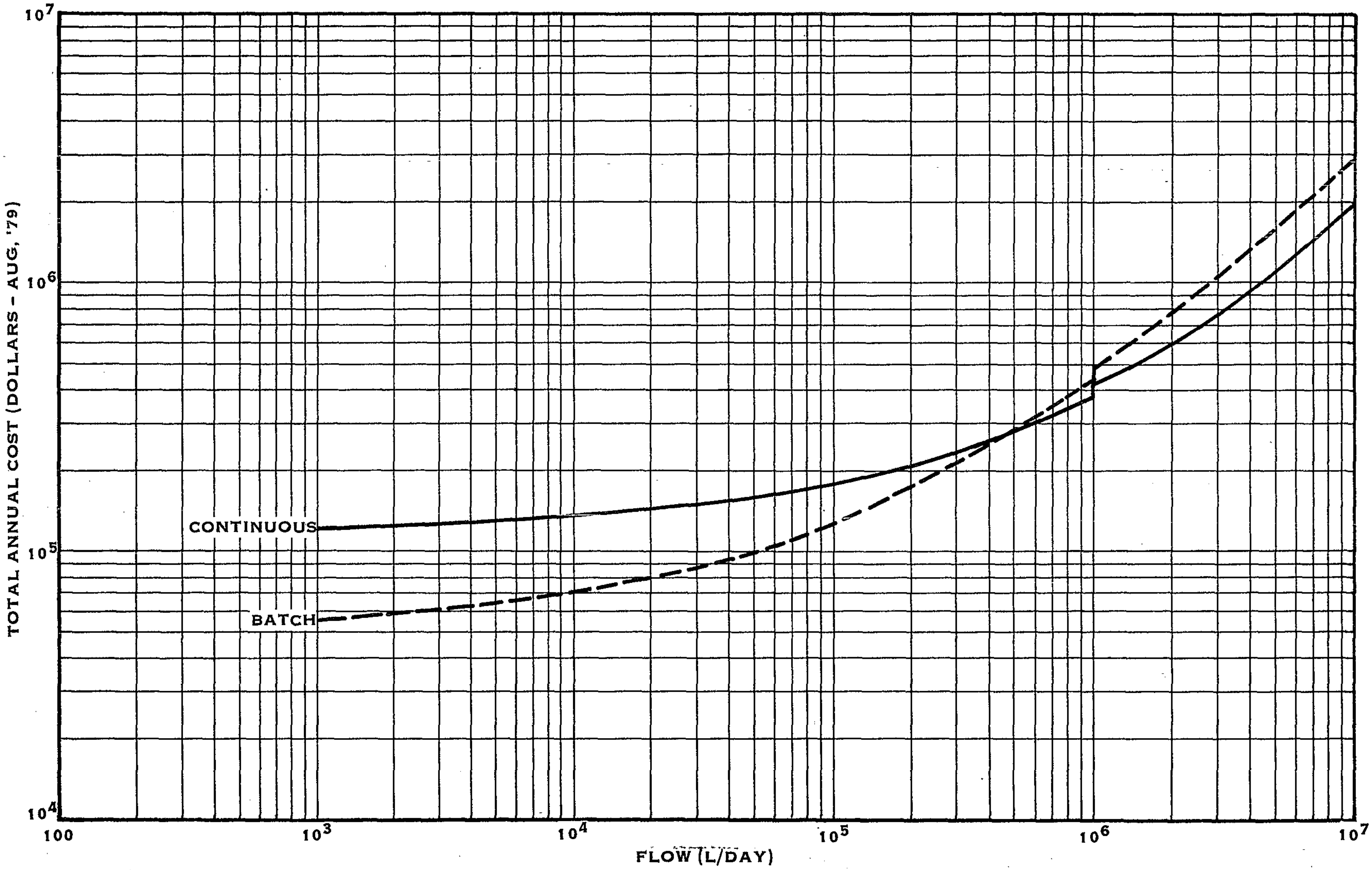


FIGURE 8-49

TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 1

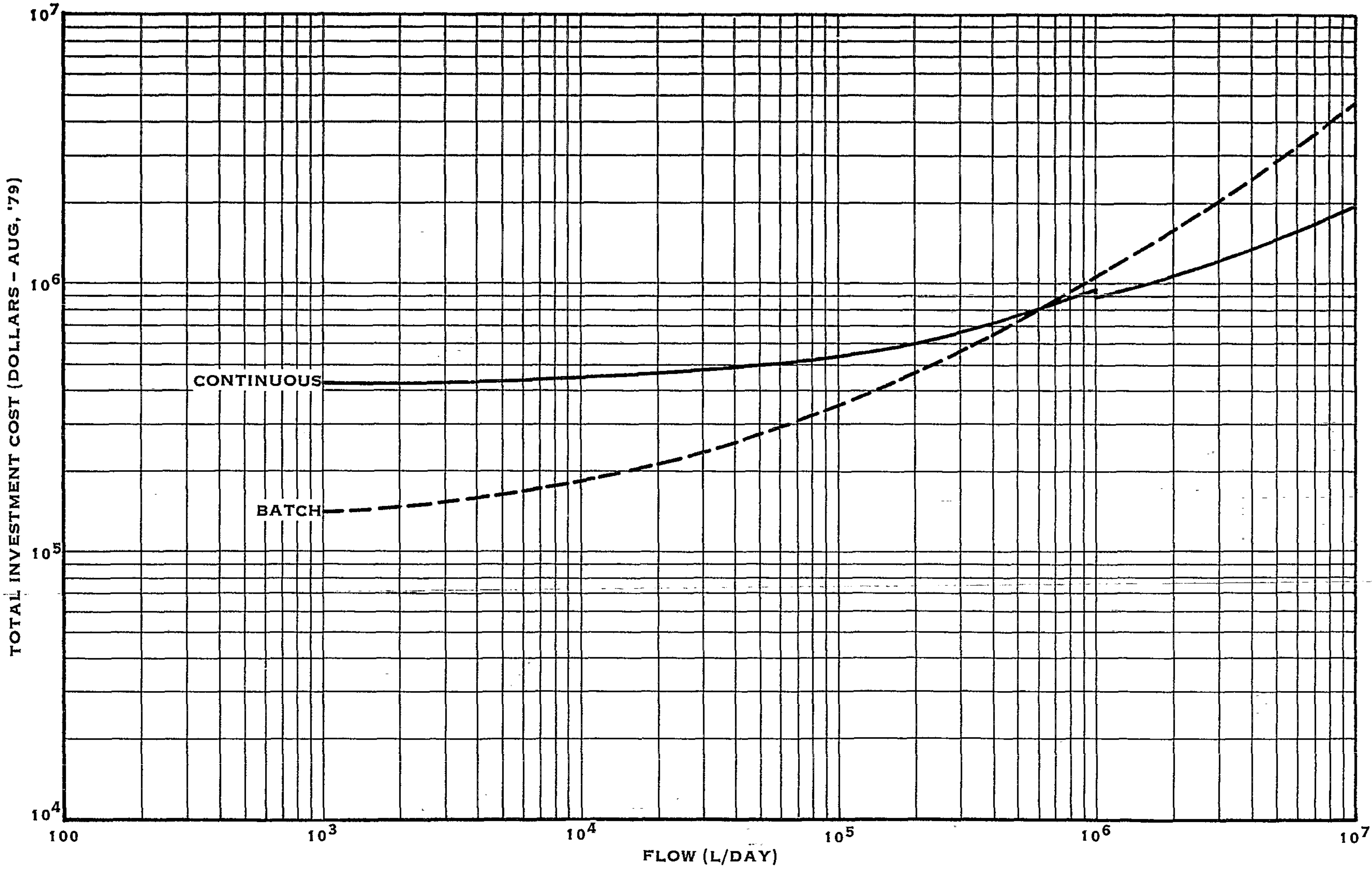


FIGURE 8-50
TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 2

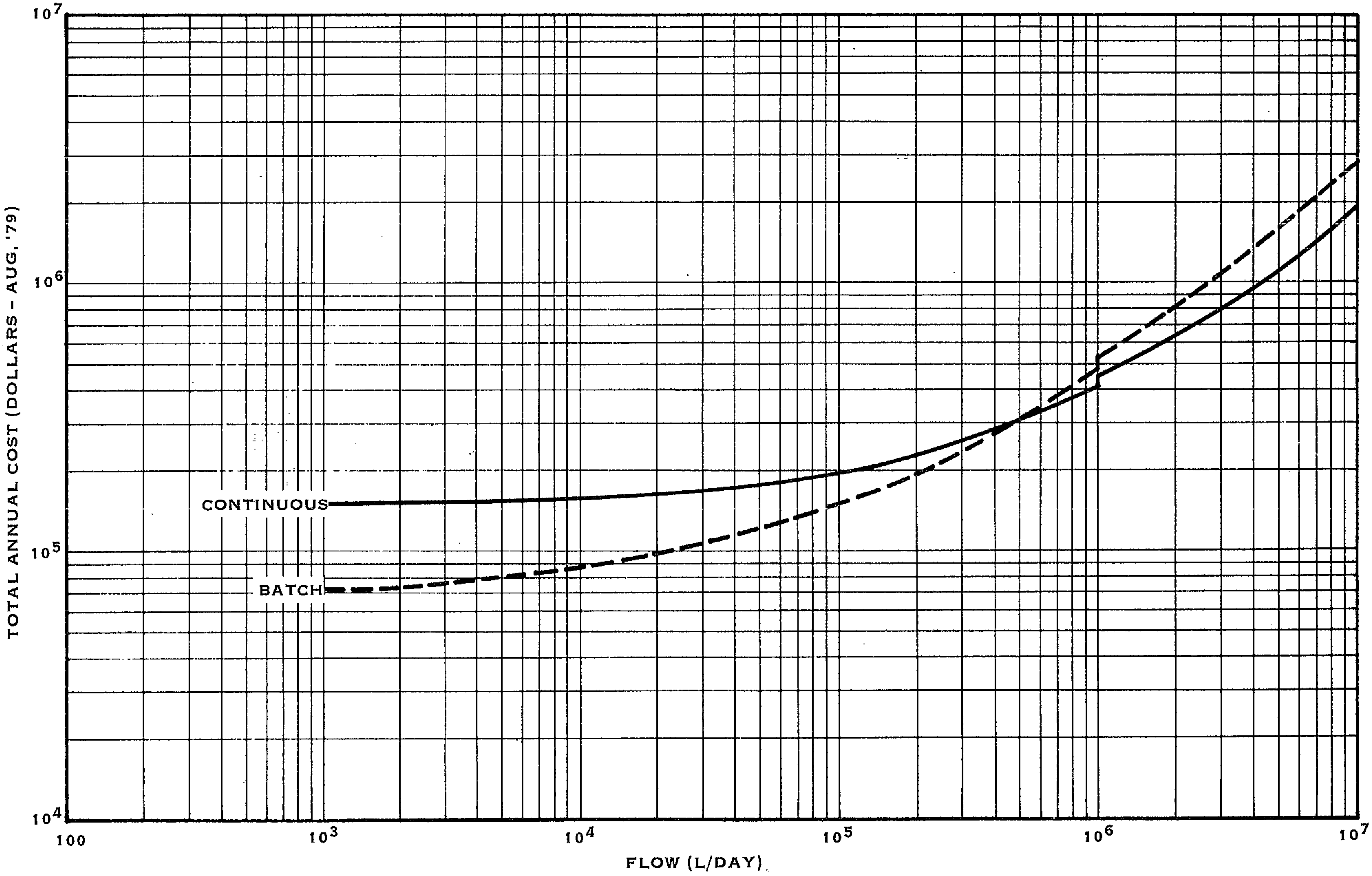


FIGURE 8-51
TOTAL ANNUAL COST VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 2

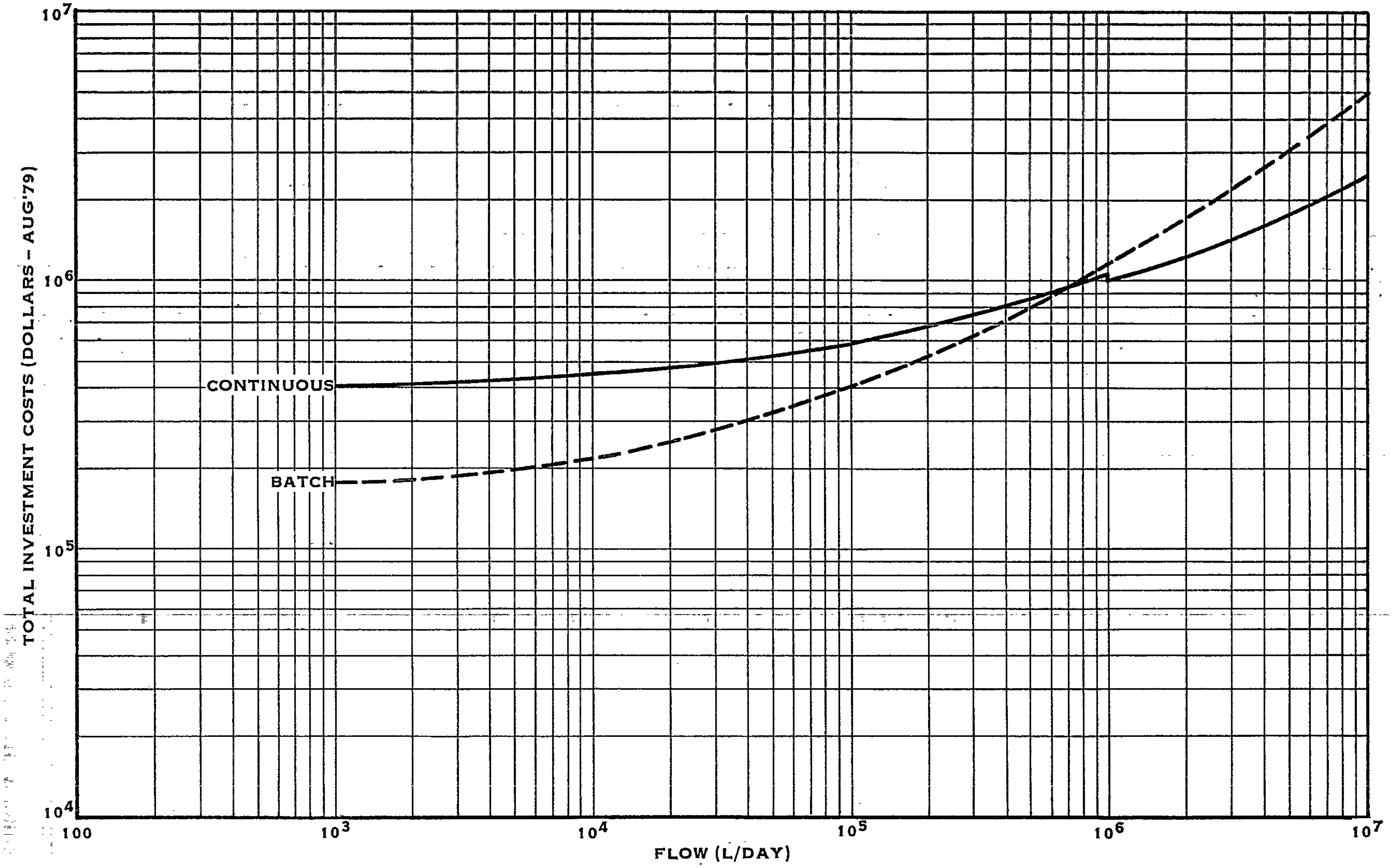


FIGURE 8-52

TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 3

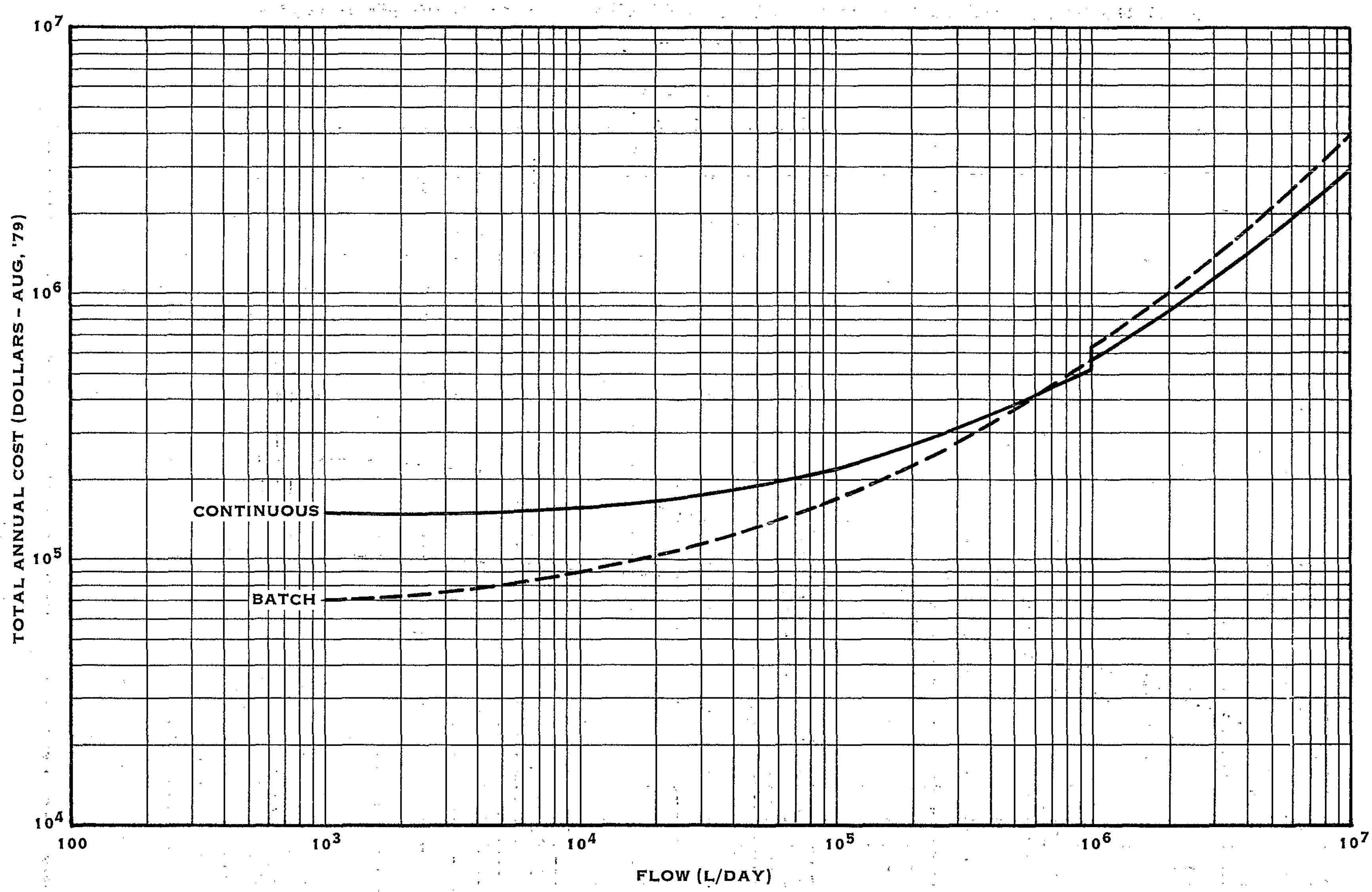


FIGURE 8-53

TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 3

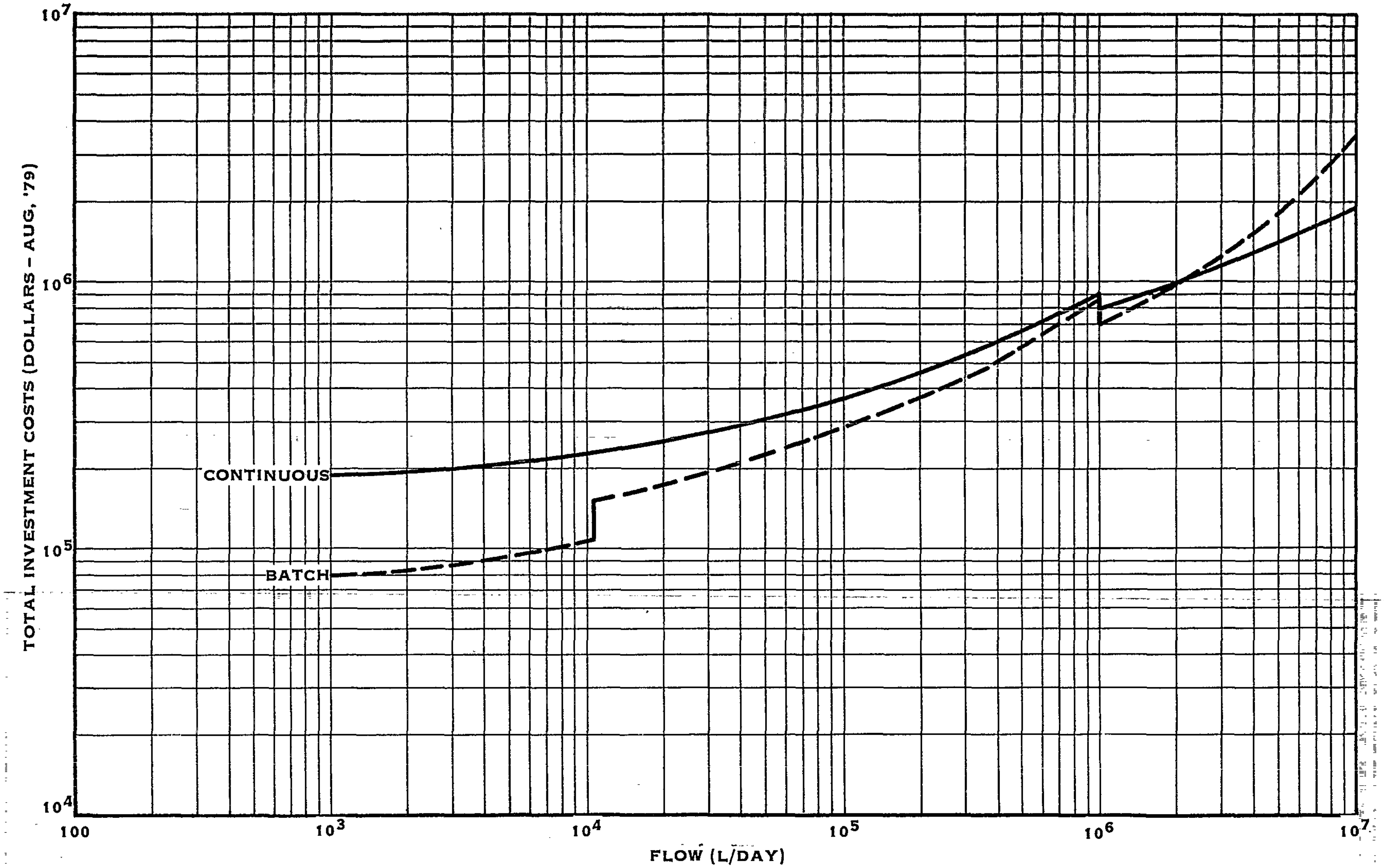


FIGURE 8-54

TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 4

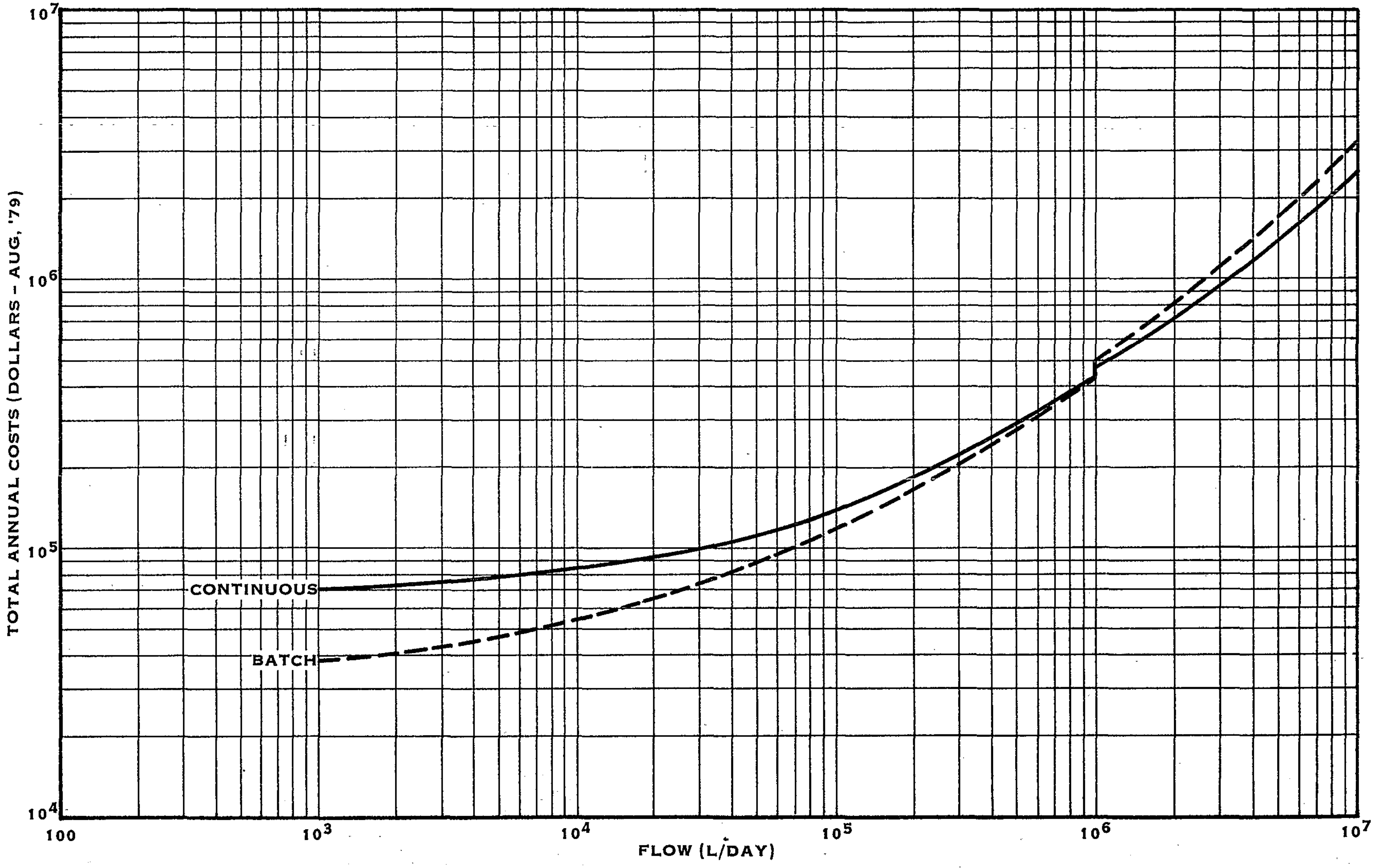


FIGURE 8-55
TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 4

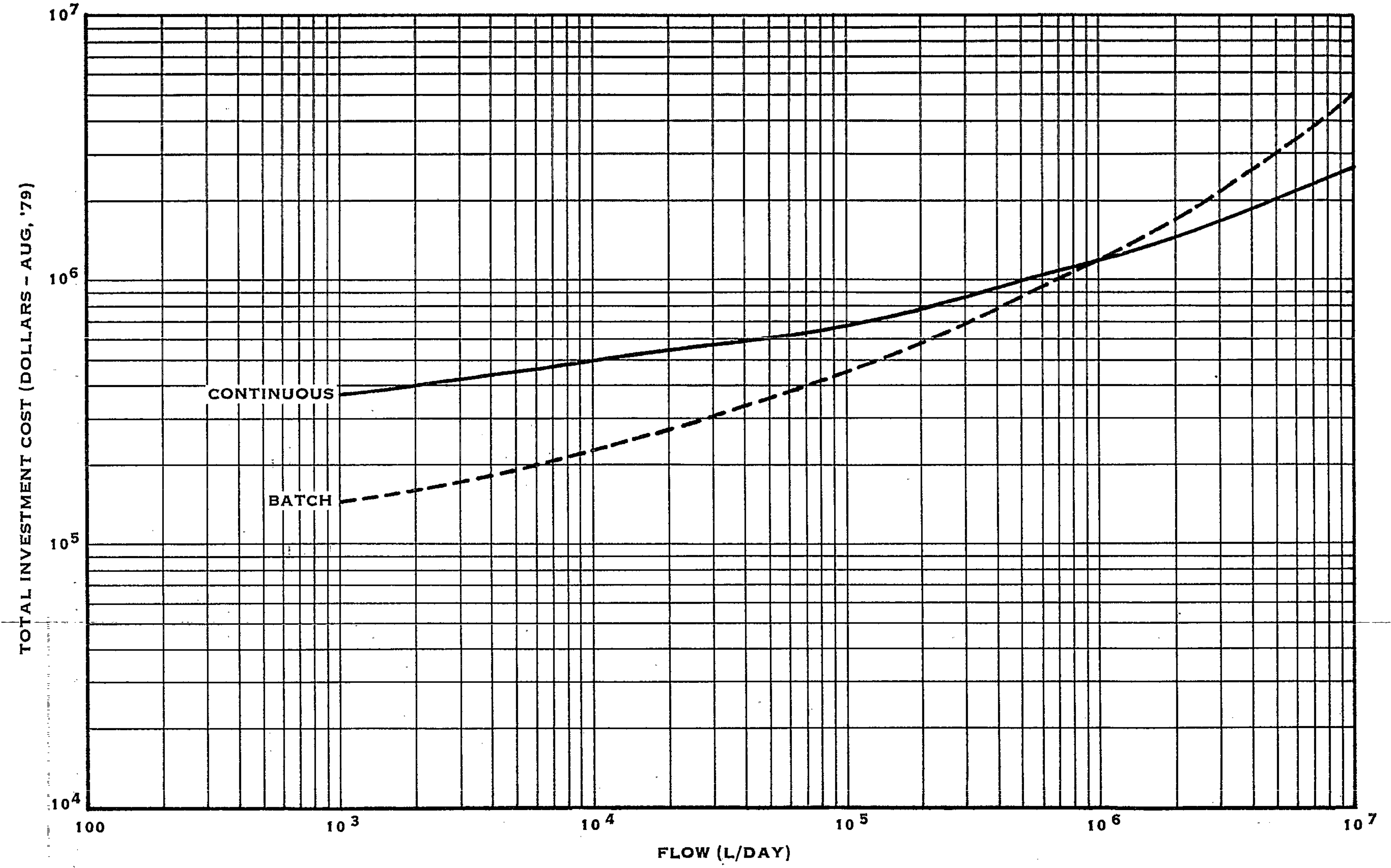


FIGURE 8-56

TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 5

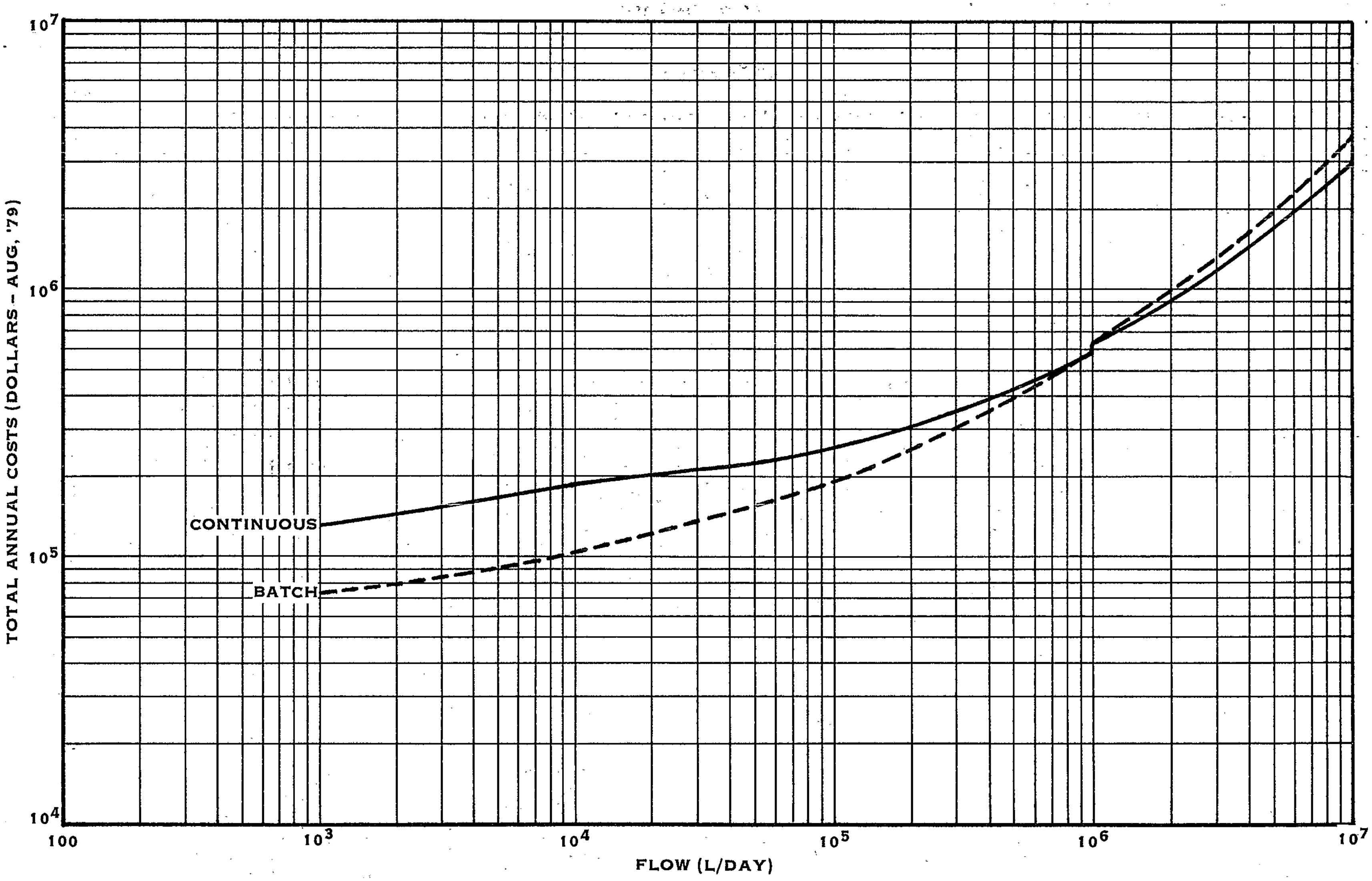


FIGURE 8-57
TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 2 TREATMENT SYSTEM, CASE 5

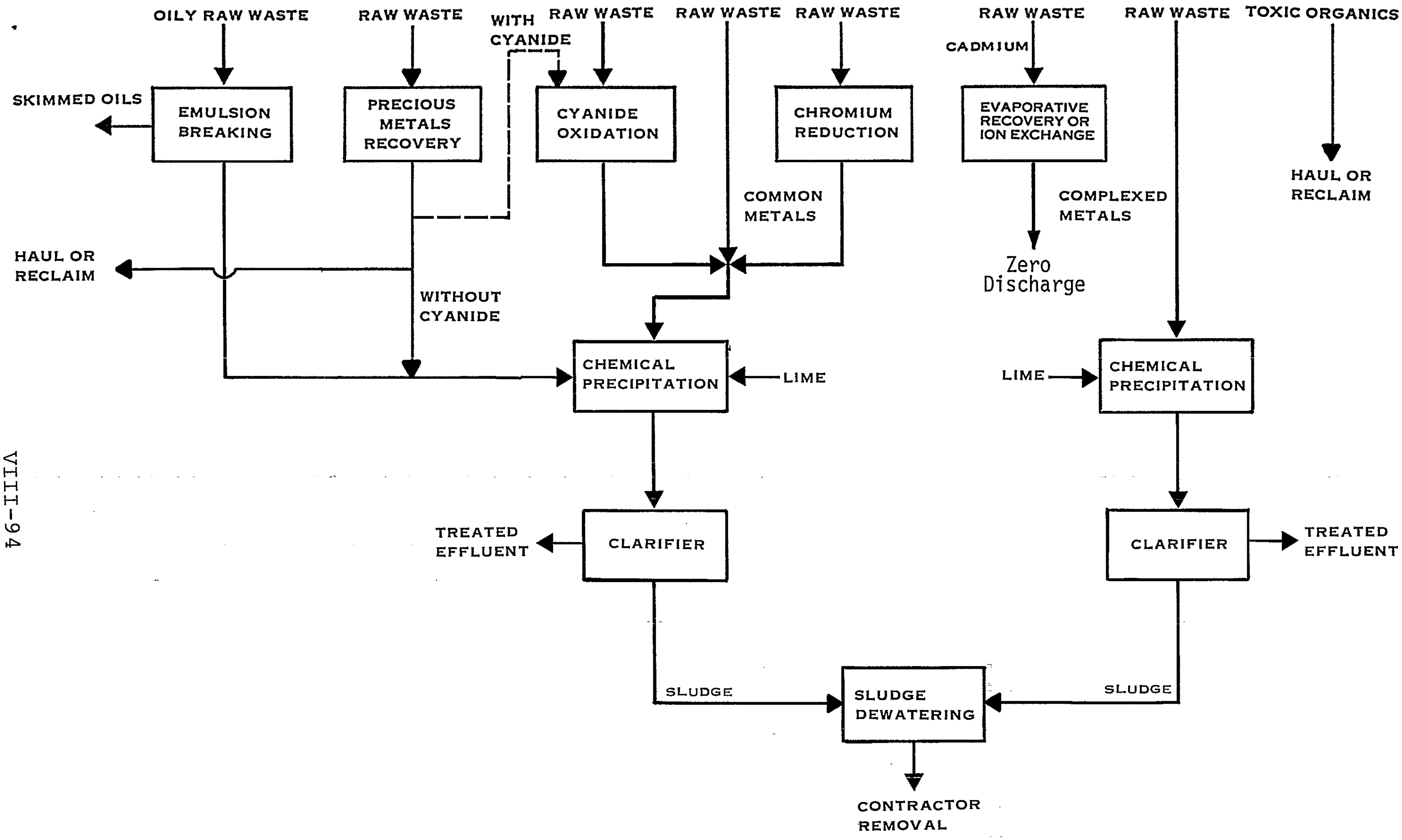


FIGURE 8-58
OPTION 3 SYSTEM

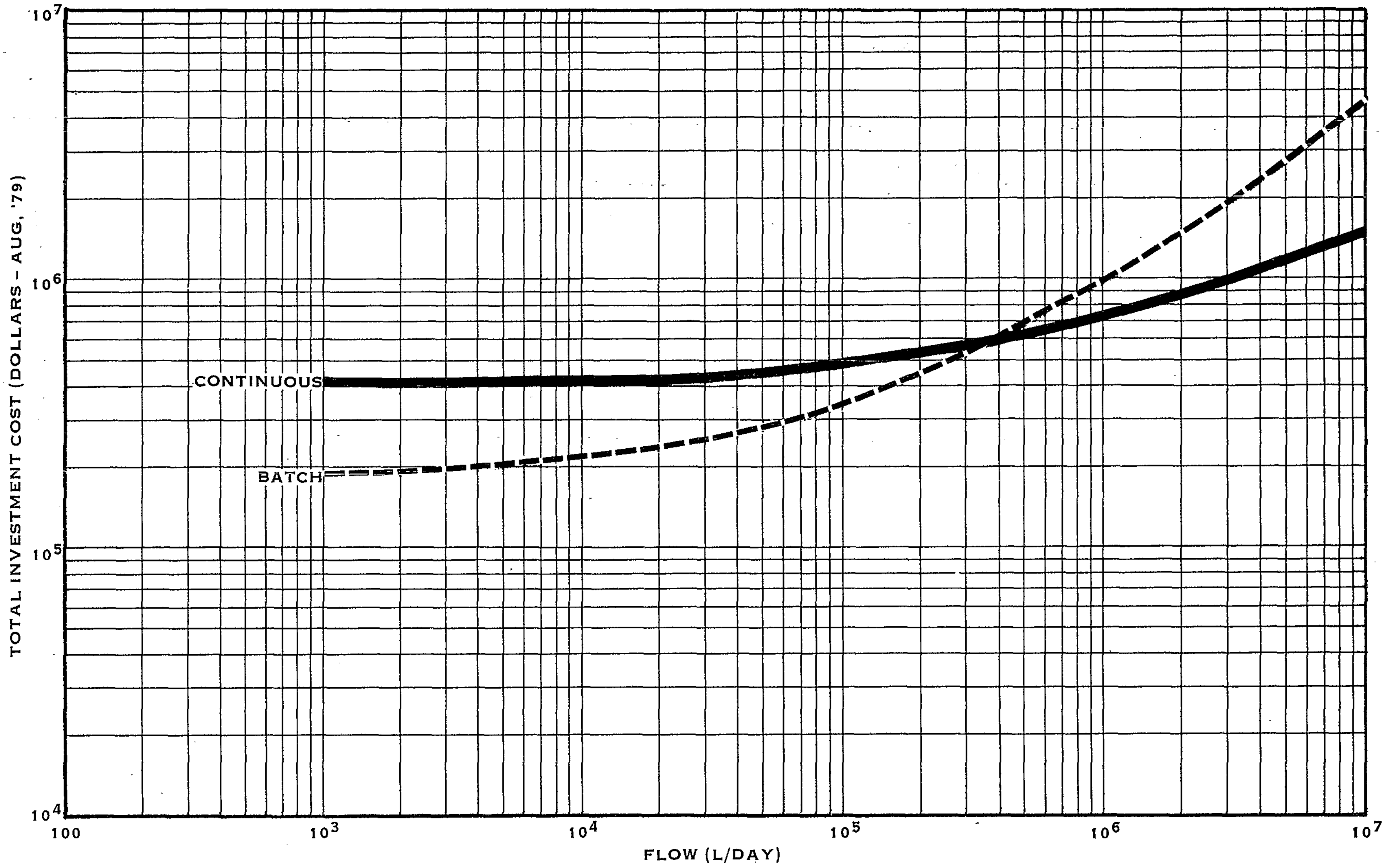


FIGURE 8-59
TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 1

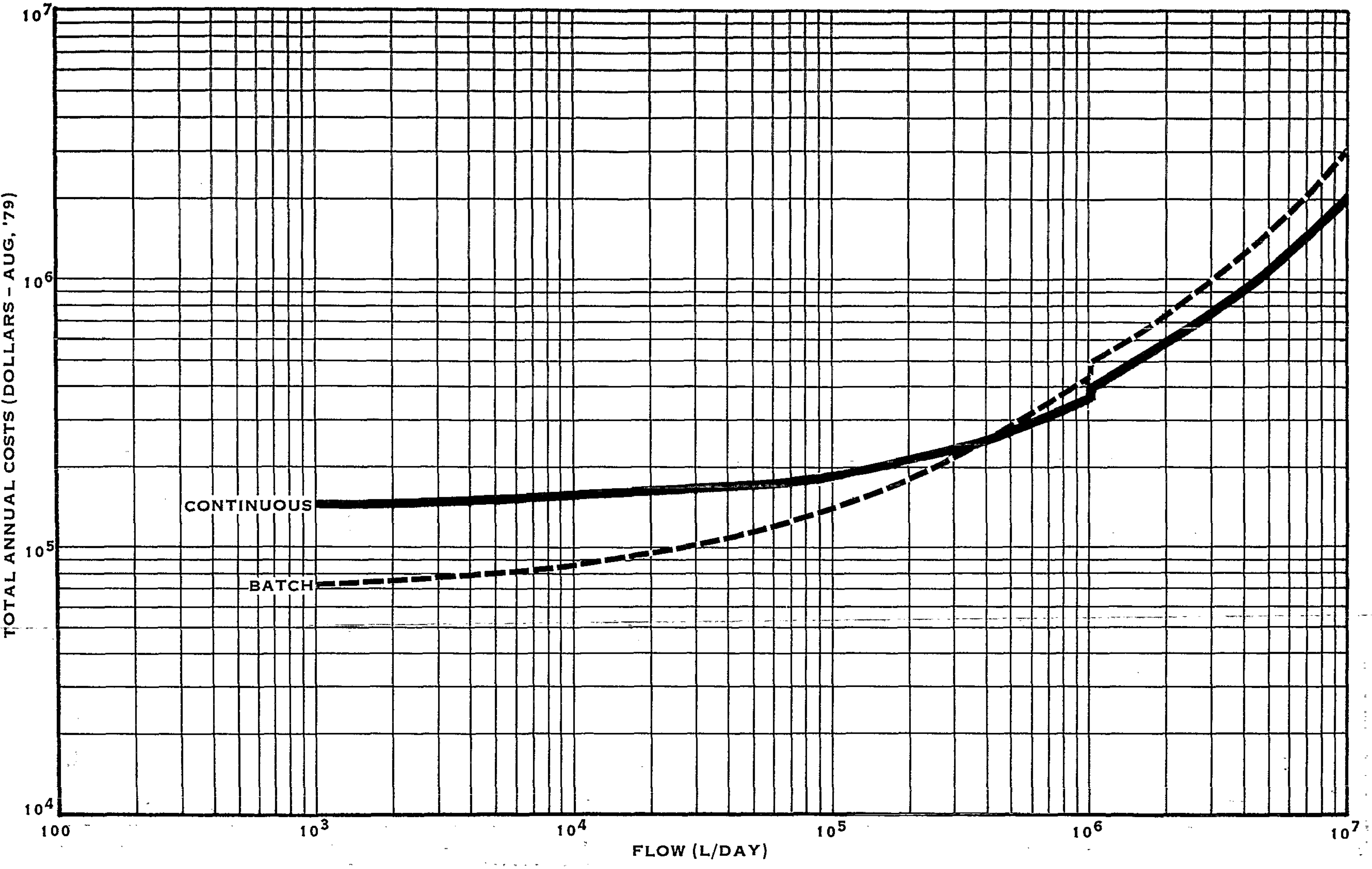


FIGURE 8-60
TOTAL ANNUAL COST VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 1

