DEVELOPMENT DOCUMENT

for

PROPOSED EFFLUENT LIMITATIONS GUIDELINES
NEW SOURCE PERFORMANCE STANDARDS

and

PRETREATMENT STANDARDS

for the

LEATHER TANNING AND FINISHING
POINT SOURCE CATEGORY

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SECTION I

CONCLUSIONS

The leather tanning and finishing industry characteristically is family-owned, not very progressive or profitable, and dominated by small plants employing less than 100 people. There are an estimated 188 leather tanning and finishing plants in the United States today comprised of 170 dischargers to publicly owned treatment works (indirect dischargers) and 18 dischargers to waters of the U.S. (direct dischargers). Total industry flow is approximately 52 million gallons daily (MGD), of which 47 MGD are discharged to POTWs and 5 MGD are discharged directly to navigable waters.

For the purpose of establishing wastewater effluent limitations guidelines and standards of performance for new sources, the Leather Tanning and Finishing Point Source Category has been subcategorized as follows:

1. Hair Pulp-Chrome Tan-Retan-Wet Finish
2. Hair Save-Chrome Tan-Retan-Wet Finish
3. Hair Save-Nonchrome Tan-Retan-Wet Finish
4. Retan-Wet Finish
5. No Beamhouse
6. Through-the-Blue
7. Shearling.

The primary criteria for subcategorizing the leather tanning and finishing industry were the type or condition of animal hide processed, method of hair removal, type of tanning agent used, and extent of finishing performed. Plant size, age, and location, wastewater characteristics, and water usage were also considered.

The most significant pollutants and pollutant parameters detected in the industry's wastewaters in terms of occurrence and concentration include: the conventional and proposed conventional pollutants BOD_5, TSS, pH, COD, and oil and grease; and the nonconventional pollutants ammonia, total Kjeldahl nitrogen (TKN), and sulfide. The following toxic pollutants were found in treated effluents at more than two plants above the nominal limits of detection:

2,4,6-trichlorophenol
chloroform
1,2-dichlorobenzene
1,4-dichlorobenzene
ethylbenzene
methylene chloride (dichloromethane)
naphthalene
pentachlorophenol
phenol

bis(2-ethylhexyl) phthalate
toluene
chromium
copper
cyanide
lead
nickel
zinc

A total of 37 toxic pollutants were detected in raw waste discharges of which 17 were also detected in biologically treated effluents.

The Agency concludes that the best practicable control technology currently available (BPT) is based upon the performance of primary treatment (coagulation-sedimentation) and "secondary" biological treatment (extended aeration activated sludge) as practiced at plant No. 47 (subcategory No. 3) and at the Berwick, Maine POTW which treats more than 90 percent tannery wastewater (subcategory No. 4). Treatment systems at plant No. 253 (subcategory No. 7), a plant in the Netherlands (subcategory No. 1), and the Hartland, Maine POTW treating 90 percent tannery wastewater (subcategory No. 1) support this conclusion because the performance of these systems equaled or surpassed the performance of plant No. 47 and the Berwick POTW. The Agency also concludes that the balance of the plants with direct discharge have inadequate treatment systems and must be upgraded to achieve effluent limitations based upon BPT performance transferred from subcategories within the leather tanning and finishing industry.

The pollutant parameters regulated by the proposed best practicable technology (BPT) are BOD_5, TSS, oil and grease, (total) chromium, and pH.

The Agency concludes that the best available technology economically achievable (BAT) builds on BPT technology with in-plant control,and pretreatment, and upgraded biological treatment by powdered activated carbon addition, and multi-media filtration. Plant No. 247 (now closed) employed physical/chemical treatment to achieve an effluent quality far better than required by BAT. The activated sludge system at plant No. 253 has achieved BAT effluent quality for some of the regulated pollutant parameters for substantial periods of time. The balance of the plants with direct discharge have inadequate treatment systems in place and technology and performance transfer is necessary to achieve BAT effluent limitations.

The pollutants regulated by the proposed best available technology economically achievable (BAT) and the new source performance standards (NSPS) are BOD_5, COD, TSS, oil and grease, TKN, ammonia, sulfide and pH, and the toxic pollutants (total) chromium and (total) phenol. No effluent limitations have been proposed for any other toxic pollutants. The control of toxics other than chromium and phenol,

which were found in significant concentrations in tannery wastewater, will be regulated by placing numerical limitations on "indicator" pollutants, including BOD_5, COD, TSS, oil and grease, TKN, ammonia, (total) chromium, and (total) phenol. EPA has concluded from available data that when the indicator pollutants are controlled, the concentrations of toxic pollutants are significantly lower than when the indicator pollutants were present in high concentrations. The Agency concludes from this data that control of the "indicator" pollutants is necessary to ensure the control of toxic pollutants.

The Agency concludes that plants with indirect discharge contribute substantial quantities of organic compounds and heavy metals, the most important of which is chromium, to the contamination of large quantities of POTW sludges. In addition, the Agency concludes that the high concentrations of nitrogen (particulary ammonia) in raw wastewater pass through POTW largely untreated, and that the high concentrations of hydrogen sulfide in raw wastewaters can and do cause severe odor and health hazard problems. In-plant controls, pretreatment of segregated streams, and primary treatment of combined streams is the technology basis of pretreatment standards for existing sources (PSES) to control the discharge of toxic pollutants, and ammonia and sulfides. This level of control will increase POTW sludge disposal alternatives, improve POTW effluent quality, and essentially eliminate odor and health hazard problems. The Agency concludes that this level of control recognizes limitations on existing interior plant space and adjacent land. Most plants will find it necessary to install a large portion of these in-plant controls and pretreatment technologies to achieve PSES limitations.

The Agency concludes that pretreatment standards for new sources (PSNS) should be based upon the same technology used for PSES plus physical/chemical treatment to achieve BAT levels of control for toxic pollutants. The Agency concluded this level of control would be necessary because POTW effluent quality which incorporates PSES may not be the same as the effluent quality based on BAT for a direct discharger.

The pollutants regulated by the proposed pretreatment standards for existing sources (PSES) are total chromium, ammonia, and sulfides. In addition to limitations for these pollutants, the proposed pretreatment standards for new sources (PSNS) also include limitations on the pollutants regulated by BAT.

The Agency concludes that the total investment cost incurred by existing sources, both direct and indirect dischargers, to achieve these effluent limitations guidelines (BPT and BAT) and pretreatment standards (PSES) is $65 million, with total annualized cost of $34 million. A total of approximately 300,000 lbs/yr of chromium will be removed by compliance with BAT effluent limitations, and more than 2 million lbs/yr of chromium will be removed from POTW sludges by

compliance with PSES. In addition, approximately 59 million lbs/yr of conventional pollutants and 2.3 million lbs/yr of nonconventional pollutants will be removed by BAT; and 172 million lbs/yr of conventional pollutants and 5.7 million lbs/yr of nonconventional pollutants will be removed by compliance with PSES.

SECTION II

RECOMMENDATIONS

Proposed effluent limitations representative of the best practicable control technologies currently available (BPT) are based upon performance characteristics of primary treatment and "secondary" biological treatment (high solids extended aeration activated sludge). Numerical limitations (lbs/1,000 lbs of raw material) are proposed for BOD_5, TSS, oil and grease, (total) chromium, and pH, and apply to all seven subcategories. See Section IX for the mass limitations.

Proposed effluent limitations for the best available technolgoy economically achievable are based upon BPT technology plus in-plant control, pretreatment, upgraded biological treatment by powdered activated carbon (PAC) addition, and multi-media filtration. Numerical limitations (lbs/1,000 lbs of raw material) are proposed for three non-toxic, non-conventional pollutants: total Kjeldahl nitrogen (TKN), ammonia, and sulfide; TKN and ammonia also serve as "indicators" for the removal of toxic pollutants. Other "indicator" pollutants for which limitations are proposed are BOD_5, COD, TSS, oil and grease, total chromium, and total phenol. The only toxic pollutants expressly controlled for direct dischargers are chromium and phenol. See Section X for the mass limitations.

The BAT "indicator" limitations on conventional pollutants have passed the cost reasonableness test (POTW cost comparison) and have been designated as the proposed BCT limitations (lbs/1,000 lbs of raw material) as well.

The proposed new source performance standards are the same as BAT for the same regulated parameters.

Proposed pretreatment standards for existing sources (PSES) are based on in-plant control and pretreatment technologies to regulate pH, chromium, sulfide, and ammonia. Limitations are expressed on a concentration basis (mg/l), while mass limitations (lbs/1,000 lbs of raw material) are also included as guidance for POTWs which may find it necessary to control the mass of pollutants introduced by system users.

Proposed pretreatment standards for new sources (PSNS) are based on in-plant control and pretreatment technology, plus physical/chemical treatment to achieve effluent quality equal to that required by BAT. Limitations are expressed on a concentration basis (mg/l), while mass limitations (lbs/1,000 lbs of raw material) are also included as guidance for POTWs which may find it necessary to control the mass of pollutants introduced by system users.

SECTION III

INTRODUCTION

PREFACE

On July 2, 1979, the United States Environmental Protection Agency (EPA) proposed regulations to control water pollution by leather tanning and finishing plants. See 44 FR 38746. The purpose of those regulations is to provide effluent limitations guidelines and standards of performance under the Clean Water Act. To promote that purpose, the proposed regulations also include monitoring requirements.

This document highlights EPA's study of the industry and explains the technical rationale for the proposed regulations.

PURPOSE AND AUTHORITY

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 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. 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 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)(E) 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.

The purpose of these proposed regulations is to provide effluent limitations guidelines for BPT, BAT, and BCT, and to establish NSPS, pretreatment standards for existing sources (PSES), and pretreatment standards for new sources (PSNS), under Sections 301, 304, 306, 307, and 501 of the Clean Water Act. To promote this purpose, the proposed regulations also establish monitoring requirements under Section 308 of the Act.

SUMMARY OF METHODOLOGY

The effluent limitations and pretreatment standards set forth herein were developed in the following manner. The original development document (1974) and the appendices to that document were acquired. The organization that prepared the original "draft" document was included on the study team so that the venefit of their experience could be obtained and the incorporation of existing data and information on the tanning industry would be facilitated.

First, EPA studied the leather tanning industry to determine whether differences in raw materials, final products, manufacturing processes, equipment, age and size of plants, water usage, wastewater constituents, or other factors required the development of separate effluent limitations and standards for different segments of the industry. This study included the identification of raw waste and treated effluent characteristics, including: 1) the sources and volume of water used, the processes employed, and the sources of pollutants and wastewaters in the plant, and 2) the constituents of wastewaters, including toxic pollutants. EPA then identified the constituents of wastewaters which should be considered for effluent limitations guidelines and standards of performance, and statistically analyzed raw waste constituents.

Next, EPA identified several distinct control and treatment technologies, including both in-plant and end-of-process technologies, which are in use or capable of being used in the leather tanning and finishing industry. The Agency compiled and analyzed historical data and newly generated data on the effluent quality resulting from the application of these technologies. The long term performance, operational limitations, and reliability of each of the treatment and control technologies were also identified. In addition, EPA considered the non-water quality environmental impacts of these technologies, including impacts on air quality, solid waste generation, water scarcity, and energy requirements.

The Agency then estimated the costs of each control and treatment technology from unit cost curves developed by standard engineering

analysis as applied to leather tanning and finishing wastewater characteristics. EPA derived unit process costs from model plant characteristics (production and flow) applied to each treatment process unit cost curve (i.e., primary coagulation-sedimentation, activated sludge, multi-media filtration, etc.). These unit process costs were added to yield total cost at each treatment level. After confirming the reasonableness of this methodology by comparing EPA cost estimates to treatment system costs supplied by the industry, the Agency evaluated the economic impacts of these costs.

Upon consideration of these factors, as more fully described below, EPA identified various control and treatment technologies as BPT, BCT, BAT, PSES, PSNS, and NSPS. The proposed regulations, however, do not require the installation of any particular technology. Rather, they require achievement of effluent limitations representative of the proper operation of these technologies or equivalent technologies.

The effluent limitations for BPT, BCT, BAT and NSPS are expressed as mass limitations (lbs/1000 lbs raw material) and are calculated by multiplying three figures: (1) effluent concentrations determined from analysis of control technology performance data, (2) wastewater flow for each subcategory, and (3) any relevant process or treatment variability factor (e.g., maximum month vs. maximum day). This basic calculation was performed for each regulated pollutant or pollutant parameter for each subcategory of the industry. Effluent limitations for PSES and PSNS are expressed as allowable concentrations in milligrams per liter (mg/l). For POTWs which may wish to impose mass limitations, the proposed regulations provide guidance on equivalent mass limitations.

Data and Information Gathering Program

In addition to the 1974 study, EPA gathered the following additional data for the proposed BPT, BAT, BCT, NSPS, PSES, and PSNS:

1. Through the Tanners' Council of America (TCA), EPA distributed one-page surveys and detailed questionnaires to about 301 addresses of tanneries, finishers, and sales offices to obtain information on specific plant situations. It was jointly agreed at the outset of the study by EPA and the TCA that authority of Section 308 of the Act would not be used to gather technical information to support this effort, except as a last resort in obtaining critical or proprietary information. EPA received survey responses from 116 tanneries and questionnaires from 89 tanneries.