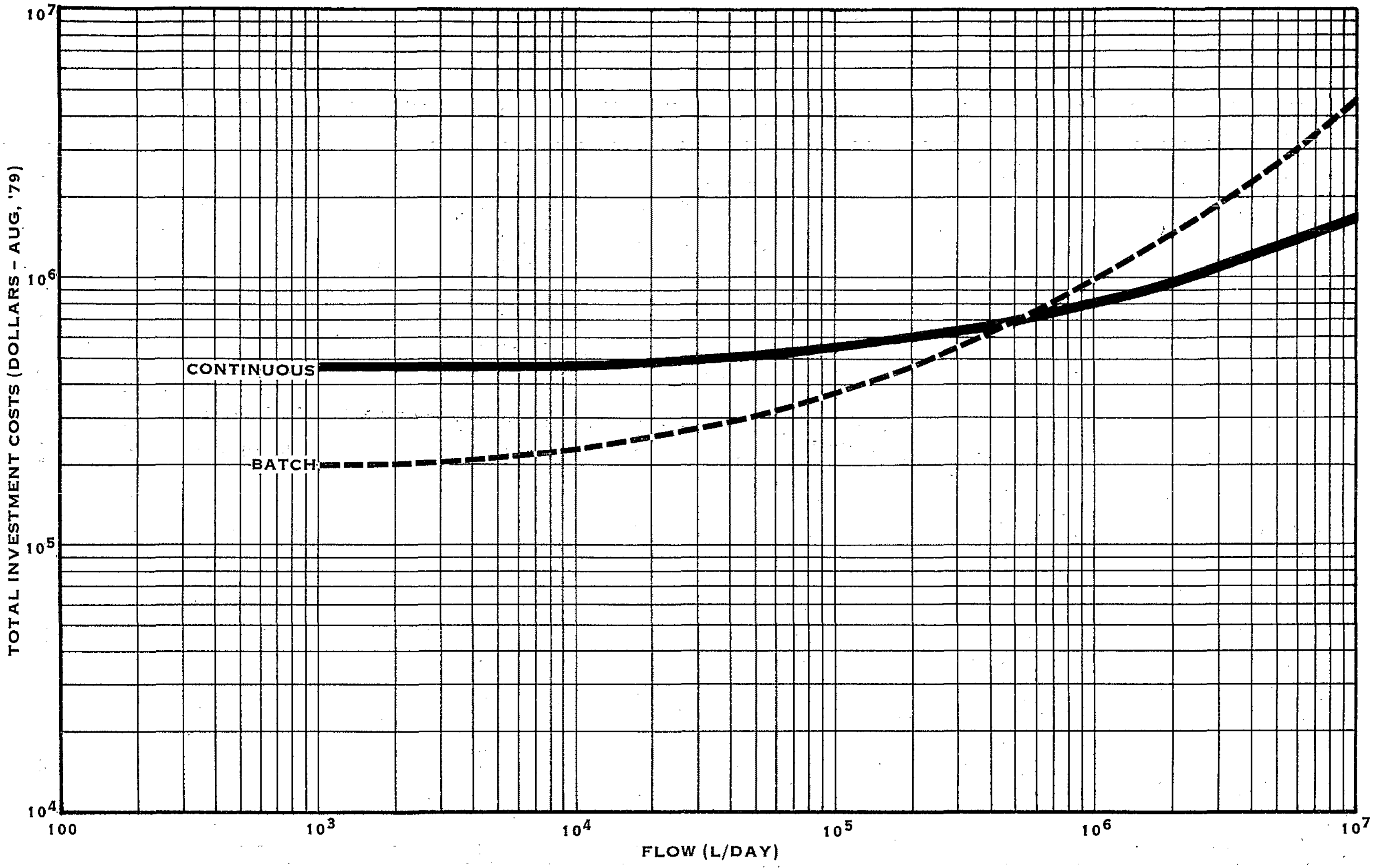


FIGURE 8-61
TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 2

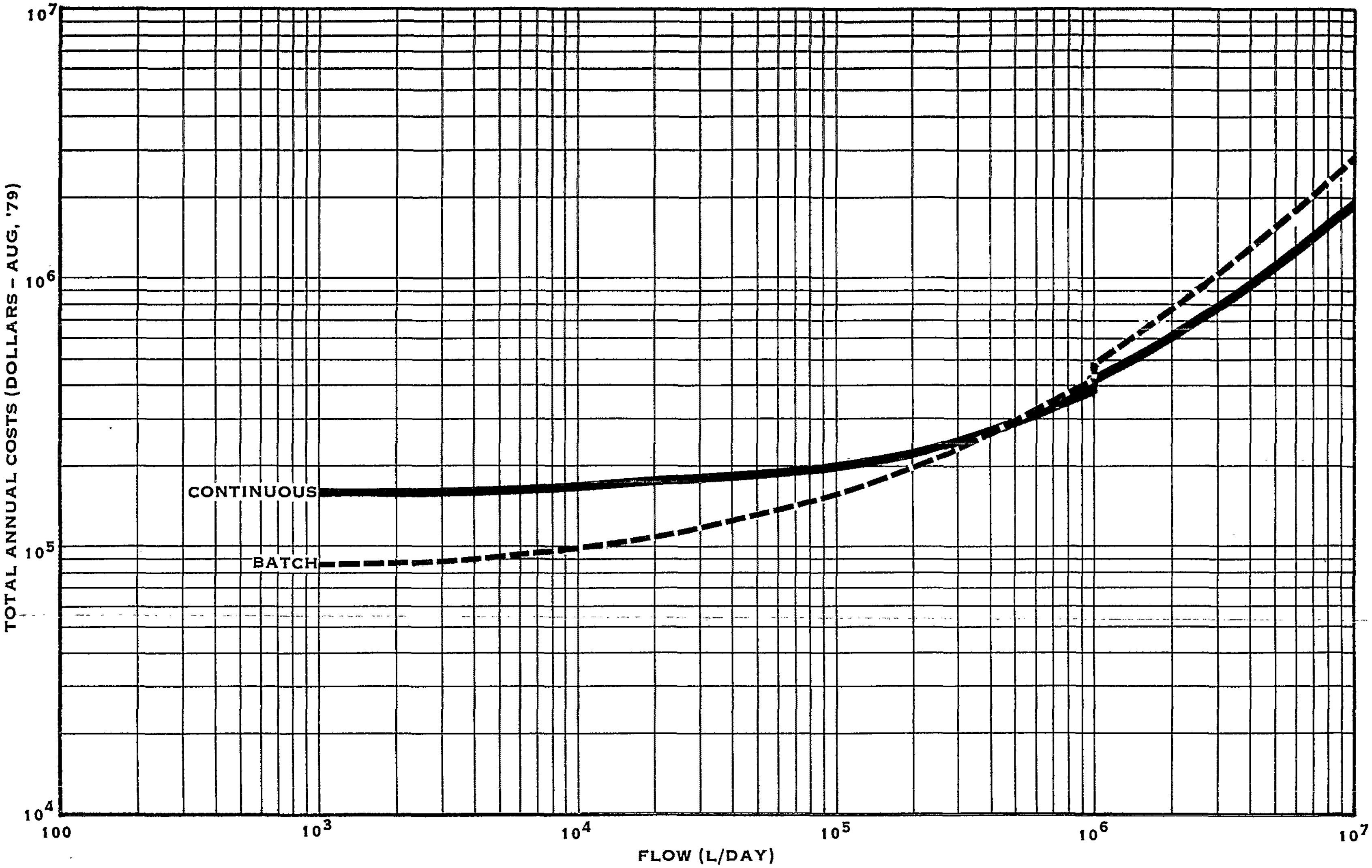


FIGURE 8-62
TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 2

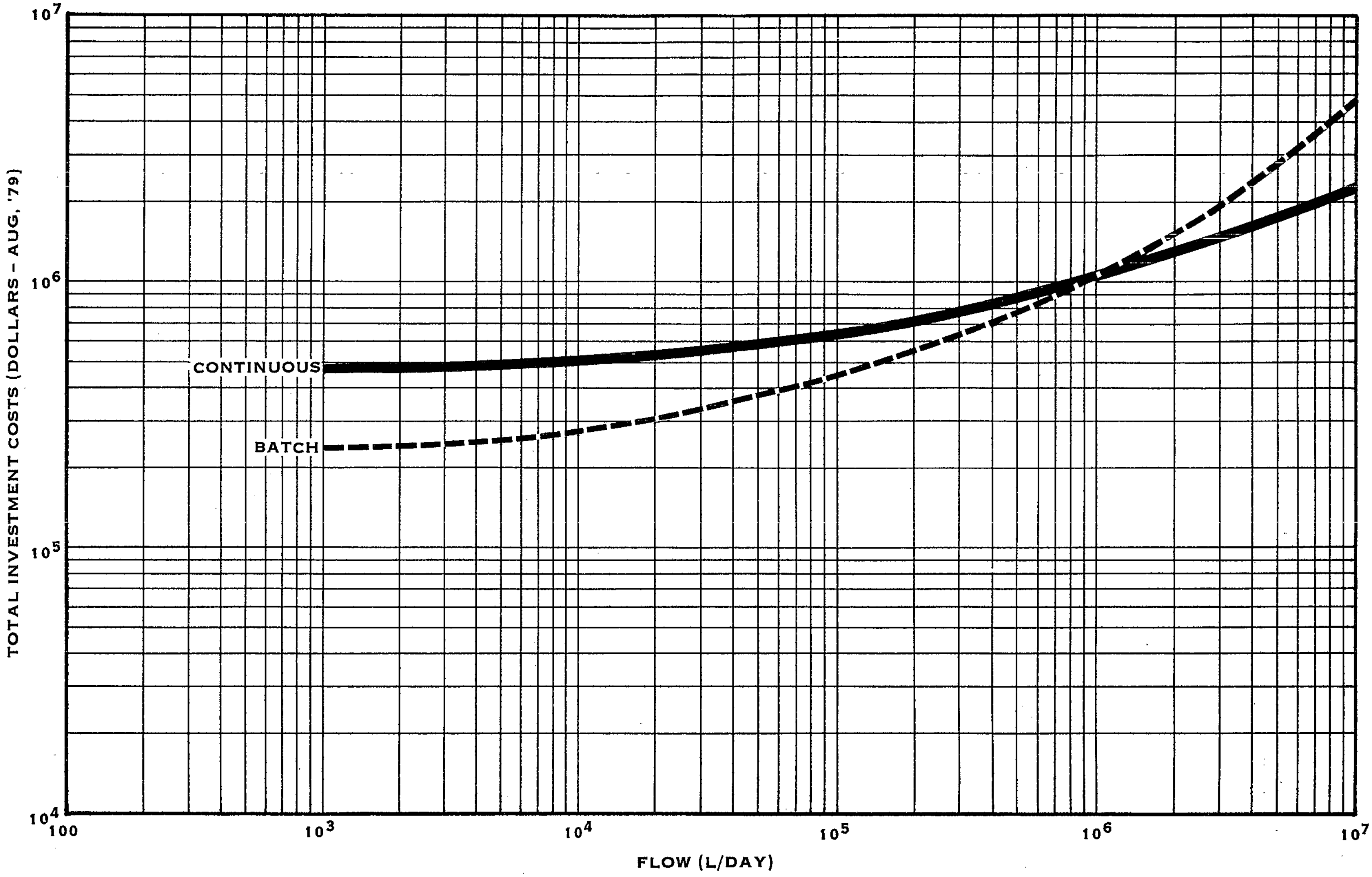


FIGURE 8-63
TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 3

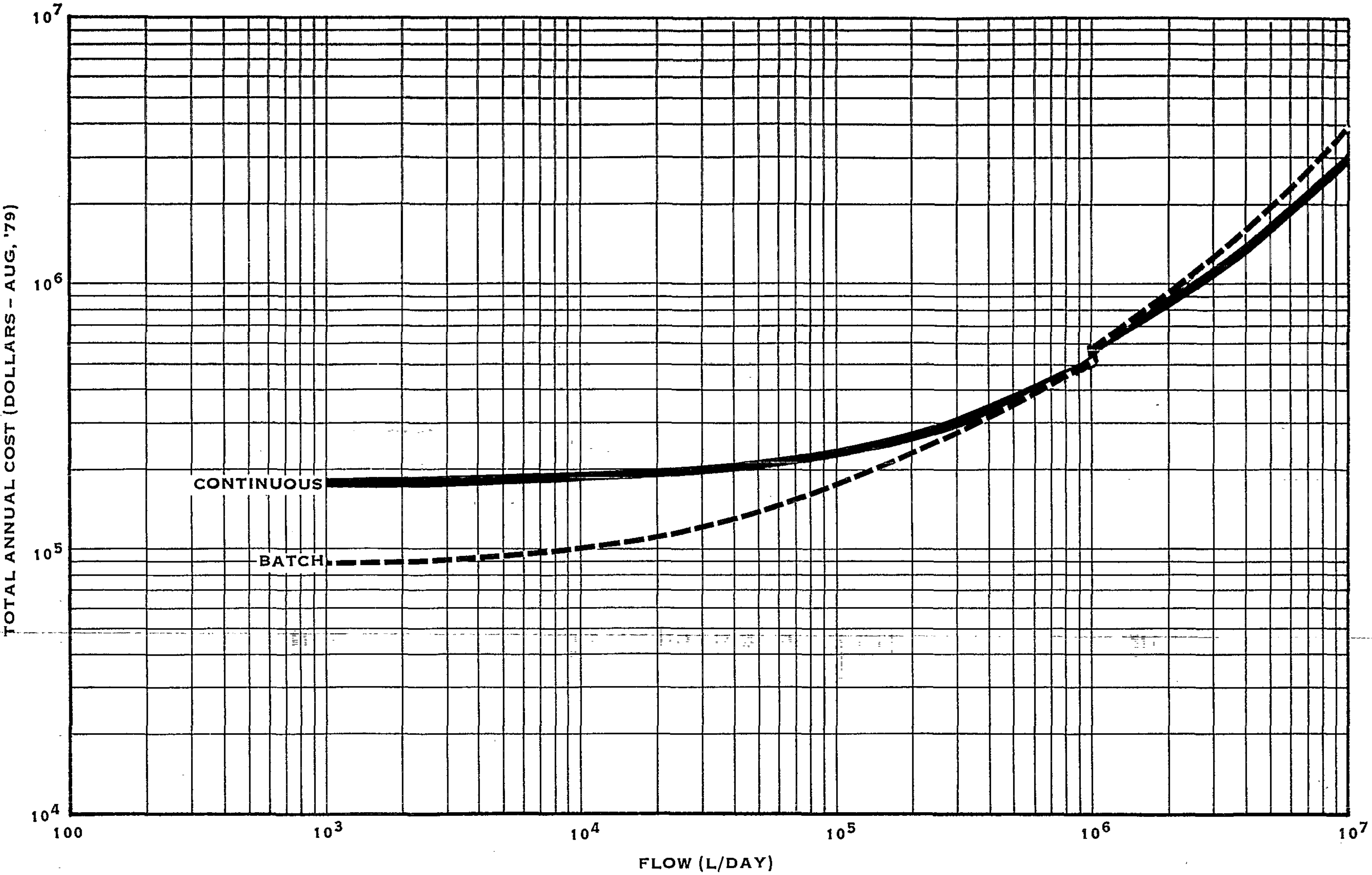


FIGURE 8-64
TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 3

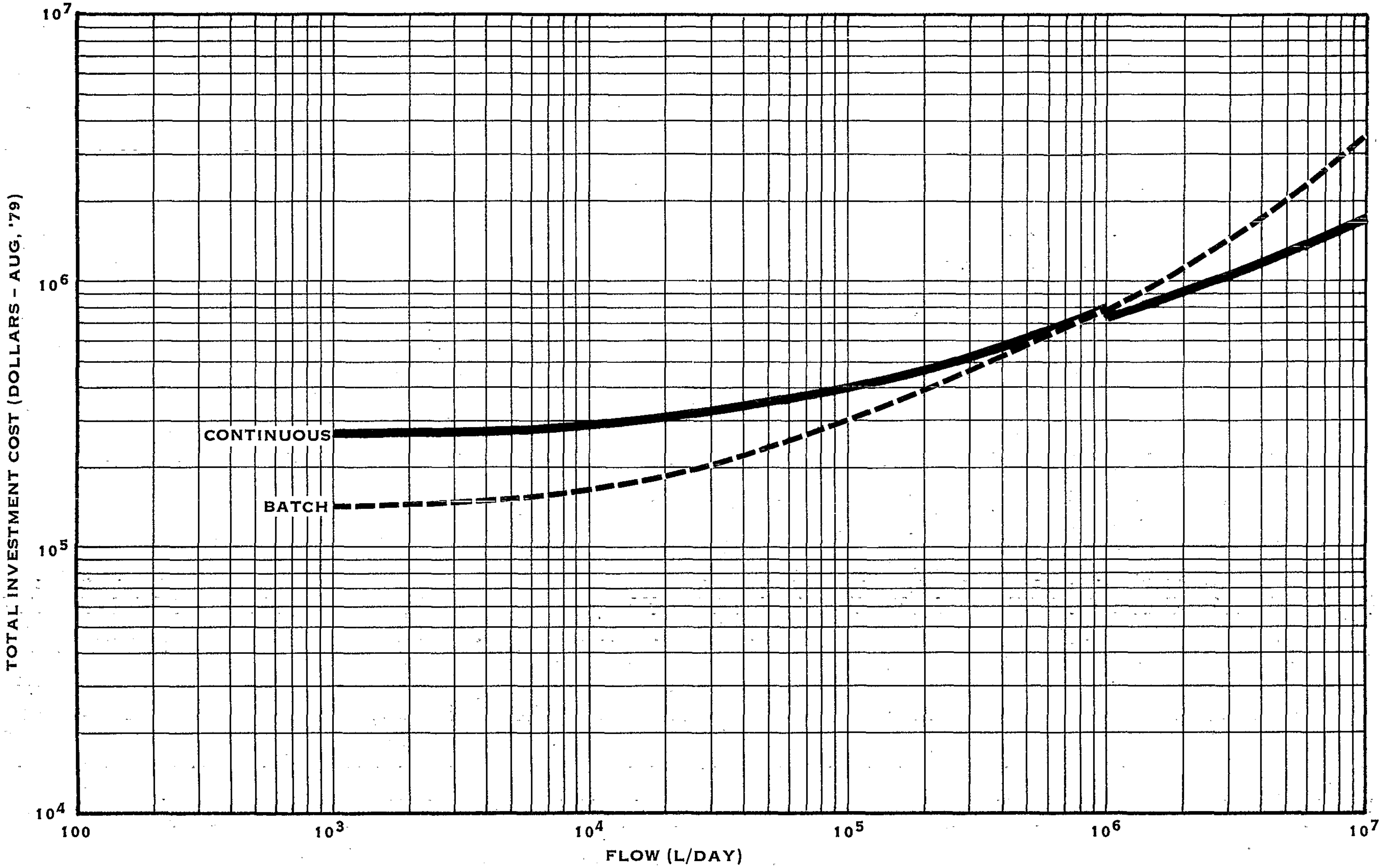


FIGURE 8-65
TOTAL INVESTMENT COST VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 4

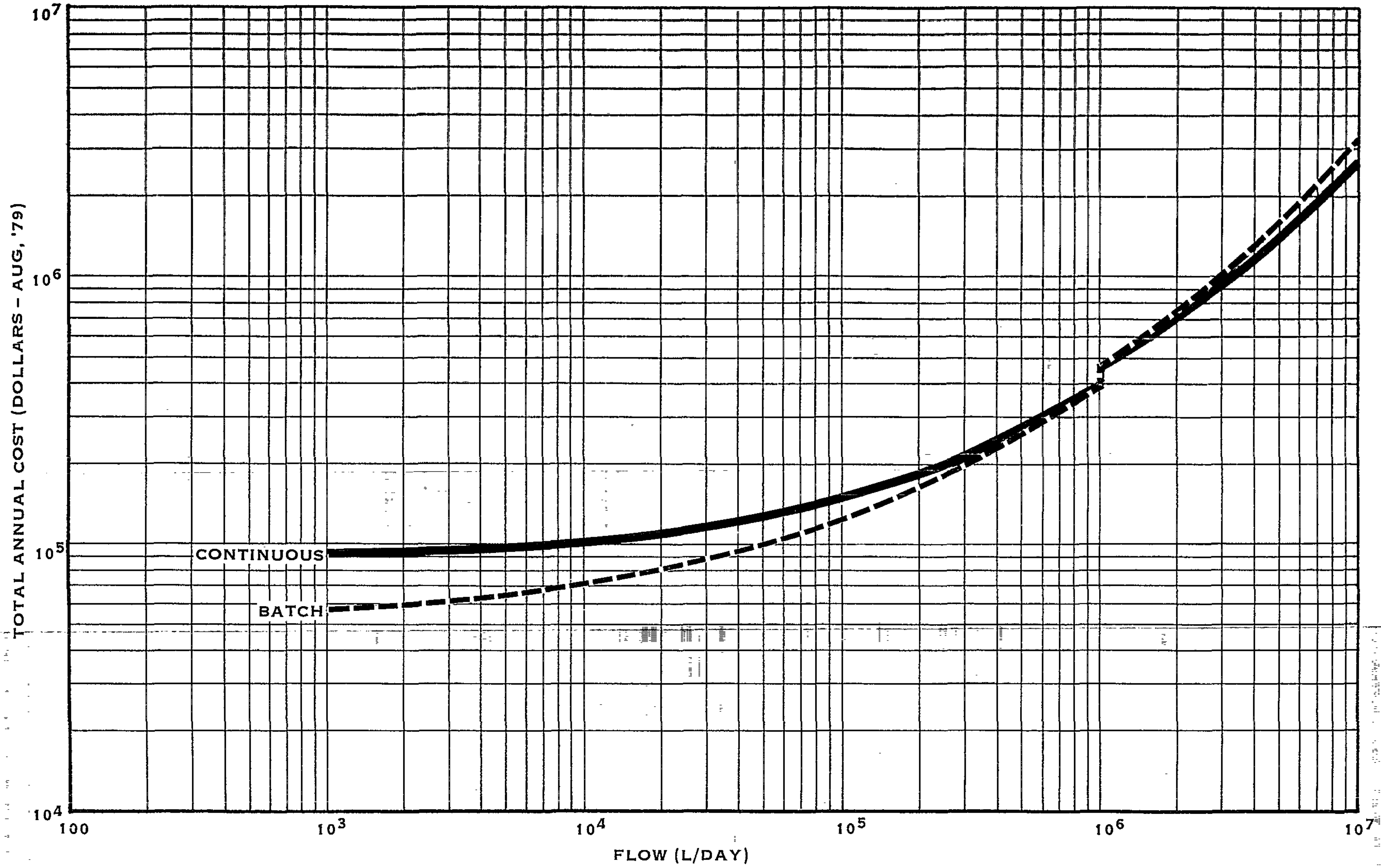


FIGURE 8-66
TOTAL ANNUAL COSTS VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 4

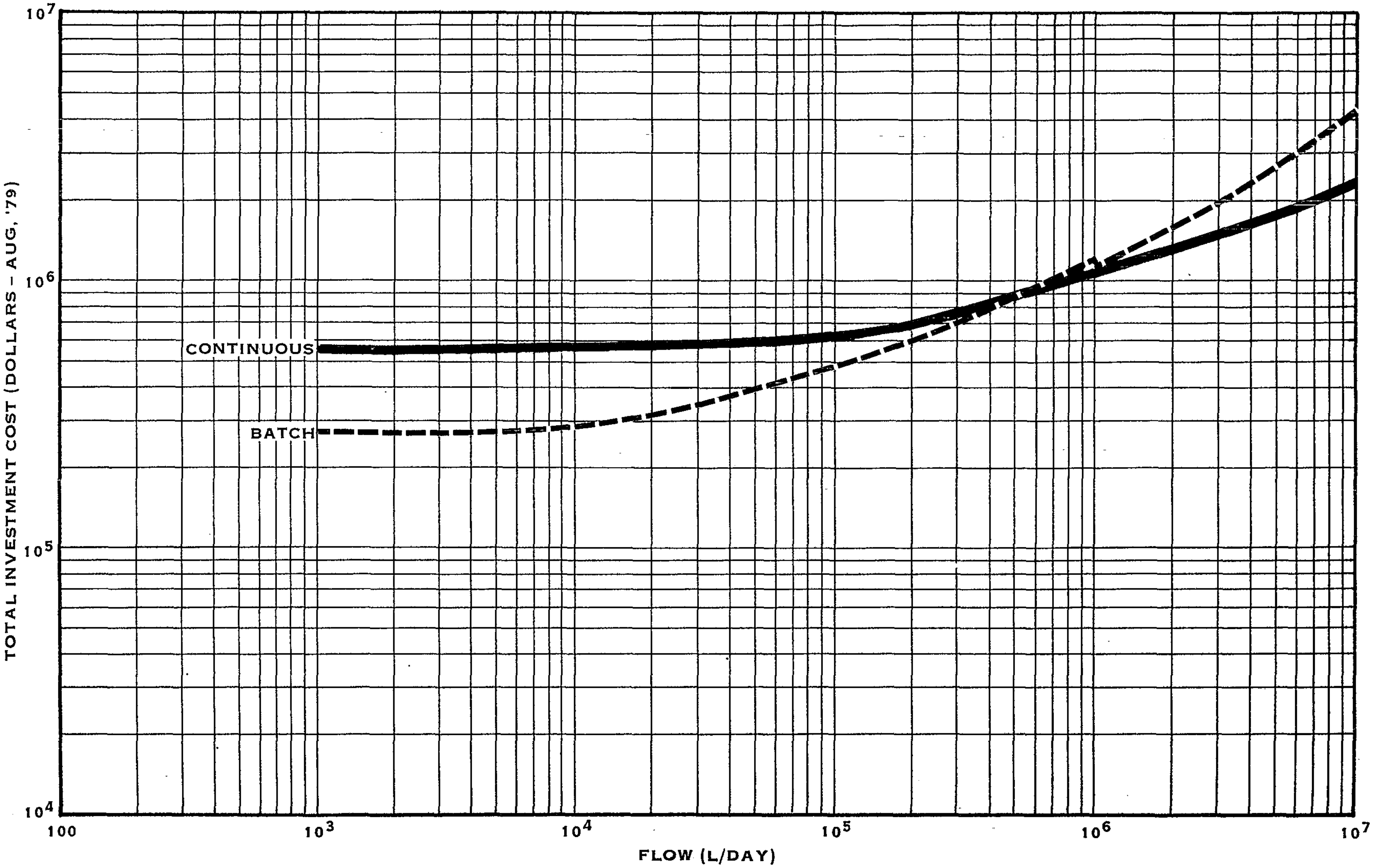


FIGURE 8-67
TOTAL INVESTMENT COSTS VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 5

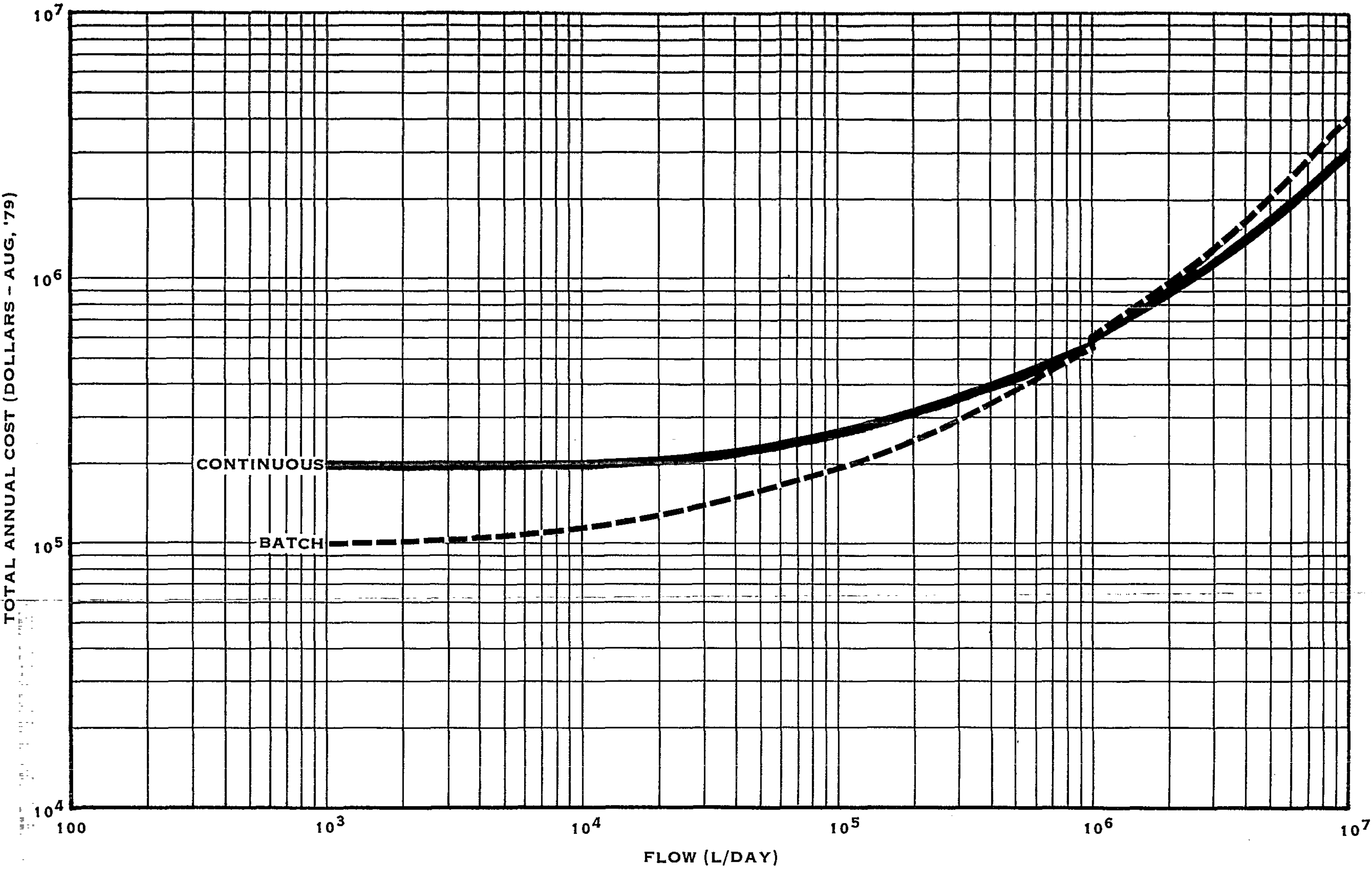


FIGURE 8-68
TOTAL ANNUAL COST VS. FLOW RATE FOR OPTION 3 TREATMENT SYSTEM, CASE 5

total system costs and do not assume any treatment in place, it is probable that most plants will require smaller expenditures to reach the specified levels of control from their present status.

The actual costs of installing and operating a system at a particular plant may be substantially lower than the tabulated values. Reductions in investment and operating costs are possible in several areas. Design and installation costs may be reduced by using plant workers. Equipment costs may be reduced by using or modifying existing equipment instead of purchasing all new equipment. Application of an excess capacity factor, which increases the size of most equipment foundation costs could be reduced if an existing concrete pad or floor can be utilized. Equipment size requirements may be reduced as a result of treatment conditions (for example, shorter retention time) for particular waste streams. Substantial reduction in both investment and operating cost may be achieved if a plant reduces its water use rate below that assumed in costing.

## IN-PROCESS FLOW REDUCTIONS

The use of in-process techniques to achieve reductions in waste flows can result in significantly reduced operating and maintenance costs. Although an additional initial investment will be required for a countercurrent rinse or other flow reducing **equipment, in most cases it will be less than the saving due to downstream treatment components may be sized for smaller flows. This reduces the initial investment for downstream treatment components**

## ECONOMIC IMPACT ANALYSIS OF SYSTEM COST ESTIMATES

The individual waste treatment component and system cost estimates presented in this section of the development document can be applied to each manufacturing facility in the Metal Finishing Category. The cost estimates can be used to estimate the value of existing in-place waste treatment components and to estimate the economic impact of a proposed level of waste treatment upon an individual manufacturing facility.

In order to establish the economic impact of the various proposed waste treatment systems upon actual Metal Finishing firms, treatment system cost estimates were developed for one hundred (100) captive indirect dischargers, one hundred three (103) captive direct dischargers, and forty (40) job shop direct dischargers. These firms were determined to be representative of the Metal Finishing Category and these cost estimates were used to assess the economic impact of the proposed regulations upon the entire

Metal Finishing Industry. Cost estimates for job shop indirect dischargers were developed only for the control of total toxic organics (TTO) because these firms are regulated under the Pretreatment Regulations for the Electroplating Point Source Category, 40 CFR Part 413 (Ref. EPA 440/1-79/003, August 1979).

System cost estimates for the previously described groups of plants were provided to the Office of Analysis and Evaluation of the EPA for use in Economic Impact Analysis (EIA) of the Metal Finishing Category. Option 3 for the new source cadmium limitations was recosted to include three sources of cadmium: cadmium plating rinses, acid stripping of cadmium plated parts, and chromating of cadmium plated parts. The revised costs were used in the economic impact analysis and the results are presented in the Metal Finishing record.

## ENERGY AND NON-WATER QUALITY ASPECTS

Energy and non-water quality aspects of the wastewater treatment technologies described in Section VII are summarized in Tables 8-12 and 8-13. Energy requirements are listed, the impact on environmental air and noise pollution is noted, and solid waste generation characteristics are summarized. The treatment processes are divided into two groups, wastewater treatment processes on Table 8-12 and sludge and solids handling processes on Table 8-13.

### Energy Aspects

Energy aspects of the wastewater treatment processes are important because of the impact of energy use on our natural resources and on the economy. Electrical power and fuel requirements (coal, oil, or gas) are listed in units of kilowatt hours per ton of dry solids for sludge and solids handling. Specific energy uses are noted in the "Remarks" column.

Evaporation as applied in Option 3 is an energy intensive technology for waste treatment. However, its energy consumption is significantly reduced by the use of double effect evaporation and by the use of countercurrent rinsing to limit the volume of wastewater flowing to the evaporator. With the effective implementation of these techniques the total energy requirements for evaporation in this category will be small and will probably not exceed the energy consumed in treating and pumping the volume of water which would be used in rinsing without these techniques.

### Non-Water Quality Aspects

It is important to consider the impact of each treatment process on air, noise, and radiation pollution of the enviroment to preclude the development of a more adverse environmental impact.

TABLE 8-12

## NON-WATER QUALITY ASPECTS OF WASTEWATER TREATMENT

| PROCESS | ENERGY REQUIREMENTS | | | NON-WATER QUALITY IMPACT | | | |
|---|---|---|---|---|---|---|---|
| | Power kwh / 1000 liters | Fuel kwh / 1000 liters | Energy Use | Air Pollution Impact | Noise Pollution Impact | Solid Waste | Solid Waste Concentration % Dry Solids |
| Chemical Reduction | 1.0 | --- | Mixing | No | No | No | --- |
| Skimming | 0.01-.3 | --- | Skimmer Drive | No | No | Yes[3] | 5-50 (oil) |
| Clarification | 0.1-3.2 | --- | Sludge Collector Drive | No | No | Yes[3] | 1-10 |
| Chemical Precipitation | 1.02 | --- | Flocculation Paddles | No | No | Yes[3] | 3-10 |
| Sedimentation | 0.1-3.2 | --- | Sludge collector Drive | No | No | Yes[3] | 1-3 |
| Reverse Osmosis | 3.0 | --- | High Pressure Pump | No | Yes[2] | Yes[4]<br>Yes[3] | 1-40 |
| Ultrafiltration | 1.25-3.0 | | High Pressure Pump | No | Yes[2] | Yes[4]<br>Yes[3] | 1-40 |
| Electrochemical Chromium Reduction | 0.2-0.8 | --- | Reactifier, Pump | No | No | Yes[3] | 1-3 |
| Chemical Oxidation by Chloride | 4.4-9.6 | --- | Mixing | No | No | No | --- |
| Chemical Emulsion Breaking | .1-3.2 | --- | Mixer, Skimmer, Sludge Pump | No | Yes[2] | Yes[3] | 5-50 (oil)<br>1-3 (TSS) |
| Deep Bed Filtration | .02-1.0 | --- | Head, Backwash Pumps | No | No | Yes[3] | Variable |
| Carbon Adsorption Throwaway | .08 | --- | Head, Backwash Pumps | No | No | Yes[3] | Variable |
| Evaporation | --- | 2,500,000 | Evaporation | Yes[1] | No | Yes[3] | 50-100 |
| Countercurrent Rinse | --- | --- | Negligible | No | No | No | --- |

## TABLE 8-13

## NON-WATER QUALITY ASPECTS OF SLUDGE AND SOLIDS HANDLING

| PROCESS | ENERGY REQUIREMENTS | | | NON-WATER QUALITY IMPACT | | | | |
|---|---|---|---|---|---|---|---|---|
| | Power kwh / ton dry solids | Fuel kwh / ton dry solids | Energy Use | Air Pollution Impact | Noise Pollution Impact | Solid Waste | Solid Waste Concentration % Dry Solids | Solid Waste Disposal Technique |
| Sludge Thickening | 29-930 | --- | Skimmer, Sludge Rake Drive | No | No | Yes[3] | 4-27 | Dewater & Landfill or Incinerate |
| Pressure Filtration | 21 | --- | High Pressure Pumps | No | No | Yes[5] | 25-50 | Landfill or Incinerate |
| Vacuum Filter | 16.7-66.8 | --- | Vacuum Pump, Rotation | No | Yes[2] | Yes[5] | 12-40 | Landfill or Incinerate |
| Centrifugation | 0.2-98.5 | --- | Rotation | No | Yes[2] | Yes[5] | 15-50 | Landfill or Incinerate |
| Landfill | --- | 20-980 | Haul, Landfil 1-10 Mile Trip | No | No | Yes[5] | N/A | N/A |
| Lagooning | --- | 36 | Removal Equipment | No | No | Yes[5] | 3-5 | Dewater & Landfill |
| Sand Bed Drying | --- | 35 | Removal Equipment | No | No | Yes[5] | 15-40 | Landfill |

1) Depends on volatiles present
2) Not objectionable
3) Wastewater pollutants have been concentrated into a solid for disposal or further treatment
4) Wastewater pollutants have been concentrated into a liquid for disposal or further treatment
5) Wastewater pollutants which have been concentrated into a solid have been further concentrated by dewatering for disposal

In general, none of the liquid handling processes causes air pollution. Alkaline chlorination for cyanide destruction and chromium reduction using sulfur dioxide also have potential atmospheric emissions. With proper design and operation, however, air pollution impacts are eliminated. Incineration of sludge or solids can cause significant air pollution which must be controlled by suitable bag houses, scrubbers, or stack gas precipitators as well as proper incinerator operation and maintenance. Care must be taken to insure that solids collected in air pollution control do not become a water pollution threat. None of the wastewater treatment processes causes objectionable noise and none of the treatment processes has any potential for radioactive radiation hazards.

The solids waste impact of each sludge dewatering process is indicated in two columns on Table 8-13. The first column shows whether effluent solids are to be expected and, if so, the solids content in qualitative terms. The second column lists typical values of percent solids of sludge or residue. The third column indicates the usual method of solids disposal associated with the process.

The processes for treating the wastewaters from this category produce considerable volumes of sludges. In order to ensure long-term protection of the environment from harmful sludge constituents, all sludges must be disposed of in accordance with the Resource Conservation and Recovery Act (RCRA).

# SECTION IX
# BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

## INTRODUCTION

This section describes the best practicable control technology currently available (BPT) for the treatment of process wastewaters generated within the Metal Finishing Category. BPT reflects existing treatment and control practices at metal finishing plants of various sizes, ages, and manufacturing processes.

The factors considered in defining BPT include the total cost of application of technology in relation to the effluent reduction benefits from such application, the age of equipment and facilities involved, the processes employed, non-water quality environmental impact (including energy requirements), and other factors considered appropriate by the Administrator. In general, the BPT technology level represents the best existing practices at plants of various ages, sizes, processes, or other common characteristics. Where existing practice is uniformly inadequate, BPT may be transferred from a different subcategory or category. Limitations based on transfer of technology must be supported by a conclusion that the technology is, indeed, transferrable and a reasonable prediction that it will be capable of achieving the prescribed effluent limits (see Tanner's Council of America v. Train Supra). BPT focuses on end-of-pipe treatment rather than process changes or internal controls, except where such are common industry practice.

## IDENTIFICATION OF BPT

Plants in the Metal Finishing Category generate process wastewater streams of several distinct types. As described in Sections V and VI, waste streams produced in this category may contain common metals (e.g., copper, nickel, zinc, etc.), precious metals (e.g., gold, palladium, silver), cyanide, hexavalent chromium, oil and grease, and a variety of toxic organic compounds (designated total toxic organics, TTO). Individual process wastewater streams characteristically contain only some of these pollutants, and metal finishing facilities generally produce several distinct streams differing in their chemical composition and treatment requirements. These considerations are reflected in prevailing wastewater treatment practices within the category, and in the identified BPT.

The BPT wastewater treatment system (Option 1 System in Section VII) for the Metal Finishing Category is illustrated in Figure 9-1. This treatment system provides for the removal of metals

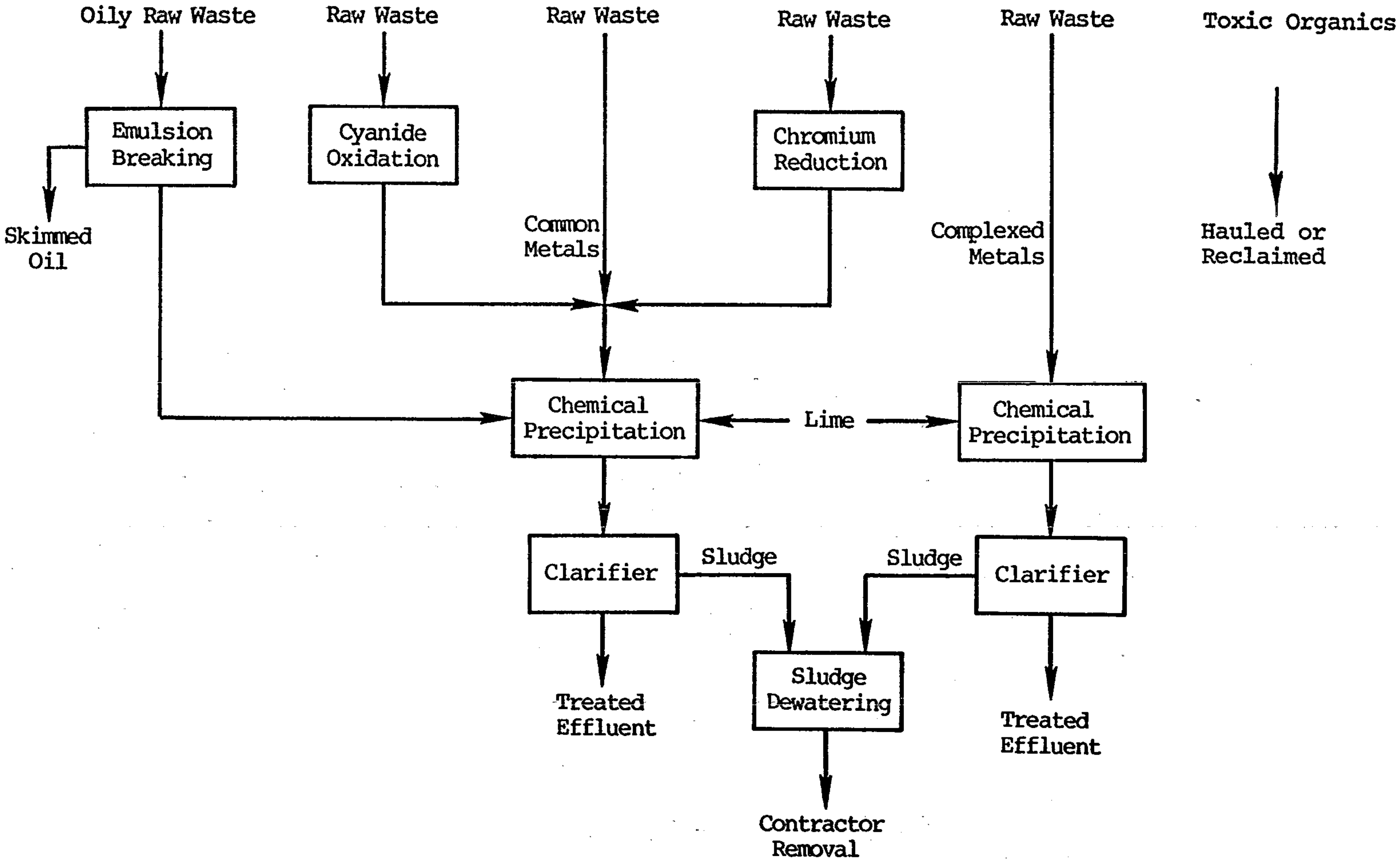


FIGURE 9-1

BPT SYSTEM

from all process wastewater streams by chemical precipitation and clarification, and specific treatment of some waste streams for the removal of other process wastewater pollutants. Extensive description of these treatment components is provided in Section VII. Individual plants in the Metal Finishing Category that do not produce all of the distinct wastewater types shown need to install only the system components necessary for the treatment of those wastewater types existing at the plant to achieve compliance with BPT.

Where some process waste streams contain complexed metals, BPT includes the segregation of these wastes and separate treatment for the precipitation of metals and removal of suspended solids. Precipitation of metals from these wastes is characteristically accomplished at a high pH (11.6 - 12.5) to induce dissociation of the metal complexes. Lime or other calcium compounds are used to adjust the pH to the high levels required to induce precipitation of the free metals as hydroxides. Sedimentation is then used in order to allow the resulting suspended solids to settle out of solution.

Waste streams containing cyanide or hexavalent chromium are also segregated for treatment in the BPT system. Cyanide bearing wastes are treated chemically to oxidize the cyanide, and streams containing hexavalent chromium are subjected to chemical chromium reduction. After these separate treatment operations are completed, these waste streams are combined with other process wastewater for the chemical precipitaion of metals and clarification.

Concentrated oily waste streams are segregated and treated for the removal of oil and grease prior to treatment for metals removal. Oils and greases are removed by gravity separation and skimming of free oils followed by chemical emulsion breaking and subsequent skimming for the removal of emulsified oils. Some oily waste streams produced in this category may contain very low concentrations of emulsified oils making chemical emulsion breaking unnecessary, while others may contain low free oil concentrations obviating the need for skimming prior to emulsion breaking. Some oily waste streams containing very low concentrations of dissolved metals may be of a quality suitable for discharge after oil removal treatment. In these cases, further treatment for metals removal with other process waste streams would not be necessary to achieve compliance with BPT.

Following separate stream treatment the effluents are combined and the metals are removed by precipitation and subsequent clarification. Precipitation is accomplished by the addition of lime, caustic, sodium carbonate, or acid to achieve a favorable pH. Most metals precipitate as hydroxides although some, such as lead and silver, preferentially form other compounds (e.g. carbonates or chlorides). The optimum pH for precipitation is generally in the range of 8.8-9.3, although it will vary somewhat depending on the specific waste composition. The use of coagulents or flocculants to enhance the effectiveness of clarification is also specifically included in BPT.

In addition to the control of toxic metals, cyanide, TSS, and pH, BPT regulates toxic organics as Total Toxic Organics. Compliance with the TTO limit can be achieved by good management practices (i.e., not dumping waste solvents into the wastewater). No additional end-of-pipe technology beyond that required for metals removal is necessary.

Alternative technologies are available which are equivalent to BPT for the removal of the pollutants encountered in the Metal Finishing Category. Some of these technologies as well as those discussed above as BPT have been described in detail in Section VII of this document. The specific technologies implemented at each individual plant to achieve compliance with BPT limitations will depend on economic and operational considerations specific to the facility.

## RATIONALE FOR THE SELECTION OF BPT

The BPT system identified above has been selected on the basis of: proven effectiveness in treating pollutants present in metal finishing process wastewaters; present practice within the category; and non-water quality considerations. All of the elements of the selected BPT are presently practiced at many plants within the Metal Finishing Category and have been proven to be reliable and effective in treating industrial wastewater. Energy requirements for these technologies are moderate. However, sludges and waste oils which prove to be hazardous must be handled and disposed of in accordance with the Resource Conservation and Recovery Act regulations.

Chemical precipitation is a proven technology which is widely applied at Metal Finishing Category plants. As is shown in Section VII, over 100 facilities employing hydroxide precipitation and sedimentation for the removal of metals from process wastewaters are identified. With appropriate control of pH and settling conditions, this technology can be effectively applied to process wastewaters containing any of the metals commonly encountered in this category. Because this technology has been applied at many facilities over extended periods of time, its performance capabilities were established on the basis of a large body of data from industrial effluents within the Metal Finishing Category.

Chemical chromium reduction is also a proven and widely applied technology. Over 300 plants in the Metal Finishing Category which employ this technology were identified. It may be implemented using a variety of equipment, reagents, and operating procedures, and is readily adaptable to the wide range of flow rates and hexavalent chromium concentrations encountered in the Metal Finishing Category. Similar to chemical precipitation, its pollutant reduction performance capabilities were established from effluent data from a number of plants within the category.

Chemical oxidation of cyanide using chlorine is also a common wastewater treatment practice within the Metal Finishing Category. Over 200 plants employing this technology were identified within the surveyed data base. As a result, considerable data establishing the reliability and performance of this technology were available from industrial sites within the Metal Finishing Category.

Treatment of process wastewater for the removal of oils and greases is common practice in the Metal Finishing Category. A variety of oil removal techniques are employed as discussed in Section VII. These correspond to the wide range of waste stream compositions encountered. The identified BPT provides for the removal of both free and emulsified oils commonly encountered in metal finishing wastewaters. Twenty-nine plants in the data base were identified which employ emulsion breaking technology. The number of plants employing skimming for the removal of oils and greases is much larger. Performance capabilities for these technologies were firmly established on the basis of extensive long-term practice in treating industrial process wastewater. The specific technologies identified as BPT are relatively simple and reliable; however, comparable effluent performance can be achieved by numerous technical alternatives.

The technical merits, present practice, and demonstrated performance of the BPT technologies are discussed in detail in Section VII. The costs and non-water quality environmental aspects of these technologies are presented in Section VIII.

## BPT LIMITATIONS

The effluent limitations attainable by application of BPT are presented in Table 9-1.

TABLE 9-1
BPT EFFLUENT LIMITATIONS
Concentration (mg/ℓ)

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Oil and Grease | 52 | 26 |
| TSS | 60 | 31 |
| pH | Within the range of 6.0 to 9.0 | |
| Alternative to total cyanide | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

These limitations are based on demonstrated performance at metal finishing plants employing the identified BPT technologies. As described in Section VII, both on-site sampling and observations, and long-term effluent monitoring data are reflected in the limitations. They therefore incorporate both plant to plant variations in raw wastes and treatment practices and the day-to-day variability of treatment system performance. The effluent concentrations shown in Table 9-1 represent levels attainable by a well run BPT system 99% of the time.

The concentrations shown are all applicable to the treated effluent prior to any dilution with sanitary wastewater, noncontact cooling water, or other non-process water. The total cyanide concentration limitation applies to the discharge from cyanide oxidation prior to mixture with any other process wastes.

As an alternative the amenable cyanide limit may apply in place of the total cyanide limit for industrial facilities with cyanide treatment and upon agreement between a source subject to those limits and the pollution control authority.

The derivation of these performance limitations from effluent data for Metal Finishing Category plants is described in detail in Section VII. After technical analysis of the effluent data and supporting information to identify plants with properly operating treatment systems, the data were screened to ensure that only effluent data corresponding to raw waste streams which contained significant levels of each pollutant were used to establish limitations for that parameter. These data were then analyzed statistically as described under Statistical Analysis (reference Section VII) to derive 99th percentile limits on both single day and monthly maximum average effluent concentrations.

## PRESENT COMPLIANCE WITH BPT

Table 9-2 shows the compliance percentages for the two data bases evaluated in developing the BPT effluent limitations: (1) the EPA sampled data base; and (2) the long term self-monitoring data base from data submitted by plants in the industry. Compliance for the self-monitoring data was determined for both daily maximum values and 10-day average values.

Tables 9-3 and 9-10 present a detailed summary of the self-monitoring data relative to compliance with the daily maximum and the monthly maximum average limitations for the regulated parameters. Table 9-3 shows the number of data points in compliance with the BPT daily maximum limitations and the total number of data points for each parameter at each plant. Table 9-4 presents the corresponding compliance percentage values. Tables 9-5 and 9-6 present the same information for total cyanide, amenable cyanide, and silver. Compliance information is presented in the same format for the maximum monthly averages in Tables 9-7 through 9-10 using 10 days as a basis.

## BENEFITS OF BPT IMPLEMENTATION

The estimated environmental benefits of the application of BPT to all plants in the Metal Finishing Category are summarized in Table 9-11. This table presents estimates of the total mass of the regulated pollutant parameters in raw wastewaters from all metal finishing plants and the remaining mass of these pollutants discharged after application of BPT at all facilities with direct discharges. The differences between these values are presented as quantitative estimates of the environmental benefits of implementing BPT. These benefits may be compared to the costs of BPT (Option 1) as presented in Section VIII.

## TABLE 9-2
## PERCENTAGE OF THE MFC DATA BASE BELOW THE BPT LIMITATIONS

| Pollutant | EPA Sampled Data* Daily Maximum | Self-Monitoring Data Daily Maximum | Self-Monitoring Data 10-Day Average |
|---|---|---|---|
| Cadmium | 100.0 | 98.8 | 97.8 |
| Chromium | 100.0 | 99.7 | 99.7 |
| Copper | 95.7 | 98.5 | 96.7 |
| Lead | 100.0 | 95.9 | 92.7 |
| Nickel | 95.6 | 99.9 | 100.0 |
| Silver | 100.0 | 70.6 | 100.0 |
| Zinc | 94.1 | 99.2 | 95.8 |
| Cyanide, total | 97.8 | 79.3 | 63.4 |
| TTO | 100.0 | | |
| Oil & grease | 100.0 | 100.0 | 100.0 |
| TSS | 100.0 | 99.8 | 100.0 |

* EPA sampled data used to develop limits (i.e., Tables 7-4 to 7-10, 7-55, 7-74).

# TABLE 9-3
## BPT SELF-MONITORING DATA COMPLIANCE SUMMARY
## DATA POINTS $\leq$ BPT DAILY MAXIMUM LIMITATIONS/TOTAL DATA POINTS

| PLANT | TSS | CADMIUM | CHROMIUM | COPPER | LEAD | NICKEL | ZINC | OIL & GREASE |
|---|---|---|---|---|---|---|---|---|
| 1067 | 148/149 | 228/230 | 230/230 | 230/230 | -- | 230/230 | 230/230 | -- |
| 3049 | 49/49 | -- | -- | -- | -- | -- | -- | 49/49 |
| 5020 | -- | -- | 228/228 | 232/232 | 217/229 | 231/231 | -- | -- |
| 6002 | -- | 6/6 | -- | -- | -- | -- | -- | -- |
| 6035 | 12/12 | 9/9 | 12/12 | -- | -- | -- | -- | -- |
| 6051 | 13/13 | 13/13 | 13/13 | 13/13 | -- | 13/13 | 13/13 | 13/13 |
| 6053 | 12/12 | -- | -- | -- | -- | -- | -- | -- |
| 6087 | 12/12 | -- | -- | 12/12 | -- | -- | -- | -- |
| 6103 | 13/13 | -- | -- | -- | -- | -- | -- | -- |
| 6107 | 10/10 | -- | 10/10 | 8/10 | -- | -- | 9/10 | -- |
| 11008 | 140/140 | 183/185 | 185/185 | 185/185 | -- | 185/185 | 184/184 | -- |
| 11477 | 69/69 | -- | -- | -- | -- | -- | -- | 66/66 |
| 12002 | -- | -- | -- | 58/58 | -- | -- | 51/51 | 55/55 |
| 17030 | -- | -- | 342/344 | -- | -- | -- | -- | -- |
| 19063 | -- | -- | 238/238 | 247/248 | 238/238 | 10/10 | -- | -- |
| 20080 | 269/269 | -- | 269/269 | -- | -- | -- | 269/269 | 269/269 |
| 20082 | -- | -- | 250/253 | 240/253 | -- | 253/253 | 249/250 | -- |
| 20116 | 243/243 | -- | 243/243 | 243/243 | -- | 243/243 | -- | -- |
| 22735 | 27/27 | -- | 35/35 | -- | -- | -- | -- | 45/45 |
| 23076 | -- | -- | 237/242 | 231/241 | -- | 239/241 | -- | -- |
| 30050 | 292/292 | -- | 289/289 | 292/292 | -- | 75/75 | -- | 287/287 |
| 30079 | -- | -- | -- | -- | -- | -- | -- | 12/12 |
| 30090 | 51/51 | -- | 49/49 | 260/260 | -- | -- | -- | 45/45 |
| 30165 | -- | -- | -- | 65/66 | 54/65 | -- | 58/66 | -- |
| 33050 | -- | -- | -- | 112/112 | -- | -- | 115/115 | -- |
| 33092 | -- | -- | -- | -- | -- | 33/33 | -- | -- |
| 34037 | -- | -- | -- | 172/184 | -- | -- | -- | -- |
| 36040 | -- | -- | 225/225 | -- | -- | 228/228 | -- | -- |
| 44045 | 50/50 | -- | -- | 49/49 | 48/49 | 49/49 | -- | -- |
| 44150 | -- | -- | -- | 124/127 | -- | -- | 42/42 | -- |
| 45741 | -- | -- | 358/358 | -- | -- | -- | -- | 49/49 |
| 47025 | 335/337 | 49/51 | 256/256 | -- | -- | -- | -- | -- |
| OVERALL | 1745/1748 | 488/494 | 3469/3479 | 2773/2815 | 557/581 | 1789/1791 | 1220/1230 | 890/890 |

-- = No data or material not used in metal finishing processes.

# TABLE 9-4
## BPT SELF-MONITORING DATA COMPLIANCE SUMMARY
## PERCENT OF DATA POINTS ≤ BPT DAILY MAXIMUM LIMITATIONS

| PLANT | TSS | CADMIUM | CHROMIUM | COPPER | LEAD | NICKEL | ZINC | OIL & GREASE |
|---|---|---|---|---|---|---|---|---|
| 1067 | 99.3 | 99.1 | 100.0 | 100.0 | -- | 100.0 | 100.0 | -- |
| 3049 | 100.0 | -- | -- | -- | -- | -- | -- | 100.0 |
| 5020 | -- | - | 100.0 | 100.0 | 94.8 | 100.0 | -- | -- |
| 6002 | -- | 100.0 | -- | - | -- | -- | -- | -- |
| 6035 | 100.0 | 100.0 | 100.0 | -- | -- | -- | -- | -- |
| 6051 | 100.0 | 100.0 | 100.0 | 100.0 | -- | 100.0 | 100.0 | 100.0 |
| 6053 | 100.0 | -- | -- | -- | -- | -- | -- | -- |
| 6087 | 100.0 | -- | -- | 100.0 | -- | -- | -- | -- |
| 6103 | 100.0 | -- | -- | -- | -- | -- | -- | -- |
| 6107 | 100.0 | -- | 100.0 | 80.0 | -- | -- | 90.0 | -- |
| 11008 | 100.0 | 98.9 | 100.0 | 100.0 | -- | 100.0 | 100.0 | -- |
| 11477 | 100.0 | -- | -- | -- | -- | -- | -- | 100.0 |
| 12002 | -- | -- | -- | 100.0 | -- | -- | 100.0 | 100.0 |
| 17030 | -- | -- | 99.4 | -- | -- | -- | -- | -- |
| 19063 | -- | -- | 100.0 | 99.6 | 100.0 | 100.0 | -- | -- |
| 20080 | 100.0 | -- | 100.0 | -- | -- | -- | 100.0 | 100.0 |
| 20082 | -- | -- | 98.8 | 94.9 | -- | 100.0 | 99.6 | -- |
| 20116 | 100.0 | -- | 100.0 | 100.0 | -- | 100.0 | -- | -- |
| 22735 | 100.0 | -- | 100.0 | -- | -- | -- | -- | 100.0 |
| 23076 | -- | -- | 97.9 | 95.9 | -- | 99.2 | -- | -- |
| 30050 | 100.0 | -- | 100.0 | 100.0 | -- | 100.0 | -- | 100.0 |
| 30079 | -- | -- | -- | -- | -- | -- | -- | 100.0 |
| 30090 | 100.0 | -- | 100.0 | 100.0 | -- | -- | -- | 100.0 |
| 30165 | -- | -- | -- | 98.5 | 83.1 | -- | 87.9 | -- |
| 33050 | -- | -- | -- | 100.0 | -- | -- | 100.0 | -- |
| 33092 | -- | -- | -- | -- | -- | 100.0 | -- | -- |
| 34037 | -- | -- | -- | 93.5 | -- | -- | -- | -- |
| 36040 | -- | -- | 100.0 | -- | -- | 100.0 | -- | -- |
| 44045 | 100.0 | -- | -- | 100.0 | 97.9 | 100.0 | -- | -- |
| 44150 | -- | -- | -- | 97.6 | -- | -- | 100.0 | -- |
| 45741 | -- | -- | 100.0 | -- | -- | -- | -- | 100.0 |
| 47025 | 99.4 | 96.1 | 100.0 | -- | -- | -- | -- | -- |
| OVERALL | 99.8 | 98.8 | 99.7 | 98.5 | 95.9 | 99.9 | 99.2 | 100.0 |

-- = No data or material not used in metal finishing processes.

## TABLE 9-5
## SINGLE OPTION - SELF-MONITORING DATA COMPLIANCE SUMMARY
## DATA POINTS ≤ BPT LIMITATIONS/TOTAL DATA POINTS

| Plant | Cyanide, Total † | Cyanide, Amenable † | Silver |
|---|---|---|---|
| 1067 | * | -- | -- |
| 3043 | 78/89 | -- | -- |
| 6002 | -- | -- | -- |
| 6051 | * | -- | -- |
| 6087 | -- | -- | 12/12 |
| 6107 | * | -- | -- |
| 11008 | 170/179 | -- | -- |
| 11125 | 0/54 | -- | 0/5 |
| 15193 | 4/12 | -- | -- |
| 20080 | 268/268 | -- | -- |
| 20082 | 200/246 | -- | -- |
| 31021 | 86/140 | 31/40 | -- |
| 36082 | 119/121 | -- | -- |
| 38223 | -- | 234/235 | -- |
| 44045 | 40/50 | -- | -- |
| 47025 | 63/139 | 216/243 | -- |
| Overall | 1028/1298 | 481/518 | 12/17 |

† Adjusted for dilution.
* Dilution factor not known.
-- No data or material not used in metal finishing processes.

## TABLE 9-6
## SINGLE OPTION - SELF-MONITORING DATA COMPLIANCE SUMMARY
## PERCENT OF DATA POINTS ≤ BPT LIMITATIONS

| Plant | Cyanide, Total † | Cyanide, Amenable † | Silver |
|---|---|---|---|
| 1067 | * | -- | -- |
| 3043 | 87.6 | -- | -- |
| 6002 | -- | -- | -- |
| 6051 | * | -- | -- |
| 6087 | -- | -- | 100.0 |
| 6107 | * | -- | -- |
| 11008 | 94.9 | -- | -- |
| 11125 | 0.0 | -- | 0.0 |
| 15193 | 33.3 | -- | -- |
| 20080 | 100.0 | -- | -- |
| 20082 | 81.3 | -- | -- |
| 31021 | 61.4 | 77.5 | -- |
| 36082 | 98.3 | -- | -- |
| 38223 | -- | 99.6 | -- |
| 44045 | 80.0 | -- | -- |
| 47025 | 45.3 | 88.9 | -- |
| Overall | 79.2 | 92.8 | 70.5 |

† Adjusted for dilution.
* Dilution factor not known.
-- No data or material not used in metal finishing processes.

# TABLE 9-7
# BPT SELF-MONITORING DATA COMPLIANCE
## 10-DAY AVERAGES ≤ BPT MONTHLY MAXIMUM AVERAGE LIMITATIONS/TOTAL NUMBER OF 10-DAY AVERAGES

| PLANT | TSS | CADMIUM | CHROMIUM | COPPER | LEAD | NICKEL | ZINC | OIL & GREASE |
|---|---|---|---|---|---|---|---|---|
| 1067 | 14/14 | 23/23 | 23/23 | 23/23 | -- | 23/23 | 23/23 | -- |
| 3049 | 4/4 | -- | -- | -- | -- | -- | -- | 4/4 |
| 5020 | -- | -- | 22/22 | 23/23 | 21/22 | 23/23 | -- | -- |
| 6002 | -- | -- | -- | -- | -- | -- | -- | -- |
| 6035 | 1/1 | -- | 1/1 | -- | -- | -- | -- | -- |
| 6051 | 1/1 | 1/1 | 1/1 | 1/1 | -- | 1/1 | 1/1 | 1/1 |
| 6053 | 1/1 | -- | -- | -- | -- | -- | -- | -- |
| 6087 | 1/1 | -- | -- | 1/1 | -- | -- | -- | -- |
| 6103 | 1/1 | -- | -- | -- | -- | -- | -- | -- |
| 6107 | 1/1 | -- | 1/1 | 0/1 | -- | -- | 0/1 | -- |
| 11008 | 14/14 | 18/18 | 18/18 | 18/18 | -- | 18/18 | 18/18 | -- |
| 11477 | 6/6 | -- | -- | -- | -- | -- | -- | 6/6 |
| 12002 | -- | -- | -- | 5/5 | -- | -- | 5/5 | 5/5 |
| 17030 | -- | -- | 34/34 | -- | -- | -- | -- | -- |
| 19063 | -- | -- | 23/23 | 24/24 | 23/23 | 1/1 | -- | -- |
| 20080 | 26/26 | -- | 26/26 | -- | -- | -- | 26/26 | 26/26 |
| 20082 | -- | -- | 24/25 | 22/25 | -- | 25/25 | 25/25 | -- |
| 20116 | 24/24 | -- | 24/24 | 24/24 | -- | 24/24 | -- | -- |
| 22735 | 2/2 | -- | 3/3 | -- | -- | -- | -- | 4/4 |
| 23076 | -- | -- | 24/24 | 23/24 | -- | 24/24 | -- | -- |
| 30050 | 29/29 | - | 28/28 | 29/29 | -- | 7/7 | -- | 28/28 |
| 30079 | -- | -- | -- | -- | -- | -- | -- | 1/1 |
| 30090 | 5/5 | - | 4/4 | 26/26 | -- | -- | -- | 4/4 |
| 30165 | -- | -- | -- | 6/6 | 3/6 | -- | 2/6 | -- |
| 33050 | -- | -- | -- | 11/11 | -- | -- | 11/11 | -- |
| 33092 | -- | -- | -- | -- | -- | 3/3 | -- | -- |
| 34037 | -- | -- | -- | 14/18 | -- | -- | -- | -- |
| 36040 | -- | -- | 22/22 | -- | -- | 22/22 | -- | -- |
| 44045 | 5/5 | -- | -- | 4/4 | 4/4 | 4/4 | -- | -- |
| 44150 | -- | -- | -- | 12/12 | -- | -- | 4/4 | -- |
| 45741 | -- | -- | 35/35 | -- | -- | -- | -- | 4/4 |
| 47025 | 33/33 | 3/4 | 25/25 | -- | -- | -- | -- | -- |
| OVERALL | 168/168 | 45/46 | 338/339 | 266/275 | 51/55 | 175/175 | 115/120 | 83/83 |

-- = No data or material not used in metal finishing processes.

# TABLE 9-8
## BPT SELF-MONITORING DATA COMPLIANCE SUMMARY
## PERCENT OF 10-DAY AVERAGES ≤ BPT MONTHLY MAXIMUM AVERAGE LIMITATIONS

| PLANT | TSS | CADMIUM | CHROMIUM | COPPER | LEAD | NICKEL | ZINC | OIL & GREASE |
|---|---|---|---|---|---|---|---|---|
| 1067 | 100.0 | 100.0 | 100.0 | 100.0 | -- | 100.0 | 100.0 | -- |
| 3049 | 100.0 | -- | -- | -- | -- | -- | -- | 100.0 |
| 5020 | -- | -- | 100.0 | 100.0 | 95.5 | 100.0 | -- | -- |
| 6002 | -- | -- | -- | -- | -- | -- | -- | -- |
| 6035 | 100.0 | -- | 100.0 | -- | -- | -- | -- | -- |
| 6051 | 100.0 | 100.0 | 100.0 | 100.0 | -- | 100.0 | 100.0 | 100.0 |
| 6053 | 100.0 | -- | -- | -- | -- | -- | -- | -- |
| 6087 | 100.0 | -- | -- | 100.0 | -- | -- | -- | -- |
| 6103 | 100.0 | -- | -- | -- | -- | -- | -- | -- |
| 6107 | 100.0 | -- | 100.0 | 0.0 | -- | -- | 0.0 | -- |
| 11008 | 100.0 | 100.0 | 100.0 | 100.0 | -- | 100.0 | 100.0 | -- |
| 11477 | 100.0 | -- | -- | -- | -- | -- | -- | 100.0 |
| 12002 | -- | -- | -- | 100.0 | -- | -- | 100.0 | 100.0 |
| 17030 | -- | -- | 100.0 | -- | -- | -- | -- | -- |
| 19063 | -- | -- | 100.0 | 100.0 | 100.0 | 100.0 | -- | -- |
| 20080 | 100.0 | -- | 100.0 | -- | -- | -- | 100.0 | 100.0 |
| 20082 | -- | -- | 96.0 | 88.0 | -- | 100.0 | 100.0 | -- |
| 20116 | 100.0 | -- | 100.0 | 100.0 | -- | 100.0 | -- | -- |
| 22735 | 100.0 | -- | 100.0 | -- | -- | -- | -- | 100.0 |
| 23076 | -- | -- | 100.0 | 95.8 | -- | 100.0 | -- | -- |
| 30050 | 100.0 | -- | 100.0 | 100.0 | -- | 100.0 | -- | 100.0 |
| 30079 | -- | -- | -- | -- | -- | -- | -- | 100.0 |
| 30090 | 100.0 | -- | 100.0 | 100.0 | -- | -- | -- | 100.0 |
| 30165 | -- | -- | -- | 100.0 | 50.0 | -- | 33.3 | -- |
| 33050 | -- | -- | -- | 100.0 | -- | -- | 100.0 | -- |
| 33092 | -- | -- | -- | -- | -- | 100.0 | -- | -- |
| 34037 | - | -- | -- | 77.8 | -- | -- | -- | -- |
| 36040 | -- | -- | 100.0 | -- | -- | 100.0 | -- | -- |
| 44045 | 100.0 | -- | -- | 100.0 | 100.0 | 100.0 | -- | -- |
| 44150 | -- | -- | -- | 100.0 | -- | -- | 100.0 | -- |
| 45741 | -- | -- | 100.0 | -- | -- | -- | -- | 100.0 |
| 47025 | 100.0 | 75.0 | 100.0 | -- | -- | -- | -- | -- |
| OVERALL | 100.0 | 97.8 | 99.7 | 96.7 | 92.0 | 100.0 | 95.8 | 100.0 |

-- = No data or material not used in metal finishing processes.

## TABLE 9-9
## SINGLE OPTION - SELF-MONITORING DATA COMPLIANCE SUMMARY 10-DAY AVERAGES ≤ BPT MONTHLY MAXIMUM AVERAGE LIMITATIONS/TOTAL NUMBER OF 10-DAY AVERAGES

| Plant | Cyanide, Total † | Cyanide, Amenable † | Silver |
|---|---|---|---|
| 1067 | * | -- | -- |
| 3043 | 6/8 | -- | -- |
| 6002 | -- | -- | -- |
| 6051 | * | -- | -- |
| 6087 | -- | -- | 1/1 |
| 6107 | * | -- | -- |
| 11008 | 15/17 | -- | -- |
| 11125 | 0/5 | -- | -- |
| 15193 | 0/1 | -- | -- |
| 20080 | 26/26 | -- | -- |
| 20082 | 12/24 | -- | -- |
| 31021 | 4/14 | 0/3 | -- |
| 36082 | 11/12 | -- | -- |
| 38223 | -- | 22/23 | -- |
| 44045 | 3/4 | -- | -- |
| 47025 | 1/13 | 17/24 | -- |
| Overall | 78/124 | 39/50 | 1/1 |

† Adjusted for dilution.
* Dilution factor not known.
-- No data or material not used in metal finishing processes.

## TABLE 9-10
## SINGLE OPTION - SELF-MONITORING DATA COMPLIANCE SUMMARY
## PERCENT OF 10-DAY AVERAGES ≤ BPT MONTHLY MAXIMUM AVERAGE LIMITATIONS

| Plant | Cyanide, Total † | Cyanide, Amenable † | Silver |
|---|---|---|---|
| 1067 | * | -- | -- |
| 3043 | 75.0 | -- | -- |
| 6002 | -- | -- | -- |
| 6051 | * | -- | -- |
| 6087 | -- | -- | 100.0 |
| 6107 | * | -- | -- |
| 11008 | 88.2 | -- | -- |
| 11125 | 0.0 | -- | -- |
| 15193 | 0.0 | -- | -- |
| 20080 | 100.0 | -- | -- |
| 20082 | 50.0 | -- | -- |
| 31021 | 28.6 | 0.0 | -- |
| 36082 | 91.7 | -- | -- |
| 38223 | -- | 95.6 | -- |
| 44045 | 75.0 | -- | -- |
| 47025 | 7.7 | 70.8 | -- |
| Overall | 62.9 | 78.0 | 100.0 |

† Adjusted for dilution.
* Dilution factor not known.
-- No data or material not used in metal finishing processes.

## TABLE 9-11

## BPT TREATMENT BENEFIT SUMMARY

Discharge (Metric tons/year)

| Pollutant Parameter | Raw Loading | BPT Effluent | BPT Benefit |
|---|---|---|---|
| Cadmium | 102 | 3 | 99 |
| Chromium, Total | 9886 | 136 | 9750 |
| Copper | 4547 | 206 | 4341 |
| Lead | 119 | 14 | 105 |
| Nickel | 557 | 237 | 320 |
| Silver | 8 | 6 | 2 |
| Zinc | 4489 | 110 | 4379 |
| TOXIC METALS TOTALS: | 19708 | 712 | 18996 |
| Cyanide, Total | 3582 | 65 | 3517 |
| Total Toxic Organics | 1170 | 30 | 1140 |
| OVERALL TOTALS: | 24460 | 807 | 23653 |

# SECTION X
# BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

## INTRODUCTION

This section describes the best available technology economically achievable (BAT) for the treatment and control of process wastewater generated within the Metal Finishing Category. BAT represents the best existing economically achievable performance of plants of various ages, sizes, processes or other shared characteristics.

The Federal Water Pollution Control Act of 1972 required that BAT represent reasonable further progress (beyond BPT) toward eliminating the discharge of all pollutants. In fact, elimination of discharge of all pollutants is required if technologically and economically achievable. The Clean Water Act of 1977 specifically defined both the conventional and toxic pollutants that must be regulated (See Section V of this document for identification of these pollutants) and also established a class of nonconventional pollutants for regulation.

BAT has been further defined as the very best control and treatment technology within a subcategory or as superior technology transferred from other industrial subcategories or categories. This definition encompasses in-plant process improvements as well as more effective end-of-pipe treatment.

## IDENTIFICATION OF BAT

BAT is the technology defined under Option 1 in Section VII of this document and is shown in Figure 10-1. For toxic metals, toxic organics, and cyanide, BAT effluent control is achieved by the BPT system described in Section IX.

For waste streams containing complexed metals, BAT will be identical to BPT. This will require the segregation of the complexed metals waste stream with separate treatment for the precipitation of metals and removal of suspended solids. Precipitation of metals from this waste stream can be accomplished by adjusting the pH of the wastewater to 11.6-12.5 in order to promote dissociation of the metal complexes and subsequent precipitation of the free metals. Sedimentation is then employed in order to allow the resulting suspended solids to settle out of solution.

The BAT treatment systems (Option 1 system in Section VII) is adequate to achieve the BAT effluent limitations presented later in this section. However, a plant may elect to supplement this system with other equipment or use an entirely different treatment technique in order to attain the BAT limitations. Alternative technologies (both end-of-pipe and in-process) are described in Section VII of this document. In-plant techniques such as evaporative recovery or reverse osmosis may substantially reduce the end-of-pipe treatment requirements.

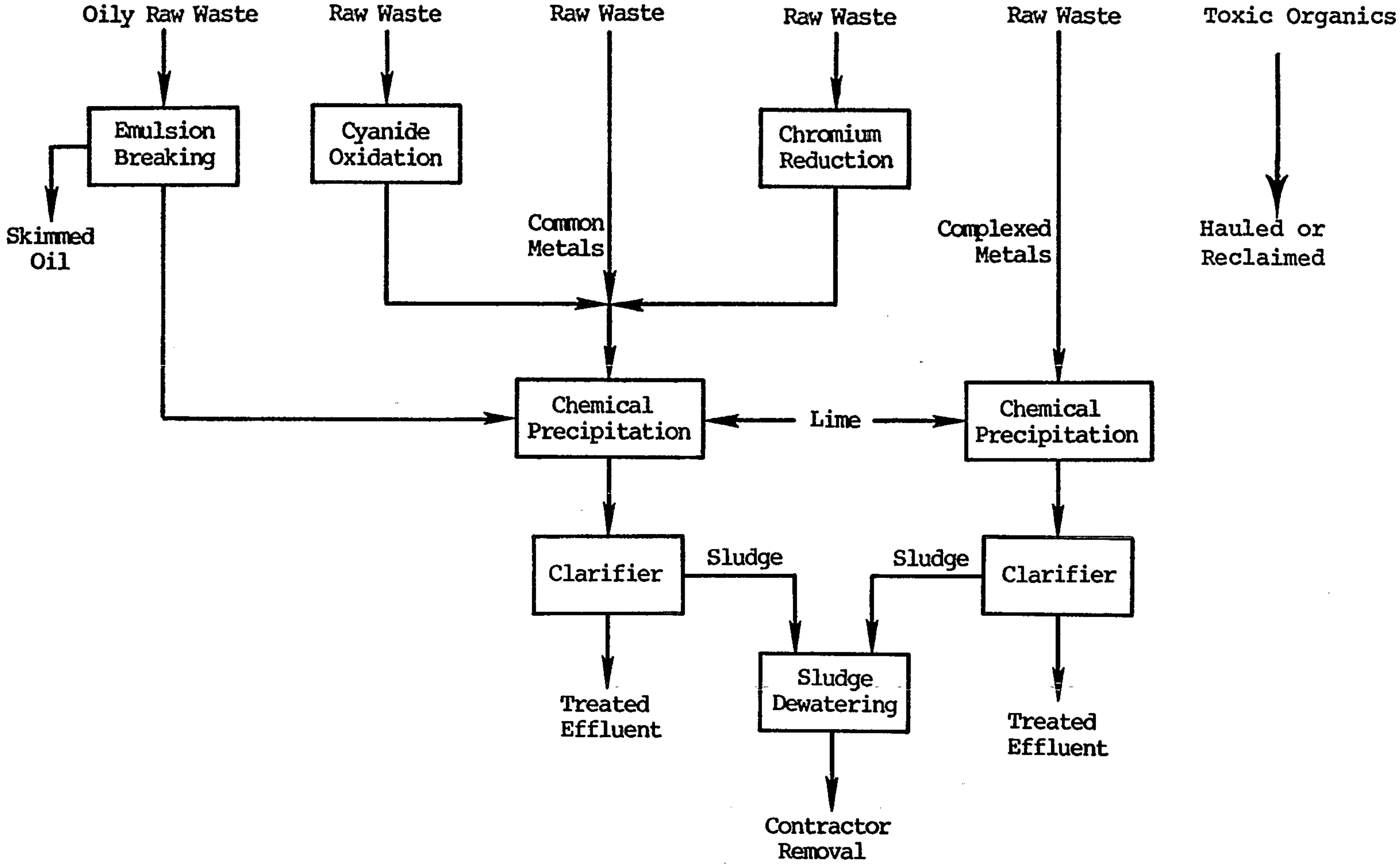


FIGURE 10-1

BAT SYSTEM

## RATIONALE FOR SELECTION OF BAT

The BAT treatment system identified previously was selected because it has been proven in metal finishing plants to represent a well demonstrated, reliable technology which achieves a high degree of toxic pollutant removal. This is demonstrated by the Option 1 system performance in Section VII.