2. EPA contacted 50 municipalities to collect information on city ordinance wastewater limitations, reasons for limitations, wastewater problems and plans for dealing with the problems. Supplementary wastewater data for local

tanneries and municipal POTW performance data were also requested. The Agency obtained extensive data for four POTWs which treat primarily leather tanning and finishing wastewater. Many POTWs, however, could not provide extensive data for parameters other than flow, pH, BOD_5, and TSS.

3. During field visits to 50 tanneries, EPA collected information on plant operations, sites, practices, processes, equipment, management concerns and attitudes, and wastewater and production data; 22 of the visited tanneries were sampled for wastewater constituents. Tanneries visited and/or sampled included facilities representing most industrial situations and operations, including plants of different sizes, ages, and locations.

4. NPDES permit data and background information on a number of tanneries were obtained from EPA regional offices. Permits included information on the tannery and waste treatment facilities and the discharge standards and schedule for compliance being set at the present time.

5. The Agency received engineering studies and reports on waste treatment facilities for several tanneries. These reports included dimensions and descriptions of the facilities, operating practices, data on wastewater quality and quantity, waste treatment design basis and criteria, treatment system problems, and cost estimates for wastewater control and treatment facilities.

6. EPA also contacted state pollution control offices to request available data and information on tannery wastewater problems and plans for dealing with these problems.

In response to the Clean Water Act of 1977 and the EPA - Natural Resources Defense Council (NRDC) Settlement Agreement (NRDC v. Train, 8 ERC 2120 (D.D.C. 1976), the updated study of this industry emphasizes the evaluation of 65 classes of potentially toxic pollutants declared toxic under section 307(a) of the Act. This group of pollutants and classes of pollutants, potentially including thousands of specific compounds, was eventually lengthened to a list of 129 priority pollutants (Table 1) which served as the basis for the proposed BAT, new source performance standards, and pretreatment standards for new and existing sources.

1. In order to obtain information and data on the priority pollutants, wastewater control and treatment practices, and in-plant process changes, EPA mailed questionnaires to all domestic tanners and to the industry's chemical suppliers. The suppliers were unable to provide significant information on the priority pollutant content of their products due to

their apparently limited knowledge of the chemical constituents of their products. Forty-six tannery questionnaires were returned, sixteen of which included detailed information on chemical usage.

2. Under Section 308 of the Act, EPA also conducted an economic survey of the industry. Questionnaires were mailed to the 188 domestic tanneries requesting production costs, balance sheet and income data, and costs for existing pollution abatement systems. Sixteen of the eighteen direct dischargers and 120 of the 170 indirect dischargers responded.

In order to determine the toxic pollutant content of leather tannery wastewater, the Agency developed a two phase wastewater sampling and analysis program. Twenty-two tanneries and two POTWs were involved, the latter with substantial tannery wastewater flows. A table describing the tanneries in this sampling program is provided in Section V. The original leather tanning study had divided the industry into six subcategories. Phase one of the wastewater analysis program sampled one plant in each of these subcategories for the presence of toxic pollutants. During the second phase of this program, the industry was re-divided into seven subcategories; sixteen representative plants and two POTWs were sampled for quantities of priority pollutants. A distribution of plant sampling is summarized in Table 2. A summary of the special wastewater sampling and analysis methods is included in Appendix A of this document.

The analytical methods used for toxic pollutant analyses are capable of detecting the presence of compounds generally at levels of parts per billion. The analytical results involve the terminology "level of detection". When results appear to indicate the absence of pollutants, they are in fact, simply reporting the lack of detection. This is because the analytical procedures are limited to a specific lower limit of concentration detectable for each compound; thus a wastewater concentration for a compound below that lower level is reported as not detected (ND). This produces results on toxic pollutants across waste treatment systems that would be questionable for standard pollutants, i.e., a toxic pollutant may not be detected in the raw wastewater but show up in the final effluent. This occurs when sample preparation requires substantial dilution for injection into the analytical equipment. This dilution may reduce the pollutant concentration to a level below the detection limit.

GENERAL DESCRIPTION OF THE INDUSTRY

The leather tanning and finishing industry is included within the U.S. Department of Commerce, Bureau of the Census Standard Industrial Classification (SIC) 3100, Leather and Leather Products. The part of the industry addressed in this report is identified as SIC 3111, Leather Tanning and Finishing.

Table 1

Recommended List of Toxic Pollutants

Revised April 1977

Compound Name

1. *acenaphthene

2. *acrolein

3. *acrylonitrile

4. *benzene

5. *benzidine

6. *carbon tetrachloride (tetrachloromethane)

*chlorinated benzenes (other than dichlorobenzenes)

7. chlorobenzene

8. 1,2,4-trichlorobenzene

9. hexachlorobenzene

*chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)

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

*chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)

17. bis(chloromethyl) ether

*Specific compounds and chemical classes as listed in the consent decree

Table 1 (Contd.)

18. bis(2-chloroethyl) ether

19. 2-chloroethyl vinyl ether (mixed)

*<u>chlorinated naphthalene</u>

20. 2-chloronaphthalene

*<u>chlorinated phenols</u> (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)

21. 2,4,6-trichlorophenol

22. para-chloro meta-cresol

23. *chloroform (trichloromethane)

24. *2-chlorophenol

*<u>dichlorobenzenes</u>

25. 1,2-dichlorobenzene

26. 1,3-dichlorobenzene

27. 1,4-dichlorobenzene

*<u>dichlorobenzidine</u>

28. 3,3'-dichlorobenzidine

*<u>dichloroethylenes</u> (1,1-dichloroethylene and 1,2-trans-dichloroethylene)

29. 1,1-dichloroethylene

30. 1,2-trans-dichloroethylene

31. *2,4-dichlorophenol

*<u>dichloropropane and dichloropropene</u>

32. 1,2-dichloropropane

33. 1,2-dichloropropylene (1,2-dichloropropene)

34. *2,4-dimethylphenol

Table 1 (Contd.)

*<u>dinitrotoluene</u>

35. 2,4-dinitrotoluene

36. 2,6-dinitrotoluene

37. *1,2-diphenylhydrazine

38. *ethylbenzene

39. *fluoranthene

*<u>haloethers</u> (other than those listed elsewhere)

40. 4-chlorophenyl phenyl ether

41. 4-bromophenyl phenyl ether

42. bis(2-chloroisopropyl) ether

43. bis(2-chloroethoxy) methane

*<u>halomethanes</u> (other than those listed elsewhere)

44. methylene chloride (dichloromethane)

45. methyl chloride (chloromethane)

46. methyl bromide (bromomethane)

47. bromoform (tribromomethane)

48. dichlorobromomethane

49. trichlorofluoromethane

50. dichlorodifluoromethane

51. chlorodibromomethane

52. *hexachlorobutadiene

53. *hexachlorocyclopentadiene

54. *isophorone

Table 1 (Contd.)

55. *naphthalene

56. *nitrobenzene

*<u>nitrophenols</u> (including 2,4-dinitrophenol and dinitrocresol)

57. 2-nitrophenol

58. 4-nitrophenol

59. 2,4-dinitrophenol

60. 4,6-dinitro-o-cresol

61 *<u>nitrosamines</u>

61. N-nitrosodimethylamine

62. N-nitrosodiphenylamine

63. N-nitrosodi-n-propylamine

64. *pentachlorophenol

65. *phenol

*<u>phthalate esters</u>

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

*<u>polynuclear aromatic hydrocarbons</u>

72. benzo(a)anthracene (1,2-benzanthracene)

Table 1 (Contd.)

73. benzo (a) pyrene (3,4-benzopyrene)

74. 3,4-benzofluoranthene

75. benzo(k)fluoranthene (11,12-benzofluoranthene)

76. chrysene

77. acenaphthylene

78. anthracene

79. benzo(ghi)perylene (1,12-benzoperylene)

80. fluorene

81. phenanthrene

82. dibenzo (a,h)anthracene (1,2,5,6-dibenzanthracene)

83. indeno (1,2,3-cd)pyrene (2,3-o-phenylpyrene)

84. pyrene

85. *tetrachloroethylene

86. *toluene

87. *trichloroethylene

88. *vinyl chloride (chloroethylene)

*<u>pesticides and metabolites</u>

89. *aldrin

90. *dieldrin

91. *chlordane (technical mixture and metabolites)

*<u>DDT and metabolites</u>

92. 4,4'-DDT

93. 4,4'-DDE (p,p'-DDX)

94. 4,4'-DDD (p,p'-TDE)

Table 1 (Contd.)

*endosulfan and metabolites

95. a-endosulfan-Alpha

96. b-endosulfan-Beta

97. endosulfan sulfate

*endrin and metabolites

98. endrin

99. endrin aldehyde

100 *heptachlor and metabolites

100. heptachlor

101. heptachlor epoxide

*hexachlorocyclohexane (all isomers)

102. a-BHC-Alpha

103. b-BHC-Beta

104. r-BHC (lindane)-Gamma

105. g-BHC-Delta

*polychlorinated biphenyls (PCB's)

106. PCB-1242 (Arochlor 1242)

107. PCB-1254 (Arochlor 1254)

108. PCB-1221 (Arochlor-1221)

109. PCB-1232 (Arochlor 1232)

110. PCB-1248 (Arochlor-1248)

111. PCB-1260 (Arochlor-1260)

112. PCB-1016 (Arochlor 1016)

113. *toxaphene

114. *antimony (total)

115. *arsenic (total)

Table 1 (Contd.)

116. *asbestos (fibrous)

117. *beryllium (total)

118. *cadmium (total)

119. *chromium (total)

120. *copper (total)

121. *cyanide (total)

122. *lead (total)

123. *mercury (total)

124. *nickel (total)

125. *selenium (total)

126. *silver (total)

127. *thallium (total)

128. *zinc (total)

129. **2,3,7,8-tetrachlorodibenzo-p-dioxin

*Specific compounds and chemical classes as listed in the consent decree

**This compound was specifically listed in the consent decree; however, due to its extreme toxicity we are recommending that laboratories <u>not</u> acquire an analytical standard for this compound.

Table 2
Distribution of Plant Sampling

Toxic Pollutant Data Set

- 12 plants - direct discharge
- 10 plants - indirect discharge
- 2 POTW
- 1259 data points from 73 sample sets, including 269 intake water data points, 416 raw wastewater data points, 312 primary treated data points, and 262 secondary treated data points
- 7 plants in hair pulp, chrome tan, retan-wet finish subcategory
- 2 plants in hair save, chrome tan, retan-wet finish subcategory
- 4 plants in hair save, non-chrome tan, retan-wet finish subcategory
- 3 plants in retan-wet finish subcategory
- 1 plant in through the blue subcategory
- 2 plants in shearling subcategory

"Leather tanning" is a general term for the numerous processing steps involved in converting animal skins or hides into leather. The three major hide and skin types used to manufacture leather are cattlehides, sheepskins, and pigskins. Cattlehides constitute the bulk of the tanning performed in the U.S., representing about 90 percent of the total estimated weight of hides tanned.[1]

Three major groups are of standard processing steps required to manufacture leather: 1) beamhouse operations which wash and soak the hides or skins and remove the attached hair, 2) tanyard processes in which the tanning agent reacts with and stabilizes the proteinaceous matter in the hides or skins, and 3) retanning and wet finishing processes which accomplish further tanning by chemical agents such as dyes, lubricants, and various finishes.

Smaller quantities of hides and skins of horses, goats, deer, elk, and other animals are also tanned each year in the U.S. In general, tanneries purchase hides and skins to manufacture leather for shoes, garments, upholstery, luggage, gloves, handbags, sporting goods, and a variety of other products.

Some plants tan and finish a single species of animal hide, while others tan and finish various combinations of animal hide types. Some tanneries have a single, very specialized end-products such as lace leather or mechanical cushions for pianos. Other tanneries produce a variety of leather types for many consumer goods and industrial uses. The variety of final products produced by the individual tannery influences the hide types required and processing operations employed by that facility.

Many tanneries produce finished leather from raw, green salted, or brine cured hides; other tanneries, however, perform only a portion of the total process. Several facilities purchase previously tanned hides or splits and perform only the retan, color, fatliquor and finishing processes. A number of tanneries purchase hides and skins which either do not require a complete beamhouse process (such as pigskins) or which have previously gone through the beamhouse (such as pickled cattlehides and pickled sheepskins).

There are currently 188 tanneries producing leather products in the United States. These tanneries are primarily located in four general areas: the New England states, Mid-Atlantic states, the Midwest, and the Pacific Coast. Most of the tanneries are family-owned, closely held corporations, although a few are divisions of large conglomerates. Approximately 40 percent of these plants have fewer than 50 employees and wastewater volumes typically less than 100,000 gallons per day. About 70 percent of these plants are more than 50 years old in terms of the physical structures which house the leathermaking processes. Although the equipment used in some plants may be relatively modern, the typical processing techniques have not changed for many years. A small number of plants, usually the larger

ones, use modern processing methods and equipment, including reuse and recovery of process water and chemicals.

Local wastewater pretreatment standards or limited land availability have caused the relocation of certain tanning operations. In areas where local publicly owned treatment works (POTW) have sufficient capacity, or where a waste treatment system can be readily implemented, some tanneries have centralized beamhouse operations. Centralization has generally occurred in locations close to the source of raw material (hides or skins). Of the 188 tanneries currently operating in the U.S., 18 discharge directly to receiving waters. POTW's provide treatment for the remainder of the industry.