Although demonstration of BAT at a single plant is adequate for its selection, the common metals Option 1 system is identified in Section VII as presently employed at over 100 known metal finishing plants. Precipitation, clarification, and filtration, has been demonstrated to be effective at several plants, although far less frequently than precipitation/clarification alone. Although precipitation/clarification/filtration was considered for BAT, it was not selected as the technology basis because of the very high incremental aggregate costs.

Compared to BPT, BAT has identical impact on energy requirements and nonwater quality aspects.

## BAT LIMITATIONS

The BAT effluent limitations are presented in Table 10-1.

TABLE 10-1
BAT EFFLUENT LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

As discussed in Section VII, these limitations represent the effluent concentrations attainable by a properly operating BAT system 99 percent of the time. The concentrations presented in Table 10-1 reflect treated effluent undiluted by sanitary wastewater, noncontact cooling water, or other nonprocess water. The total cyanide concentration limitation applies to the discharge from cyanide oxidation prior to mixture with any other process wastes. As an alternative to the total cyanide limit, cyanide amenable limit may apply in place of total cyanide for a facility with cyanide treatment and contingent on agreement between the facility and the pollution control authority.

The development of these effluent limitations from performance measurements of existing BAT systems is described in Section VII. The statistical rationale used in developing these limitations is presented at the end of Section VII under the heading of Statistical Analysis.

## PRESENT COMPLIANCE WITH BAT

The percent compliance with BAT for the EPA sampled data base and the long-term self-monitoring data base is the same as for BPT for the toxic metals and cyanide as presented in Tables 9-2 to 9-10.

## BENEFITS OF BAT IMPLEMENTATION

Since the BAT treatment system is identical to the BPT system, no increased environmental benefit above that derived from BPT treatment is attained.

# SECTION XI
# NEW SOURCE PERFORMANCE STANDARDS

## INTRODUCTION

This section describes the new source performance standards (NSPS) for the treatment and control of process wastewaters generated within the Metal Finishing Category. NSPS reflects existing treatment and control practices or demonstrations that are not necessarily in common practice.

The Federal Water Pollution Control Act of 1972 required that NSPS represent the best available demonstrated control technology, processes, and operating methods. Where practicable, no pollutant discharge at all is to be allowed. Where pollutant discharge is unavoidable, these standards are to represent the greatest degree of effluent reduction achievable. They apply to new sources, which are defined as any building, structure, facility, or installation that discharges pollutants and for which construction is started after promulgation of the standards.

## IDENTIFCATION OF NSPS

NSPS is the technology defined under Treatment of Common Metals Wastes - Option 3 in Section VIII of this Development Document. The NSPS waste treatment system is shown in Figure 11-1. For common metals, precious metals, oil and grease and cyanide wastes, NSPS is achieved by the previously described BPT and BAT treatment systems, plus the use of in-process treatment modifications for controlling the discharge of cadmium. The BPT or BAT waste treatment systems have been previously described in Sections IX and X of the document.

The in-process modifications for controlling cadmium consist of using evaporative recovery or ion exchange on segregated cadmium bearing waste streams prior to mixing with other common metals bearing wastewaters for end-of-pipe treatment. These in-process modifications will reduce cadmium discharges to the background levels detailed in Section VII of the document.

For complexed metal bearing waste streams, NSPS will be identical to the BPT and BAT waste systems. This requires segregation of the complexed metals waste stream with separate treatment for the precipitation of metals and removal of suspended solids. Precipitation of metals from this waste stream is accomplished by pH adjustment of the wastewater to 11.6-12.5 in order to promote dissociation of the metal complexes and subsequent precipitation of the free metals. This is followed by sedimentation in order to allow the resulting suspended solids to settle out of solution.

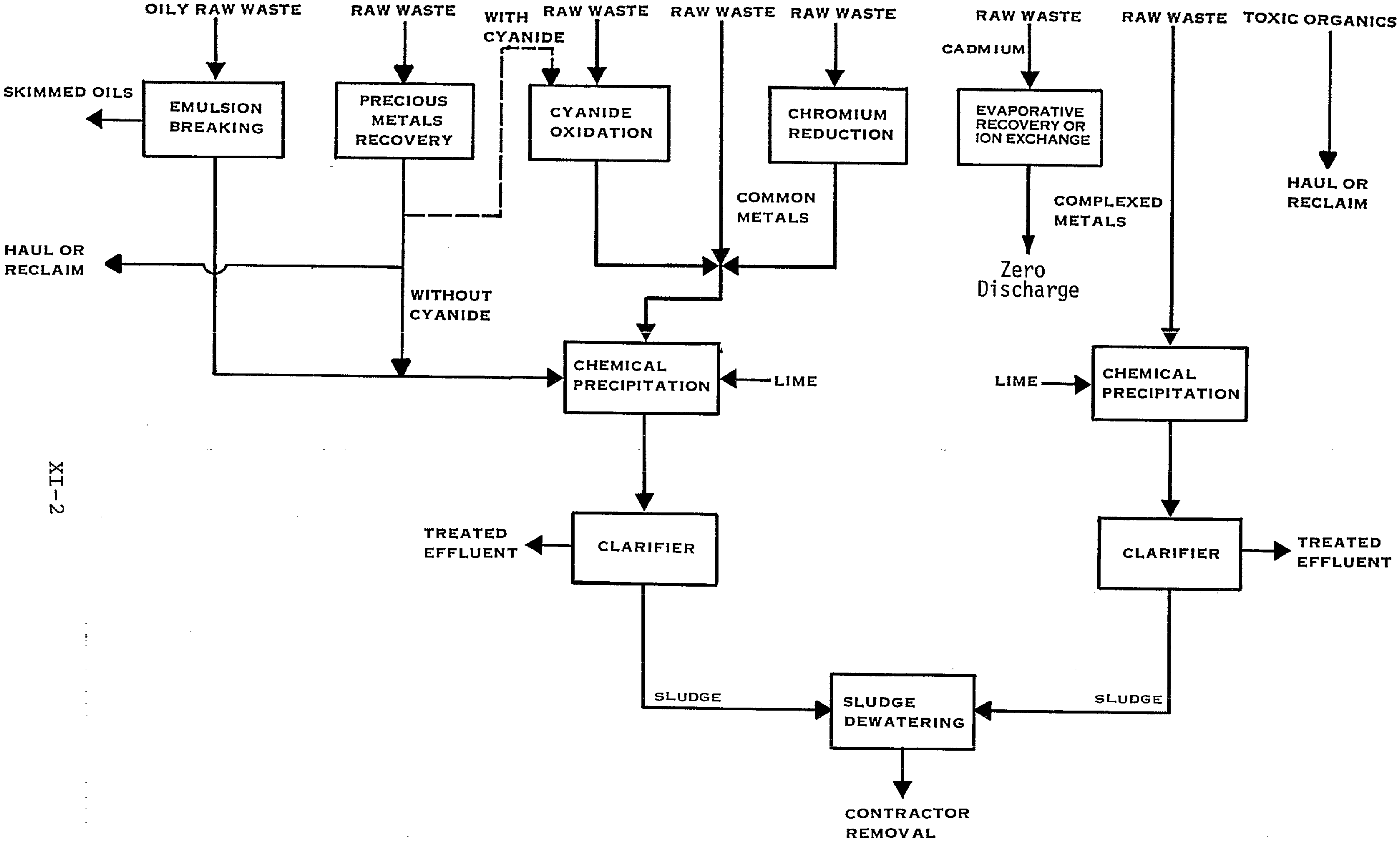


FIGURE 11-1
NSPS SYSTEM

The NSPS treatment system will, with proper operation, achieve the NSPS effluent limitations presented later in this section. However, a plant may elect to supplement this system with other equipment or use an entirely different treatment technique in order to attain the NSPS limitations. Alternative technologies (both end-of-pipe and in-process) are described in Section VII of this document. In-plant treatment modifications such as the use of evaporated recovery may substantially reduce end-of-pipe treatment requirements.

## RATIONALE FOR SELECTION OF NSPS TECHNOLOGY

The NSPS treatment components identified previously for control of cadmium were selected because they have been proven in metal finishing plants to represent reasonable performance improvement beyond the BPT and BAT levels of treatment. This improvement is demonstrated by the comparison of Option 1 and Option 3 system performance for cadmium in Section VII.

Option 3 effluent limitations for cadmium represent background levels detected in effluents from plants which do not apply this metal in their production operations. Because the technology basis eliminated the discharge from cadmium wastewater sources, this limit is appropriate. In using data indirectly, the Agency has been conservative in two ways. First, the background levels used to develop the standards are raw waste concentrations; the technology basis of precipitation/clarification is expected to result in further removal. Second, the highest two plants were used for the derivation of the long term average. The conservative nature of this procedure can be seen by comparing the new source average with the EPA sampled discharges of cadmium from precipitation/clarification. (A detailed explanation of this approach and the data supporting the reasonableness of this approach are provided in Section VII.)

When compared to BPT and BAT, NSPS has only minor incremental impact upon energy requirements and other nonwater quality aspects.

## NSPS LIMITATIONS

The NSPS effluent limitations are presented in Table 11-1.

## TABLE 11-1
## NSPS EFFLUENT LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.11 | 0.07 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Oil and Grease | 52 | 26 |
| TSS | 60 | 31 |
| pH | Within the range of 6.0 to 9.0 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

As discussed in Section VII of this document, these limitations represent the effluent concentrations attainable by a well operating NSPS system 99 percent of the time. The concentrations presented in Table 11-1 reflect treated effluent undiluted by sanitary wastewater, non-contact cooling water, or other non-process water. The total cyanide concentration limitation applies to the discharge from in-process modifications (for this pollutant) prior to mixture with any other process wastes. As an alternative to the total cyanide limit, a facility with cyanide treament may apply the cyanide amenable limit in place of the total cyanide limit upon agreement between the facility and the pollution control authority. The cadmium limitation applies to the discharge from in-process modifications (for this pollutant) prior to mixture with any other process wastes.

The development of the NSPS effluent limitations is described in Section VII under Common Metals Waste Treatment System Performance - Option 3, and the statistical rationale is presented at the end of Section VII under the heading of Statistical Analysis.

## PRESENT COMPLIANCE WITH NSPS

The NSPS compliance for all parameters other than cadmium is the same as that presented in Section IX (for BPT) because the NSPS limitations for all parameters other than cadmium are identical tothe BPT limitations. Present compliance with the Option 3 cadmium limitation cannot be determined because data are not available from metal finishing plants using the specified technology.

## BENEFITS OF NSPS IMPLEMENTATION

Table 11-2 shows the estimated benefit of reduced cadmium discharge in terms of concentration reduction that results from the implementation of the NSPS limitations. An incremental reduction benefit of 0.19 mg/ℓ of cadmium would be achieved. The estimated environmental benefits for all pollutant parameters other than cadmium were presented in Section IX (for BPT) and Section X (for BAT). Quantitative benefits cannot be determined for NSPS because installation of future facilities cannot be predicted, and the wastewater flow rates from new sources cannot be projected.

TABLE 11-2
NSPS TREATMENT BENEFIT SUMMARY
Concentration Reduction (mg/l)

| Pollutant Parameter | Average BPT/BAT Effluent | Average NSPS Effluent | Average NSPS Reduction |
|---|---|---|---|
| Cadmium | 0.13 | 0.06 | 0.07 |

# SECTION XII
# PRETREATMENT STANDARDS

## INTRODUCTION

This section describes the pretreatment standards for existing sources (PSES) and the pretreatment standards for new sources (PSNS) for the treatment of wastewaters generated within the Metal Finishing Category that are discharged to a publicly owned treatment works (POTW). These standards are intended to provide an equivalent degree of toxic metals and toxic organic pollutant removal as provided by direct discharge limitations.

The Federal Water Pollution Control Act of 1972 stated that the pretreatment standards shall prevent the discharge to a POTW of any pollutant that may interfere with, pass through, or otherwise be incompatible with the POTW. The Clean Water Act of 1977 further stipulated that industrial discharges must not interfere with use and disposal of municipal sludges. In accordance with the Clean Water Act, individual POTWs may specify more stringent standards or (after meeting specified criteria) may relax the standards presented here.

## IDENTIFICATION OF PRETREATMENT TECHNOLOGY

Pretreatment technology for PSES is the same as that defined in Section X for BAT, and pretreatment technology for PSNS is the same as that defined in Section XI for NSPS, with the exception that oil and grease and TSS are not regulated parameters. In addition, the Agency is allowing 31 months for compliance with the metals, cyanide, and total toxic organics standards. However, the Agency believes that toxic organics should not be uncontrolled for this period and has, therefore, established an interim TTO limit based on data prior to precipitation/clarification and reflecting proper management of toxic organics. The interim TTO limit has been established with a compliance date of June 30, 1984.

## RATIONALE FOR SELECTION OF PRETREATMENT TECHNOLOGY

Toxic metals, and toxic organics may pass through a POTW, or they may contaminate its sludge, or they may interfere with the treatment process. These pollutants must therefore be controlled by pretreatment.

## PRETREATMENT STANDARDS

Pretreatment standards for existing sources are the same as BAT (reference Section X) for existing sources with the exception of the interim TTO limit. The PSES interim TTO daily maximum limitation is 4.57 mg/ℓ and applies to the TTO concentration in the total plant raw wastewater. Pretreatment standards for new sources are the same as NSPS (reference Section XI) for new sources, with the exception of control of oil and grease, TSS, and pH. Table 12-1 quantifies the PSES requirements and Table 12-2 presents the requirements for PSNS. Although specific control of TSS is not required, it will be effectively controlled by the need to control metals.

## PRESENT COMPLIANCE WITH PRETREAMENT STANDARDS

The percent compliance for EPA sampled plants with the interim TTO limitation is 100 percent for plants which appear to properly manage toxic organic wastes. Compliance with PSES for metals, cyanide and TTO (final) is the same as that presented in Section IX for BPT. Compliance with PSNS is discussed in Section XI for NSPS.

## BENEFITS OF IMPLEMENTATION

Table 12-3 shows for existing sources the estimated benefit of reduced metals, cyanide, and total toxic organics discharge in terms of metric tons of pollutant per day that results from the implementation of the pretreatment limitations. A reduction of toxic metals (52549 metric tons/year), total cyanide (7699 metric tons/year), and total toxic organics (4098 metric tons/year) may be achieved by pretreatment prior to discharge to the municipal sewer. Benefits derived from implementing new source performance standards cannot be predicted. However, the impact on cadmium effluent concentration reduction is presented in Section 11, Table 11-2.

## TABLE 12-1
## PSES LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO (interim) | 4.57 | |
| TTO (final) | 2.13 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

## TABLE 12-2
## PSNS LIMITATIONS

| Pollutant or Pollutant Parameter | Daily Maximum | Maximum Monthly Average |
|---|---|---|
| Cadmium | 0.11 | 0.07 |
| Chromium, total | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide, total | 1.20 | 0.65 |
| TTO | 2.13 | |
| Alternative to total cyanide: | | |
| Cyanide, amenable to chlorination | 0.86 | 0.32 |

## TABLE 12-3
## PRETREATMENT BENEFIT SUMMARY

Discharge (kkg/yr)

| Pollutant Parameter | Raw Loading | Pretreatment Effluent | Pretreatment Benefit |
|---|---|---|---|
| Cadmium | 223 | 6 | 217 |
| Chromium, Total | 21638 | 296 | 21342 |
| Copper | 9952 | 451 | 9501 |
| Lead | 261 | 30 | 231 |
| Nickel | 12190 | 522 | 11668 |
| Silver | 18 | 14 | 4 |
| Zinc | 9826 | 240 | 9586 |
| TOXIC METALS TOTALS: | 54108 | 1559 | 52549 |
| Cyanide, Total | 7841 | 142 | 7699 |
| Total Toxic Organics | 4164 | 66 | 4098 |
| OVERALL TOXIC TOTALS: | 66113 | 1767 | 64346 |

# SECTION XIII
# INNOVATIVE TECHNOLOGY

## INTRODUCTION

The Clean Water Act of 1977, Public Law 95-217, provides that direct discharging facilities which make use of innovative technology that results in an effluent reduction greater than that required by the limitations may have a date of July 1, 1987 for compliance with the limitations.

Specifically, this compliance date extension is authorized by Section 47 of the Act and is reproduced herein for reference:

### INNOVATIVE TECHNOLOGY

Compliance date extension. Supra.

Sec. 47. Section 301 of the Federal Water Pollution Control Act is amended by adding at the end thereof a new subsection as follows:

"(k) In the case of any facility subject to a permit under section 402 which proposes to comply with the requirements of subsection (b) (2) (A) of this section by replacing existing production capacity with an innovative production process which will result in an effluent reduction significantly greater than that required by the limitation otherwise applicable to such facility and moves toward the national goal of eliminating the discharge of all pollutants, or with the installation of an innovative control technique that has a substantial likelihood for enabling the facility to comply with the applicable effluent limitation by achieving a significantly greater effluent reduction than that required by the applicable effluent limitation and moves toward the national goal of eliminating the discharge of all pollutants, or by achieving the required reduction with an innovative system that has the potential for significantly lower costs than the system which have been determined by the Administrator to be economically achievable, the Administrator (or the State with an approved program under section 402, in consultation with the Administrator) may establish a date for compliance under subsection (b) (2) (A) of this section no later than July 1, 1987, if it is also determined that such innovative system has the potential for industry wide application".

This section describes pollution control techniques that have the capability of achieving the significant effluent reduction necessary to qualify as an innovative technology.

## INNOVATIVE TECHNOLOGY CANDIDATES

This section presents information on various innovative technologies available to the industry for use in wastewater treatment and control. The innovative technologies described in this section may not be applicable to all metal finishing facilities as the appropriateness of these technologies is dependent on a number of factors, including the design and operating characteristics of a facility. Currently, the appropriateness of these innovative technologies should be determined on a plant-by-plant basis. However, the innovative technologies described in this section have been reported to be effective for wastewater treatment and control at plants in the metal finishing industry. These technologies, if properly applied, can qualify as innovative technologies. Included among these candidate systems are evaporative systems, ion exchange, electrolytic recovery systems, electrodialysis, reverse osmosis, and electrochemical chromium regeneration. A discussion of water reducing controls is also presented in this section.

Descriptions of evaporation, ion exchange, electrolytic recovery, reverse osmosis, and electrochemical chromium regeneration technologies are provided in Section VII along with information on application, performance, and demonstration status in the Metal Finishing industry.

An index to these technologies is provided in Table XIII-1. Electrodialysis is described below.

TABLE 13-1

INDEX TO INNOVATIVE TECHNOLOGY CANDIDATES DESCRIBED IN SECTION VII

| TECHNOLOGY | PAGE |
|---|---|
| Evaporation | VII-76, 100, 124, 153 |
| Ion Exchange | VII-80, 102, 114, 124 |
| Reverse Osmosis | VII-178 |
| Electrolytic Recovery | VII-102 |
| Electrochemical Chromium Regeneration | VII-123 |

## Electrodialysis

Electrodialysis is a process in which dissolved species are exchanged between two liquids through selective semipermeable membranes. An electromotive force causes concentration of the species from a waste stream, thereby providing purified water.

Water to be treated by electrodialysis is pumped through a standard cartridge filter and into the membrane stack. The stack consists of about fifty cell pairs operated in parallel flow. Each cell pair consists of an anion-selective membrane, a cation-selective membrane, and membrane spacers. These membranes and a membrane from the adjacent cell pair define a diluting compartment and a concentrating compartment.

Water to be treated flows through the diluting compartments. As it does so, the contained ions (e.g. nickel and sulfate) are drawn toward the electrodes at either end of the stack. Negative and positive ions are drawn in opposite directions through the selective membranes on either side of the diluting compartment into the adjacent concentrating compartments. Water of hydration goes with them. The ions continue in each direction across the concentrating compartments but are trapped there because they are blocked by membranes having a selectivity opposite to the one they passed through. The net effect is that the water passing through the diluting compartments is deionized, while a concentrate (the ions and their water of hydration) is formed in the concentrating compartments (the concentrating compartments have no inlet, only an outlet).

The end (electrode) compartments are different. They are continously flushed with a common-ion liquid (e.g. sodium sulfate for nickel sulfate plating solution) to remove oxygen, hydrogen, and chlorine formed by electrolysis at the electrodes. These gases are vented from the electrode wash solution reservoir.

The overall effect is that the total mineral content of the treated water is reduced to about 1,000 mg/l. Further reduction in concentration is not efficient and is not practical because of excessive electrolysis. Thus, electrodialysis functions more like ion exchange than like reverse osmosis and evaporation. That is, ions are removed from wastewater rather than concentrated. Non-ionic constituents such as organic brighteners remain in the treated water rather than in the concentrate.

Figure 13-1 shows the application of a simple electrodialysis cell to separate potassium sulfate solution ($K_2SO_4$) into its components. Practical electrodialysis installations contain from ten to hundreds of compartments between one pair of electrodes. The application of an electric charge draws the cations to the cathode and anions to the anode. Industrial wastewater containing metallic salts enters the center cell,

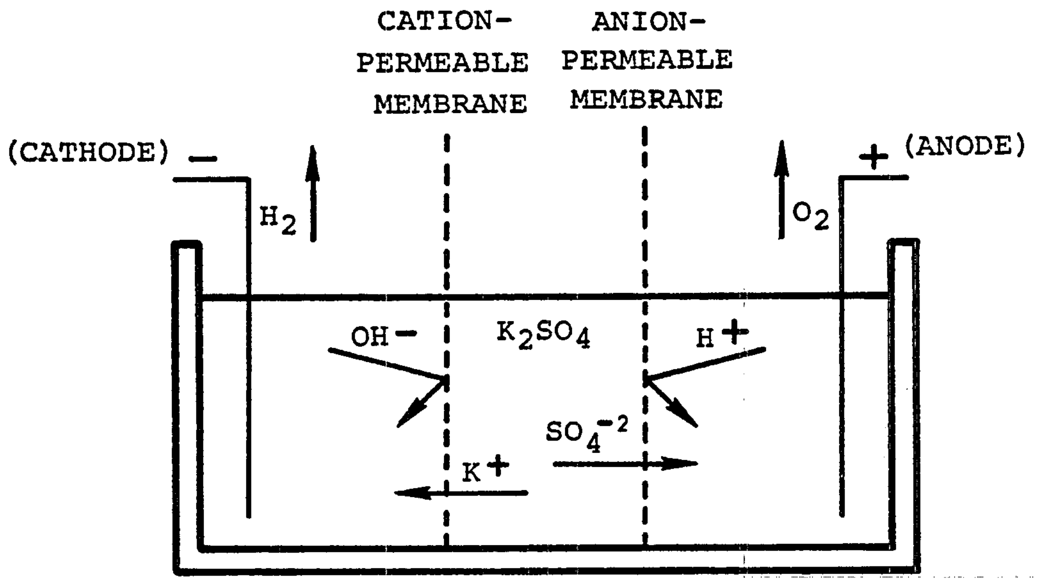


FIGURE 13-1

SIMPLE ELECTRODIALYSIS CELL

and the charge takes the positive ions to the cathode and negative ions to the anode. The result is a significant reduction in salt concentration in the center cell with an increase in solution concentrations in the adjacent cells. Thus, the water from the center of each of three adjacent cells is purified and metal ions are concentrated in the cathode cell, with sulfates, chlorides, etc., concentrated in the anode cell. At the outlet end of the cell stack, streams are drawn off from the individual cells either as the purified water or as concentrate for recovery or for further treatment.

Figure 13-2 illustrates the operation of a seven chamber conventional electrodialysis cell. In large electrodialysis installations, two or more stacks are linked in series. The dilute effluent from the first stage is passed through an identical second stage, and so forth, with the effluent from the final stage reaching the desired concentration.

## Application

The functional characteristics just described are the key to potential application. Electrodialysis treated water is not pure enough for a final rinse. Adding a reverse osmosis unit would achieve adequately pure water, with the RO concentrate returning to the ED feed. The standard setup, however, is recirculation of a dead rinse (following the plating tank) through the ED unit and back. This maintains a low concentration (about 1,000 mg/l of total mineral content) in the dead rinse, minimizing the flow needed in the following running rinses. If desired, these running rinses could be counterflowed through an RO unit, with the concentrate directed to the ED unit.

Present applications include nickel, gold (cyanide and citrate), silver, and cadmium plating. Any type of plating solution is potentially recoverable for direct return to the plating tank. Electrodialysis has been shown to be an effective method for concentrating rinse waters to a high percentage of bath strength. Nickel, copper, cyanide, chromic acid, iron and zinc can be removed from process wastes by electrodialysis. The natural evaporation taking place in a plating bath will often be sufficient to allow electrodialysis to be used to close the loop without the addition of an evaporator.

At the time of the sampling visit, conventional electrodialysis was being used by plant ID 20064 as a means of concentrating and recovering chromic acid etch solution. Electrodialysis can be combined with an existing treatment system for recovery of metals, or it can be used with other treatment to effect recirculation of rinse water. Many possibilities exist for electrodialysis and with recent developments in membrane materials and cathode design and increased knowledge of their applications, it may become a major form of treatment for metals.

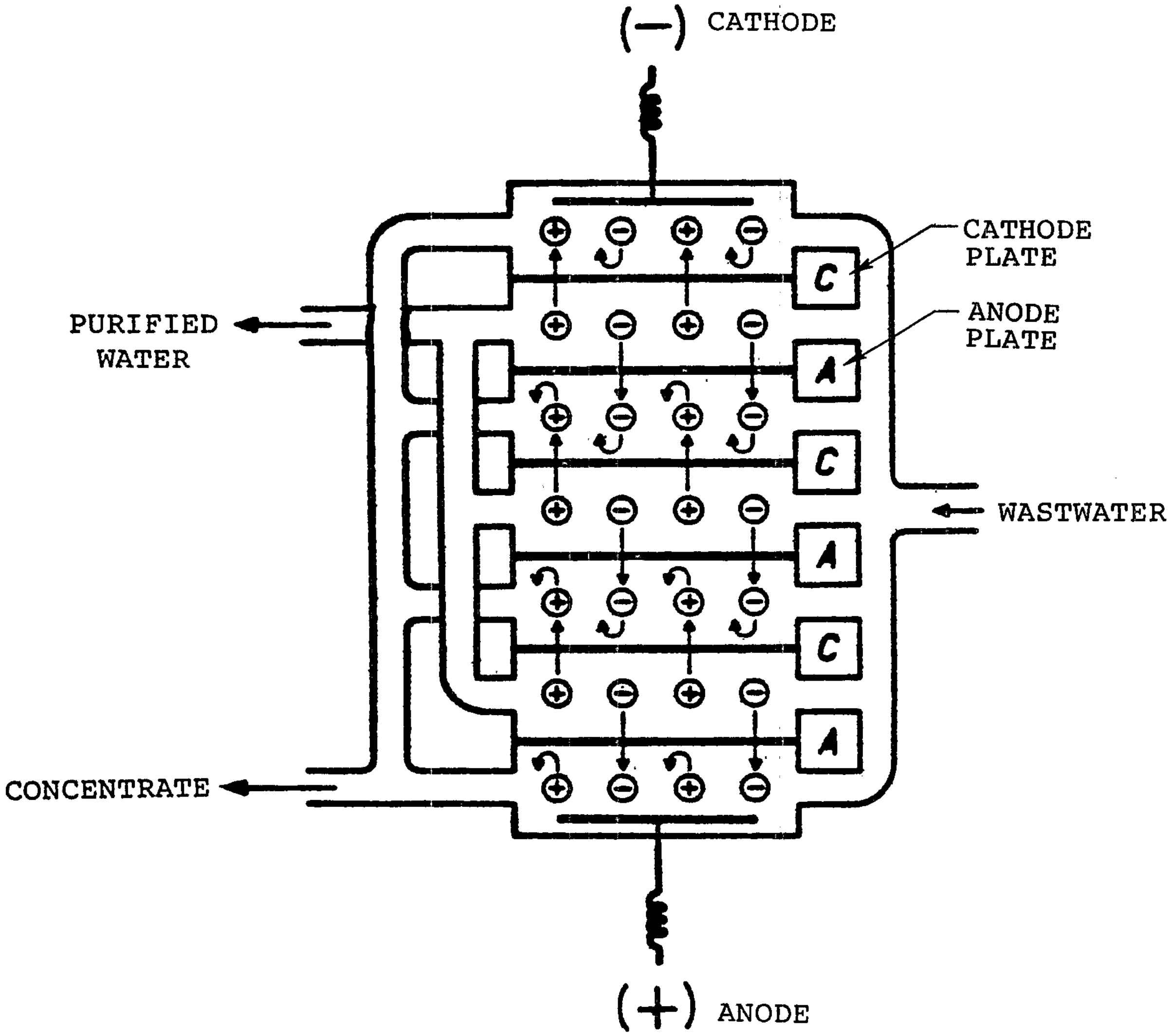


FIGURE 13-2

MECHANISM OF THE ELECTRODIALYTIC PROCESS

Performance

Little information is available on performance for treatment of chromic acid; however, information is available on copper cyanide performance. Copper cyanide rinse water is treated in an electrodialysis unit for return of the concentrated chemicals to the process bath. The copper cyanide chemicals in the rinse water can be concentrated to slightly more than 70 percent of the bath strength. For most copper cyanide plating, this concentration may be sufficient to permit the direct return of all chemicals to the processing operation. One manufacturer guarantees 94 percent recovery of dragged-out plating metals. Figure 13-3 shows an electrodialysis recovery system.

Demonstration Status

Commercial electrodialysis units are manufactured by at least two major suppliers to the metal finishing industry. At least 20 units have been installed.

Three metal finishing plants in our data base indicate the use of electrodialysis. These plant ID's are: 20064, 20069, and 41003.

## Advanced Electrodialysis

This particular electrodialysis system is used to oxidize chromium (in spent chromic acid) from a trivalent form to a hexavalent form. Its design uses a circular, permeable anode, separated from the cathode by perfluorosulfonic membrane. The anode material is a specially designed lead alloy. The cathode is made from Hastelloy C tubing, which is a nickel alloy. The cathode is located in the center of the circular, permeable anode and has a catholyte (10 percent sulfuric acid) which is circulating through it and surrounds the cathode. This solution is used as a transfer solution. Figure 13-4 shows the physical construction of this circular electrodialysis cell.

The etchant is pumped in at the bottom of the unit through the anode so that it remains in the chamber between the anode and the perfluorosulfonic membrane. Chromium in the trivalent form is contained in the etchant and, when a current is passed through this etchant solution, electrons are stripped from the trivalent chromium causing oxidation of the trivalent chromium to hexavalent chromium. The newly stripped electrons migrate through the perfluorosulfonic membrane into the catholyte solution. Converted hexavalent chromium is pumped back into the chromium etch tank for reuse, while at the same time the catholytic solution is being recirculated. The reaction which occurs at the anode is as follows:

$$Cr^{+3} + 12\ H_2O + 3e- = CrO_4^{-2} + 8H_3O^{+1} + 6e-$$

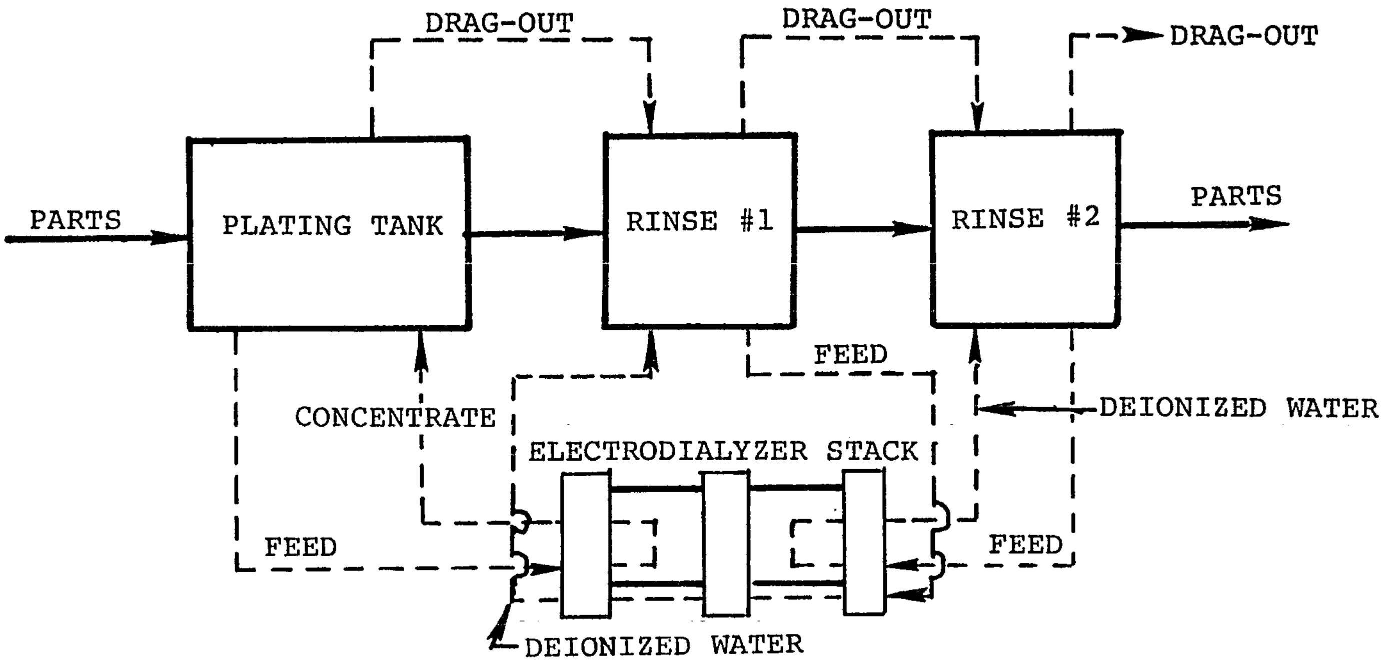


FIGURE 13-3

ELECTRODIALYSIS RECOVERY SYSTEM

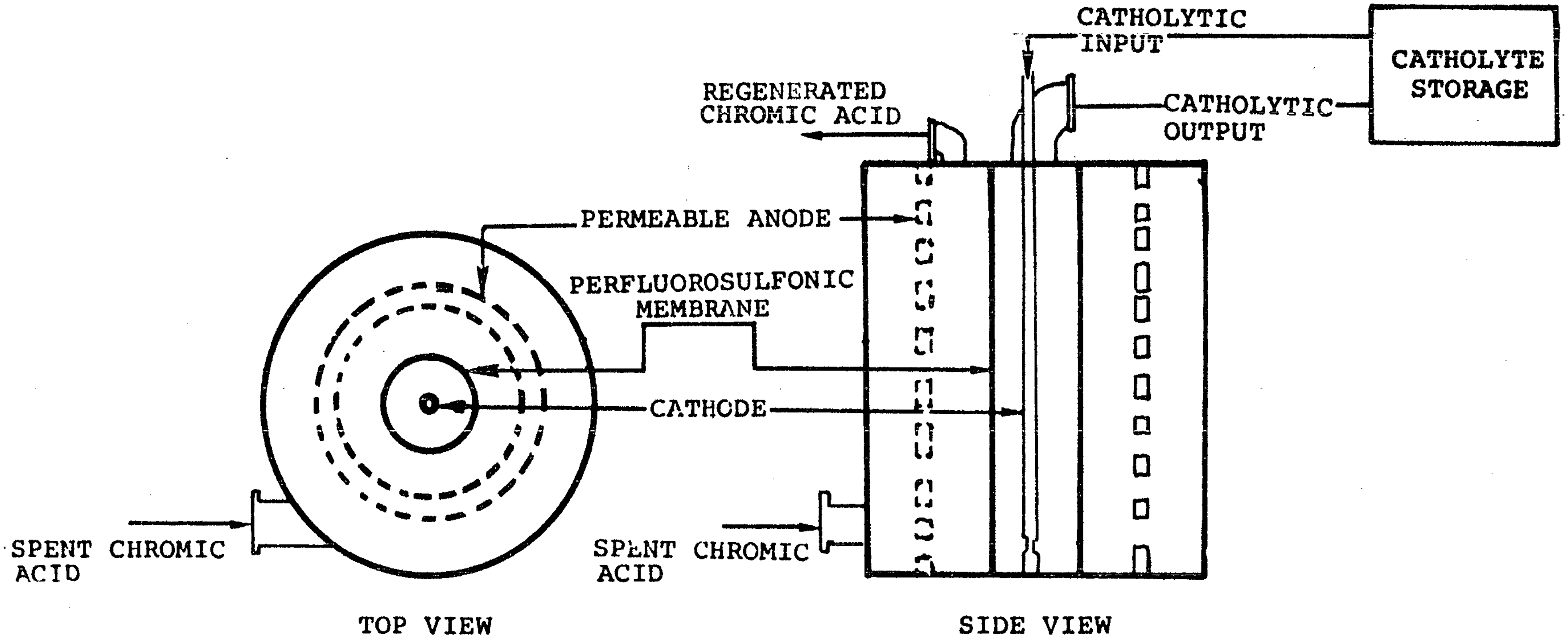


FIGURE 13-4

ELECTRODIALYSIS CELL

This reaction is continually taking place as both the etchant and the catholyte are circulated through the cell.

Application

Electrodialysis of chromium, oxidizing trivalent chromium to hexavalent chromium, is not a widely practiced method of waste treatment as yet. It is, however, a very efficient method for waste treatment of chromium, and it is used at one company visited (ID 20064). This electrodialysis cell closes the loop on chromium so that there is no need to reduce hexavalent chromium. The only application, current or predicted, for this electrodialysis cell system is the oxidation of chromium wastes.

Performance

The electrical efficiency of the unit varies with the concentration of both hexavalent chromium and trivalent chromium. The electrochemical efficiency of the unit is generally between 50 to 90 percent, depending on the concentrations. This corresponds to an energy consumption of 8 to 16 kwh/kg of chromic acid from reduced chromium. The metal removed efficiency of the electrodialysis unit is 90 percent for 8 mg/l of trivalent chromium and 95 percent for 12 mg/l.

## Water Reducing Controls for Electroplaters

To minimize pollution problems, electroplaters have discovered that relatively simple strategies can effectively be made operational. First, water can be used more efficiently. Second, water can be kept clean to begin with and, therefore, will not be a problem that requires wastewater treatment.

Efficient water use means getting the most rinsing from each gallon of water. A single rinse tank is the least efficient means to obtain adequate rinsing because a much larger volume of water must be used in comparison to counterflow rinsing. (Counterflow rinsing is an effective flow reduction technique but it can also be expensive.) Electroplaters have found that using rinse water two or three times before it is purified or discarded not only reduces water consumption, but it can actually improve rinsing and save process chemicals. Moreover, rinse water reuse techniques are not expensive to implement and are not subject to space constraints to the same extent as counterflow rinsing.

Low cost pollution control strategies further benefit electroplating firms by reducing costs for raw water and wastewater treatment. In addition, the strategies can often be operated by in-shop fabrication instead of expensive high technology controls or end-of-pipe treatment. Two effective and inexpensive technologies that may be used to minimize pollution problems are described in this section, multiple dragout and reactive rinsing.

## Multiple Drag-Out Control: Techniques and Effectiveness

By controlling the amount of plating solution that is dragged from work pieces upon their removal from the process tank, the amount of contamination in subsequent rinse tanks can be reduced. A dragout tank, consisting of nothing more than a still rinse, installed immediately following the plating process will capture some of the contamination.

The multiple dragout method uses the same number of rinse tanks as counterflow rinsing. The difference is that instead of a single dragout tank and several running rinse tanks, several dragout tanks and a single running rinse tank are used.

Most of the solution dragged from the plating tank is captured in the first dragout tank. The multiple drag-out tank protect the running rinse from intense contamination and often allows the rinsewater to be discharged with little or no treatment because it already meets the Federal standards. As a result, the multiple drag-out method greatly reduces the cost the wastewater treatment. Likewise, because wastewater treatment is minimized so is sludge generation and sludge management costs.

Periodically, some of the solution from the first tank must be drained and replaced by the less contaminated solution from the second drag-out tank. Fresh water is than used to fill the second tank. The solution drained from the first drag-out tank can be (1) recycled to the plating process; (2) processed to recover the metals; or (3) sent to a waste treatment plant. Multiple drag-out tanks are a simple and efficient means to reduce drag-out contamination. Two or more drag-out tanks operated in series assure almost complete control of drag-out losses.

## Reactive Rinsing: Techniques and Effectiveness

Reactive rinsing means reusing or recycling the rinse water. By flowing rinse water back through the electroplating process and taking advantage of the chemical reactivity of contaminated water, water use can be minimized.

As an example, consider a nickel plating process composed of an alkaline cleaning tank, an acid dip tank, and a plating tank, with a rinse tank after each process. In a conventional plating process, water would be individually fed to each rinse tank. Using reactive rinsing, water fed to the rinse tank following the planting tank would supply the rinse tank following the acid dip; the water from this rinse would supply the tank following the alkaline cleaner.

Reactive rinsing allows a pH neutralization reaction to occur as the rinse water from the acid dip is fed back to the rinse water from the alkaline cleaner. The reaction does not harm the plating process, and actually improves the rinsing effectiveness following the cleaner. Cleaner solution is greasy and hard to rinse; however, with acid rinsewater the alkaline solution is neutralized and rinses easily. Drag-out contamination may also be reduced because rinse water from the tank following the plating tank (i.e., water containing drag-out) is fed back to the rinse tank preceding the plating tank. Accordingly, the drag-in to the nickel tank will contain some nickel solution.

This example describes an in-process, counterflow reactive rinsing technique, other reactive rinsing opportunities are possible. Depending upon the particular plating process, it may be possible to feed rinse water forwards. In some instances, it is be possible to feed rinse water across processes to obtain the desired reaction. The possibilities for interprocess reuse at plating shops are great but have been largely unexplored.

## SECTION XIV
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# SECTION XVI

## GLOSSARY

Abrasive Belt Grinding - Roughing and/or finishing a workpiece by means of a power-driven belt coated with an abrasive, usually in particle form, which removes material by scratching the surface.

Abrasive Belt Polishing - Finishing a workpiece with a power-driven abrasive-coated belt in order to develop a very good finish.

Abrasive Blasting - (Surface treatment and cleaning.) Using dry or wet abrasive particles under air pressure for short durations of time to clean a metal surface.

Abrasive Cutoff - Severing a workpiece by means of a thin abrasive wheel.

Abrasive Jet Machining - Removal of material from a workpiece by a high-speed stream of abrasive particles carried by gas from a nozzle.