Beginning in the mid-1960's and continuing until 1974, the domestic leather tanning and finishing industry experienced a steady decline in the number of plants, production volume, and profits. This trend, as indicated in Table 3, was attributed to: 1) greater foreign demand for cattlehide, which caused an increase in raw material cost, and 2) competition from foreign countries in the finished leather products market.

The industry's economic situation has continued to decline, despite a short-term improvement from 1974 to 1976; nevertheless, it may stabilize in the future as the demand for leather products balances relative to leather substitutes. Prospects for new plants vary among segments of the industry; entry of new plants appears likely for tanneries which can take advantage of strong demand and economies of scale.

STANDARD MANUFACTURING PROCESSES

Animal skin is composed of outer and inner (epidermal and dermal) layers and it is the inner (dermal) layer which constitutes the leather-making portion of the skins and hides. This dermal layer consists mainly of the protein collagen. Tanning is essentially the reaction of collagen fibers with tannin, chromium, alum, or other tanning agents which help stabilize, or preserve, the skin and make it useful.

Water is essential to leathermaking and is used in virtually all manufacturing processes. Various chemical preservatives, biocides, coloring pigments, and solvents also are integral to producing leather from animal hides or skins. The standard manufacturing processes characteristic of the industry are shown schematically in Figure 1. Each of the four major process groups (beamhouse, tan, retan, and wet finish) consists of specific subprocesses.

For the purpose of this study, EPA defines a manufacturing process as a single step in the complete manufacturing operation where alternative steps may result in different waste characteristics. A process can consist of one or a series of subprocesses. In any

Table 3 Production and Marketing Trends in the Leather Tanning and Finishing Industry

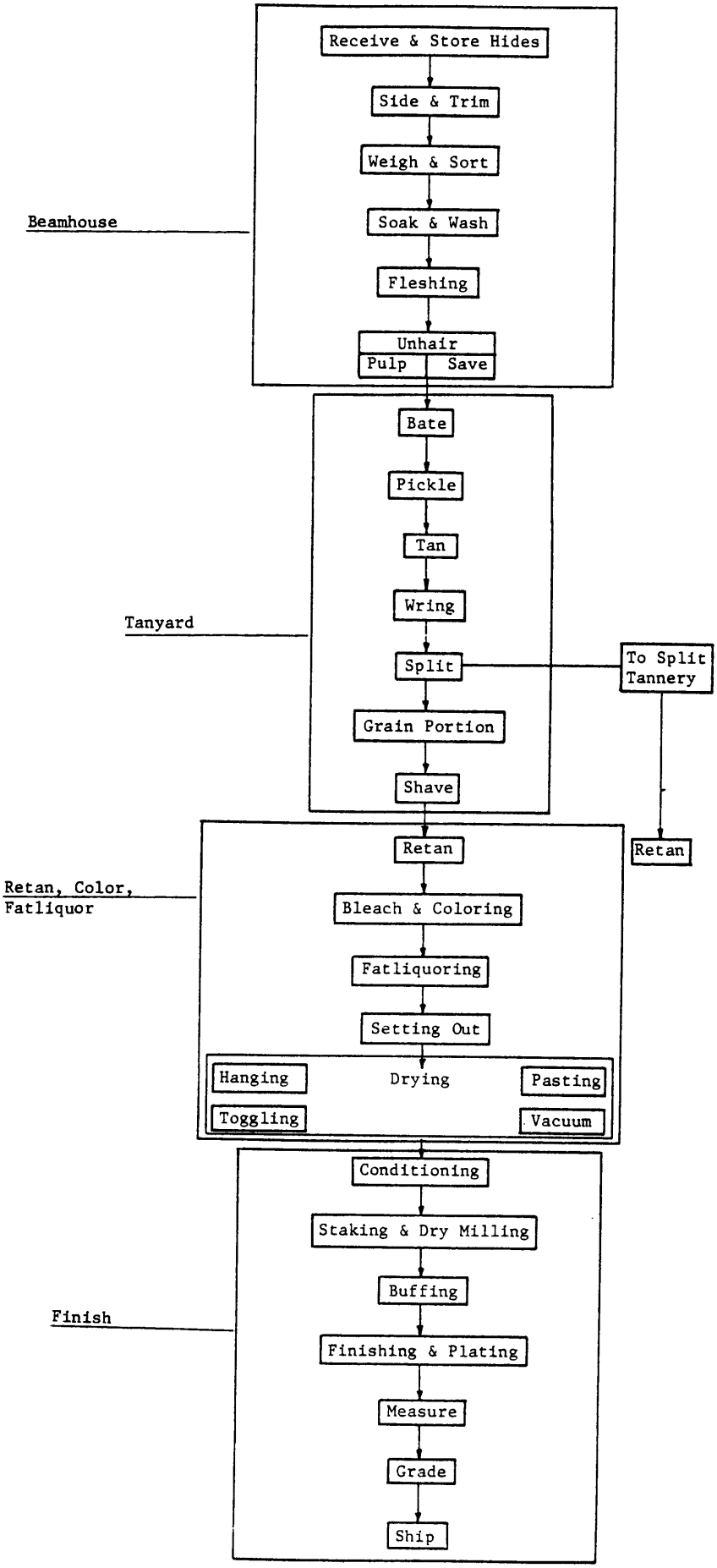
Year	Total Tanning Industry Production[2]	Total Industry Value of Shipments[1]	Cattle Hides[1] Net Exports	Leather[1] Imports	Exports[1]
	(1000 Equiv. Hides)	(Million Dollars)	(1000 Hides)	($1,000)	($1,000)
1965	32,697	857	13,019	66,998	39,474
1966	32,252	940	13,984	74,996	41,583
1967	30,861	870	11,634	68,045	42,321
1968	31,884	878	12,359	81,429	45,324
1969	28,388	854	14,513	85,805	41,586
1970	25,941	794	14,844	87,384	36,736
1971	25,267	838	15,694	83,273	42,832
1972	24,661	1060	17,292	138,795	66,706
1973	21,062	1082	16,177	127,381	82,914
1974	19,998	980	17,924	124,513	102,116
1975	21,894	1105	20,329	87,953	140,497
1976*	23,000	1200			

*Estimated

Source: (1) U.S. Department of Commerce

(2) Tanners Council of America, Inc.

Figure 1 GENERAL PROCESS FLOWSHEET FOR LEATHER TANNING AND FINISHING INDUSTRY



defined process, subprocesses remain the same. This concept of manufacturing steps seems to best allow for the variation of processes used by different plants.

The discussion and description of tannery processes which follow are based on the three major hide and skin types produced in the U.S.: cattlehides, sheepskins, and pigskins. The processes and subprocesses discussed represent those most typical of the industry.

Cattlehide Tannery Processes

Much of the following process description of a typical cattlehide tannery was developed in detail from the book, Leather Facts[2], and from industry questionnaires and plant visit reports. Detailed descriptions of typical cattlehide tannery process and subprocess operations follow.

Receiving and Storage. Nearly all cattlehides received at tanneries are either green salted or brine-cured hides, with the brine-cured hides predominant. In the few isolated cases where transit time is short, fresh green hides (without prior curing) are sent directly from a meat packer to a tannery for immediate processing.

After being trimmed and graded, green hides are cured at the packinghouse by spreading the hides, flesh side up, and covering them with salt. Another layer of hides is placed over the salted hides, again flesh side up, and covered with salt. This process continues until the pack of hides is about 5 to 6 feet high. A heavy layer of salt is placed on the top layer of hides. The natural fluids from the hides dissolve a portion of the salt to form a brine, allowing the salt to be absorbed. Through diffusion and osmosis, the salt reduces the moisture content in the hide. A pack of hides is typically cured for 10 to 30 days. After the green salted hides have been cured adequately the pack is reopened and the excess salt is shaken off each hide. The cured hides are then folded individually, repacked and shipped in packs, either to other tanneries or to warehouses for storage. The size of the pack depends on a number of variables, such as size of the packing plant, size of shipments, and method of shipment.

Brine-cured hides are prepared either at the packing plant or at a separate hide processing facility. Fresh hides are agitated in a saturated brine solution for two or three days, until the salt has replaced a desired amount of moisture within the hide. This process also cleanses the hides of manure and other foreign matter. The hides are then removed, drained, and bundled in a manner similar to that used for green salted hides. Fleshing may occur before or after brining. "Safety salt" is usually sprinkled on each hide before shipment. Because the brining process takes less time than salt-curing, it is preferred by packers and hide curing establishments which do not want to hold a large inventory of hides. The brining

process also produces cleaner hides, which are more attractive to the tanners. Increased use of brine-cured hides in recent years demonstrates these preferences by both packer and tanner.

Normally the tannery receives the cured hides in a large, cool, well ventilated area designed to preserve the moisture content at which they were received; packs are usually stored in the form in which they are received. From storage, they are taken to the beamhouse, where they are prepared for tanning.

Beamhouse Processes. There are four typical processing steps in the beamhouse: 1) side and trim; 2) soak and wash; 3) fleshing; and 4) unhairing.

Side and Trim.

The typical first step in preparing hides for processing is to trim off the heads, long shanks, and other perimeter areas which do not produce good leather. The hides are then cut lengthwise along the backbone, head to tail, to make two sides. In some instances, hides are halved or sided after unhairing or tanning. Trimmings are often collected for shipment to glue factories or other by-product manufacturers.

Soak and Wash.

The hides soak in vats (with or without paddles), drums, or hide processors (concrete mixers with special linings) for 8 to 20 hours to restore moisture which the hides have lost as a result of the curing process. They gradually absorb water, becoming softer and cleaner. Washing then removes dirt, salt, blood, manure, and non-fibrous proteins. There may be some variation in the quantity of such waste materials according to the time of year and the source of hides. According to the type of leather produced, additional washes (rinses) may also follow several subprocesses including unhairing, bating, tanning, and coloring. A rinse operation may also precede the coloring of hides or skins.

Fleshing.

Fleshing is a mechanical operation which removes excess flesh, fat and muscle from the interior of the skins. The fleshing machine carries the hide through rollers and across rotating spiral blades which remove the flesh from the hide. Cold water is necessary to keep the fat congealed, but the fat does represent an additional waste load.

Many hides are fleshed at packing plants or at separate hide processing facilities, particularly brined hides. Removal of flesh prior to liming is referred to as green fleshing; removal

after liming is referred to as lime fleshing. In any case, fleshings (i.e., the removed particles) are normally recovered and sold to plants for rendering or conversion to glue. Properly handled, this operation contributes very little liquid or solid waste. On-site rendering of fleshings, however, does contribute an additional waste stream (stick liquor), which is relatively low-volume but extremely concentrated.

Unhairing.

The removal of hair usually employs calcium hydroxide, sodium sulfhydrate, and sodium sulfide as the dehairing (depilatory) chemicals. These chemicals: 1) destroy the hair or attack the hair roots, 2) loosen the epidermis, and 3) remove certain soluble skin proteins.

Fleshed hides are placed in paddle vats containing water and the depilatory chemicals. The concentration of chemicals, the water temperature, and the amount of agitation directly affect the rate at which unhairing proceeds. In a pulp or brine unhairing operation, concentrated chemicals and high temperatures dissolve the entire hair within a few hours. If the hair is saved for its commercial value, a longer procedure using weaker solutions and lower temperatures is employed. This process attacks the hair roots only. The loosened hair can then be collected, washed, dried, and either sold where markets exist, or landfilled.

Where chemical treatment alone does not remove all of the hair or hair roots, the process can be completed on an unhairing machine. This is very similar to a fleshing machine, except the cylinder blades are blunt and rub the hide rather than cut it.

The lime and sulfide chemicals used in the unhairing process produce a concentrated alkaline solution, causing the hide fibers to absorb large amounts of moisture. This makes the hide swell to about twice its normal thickness, a phenomenon called alkaline swelling. Some tanners relime the hides prior to deliming to ensure complete hair removal and uniformity of alkaline swelling within the hide substance prior to deliming. Use of this subprocess depends upon the nature of the hides being processed and the types of final products desired.

A few tanneries now use a hybrid hair removal process, which compromises the two extremes of pulping (dissolving) and saving the hair. The semi-pulp unhairing process is a natural outgrowth of the traditional hair save operation. In many cases, by-product hair markets no longer exist or the cost of hair washing, baling, and selling exceeds income for the hair. In these instances, tanners have simply made marginal increases in the concentration of unhairing chemicals, and retained the use of unhairing machines. This falls short of complete changeover to a

hair pulp beamhouse, but retains the hair save option and maintains a process with which the operator is basically familiar. In these cases, raw waste loads tend to be about the same as for complete pulping of hair.

Tanyard Processes. Hides are brought from the beamhouse to the tanyard for further preparation and then tanning. Tanyard processes are described below.

Bating.

Bating is a two-step process consisting of deliming and enzyme addition. Residual alkaline chemicals used in the unhairing process are present in fairly large amounts and must be removed prior to tanning. In deliming, salts of ammonium sulfate or ammonium chloride convert the residual lime into soluble compounds which later can be washed free of the system. As this step progresses, the excessive alkaline swelling begins to disappear, and the skins return to their normal thickness. The deliming chemicals also properly condition the pH for receiving the bate.

Bates are enzymes similar to those found in the digestive systems of animals. These natural catalysts facilitate separation of the collagen protein fibers through hydrolytic destruction of peptide bonds which cross-link the chains of amino acids. Bating also attacks and destroys most of the remaining undesirable constituents of the skin, such as hair roots and pigments. Removal of these materials softens the grain surface and gives it a cleaner appearance. Modern bates are actually mixtures of chemical deliming agents and selected enzymes, permitting simultaneous operation of both phases of this subprocess.

As in unhairing, the amount of bating chemicals, the temperature, and the reaction time are critical. Commercial processes vary in length from a few hours to overnight, depending on the nature of the skins being handled. At the conclusion of bating, the hides are thoroughly washed to remove all of the substances that have been loosened or dissolved.

Pickling.

Pickling prepares the hides to accept the tanning agents by providing an acid environment - an essential step in chrome tanning. Chrome tanning agents have minimum solubility under alkaline conditions; the acid environment thus prevents precipitation of chromium salts. Pickling most commonly uses sulfuric acid, with common salt or brine first added to the system. If acid alone were to be added, excessive swelling (similar to alkaline swelling) would develop, either producing

inferior leather or converting the hide into an untannable gelatinous mass.

Controlled acid swelling helps separate collagen protein fibers, which facilitates further complexing of the hide by the tanning agent (i.e., trivalent chrome) and, thus, more complete stabilization. The salt and acid solution completely penetrates the hide in a few hours.

The pickling operation is a preserving technique in its own right and skins can remain in this state for extended periods of time.

Tanning.

Tanning agents convert the raw collagen fibers of the hide into a stable product which is no longer susceptible to putrefaction or rotting. They also significantly improve many of the mechanical properties of the raw material including dimensional stability, resistance to abrasion, chemical resistance, heat resistance, flexibility, and the ability to endure repeated cycles of wetting and drying.

The predominant tanning agents used in the U.S. are trivalent chromium and vegetable tannins extracted primarily from specific tree barks. Other principal tanning agents include alum and syntans.

Vegetable tanning is an older process performed in a solution containing plant extracts. This method is applicable to the production of heavy leathers, such as sole leather, mechanical leather, and saddle leather. Vegetable tanning usually takes place in vats because of the longer reaction times involved. Recycling of vegetable tan solutions is becoming more common in the industry; unrecycled solutions may be used for retanning or may be evaporated for recovery and reuse.

Tanners generally prefer chromium tanning because it produces leather that best combines most of the chemical and physical properties preferred for the majority of leather uses. Chromium tanning also takes place in a shorter period of time (4 to 6 hours) than vegetable tanning.

The chemical state of the tanning agent, as well as the condition of the hides and interior of the drum, is important with regard to the thorough penetration of the chromium into the hide. The addition of sodium bicarbonate and formic acid (masking agent) increase the affinity of the separated collagen protein fibers for the chrome.

The older and more traditional method of chrome tanning, known as the "two-bath" method, entailed the use of hexavalent chromium,

which can be very toxic. The hexavalent chrome penetrates the hide during the first bath; the second bath introduces a reducing agent (such as thiosulfate) which "blues" the hides by in situ chemical reduction of chromium to the trivalent state. This process complexes the proteins.

Very few tanners have continued the use of the "two bath" method. The dangers of handling hexavalent chromium and the reduced processing time and chemical cost incurred in the use of trivalent chromium have encouraged the tanning industry to de-emphasize the traditional process.

Some tanners still purchase hexavalent chromium (bichromate, dichromate) and reduce it on-site to the trivalent state with dextrose or molasses and acid. This approach results primarily from the cost differentials between hexavalent and trivalent chromium in certain geographical areas. The danger of toxic hexavalent chromium spills exists even where adequate operator control is exercised, although certain tanneries have minimized these occurrences through the implementation of improved management practices.

Wringing.

In preparation of the blue hide for splitting, excess moisture is removed from the hide by wringing. The hides are fed through a machine equipped with two large rollers very similar to a clothes wringer.

The process at this point yields "wet-blue stock", which is either taken through retanning and wet finishing at the same plant, or sold to another plant which produces the finished leather products. Plants in the through-the-blue segment of the industry have no wet processing operations beyond this point.

Splitting and Shaving.

Splitting adjusts the thickness of the tanned hide to the requirements of the finished product. Hide thickness varies, depending partly on the age of the animal; different parts of the skin will also have various thicknesses. Splitting yields a grain portion of uniform thickness and a split (or fleshed) side. The split layer can be processed separately at the same facility or sold to split tanneries for use in suede types of leather.

Shaving removes any remaining fleshy matter from the grain portion of the hide, where the thickness was insufficient for contact with the splitting knife. The shaving machine also can adjust the tanned skin to meet exact specifications.

Retan, Color, Fatliquor, and Finishing Processes. To give the tanned hide special or desired characteristics, a tannery may employ further processing steps, as described below.

Retanning.

Most tanners have neither the equipment nor the low-cost labor to support multiple beamhouse and tanyard formulae for various finished leather products. Most hides are therefore subjected to identical processing through the blue state. The primary function of retanning is to impart characteristics to the finished leather which it lacks following the initial tanning step. The more common retanning agents are chromium, vegetable extracts, and syntans. Other agents such as as zirconium and gluteraldehyde, however, are used for very small quantities of leather. Retanning usually takes place in a drum during a one- or two-hour perod.

Vegetable extracts help to minimize any variation that may exist between different parts of the chrome tanned hide. Syntans are man-made chemicals which are used extensively in the manufacture of the softer side leathers. Because of their pronounced bleaching effect on the bluish-green color of chrome tannage, syntans are used in making white or pastel shades of leather.

Bleaching.

After tanning, hides can be bleached in vats or drums containing sodium bicarbonate and sulfuric acid. This is commonly practiced in the sole leather industry.

Coloring.

Dyes are added to the same drums used for retanning. Two important factors in coloring are: 1) skin variability, such as varying pigmentation, and 2) color penetration, or the depth to which the coloring material passes into the leather.

Typical dyestuffs are aniline based, and combine with the skin fibers to form an insoluble compound. Shades and degrees of penetration can be varied by controlling pH, which affects the affinity of the dye for the leather fibers.

Fatliquoring.

The fatliquoring process lubricates the fibers so that they can slide over one another. Oils and related fatty substances in fatliquors replace the natural oils lost in the beamhouse and tanyard processes. Chemical emulsifiers added to the fatliquor ingredients permit their dispersion in water. Fatliquoring requires approximately one hour to complete. Use of differing

amounts of oil permits the tannery to vary the firmness of the final product.

Fatliquors typically and predominantly are either of animal or vegetable origin, or are synthetics made from modified mineral-based oils. Straight-chain aliphatic mineral oils are used in very small quantities for specialty products such as mechanical and heavy shoe leathers.

Finishing.

The finishing process includes all of the operations performed on the hide following the fatliquoring operation. Generally, trimmings and dust collected during these processing steps are disposed of as solid wastes; however, dust may also enter the plant's liquid waste stream. There are a number of finishing steps:

Setting out smooths and stretches the skin while compressing and squeezing out excess moisture.

Drying uses four methods:

1) hanging, in which hides are draped over a horizontal shaft and passed through a large drying oven;

2) toggling, in which the skins dry in a stretched position on frames which are slid into channels of a drying oven;

3) pasting, in which the skins are pasted onto plates which are subsequently placed in a drying oven; and

4) vacuum drying, in which hides are smoothed out on a heated steel plate and covered by a perforated belt or cloth-covered steel plate. A vacuum then extracts water from the leather.

Unlike the first three drying processes, which require 4 to 7 hours per skin, vacuum drying can be accomplished in only three to nine minutes. Shrinkage of the leather, however, has inhibited widespread adoption of vacuum drying by the industry.

Conditioning involves spraying a mist on the hides, which are then piled on a table, wrapped in a watertight cover, and kept overnight to permit uniform moisture distribution within the leather.

Staking stretches and flexes the leather on automatic equipment to make it soft and pliable.

Dry milling tumbles the hides in a large drum.

Buffing smoothes or "corrects" irregularities in the grain surface by mechanical abrasion.

Finishing may be applied to the leather, depending on the end use and type of hide. Various finishes, both water-base and solvent-base, provide abrasion and stain resistance and enhance color. Solvent-based coatings are employed only for special high-luster finishes. Use of these coatings has been curtailed largely due to handling difficulties and their inherent fire hazard.

Plating is the final processing step, which influences the appearance and feel of leather. It smoothes the surface of the coating materials, while bonding them firmly to the grain. The finishing and plating operations occur in conjunction with each other over a period of four to five days. Hides may also be embossed (stamped with a particular pattern).

After finishing, the surface area of the hide is determined, and the product is graded for temper, uniformity of color and thickness, and the extent of any surface defects.

Sheepskin Tannery Processes

The manufacture of leather from sheepskin is similar to cattlehide tanning, except that the beamhouse process typically is absent. In addition, sheepskins require degreasing prior to tanning. The processes and subprocesses which differentiate sheepskin tanning from cattlehide operations are described below.

Tanyard Processes. U.S. tanneries receive sheepskins from both domestic and foreign sources. Imported skins generally arrive in a pickled condition, preserved for shipment and storage by immersion in a solution of brine and acid. Excess solution is drained prior to handling the skins, which are normally tied in bundles of one dozen. The wool is removed from the skins at the packinghouse or wool-pullery before the skins are processed to the pickled condition. Skins which arrive with the wool intact are referred to as shearlings. Shearling skins are cured in a salt brine only.

The hides normally are stored in the bundles as received. Some tanneries indicated that pickled skins held for extended periods should be kept below 30 degrees C (86 degrees F) to avoid deterioration. Biocides, such as chlorinated phenolics, retard bacterial action and lengthen storage time.

From storage, skins are taken from the bundles, inspected, and fleshed. Tanneries which receive fleshed sheepskins will usually reflesh them after tanning; typically, however, sheepskin hides are fleshed after a wash and soak operation. Fleshing is done on the same type of machine employed for processing cattlehides. The skin is carried through rollers and across rotating spiral blades which remove

the attached flesh. Fleshings and trimmings are collected as solid waste.

The fleshed skins are placed in drums, soaked, and washed. An added solvent or detergent then removes grease. Grease by-products are recovered from those skins which have had the wool removed. When solvent degreasing is employed, the solvent is recovered for reuse.

Shearlings require substantially more water in the soaking and washing operations. Grease recovery is not a conventional practice for shearling tanneries; these hides may be pickled in a process similar to that described for cattlehides.

Sheepskins may be either chrome or vegetable tanned, although the majority are tanned with chrome. Pickled skins require no liming or bating. Degreased skins are placed in drums with salt water and mixtures of basic chromium sulfate for chrome tanning or solutions of the natural tannins for vegetable tanning.

In some cases, a refleshing operation follows the tanning of sheepskins.

Retan, Color, Fatliquor, and Finishing Processes. The retan processing step proceeds in a manner similar to the cattlehide retanning operation.

Skins to be colored are immersed in a dye solution contained in drums. Generally, synthetic dyes are used, and sometimes shearlings are bleached prior to coloring.

Fatliquoring takes place in the same drum used for coloring and is designed to replace the natural oils of the skin lost in the tanning process. The process is similar to cattlehide fatliquoring.

A number of operations follow the sheepskin coloring and fatliquoring steps, including drying, skiving, staking, carding, clipping, sanding, and buffing. These are essentially dry operations which generate some solid wastes (trimmings and skivings). Dust from sanding and buffing may be collected dry or may become part of the waste flow.

Pigskin Tannery Processes

The tanning of pigskins differs from cattlehide tanning in the lack of a beamhouse process; most skins have the external hair removed at the packinghouse. Skin degreasing is an essential tanyard subprocess. The major processes required for pigskin tanning are described as follows:

Tanyard Processes. Tanneries receive nearly all pigskins as fresh, frozen skins although they can be brined and refrigerated. They usually are tied in bundles of 40 to 50 pounds each. In some cases,

frozen skins may be delivered in paper bags. Most tanneries use refrigerated storage for skins held before tanning.

Most pigskin tanneries use solvent degreasing. The skins are placed in drums, then soaked and washed in warm water to bring them up to a suitable temperature for degreasing. Solvent is then added to the drums and the skins are tumbled to facilitate grease removal. The solution of solvent, grease, and water is pumped from the drums to large tanks, where some separation occurs. This allows decanting and discharge of the water fraction to the plant sewer. From the tanks the solvent and grease mixture is sent to a stripping column, which recovers the solvent for reuse. Grease is then recovered as a by-product.

Some tanneries have adopted an alternate degreasing method in which the skins are tumbled in hot water and detergent. Following this operation, the degreasing solution is diverted to holding tanks where grease by-products are recovered by decanting or skimming from the top of the tanks.

The skins are then placed in tanning drums with a lime slurry and sharpeners. This step is to remove the embedded portion of the hair from the skins.

The bating operation, similar to that used in cattlehide tanning, takes place in the same drums used for liming.

Also, as in the cattlehide tanning, the pickling step places the skins in an acid bath to prevent precipitation of chromium salts and facilitate tanning. The required constituents are added to the same drums used for bating and liming.