Abrasive Machining - Used to accomplish heavy stock removal at high rates by use of a free-cutting grinding wheel.

Acceleration - See Activation.

Acceptance Testing - A test, or series of tests, and inspections that confirms product functioning in accordance with specified requirements.

Acetic Acid - (Ethanoic acid, vinegar acid, methanecarboxylic acid) $CH_3COOH$. Glacial acetic acid is the pure compound (99.8% min.), as distinguished from the usual water solutions known as acetic acid. Vinegar is a dilute acetic acid.

Acid Cleaning - Using any acid for the purpose of cleaning any material. Some methods of acid cleaning are pickling and oxidizing.

Acid Dip - An acidic solution for activating the workpiece surface prior to electroplating in an acidic solution, especially after the workpiece has been processed in an alkaline solution.

Acidity - The quantitative capacity of aqueous solutions to react with hydroxyl ions. It is measured by titration with a standard solution of a base to a specified end point. Usually expressed as milligrams per liter of calcium carbonate.

Act - Federal Water Pollution Control Act Amendments of 1972.

Activitated Sludge Process - Removes organic matter from sewage by saturating it with air and biological active sludge.

Activation - The process of treating a substance by heat, radiation or the presence of another substance so that the first mentioned substance will undergo chemical or physical change more rapidly or completely.

Additive Circuitry - 1. Full - Circuitry produced by the buildup of an electroless copper pattern upon an unclad board. 2. Semi - Circuitry produced by the selective "quick" etch of an electroless layer; this copper layer was previously deposited on an unclad board.

Administrator - Means the Administrator of the United States Environmental Protection Agency.

Adsorption - The adhesion of an extremely thin layer of molecules (as of gas, solids or liquids) to the surface of solid or liquids with which they are in contact.

Aerobic - Living, active, or occurring only in the presence of oxygen.

Aerobic Biological Oxidation - Any waste treatment process utilizing organisms in the presence of air or oxygen to reduce the pollution load or oxygen demand of organic substance in water.

Aerobic Digestion - (Sludge Processing) The biochemical decomposition of organic matter, by organisms living or active only in the presence of oxygen, which results in the formation of mineral and simpler organic compounds.

Aging - The change in properties (eg. increase in tensile strength and hardness) that occurs in certain metals at atmospheric temperature after heat treatment.

Agitation of Parts - The irregular movement given to parts when they have been submerged in a plating or rinse solution.

Air Agitation - The agitation of a liquid medium through the use of air pressure injected into the liquid.

Air Flotation - See Flotation

Air Pollution - The presence in the outdoor (ambient) atmosphere of one air pollutants or any combination thereof in such quantities and of such characteristics and duration as to be, or be likely to be, injurious to public welfare, to the health of human, plant or animal life, or to property, or as unreasonably to interfere with the enjoyment of life and property.

Air-Liquid Interface - The boundary layer between the air and the liquid in which mass transfer is diffusion controlled.

Aldehydes Group - A group of various highly reactive compounds typified by actaldehyde and characterized by the group CHO.

Algicides - Chemicals for preventing the growth of algae.

Alkaline Cleaning - A process for cleaning basis material where mineral and animal fats and oils must be removed from the surface. Solutions at high temperatures containing casutic soda, soda ash, alkaline silicates and alkaline phosphates are commonly used.

Alkalinity - The capacity of water to neutralize acids, a property imparted by the water's content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates.

Alloy Steels - Steels with carbon content between 0.1% to 1.1% and containing elements such as nickel, chromium, molybdenum and vanadium. (The total of all such alloying elements in these type steels is usually less than 5%.)

Aluminizing - Forming an aluminum or aluminum alloy coating on a metal by hot dipping, hot spraying or diffusion.

Amines - A class of organic compounds of nitrogen that may be considered as derived from ammonia ($NH_3$) by replacing one or more of the hydrogen atoms by organic radicals, such as $CH_3$ or $C_6H_5$, as in methylamine and aniline. The former is a gas at ordinary temperature and pressure, but other amines are liquids or solids. All amines are basic in nature and usually combine readily with hydrochloric or other strong acids to form salts.

Anaerobic Biological Treatment - Any waste treatment process utilizing anaerobic or facultative organisms in the absence of air to reduce the organic matter in water.

Anaerobic Digestion - The process of allowing sludges to decompose naturally in heated tanks without a supply of oxygen.

Anaerobic Waste Treatment - (Sludge Processing) Waste stabilization brought about through the action of microorganisms in the absence of air or elemental oxygen.

Anhydrous - Containing no water.

Anions - The negatively charged ions in solution, e.g., hydroxyl.

Annealing - A process for preventing brittleness in a metal part. The process consists of raising the temperature of the metal to a pre-established level and slowly cooling the steel at a prescribed rate.

Annual Capital Recovery Cost - Allocates the initial investment and the interest to the total operating cost. The capital recovery cost is equal to the initial investment multiplied by the capital recovery factor.

Anode - The positively charged electrode in an electrochemical process.

Anodizing - The production of a protective oxide film on aluminum or other light metal by passing a high voltage electric current through a bath in which the metal is suspended.

Aquifer - Water bearing stratum.

Ash - The solid residue left after complete combustion.

Assembly - The fitting together of manufactured parts into a complete machine, structure, or unit of a machine.

Atmospheric Evaporation - Evaporation at ambient pressure utilizing a tower filled with packing material. Air is drawn in from the bottom of the tower and evaporates feed material entering from the top. There is no recovery of the vapors.

Atomic Absorption - Quantitative chemical instrumentation used for the analysis of elemental constituents.

Automatic Plating - 1. Full - Plating in which the workpieces are automatically conveyed through successive cleaning and plating tanks. 2. Semi - Plating in which the workpieces are conveyed automatically through only one plating tank.

Austempering - Heat treating process to obtain greater toughness and ductility in certain high-carbon steels. The process is characterized by interrupted quenching and results in the formation of bainite grain structure.

Austenitizing - Heating a steel to a temperature at which the structure transforms to a solution of one or more elements in face-centered cubic iron. Usually performed as the essential preliminary of heat treatment, in order to get the various alloying elements into solid solution.

Barrel Finishing - The process of polishing a workpiece using a rotating or vibrating container and abrasive grains or other polishing materials to achieve the desired surface appearance.

Barrel Plating - Electroplating of workpieces in barrels (bulk).

Basis Metal or Material - That substance of which the workpieces are made and that receives the electroplate and the treatments in preparation for plating.

Batch Treatment - A waste treatment method where wastewater is collected over a period of time and then treated prior to discharge.

Bending - Turning or forcing by a brake press or other device from a straight or even to a curved or angular condition.

Best Available Technology Economically Achievable (BAT) - Level of technology applicable to effluent limitations to be achieved by 1984 for industrial discharges to surface waters as defined by Section 301(b) (2) (A) of the Act.

Best Practicable Control Technology Currently Available - Level of technology applicable to effluent limitations to be achieved for industrial discharges to surface waters as defined by Section 301 (b) (1) (A) of the Act.

Biochemical Oxygen Demand (BOD) - The amount of oxygen in milligrams per liter used by microorganisms to consume biodegradable organics in wastewater under aerobic conditions.

Biodegradability - The susceptibility of a substance to decomposition by microorganisms; specifically, the rate at which compounds may be chemically broken down by bacteria and/or natural environmental factors.

Blanking - Cutting desired shapes out of sheet metal by means of dies.

Blowdown - The minimum discharge of recirculating water for the purpose of discharging materials contained in the water, the further build-up of which would cause concentration in amounts exceeding limits established by best engineering practice.

BOD5 - The five-day Biochemical Oxygen Demand (BOD5) is the quantity of oxygen used by bacteria in consuming organic matter in a sample of wastewater over a five-day period. BOD from the standard five-day test equals about two-thirds of the total BOD. See Biochemical Oxygen Demand.

Bonding - The process of uniting using an adhesive or fusible ingredient.

Boring - Enlarging a hole by removing metal with a single or occasionally a multiple point cutting tool moving parallel to the axis of rotation of the work or tool. 1. Single-Point Boring - Cutting with a single-point tool. 2. Precision Boring - Cutting to tolerances held within narrow limits. 3. Gun Boring - Cutting of deep holes. 4. Jig Boring - Cutting of high-precision and accurate location holes. 5. Groove Boring - Cutting accurate recesses in hole walls.

Brazing - Joining metals by flowing a thin layer, capillary thickness, of non-ferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term brazing is used where the temperature exceeds 425°C(800°F).

Bright Dipping - The immersion of all or part of a workpiece in a media designed to clean or brighten the surface and leave a protective surface coating on the workpiece.

Brine - An aqueous salt solution.

Broaching - Cutting with a tool which consists of a bar having a single edge or a series of cutting edges (i.e., teeth) on its surface. The cutting edges of multiple-tooth, or successive single-tooth, broaches increase in size and/or change in shape. The broach cuts in a straight line or axial direction when relative motion is produced in relation to the workpiece, which may also be rotating. The entire cut is made in single or multiple passes over the workpiece to shape the required surface contour. 1. Pull Broaching - Tool pulled through or over workpiece. 2. Push Broaching - Tool pushed over or through workpiece. 3. Chain Broaching - A continuous high production surface broach. 4. Tunnel Broaching - Work travels through an enclosed area containing broach inserts.

Bromine Water - A nonmetallic halogen liquid, normally deep red, corrosive and toxic, which is used as an oxidizing agent.

Buffing - An operation to provide a high luster to a surface. The operation, which is not intended to remove much material, usually follows polishing.

Buffing Compounds - Abrasive contained by a liquid or solid binder composed of fatty acids, grease, or tallow. The binder serves as lubricant, coolant, and an adhesive of the abrasive to the buffing wheel.

Burnishing - Finish sizing and smooth finishing of a workpiece (previously machined or ground) by displacement, rather than removal, of minute surface irregularities with smooth point or line-contact, fixed or rotating tools.

Calendering - Process of forming a continuous sheet by squeezing the material between two or more parallel rolls to impart the desired finish or to insure uniform thickness.

Calibration - The application of thermal, electrical, or mechanical energy to set or establish reference points for a part, assembly or complete unit.

Calibration Equipment - Equipment used for calibration of instruments.

Capital Recovery Costs - Allocates the initial investemnt and the interest to the total operating cost. The capital recovery cost is equal to the initial investment multiplied by the capital recovery factor.

Capital Recovery Factor - Capital Recover Factor is defined as: $i + i/(a - 1)$ where $i$ = interest rate, $a = (1 + i)$ to the power $n$, $n$ = interest period in years.

Captive Facility - A facility which owns more than 50 percent (annual area basis) of the materials undergoing metal finishing.

Captive Operation - A manufacturing operation carried out in a facility to support subsequent manufacturing, fabrication, or assembly operations.

Carbides - Usually refers to the general class of pressed and sintered tungsten carbide cutting tools which contain tungsten carbide plus smaller amounts of titanium and tantalum carbides along with cobalt which acts as a binder. (It is also used to describe hard compounds in steels and cast irons.)

Carbon Adsorption - Activated carbon contained in a vessel and installed in either a gas or liquid stream to remove organic contaminates. Carbon is regenerable when subject to steam which forces contaminant to desorb from media.

Carbon Bed Catalytic Destruction - A non-electrolytic process for the catalytic oxidation of cyanide wastes using filters filled with low-temperature coke.

Carbon Steels - Steel which owes its properties chiefly to various percentage of carbon without substantial amounts of other alloying elements.

Carbonate - A compound containing the acid radical of carbonic acid ($CO_3$ group).

Carbonitriding - Process for case or core hardening of metals. The heated metals absorb carbon in a gaseous atmosphere.

Carburizing - (Physical Property Modification) Increasing the carbon content of a metal by heating with a carburizing medium (which may be solid, liquid or gas) usually for the purpose of producing a hardened surface by subsequent quenching.

Carcinogen - Substance which causes cancerous growth.

Case Hardening - A heat treating method by which the surface layer of alloys is made substantially harder than the interior. (Carburizing and nitriding are common ways of case hardening steels.)

Cast - A state of the substance after solidification of the molten substance.

Casthouse - The facility which melts metal, holds it in furnaces for degassing (fluxing) and alloying and then casts the metal into pigs, ingots, billets, rod, etc.

Casting - The operation of pouring molten metal into a mold.

Catalytic Bath - A bath containing a substance used to accelerate the rate of chemical reaction.

Category - Also point source category. A segment of industry for which a set of effluent limitations has been established.

Cathode - The negatively charged electrode in an electrochemical process.

Cation - The positively charged ions in a solution.

Caustic - Capable of destroying or eating away by chemical action. Applies to strong bases and characterized by the presence of hydroxyl ions in solution.

Caustic Soda - Sodium hydroxide, NaOH, whose solution in water is strongly alkaline.

Cementation - The electrochemical reduction of metal ions by contact with a metal of higher oxidation potential. It is usually used for the simultaneous recovery of copper and reduction of hexavalent chromium with the aid of scrap iron.

Centerless Grinding - Grinding the outside or inside of a workpiece mounted on rollers rather than on centers. The workpiece may be in the form of a cylinder or the frustrum of a cone.

Central Treatment Facility - Treatment plant which co-treats process wastewaters from more than one manufacturing operation or co-treats process wastewaters with non-contact cooling water, or with non-process wastewaters (e.g., utility blowdown, miscellaneous runoff, etc.).

Centrifugation - An oil recovery step employing a centrifuge to remove water from waste oil.

Centrifuge - A device having a rotating container in which centrifugal force separates substances of differing densities.

Chelated Compound - A compound in which the metal is contained as an integral part of a ring structure and is not readily ionized.

Chelating Agent - A coordinate compound in which a central atom (usually a metal) is joined by covalent bonds to two or more other molecules or ions (called ligands) so that heterocyclic rings are formed with the central (metal) atom as part of each ring. Thus, the compound is suspending the metal in solution.

Chemical Brightening - Process utilizing an addition agent that leads to the formation of a bright plate or that improves the brightness of the deposit.

Chemical Deposition - Process used to deposit a metal oxide on a substrate. The film is formed by hydrolysis of a mixture of chlorides at the hot surface of the substrate. Careful control of the water mixture insures that the oxide is formed on the substrate surface.

Chemical Etching - To dissolve a part of the surface of a metal or all of the metal laminated to a base.

Chemical Machining - Production of derived shapes and dimensions through selective or overall removal of metal by controlled chemical attack or etching.

Chemical Metal Coloring - The production of desired colors on metal surfaces by appropriate chemical or electrochemical action.

Chemical Milling - Removing large amounts of stock by etching selected areas of complex workpieces. This process entails cleaning, masking, etching, and demasking.

Chemical Oxidation - (Including Cyanide) The addition of chemical agents to wastewater for the purpose of oxidizing pollutant material.

Chemical Oxygen Demand (COD) - The amount of oxygen in milligrams per liter to oxidize both organic and oxidizable inorganic compounds.

Chemical Precipitation - A chemical process in which a chemical in solution reacts with another chemical introduced to that solution to form a third substance which is partially or mainly insoluble and, therefore, appears as a solid.

Chemical Recovery Systems - Chemical treatment to remove metal or other materials from wastewater for later reuse.

Chemical Reduction - A chemical reaction in which one or more electrons are transferred to the chemical being reduced from the chemical initiating the transfer (reducing agent).

Chemical Treatment - Treating contaminated water by chemical means.

Chip Dragout - Cutting fluid or oil adhering to metal chips from a machining operation.

Chlorinated Hydrocarbons - Organic compounds containing chlorine such as many insecticides.

Chlorination - The application of chlorine to water generally for purposes of disinfection, but frequently for accomplishing other biological or chemical results.

Chromate Conversion Coating - Protective coating formed by immersing metal in an aqueous acidified solution consisting substantially of chromic acid or water soluble salts of chromic acid together with various catalysts or activators.

Chromatizing - To treat or impregnate with a chromate (salt of ester of chromic acid) or dichromate, especially with potassium dichromate.

Chrome-Pickle Process - Forming a corrosion-resistant oxide film on the surface of magnesium base metals by immersion in a bath of an alkaline bichromate.

Clarification - The composite wastewater treatment process consisting of flash mixing of coagulants, pH adjusting chemicals, and/or polyelectrolytes, flocculation, and sedimentation.

Clarifier - A unit which provides for settling and removal of solids from wastewater.

Cleaning - The removal of soil and dirt (including grit and grease) from a workpiece using water with or without a detergent or other dispersing agent.

See Vapor Degreasing
Solvent Cleaning
Contaminant Factor
Acid Cleaning
Emulsion Cleaning
Alkaline Cleaning
Salt Bath Descaling
Pickling
Passivate
Abrasive Blast Cleaning
Sonic and Ultrasonic Cleaning

Closed-Loop Evaporation System - A system used for the recovery of chemicals and water from a chemical finishing process. An evaporator concentrates flow from the rinse water holding tank. The concentrated rinse solution is returned to the bath, and distilled water is returned to the final rinse tank. The system is designed for recovering 100 percent of chemicals normally lost in dragout for reuse in the process.

Closed Loop Rinsing - The recirculation of rinse water without the introduction of additional makeup water.

Coagulation - A chemical reaction in which polyvalent ions neutralize the repulsive charges surrounding colloidal particles.

Coating See Aluminum Coating
Hot Dip Coating
Ceramic Coating
Phosphate Coating
Chromate Conversion Coating
Rust-Preventive Compounds
Porcelain Enameling

COD - See Chemical Oxygen Demand

Cold Drawing - A process of forcing material through dies or other mandrels to produce wire, rod, tubular and some bars.

Cold Heading - A method of forcing metal to flow cold into enlarged sections by endwise squeezing. Typical coldheaded parts are standard screws, bolts under 1 in. diameter and a large variety of machine parts such as small gears with stems.

Cold Rolling - A process of forcing material through rollers to produce bars and sheet stock.

Colorimetric - A procedure for establishing the concentration of impuritites in water by comparing its color to a set of known color impurity standards.

Common Metals - Copper, nickel, chromium, zinc, tin, lead, cadmium, iron, aluminum, or any combination thereof.

Compatible Pollutants - Those pollutants which can be adequately treated in publicly-owned treatment works without upsetting the treatment process.

Complexing Agent - A compound that will join with a metal to form an ion which has a molecular structure consisting of a central atom (the metal) bonded to other atoms by coordinate covalent bonds.

Composite Wastewater Sample - A combination of individual samples of water or wastewater taken at selected intervals, generally hourly for some specified period, to minimize the effect of the variability of the individual sample. Individual samples may have equal volume or may be proportioned to the flow at time of sampling.

Conductance - See Electrical Conductivity.

Conductivity Surface - A surface that can transfer heat or electricity.

Conductivity Meter - An instrument which displays a quantitative indication of conductance.

Contact Water - See Process Wastewater.

Contamination - Intrusion of undesirable elements.

Continuous Treatment - Treatment of waste streams operating without interruption as opposed to batch treatment; sometimes referred to as flow=through treatment.

Contractor Removal - Disposal of oils, spent solutions, or sludge by a scavenger service.

Conversion Coating - A coating produced by chemical or electrochemical treatment of a metallic surface that gives a superficial layer containing a compound of the metal. For example, chromate coating on zinc and cadmium, oxide coatings on steel.

Coolant - See Cutting Fluids.

Cooling Water - Water which is used to absorb and transport heat generated in a process or machinery.

Copper Flash - Quick preliminary deposition of copper for making surface acceptable for subsequent plating.

Coprecipitation of Metals - Precipitation of a metal with another metal.

Corrosion Resistant Steels - A term often used to describe the stainless steels with high nickel and chromium alloy content.

Cost of Capital - Capital recovery costs minus the depreciation.

Counterboring - Removal of material to enlarge a hole for part of its depth with a rotary, pilot guided, end cutting tool having two or more cutting lips and usually having straight or helical flutes for the passage of chips and the admission of a cutting fluid.

Countercurrent Rinsing - Rinsing of parts in such a manner that the rinse water is removed from tank to tank counter to the flow of parts being rinsed.

Countersinking - Beveling or tapering the work material around the periphery of a hole creating a concentric surface at an angle less than 90 degrees with the centerline of the hole for the purpose of chamfering holes or recessing screw and rivet heads.

Crystalline Solid - A substance with an ordered structure, such as a crystal.

Crystallization - 1. Process used to manufacture semiconductors in the electronics industry. 2. A means of concentrating pollutants in wastewaters by crystallizing out pure water.

Curcumine or Carmine Method - A standard method of measuring the concentration of boron (B) within a solution.

Cutting Fluids - Lubricants employed to ease metal and machining operations, produce surface smoothness and extend tool life by providing lubricity and cooling. Fluids can be emulsified oils in water, straight mineral oils when better smoothness and accuracy are required, or blends of both.

Cyaniding - A process of case hardening an iron-base alloy by the simultaneous absorption of carbon and nitrogen by heating in a cyanide salt. Cyaniding is usually followed by quenching to produce a hard case.

Cyclone Separator - A device which removes entrained solids from gas streams.

Dead Rinse - A rinse step in which water is not replenished or discharged.

Deburring - Removal of burrs or sharp edges from parts by filing, grinding or rolling the work in a barrel with abrasives suspended in a suitable medium.

Deep Bed Filtration - The common removal of suspended solids from wastewater streams by filtering through a relatively deep (0.3-0.9 m) granular bed. The porous bed formed by the granular media can be designed to remove practically all suspended particles by physical-chemical effects.

Degassing - (Fluxing) The removal of hydrogen and other impurities from molten primary aluminum in a casthouse holding furnace by injecting chlorine gas (often with nitrogen and carbon).

Degradable - That which can be reduced, broken down or chemically separated.

Demineralization - The removal from water of mineral contaminants usually present in ionized form. The methods used include ion-exchange techniques, flash distillation or electrolysis.

Denitrification (Biological) - The reduction of nitrates to nitrogen gas by bacteria.

Deoxidizing - The removal of an oxide film from an alloy such as aluminum oxide.

Depreciation - Decline in value of a capital asset caused either by use or by obsolescence.

Descaling - The removal of scale and metallic oxides from the surface of a metal by mechanical or chemical means. The former includes the use of steam, scale-breakers and chipping tools, the latter method includes pickling in acid solutions.

Desmutting - The removal of smut (matter that soils or blackens) generally by chemical action.

Dewatering - (Sludge Processing) Removing water from sludge.

Diaminobenzidene - A chemical used in the standard method of measuring the concentrations of selenium in a solution.

Dibasic Acid - An acid capable of donating two protons (hydrogen ions).

Dichromate Reflux - A standard method of measuring the chemical oxygen demand of a solution.

Die Casting - (hot chamber, vacuum, pressure) Casting are produced by forcing molten metal under pressure into metal mold called dies. In hot chamber machines, the pressure cylinder is submerged in the molten metal resulting in a minimum of time and metal cooling during casting. Vacuum feed machines use a vacuum to draw a measured amount of melt from the molten bath into the feed chamber. Pressure feed systems use a hydraulic or pneumatic cylinder to feed molten metal to the die.

Digestion - A standard method of measuring organic nitrogen.

Dipping - Material coating by briefly immersing parts in a molten bath, solution or suspension.

Direct Labor Costs - Salaries, wages and other direct compensations earned by the employee.

Discharge of Pollutant(s) - 1. The addition of any pollutant to navigable waters from any point source. 2. Any addition of any pollutant to the waters of the continguous zone or the ocean from any point source, other than from a vessel or other floating craft. The term "discharge" includes either the discharge of a single pollutant or the discharge of multiple pollutants.

Dispersed-air Flotation - Separation of low density contaminants from water using minute air bubbles attached to individual particles to provide or increase the buoyancy of the particle. The bubbles are generated by introducing air through a revolving impeller or porous media.

Dissolved-air Floatation - Separation of low density contaminants from water using minute air bubbles attached to individual particles to provide or increase the buoyancy of the particle. The air is put into solution under elevated pressure and later released under atmospheric pressure or put into solution by aeration at atmospheric pressure and then released under a vacuum.

Dissolved Oxygen (DO) - The oxygen dissolved in sewage, water, or other liquid, usually expressed in milligrams per liter or percent of saturation. It is the test used in BOD determination.

Distillation - Vaporization of a liquid followed by condensation of the vapor.

Distillation Refining - A metal with an impurity having a higher vapor pressure than the base metal can be refined by heating the metal to the point where the impurity vaporizes.

Distillation-Silver Nitrate Titration - A standard method of measuring the concentration of cyanides in a solution.

Distillation-SPADNS - A standard method of measuring the concentration of fluoride in a solution.

Dollar Base - A period in time in which all costs are related. Investment costs are related by the Sewage Treatment Plant Construction Cost Index. Supply costs are related by the "Industrial Commodities" Wholesale Price Index.

Drag-in - Water or solution carried into another solution by the work and the associated handling equipment.

Dragout - The solution that adheres to the objects removed from a bath, more precisely defined as that solution which is carried past the edge of the tank.

Dragout Reduction - Minimization of the amount of material (bath or solution) removed from a process tank by adherring to the part or its transfer device.

Drainage Phase - Period in which the excess plating solution adhering to the part or workpiece is allowed to drain off.

Drawing - Reduction of cross section area and increasing the length by pulling metal through conical taper dies.

Drawing Compounds - See Wire Forming Lubricants.

Drilling - Hole making with a rotary, end-cutting tool having one or more cutting lips and one or more helical or straight flutes or tubes for the ejection of chips and the passage of a cutting fluid. 1. Center Drilling - Drilling a conical hole in the end of a workpiece. 2. Core Drilling - Enlarging a hole with a chamer-edged, multiple-flute drill. 3. Spade Drilling - Drilling with a flat blade drill tip. 4. Step Drilling - Using a multiple diameter drill. 5. Gun Drilling - Using special straight flute drills with a single lip and cutting fluid at high pressures for deep hole drilling. 6. Oil Hole or Pressurized Coolant Drilling - Using a drill with one or more continuous holes through its body and shank to permit the passage of a high pressure cutting fluid which emerges at the drill point and ejects chips.

Drip Station - Empty tank over which parts are allowed to drain freely to decrease end dragout.

Drip Time - The period during which a part is suspended over baths in order to allow the excessive dragout to drain off.

Drying Beds - Areas for dewatering of sludge by evaporation and seepage.

EDTA Titration - EDTA - ethylenediamine tetraacetic acid ( or its salts). A standard method of measuring the hardness of a solution.

Effluent - The water and the quantities, rates, and concentrations of chemical, physical, biological, and other constituents which are discharged from point sources.

Effluent Limitation - Any restriction (including schedules of compliance) established by a state or the federal EPA on quantites, rates, and concentrations of chemical, physical, biological, and other constituents which are discharged from point sources into naviigable waters, the waters of the contiguous zone, or the ocean.

Electrical Conductivity - The property which allows an electric current to flow when a potential difference is applied. It is the reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature. It is expressed as micromhos per centimeter at temperature degrees Celsius.

Electrical Discharge Machining - Metal removal by a rapid spark discharge between different polarity electrodes, one the workpiece and the other the tool separated by a gap distance of 0.0005 in. to 0.035 in. The gap is filled with dielectric fluid and metal particles which are melted, in part vaporized and expelled from the gap.

Electrobrightening - A process of reversed electro-deposition which results in anodic metal taking a high polish.

Electrochemical Machining (ECM) - A machining process whereby the part to be machined is made the anode and a shaped cathode is maintained in close proximity to the work. Electrolyte is pumped between the electrodes and a potential applied with the result that metal is rapidly dissolved from the workpiece in a selective manner and the shape produced on the workpiece complements that of the cathode.

Electrocleaning - The process of anodic removal of surface oxides and scale from a workpiece.

Electrode - Conducting material for passing electric current into or out of a solution by adding electrons to or taking electrons from ions in the solution.

Electrodialysis - A treatment process that uses electrical current and and arrangement of permeable membranes to separate soluble minerals from water. Often used to desalinate salt or brackish water.

Electroless Plating - Deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited.

Electrolysis - The chemical decomposition by an electric current of a substance in a dissolved or molten state.

Electrolyte - A liquid, most often a solution, that will conduct an electric current.

Electrolytic Cell - A unit apparatus in which electrochemical reactions are produced by applying electrical energy or which supplies electrical energy as a result of chemical reactions and which includes two or more electrodes and one or more electrolytes contained in a suitable vessel.

Electrolytic Decomposition - An electrochemical treatment used for the oxidation of cyanides. The method is practical and economical when applied to concentrated solutions such as contaminated baths, cyanide dips, stripping solutions, and concentrated rinses. Electrolysis is carried out at a current density of 35 amp/sq. ft. at the anode and 70 amp/sq. ft. at the cathode. Metal is deposited at the cathode and can be reclaimed.

Electrolytic Oxidation - A reaction by an electrolyte in which there is an increase in valence resulting from a loss of electrons.

Electrolytic Reduction - A reaction in which there is a decrease in valence resulting from a gain in electrons.

Electrolytic Refining - The method of producing pure metals by making the impure metal the anode in an electrolytic cell and depositing a pure cathode. The impurities either remain undissolved at the anode or pass into solutions in the electrolyte.

Electrometallurgical Process - The application of electric current to a metallurgical process either for electrolytic deposition or as a source of heat.

Electrometric Titration - A standard method of measuring the alkalinity of a solution.

Electron Beam Machining - The process of removing material from a workpiece by a high velocity focused stream of electrons which melt and vaporize the workpiece at the point of impingerent.

Electroplating - The production of a thin coating of one metal on a surface by electrodeposition.

Electropolishing - Electrolytic corrosion process that increases the percentage of specular reflectance from a metallic surface.

Embossing - Raising a design in relief against a surface.

Emulsified Oil and Grease - An oil or grease dispersed in an immiscible liquid usually in droplets of larger than colloidal size. In general suspension of oil or grease within another liquid (usually water).

Emulsifying Agent - A material that increases the stability of a dispersion of one liquid in another.

Emulsion Breaking - Decreasing the stability of dispersion of one liquid in another.

Emulsion Cleaning - A cleaning process using organic solvents dispersed in an aqueous medium with the aid of an emulsifying agent.

End-of-Pipe Treatment - The reduction and/or removal of pollutants by treatment just prior to actual discharge.

Environmental Protection Agency - the United States Environmental Protection Agency.

EPA - See Environmental Protection Agency.

Equalization - (Continuous Flow) - The balancing of flow or pollutant load using a holding tank for a system that has widely varying inflow rates.

Equilibrium Concentration - A state at which the concentration of chemicals in a solution remain in a constant proportion to one another.

Ester - An organic compound corresponding in structure to a salt in inorganic chemistry. Esters are considered as derived from the acids by the exchange of the replaceable hydrogen of the latter for an organic alkyl radical. Esters are not ionic compounds, but salts usually are.

Etchant - The material used in the chemical process of removing glass fibers and epoxy between neighboring conductor layers of a PC board for a given distance.

Etching - A process where material is removed by chemical action.

Evaporation Ponds - Liquid waste disposal areas that allow the liquid to vaporize to cool discharge water temperatures or to thicken sludge.

Excess Capacity Factor - A multiplier on process size to account for shutdown for cleaning and maintenance.

Extrusion - A material that is forced through a die to form lengths of rod, tube or special sections.

4-AAP Colorimetric - A standard method of measurement for phenols in aqueous solutions.

Fermentation - A chemical change to break down biodegradable waste. The change is induced by a living organism or enzyme, specifically bacteria or microorganisms occurring in unicellular plants such as yeast, molds, or fungi.

Ferrite - A solid solution in which alpha iron is present.

Ferrous - Relating to or containing iron.

Filtrate - Liquid after passing through a filter.

Filtration - Removal of solid particles from liquid or particles from air or gas stream by means of a permeable membrane. Types: Gravity, Pressure, Microstraining, Ultrafiltration, Reverse Osmosis (Hyperfiltration).

Flameless Atomic Absorption - A method of measuring low concentration values of certain metals in a solution.

Flame Hardened - Surface hardened by controlled torch heating followed by quenching with water or air.

Flame Spraying - The process of applying a metallic coating to a workpiece whereby finely powdered fragments or wire, together with suitable fluxes, are projected through a cone of flame onto the workpiece.

Flash Evaporation - Evaporation using steam heated tubes with feed material under high vacuum. Feed material "flashes off" when it enters the evaporation chamber.

Flocculation - The process of separating suspended solids from wastewater by chemical creation of clumps or flocs.

Flotation - The process of removing finely divided particles from a liquid suspension by attaching gas bubbles to the particles, increasing their buoyancy, and thus concentrating them at the surface of the liquid medium.

Fluxing - (Degassing) The removal of oxides and other impurities from molten primary aluminum in a casthouse holding furnace by injecting chlorine gas (often with nitrogen and carbon monoxide).

Fog - A type of rinse consisting of a fine spray.

Forming Compounds (Sheet) - Tightly adhering lubricants composed of fatty oils, fatty acids, soaps, and waxes and designed to resist the high surface temperatures and pressures the metal would otherwise experience in forming.

Forming Compounds (Wire) - Tightly adhering lubricants composed of solids (white lead, talc, graphite, or molybdenum disulfide) and solible oils for cooling and corrosion protection. Lubricants typically contain sulfur, chlorine, or phsophate additives.

Free Cyanide - 1. True - the actual concentration of cyanide radical or equivalent alkali cyanide not combined in complex ions with metals in solutions. 2. Calculated - the concentration of cyanide or alkali cyanide present in solution in excess of that calculated as necessary to form a specified complex ion with a metal or metals present in solution. 3. Analytical - the free cyanide content of a solution as determined by a specified analytical method.

Freezing/Crystallization - The solidification of a liquid into aggregations of regular geometric forms (crystals) accomplished by subtraction of heat from the liquid. This process can be used for removal of solids, oils, greases, and heavy metals from industrial wastewater.

Galvanizing - The deposition of zinc on the surface of steel for corrosion protection.

Gas Carburizing - The introduction of carbon into the surface layers of mill steel by heating in a current of gas high in carbon.

Gas Chromotagrophy - Chemical analytical instrumentation generally used for quantitative organic analysis.

Gas Nitriding - Case hardening metal by heating and diffusing nitrogen gas into the surface.

Gas Phase Separation - The process of separating volatile constituents from water by the application of selective gas permeable membranes.

Gear Forming - Process for making small gears by rolling the gear material as it is pressed between hardened gear shaped dies.

Glass Fiber Filtration - A standard method of measuring total suspended solids.

Good Housekeeping - (In-Plant Technology) Good and proper maintenance minimizing spills and upsets.

GPD - Gallons per day.

Grab Sample - A single sample of wastewater taken without regard to time or flow.

Gravimetric 103-105C - A standard method of measuring total solids in aqueous solutions.

Gravimetric 550C - A standard method of measuring total volatile solids in aqueous solutions.

Gravity Filtration - Settling of heavier and rising of lighter constituents within a solution.

Gravity Flotation - The separation of water and low density contaminants such as oil or grease by reduction of the wastewater flow velocity and turbulence for a sufficient time to permit separation due to difference in specific gravity. The floated material is removed by some skimming technique.

Gray Cast Irons - Alloys primarily of iron, carbon and silicon along with other alloying elements in which the graphite is in flake form. (These irons are characterized by low ductility but have many other properties such as good castability and good damping capacity.)

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

**Grease Skimmer** - A device for removing floating grease or scum from the surface of wastewater in a tank.

**Grinding** - The removal of stock from a workpiece by use of abrasive grains held by a rigid or semi rigid binder. 1. Surface Grinding - Producing a flat surface with a rotating grinding wheel as the workpiece passes under the wheel. 2. Cylindrical Grinding - Grinding the outside diameters of cylindrical workpieces held between centers. 3. Internal Grinding - Grinding the inside of a rotating workpiece by use of a wheel spindle which rotates and reciprocates through the length of depth of the hole being ground.

**Grinding Fluids** - Water based, straight oil, or synthetic based lubricants containing mineral oils, soaps, or fatty materials lubricants serve to cool the part and maintain the abrasiveness of the grinding wheel face.

**Hammer Forging** - Heating and pounding metal to shape it into the desired form.

**Hardened** - Designates condition produced by various heat treatments such as quench hardening, age hardening and precipitation hardening.

**Hardness** - A characteristic of water, imparted by salts of calcium, magnesium and iron such as bicarbonates, carbonates, sulfates, chlorides and nitrates, that cause curdling of soap, deposition of scale, damage in some industrial processes and sometimes objectionable taste. It may be dtermined by a standard laboratory procedure or computed from the amounts of calcium and magnesium as well as iron, aluminum, manganese, barium, strontium, and zinc and is expressed as equivalent calcium carbonate.

**Heading** - (Material forming) Upsetting wire, rod or bar stock in dies to form parts having some of the cross-sectional area larger than the original. Examples are bolts, rivets and screws.

**Heat Resistant Steels** - Steel with high resistance to oxidation and moderate strength at high temperatures above 500 Degrees C.

Heat Treatment - The modification of the physical properties of a workpiece through the application of controlled heating and cooling cycles. Such operations are heat treating, tempering, carburizing, cyaniding, nitriding, annealing, normalizing, austenizing, quenching, austempering, siliconizing, martempering, and malleabilizing are included in this definition.

Heavy Metals - Metals which can be precipitated by hydrogen sulfide in acid solution, e.g., lead, silver, gold, mercury, bismuth, copper, nickel, iron, chromium, zinc, cadmium, and tin.

High Energy Forming - Processes where parts are formed at a rapid rate by using extremely high pressures. Examples: Explosive forming, Electrohydraulic forming.

High Energy Rate Forging (HERF) - A closed die process where hot or cold deforming is accomplished by a high velocity ram.

Hobbing - Gear cutting by use of a tool resembling a worm gear in appearance, having helically-spaced cutting teeth. In a single-thread hob, the rows of teeth advance exactly one pitch as the hob makes one revolution. With only one hob, it is possible to cut interchangeable gears of a given pitch of any number of teeth within the range of the hobbing machine.

Honing - A finishing operation using fine grit abrasive stones to produce accurate dimensions and excellent finish.

Hot Compression Molding - (Plastic Processing) A technique of thermoset molding in which preheated molding compound is closed and heat and pressure (in the form of a downward moving ram) are applied until the material has cured.

Hot Dip Coating - The process of coating a metallic workpiece with another metal by immersion in a molten bath to provide a protective film.

Hot Rolled - A term used to describe alloys which are rolled at temperatures above the recrystallization temperature. (Many alloys are hot rolled, and machinability of such alloys may vary because of differences in cooling conditions from lot to lot.

Hot Stamping - Engraving operation for marking plastics in which roll leaf is stamped with heated metal dies onto the face of the plastics. Ink compounds can also be used.

Hot Upset Forging - The diameter is locally increased i.e. to upset the head of a bolt, the end of the barstock is heated and then deformed by an axial blow often into a suitably shaped die.

Hydrofluoric Acid - Hydrogen fluoride in aqueous solution.

Hydrogen Embrittlement - Embrittlement of a metal or alloy caused by absorption of hydrogen during a pickling, cleaning, or plating process.

Hydrometallurgical Process - The treatment of ores by wet processes such as leaching.

Hydrophilic - A surface having a strong affinity for water or being readily wettable.

Hydrophobic - A surface which is non-wettable or not readily wettable.

Hydrostatic Pressure - The force per unit area measured in terms of the height of a column of water under the influence of gravity.

Immersed Area - Total area wetted by the solution or plated area plus masked area.

Immersion Plate - A metallic deposit produced by a displacement reaction in which one metal displaces another from solution, for example: $Fe + Cu(+2) = Cu + Fe(+2)$

Impact Deformation - The process of applying impact force to a workpiece such that the workpiece is permanently deformed or shaped. Impact deformation operations such as shot peening, peening, forging, high energy forming, heading, or stamping.

Incineration - (Sludge Disposal) The combustion (by burning) of organic matter in wastewater sludge after dewatering by evaporation.

Incompatible Pollutants - Those pollutants which would cause harm to, adversely affect the performance of, or be inadequately treated in publicly-owned treatment works.

Independent Operation - Job shop or contract shop in which electroplating is done on workpieces owned by the customer.

Indirect Labor Costs - Labor-related costs paid by the employer other than salaries, wages and other direct compensation such as social security and insurance.

Induction Hardened - Surface or through hardened using induction heating followed by quenching with water or air.

Industrial User - Any industry that introduces pollutants into public sewer systems and whose wastes are treated by a publicly-owned treatment facility.

Industrial Wastes - The liquid wastes from industrial processes, as distinct from domestic or sanitary wastes.

Inhibition - The slowing down or stoppage of chemical or biological reactions by certain compounds or ions.

In-Process Control Technology - The regulation and the conservation of chemicals and the reduction of water usage throughout the operations as opposed to end-of-pipe treatment.

Inspection - A checking or testing of something against standards or specification.

Intake Water - Gross water minus reuse water.

Integrated Chemical Treatment - A waste treatment method in which a chemical rinse tank is inserted in the plating line between the process tank and the water rinse tank. The chemical rinse solution is continuously circulated through the tank and removes the dragout while reacting chemicals with it.

Integrated Circuit (IC) - 1. A combination of interconnected circuit elements inseparably associated on or within a continuous substrate. 2. Any electronic device in which both active and passive elements are contained in a single package. Methods of making an integrated circuit are by masking process, screening and chemical deposition.

Intraforming - A method of forming by means of squeezing.

Investment Costs - The capital expenditures required to bring the treatment or control technology into operation.

Ion Exchange - A reversible chemical reaction between a solid (ion exchanger) and a fluid (usually a water solution) by means of which ions may be interchanged from one substance to another. The superficial physical structure of the solid is not affected.

Ion Exchange Resins - Synthetic resins containing active groups (usually sulfonic, carboxylic, phenol, or substituted amino groups) that give the resin the property of combining with or exchanging ions between the resin and a solution.

Ion-Flotation Technique - Treatment for electroplating rinse waters (containing chromium and cyanide) in which ions are separated from solutions by flotation.

Iridite Dip Process - Dipping process for zinc or zinc-coated objects that deposits protective film that is a chromium gel, chromium oxide, or hydrated chromium oxide.

Isolation - Segregation of a waste for separate treatment and/or disposal.

Job Shop - A facility which owns not more than 50 percent (annual area basis) of the materials undergoing metal finishing.

Kiln - (Rotary) A large cylindrical mechanized type of furnace.

Kinematic Viscosity - The viscosity of a fluid divided by its density. The C.G.S. unit is the stoke (cm2/sec).

Knurling - Impressing a design into a metallic surface, usually by means of small, hard rollers that carry the corresponding design on their surfaces.