Pigskins may be either chrome tanned or vegetable tanned. The major pigskin tanner in this country, however, uses strictly the chrome tanning process. Chrome tanning is conducted in the same drums used for liming, bating, and pickling by immersion in a solution of chromium sulfate. The current practice is to fully tan the skins in this operation, eliminating any need for a retan operation to produce a final product.

After being tanned, the skins are tumble dried, split and shaved to obtain the desired thickness. Since the split portion of the pigskin has no commercial value as leather, it is baled with other scrap and sold as a fertilizer component. The grain sides are subjected to subsequent processing operations.

<u>Color, Fatliquor, and Finishing Processes</u>. Typically, tanned pigskins are colored by immersion in a solution containing a synthetic dye. The process considerations are similar to those involved in cattlehide tanning.

The purpose and methodology associated with the fatliquoring processing step for pigskins parallel those outlined for cattlehide and sheepskin fatliquoring.

A number of operations typically follow the color and fatliquor steps. These are principally dry subprocesses similar to those described for cattlehide tanning.

SECTION IV

INDUSTRY SUBCATEGORIZATION

SUMMARY

In developing effluent limitations guidelines, new source performance standards and pretreatment standards for the leather tanning industry, it was necessary to segment the industry into relatively homogeneous groups or subcategories. EPA found that the most significant factor for subcategorizing regulated industries is the product, which accounts for such factors as the types of raw materials processed and the manufacturing processes employed.

The raw material of the leather tanning industry is the hide or skin type subjected to the processing operations. Manufacturing processes then relate to the type of raw material received by the facility. For example, some tanneries process previously tanned hides or skins, thus eliminating the need for beamhouse operations. Other significant process considerations include the tanning process utilized and the presence of finishing operations, including retanning.

In subcategorizing industries, EPA also examines plant size, age and location (including climate), wastewater characteristics and treatability, engineering aspects of various control technologies, costs, economic impacts, and other factors. In most cases, these factors do not justify additional subcategorization, but substantiate subcategorization based on commodity (raw material and process).

The factors considered for subcategorizing the leather tanning industry are summarized as follows:

1. raw material

   a. cattlehide,

   b. split,

   c. pickled sheepskin,

   d. shearling,

   e. pigskin;

2. manufacturing processes

   a. beamhouse operations,

   b. tanning process (chrome, vegetable, alum),

   c. finishing operations (including retanning);

3. plant size

4. plant age

5. plant location and inherent climate

6. wastewater characteristics and treatability

7. engineering aspects of the application of various treatment technologies

8. non-water quality impacts

9. costs

10. economic impact.

EPA has determined that raw material and manufacturing process are the most significant factors in subcategorizing the leather tanning point source category. Seven subcategories have been developed (originally six). Four of the subcategories primarily cover the cattlehide to leather segment of the industry; two subcategories cover operations which have no beamhouse and the seventh subcategory covers shearling tanning (sheepskin with hair intact).

The seven subcategories are defined as follows:

1. Hair Pulp/Chrome Tan/Retan-Wet Finish - facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving the hair (hair pulp); tanning with chrome; and retanning and wet finishing.

2. Hair Save/Chrome Tan/Retan-Wet Finish - facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically loosening and mechanically removing the hair; tanning with chrome; and retanning and wet finishing.

3. Hair Save/Non-Chrome Tan/Retan-Wet Finish - facilities which process raw or cured cattle or cattle-like hides into finished leather by chemically loosening and mechanically removing the hair; tanning with primarily vegetable tannins, alum, syntans, oils, or other chemicals; and retanning and wet finishing.

4. Retan-Wet Finish - facilities which process previously unhaired and tanned hides or splits into finished leather through retanning and wet finishing processes including coloring, fatliquoring, and mechanical conditioning.

5. No Beamhouse - facilities which process previously unhaired and pickled cattlehides, sheepskins or pigskins into finished leather by

tanning with chrome or other agents, followed by retanning and wet finishing.

6. Through-the-Blue - facilities which process raw or cured cattle or cattle-like hides into the blue tanned state only, by chemically dissolving or loosening the hair and tanning with chrome, with no retanning or wet finishing.

7. Shearling - facilities which process raw or cured sheep or sheep-like skins into finished leather by retaining the hair on the skin; tanning with chrome or other agents; and retanning and wet finishing.

RATIONALE FOR SUBCATEGORIZATION

Raw Material

The hide or skin type received by a tannery imposes specific processes on the manufacture of leather products. This relationship between raw material and manufacturing process establishes hide or skin type as a basis for industry subcategorization.

The original development document grouped tanneries into six segments. Table 4 compares the original listing of six industry segments to the seven subcategories which are defined in this document. The updated industry subcategorization segregates shearling tanning from the other no beamhouse operations because of the nature of the raw material. Preparation of the sheepskins for tanning with the wool intact requires significantly more washing than is required for pickled skins. This results in higher flows and waste loads for shearling operations, which therefore warrant a distinct subcategory.

The presence and length of hair on the hides or skins being tanned determines the manufacturing processes required and helps determine the character of the plant waste stream. Removal of hair (beamhouse subprocesses) increases tannery waste loads in terms of most pollutant parameters such as BOD_5, COD, TSS, TKN, etc. Hair length (as with shearlings) also affects waste generation, especially water use. For the purpose of subcategorizing tanneries three basic hide/skin types are important:

1. Cattlehide or cattle-like hide - short hair, relatively heavy hides or skins (includes splits). Deerskin, horsehide, cow bellies, and other similar hides are included in this group.

2. Sheep or sheep-like skins - long hair and relatively light skins (includes shearlings). Goatskin and other similar hides are included in this group.

3. Pig or pig-like skins - short hair or hairless, and relatively light skins. This group includes only skins which have little or no hair.

Table 4 Subcategory Comparison by Principal Processes

Present Document Subcategory	EPA Development Document March 1974 Subcategory
1. Hair Pulp, Chrome Tan, Retan-Wet Finish	1
2. Hair Save, Chrome Tan, Retan-Wet Finish	2
3. Hair Save, Non-Chrome Tan, Retan-Wet Finish	3
4. Retan-Wet Finish	4
5. No Beamhouse	5
6. Through-the-Blue	6
7. Shearlings	5

Manufacturing Processes

Beamhouse Operations. The existence of or type of beamhouse operation in a leather tannery is a significant factor in subcategorization. Unhairing operations typically contribute high raw waste flows and loadings at tanneries with a beamhouse. The specific unhairing process (i.e., hair pulp or hair save) also affect beamhouse waste characteristics and loadings, since hair dissolving (or pulping) contributes lower flows but more pollutant discharges. In addition, preliminary treatment of segregated beamhouse wastewaters is necessary for plants which include these subprocesses. EPA has therefore subcategorized the tanning industry to reflect the following variations of beamhouse operations:

1. Pulp hair - hair is chemically dissolved from the hide/skin and enters the liquid waste stream.

2. Save hair (and wool pullery) - hair (or wool) is chemically softened and mechanically removed. The major portion of the hair is removed as a solid, thus preventing it from entering the liquid waste stream. Residual roots and fragments may be lost to the waste stream.

3. No beamhouse - hides or skins are received with the hair already removed; a beamhouse operation is therefore not needed and the tannery does not generate the beamhouse-type waste stream. Raw materials that require little or no hair removal, such as pickled sheepskin or cattlehides, shearlings, and pigskin are included in this group.

Tanning Process. This process is primarily a function of the tanning agent used. The industry in the U.S. employs various agents, including chrome, vegetable tannins, alum and syntans. Non-chrome tanning methods may generate highly colored waste streams, but flows and waste loads are slightly less than those observed for chrome tanning operations. Facilities which only retan and finish previously tanned hides should be considered separately because the resulting waste streams contain reduced mass of residual tanning compounds, such as chromium.

Since tanning processes influence the flow, waste characteristics and pollutant loadings for each tannery's waste stream, industry subcategorization reflects the tanning process as follows:

1. Chrome tanning - at least 20 percent of the total tonnage is tanned with this agent. A significant number of plants use only this tanning method and for most facilities, chrome represents the primary tanning agent.

2. Non-chrome tanning - less than 20 percent of the total hide tonnage is chrome tanned. The primary non-chrome tanning agents are of vegetable tannins (primarily extracts from specific types of tree

bark) with significantly less utilization of alum, and synthetic agents.

3. Previously tanned - no tanning is carried out because the plant receives fully tanned hides which require only retanning and finishing.

Retanning and Wet Finishing Operations. The presence or absence of retanning and wet finishing (coloring, fatliquoring, etc.) is significant for industry subcategorization. These processes contribute significantly to the total waste stream of tanneries with or without a beamhouse, most importantly to total water use. At No Beamhouse tanneries, retanning and wet finishing operations have a considerable impact on total waste flows and pollutant loadings.

Some tanneries restrict processing to retanning and wet finishing of hides and skins received in the tanned state. These facilities incur water usage and raw waste loadings which are considerably less than those observed for more complex tanneries conducting beamhouse and tanning operations.

Plants which start with "crust" leather (wet finishing previously completed) are not considered tanneries and were excluded from this study.

Plant Size. EPA defines the size of a tannery as the number or weight of hides and skins processed in a day. Most subcategories contain a wide range of plant sizes or production levels. The ratio of flows and raw pollutant loadings to units of production remains constant, however, essentially independent of plant size for each subcategory. The Agency found no other factors which coincide with plant size to be relevant for subcategorizing the industry.

Plant Age. No consistent difference in plant operations or wastewater generation was associated with tannery age. The physical structures for most plants are quite old, but even the newer plants have processing equipment similar or identical to much of the equipment found in the older tanneries. In fact, many older plants have certain pieces of processing equipment which are quite modern, such as hide processors, "Turbotan" processors, and "Idronova" separation equipment.

Plant Location and Climate. There was apparently no detectable relationship between plant location and raw waste loadings; neither do tannery location and raw material source necessarily coincide. Hides and skins are usually purchased for specific product applications. With rare exceptions, the geographical location of a plant and its source of raw material are basically independent.

Climate, directly related to geographical location, also does not influence the processing activities of tanneries in the seven

subcategories. For a given raw material, the selection of processing steps remains the same. Water usage and raw waste loads are not affected by climate, since they are primarily a function of hide or skin type and manufacturing processes employed. Furthermore, the Agency found that climate does not affect the treatability of wastewaters and achievable final effluent concentrations. Climate does, however, affect the specifics of design, equipment selection, and especially operational requirements of treatment systems. Plants in northern cold climate areas can be expected to incur somewhat higher costs to ensure consistent operation during winter months. Where appropriate, these factors have been considered in development treatment system component costs with no difference in economic impacts identified. No differences were identified in non-water quality impacts attributable to climate. Therefore, further subcategorization of the leather tanning industry based on climate is not warranted.

Wastewater Characteristics and Treatability. To assess the subcategorization of the leather tanning industry regarding wastewater characteristics and treatability, the Agency reviewed information from various sources. Substantial data for conventional pollutant parameters and for sulfide and chromium were available; however, information for other toxic pollutants was limited essentially to that generated during the course of this study. The data for flow, BOD_5, suspended solids, sulfide, and chromium supports the updated industry subcategorization set forth above. Aside from chromium, toxic pollutants provided no basis to alter the subcategories identified principally on the basis of raw material and manufacturing processes.

Same or similar treatment technologies are capable of treating the raw wastewaters associated with the various industry segments. The preliminary treatment technologies vary with subcategory by presence or absence of beamhouse operations and tanyard operations including deliming (ammonia substitution) and tanning (chrome recovery). End-of-pipe treatment technology was found to be equally applicable to all subcategories after differences in raw waste loads were accounted for by preliminary treatment. Climate, as noted above, does not adversely affect the considered treatment process. There is therefore no need to subcategorize industry operations in terms of wastewater characteristics and treatability since the same final effluent concentrations can be achieved by plants in all subcategories. Only the mass limitations (lb/1,000 lbs) vary according to water use (gal/lb) in each subcategory.

The principal wastewater characteristics considered for subcategorization were: 1.) 5-day biochemical oxygen demand (BOD_5) expressed in kilograms (kg) per thousand kilograms (kkg) of hide, or pounds (lb) per thousand pounds (1000 lb); and 2.) flow in litres per kg (gallons/lb) of hide. BOD_5 is associated with all tannery wastewater; it is present, however, at different levels depending on the nature of the raw material and the manufacturing processes. BOD_5

provides the best measure of plant operation and treatment effectiveness among the wastewater parameters measured, and more data is available for BOD_5 than for any other pollutant parameter. Flow per unit of unprocessed hide weight reflects many factors, including: 1) type of hide or skin processed; 2) presence of any of the three major process groupings (beamhouse, tanyard, retan-wet finish) in the operation; 3) degree of process variation; and 4) housekeeping practices.

Total suspended solids (TSS) data serve to reinforce the conclusions developed from BOD_5 and flow in that presence of unhairing operations substantially increases the TSS content of raw waste loads. Another parameter, chemical oxygen demand (COD), is also much higher where beamhouse operations are present. COD is also a measure of refractory organic matter in wastewater, including some of the non-biodegradable toxic pollutants. Further, COD is a good indicator of change, but does not relate directly to the biodegradation occurring in biological treatment processes. However, BOD_5, TSS, and COD are all reduced to some degree by the same tannery wastewater treatment technology.

Sulfides and total chromium are other pollutant parameters considered significant for industry subcategorization. Trivalent chromium is recognized as an important constituent of tannery wastewater, hence the distinction between "chrome" and "non-chrome" tanneries in the subcategorization. The amount of chromium in the wastewater reflects whether a plant operates both tanning and retanning processes, or merely retans partially processed stock. Sulfides originate from chemicals used in the beamhouse unhairing operations and from residues of these chemicals in the hides. The amount of sulfide present in the wastewater reflects the type of unhairing process used.

Both chrome and sulfide levels are controllable through in-plant measures and efficient treatment processes. In-plant controls are generally dictated on the basis of pollutant levels present in the process stream. In the case of chrome and sulfide, pollutant levels are a function of the process, which in turn is reflected in the subcategorization. With the proper in-plant controls and preliminary treatment in place, all subcategories can use the same end-of-pipe technologies for effluent treatment.

EPA also considered a number of additional waste load parameters. Among these were nitrites and nitrates, Kjeldahl nitrogen, ammonia, total dissolved solids, total volatile solids, oil and grease, chlorides, total alkalinity, phenols, and fecal coliform. In each case, data for these pollutants did not indicate a need for further subcategorization on the basis of either these additional waste load parameters or their treatability.

The Agency found a total of 37 of the 129 toxic pollutants in untreated tannery wastewaters. The number present per subcategory

varied from 33 for subcategory one tanneries to 19 for tanneries in subcategory seven. (See Tables 6A - 12A, Section 5).

Comparison among subcategories and constituents, however, found consistency for the acid fraction organics (i.e., phenol and substituted phenolics) and the inorganics (cyanide, chromium, zinc, lead, nickel, and copper). These toxic pollutant groups were found in the wastewaters of all sampled plants; and therefore these constituents are probably present in all seven subcategories. A pattern is visible for a single parameter, chromium. This observation supports the subcategorization rationale which reflects the differences in chromium concentrations present in the untreated wastewaters. EPA found no discernable pattern in the concentration of the remaining toxic pollutants and pollutant groups (volatile organics, pesticides, and PCB's, etc.).

Because the presence of toxic constituents varied within the individual subcategories with no discernible pattern, their treatment does not appear to be a factor in subcategorization. Raw wastewaters generated by the various segments of the tanning industry are amenable to the same treatment processes.

Climate, particularly severe cold, has dictated the type of secondary wastewater treatment and the specific design parameters selected in some instances. However, the ultimate treatability of toxic pollutants is not influenced by climate, assuming careful design, and diligent operation and maintenance of extended aeration activated sludge treatment systems. In fact, certain treatment facilities operating in the most severe northern climates represent model systems for the tanning industry (see Section VII).

Differences in raw waste loading among tanneries are accounted for by varying the degree of in-plant control and pretreatment rather than variation in end-of-pipe technology or the achievable final effluents. The presence of beamhouse operations, for example, requires the control of sulfide and proteinaceous material prior to end-of-pipe treatment.

SECTION V

WATER USE AND WASTE CHARACTERISTICS

The purpose of this section is to describe the sources, volumes, and characteristics of wastewaters in the leather tanning and finishing industry. The data base consists of 4,060 data points for 87 plants during the period of 1973 to 1978. Data from the original study were used for comparison purposes to highlight trends and questionable data, but were not included in this study. Detailed information for individual tanneries documents this report.

In reviewing this data base, EPA has observed variability in the data reported by tanners and gathered by EPA. Some of this variability may be the result of differences in production processes and scheduling, as well as sampling procedures, analytical techniques, and possible reporting errors. EPA has attempted to ascertain the causes of variability and has taken variability into account in describing and interpreting raw waste characteristics presented below.

The leather tanning and finishing industry uses water in large quantities for several purposes:

1. for soaking and washing unprocessed hides;

2. as a medium which allows chemicals to react with hides/skins;

3. as a carrier for dyes and pigments which impart the desired color to the final product; and

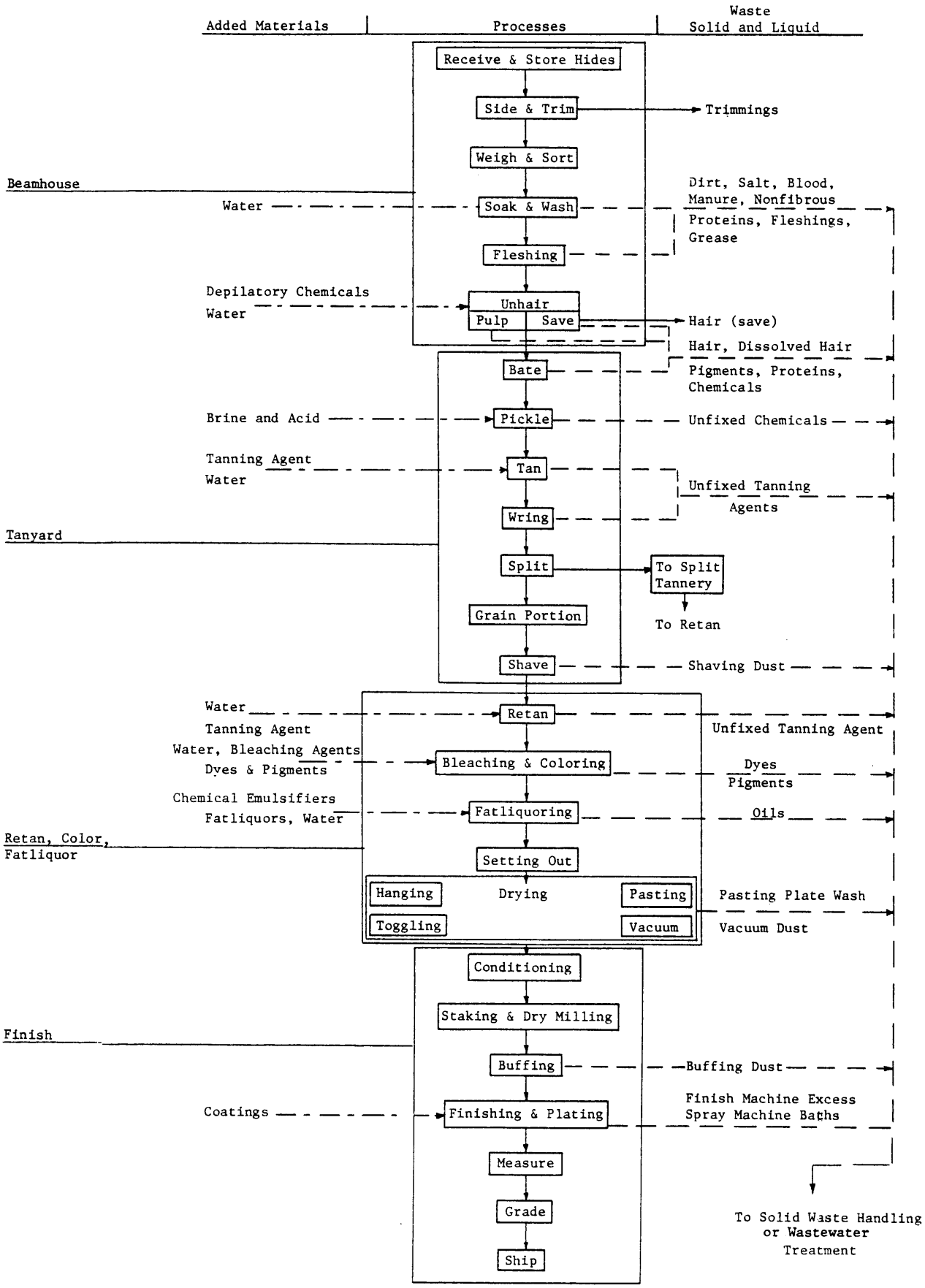
4. for cleaning processing areas and equipment.

Figure 2 shows the sequence of subprocesses associated with tannery operations. This illustration also indicates the origin of solid waste and major liquid waste streams for each process, and the primary physical contaminants within each waste stream.

Recycling and reuse of several waste streams is a continuing and growing trend in the industry. Streams such as the spent chrome and vegetable tanning solutions, unhairing lime-sulfide liquor, and the pickling solution are those most frequently considered for reuse, recycle, or materials recovery. Among U.S. tanners, the chrome tanning solution is most often managed for reuse. Pickling solution has also received considerable attention with regard to reuse. European tanneries are reported as giving serious consideration to the recovery of proteins from the beamhouse waste stream; this measure would reduce tannery waste loads while producing a by-product of value[3]. The following discussion of subprocesses as a source of wastewater, however, will address standard U.S. manufacturing practices.

Figure 2

PRODUCT AND WASTEWATER FLOW FOR GENERALIZED LEATHER TANNING AND FINISHING PLANTS



Wastewater of various quantities and pollutant loads originate from every wet process in a tannery. Depending on the nature of the dry finishing operations, such as embossing, the resulting waste stream is either intermittent and relatively small, or nonexistent. Historical information and knowledge of actual processing operations indicate that tannery wastewaters contain soluble and suspended organic matter, including grease and oils; solids; inorganic materials such as salt; chromium salts; sulfide; ammonia; small quantities of nutrients; and in some cases coliform. In addition to chromium, other toxic pollutants are present in the various waste streams as a result of the chemical processes characteristic of the tanning industry. These constituents enter the waste stream as proteinaceous matter, hair, tissue, unfixed chemicals, tanning agents, extracts, dyes, pigments, dirt, grit, and manure.

Water use and wastewater characteristics throughout the industry are discussed in more detail below.

WATER USE

The volume of water used (and plant effluent) depends on the major processes employed at a specific tannery. Variations in processing techniques are recognized in the subcategorization of the industry. Water use and specific sources of wastewater are discussed, by subcategory, as follows:

Subcategory One (Hair Pulp/Chrome Tan/Retan-Wet Finish)

Tanneries in this subcategory primarily process brine-cured or green salted cattlehides into finished leather. Various amounts of water are used in performing the three wet processing operations: beamhouse, tanyard, and retan-wet finish. Water use for typically employed individual subprocesses is described in the following paragraphs.

Soak and Wash. The purpose of this operation is to remove salt, restore the moisture content of the hides, and remove any foreign material such as dirt and manure. Brine-cured hides are soaked and washed simply to remove salt, while green salted hides require the removal of manure and dirt, as well as salt. The quantity of manure and dirt varies with the season of the year and the origin of the hide. Industry data estimate the wastewater volume from this subprocess to be about 20 percent of the total wastewater flow. Primary waste constituents from the soak and wash process are BOD_5, COD, suspended solids, and dissolved solids (including sodium chloride).

Fleshing. Fleshing follows the soak and wash operation if this was not done previously. Fleshings are isolated as a solid waste and, when handled properly, do not make a significant contribution to the total waste loads of a cattlehide tannery.

Unhairing. Pulping to remove hair involves the addition of lime and sharpeners (e.g., sodium sulfhydrate) in relatively high concentrations. The process dissolves the proteinaceous hair enough to dissipate it in the unhairing solution. As reported by various tanneries, this segment of beamhouse operations generates between 20 and 38 percent of the total tannery flow, an average of 32 percent for those facilities reporting such information. Because of the nature of this subprocess, the BOD_5 and other waste constituents (particularly sulfides and nitrogen) are present in relatively high concentrations.

Bating and Pickling. The bating subprocess delimes, reduces swelling, peptizes the fibers, and removes protein degradation products. Major chemical additions are ammonium sulfate to reduce pH to an acceptable level and enzyme to condition the protein matter.

Following the bating process, hides are prepared for tanning by pickling. Pickling solutions contain primarily sulfuric acid and salt, although small amounts of wetting agent and biocide are sometimes added. Since protein degradation products, lime, and other waste material are removed through bating, the quantities of BOD_5, suspended solids, and nitrogen are relatively low. Principal waste constituents are the acid and salt. Bate and pickle wastewater volumes, reported as a combined total by several tanneries, range from 9 to 50 percent of the plant flow, an average of 26 percent for the combined process flow.

Tanning. Chrome tanning employs a chromium sulfate or a chrome tanning solution as the tanning agent. Other chemical additives include sodium formate and soda ash. The chromium must be in the trivalent form and must be dissolved in an acidic medium to accomplish desired results.

For those plants reporting data, the median and average flows associated with the tanning process were found to be 4.4 and 6.6 percent of total plant water use. The spent chrome tanning solution represents a relatively low waste load in terms of BOD_5 and suspended solids; this waste stream, however, is the principal source of trivalent chromium in the plant effluent.

Some tanneries prepare trivalent chromium by reducing dichromate solution to the trivalent form, using glucose (molasses) as a reducing agent. The only entry of hexavalent chromium into the plant effluent is by spillage of unreduced bichromate or dichromate from reducing equipment, or from tanning drums by those very few plants which still utilize the more traditional "two bath" method of tanning.

Retanning, Coloring and Fatliquoring. The chrome tanned hides normally remain in the same drums for these three subprocesses. Retanning increases the penetration of tanning solution into the hides after splitting and uses either chrome, vegetable, or synthetic tanning agents. Because retanning uses the low concentrations of

chemicals, the wastewater strength is not high and does not represent a significant portion of the total waste flow.