Lagoon - A man-made pond or lake for holding wastewater for the removal of suspended solids. Lagoons are also used as retention ponds, after chemical clarification to polish the effluent and to safeguard against upsets in the clarifier; for stabilization of organic matter by biological oxidation; for storage of sludge; and for cooling of water.

Laminate - 1. A composite metal, wood or plastic usually in the form of sheet or bar, composed of two or more layers so bonded that the composite forms a structural member. 2. To form a product of two or more bonded layers.

Landfill - Disposal of inert, insoluble waste solids by dumping at an approved site and covering with earth.

Lapping - An abrading process to improve surface quality by reducing roughness, waviness and defects to produce accurate as well as smooth surfaces.

Laser Beam Machining - Use of a highly focused mono-frequency collimated beam of light to melt or sublime material at the point of impingement on a workpiece.

Leach Field - A area of ground to which wastewater is discharged. Not considered an acceptable treatment method for industrial wastes.

Leaching - Dissolving out by the action of a percolating liquid, such as water, seeping through a landfill.

Ligands - The molecules attached to the central atom by coordinate covalent bonds.

Liquid/Liquid Extraction - A process of extracting or removing contaminant(s) from a liquid by mixing contaminated liquid with another liquid which is immiscible and which has a higher affinity for the contaminating substance(s).

Liquid Nitriding - Process of case hardening a metal in a molten cyanide bath.

Liquid Phase Refining - A metal with an impurity possessing a lower melting point is refined by heating the metal to the point of melting of the low temperature metal. It is separated by sweating out.

Machining - The process of removing stock from a workpiece by forcing a cutting tool through the workpiece removing a chip of basis material. Machining operations such as turning, milling, drilling, boring, tapping, planing, broaching, sawing and filing, and chamfering are included in this definition.

Maintenance - The upkeep of property or equipment.

Malleablizing - Process of annealing brittle white cast iron in such a way that the combined carbon is wholly or partly transformed to graphitic or temper carbon nodules in a ferritic or pearlitic microstructure, thus providing a ductile and machinable material.

Manual Plating - Plating in which the workpieces are conveyed manually through successive cleaning and plating tanks.

Maraged - Describes a series of heat treatments used to treat high strength steels of complex composition (maraging steels) by aging of martensite.

Martensite - An acicular or needlelike microstructure that is formed in quenched steels. (It is very hard and brittle in the quenched form and, therefore, is usually tempered before being placed into service. The harder forms of tempered martensite have poorer machinability.)

Martempering - Quenching an austentized ferrous alloy in a medium at a temperature in the upper part of the martensite range, or slightly above that range, and holding it in the medium until the temperature throughout the alloy is substantially uniform. The alloy is then allowed to cool in air through the martensite range.

Masking - The application of a substance to a surface for the prevention of plating to said area.

Material Modification - (In-Plant Technology) Altering the substance from which a part is made.

Mechanical Agitation - The agitation of a liquid medium through the use of mechanical equipment such as impellers or paddles.

Mechanical Finish - Final operations on a product performed by a machine or tool. See: Polishing, Buffing, Barrel Finishing, Shot Peening, Power Brush Finishing.

Mechanical Plating - Providing a coating wherein fine metal powders are peened onto the part by tumbling or other means.

Membrane - A thin sheet of synthetic polymer through the apertures of which small molecules can pass, while larger ones are retained.

Membrane Filtration - Filtration at pressures ranging from 50 to 100 psig with the use of membranes or thin films. The membranes have accurately controlled pore sites and typically low flux rates.

Metal Ion - An atom or radical that has lost or gained one or more electrons and has thus acquired an electric charge. Positively charged ions are cations, and those having a negative charge are anions. An ion often has entirely diffemt properties from the element (atom) from which it was formed.

Metal Oxidation Refining - A refining technique that removes impurities from the base metal because the impurity oxidizes more readily than the base. The metal is heated and oxygen supplied. The impurity upon oxidizing separates by gravity or volatilizes.

Metal Paste Production - Manufacture of metal pastes for use as pigments by mixing metal powders with mineral spirits, fatty acids and solvents. Grinding and filtration are steps in the process.

Metal Powder Production - Production of metal particles for such uses as pigments either by milling and grinding of scrap or by atomization of molten metal.

Metal Spraying - Coating metal objects by spraying molten metal upon the surface with gas pressure.

Microstraining - A process for removing solids from water, which consists of passing the water stream through a microscreen with the solids being retained on the screen.

Milling - Using a rotary tool with one or more teeth which engage the workpiece and remove material as the workpiece moves past the rotating cutter. 1. Face Milling - Milling a surface perpendicular cutting edges remove the bulk of the material while the face cutting edges provide the finish of the surface being generated. 2. End Milling - Milling accomplished with a tool having cutting edges on its cylindrical sufaces as well as on its end. In end milling - peripheral, the peripheral cutting edges on the cylindrical surface are used; while in end milling-slotting, both end and peripheral cutting edges remove metal. 3. Slide and Slot Milling - Milling of the side or slot of a workpiece using a peripheral cutter. 4. Slab Milling - Milling of a surface parallel to the axis of a helical, multiple-toothed cutter mounted on an arbor. 5. Straddle Milling - Peripheral milling a workpiece on both sides at once using two cutters spaced as required.

Molecule - Chemical units composed of one or more atoms.

Monitoring - The measurement, sometimes continuous, of water quality.

Multi-Effect Evaporator - A series of evaporations and condensations with the individual units set up in series and the latent heat of vaporization from one unit used to supply energy for the next.

Multiple Operation Machinery - Two or more tools are used to perform simultaneous or consecutive operations.

Multiple Subcategory Plant - A plant discharging process wastewater from more than one manufacturing process subcategory.

National Pollutant Discharge Elimination System (NPDES) - The federal mechanism for regulating point source discharge by means of permits.

Navigable Waters - All navigable waters of the United States; tributaries of navigable waters of the United States; interstate waters,intrastate lakes, rivers and streams which are utilized for recreational or other purposes.

Neutralization - Chemical addition of either acid or base to a solution such as the pH is adjusted to 7.

New Source - Any building, structure, facility, or installation from which there is or may be the discharge of pollutants, the construction of which is commenced after the publication of proposed regulations prescribing a standard of performance under Section 306 of the Act which will be applicable to such source if such standard is thereafter promulgated in accordance with Section 306 of the Act.

Nitriding - A heat treating method in which nitrogen is diffused into the surface of iron-base alloys. (This is done by heating the metal at a temperature of about 950 degrees F in contact with ammonia gas or other suitable nitrogenous materials. The surface, because of formation of nitrides becomes much harder than the interior. Depth of the nitrided surface is a function of the length of time of exposure and can vary from .0005" to .032" thick. Hardness is generally in the 65 to 70 Rc range, and, therefore, these structures are almost always ground.)

Nitriding Steels - Steels which are selected because they form good case hardened structures in the nitriding process. ( In these steels, elements such as aluminum and chromium are important for producing a good case.)

Nitrification (Biological) - The oxidation of nitrogenous matter into nitrates by bacteria.

Noble Metals - Metals below hydrogen in the electromotive force series; includes antimony, copper, rhodium, silver, gold, bismuth.

Noncontact Cooling Water - Water used for cooling which does not come into direct contact with any raw material, intermediate product, waste product, or finished product.

Nonferrous - No iron content.

Non-Water Quality Environmental Impact - The ecological impact as a result of solid, air, or thermal pollution due to the application of various wastewater technologies to achieve the effluent guidelines limitations. Associated with the non-water quality aspect is the energy impact of wastewater treatment.

Normalizing - Heat treatment of iron-base alloys above the critical temperature, followed by cooling in still air. (This is often done to refine or homogenize the grain structure of castings, forgings and wrought steel products.)

Notching - Cutting out various shapes from the edge or side of a sheet, strip, blank or part.

NPDES - See National Pollutant Discharge Elimination System.

Oil Cooker - Open-topped vessel contining a heat source and typically maintained at 68°C (180°F) for the purpose of driving off excess water from waste oil.

Operation and Maintenance Costs - The cost of running the wastewater treatment equipment. This includes labor costs, material and supply costs, and energy and power costs.

Organic Compound - Any substance that contains the element carbon, with the exception of carbon dioxide and various carbonates.

ORP Recorders - Oxidation-reduction potential recorders.

Oxidants - Those substances which aid in the formation of oxides.

Oxidizable Cyanide - Cyanide amenable to oxidation.

Oxidizing - Combining the material concerned with oxygen.

Paint Stripping - The term "paint stripping" shall mean the process of removing an organic coating from a workpiece or painting fixture. The removal of such coatings using processes such as caustic, acid, solvent and molten salt stripping are included.

Parameter - A characteristic element of constant factor.

Passivation - The changing of the chemically active surface of a metal to a much less reactive state by means of an acid dip.

Patina - A blue green oxidation of copper.

Pearlite - A microstituent found in iron-base alloys consisting of a lamellar (Patelike) composite of ferrite and iron carbide. (This structure results from the decomposition of austenite and is very common in cast irons and annealed steels.)

Peening - Mechanical working of metal by hammer blows or shot impingement.

pH - A unit for measuring hydrogen ion concentrations. A pH of 7 indicates a "neutral" water or solution. A pH lower than 7, a solution is acidic. At pH higher than 7, a solution is alkaline.

pH Buffer - A substance used to stabilize the acidity or alkalinity in a solution.

Phenols - A group of aromatic compounds having the hydroxyl group directly attached to the benzene ring. Phenols can be a contaminant in a waste stream from a manufacturing process.

Phosphate Coating - Process of forming a conversion coating on iron or steel by immersing in a hot solution of manganese, iron or zinc phosphate. Often used on a metal part prior to painting or porcelainizing.

Phosphate - Salts or esters of phosphoric acid.

Phosphatizing - Process of forming rust-resistant coating on iron or steel by immersing in a hot solution of acid manganese, iron or zinc phosphates.

Photoresists - Thin coatings produced from organic solutions which when exposed to light of the proper wave length are chemically changed in their solubility to certain solvents (developers). This substance is placed over a surface which is to be protected during processing such as in the etching of printer circuit boards.

Photosensitive Coating - A chemical layer that is receptive to the action of radiant energy.

Pickling - The immersion of all or part of a workpiece in a corrosive media such as acid to remove scale and related surface coatings.

Planing - Producing flat surfaces by linear reciprocal motion of the work and the table to which it is attached relative to a stationary single-point cutting tool.

Plant Effluent or Discharge After Treatment - The wastewater discharged from the industrial plant. In this definition, any waste treatment device (pond, trickling filter, etc.) is considered part of the industrial plant.

Plasma Arc Machining - The term "plasma arc machining" shall mean the process of material removal or shaping of a workpiece by a high velocity jet of high temperature ionized gas.

Plated Area - Surface upon which an adherent layer of metal is deposited.

Plating - Forming an adherent layer of metal upon an object.

Point Source - Any discernible, confined, and discrete conveyance including, but not limited to, any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft from which pollutants are or may be discharged.

Point Source Category - See Category.

Polishing - The process of removing stock from a workpiece by the action of loose or loosely held abrasive grains carried to the workpiece by a flexible support. Usually, the amount of stock removed in a polishing operation is only incidental to achieving a desired surface finish or appearance.

Polishing Compounds - Fluid or grease stick lubricants composed of animal tallows, fatty acids, and waxes. Selection depends on surface finish desired.

Pollutant - Dredged spoil, solid waste, incinerator residue, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials, heat, wrecked or discarded equipment, rock, sand, cellar dirt and industrial, municipal and agricultural waste discharged into water. It does not mean (1) sewage from vessels or (2) water, gas, or other material which is injected into a well to facilitate production of oil or gas, or water derived in association with oil or gas production and disposed of in a well, if the well, used either to facilitate production or for disposal purposes, is approved by authority of the State in which the well is located, and if such State determines that such injection or disposal will not result in degradation of ground or surface water resources.

Pollutant Parameters - Those constituents of wastewater determinded to be detrimental and, therefore, requiring control.

Pollution - The man-made or man-induced alternation of the chemical, physical, biological, and radiological integrity of water.

Polychlorinated Biphenyl (PCB) - A family of chlorinated biphenyls with unique thermal properties and chemical inertness which have a wide variety of uses as plasticizers, flame retardants and insulating fluids. They represent a persistent contaminant in waste streams and receiving waters.

Polyelectrolyte - A high polymer substance, either natural or synthetic, containing ionic constituents; they may be either cationic or anionic.

Post Curring - Treatment after changing the physical properties of a material by chemical reaction.

Pouring - (Casting and Molding) Transferring molten metal from a furnace or a ladle to a mold.

Power Brush Finishing - This is accomplished (wet or dry) using a wire or nonmetallic-fiber-filled brush used for deburring, edge blending and surface finishing of metals.

Precious Metals - Gold, silver, iridium, palladium, platinum, rhodium, ruthenium, indium, osmium, or combination thereof.

Precipitate - The discrete particles of material rejected from a liquid solution.

Precipitation Hardening Metals - Certain metal compositions which respond to precipitation hardening or aging treatment.

Pressure Deformation - The process of applying force, (other than impact force), to permanently deform or shape a workpiece. Pressure deformation operations may include operations such as rolling, drawing, bending, embossing, coining, swaging, sizing, extruding, squeezing, spinning, seaming, piercing, necking, reducing, forming, crimping, coiling, twisting, winding, flaring or weaving.

Pressure Filtration - The process of solid/liquid phase separation effected by passing the more permeable liquid phase through a mesh which is impenetrable to the solid phase.

Pretreatment - Treatment of wastewaters from sources before introduction into municipal treatment works.

Primary Settling - The first treatment for the removal of settleable solids from wastewater which is passed through a treatment works.

Primary Treatment - The first stage in wastewater treatment in which floating or settleable solids are mechanically removed by screening and sedimentation.

Printed Circuit Boards - A circuit in which the interconnecting wires have been replaced by conductive strips printed, etched, etc., onto an insulating board. Methods of fabrication include etched circuit, electroplating, and stamping.

Printing - A process whereby a design or pattern in ink or types of pigments are impressed onto the surface of a part.

Process Modification - (In-Plant Technology) Reduction of water pollution by basic changes in a manufacturing process.

Process Wastewater - Any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product.

Process Water - Water prior to its direct contact use in a process or operation. (This water may be any combination of raw water, service water, or either process wastewater or treatment facility effluent to be recycled or reused).

Punching - A method of cold extruding, cold heading, hot forging or stamping in a machine whereby the mating die sections control the shape or contour of the part.

Pyrolysis - (Sludge Removal) Decomposition of materials by the application of heat in any oxygen-deficient atmosphere.

Pyrazolone-Colorimetric - A standard method of measuring cyanides in aqueous solutions.

Quantity GPD - Gallons per day.

Quenching - Rapid cooling of alloys by immersion in water, oil, or gases after heating.

Racking - The placement of parts on an apparatus for the purpose of plating.

Rack Plating - Electroplating of workpieces on racks.

Radiography - A nondestructive method of internal examination in which metal or other objects are exposed to a beam of x-ray or gamma radiation. Differences in thickness, density or absorption, caused by internal discontinuities, are apparent in the shadow image either on a fluorescent screen or on photographic film placed behind the object.

Raw Water - Plant intake water prior to any treatment or use.

Reaming - An operation in which a previously formed hole is sized and contoured accurately by using a rotary cutting tool (reamer) with one or more cutting elements (teeth). The principal support for the reamer during the cutting action is obtained from the workpiece. 1. Form Reaming - Reaming to a contour shape. 2. Taper Reaming - Using a special reamer for taper pins. 3. Hand Reaming - Using a long lead reamer which permits reaming by hand. 4. Pressure Coolant Reaming (or Gun Reaming) - Using a multiple-lip, end cutting tool through which coolant is forced at high pressure to flush chips ahead of the tool or back through the flutes for finishing of deep holes.

Receiving Waters - Rivers, lakes, oceans, or other water courses that receive treated or untreated wastewaters.

Recirculating Spray - A spray rinse in which the drainage is pumped up to the spray and is continually recirculated.

Recycled Water - Process wastewater or treatment facility effluent which is recirculated to the same process.

Recycle Lagoon - A pond that collects treated wastewater, most of which is recycled as process water.

Reduction - A reaction in which there is a decrease in valence resulting from a gain in electrons.

Redox - A term used to abbreviate a reduction-oxidation reaction.

Residual Chlorine - The amount of chlorine left in the treated water that is available to oxidize contaminants.

Reverse Osmosis - The application of pressure to the surface of solution through a semipermeable membrane that is too dense to permit passage of the solute, leaving behind the dissolved solids (concentrate).

Reused Water - Process wastewater or treatment facility effluent which is further used in a different manufacturing process.

Ring Rolling - A metals process in which a doughnut shaped piece of stock is flattened to the desired ring shape by rolling between variably spaced rollers. This process produces a seamless ring.

Rinse - Water for removal of dragout by dipping, spraying, fogging, etc.

Riveting - Joining of two or more members of a structure by means of metal rivets, the undeaded end being upset after the rivet is in place.

Routing - Cutting out and contouring edges of various shapes in a relatively thin material using a small diameter rotating cutter which is operated at fairly high speeds.

Running Rinse - A rinse tank in which water continually flows in and out.

Rust Prevention Compounds - Coatings used to protect iron and steel surfaces, against corrosive environment during fabrication, storage, or use.

Salt - 1. The compound formed when the hydrogen of an acid is replaced by a metal or its equivalent (e.g., an NH4 radical).
Example: $HCl + NaOH = NaCl + H_2O$
This is typical of the general rule that the reaction of an acid and a base yields a salt and water. Most salts ionize in water solution. 2. Common salt, sodium chloride, occurs widely in nature, both as deposits left by ancient seas and in the ocean, where its average concentration is about 3%.

Salt Bath Descaling - Removing the layer of oxides formed on some metals at elevated temperatures in a salt solution. See: Reducing, Oxidizing, Electrolytic.

Sand Bed Drying - The process of reducing the water content in a wet substance by transferring that substance to the surface of a sand bed and allowing the processes of drainage through the sand and evaporation to effect the required water separation.

Sand Blasting - The process of removing stock including surface films, from a workpiece by the use of abrasive grains pneumatically impinged against the workpiece.

Sand Filtration - A process of filtering wastewater through sand. The wastewater is trickled over the bed of sand where air and bacteria decompose the wastes. The clean water flows out through drains in the bottom of the bed. The sludge accumulating at the surface must be removed from the bed periodically.

Sanitary Water - The supply of water used for sewage transport and the continuation of such effluents to disposal.

Sanitary Sewer - Pipes and conveyances for sewage transport.

Save Rinse - See Dead Rinse.

Sawing - Using a toothed blade or disc to sever parts or cut contours. 1. Circular Sawing - Using a circular saw fed into the work by motion of either the workpiece or the blade. 2. Power Band Sawing - Using a long, multiple-tooth continuous band resulting in a uniform cutting action as the workpiece is fed into the saw. Power Hack Sawing - Sawing in which a reciprocating saw blade is fed into the workpiece.

Scale - Oxide and metallic residues.

Screening - Selectively applying a resist material to a surface to be plated.

Secondary Settling - Effluent from some prior treatment process flows for the purpose of removing settleable solids.

Secondary Treatment - The second step in most sanitary waste treatment plants in which bacteria consume the organic portions of the waste. This removal is accomplished by trickling filters, an activated sludge unit, or other processes.

Sedimentation - The process of subsidence and deposition of suspended matter carried by water, wastewater, or other liquids by gravity. It is usually accomplished by reducing the velocity of the liquid below the point at which it can transport the suspended material. Also called settling.

Sensitization - The process in which a substance other than the catalyst is present to facilitate the start of a catalytic reaction.

Sequestering Agent - An agent (usually a chemical compound) that "sequesters" or holds a substance in suspension.

Series Rinse - A series of tanks which can be individually heated or level controlled.

Service Water - Raw water which has been treated preparatory to its use in a process or operation; i.e., makeup water.

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

Settling Ponds - A large shallow body of water into which industrial wastewaters are discharged. Suspended solids settle from the wastewaters due to the large retention time of water in the pond.

Shaping - Using single point tools fixed to a ram reciprocated in a linear motion past the work. 1. Form Shaping - Shaping with a tool ground to provide a specified shape. 2. Contour Shaping - Shaping of an irregular surface, usually with the aid of a tracing mechanism. 3. Internal Shaping - Shaping of internal forms such as keyways and guides.

Shaving - 1. As a finishing operation, the accurate removal of a thin layer by drawing a cutter in straight line motion across the work surfaces. 2. Trimming parts like stampings, forgings and tubes to remove uneven sheared edges or to improve accuracy.

Shearing - The process of severing or cutting of a workpiece by forcing a sharp edge or opposed sharp edges into the workpiece by forcing a sharp edge or opposed sharp edges into the workpiece stressing the material to the point of sheer failure and separation.

Shipping - Transporting.

Shot Peening - Dry abrasive cleaning of metal surfaces by impacting the surfaces with high velocity steel shot.

Shredding - (Cutting or Stock Removal) Material cut, torn or broken up into small parts.

SIC - Standard Industrial Classification - Defines industries in accordance with the composition and structure of the economy and covers the entire field of economic activity.

Silica - ($SiO_2$) Dioxide of silicon which occurs in crystalline form as quartz, cristohalite, tridymite. Used in its pure form for high-grade refractories and high temperature insulators and in impure form (i.e. sand) in silica bricks.

Siliconizing - Diffusing silicon into solid metal, usually steel, at an elevated temperature for the purposes of case hardening thereby providing a corrosion and wear-resistant surface.

Sintering - The process of forming a mechanical part from a powdered metal by bonding under pressure and heat but below the melting point of the basis metal.

Sizing 1. Secondary forming or squeezing operations, required to square up, set down, flatten or otherwise correct surfaces, to produce specified dimensions and tolerances. See restriking. 2. Some burnishing, broaching, drawing and shaving operations are also called sizing. 3. A finishing operation for correcting ovality in tubing. 4. Powder metal. Final pressing of a sintered compact.

Skimming - The process of removing floating solid or liquid wastes from a wastewater stream by means of a special tank and skimming mechanism prior to treatment of the water.

Slaking - The process of reacting lime with water to yield a hydrated product.

Sludge - Residue produced in a waste treatment process.

Sludge Dewatering - The removal of water from sludge by introducing the water sludge slurry into a centrifuge. The sludge is driven outward with the water remaining near the center. The water is withdrawn and the dewatered sludge is usually landfilled.

Slurry - A watery suspension of solid materials.

Snagging - Heavy stock removal of superfluous material from a work piece by using a portable or swing grinder mounted with a coarse grain abrasive wheel.

Soldering - The process of joining metals by flowing a thin (capillary thickness) layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term soldering is used where the temperature range falls below 425°C (800°F).

Solids - (Plant Waste) Residue material that has been completely dewatered.

Solute - A dissolved substance.

Solution - Homogeneous mixture of two or more components such as a liquid or a solid in a liquid.

Solution Treated - (Metallurgical) A process by which it is possible to dissolve micro-constituents by taking certain alloys to an elevated temperature and then keeping them in solution after quenching. (Often a solution treatment is followed by a precipitation or aging treatment to improve the mechanical properties. Most high temperature alloys which are solution treated and aged machine better in the solution treated state just before they are aged.)

Solvent - A liquid used to dissolve materials. In dilute solutions the component present in large excess is called the solvent and the dissolved substance is called the solute.

Solvent Cleaning - Removal of oxides, soils, oils, fats, waxes, greases, etc. by solvents.

Solvent Degreasing - The removal of oils and grease from a workpiece using organic solvents or solvent vapors.

Specific Conductance - The property of a solution which allows an electric current to flow when a potential difference is applied.

Spectrophotometry - A method of analyzing a wastewater sample by means of the spectra emitted by its constituents under exposure to light.

Spray Rinse - A process which utilizes the expulsion of water through a nozzle as a means of rinsing.

Spinning - Shaping of seamless hollow cylindrical sheet metal parts by the combined forces of rotation and pressure.

Spotfacing - Using a rotary, hole piloted end facing tool to produce a flat surface normal to the axis of rotation of the tool on or slightly below the workpiece surface.

Sputtering - The process of covering a metallic or non-metallic workpiece with thin films of metal. The surface to be coated is bombarded with positive ions in a gas discharge tube, which is evacuated to a low pressure.

Squeezing - The process of reducing the size of a piece of heated material so that it is smaller but more compressed than it was before.

Stainless Steels - Steels which have good or excellent corrosion resistance. (One of the common grades contains 18% chromium and 8% nickel. There are three broad classes of stainless steels - ferritic, austenitic, and martensitic. These various classes are produced through the use of various alloying elements in differing quantities.

Staking - Fastening two parts together permanently by recessing one part within the other and then causing plastic flow at the joint.

Stamping - A general term covering almost all press operations. It includes blanking, shearing, hot or cold forming, drawing, bending and coining.

Stamping Compounds - See Forming Compounds (Sheet).

Standard of Performance - Any restrictions established by the Administrator pursuant to Section 306 of the Act on quantities, rates and concentrations of chemical, physical, biological, and other constituents which are or may be discharged from new sources into navigable waters, the waters of the contiguous zone or the ocean.

Stannous Salt - Tin based compound used in the acceleration process. Usually stannous chloride.

Utill Rinse - See Dead Rinse.

Storm Water Lake - Reservoir for storage of storm water runoff collected from plant site; also, auxiliary source of process water.

Stress Relieved - The heat treatment used to relieve the internal stresses induced by forming or heat treating operations. (It consists of heating a part uniformly, followed by cooling slow enough so as not to reintroduce stresses. To obtain low stress levels in steels and cast irons, temperatures as high as 1250 degrees F may be required.)

Strike - A thin coating of metal (usually less than 0.0001 inch in thickness) to be followed by other coatings.

Stripping - The removal of coatings from metal.

Subcategory or Subpart - A segment of a point source for which specific effluent limitations have been established.

Submerged Tube Evaporation - Evaporation of feed material using horizontal steam-heat tubes submerged in solution. Vapors are driven off and condensed while concentrated solution is bled off.

Subtractive Circuitry - Circuitry produced by the selective etching of a previously deposited copper layer.

Substrates - Thin coatings ( as of hardened gelatin) which act as a support to facilitate the adhesion of a sensitive emulsion.

Surface Tension - A measure of the force opposing the spread of a thin film of liquid.

Surface Waters - Any visible stream or body of water.

Surfactants - Surface active chemicals which tend to lower the surface tension between liquids, such as between acid and water.

Surge - A sudden rise to an excessive value, such as flow, pressure, temperature.

Swaging - Forming a taper or a reduction on metal products such as rod and tubing by forging, squeezing or hammering.

Tank - A receptacle for holding transporting or storing liquids.

**Tapping** - Producing internal threads with a cylindrical cutting tool having two or more peripheral cutting elements shaped to cut threads of the desired size and form. By a combination of rotary and axial motion, the leading end of the tap cuts the thread while the tap is supported mainly by the thread it produces.

**Tempering** - Reheating a quench-hardened or normalized ferrous alloy to a temperature below the transformation range then cooling at any rate desired.

**Testing** - The application of thermal, electrical, or mechanical energy to determine the suitability or functionality of a part, assembly or complete unit.

**Thermal Cutting** - The term "thermal cutting" shall mean the process of cutting, slotting or piercing a workpiece using an oxy-acetylene oxygen lance or electric arc cutting tool.

**Thermal Infusion** - The process of applying a fused zinc, cadmium or other metal coating to a ferrous workpiece by imbueing the surface of the workpiece with metal powder or dust in the presence of heat.

**Thickener** - A device or system wherein the solid contents of slurries or suspensions are increased by gravity settling and mechanical separation of the phases, or by flotation and mechanical separation of the phases.

**Thickening** - (Sludge Dewatering) Thickening or concentration is the process of removing water from sludge after the initial separation of the sludge from wastewater. The basic objective of thickening is to reduce the volume of liquid sludge to be handled in subsequent sludge disposal processes.

**Threading** - Producing external threads on a cylindrical surface. 1. Die Threading - A process for cutting external threads on cylindrical or tapered surfaces by the use of solid or self-operning dies. 2. Single-Point Threading - Turning threads on a lathe. 3. Thread Grinding - See definition under grinding. 4. Thread Milling - A method of cutting screw threads with a milling cutter.

**Threshold Toxicity** - Limit upon which a substance becomes toxic or poisonous to a particular organism.

**Through Hole Plating** - The plating of the inner surfaces of holes in a PC board.

**Titration** - 1. A method of measuring acidity of alkalinity. 2. The determination of a constituent in a known volume of solution by the measured addition of a solution of known strength for completion of the reaction as signaled by observation of an end point.

Total Chromium - The sum of chromium in all valences.

Total Cyanide - The total content of cyanide expressed as the radical CN- or alkali cyanide whether present as simple or complex ions. The sum of both the combined and free cyanide content of a plating solution. In analytical terminology, total cyanide is the sum of cyanide amenable to oxidation by chlorine and that which is not according to standard analytical methods.

Total Dissolved Solids (TDS) - The total amount of dissolved solid materials present in an aqueous solution.

Total Metal - Sum of the metal content in both soluble and insoluble form.

Total Organic Carbon (TOC) - TOC is a measure of the amount of carbon in a sample originating from organic matter only. The test is run by burning the sample and measuring the $CO_2$ produced.

Total Solids - The sum of dissolved and undissolved constituents in water or wastewater, usually stated in milligrams per liter.

Total Suspended Solids (TSS) - Solids found in wastewater or in the stream, which in most cases can be removed by filtration. The origin of suspended matter may be man-made or of natural sources, such as silt from erosion.

Total Volatile Solids - Volatile residue present in wastewater.

Tool Steels - Steels used to make cutting tools and dies. (Many of these steels have considerable quantities of alloying elements such as chromium, carbon, tungsten, molybdenum and other elements. These form hard carbides which provide good wearing qualities but at the same time decrease machinability. Tool steels in the trade are classified for the most part by their applications, such as hot work die, cold work die, high speed, shock resisting, mold and special purpose steels.)

Toxic Pollutants - A pollutant or combination of pollutants including disease causing agents, which after discharge and upon exposure, ingestion, inhalation or assimilation into any organism either directly or indirectly cause death, disease, cancer, genetic mutations, physiological malfunctions (including malfunctions in such organisms and their offspring.

Treatment Facility Effluent - Treated process wastewater.

Trepanning - Cutting with a boring tool so designed as to leave an unmachined core when the operation is completed.

Trickling Filters - A filter consisting of an artificial bed of coarse material, such as broken stone, clinkers, slate, salts, or brush over which an effluent is distributed and applied in drops, films, or spray from troughs, drippers, moving distributors, or fixed nozzles and through which it trickles to the underdrains giving opportunity for the formation of zoological slimes which clarify and oxidize the effluent.

Tumbling - See Barrel Finishing.

Tubidimeter - An instrument for measurement of turbidity in which a standard suspension is usually used for reference.

Turbidity - 1. A condition in water or wastewater caused by the presence of suspended matter resulting in the scattering and absorption of light rays. 2. A measure of fine suspended matter in liquids. 3. An analytical quantity usually reported in arbitrary turbidity units determined by measurements of light diffraction.

Turning - Generating cylindrical forms by removing metal with a single-point cutting tool moving parallel to the axis of rotation of the work. 1. Single-Point Turning - Using a tool with one cutting edge. 2. Face Turning - Turning a surface perpendicular to the axis of the workpiece. 3. Form Turning - Using a tool with a special shape. 4. Turning Cutoff - Severing the workpiece with a special lathe tool. 5. Box Tool Turning - Turning the end of workpiece with one or more cutters mounted in a boxlike frame, primarily for finish cuts.

Ultrafiltration - A process using semipermeable polymeric membranes to separate molecular or colloidal materials dissolved or suspended in a liquid phase when the liquid is under pressure.

Ultrasonic Agitation - The agitation of a liquid medium through the use of ultrasonic waves.

Ultrasonic Cleaning - Immersion cleaning aided by ultrasonic waves which cause microagitation.

Ultrasonic Machining - Material removal by means of an ultrasonic-vibrating tool usually working in an abrasive slurry in close contact with a workpiece or having diamond or carbide cutting particles on its end.

Unit Operation - A single, discrete process as part of an overall sequence, e.g., precipitation, settling and filtration.

Vacuum Deposition - Condensation of thin metal coatings on the cool surface of work in a vacuum.

Vacuum Evaporization - A method of coating articles by melting and vaporizing the coating material on an electrically heated conductor in a chamber from which air has been exhausted. The process is only used to produce a decorative effect. Gold, silver, copper and aluminum have been used.

Vacuum Filtration - A sludge dewatering process in which sludge passes over a drum with a filter medium, and a vacuum is applied to the inside of the drum compartments. As the drum rotates, sludge accumulates on the filter surface, and the vacuum removes water.

Vacuum Metalizing - The process of coating a workpiece with metal by flash heating metal vapor in a high-vacuum chamber containing the workpiece. The vapor condenses on all exposed surfaces.

Vapor Blasting - A method of roughing plastic surfaces in preparation for plating.

Vapor Degreasing - Removal of soil and grease by a boiling liquid solvent, the vapor being considerably heavier than air. At least one constituent of the soil must be soluble in the solvent.

Vapor Plating - Deposition of a metal or compound upon a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting points of either the deposit or the basis material.

Viscosity - The resistance offered by a real fluid to a shear stress.

Volatile Substances - Material that is readily vaporizable at a relatively low temperature.

Volumetric Method - A standard method of measuring settleable solids in an aqueous solution.

Waste Discharged - The amount (usually expressed as weight) of some residual substance which is suspended or dissolved in the plant effluent.

Wastewater Constituents - Those materials which are carried by or dissolved in a water stream for disposal.

# APPENDIX A

## EXHIBIT 1

## Statistical Analysis of Cadmium (except new sources), Chromium, Copper, Lead, Nickel, Silver, Zinc, Cyanide, Total Suspended Solids and Oil and Grease

### Background

This exhibit provides documentation of the data and methods used to determine final effluent guidelines limitations for the Metal Fininshing industry. Limitations are expressed in concentration units (mg/l); production based limitations were not developed because flow data were fragmentary and relationships of flow to other indices of production were not reliable. The Final Regulation for Effluent Limitations, Guidelines, and Standards for the Metal Finishing Point Source Category specifies daily maximum and 10 day average limitations for Best Practicable Control Technology Currently Available (BPT), Best Available Technology Economically Achievable (BAT), Pretreatment Standards for Existing Sources (PSES) Pretreatment Standards for New Sources (PSNS) and New Source Performance Standards (NSPS).

Unless mentioned otherwise, limitations for the following pollutants under each standard are based on the methodology, data, and results presented in this exhibit. The standards will limit cadmium (Cd), total chromium ($Cr^T$), copper (Cu), lead (Pb), nickle (Ni), silver (Ag), zinc (Zn), total cyanide ($Cn^T$), and amenable cyanide ($Cn^A$). Oil and Grease (OG), total suspended solids (TSS) and pH are regulated only under BPT and NSPS, and are derived in accord with this exhibit. The development of new source (PSNS and NSPS) Cd limits are discussed in another exhibit. Guidance limitations for hexavalent chromium ($Cr^{6+}$) are also established here. The establishment of limits for TTO standards are discussed in another exhibit.

Details regarding the technical background and justification for effluent guidelines for the Metal Finishing Category are discussed in chapter VII of the "Final Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category".

Several appendices are referred to in this exhibit. They include computer printouts which support the results reported here. These printouts are voluminous and are not attached physically to this exhibit. They have, however, been entered into the administrative record supporting the metal finishing rulemaking; the titles to the Appendices are listed in Table 1.

### Data

Two data sets are used for the development of the limitations; a set of EPA collected and analyzed wastewater data, (refered to as EPA data) and a data set of the results from self monitoring samples, collected and analyzed by metal finishing plants as part of their compliance monitoring activities, (refered to as self monitoring data).

The EPA data are analytical results of samples collected at metal finishing plants before and after wastewater treatment. The availability of paired raw and treated waste data allows assessment of treatment when pollutants are present in significant concentrations in the raw waste. Daily samples were generally taken over a 1 to 3 day period (in some cases, as many as 6 daily samples were taken at a plant). Total suspended solids (TSS) and pH were measured and if the treated waste samples had TSS concentrations greater than 50 mg/l or pH less than 7.0, the entire sample was deleted for all pollutants measured. Plants with complexing, dilution, or poor operation were deleted.* Plants that were not option 1 (precipitation-clarification) metal finishing plants were also deleted. Effluent observations which were greater than influent observations taken on the same day were deleted. Also, effluent observations identified by an iterative procedure were deleted. The iterative procedure is intended to remove treated effluent values associated with low pollutant mesurements in untreated wastewater and is described in Appendix A. The values remaining, after all the deletions are listed in Appendix A. The treated effluent concentrations as listed in Appendix A for all pollutants, except Cd and Pb, are used to calculate long term average pollutant concentrations in treated wastewater. Cadmium and Pb means are from the self monitoring data discussed below. Table 2 lists the pollutants, the number of observations, and the number of plants used from the EPA sampling data.

The self monitoring data were obtained from metal finishing plants where sampling, analysis, and reporting of treated waste waters were conducted by industry without EPA's direct involvement. Analytical methodology is reported to have followed acceptable EPA methods. To the extent information was available, plants were checked for properly constructed and managed Option 1 treatment systems. Raw waste data were not available for the self monitoring data to measure treatment when pollutants are present in significant concentrations in the raw waste; as an alternative the Agency used a pollutant only when there was an identifiable process source of the pollutant. Self monitoring data were used for the evaluation of variability, which will be presented in the following data-analysis section. Table 3 lists the pollutants, the number of observations and the number of plants chosen from the self monitoring data.

When pollutant concentrations were too low to be quantified they were reported as below a detection limit (DL). For a particular pollutant-plant data set, DL's could differ depending on the laboratory, sample dilution, or methodology. Values reported at below a DL were set equal to zero for the purpose of estimating variability and central tendency. This was done for the

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* The cut-off criteria are: 1) plants that had complexing agents unoxidized cyanide or nonsegregated wastes; 2) plants which had effluent flow significantly greater than the corresponding raw waste flows were deleted; 3) plants that experienced difficulties in system operation during the sampling period were excluded. These difficulties include a few hours operation at very low pH (approximately 4.0), observed operator error, an inoperative chemical feed system, improper chemical usage, improperly maintained equipment, high flow slugs during the sampling period, and excessive surface water intrusion (heavy rains).

following reasons: the data above the DL were found to generally fit the lognormal distribution; the assignment of the value zero to DL observations is recommended for estimation from data sets that are mixtures of DL observations and observations that fit the lognormal (see Owen and DeRouen, "Estimation of the Mean for Lognormal Data Containing Zeroes and Left Censored Values, with Applications to the Measurement of Worker Exposure to Air Contaminents", Biometrics (1980), V. 36, pp. 707-719). Appendix B is a listing of the self monitoring data and Appendix C presents summary statistics of the self monitoring data.

## Analysis

### Lognormal Goodness-of-Fit

Lognormality was examined graphically and tested for each pollutant-plant combination in the self monitoring data base in Appendix B. The distributional form of each plant-pollutant combination data set is displayed in Appendix D as empirical frequency histograms of the data, before logarithmic transformation. A majority of the histograms have the general shape of the lognormal distribution, i.e., positive skewness and long "tails" to the right. The larger data sets tend to display the lognormal characteristics more than the smaller data sets. This is not surprising since the lognormal distribution has provided a satisfactory fit to effluent data for a wide range of industrial categories and pollutants. The visual suggestion of lognormality is best revealed in the larger sets as distributional shapes cannot be identified with only a few observations.

Three goodness-of-fit tests were performed on the natural logarithims of the self-monitoring data for each pollutant-plant combination for which sufficient data were available. (Appendix E) If the distribution of the logarithms of the data are not significantly different from the normal distribution then the assumption of lognormality is reasonable. The Kolmogorov-Smirnov test (KS), the Anderson-Darling test (AD) and the D'Agostino test (DA) were applied to each pollutant-plant data set. These procedures test the null hypothesis that the distribution of the logs of the observed values follow a normal distribution. The DA test was not performed in some cases because the data did not meet the minimum sample size required for the test. The three tests together provide a thorough examination of the distributional form because the KS is a general test of normality, the AD is sensitive to normality departures in the tails, and DA is sensitive to normality departures in the higher moments. Table 4 summarizes the results of the 3 significance tests and indicates that the pollutant distributions within each plant frequently follow a lognormal distribution. Appendix F contains time plots of the data which permit visual inspection of data structure over time.

### Daily Variability Factors

A variability factor (VF) for a pollutant-plant combination is defined as the ratio of the lognormally estimated 99th percentile of the distribution of within-plant pollutant values to the arithmetic mean of the same values. In cases where there were DL observations present in the data, a generalized form of the lognormal disbribution, known as the delta lognormal distribution (DLN) was used to model the data. The delta lognormal distribution is described in Chapter 9 of The Lognormal Distribution, by Aitchison and Brown, Cambridge

University Press, 1963. The DLN is a mixed probability distribution, having both discrete and continuous portions. The discrete portion models the possibility of observing a DL value while the continuous portion is a lognormal probability distribution and models the distribution of all values above the DL.

The 99th percentile for the DLN is

$$\xi = \exp(\mu + \nu_{q}{}'\sigma)$$

where

$$q' = (.99 - \delta)/(1 - \delta)$$

and

$\delta$ = probability of observing a DL value

$\nu_{q'}$ is the quantile of order q' of the N(0,1) distribution

$\nu_{q}{}' = 2.326$ if $\delta = 0$

The 99th percentile is estimated by using the following estimates of the DLN parameters in the above formulae:

$\hat{\delta} = \frac{n_o}{n}$ where $n_o$ is the number of DL values and n is the total number of values

$\hat{\mu} = \overline{x} = \sum_{i=1}^{n_i} x_i/n_1$ where $x_i = \ln y_i$ for non DL values of y, $n_1$ is the number of non DL values, and $\overline{x}$ is the logmean of the non DL values

$$\hat{\sigma}^2 = \sum_{i=1}^{n_1} (x_i - \overline{x})^2/(n_1 - 1).$$

The DLN 99th percentile was not estimated if greater than 50% of the observations for a pollutant-plant data set were DL values. This is because a large proportion of DL observations can introduce mathematical instabilities into the estimates and result in extremely exaggerated and unreliable measures of variability.