The most variable process in the tannery is coloring. There are hundreds of different kinds of dyes, both synthetic and vegetable based. Synthetic dyes are the most widely used in the industry and usually require the addition of acid to facilitate dye uptake in the leather. The fatliquoring operation can be performed either before or after coloring. Ultimate use of the leather product dictates the type and amount of oil required for this subprocess.

Drying by the pasting method requires a small amount of water, first to prepare the mixture and then to wash it off. Even though the volume is very small, pollutants associated with the starch can be present in relatively high concentrations Several tanneries report the reuse of paste mixtures, which minimizes the amount of material entering the waste stream.

Process effluent from wet finishing (retan, color and fatliquoring) is considered high-volume, low-strength wastewater, compared to the waste streams associated with beamhouse and tanyard operations. Because wet finishing imparts color to the process water, recycling is not normally practiced. The wastewater volumes from the combined subprocesses, reported as a percentage of total tannery flow, are highly variable, ranging from 12 to 30 percent.. Because few tanneries reported flow information for these operations, presentation of an average value could not be computed.

Finishing. Because leather finishing operations are basically dry, they contribute the lowest wastewater flow of any tannery process. There is some wet processing, such as wetting the hides to facilitate handling in the staking or tacking operations, but most leather finishers do not have a contaminated discharge resulting from their processing activities.

Subcategory Two (Hair Save/Chrome Tan/Retan-Wet Finish)

Except for the unhairing operation, the major processing steps employed to convert cattlehide into leather are similar to those described for Subcategory One. In the hair save unhairing operation, the hair is loosened for subsequent machine removal. The depilatory chemicals utilized are the same as those characteristic of hair pulping, but are present in lower concentrations.

The second step in the hair save operation is machine removal of hair from the hide. Removed hairs require washing only if they are to be baled and sold; otherwise they are handled as solid wastes.

The average water consumption of hair save operations is approximately 20 percent greater than for hair pulp tanneries. The higher water use is associated with machine removal and washing of the hair. The

resulting waste is characterized by a high alkalinity, pH, sulfide, and nitrogen content. The reaction of the unhairing solution with the proteinaceous matter contributes the nitrogen. Other waste constituents include BOD_5, COD, suspended solids, and dissolved solids, a portion of which is the sodium chloride remaining from the soak and wash operation. The levels of these pollutant parameters are significantly less per unit production than the levels for hair pulp operations.

Subcategory Three (Hair Save/Non-Chrome Tan/Retan-Wet Finish)

The principal difference between this subcategory and Subcategory Two is the tanning operation. Cattlehides leaving the beamhouse are bated and pickled in a similar manner, but tanned with such agents as alum, zirconium, and other metal salts, as well as syntans, gluteraldehyde, and formaldehyde. Vegetable tannins accomplish the major portion of non-chrome tanning.

Spent solutions from the vegetable tanning process are quite different from chrome solutions. The reaction rate of vegetable tannins with the hides is much slower than that associated with chrome. Because of the longer contact time, the process normally proceeds in vats with some type of gentle agitation. In some instances, the hides pass through a series of vats with varying solution strengths. Process solution conservation is prevalent due to the cost of tanning agents.

Portions of the solution which enter the waste stream generally result from drag-out or planned blow-down to maintain the integrity of the solution. The semi-batch approach to vegetable tanning yields lower flows than those for chrome tanning (Subcategory Two). With regards to pollutant parameters, vegetable tanning is a significant source of BOD_5 and color. Although the retanning and fatliquoring steps are similar to those employed for chrome-tanned hides, vegetable-tanned leathers are surface-dyed by spraying the desired color on the leather surface.

Subcategory Four (Retan-Wet Finish)

Tanneries in this subcategory receive previously tanned hides or splits for retanning and finishing. Either chrome, vegetable or synthetic tanning agents can be used for retanning. Wastewater sources for the wet finishing steps (coloring, fatliquoring, and drying) are comparable to the description provided for Subcategory One. Without the beamhouse and tanyard operations, flow and waste loads (BOD_5, TSS, COD, and sulfide) per unit of production decrease substantially from those associated with the preceding subcategories. The average flow for a retan-wet finish facility is less than one-half of the volume characteristic of tanneries with beamhouse and tanyard processes.

Subcategory Five (No Beamhouse)

This subcategory primarily includes plants which tan unhaired pigskins and pickled sheepskins. Tanneries may also receive pickled and unhaired cattlehides which are subjected to tanyard and retan-wet finish processes as outlined for the preceding subcategories.

Unhaired, pickled sheepskins require fleshing if this has not previously been done. Previously fleshed skins usually require refleshing after tanning. Pigskins are not subjected to this operation.

Grease removal is necessary for both sheepskins and pigskins and follows the soak and wash step. Utilizing the same drums, degreasing proceeds by one of two methods: 1) hot water with detergent, or 2) solvent addition. In either case, the grease is separated and recovered as a by-product having some commercial value. For pigskins, the total amount of grease removed from the skin can approach 10 percent of the skin weight.[1] The quantity entering the waste stream is usually a small part of the total. In solvent degreasing, the solvent is recovered for reuse. BOD_5, COD, and suspended solids are other constituents in waste streams generated by this operation.

Prior to tanning pigskins, the tanneries must remove the embedded portion of the hair from the skins. This step is accomplished in drums containing a lime slurry and sharpeners; the bating operation, comparable to the cattlehide process, occurs in the same drums. The pickling step follows to prepare the skins for tanning.

Sheepskins and pigskins may be tanned with chrome or vegetable tannins, although the majority of tanneries utilize the chrome tanning method. The conventional practice is to tan pigskins completely, thus eliminating the need for a retan operation. Tanned sheepskins are retanned in a manner similar to cattlehides. The wet finishing operations for both types of skins are equivalent to those described for Subcategory One.

Elimination of the beamhouse results in lower average flow and waste loads per unit of production than is typical for Subcategories One, Two and Three; however, the No-Beamhouse segment generates higher flows and waste loads than tanneries which only retan and wet finish (Subcategory Four).

Subcategory Six (Through-the-Blue)

Facilities in Subcategory Six process raw or cured cattlehides through the blue tanned state only. The remaining steps to produce finished leather are performed by other tanneries which characterize Subcategory Four.

Unhairing of the hides may use either the hair pulp or the hair save method. Hair pulping results in the higher waste loads, while hair save uses more water. Following bating and pickling, the unhaired hides are chrome tanned to the blue stage.

Average wastewater flows for through-the-blue tanneries are lower than those for Subcategory Five (No Beamhouse) tanneries, but greater than facilities which only retan and wet finish. The beamhouse process increases the pollutant content of the total plant waste stream to levels approaching those observed for Subcategories One and Two.

Subcategory Seven (Shearling)

This subcategory consists of tanneries which process raw or cured sheepskins into finished leather with the hair (wool) intact. The major processing operations include tanyard and retan-wet finish.

Prior to the tanning operation, the skins are soaked and washed to cleanse them of foreign matter. This step requires substantially more water for shearlings than for unhaired hides or skins. The shearling hides are fleshed after washing. Degreasing follows, using either of the two methods described for Subcategory Five; however, grease recovery is not normally practiced by shearling tanneries.

Unlike unhaired sheepskins, shearling hides are pickled in the manner characteristic of cattlehide processing, prior to tanning. They do not, however, require liming and bating. Tanning may be accomplished with chrome or vegetable tannins, although the chrome method is generally preferred. The retanning and wet finishing steps for shearlings follow.

Because shearling hides are processed with the hair intact, average water consumption is more than four times the volume per unit of production observed for Subcategory Five, which essentially employs the same processing steps. The longer hair and the absence of grease recovery are major factors contributing to the higher waste loads for suspended solids as well as oil and grease.

WASTE CHARACTERIZATION

Background

The characteristics of untreated wastewaters are based on: 1) historical data collected from the industry and various other sources; and 2) the sampling program undertaken during the course of this study. EPA defines raw waste as the total plant effluent available for sampling at the first access point in the tannery. This is typically a catch basin or wet well, frequently equipped with an integral screening device. The raw waste characteristics thus reflect the pollutant load reduction achieved by screening, which is usually minimal.

The Agency analyzed the following standard tannery processes and subprocesses: beamhouse, tanyard, retan, color, fatliquor, and finishing. The primary inputs to these operations are water and such chemicals as lime, sodium sulfide, sodium sulfhydrate, ammonium salts, enzymes, basic chromium sulfates, vegetable tanning extracts and compounds, mineral acids, alum, natural and synthetic fatliquors, acid dyes, some solvent coatings, and sodium chloride.

Depending on its origin, a waste stream may consist of such materials as dirt, manure, salt, fleshings, grease, hair, unfixed chemicals and tanning agents, proteins, dyes, pigments, oil, and leather dust. The pollutant parameters historically used to characterize the raw waste from tanneries are flow, BOD_5 total suspended solids, oil and grease, total chromium, ammonia, and sulfide. Information regarding other classical pollutant parameters, including solids and nutrients are also available from selected sources. EPA collected data regarding toxic pollutants through a sampling program described previously in Section III. With the exception of chromium, the analytical results represent first-time data generated for toxic pollutants present in leather tanning and finishing wastewaters.

Relating wastewater volumes and pollutant parameters to production is one way of gaining perspective on the waste generated by tannery operations. Traditionally, flows as well as "classical" pollutant loadings have been related to production (defined as the weight of hides/skins processed) for the purpose of normalizing the data. Production level, in terms of hide/skin weight processed per operating day, for a given plant was computed from the number and average weight of hides reported by the tannery during year-round operation. This approach was taken because the weight of raw material processed on a given day is subject to variations for both the average weight per hide/skin and the actual number handled. The mix of unprocessed hide conditions (green-salted, brine-cured, fresh, etc.) and the variable amounts of extraneous matter attached to the hides contributed substantially to variations in production levels. These factors can also influence the waste flows and loadings.

Wastewater flow is generally presented as the ratio of total volume to production level per operating day. Other wastewater characteristics (classical pollutants) are expressed in terms of pollutant mass per 1,000 units of production. The data indicate the presence of toxic constituents in a waste stream; however, a mass relationship between toxic pollutant levels and production is unclear at this time. The presence of specific constituents demonstrates to some extent the manufacturing process being employed.

Flow ratios and raw waste loadings based on historical information are presented for each subcategory. The Agency calculated "classical" pollutant values from concentrations in milligrams per litre (mg/l), flow in gallons per day (gpd), and production levels expressed as 1,000-lb units of incoming raw material. The data base for these

parameters has been established by industry, governmental sources, sampling, and plant visits.

EPA tested the raw waste load data base for classical parameters to determine the best fit among three types of statistical distributions: normal, log-normal and three parameter log. Flow data were evaluated for all subcategories and pollutant loadings for four subcategories (where sufficient data for statistical analysis was available), representing 43 data sets. Twenty-five (60 percent) of these data sets were log-normally distributed, including four of seven low data sets. In a log-normal distribution, the logarithms of the data points are normally distributed thus allowing application of conventional statistical analysis. The distribution is generally characterized by a clustering of most lower and middle range data points with a small number of high value data points. The Agency decided that the log-normal distribution was most representative and appropriate to all data sets. In this form, the most meaningful indicator of the central tendancy of the data is the geometric mean; hence, all classical pollutant loads for the seven subcategories of the leather tanning industry reflect geometric means (logarithmic averages).

The Agency sampled a cross-section of the leather tanning industry to determine the presence and levels of toxic pollutants, as noted previously by Table 2 (Section III). Table 5 lists the processes, hide material, and finished products for each of the 22 tanneries which participated in the sampling and analysis program.

Several toxic pollutants are major ingredients of chemicals used in tannery processes; several others are used as solvents and dye carriers. Many occur as minor or trace components in other chemicals. The most heavily used toxic pollutant in leather tanning is chromium, but there are several others used in significant amounts. These include:

1. syntans based on naphthalene and phenol;
2. 4-nitrophenol (a biocide, as well as a waterproofing agent);
3. pentachlorophenol (a preservative and biocide);
4. hexachloroethane, ethylbenzene and toluene solvents;
5. 2,4,6-trichlorophenol (a biocide);
6. biocides based on cresol; and
7. heavy metals (organometallic dyes).