For each pollutant-plant combination a DLN 99th percentile was estimated and divided by the arithmetic mean (AM) from the same pollutant-plant combination to estimate the daily VF. The median VF of all the plants that had data on a particular pollutant was then used as the daily VF for that pollutant. Table 5 presents the median daily VF for each pollutant. Appendix E is a listing of each pollutant-plant combination and the corresponding goodness-of-fit results, DLN parameter estimates, 99th percentiles, AMs, and VFs.

Usable Self monitoring data were not available for silver so the average median variability factor for $Cr^T$, Cu, Pb, Ni, Cd and Zn was used as an estimate of the Ag VF.

## Ten Day Variability Factors

Ten day variability factors were determined on the basis of the assumption that averages of 10 samples drawn from the distribution of daily values are approximately lognormally distributed. This characteristic of small sample averages drawn from underlying distributions that are lognormally distributed has been observed in effluent data from many different industry categories for a wide variety of pollutants. This assumption was used as the basis of four sample average monthly limitations in the effluent guideline regulations for pretreatment standards for the electroplating industry. The assumption of lognormality for the 10 day averages was also verified empirically by constructing averages of sequences of 10 observations in the self monitoring data base and examining their distributions. The listing of the 10 day average data are in Appendix G. Summary statistics of the 10 day average are in Appendix H and the empirical distributions of 10 day averages are listed in Appendix I. Lognormal goodness-of-fit tests of the ten day average distributions are shown in Appendix J. In general, the lognormal provides a reasonable fit to the data. Appendix K presents plots of temporally sequential 10 day average data which permit visual inspection of data structure over time.

The empirical distributions were used to estimate 10 day VF's using a methodology identical to the calculation of the daily VFs. That is, the data were fit to a lognormal distribution and the VF was determined by the ratio of the estimated 99th percentile to the arithmetic mean. The DLN model was used in some cases because there were several instances in the self monitoring data when there are series of ten or more DL values in a row. Table 6 lists the 10 day average variability factors for each pollutant.

## Effluent Limitations

The maximum daily and 10 day average effluent limitations were determined by multiplying the long term average pollutant concentrations and the daily and 10 day average variability factors, respectively. The long term average concentration was determined by the arithmetic average of the EPA sample data for each pollutant with the exception of Cd and Pb. For Cd and Pb the arithmetic average of the self monitoring data was used. The AMs, daily VFs, 10 day VFs and resulting limitations are shown in Tables 5 and 6. The VFs shown in Tables 5 and 6 are the median plant VFs of daily and 10 day VFs for each pollutant.

## Alternative Methodologies Considered

Effluent limitations for the MF industry were determined on the basis of median VFs and average effluent concentrations. Given the data on hand, however, other methods of combining or averaging the results across plants to form limitations are possible and reasonable alternatives. During the development of daily maximum limitations for the MF regulation a variety of methodologies were examined. These exploratory analyses were conducted to examine reasonable alternatives and ensure that methods used to develop the final limitations were both appropriate and consistent with methods used previously in the proposed metal finishing regulations. Consideration was also given to identifying plants whose data exerted excessive influences on the results.

The daily maximum limitations that result from the various alternatives considered are shown in Tables 7 and 8. Although the results in Tables 7 and 8 include plant 11118, it was discovered that for the pollutants reported for this plant ($Cr^T$, Zn, Ni, $Cn^T$, Cu, Pb, Cd), the mean concentration or variability were excessive relative to the other plants with data for a particular pollutant. This led to an engineering assessment of the plant's wastewater treatment system. Because plant 11118 was not isolating complexing wastewaters that plant was not operating as an option 1 plant during the time the self monitoring data were collected. Therefore, plant 11118 is not used in final limitations. Column II in Table 7 lists the limitations including plant 11118 calculated using the same methodology used to calculate the final limitations in Table 5 which do not include 11118.

The proposed and final limitations for MF used median plant VFs. During the examination of other alternatives weighted mean VFs were also considered and limitations based on these are listed in columns III and V of Table 7. The median has the convienient interpretation of being the "middle most" value in a set of data while the weighted mean procedure is an objective way of combining data from sources providing unequal amounts of observations.

The EPA sampling data were also evaluated under various methodologies. For both proposed and final limitations EPA data were used to establish a long term average performance level for each pollutant (except Cd and Pb). The EPA data for each pollutant were summarized as an AM and as a mean estimated by fitting the data to a lognormal distribution. Each mean was then used in combination with weighted mean self monitoring VF's and median self monitoring VFs. These limitations are listed in columns II through V of Table 7. The EPA data were also used to estimate limitations without the use of self monitoring data. These values are shown in column VI of Table 7.

Table 8 shows alternative limitation values based on the self monitoring data only. In each case the variability factors and means were determined on the basis of estimates of lognormal means and 99th percentiles calculated by fitting the data to a lognormal distribution. The estimated lognormal means are slightly different from the AM of the data but given that the data fit a lognormal distribution it would be appropriate to use an estimated lognormal mean. The AM and estimated lognormal mean are both estimates of the mean of the distribution and thus either could be reasonable. Arithmetic means are, of course, more easily understood and were used in proposal.

Appendix L details the results of alternative methods for computing 10 Day (average monthly) limitations.

# TABLE 1

## List of Appendices Which Can Be Found in the Administrative Record

| Appendix | Title |
|---|---|
| A | A Listing of the EPA Data Used for the Long Term Mean |
| B | A Listing of the Self Monitoring Data Used for Estimating Variability |
| C | Summary Statistics of the Self Monitoring Data |
| D | Empirical Frequency Histograms of the Self Monitoring Data |
| E | Listing of Goodness-of-Fit Results, Delta Lognormal Parameter Estimates, 99th Percentiles, Arithmetic Means and Variability Factors for Each Pollutant-Plant Combination in the Self Monitoring Data Base |
| F | Plots Over Time of the Daily Self Monitoring Pollutant Concentrations for Each Pollutant-Plant Combination |
| G | A Data Listing of the 10 Day Average Data Derived from the Self Monitoring Daily Data |
| H | Summary Statistics of the 10 Day Average Self Monitoring Data |
| I | Empirical Frequency Histograms of the 10 Day Average Data Derived from the Self Monitoring Daily Data |
| J | Listing of Goodness-of-Fit Results, Delta Lognormal Parameter Estimates, 99th Percentiles, Arithmetic Means, and Variability Factors for Each Pollutant-Plant Combination in the Derived 10 Day Average Data Derived from the Self Monitoring Data |
| K | Plots of Temporally Sequential 10 Day Average Data of the Daily Self Monitoring Pollutant Concentrations for Each Pollutant-Plant Combination |
| L | Listing of 10 Day Limitations Using Various Alternative Methodologies. |

# TABLE 2

## A Summary of the Pollutants, Number of Plants, and Number of Observations Used to Establish the EPA Long Term Averages

| Pollutant | # of Plants | # of Observations |
|---|---|---|
| TSS | 36 | 78 |
| OG | 16 | 30 |
| Cd[1] | 6 | 485 |
| $Cr^T$ | 20 | 38 |
| $Cr^{6+}$ | 5 | 10 |
| Cu | 22 | 47 |
| Pb[1] | 5 | 620 |
| Ni | 20 | 45 |
| Zn | 17 | 34 |
| $Cn^T$ | 15 | 45 |
| $Cn^A$ | 15 | 43 |
| Ag | 2 | 5 |

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[1] Data are from the self monitoring data set.

## TABLE 3

## A Summary of the Pollutants, Number of Plants and Number of Observations Used from the Self Monitoring Data

| Pollutant | # of Plants | # of Observations |
|---|---|---|
| TSS | 20 | 1777 |
| OG | 12 | 893 |
| Cd* | 4 | 463 |
| $Cr^T$* | 20 | 3270 |
| $Cr^{6+}$ | 9 | 1811 |
| Cu* | 19 | 2743 |
| Pb* | 4 | 581 |
| Ni* | 14 | 1750 |
| Zn* | 11 | 1216 |
| $Cn^T$* | 13 | 1198 |
| $Cn^A$ | 1 | 28 |

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* Plant 11118 is not included in the summary.

## TABLE 4

## A Summary of Normality Tests Applied to the Natural Logarithims of the Daily Self Monitoring Metal Finishing Data for Each Pollutant-Plant Combination

| | KS | | | AD | | | DA | | |
|---|---|---|---|---|---|---|---|---|---|
| | Total # | Accept[1] # | Accept[1] % | Total # | Accept[1] # | Accept[1] % | Total # | Accept[1] # | Accept[1] % |
| TSS | 20 | 20 | 100 | 20 | 12 | 60 | 11 | 10 | 91 |
| OG | 12 | 10 | 83 | 12 | 8 | 67 | 8 | 6 | 75 |
| Cd | 4 | 4 | 100 | 4 | 2 | 50 | 3 | 2 | 67 |
| $Cr^T$ | 9 | 9 | 100 | 9 | 4 | 44 | 9 | 6 | 67 |
| $Cr^{6+}$ | 9 | 9 | 100 | 9 | 2 | 22 | 8 | 2 | 25 |
| Cu | 19 | 17 | 90 | 19 | 10 | 53 | 15 | 9 | 60 |
| Pb | 4 | 4 | 100 | 4 | 2 | 50 | 4 | 2 | 50 |
| Ni | 14 | 13 | 93 | 14 | 7 | 50 | 10 | 6 | 60 |
| Zn | 10 | 9 | 90 | 10 | 6 | 60 | 7 | 5 | 71 |
| $Cn^T$ | 10 | 10 | 100 | 10 | 3 | 30 | 8 | 5 | 63 |
| $Cn^A$ | 1 | 1 | 100 | 1 | 1 | 100 | 1 | 1 | 100 |

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K-S - Kolmogorov-Smirnov test.
A-D - Anderson Darling test.
D-A - D'Agostino test.

[1] Fail to reject the null hypothesis that the data are from a lognormal distribution.

# TABLE 5

## Metal Finishing Daily Median Variability Factors, EPA Arithmetic Means, and the Daily Maximum Limitations for Each Pollutant Parameter

| | VF[1] | $\overline{X}$[2] (mg/1) | DAILY LIMIT[3] (mg/1) |
|---|---|---|---|
| TSS | 3.59 | 16.8 | 60.0 |
| OG | 4.36 | 11.8 | 52.0 |
| Cd | 5.31 | 0.130 | 0.69 |
| $Cr^T$ | 4.85 | 0.572 | 2.77 |
| $Cr^{6+}$ | 5.04 | 0.032 | 0.16 |
| Cu | 4.15 | 0.815 | 3.38 |
| Pb | 3.52 | 0.197 | 0.69 |
| Ni | 4.22 | 0.942 | 3.98 |
| Zn | 4.75 | 0.549 | 2.61 |
| $Cn^T$ | 6.68 | 0.180 | 1.20 |
| $Cn^A$ | 14.31* | 0.060 | 0.86 |
| Ag | 4.47 | 0.096 | 0.43 |

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[1] Median plant variability factor calculated for each pollutant-plant combination by taking the ratio of the estimated delta lognormal 99th percentile to the arithmetic mean.

[2] Arithmetic mean of the EPA sampled data.

[3] VF • $\overline{X}$ = Daily maximum limitation.

* VF based on only one plant with data suitable for estimating variability.

## TABLE 6

## Metal Finishing Ten Day Median Variability Factors, EPA Arithmetic Means, and the Daily Maximum Limitations for Each Pollutant Parameter

| | $VF^1_{10}$ | $\overline{X}^2$ (mg/1) | 10 Day Limit$^3$ (mg/1) |
|---|---|---|---|
| TSS | 1.85 | 16.8 | 31.0 |
| OG | 2.18 | 11.8 | 26.0 |
| Cd | 2.02 | 0.130 | 0.26 |
| $Cr^T$ | 2.98 | 0.572 | 1.71 |
| $Cr^{6+}$ | 3.05 | 0.032 | 0.10 |
| Cu | 2.54 | 0.815 | 2.07 |
| Pb | 2.19 | 0.197 | 0.43 |
| Ni | 2.53 | 0.942 | 2.38 |
| Zn | 2.70 | 0.549 | 1.48 |
| $Cn^T$ | 3.61 | 0.180 | 0.65 |
| $Cn^A$ | 5.31 | 0.060 | 0.32 |
| Ag | 2.49 | 0.096 | 0.24 |

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[1] Median plant 10 day average variability factor calculated for each pollutant-plant combination by taking the ratio of the delta lognormal 99th percentile (with detection limits equal to zero) to the arithmetic mean.

[2] Arithmetic mean of the EPA sampled data.

[3] $VF_{10} \cdot \overline{X}$ = 10 day average maximum limitation.

## TABLE 7

### Metal Finishing Alternative Daily Maximum Limitations

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| | PROPOSED LIMITS | MEDIAN VF ° EPA $\overline{X}$ | WEIGHTED $\overline{VF}$ ° EPA $\overline{X}$ | MEDIAN VF ° EPA LN MEAN | WEIGHTED $\overline{VF}$ ° EPA LN MEAN | EPA SAMPLING DATA ONLY (LN) |
| TSS | 60.1 | 60.8 | 63.3 | 51.8 | 54.6 | 52.1 |
| O&G | 42.2 | 51.8 | 67.0 | 39.8 | 51.5 | 26.7 |
| Cd | 1.29** | 1.41** | 0.80** | 0.07 | 0.04 | 0.014 |
| $Cr^T$ | 2.87 | 2.94 | 2.55 | 1.90 | 1.65 | 1.11 |
| $Cr^{6+}$ | 0.18 | 0.16 | 0.14 | * | * | * |
| Cu | 3.72 | 3.56 | 3.89 | 1.90 | 2.08 | 1.35 |
| Pb | 0.67** | 0.80** | 0.79** | 0.19 | 0.19 | 0.08 |
| Ni | 3.51 | 4.17 | 3.83 | 3.20 | 2.94 | 2.29 |
| Zn | 2.64 | 2.40 | 2.39 | 0.92 | 0.91 | 0.62 |
| $Cn^T$ | 1.30 | 1.29 | 1.12 | * | * | * |
| $Cn^A$ | 0.54 | 0.71 | 0.71 | * | * | * |

I Limits Proposed for Metal Finishing, August, 1982.

II Product of Self Monitoring Data Median Variability Factor (VF) based on lognormal and EPA MF data arithmetic mean ($\overline{X}$).

III Product of Self Monitoring Data Weighted Average $\overline{VF}$ and EPA MF data $\overline{X}$.

IV Product of Self Monitoring Data Median VF and EPA MF data lognormal mean.

V Product of Self Monitoring Data Weighted Average VF and EPA MF data lognormal mean.

VI EPA MF data only, lognormal 99th percentile estimate.

* EPA MF data required to estimate lognormal mean not available.

** The arithmetic means of the EPA data were not used for these limitations. Instead, the arithmetic means of the self monitoring data were used.

TABLE 8

Metal Finishing Alternative Daily Maximum Limitations
Self Monitoring Data Only

|  | I<br>MEDIAN VF ° WTG. LN MEAN | II<br>WTG. $\overline{VF}$ ° WTG. LN MEAN | III<br>MEDIAN VF ° MED. LN MEAN | IV<br>WTG. $\overline{VF}$ ° MED. LN MEAN |
|---|---|---|---|---|
| TSS | 32.9 | 34.7 | 28.2 | 30.8 |
| O&G | 12.7 | 16.4 | 13.2 | 17.0 |
| Cd | 1.46 | 0.83 | 0.97 | 0.56 |
| $Cr^T$ | 1.02 | 0.88 | 0.81 | 0.70 |
| $Cr^{6+}$ | 0.10 | 0.09 | 0.09 | 0.07 |
| Cu | 1.91 | 2.09 | 0.92 | 1.01 |
| Pb | 0.78 | 0.77 | 0.85 | 0.84 |
| Ni | 1.73 | 1.59 | 1.36 | 1.25 |
| Zn | 1.88 | 1.88 | 1.36 | 1.35 |
| $Cn^T$ | 3.51 | 1.30 | 0.75 | 0.65 |
| $Cn^A$ | * | * | * | * |

I Product of Median plant variability factors based on lognormal and weighted average of plant estimated lognormal means.

II Product of weighted average of plant lognormal variability factors and weighted average of plant lognormal means.

III Product of median plant lognormal variability factors and median of plant lognormal mean.

IV Product of weighted average of plant lognormal variability factors and median of plant lognormal means.

* Self monitoring data on $Cn^A$ suitable for estimation were available from only one plant with excessive variability. Accordingly, limitation values were not calculated.

# EXHIBIT 2

## Analysis of Total Toxic Organic (TTO) Data

### Background

The final effluent guideline regulation for the Metal Finishing (MF) industry contains limitations on TTO. The purpose of including TTO limitations is to require MF facilities to practice control of the release of toxic organics, into process wastewaters. This exhibit documents the data and analysis used to determine two daily limitations for TTO. The data sources and industrial sector to which each limitation applies are outlined in Table 1.

### Data

Total toxic organic data are presented in Appendix A. Each value is the sum of all toxic organic compounds found in the sample. In Chapter 6 there is a description of the toxic organic chemicals whose concentrations are summed to arrive at TTO, when toxic organic chemicals were reported below the detection limit (DL) the measurement was assigned a value equal to the DL. This yields TTO concentrations that tend to be slightly higher than actual concentrations and results in less stringent limitations than would be obtained by setting DL values equal to zero or some value between zero and the detection limit. TTO concentrations calculated by setting the DL values equal to zero (DL = 0) were also calculated; (indicated by "<" in the Table). Although summary information was examined for TTO concentrations generated using the DL=0 technique, no limitations were developed using these data.

Plants with TTO data were divided into three categories: Option 1 plants, (plants with precipitation-clarification) Option 2 plants (plants with precipitationclarification plus filtration) and other than Option 1 and Option 2 plants. Option 1 plants were used to estimate end-of-pipe TTO limits. These data are shown in Table 2; descriptive information regarding the limit derived from the data is in Table 1, section A. Raw waste TTO limits were estimated using the raw waste TTO data from all three categories. These data are shown in Table 3; descriptive information regarding the limit derived from these data is in Table 1, section B.

The data were also classified on the basis of other characteristics. This was done to investigate combinations of plants that would be expected, on the basis of processes, pre- and post-process water quality characteristics, products, or type of work, to generate larger amounts of TTO than other groups of plants. The processes were classified into two categories, painting and solvent degreasing (these two processes were specifically examined because they have higher TTO concentrations in the raw waste than metals finishers without these processes). Classifications were also provided for the raw waste stream, oil and grease (OG) concentration (which is an indicator of certain processes), and the TTO concentration in the plant's influent water supply ("supply stream"). The raw waste stream oil and grease data were used to place plants into groups with concentrations above and below 100 mg/l OG. The supply stream TTO data were used to categorize plants into groups with concentrations above and below 0.1 mg/l TTO. There were three product categories: printed circuit board manufacturing, automotive, and auto assembly. The type of work also considered, i.e., plants were classified as job shops or captives. If their work was partially job order or partially captive, then a percentage of involvement was generally provided. This array of classifications allows examination of the TTO characteristics of various components of the Metal Finishing Industry. The number of plants and observations used for the Option 1, treated effluent based analysis within each of the above described categories and various combinations are reported in Table 2. Similar information for the raw waste based analysis of the Option 1, Option 2, and other than Option 1 or Option 2 plants are reported in Table 3. The overall EPA metal finishing TTO data base is comprised of 75 observations from 29 plants. There were from 1 to 4 observations per plant.

## Analysis

Metal Finishing plants that paint and also solvent degrease (P&SD) discharge more toxic organic chemicals than any other sector of the metal finishing industry, with the partial exception of the automobile assembly plants (AA) (Tables 2 and 3). The P&SD group is the intersection of the painting group and the solvent degreasing group; i.e. it includes only plants that fit in both groups. P&SD plants were used to establish an overall mean. The overall mean specifically includes the AA plants because the AA plants are a subset of the P&SD plants. The P&SD group represents a more reasonable measure of process control than the AA plants; because P&SD plants are identifiable by the use of solvent degreasers and paints which are linked to the process rather than to the type of product produced. Finally, and significantly, there are more observations in the P&SD group (N=4 for the end-of-pipe data and N=5 for the untreated waste data) than in the AA group (N=2). Data based on process and larger sample sizes give a better measure of appropriate levels.

The painting or solvent degreasing group (PorSD) is the union of painting and solvent degreasing plants -- it includes plants from either group -- and is used to estimate overall variability. It is appropriate to estimate variability from the PorSD group because it corresponds with the processes used in the P&SD group which provided the mean and because there are more observations in the PorSD group than in the P&SD (Tables 2 and 3). The variability of the PorSD group is expressed as a variability factor (VF) which is calculated by dividing the lognormal estimate of the 99th percentile by the arithmetic mean. Details of the formulae and calculations are presented in Appendix B. Table 4 lists the data used for the treated effluent analysis; Table 5 lists the data used for the raw waste analysis.

The daily limitations are presented in Table 6. The VF from the PorSD group is multiplied by the arithmetic mean from the P&SD group to calculate the daily limitations.

In conclusion, these limitations are rather high as a result of the heavy consideration given to the painting and/or solvent degreasing operations at some MF plants. By comparison, if the entire data set was used, the daily maximum limitations for the raw waste option 1, option 2, and other than option 1 and option 2 plants would be 0.71 mg/l TTO and for the treated effluent of option 1 plants the daily maximum limitation would be 0.19 mg/l TTO.

## TABLE 1

## AN OUTLINE OF EACH TTO LIMITATION (A AND B) DESCRIBING THE DATA SOURCE AND INDUSTRIAL APPLICATION

A. Limits calculated using TTO concentrations after treatment of toxic metals with option 1 technology (precipitation-clarification).

  a. DATA SOURCE: Treated wastes of option 1 plants.

  b. APPLICATION: Applies to Metal Finishing (MF) and Electroplating Pretreatment (part 413, PSES) plants expected to treat toxic metals with precipitation-clarification treatment.

B. Limits calculated using TTO concentrations before treatment of waste waters.

  a. DATA SOURCE: Raw wastes, prior to treatment from option 1, option 2, and non option 1 or option 2 plants.

  b. APPLICATION: An interim limit for MF that applies prior to complying with limits in A, above. This is also a limit that applies to part 413, PSES for plants which are not expected to treat toxic metals with precipitation-clarification technology, namely, those discharging less than 10,000 gals/day.

## TABLE 2

## SUMMARY OF TTO (mg/l) DATA FROM THE TREATED EFFLUENT OF OPTION 1 METAL FINISHING PLANTS

| Subset | # of Plants | # of Observations | $\overline{X}$ | $\mu$ | $\sigma_p$ |
|---|---|---|---|---|---|
| Solvent Degreasing | 9 | 18 | 0.209 | -2.257 | 1.019 |
| Solvent Degreasing & not Painting | 5 | 14 | 0.144 | -2.630 | 1.019 |
| Painting | 7 | 10 | 0.231 | -1.854 | 0.521 |
| Painting & not Solvent Degreasing | 3 | 6 | 0.095 | -2.593 | 0.521 |
| Neither Painting nor Solvent Degreasing | 17 | 51 | 0.030 | -4.309 | 0.850 |
| Either painting or Solvent Degreasing | 12 | 24 | 0.180 | -2.33 | 0.948 |
| Painting and Solvent Degreasing | 4 | 4 | 0.434 | -.931 | -- |
| Printed Circuit Board Manufactuers | 4 | 12 | 0.166 | -2.318 | 1.061 |
| Automobile Assembly Plants | 2 | 2 | 0.536 | -0.643 | -- |
| 100% Jobshops | 11 | 32 | 0.046 | -3.934 | 0.864 |
| Any Jobshop Work | 14 | 41 | 0.064 | -3.808 | 0.939 |
| 100% Captive | 16 | 38 | 0.088 | -3.646 | 0.783 |
| Any Captive Work | 19 | 47 | 0.095 | -3.590 | 0.882 |
| TTO in the water supply greater than 0.1 mg/l | 3 | 6 | 0.171 | -1.904 | 0.423 |
| TTO in the water supply less than 0.1 mg/l | 21 | 52 | 0.084 | -3.796 | 0.909 |
| O&G in the raw waste greater than 100 mg/l | 4 | 6 | 0.231 | -1.714 | 0.521 |
| O&G in the raw waste less than 100 mg/l | 22 | 62 | 0.064 | -3.845 | 0.838 |
|  | === | === | ===== | ====== | ===== |
| TOTAL | 29 | 75 | 0.078 | -3.694 | 0.875 |

$\overline{X}$ = arithmetic mean, $\mu$ = log mean, $\sigma_p$ = pooled within plant log standard deviation.

## TABLE 3

## SUMMARY OF TTO (mg/l) DATA FROM THE RAW WASTE OF OPTION 1, OPTION 2, and OTHER THAN OPTION 1 & OPTION 2 METAL FINISHING PLANTS

| Category | # of Plants | # of Observations | $\overline{X}$ | $\mu$ | $\sigma_p$ |
|---|---|---|---|---|---|
| Solvent Degreasing | 11 | 23 | 0.381 | -1.965 | 1.149 |
| Solvent Degreasing & not Painting | 6 | 18 | 0.186 | -2.467 | 1.149 |
| Painting | 10 | 17 | 0.473 | -1.542 | 0.658 |
| Painting & not Solvent Degreasing | 5 | 12 | 0.220 | -2.172 | 0.658 |
| Neither Painting nor Solvent Degreasing | 20 | 56 | 0.112 | -3.434 | 0.579 |
| Either Painting or Solvent Degreasing | 16 | 35 | 0.326 | -2.032 | 1.012 |
| Painting and Solvent Degreasing | 5 | 5 | 1.081 | -0.156 | -- |
| Printed Circuit Board Manufactuers | 4 | 12 | 0.249 | -2.156 | 1.378 |
| Automobile Assembly Plants | 2 | 2 | 1.354 | 0.284 | -- |
| 100% Jobshops | 13 | 36 | 0.089 | -3.189 | 0.608 |
| Some Jobshop Work | 16 | 45 | 0.124 | -3.198 | 0.842 |
| 100% Captive | 21 | 49 | 0.247 | -2.734 | 0.658 |
| Some Captive Work | 24 | 58 | 0.250 | -2.808 | 0.848 |
| TTO in the water supply greater than 0.1 mg/l | 3 | 7 | 0.431 | -1.430 | 0.898 |
| TTO in the water supply less than 0.1 mg/l | 27 | 69 | 0.164 | -3.1003 | 0.664 |
| O&G in the raw waste greater than 100 mg/l | 5 | 9 | 0.456 | -2.022 | .250 |
| O&G in the raw waste less than 100 mg/l | 31 | 82 | 0.165 | -2.982 | 0.778 |
|  | == | == | ===== | ====== | ===== |
| TOTAL | 45 | 90 | 0.194 | -2.095 | .752 |

$\overline{X}$ = arithmetic mean $\mu$ = log mean $\sigma_p$ = pooled within plant log standard deviation.

TABLE 4

## A SUMMARY OF THE DATA USED TO CALCULATE LIMITS FOR THE TREATED EFFLUENT OF OPTION 1 METAL FINISHING PLANTS

| | | | CATEGORY | |
|---|---|---|---|---|
| PLANT | TTO[1] mg/l | ln TTO | P or SD[2] | P & SD[3] |
| 2032 | 0.082 | -2.501 | x | |
| | 0.207 | -1.575 | | |
| | 0.081 | -2.513 | | |
| 4069 | 0.254 | -1.370 | x | |
| | 0.131 | -2.033 | | |
| | 0.322 | -1.133 | | |
| 4071 | 0.032 | -3.442 | x | |
| | 0.040 | -3.219 | | |
| | 0.093 | -2.375 | | |
| 6019 | 0.483 | -0.728 | x | x |
| 17061 | 0.699 | -0.358 | x | |
| | 0.020 | -3.912 | | |
| | 0.034 | -3.381 | | |
| 20005 | 0.430 | -0.844 | x | x |
| 20103 | 0.181 | -1.709 | x | x |
| 9025 | 0.008 | -4.828 | x | |
| 28699 | 0.643 | -0.442 | x | x |
| 30165 | 0.130 | -2.040 | x | |
| 44062 | 0.228 | -1.478 | x | |
| | 0.122 | -2.104 | | |
| | 0.081 | -2.513 | | |
| 34051 | 0.016 | -4.135 | x | |
| | 0.007 | -4.962 | | |

---

[1] Concentrations of TTO after processing by the treatment facility.

[2] Painting or Solvent Degreasing is performed at the plant.

[3] Painting and Solvent Degreasing is performed at the plant.

x Indicates category membership.

# TABLE 5

## A SUMMARY OF THE DATA USED TO CALCULATE LIMITS FOR THE RAW WASTE OF OPTION 1, OPTION 2, AND OTHER THAN OPTION 1 OR OPTION 2 METAL FINISHING PLANTS

| | | | CATEGORY | |
|---|---|---|---|---|
| PLANT | TTO[1] mg/l | ln TTO | P or SD[2] | P & SD[3] |
| 2032 | 1.161 | 0.149 | x | |
| | 0.031 | -3.474 | | |
| | 0.109 | -2.216 | | |
| 4069 | 0.022 | -3.817 | x | |
| | 0.113 | -2.180 | | |
| | 0.178 | -1.726 | | |
| 4071 | 0.032 | -3.147 | x | |
| | 0.040 | -2.017 | | |
| | 0.093 | -2.040 | | |
| 4282 | 0.283 | -1.262 | x | x |
| 6019 | 0.473 | -0.749 | x | x |
| 9025 | 0.000 | - - | x | |
| | 0.251 | -1.382 | | |
| | 0.289 | -1.241 | | |
| 17061 | 0.888 | -0.119 | x | |
| | 0.036 | -3.324 | | |
| | 0.141 | -1.959 | | |
| 20103 | 1.938 | 0.662 | x | x |
| 28699 | 1.619 | 0.482 | x | x |
| 44062 | 0.098 | -2.323 | x | |
| | 0.110 | -2.207 | | |
| | 0.107 | -2.235 | | |
| 30165 | 0.140 | -1.966 | x | |
| 34051 | 0.091 | -2.397 | x | |
| | 0.095 | -2.354 | | |
| | 0.111 | -2.198 | | |
| 17050 | 1.083 | 0.090 | x | |
| | 0.477 | -0.740 | | |

## TABLE 5 (CON'D)

## A SUMMARY OF THE DATA USED TO CALCULATE LIMITS FOR THE RAW WASTE OF OPTION 1, OPTION 2, AND OTHER THAN OPTION 1 OR OPTION 2 METAL FINISHING PLANTS

|  |  |  | CATEGORY |  |
|---|---|---|---|---|
| PLANT | TTO[1] mg/l | ln TTO | P or SD[2] | P & SD[3] |
| 18538 | 0.064 | 0.030 | x |  |
|  | 0.012 | 0.056 |  |  |
|  | 0.009 | 0.001 |  |  |
| 2033 | 0.028 | -3.576 | x |  |
|  | 0.030 | -3.507 |  |  |
|  | 0.011 | -4.510 |  |  |
| 33692 | 1.090 | 0.086 | x | x |

---

[1] Concentrations of TTO before processing by the treatment facility.

[2] Painting or Solvent Degreasing is performed at the plant.

[3] Painting and Solvent Degreasing is performed at the plant.

x Indicates category membership.

## TABLE 6

## DAILY LIMITATIONS FOR TTO (mg/l) IN THE METAL FINISHING INDUSTRY

| | $\overline{Y}_{P\&SD}$ | $\overline{Y}_{P\text{ or }SD}$[2] | $\overline{Y}_{.99}$[3] | $VF_{P\text{ or }SD}$[4] | LIMIT[5] |
|---|---|---|---|---|---|
| Raw Waste[6] | 1.081 | 0.326 | 1.380 | 4.23 | 4.57 |
| Treated Effluents[7] | 0.434 | 0.180 | 0.883 | | 2.13 |

---

[1] Arithmetic mean of plants that paint and solvent degrease.

[2] Arithmetic mean of plants that either paint or solvent degrease.

[3] Lognormal estimates of the 99th percentile (Appendix B) from plants that paint or solvent degrease.

[4] Variability factor from plants that paint or solvent degrease, $VF = X_{.99}/\overline{X}_{P\text{ or }SD}$.

[5] Limitation = $VF_{P\text{ or }SD} \cdot \overline{X}_{P\&SD}$

[6] TTO concentrations from the raw wastewater of option 1, option 2, and nonoption 1 or 2 metal finishing plants.

[7] TTO concentrations from the treated wastewater option 1 metal finishing plants.

EXHIBIT 2

APPENDIX A

## METAL FINISHING - OPTION 1 PLANTS FOR TTO DATA BASE

| Plant ID | Job Shop | Captive | PCBM | Metal Finishing Plant | Solvent Degreasing | Painting | Automotive Plant | Auto Assembly Plant | Supply Water Sampled | Water Supply TTO >0.1 mg/ℓ | Total Raw O&G >100 mg/ℓ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2032 | 10% | 90% | ✓ | ✓ | ✓ | | | | | | |
| 4069 | | ✓ | ✓ | ✓ | ✓ | | | | ✓ | ✓ | |
| 4071 | | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | |
| 4282 | | ✓ | | ✓ | ✓ | ✓ | | | ✓ | ✓ | |
| 4892* | | ✓ | | ✓ | ✓ | ✓ | | ✓ | ✓ | ✓ | |
| 6019 | | ✓ | | ✓ | ✓ | ✓ | | | | | |
| 6090 | ✓ | | | ✓ | | | | | ✓ | | |
| 6091 | ✓ | | | ✓ | | | | | | | |
| 6110 | ✓ | | | ✓ | | | | | ✓ | | |
| 6960 | ✓ | | | ✓ | | | | | ✓ | | |
| 9025 | | ✓ | | ✓ | | ✓ | | | | | |
| 9052 | | ✓ | | ✓ | | | | | ✓ | | |
| 12061 | ✓ | ✓** | | ✓ | | | | | | | |
| 15193* | | ✓ | | ✓ | ✓ | ✓ | | | ✓ | | |
| 15608 | | ✓ | | ✓ | | | | | ✓ | | |
| 17061 | 70% | 30% | ✓ | ✓ | ✓ | | | | ✓ | | |
| 19068 | ✓ | | | ✓ | | | | | | | |
| 20005 | | ✓ | | ✓ | ✓ | ✓ | | ✓ | ✓ | | |
| 20022 | ✓ | | | ✓ | | | | | ✓ | | |
| 20083 | 75% | 25% | | ✓ | | | | | ✓ | | |
| 20103 | | ✓ | | ✓ | ✓ | ✓ | | | ✓ | | ✓ |
| 21003 | | ✓ | | ✓ | | | | | ✓ | | |
| 21051* | 40% | 60% | | ✓ | | | | | ✓ | | |
| 27046 | | ✓ | | ✓ | | | | | ✓ | | |
| 28699 | | ✓ | | ✓ | ✓ | ✓ | | ✓ | ✓ | | ✓ |
| 30054 | | ✓ | | ✓ | | | | | ✓ | ✓ | |
| 30165 | | ✓ | | No | | ✓ | ✓ | | ✓ | | ✓ |
| 34050 | | ✓ | | ✓ | | | | | ✓ | | |
| 34051 | ✓ | | | ✓ | ✓ | | | | ✓ | | |
| 38051 | ✓ | | | ✓ | | | | | ✓ | | |
| 38052 | ✓ | | | ✓ | | | | | ✓ | | |
| 41051 | | ✓ | | ✓ | | | | | | | |
| 44062 | ✓ | | | ✓ | | ✓ | | | ✓ | | ✓ |

* No total raw waste or total effluent TTO data available.

** Electroplating-captive, wire drawing - job shop - no percentage breakdown supplied General Cable Corporation (likely captive).

# METAL FINISHING - OPTION 1 PLANTS
TTO DATA BASE

| Plant ID | Total Raw | Total Effluent | Example Streams | |
|---|---|---|---|---|
| 2032 | ✓ | ✓ | | |
| 4069 | ✓ | ✓ | ✓ | |
| 4071 | ✓ | ✓ | ✓ | |
| 4282 | ✓ | | | |
| 4892 | | | ✓ | |
| 6019 | ✓* | ✓ | ✓ | * Total raw TTO from precision and accuracy study. |
| 6090 | ✓ | ✓ | ✓ | |
| 6091 | | ✓ | ✓ | |
| 6110 | ✓ | ✓ | | |
| 6960 | ✓ | ✓ | | |
| 9025 | ✓ | ✓ | | |
| 9052 | ✓ | ✓ | | |
| 12061 | ✓* | ✓ | | * 14-0 - total raw not available. |
| 15193 | | | ✓ | |
| 15608 | ✓ | ✓ | | |
| 17061 | ✓ | ✓ | | |
| 19068 | ✓* | ✓ | | * 14-0 - no TTO raw waste data. |
| 20005 | | ✓ | ✓ | |
| 20022 | ✓ | ✓ | ✓ | |
| 20083 | ✓ | ✓ | ✓ | |
| 20103 | ✓ | ✓* | ✓ | * 21-1 - no TTO effluent data. |
| 21003 | ✓ | ✓ | | |
| 21051 | | | ✓ | |
| 27046 | ✓* | ✓ | | * 15-2 - no TTO raw waste data. |
| 28699 | ✓ | ✓ | ✓ | |
| 30054 | ✓ | ✓ | | |
| 30165 | ✓ | ✓ | ✓ | |
| 38052 | ✓ | ✓ | | |
| 41051 | ✓ | ✓ | | |
| 44062 | ✓ | ✓ | | |
| 34050 | | ✓ | ✓ | |
| 34051 | ✓ | ✓* | | *15-0 - no TTO effluent data. |
| 38051 | ✓ | ✓ | | |

## TTO DATA SUMMARY - METAL FINISHING - OPTION 1 PLANTS

TTO Concentration (mg/ℓ)

| | RAW | | EFFLUENT | |
|---|---|---|---|---|
| | With < | W/O < | With < | W/O < |
| 2032-15-0 | 1.161 | 1.158 | 0.082 | 0.075 |
| 2032-15-2 | 0.031 | 0.026 | 0.207 | 0.202 |
| 2032-15-5 | 0.109 | 0.103 | 0.081 | 0.074 |
| 4069-15-0/1 | 0.022 | 0.014 | 0.254 | 0.245 |
| 4069-15-2/3 | 0.113 | 0.109 | 0.131 | 0.121 |
| 4069-15-4 | 0.178 | 0.175 | 0.322 | 0.322 |
| 4071-15-0 | 0.043 | 0.035 | 0.032 | 0.019 |
| 4071-15-1 | 0.133 | 0.124 | 0.040 | 0.032 |
| 4071-15-3 | 0.130 | 0.121 | 0.093 | 0.089 |
| 4282-21-0 | 0.283 | 0.283 | ---- NO DATA ---- | |
| 6090-14-0 | 0.097 | 0.093 | 0.203 | 0.199 |
| 6090-15-1 | 0.486 | 0.475 | 0.052 | 0.043 |
| 6090-15-2 | 8.466 | 8.458 | 36.355 | 37.342 |
| 6091-15-0 | -- | -- | 0.019 | 0.015 |
| 6091-15-1 | -- | -- | 0.001 | 0 |
| 6091-15-2 | -- | -- | 0.019 | 0.018 |
| 6110-15-0 | 0.010 | 0 | 0.006 | 0.001 |
| 6110-15-1 | 0.009 | 0 | 0.005 | 0 |
| 6110-15-2 | 0.009 | 0 | 0.006 | 0 |
| 6960-15-0/1 | 0.104 | 0.099 | 0.056 | 0.049 |
| 6960-15-2/3 | 0.204 | 0.198 | 0.144 | 0.142 |
| 6960-15-4/5 | 0.059 | 0.052 | 0.038 | 0.036 |
| 9025-15-0 | 0 | 0 | 0 | 0 |
| 9025-15-1 | 0.251 | 0.248 | 0.008 | 0 |
| 9025-15-2 | 0.289 | 0.285 | 18.005 | 18.0 |

FOOTNOTE:

-- = No total plant wastewater TTO data available.
No Data = No toxic organics data available.

# TTO DATA SUMMARY - METAL FINISHING - OPTION 1 PLANTS

TTO Concentration (mg/ℓ)

| | RAW | | EFFLUENT | |
|---|---|---|---|---|
| | With < | W/O < | With < | W/O < |
| 9052-15-0 | 0.009 | 0 | 0.010 | 0 |
| 9052-15-1 | 0.040 | 0.034 | 0.002 | 0 |
| 9052-15-2 | 0.012 | 0.003 | 0.007 | 0 |
| 12061-14-0 | -- | -- | 0.037 | 0.037 |
| 12061-15-0 | 0.006 | 0.0001 | 0.005 | 0 |
| 12061-15-1 | 0.030 | 0.030 | 0.014 | 0 |
| 12061-15-2 | 0.006 | 0.0001 | 0.008 | 0.0001 |
| 15608-15-0 | 0.019 | 0 | 0.004 | 0.0001 |
| 15608-15-1 | 0.038 | 0.032 | 0.013 | 0 |
| 15608-15-2 | 0.017 | 0.0001 | 0.015 | 0.0001 |
| 17061-14-1 | 0.888 | 0.886 | 0.699 | 0.696 |
| 17061-15-1 | 0.036 | 0.031 | 0.020 | 0.012 |
| 17061-15-3 | 0.141 | 0.139 | 0.034 | 0.011 |
| 19068-14-0 | ----- NO DATA ----- | | 0.025 | 0.020 |
| 19068-15-1 | 0.120 | 0.119 | 0.017 | 0.010 |
| 19068-15-2 | 0.202 | 0.196 | 0.016 | 0.013 |
| 10005-21-0 | -- | -- | 0.430 | 0.357 |
| 20022-15-0 | 0.020 | 0.0009 | 0.008 | 0.0003 |
| 20022-15-1 | 0.008 | 0 | 0.016 | 0 |
| 20022-15-2 | 0.007 | 0 | 0.009 | 0 |
| 20083-15-0/1 | 0.002 | 0.0004 | 0.004 | 0 |
| 20083-15-2/3 | 0.003 | 0 | 0.004 | 0 |
| 10083-15-4/5 | 0.003 | 0.0001 | 0.007 | 0.0001 |
| 20103-21-0 | 1.938 | 1.868 | 0.181 | 0.061 |
| 20103-21-1 | 12.866 | 12.826 | ----- NO DATA ----- | |
| 21003-15-0 | 0.034 | 0.024 | 0.002 | 0.002 |
| 21003-15-1 | 0.040 | 0.034 | 0.035 | 0.028 |
| 21003-15-2 | 0.014 | 0 | 0.008 | 0.007 |

FOOTNOTE:

-- = No total plant wastewater TTO data available.
No Data = No toxic organics data available.

## TTO DATA SUMMARY - METAL FINISHING - OPTION 1 PLANTS
(Continued)
TTO Concentration (mg/ℓ)

| | RAW | | EFFLUENT | |
|---|---|---|---|---|
| | With < | W/O < | With < | W/O < |
| 27046-15-0 | 0.426 | 0.420 | 0.012 | 0 |
| 27046-15-1 | 0.400 | 0.398 | 0.002 | 0 |
| 27046-15-2 | ------ NO DATA ----- | | 0.007 | 0 |
| 28699-12-0 | 1.619 | 1.619 | 0.643 | 0.643 |
| 30054-15-0 | 0.364 | 0.354 | 0.067 | 0.060 |
| 30054-15-1 | 0.769 | 0.761 | 0.140 | 0.138 |
| 30054-15-2 | 1.287 | 1.282 | 0.109 | 0.108 |
| 30165-21-0 | 0.140 | 0.070 | 0.130 | 0.060 |
| 34050-15-0 | -- | -- | 0.007 | 0 |
| 34050-15-1 | -- | -- | 0.020 | 0.011 |
| 34050-15-2 | -- | -- | 0.007 | 0 |
| 34051-15-0 | 0.091 | 0.086 | -- | -- |
| 34051-15-1 | 0.095 | 0.084 | 0.016 | 0 |
| 34051-15-2 | 0.111 | 0.110 | 0.007 | 0 |
| 38051-15-0 | 0.224 | 0.214 | 0.007 | 0 |
| 38051-15-1 | 0.259 | 0.255 | 0.005 | 0 |
| 38051-15-2 | 0.097 | 0.094 | 0.003 | 0 |
| 38052-15-0 | 0.099 | 0.096 | 0.180 | 0.173 |
| 38051-15-1 | 0.192 | 0.188 | 0.012 | 0 |
| 38052-15-2 | 0.200 | 0.199 | 0.109 | 0.101 |
| 41051-15-0 | 0.014 | 0.001 | 0.013 | 0 |
| 41051-15-1 | 0.020 | 0.014 | 0.024 | 0.018 |
| 41051-15-2 | 0.023 | 0.018 | 0.012 | 0 |
| 44062-15-0 | 0.098 | 0.087 | 0.228 | 0.227 |
| 44062-15-1 | 0.110 | 0.101 | 0.122 | 0.110 |
| 44062-15-2 | 0.107 | 0.097 | 0.081 | 0.074 |
| 6019 | -- | -- | 0.485 | 0.485 |
| 6019 (P&A) | 0.473 | 0.473 | 0.483 | 0.483 |

<u>FOOTNOTE</u>:

-- = No total plant wastewater TTO data available.
No Data = No toxic organics data available.

## METAL FINISHING - OPTION 2 PLANTS FOR TTO DATA BASE

| Plant ID | Job Shop | Captive | PCBM | Metal Finishing Plant | Solvent Degreasing | Painting | Automotive Plant | Auto Assembly Plant | Supply Water Sampled | Water Supply TTO >0.1 mg/ℓ | Total Raw O&G >100 mg/ℓ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12075 | | ✓ | | ✓ | | | | | ✓ | | ✓ |
| 14062* | | ✓ | | ✓ | ✓ | ✓ | | | ✓ | | |
| 17050 | | ✓ | | ✓ | | ✓ | | | ✓ | | |
| 18538 | | ✓ | | ✓ | | ✓ | | | ✓ | | |
| 31031* | | ✓ | | ✓ | ✓ | ✓ | | | ✓ | ✓ | |
| 36048 | | ✓ | | ✓ | ✓ | | | | ✓ | | |

* No total raw waste or total effluent TTO data available.

## METAL FINISHING - OPTION 2 PLANTS
## TTO DATA BASE

| Plant ID | Total Raw | Total Effluent | Example Streams |
|---|---|---|---|
| 12075 | ✓ | ✓ | ✓ |
| 14062 | | | ✓ |
| 17050 | ✓* | ✓ | ✓ |
| 18538 | ✓ | ✓ | |
| 31031 | | | ✓ |
| 36048 | | ✓ | ✓ |

*14-0 - no TTO raw waste data.

## TTO DATA SUMMARY - METAL FINISHING - OPTION 2 PLANTS

TTO Concentration (mg/ℓ)

| | RAW | | EFFLUENT | |
|---|---|---|---|---|
| | With < | W/O < | With < | W/O < |
| 12075-15-0/1 | 0.028 | 0.0003 | 0.043 | 0.025 |
| 12075-15-2/3 | 0.021 | 0.0004 | 0.010 | 0 |
| 12075-15-4/5 | 0.042 | 0.020 | 0.007 | 0 |
| 17050-14-0 | -- | -- | 0.400 | 0.400 |
| 17050-15-0 | 1.083 | 1.081 | 0.003 | 0 |
| 17050-15-1 | 0.477 | 0.475 | 0.037 | 0.032 |
| 18538-14-0 | 0.064 | 0.019 | 0.030 | 0 |
| 18538-15-3 | 0.012 | 0.004 | 0.056 | 0.055 |
| 18538-15-5 | 0.009 | 0 | 0.001 | 0 |
| 36048-15-0/1 | -- | -- | 0.415 | 0.413 |
| 36048-15-2/3 | -- | -- | 0.103 | 0.097 |
| 36048-15-4/5 | -- | -- | 0.091 | 0.081 |

**FOOTNOTE:**

-- = No total plant wastewater TTO data available.
No Data = No toxic organics data available.

# METAL FINISHING - OTHER THAN OPTION 1 OR 2 PLANTS FOR THE TTO DATA BASE

| Plant ID | Job Shop | Captive | PCBM | Metal Finishing Plant | Solvent Degreasing | Painting | Automotive Plant | Auto Assembly Plant | Supply Water Sampled | Water Supply TTO >0.1 mg/ℓ | Total Raw O&G >100 mg/ℓ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2033 | | ✓ | | ✓ | ✓ | | | | ✓ | | |
| 3043 | | ✓ | | ✓ | | ✓ | | | ✓ | ✓ | |
| 11103 | ✓ | | | ✓ | | | | | ✓ | | |
| 11108 | ✓ | | | ✓ | | | | | ✓ | | |
| 12065 | ✓ | | | ✓ | | | | | ✓ | | |
| 13042 | | ✓ | | ✓ | ✓ | ✓ | | | | | |
| 19069 | | ✓ | | ✓ | | | | | ✓ | | |
| 20170 | | ✓ | | ✓ | ✓ | ✓ | | | ✓ | | |
| 21066 | | ✓ | | ✓ | | | | | ✓ | | |
| 30166 | | ✓ | | NO | ✓ | | | | ✓ | | |
| 31032 | | ✓ | ✓ | ✓ | ✓ | | | | | | |
| 33692 | | ✓ | | ✓ | ✓ | ✓ | | ✓ | | | |
| 36178 | | ✓ | | NO | | ✓ | | ✓ | ✓ | | |
| 38040 | | ✓ | | ✓ | ✓ | ✓ | | | | | |
| 38217 | | ✓ | | ✓ | ✓ | ✓ | | | | | |
| 40060 | ✓ | | | ✓ | | | | | ✓ | | |

## METAL FINISHING - OTHER THAN OPTION 1 OR 2 PLANTS FOR THE TTO DATA BASE

| Plant ID | Total Raw | Total Effluent | Example Streams |
|---|---|---|---|
| 2033 | ✓ | ✓ | |
| 3043 | | | ✓ |
| 11103 | ✓ | ✓ | ✓ |
| 11108 | ✓ | ✓ | |
| 12065 | | ✓ | ✓ |
| 21066 | ✓ | ✓* | |
| 20170 | | | ✓ |
| 31032 | | | ✓ |
| 30166 | | | ✓ |
| 36178 | ✓ | ✓ | ✓ |
| 40060 | ✓ | ✓ | ✓ |
| 19069 | | ✓ | |
| 33692 | ✓ | ✓ | |
| 38040 | | ✓ | ✓ |
| 38217 | | ✓ | ✓ |
| 13042 | | ✓ | ✓ |

*15-0 - No TTO effluent data.

## TTO DATA SUMMARY - METAL FINISHING PLANTS
## OTHER THAN OPTION 1 or 2
## TTO Concentration (mg/ℓ)

| | RAW | | EFFLUENT | |
|---|---|---|---|---|
| | With < | W/O < | With < | W/O < |
| 2033-15-0/1 | 0.028 | 0.012 | 0.014 | 0.011 |
| 2033-15-2/3 | 0.030 | 0.019 | 0.010 | 0.0007 |
| 2033-15-4/5 | 0.011 | 0.003 | 0.014 | 0.013 |
| 11103-15-0 | 0.084 | 0.069 | 0.011 | 0.0001 |
| 11103-15-2/3 | 0.010 | 0.0001 | 0.009 | 0.0001 |
| 11103-15-4 | 0.013 | 0.0001 | 0.009 | 0.0001 |
| 11108-15-0 | 0.011 | 0 | 0.005 | 0 |
| 11108-15-1 | 0.005 | 0.003 | 0.006 | 0 |
| 11108-15-2 | 0.007 | 0 | 0.001 | 0.001 |
| 12065-14-1 | -- | -- | 2.52 | 2.52 |
| 12065-15-2 | -- | -- | 0.189 | 0.168 |
| 12065-15-4 | -- | -- | 0.153 | 0.144 |
| 13042-21-1 | -- | -- | 0.165 | 0.165 |
| 19069-15-0 | -- | -- | 0.005 | 0 |
| 19069-15-1 | -- | -- | 0.007 | 0 |
| 19069-15-2 | -- | -- | 0.007 | 0 |
| 21066-15-0 | 0.012 | 0 | ----- NO DATA ----- | |
| 21066-15-1 | 0.011 | 0.001 | 0.009 | 0 |
| 21066-15-3 | 0.014 | 0.003 | 0.011 | 0 |
| 33692-23-0 | 1.09 | 1.08 | 0.823 | 0.763 |
| 33692-23-1 | 13.50 | 13.49 | 0.433 | 0.373 |
| 36178-21-0 | 0.285 | 0.285 | 0.257 | 0.257 |
| 36178-21-1 | 0.326 | 0.326 | 0.140 | 0.140 |
| 36178-21-2 | 2.005 | 2.005 | 0.120 | 0.120 |
| 38040-23-0 | -- | -- | 0.288 | 0.218 |
| 38040-23-1 | -- | -- | 0.377 | 0.327 |
| 38217-23-0 | -- | -- | 0.673 | 0.634 |
| 40060-15-0 | .008 | .0001 | 0.012 | 0 |
| 40060-15-1 | .009 | 0 | 0.012 | 0 |

<u>FOOTNOTE</u>:

-- = No total plant wastewater TTO data available.
No Data = No toxic organics data available.

EXHIBIT 2

## APPENDIX B

# DEFINITIONS

| | |
|---|---|
| $K$ | total number of plants |
| $n_i$ | number of observations at plant i |
| $\sum_{i=1}^{K} n_i = N$ | total number of observations |
| $Y_{ij}$ | concentration of TTO in mg/l, observation j at plant i; $j = 1, \ldots, n_i$, $i = 1, \ldots, K$ |
| $\ln Y_{ij} = X_{ij}$ | natural logarithm of TTO in mg/l |
| $\mu = \sum_{i=1}^{K} \sum_{j=1}^{n_i} X_{ij}/N$ | mean of the logs |
| $\sigma^2 i = \sum_{j=1}^{n_i} (\overline{X}_i - X_{ij})/n_i - 1$ | within plant variance, for plant i |
| $\sigma_p^2 = \frac{\sum_{i=1}^{K} (n_i - 1)\ \sigma^2_i}{\sum_{i=1}^{K} (n_i - 1)}$ | pooled within plant variance |
| $\sigma_p = \sqrt{\sigma_p^2}$ | pooled within plant standard deviation |
| $E(Y) = e^{\mu + \sigma_p 2/2}$ | estimated mean (expected value) of the distribution of Y |
| $Y_{.99} = e^{\mu + 2.326\ (\sigma)_p}$ | estimated 99th percentile |
| $\overline{Y} = \sum_{i=1}^{k} \sum_{j=1}^{n_i} Y_{ij}/N$ | arithmetic mean of all observations |

# METAL FINISHING - TTO
# RAW WASTE - OPTION 1, OPTION 2, AND OTHERS

## Daily Data

**P or SD:**

$N = 35$

$\mu = 2.032$

$\sigma^2_p = 1.024$

$\sigma_p = 1.012$

$$Y_{.99} = e^{-2.032+2.326(1.021)}$$

$$= e^{0.322}$$

$$= 1.380$$

$$E(Y) = e^{-2.032+0.5(1.024)}$$

$$= e^{-1.520}$$

$$= 0.219$$

$\overline{Y} = 0.326$

**P&SD:**

$N = 5$

$\overline{Y} = 1.081$

## METAL FINISHING - TTO
## TREATED EFFLUENT - OPTION 1

Daily Data

P or SD:

$N = 24$

$\mu = 2.33$

$\sigma_p^2 = 0.899$

$\sigma_p = 0.948$

$$Y_{.99} = e^{-2.33+2.326(.948)}$$
$$= e^{-.125}$$

$$= 0.883$$

$$E(Y) = e^{-2.33+.5(.899)}$$

$$= e^{-1.88}$$

$$= 0.153$$

$\overline{Y} = 0.180$

P&SD:

$N = 4$

$\overline{Y} = 0.434$

EXHIBIT #3

# Analysis of New Source Cadmium (Cd) Data

## Introduction

This exhibit documents the data and methodology used to determine New Source Performance Standards (NSPS) and Pretreatment Standards for New Sources (PSNS) for the Metal Finishing Industry for Cadmium (Cd). The NSPS for Cd will require treatment of the segregated waste from Cd plating, acid cleaning of Cd plated parts, and chromating of Cd plated parts with evaporative recovery or ion exchange technology. These processes are the major sources of Cd in the Metal Finishing Industry, but there are no known metal finishing plants in existence that have all components of the treatment technology required by NSPS. Some plants, for example, have evaporative recovery applied to their Cd plating operation, but not the acid cleaning or chromating which is instead commingled with other wastes prior to wastewater treatment.

The evaporative recovery and ion exchange technologies are capable of eliminating the discharge from Cd related processes and thereby reducing concentrations of Cd to extremely low levels. In order to estimate treated effluent Cd concentrations achievable using these technologies, we have examined data on Cd concentrations in the untreated wastewater from metal finishing plants that do not plate Cd. It has been found that in the untreated wastes of plants not involved with Cd plating, measurable quantities of Cd still exist, possibly from source waters or from the waste water of operations that do not plate Cd but contain low concentrations of Cd. Therefore, in order to establish NSPS limits for Cd we have assumed that background concentrations from the raw waste streams of metal finishing plants not involved with Cd plating are similar to the Cd concentrations in wastewaters that have been treated according to NSPS requirements.

## Data

The data from plants not involved with Cd plating are listed in Appendix A and include measurements of Cd (mg/l) in raw (untreated) wastewater. The sampling and analyses were conducted by EPA. There are a total of 61 measurements from 27 plants. Eight of the 27 plants have single observations. The data range from 0.005 mg/l to 0.095 mg/l Cd.

## Analysis

The data were assumed to follow a lognormal distribution by plant. The lognormal has been found to provide a satisfactory fit to effluent data for a wide range of industrial categories and pollutants.* This data base includes too few values from any given plant to confirm the assumption of lognormality; however they do not contradict it. Cadmium concentrations have been transformed using the natural logarithm function and are hereafter refered to as logs. (The symbol "ln" means natural logarithm).

Because the data exhibited large plant to plant variation, several methods of grouping the plants into subsets with statistically homogenous means were examined. The subsets are based on a statistical partitioning of the data. They should reflect variation in underlying unidentifiable sources of cadmium. The purpose of this exercise was to assess the possibility of determining limitations on the basis of groups of statistically homogenous plant values. Subsets were chosen based on several statistical comparisons of plant means: Duncan's multiple range test, Student-Newman-Keuls, Scheffe's, and Tukey's tests. These tests examine the log means of plants with multiple observations and place them into groups with nonsignificantly different means. The groups can overlap, for example, a given plant or several plants can have log means that are intermediate in size between two groups (a larger mean group and a smaller mean group). The plants with intermediate log means are not statistically larger than the small mean group, and not statistically smaller than the large mean group; therefore, these plants fall in the overlap between the two groups and it would be reasonable to include them in both or either group(s). Thus, subset definition, because of the overlap, is somewhat flexible. Five groupings emerged that were supported by the four mean comparison tests. These are shown in Appendix B.

The large variation in Cd levels among the 5 groups of plants suggested that limitations could be based reasonbly on subsets of the plants that were homogenous statistically. Accordingly, the NSPS Cd limits are based on subsets of the plants with the largest mean Cd concentrations. The data from these subsets are shown in Table 1. The plants with the statistically largest mean are designated as subset 2. Plants in the group with the next largest mean are included in subset 1 along with the two plants in 2. Although only plants with multiple observations were included in the multiple comparison tests, plants with single observations that fell within the group ranges are also listed in Table 1. The mean used in determining the NSPS Cd limits was taken from subset 2 (the set with the largest mean.) The variance estimate used to determine variability was taken from subset 1 because this provided a reasonable quantity of data with which to estimate the variance and an F test showed that the pooled within plant variance for subset 1 was significantly greater than the variance for the other subsets combined.

---

* The methodology used here for fitting the lognormal distribution to effluent data across plants is discussed in detail in the Final Development Document for the Porcelain Enameling Industry, EPA 440/1-82/072.

Table 2 presents several statistics that summarize the entire data set and statistics based on three methods of partitioning the Cd raw waste concentration data into subsets.

The limits are based upon the variability of subset 1 and the mean of subset 2. The variability is expressed as a variability factor (VF) and calculated by dividing the estimated 99th percentile (daily and 10-day 99th percentile estimates as described in Appendix C) from subset 1 by the arithmetic mean from subset 1. The mean Cd concentration is obtained from subset 2; the subset 2 arithmetic mean is then multiplied by the subset 1 variability factors to arrive at daily maximum and 10-day average maximum limitations (shown in Table 3). This multiplication, therefore, used both the highest variability group and the highest mean concentration group, producing a limit that is larger than would result from reliance on any single group.

In conclusion, it should be noted that the limitations in Table 3 are large relative to the limitations calculated using the entire data set. If all 61 observations had been used for the VF and the overall mean, the daily maximum and 10-day average maximum limitations would be 0.017 and 0.0115 mg/l of Cd respectively. (see Table 2). This serves to illustrate the effect of using subsets of plants for the purpose of determining limitations.

TABLE 1

Subsets of Cd (mg/l) Concentrations that have Higher Values
(Subsets with lower values are presented in Appendix B)

| Plant | Raw Cd (mg/l) | ln Cd | Subsets | |
|---|---|---|---|---|
| 4065 | 0.005 | -5.2983 | 1 | |
| | 0.032 | -3.4420 | | |
| 6074 | 0.019 | -3.9633 | 1 | |
| | 0.021 | -3.8632 | | |
| | 0.033 | -3.4112 | | |
| 6083 | 0.013 | -4.3428 | 1 | |
| 6731 | 0.015 | -4.1997 | 1 | |
| | 0.017 | -4.0745 | | |
| | 0.019 | -3.9633 | | |
| 15070 | 0.009 | -4.7105 | 1 | |
| | 0.013 | -4.3428 | | |
| | 0.014 | -4.2687 | | |
| 19063 | 0.011 | -4.5099 | 1 | |
| | 0.012 | -4.4228 | | |
| | 0.013 | -4.3428 | | |
| 20080 | 0.024 | -3.7297 | 1 | |
| 27044 | 0.022 | -3.8167 | 1 | |
| 31020 | 0.021 | -3.8632 | 1 | |
| 31022 | 0.011 | -4.5099 | 1 | |
| | 0.013 | -4.3428 | | |
| 33024 | 0.095 | -2.3539 | 1 | 2 |
| 33073 | 0.013 | -4.3428 | 1 | |
| | 0.013 | -4.3428 | | |
| | 0.015 | -4.1997 | | |
| 36041 | 0.042 | -3.1701 | 1 | 2 |
| | 0.042 | -3.1701 | | |
| | 0.053 | -2.9375 | | |

N = 27

## TABLE 2

## Estimates for NSPS Cd (mg/1) in the Metal Finishing Industry

| Daily | E(Y) | $Y_{.99}$ | $\bar{Y}$ | $\mu$ | $\sigma p$ |
|---|---|---|---|---|---|
| All plants | 0.0093 | 0.017 | 0.013 | -4.726 | 0.2937 |
| All plants except plant 33024 | 0.0089 | 0.017 | 0.012 | -4.765 | 0.2937 |
| Subset A Plants | 0.0197 | 0.045 | 0.023 | -3.998 | 0.3885 |
| Subset B Plants | 0.0551 | 0.075 | 0.075 | -2.908 | 0.1342 |

| 10 Day | $Y_{.99}$ (10) | $\mu_{10}$ | $\sigma_{10}$ |
|---|---|---|---|
| All plants | 0.012 | -4.683 | 0.0947 |
| All plants except plant 33024 | 0.009 | -4.722 | 0.0947 |
| Subset A Plants | 0.026 | -3.931 | 0.1273 |
| Subset B Plants | 0.061 | -2.900 | 0.0424 |

E(Y) = estimated lognormal mean
$Y_{.99}$ = estimated lognormal 99th percentile
$\mu$ = estimated log mean
$\sigma$ = estimated pooled within plant log standard deviation
$Y_{.99}(10)$ = estimated 10 day average 99th percentile
$\mu_{10}$ = estimated 10 day log mean
$\sigma_{10}$ = estimated 10 day log standard deviation

## TABLE 3

## A Summary of Values Used to Estimate the NSPS Cd Limitations

| | $\overline{Y}_A$[1] | $\overline{Y}_B$[2] | $\overline{Y}_{.99}$[3] | $VF_A$[4] | Limit[5] |
|---|---|---|---|---|---|
| Daily | 0.023 | 0.058 | 0.045 | 1.96 | 0.114 |
| 10-Day | | | 0.026 | 1.13 | 0.066 |

---

[1] Arithmetic mean of subset A.

[2] Arithmetic mean of subset B.

[3] Lognormal estimates of 99th percentile, daily and 10-day, based on data from subset A.

[4] Variability Factors from subset A, $VF_A = Y_{.99}/\overline{Y}_A$.

[5] Limitation = $VF_A \cdot \overline{Y}_B$.

EXHIBIT 3

APPENDIX A

## Cd DATA BASE

| Observation Number | Plant ID | Raw (mg/l) | Observation Number | Plant ID | Raw (mg/l) |
|---|---|---|---|---|---|
| 1. | 6101-12-1 | .001 | 32. | 40062-8-0 | .008 |
| 2. | 6101-12-1 | .002 | 33. | 33065-9-1 | .009 |
| 3. | 19068-14-0 | .002 | 34. | 15070-1-3 | .009 |
| 4. | 11477-22-1 | .002 | 35. | 19063-1-1 | .011 |
| 5. | 11477-22-2 | .002 | 36. | 31022-1-2 | .011 |
| 6. | 15010-12-2 | .004 | 37. | 19063-1-2 | .012 |
| 7. | 15010-12-3 | .005 | 38. | 20083-1-5 | .012 |
| 8. | 4065-8-1 | .005 | 39. | 20082-1-6 | .012 |
| 9. | 4069-8-1 | .005 | 40. | 31022-1-0 | .013 |
| 10. | 4069-8-1 | .005 | 41. | 33073-1-1 | .013 |
| 11. | 5020-1-4 | .005 | 42. | 33073-1-3 | .013 |
| 12. | 5020-1-5 | .005 | 43. | 6083-1-2 | .013 |
| 13. | 5020-1-6 | .005 | 44. | 15070-1-1 | .013 |
| 14. | 19051-6-0 | .005 | 45. | 19063-1-3 | .013 |
| 15. | 20078-1-2 | .005 | 46. | 15070-1-2 | .014 |
| 16. | 20078-1-3 | .005 | 47. | 33073-1-2 | .015 |
| 17. | 20078-1-4 | .005 | 48. | 6731-1-1 | .015 |
| 18. | 20078-1-7 | .005 | 49. | 6731-1-2 | .017 |
| 19. | 36040-1-1 | .005 | 50. | 6074-1-1 | .019 |
| 20. | 36040-1-1 | .005 | 51. | 6731-1-3 | .019 |
| 21. | 36040-1-1 | .005 | 52. | 6074-1-1 | .021 |
| 22. | 31021-1-2 | .005 | 53. | 31020-1-1 | .021 |
| 23. | 31021-1-3 | .005 | 54. | 27044-1-0 | .022 |
| 24. | 20083-1-3 | .006 | 55. | 20080-1-1 | .024 |
| 25. | 33692-23-1 | .006 | 56. | 4065-8-1 | .032 |
| 26. | 31021-1-1 | .006 | 57. | 6074-1-1 | .033 |
| 27. | 33070-1-1 | .007 | 58. | 36041-1-2 | .042 |
| 28. | 5020-1-3 | .007 | 59. | 36041-1-3 | .042 |
| 29. | 33065-9-1 | .007 | 60. | 36041-1-1 | .053 |
| 30. | 33070-1-3 | .008 | 61. | 33024-6-0 | .095 |
| 31. | 40062-8-0 | .008 |  |  |  |

EXHIBIT 3

APPENDIX B

```
                      NEW SOURCE CADMIUM DATA IN MG/L
                    NATURAL LOGARITHIMS OF CADMIUM (MG/L)

                      GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE:  LNRAWCD                  NAT LOG OF CONC. FOR NS CD MG/L

SOURCE                    DF                  SUM OF SQUARES     MEAN SQUARES

MODEL                     19                     30.37781823       1.59883254

ERROR                     33                      2.84653212       0.08625885

CORRECTED TOTAL           52                     33.22435035


MODEL F =              18.54                                 PR > F = 0.0001


R-SQUARE                C.V.                        ROOT MSE     LNRAWCO MEAN

0.914324              6.1396                      0.29369808      -4.78368585


SOURCE                    DF                 TYPE I SS   F VALUE    PR > F

PLANT                     19               30.37781823     18.54    0.0001


SOURCE                    DF               TYPE III SS   F VALUE    PR > F

PLANT                     19               30.37781823     18.54    0.0001
```

```
                        NEW SOURCE CADMIUM DATA IN MG/L
                     NATURAL LOGARITHIMS OF CADMIUM (MG/L)

                        GENERAL LINEAR MODELS PROCEDURE

DUNCAN'S MULTIPLE RANGE TEST FOR VARIABLE:  LNRAWCD
NOTE:  THIS TEST CONTROLS THE TYPE 1 COMPARISONWISE ERROR RATE, NOT THE
       EXPERIMENTWISE ERROR RATE.

                  ALPHA = 0.05     DR = 33     MSE = .0862585

WARNING:  CELL SIZES ARE NOT EQUAL.
HARMONIC MEAN OF CELL SIZES = 2.5
**MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.***

DUNCAN   CLUSTERS                    MEAN         N        PLANT            GROUPING

            A                      -3.0925        3       36041            1
--------------------------------------------------------------------------------

            B                      -3.7459        3        6074            2
            B
        C   B                      -4.0792        3        6731
        C   B
        C   B   D                  -4.2951        3       33073
        C       D
        C       D                  -4.3702        2        4065
        C       D
        C       D                  -4.4252        3       19063
        C       D
        C       D                  -4.4263        2       31022
        C       D
        C       D                  -4.4407        3       15070
--------------------------------------------------------------------------------
        C       D
        C   E   D                  -4.6539        3       20083            3
            E   D
        F   E   D                  -4.5283        2       40062
        F   E   D
        F   E   D                  -4.8362        2       33065
        F   E   D
        F   E   D                  -4.8951        2       33070
--------------------------------------------------------------------------------
        F   E
        F   E                      -5.2142        4        5020            4
        F   E
        F   E                      -5.2375        3       31021
        F
        F                          -5.2983        4       20078
        F
        F                          -5.2983        2        4069
        F
        F                          -5.2983        3       36040
        F
        F                          -5.4099        2       15010
--------------------------------------------------------------------------------

            G                      -6.2146        2       11477            5
            G
            G                      -6.5612        2        6101
```

```
                        NEW SOURCE CADMIUM DATA IN MG/L
                     NATURAL LOGARITHIMS OF CADMIUM (MG/L)

                        GENERAL LINEAR MODELS PROCEDURE

STUDENT-NEWMAN-KEULS TEST FOR VARIABLE:  LNRAWCD
NOTE:  THIS TEST CONTROLS THE TYPE I EXPERIMENTWISE ERROR RATE UNDER THE COMPLETE
       NULL HYPOTHESIS BUT NOT UNDER PARTIAL NULL HYPOTHESES

                  ALPHA = 0.05     DF = 33     MSE = .0862585

WARNING:  CELL SIZES ARE NOT EQUAL.
HARMONIC MEAN OF CELL SIZES = 2.5

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICNATLY DIFFERENT.

SNK      CLUSTERS                    MEAN        N        PLANT        GROUPING

               A                   -3.0925       3        36041            1
-------------------------------------------------------------------------------

               B                   -3.7459       3         6074            2
               B
       C       B                   -4.0792       3         6731
       C       B
       C       B                   -4.2951       3        33073
       C       B
       C       B   D               -4.3702       2         4065
       C       B   D
       C   E   B   D               -4.4252       3        19063
       C   E   B   D
       C   E   B   D               -4.4263       2        31022
       C   E   B   D
       C   E   B   D               -4.4407       3        15070
       C   E       D
-------------------------------------------------------------------------------
       C   E   F   D               -4.6539       3        20083            3
       C   E   F   D
       C   E   F   D               -4.8283       2        40062
       C   E   F   D
       C   E   F   D               -4.8362       2        33065
       C   E   F   D
       C   E   F   D               -4.8951       2        33070
           E   F   D
-------------------------------------------------------------------------------
           E   F   D               -5.2142       4         5020            4
           E   F   D
           E   F   D               -5.2375       3        31021
           E   F
           E   F                   -5.2983       4        20078
           E   F
           E   F                   -5.2983       2         4069
           E   F
           E   F                   -5.2983       3        36040
               F
               F                   -5.4099       2        15010
-------------------------------------------------------------------------------
```

## NEW SOURCE CADMIUM DATA IN MG/L
## NATURAL LOGARITHIMS OF CADMIUM (MG/L)

## GENERAL LINEAR MODELS PROCEDURE

```
SNK      CLUSTERS                 MEAN       N      PLANT      GROUPING

             G                 -6.2146       2      11471          5
             G
             G                 -6.5612       2       6101
```

```
                        NEW SOURCE CADMIUM DATA IN MG/L
                     NATURAL LOGARITHIMS OF CADMIUM (MG/L)

                        GENERAL LINEAR MODELS PROCEDURE

TUKEY'S STUDENTIZED RANGE (HSD) TEST FOR VARIABILE:  LNRAWCD
NOTE:  THIS TEST CONTROLS THE TYPE I EXPERIMENTWISE ERROR RATE, BUT GENERALLY
       HAS A HIGHER TYPE II ERROR RATE THAN REGWQ.

                  ALPHA = 0.05      DF = 33     MSE = .0862585

CRITICAL VALUE OF STUDENTIZED RANGE = 5.432
MINIMUM SIGNIFICANT DIFFERENCE = 1.009

WARNING:  CELL SIZES ARE NOT EQUAL.
HARMONIC MEAN OF CELL SIZES = 2.5

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

TUKEY    CLUSTERS                    MEAN        N        PLANT         GROUPING

               A                   -3.0925       3        36041            1
-------------------------------------------------------------------------------
               A
       B       A                   -3.7459       3         6074            2
       B       A
       B       A   C               -4.0792       3         6731
       B           C
       B       D   C               -4.2951       3        33073
       B       D   C
       B       D   C               -4.3702       2         4065
       B       D   C
       B   E   D   C               -4.4252       3        19063
       B   E   D   C
       B   E   D   C               -4.4263       2        31022
       B   E   D   C
       B   E   D   C               -4.4407       3        15070
-------------------------------------------------------------------------------
       B   E   D   C
       B   E   D   C               -4.6539       3        20083            3
           E   D   C
           E   D   C               -4.8283       2        40062
           E   D   C
           E   D   C               -4.8362       2        33065
           E   D   C
           E   D   C               -4.8951       2        33070
           E   D
-------------------------------------------------------------------------------
       F   E   D                   -5.2142       4         5020            4
       F   E   D
       F   E   D                   -5.2375       3        31021
       F   E   D
       F   E   D                   -5.2983       4        20078
       F   E   D
       F   E   D                   -5.2983       2         4069
       F   E   D
       F   E   D                   -5.2983       3        36040
       F   E
       F   E                       -5.4099       2        15010
       F
-------------------------------------------------------------------------------
```

## NEW SOURCE CADMIUM DATA IN MG/L
## NATURAL LOGARITHIMS OF CADMIUM (MG/L)

## GENERAL LINEAR MODELS PROCEDURE

| TUKEY | CLUSTERS | MEAN | N | PLANT | GROUPING |
|---|---|---|---|---|---|
| | G | -6.2146 | 2 | 11477 | 5 |
| | G | | | | |
| | G | -6.6512 | 2 | 6101 | |

```
                        NEW SOURCE CADMIUM DATA IN MG/L
                     NATURAL LOGARITHIMS OF CADMIUM (MG/L)

                        GENERAL LINEAR MODELS PROCEDURE

SCHEFFE'S TEST FOR VARIABILE:  LNRAWCD
NOTE:  THIS TEST CONTROLS THE TYPE I EXPERIMENTWISE ERROR RATE, BUT GENERALLY
       HAS A HIGHER TYPE II ERROR RATE THAN REGWF FOR ALL PAIRWISE COMPARISONS.

                  ALPHA = 0.05     DF = 33     MSE = .0862585

CRITICAL VALUE OF T = 1.38254
MINIMUM SIGNIFICANT DIFFERENCE = 1.58307

WARNING:  CELL SIZES ARE NOT EQUAL.
HARMONIC MEAN OF CELL SIZES = 2.5

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

SCHEFFE  CLUSTERS                    MEAN        N        PLANT        GROUPING

               A                   -3.0925       3        36041            1
               A
       B       A                   -3.7459       3         6074            2
       B       A
       B       A   C               -4.0792       3         6731
       B       A   C
       B       A   C               -4.2951       3        33073
       B       A   C
       B       A   C               -4.3702       2         4065
       B       A   C
       B       A   C               -4.4252       3        19063
       B       A   C
       B       A   C               -4.4263       2        31022
       B       A   C
       B       A   C               -4.4407       3        15070
       B       A   C
       B   D   A   C               -4.6539       3        20083            3
       B   D       C
       B   D       C               -4.8283       2        40062
       B   D       C
       B   D       C               -4.8362       2        33065
       B   D       C
       B   D       C               -4.8951       2        33070
       B   D       C
       B   D   E   C               -5.2142       4         5020            4
       B   D   E   C
       B   D   E   C               -5.2375       3        31021
       B   D   E   C
       B   D   E   C               -5.2983       4        20078
       B   D   E   C
       B   D   E   C               -5.2983       2         4069
       B   D   E   C
       B   D   E   C               -5.2983       3        36040
           D   E   C
           D   E   C               -5.4099       2        15010
```

```
                         NEW SOURCE CADMIUM DATA IN MG/L
                      NATURAL LOGARITHIMS OF CADMIUM (MG/L)

                         GENERAL LINEAR MODELS PROCEDURE

SCHEFFE  CLUSTERS                  MEAN        N       PLANT        GROUPING

           D   E                 -6.2146       2       11477            5
           D   E
               E                 -6.5612       2        6101
```

EXHIBIT 3
APPENDIX C

# Definitions

| | |
|---|---|
| $K$ | total number of plants |
| $n_i$ | number of observations at plant i |
| $\sum_{i=1}^{K} n_i = N$ | total number of observations |
| $Y_{ij}$ | concentration of Cd in mg/l, observation j at plant i; j=1, ..., $n_i$, i=1, ..., K |
| $\ln Y_{ij} = X_{ij}$ | natural logarithm of Cd observation in mg/l |
| $\mu = \sum_{i=1}^{K} \sum_{j=1}^{n_i} X_{ij}/N$ | mean of the log |
| $\sigma^2{}_i = \sum_{j=1}^{n_i} (\overline{X}_i - X_{ij})/n_i-1$ | within plant variance, plant i |
| $\dfrac{\sigma^2_p = \sum_{i=1}^{K} (n_i-1)\,\sigma^2_i}{\sum_{i=1}^{K} (n_i-1)}$ | pooled within plant variance |
| $\sigma_p = \sqrt{\sigma^2_p}$ | pooled within plant standard deviation |
| $E(Y) = e^{\mu + \sigma^2/2}$ | estimated mean (expected value) of the distribution of Y |
| $Y_{.99} = e^{\mu} + 2.326^{\sigma P}$ | estimated 99th percentile of the distribution of Y |
| $\overline{Y} = \sum_{i=1}^{K} \sum_{j=1}^{n_i} Y_{ij}/N$ | arithmetic mean of all observations |
| $\mu\ (10) = \mu + \sigma^2_p/2 - (0.5)\ln\left(\frac{e^{\sigma^2}}{10} + \frac{10-1}{10}\right)$ | 10-day log mean estimate |

## Definitions (Con'd)

| | |
|---|---|
| $\sigma^2(10) = \ln \frac{e^{\sigma^2}}{10} + \frac{10-1}{10}$ | 10-day log variance estimate |
| $Y_{.99}(10) = e^{\mu 10 + 2.326\sigma 10}$ | 10-day 99th percentile estimate |

# Metal Finishing - NSPS Cd

## All Data

### Daily

$N = 61$ VF - with plant 33024

$\mu = 4.726$ Overall Mean - with plant 33024

$\sigma^2_p = 0.08626$

$\sigma_p = 0.29370$

$$Y_{.99} = e^{-4.726+2.326(0.2937)}$$

$$= e^{-4.726+.6832} = e^{-4.0429}$$

$$= 0.018$$

$$E(Y) = e^{-4.726+.5(.08626)}$$
$$= 0.0093$$

### 10 Day

$$\mu_{10} = \mu + .5(\ \sigma^2\ ) - (.5)\ \ln\ \frac{e^{\sigma^2}}{n} + \frac{n-1}{n}$$

$$= -4.726 + .5(.08626) - (.5)\ln \frac{e^{.08626}}{10} + .9$$

$$= -4.6874$$

$$\sigma^2_{10} = \ln\ \frac{e^{\sigma^2}}{n} + \frac{n-1}{n}$$

$$= \ln \frac{e^{.08626}}{10} + \frac{9}{10}$$

$$= .00897$$ $\sigma_{10} = .0947$

$$Y_{.99}(10) = e^{\mu_{10} + 2.326\ \sigma_{10}}$$

$$= e^{-4.6874+2.326(.0947)}$$

$$= .0115$$

## Metal Finishing - NSPS Cd

**All Data Without Plant 33024**

**Daily**

VF - without plant 33024

Overall Mean - without plant 33024

$N = 60$

$\mu = -4.765$

$\sigma^2{}_p = 0.08626$

$\sigma_p = .29370$

$$Y_{.99} = e^{-4.765+2.326(.2937)}$$

$$= .017$$

$$E(Y) = e^{-4.765+(.5).08626}$$

$$= 0.0089$$

**10 Day**

$$\mu_{10} = \mu + .5(\sigma^2) - (.5)\ln \left(\frac{e^{\sigma^2}}{n} + \frac{n-1}{n}\right)$$

$$= -4.765 + .0387$$

$$= -4.7264$$

$\sigma^2{}_{10} = .00897$

$\sigma_{10} = .0947$

$$Y_{.99(10)} = e^{-4.7264+2.326(.00897)}$$

$$= .0091$$

## Metal Finishing - NSPS Cd
## Using High Effluent Concentration Plants
## Subset A

**Daily**

VF - using subset A

Overall Mean - using subset A

$N = 27$

$\mu = -3.998$

$\sigma^2_p = 0.1510$

$\sigma_p = 0.3886$

$Y_{.99} = e^{-3.998+2.326(0.3886)}$

$= 0.045$

$E(Y) = e^{-3.998+0.5(.1510)}$

$= .0198$

**10 Day**

$$\mu_{10} = \mu + .5\ (\ \sigma^2\ ) - (.5)\ln\ \frac{e^{\sigma^2}}{n} + \frac{n-1}{n}$$

$$= -3.998 + (.5)(.1510) - (.5)\ln\ \frac{e^{.1510}}{10} + .9$$

$= -3.9306$

$$\sigma^2_{10} = \ln\ \frac{e^{.1510}}{10} + .9$$

$= .0162$

$\sigma_{10} = .1273$

$Y_{.99(10)} = e^{-3.9306+2.326(.1273)}$

$= .0264$

## Metal Finishing - NSPS Cd
## Using High Effluent Concentration Plants
## Subset B

Daily

VF - using subset B

Overall Mean - using subset B

$N = 4$

$\mu = -2.908$

$\sigma_p^2 = 0.0180$

$\sigma_p = 0.1342$

$Y_{.99} = e^{-2.908+2.326(.1342)}$

$= .0746$

$E(X) = e^{-2.908+0.5(.0180)}$

$= .0551$

$\overline{X} = .058$

10-Day

$$\mu_{10} = \mu + .5\ (\ \sigma^2\ ) - (.5)\ln \frac{e^{\sigma^2}}{n} + \frac{n-1}{n}$$

$$= -2.908 + .5(.018) - (.5)\ln \frac{e^{.018}}{10} + \frac{9}{10}$$

$$= -2.900$$

$$\sigma_{10}^2 = \ln \frac{e^{.018}}{10} + \frac{9}{10}$$

$$= .0018$$

$$\sigma_{10} = .0424$$

$$Y_{.99(10)} = e^{-2.90+2.326(.0424)}$$

$$= .0610$$