Other inorganic toxic pollutants found in addition to chromium were zinc, lead, nickel, copper, and cyanide. The metals typically originate in organo-metallic dyes. Cyanide also is found in dyes, and

TABLE 5 PLANT CHARACTERISTICS OF TANNERIES SAMPLED FOR TOXIC POLLUTANTS

TANNERY NUMBER	SUBCATEGORY	TANNERY PROCESSES: HAIR-PULP	HAIR-SAVE	WOOL PULL	CHROME TAN	VEGETABLE TAN	RETAN	COLOR	FATLIQUOR	FINISH	HIDE--MATERIALS	FINISHED PRODUCT	DEMOGRAPHIC INFORMATION: LOCATION	AGE IN YEARS (1979)	AVERAGE NUMBER OF EMPLOYEES
237	1	X			X		X	X	X	X	Cattle--green salted; brine cured	Shoe upper	Minnesota	104	400
57	1	X			X		X	X	X	X	Cattle--green salted; brine cured	Shoe upper, garment, patent	Maine	21	600
10	1	X		X	X		X	X	X	X	Cattle--fresh, sheepskin shearling	Shoe upper, miscellaneous	California	102	200
60	1	X			X			X	X	X	Cattle--green salted, brine cured	Upholstery, bags	Maryland	3	280
245	1	X			X		X	X	X	X	Cattle--green salted	Shoe upper, bags	New Hampshire	27	200
184	1	X	X		X		X	X	X	X	Cattle--brine cured	Shoe upper, bags	Tennessee	30	260
13	1	X			X		X	X	X	X	Cattle--fresh and brine cured	Shoe upper	California	122	375
248	2		X		X		X	X	X		Cattle--brine cured	Shoe upper, bags	New Hampshire	56	50
320	2		X		X		X	X	X	X	Cattle--green salted, brine cured	Shoe upper	New York	102	300
410	3		X		X*	X*	X	X	X	X	Cattle--brine cured	Sole, waistbelt	Virginia	52	250
47	3	X				X**		X	X	X	Steers, cows, calves--brine cured	Alum lace leather	Kentucky	112	32
397	3		X			X			X	X	Steers, cows, calves--brine cured	Sole, curried leather	Pennsylvania	+	220
415	3		X			X	X	X	X	X	Steer	Sole leather	West Virginia	+	+
50	4						X	X	X	X	Thru-the-blue sides	Shoe upper, bag, belt	Maine	42	400
97	4						X	X	X	X	Splits--tanned	Shoe upper	Massachusetts	17	35
247	4						X	X	X	X	Thru-the-blue cattle, pig, buffalo	Shoe upper, bag, belt, garment	New Hampshire	25	60
54	5				X		X	X	X	X	Pickled lambskins	Garment	Maine	18	93
197	5				X		X	X	X	X	Pickled sheepskins & lambskins	Garment and shoe lining	Massachusetts	83	130
75	5				X	X			X	X	Pickled cow bellies	Shoe lining, work gloves	Massachusetts	>25	55
444	6	X			X						Cattle--brine cured	Thru-the-blue tanned sides	Missouri	8	100
253	7				X	X		X	X		Wet salted shearlings	Garment	New Hampshire	77	135
500	7				X		X	X	X		Salted shearlings	Garment	California	110	250

*Chrome tan ∿ 30 percent, vegetable tan ∿ 70 percent.

**Alum tannage.

+Data not available

probably in natural tannins as well. Many tanners do not know the specific ingredients of the chemical formulations they are using; many suppliers do not know the ingredients or purposes of their products or their uses in tanneries. These observations are particularly true for chemicals used only in small quantities. Some suppliers sell a "service" to the tanneries, i.e., each product is prepared for a tanner to perform a specific function. Such ingredients are viewed in functional terms only and not as chemicals reacting in a predictable manner.

As in water use, the levels and types of pollutants discharged by a plant are a function of its specific manufacturing processes. Each subcategory is assessed below in terms of wastewater generation characteristics.

Subcategory One

The primary constituents of the soak and wash waste stream are BOD_5, COD, suspended solids, and dissolved solids. For a cattlehide tannery with this operation preceding hair pulping and chrome tanning, typical ranges for BOD_5 and suspended solids range from 7 to 22 and 8 to 43 kg per kkg of hide (lb/1,000 lb of hide), respectively. Because the incoming hides are generally either brine-cured or green-salted, the salt must be removed in preparation for unhairing. This removal results in relatively high total solids values, ranging from 143 to 267 kg per kkg of hide (lb/1,000 lb of hide).

The liming and unhairing process is one of the principal contributors to the plant effluent. Spent unhairing liquors contain very high concentrations of proteinaceous organic matter, dissolved and suspended inorganic solids, and sulfides (mostly in the dissolved form) in a highly alkaline solution. Most sulfides found in tannery wastewater comes from spent unhairing liquors, although some potentially significant amounts, depending upon the specific processes and formulations, carry over into spent tanning and retanning liquors. The BOD_5 content of the waste from this operation may range from 53 to 67 kg (lb) per 1,000 kg (lb) of cattlehide processed. Concurrently, the estimated total nitrogen levels range from 11 to 15 kg (lb) per 1,000 kg (lb) of raw material.[1]

In the bating of unhaired hides, lime reacts with ammonium sulfate to produce calcium sulfate, which enters the plant effluent. The total nitrogen content of the waste stream varies from 5 to 8 kg (lb) per 1,000 kg (lb) of hide, with ammonia constituting two-thirds.[1] The pickling step which follows generates relatively low levels of pollutants including BOD_5, suspended solids, and nitrogen.

The chrome tanning operation generates significant wastes because it is the major source of chromium in the total plant effluent; however, the organic content of the spent tanning solution, including BOD_5 and suspended solids, is generally low.

The wet finishing operations, which include retanning, coloring and fatliquoring, generate high-volume, low-strength wastewaters compared to the effluents from beamhouse and tanyard processes. The temperature of the retan, color, and fatliquor waste streams is high, typically exceeding 37.7 degrees C (100 degrees F).[1] Use of high temperatures in retanning ensures maximum chromium uptake, thereby reducing its discharge to the total waste stream.

As Subcategory One represents the largest portion of the leather tanning industry, considerable data were available for characterizing its wastewaters, particularly for classical parameters. Table 6 summarizes the classical parameters, including flow, which were employed to characterize the raw loads associated with this industry segment. The values for flow and selected waste constituents represent subcategory averages, flow values are shown in gallons per pound and values for waste constituents are shown in lb per 1,000 lbs (kg/kkg). Table 6A summarizes the toxic pollutants present in Subcategory One; constituents are characterized by pollutant type, times found, and concentration.

Subcategory Two

The principal difference between Subcategories One and Two is the method of removing hair from cattlehides. Although water use is greater for machine removal and washing of hair, the waste loads associated with the hair save process are substantially less than those for hair pulp operations. The proteinaceous hair does not dissolve totally in the unhairing solution for the hair save process. This results in a lower BOD_5 content in the waste stream, ranging from 17 to 58 kg (lb) per 1,000 kg (lb) of raw material. The total nitrogen and sulfide content also decrease correspondingly. The remaining tannery operations essentially are the same as Subcategory One, thereby contributing similar waste loads.

Tables 7 and 7A summarize the raw wastewater characteristics for Subcategory Two in terms of classical parameters and toxic pollutants. Flow and classical pollutants have been normalized based on production and are presented as subcategory averages.

Subcategory Three

The tanning of cattlehides by non-chrome methods distinguishes this segment from Subcategory Two. The most significant difference between the raw waste loads of the two subcategories occurs in the total chromium content. The use of non-chrome tanning agents reduces the average chromium level observed in Subcategory Three to approximately 27 percent of that characteristic of Subcategory Two. The small amount of chromium present in the effluent from non-chrome tanneries, compared to Subcategories one and two, generally originates in the retanning operations which may require chromium salts.

Table 6

Raw Waste Characteristics for Subcategory 1
Hair Pulp, Chrome Tan, Retan - Wet Finish

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	31	453	0.419 - 10.75	4.6
BOD5				
mg/l	16	205	213 - 4300	1620
lb/1000 lb	16	172	2.10 - 275	62.3
TSS				
mg/l	17	208	24.8 - 36,100	2410
lb/1000 lb	17	175	1.45 - 941	92.3
COD				
mg/l	12	174	182 - 27,200	4640
lb/1000 lb	12	148	6.01 - 612	178
Oil & Grease				
mg/l	14	75	15.4 - 10,000	401
lb/1000 lb	14	75	0.411 - 261	15.4
Total Cr.				
mg/l	16	178	3.05 - 345	76
lb/1000 lb	16	148	0.062 - 20.5	2.9
Sulfide				
mg/l	11	169	0.800 - 198	64
lb/1000 lb	11	139	0.021 - 9.94	2.47
TKN				
mg/l	10	58	90.0 - 626	328
lb/1000 lb	10	53	3.17 - 32.5	12.6
Ammonia				
mg/l	10	168	17.0 - 380	104
lb/1000 lb	10	138	0.417 - 20.6	3.98
Phenol				
mg/l	6	15	0.140 - 110	1.0
lb/1000 lb	6	15	0.007 - 2.87	0.038

TABLE 6A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

Toxic Pollutant	Subcategory 1: Hair Pulp, Chrome Tan, Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration [1]	Concentration Range [1]
Volatile Organics				
benzene	3	3	15	10-20
1,2-dichloroethane	3		ND*	
1,1,1-trichloroethane	3	1	Present	
1,1,2,2-tetrachloroethane	3	1	10	
chloroform	3	1	20	
dichloromethane	3	3	10	10
1,2-trans-dichloroethene	3	1	30	
trichloroethene	3	1	20	
tetrachloroethene	3	1	150	
toluene	3	3	275	150-400
1,1-dichloroethane	3	1	20	
bromodichloromethane	3		ND	
trichlorofuoromethane	3		ND	
ethylbenzene	3	2	88	88
1,1,2-trichloroethane	3	1	10	
chlorobenzene	3		ND	
Smi-Volatile Organics - Amines				
n-nitrosodiphenylamine	3		ND	
benzidine	3	1	27	
1,2-diphenylhydrazine	3		ND	
3,3'-dichlorobenzidine	3		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	3		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	3	1	255	
1,3-dichlorobenzene	3		ND	
1,4-dichlorobenzene	3	1	54	
1,2,4-trichlorobenzene	3		ND	
hexachlorobenzene	3		ND	
2-chloronaphthalene	3		ND	

* ND = Not detected

[1] concentrations in ug/l

TABLE 6A Cont'd

Toxic Pollutant	Subcategory 1: Hair Pulp, Chrome Tan, Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	3	3	3700	3000-4400
total phenol	3	3	9010	650-4200
2,4-dichlorophenol	3		ND	
2,4-dimethylphenol	3	1	Present	
2,4,6-trichlorophenol	3	2	3390	880-5900
pentachlorophenol	3		ND	
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	3	1	51	
dimethyl phthalate	3	1	118	
diethyl phthalate	3		ND	
di-n-butyl phthalate	3		ND	
butyl benzyl phthalate	3		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	3	1	425	
isophorone	3		ND	
fluorene	3		ND	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	3	1	16	
acenaphthene	3	1	32	
chrysene	3		ND	
fluoranthene	3		ND	
naphthalene	3	2	46	24-67
phenanthrene/anthracene	3	1	94	
pyrene	3		ND	
Pesticides & PCB's				
alpha and beta BHC	3		ND	
chlordane	3		ND	
Inorganics				
cyanide	2	2	40	20-60
chromium	3	3	79667	43000-18000
copper	3	3	173	50-380
lead	3	3	1667	1100-2400
nickel	3	3	40	20-60
zinc	3	3	427	200-580

Table 7

Raw Waste Characteristics for Subcategory 2
Hair Save, Chrome Tan, Retan - Wet Finish

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	12	254	0.600 - 41,294	5.5
BOD5				
mg/l	7	101	140 - 2790	983
lb/1000 lb	7	98	5.45 - 600	45.1
TSS				
mb/l	7	82	94.0 - 8,580	1930
lb/1000 lb	7	79	5.26 - 596	88.3
COD				
mg/l	5	30	704 - 5700	2610
lb/1000 lb	5	27	62.6 - 230	119.7
Oil & Grease				
mg/l	5	30	49.3 - 620	244
lb/1000 lb	5	27	2.90 - 44.6	11.2
Total Cr.				
mg/l	6	56	0.006 - 392	31
lb/1000 lb	6	53	0.001 - 6.87	1.4
Sulfide				
mg/l	6	70	0.030 - 300	20
lb/1000 lb	6	67	0.004 - 16.1	0.92
TKN				
mg/l	5	56	63.0 - 3650	137
lb/1000 lb	5	53	0.617 - 147	6.3
Ammonia				
mg/l	5	31	0.400 - 660	90
lb/1000 lb	5	28	0.012 - 38.9	4.15
Phenol				
mg/l	4	24	0.440 - 6.80	2.2
lb/1000 lb	4	21	0.016 - 0.238	0.1

TABLE 7A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

Toxic Pollutant	Subcategory 2: Hair Save, Chrome Tan, Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration [1]	Concentration Range [1]
Volatile Organics				
benzene	2	1	10	
1,2-dichloroethane	2		ND*	
1,1,1-trichloroethane	2	1	10	
1,1,2,2-tetrachloroethane	2		ND	
chloroform	2	2	26	10-41
dichloromethane	2		ND	
1,2-trans-dichloroethene	2		ND	
trichloroethene	2		ND	
tetrachloroethene	2	1	10	
toluene	2	2	80	10-150
1,1-dichloroethane	2		ND	
bromodichloromethane	2		ND	
trichlorofluoromethane	2		ND	
ethylbenzene	2	1	150	
1,1,2-trichloroethane	2		ND	
chlorobenzene	2	1	10	
Semi-Volatile Organics - Amines				
n-nitrosodiphenylamine	2		ND	
benzidine	2		ND	
1,2-diphenylhydrazine	2		ND	
3,3′-dichlorobenzidine	2		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	2		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	2		ND	
1,3-dichlorobenzene	2		ND	
1,4-dichlorobenzene	2		ND	
1,2,4-trichlorobenzene	2		ND	
hexachlorobenzene	2		ND	
2-chloronaphthalene	2		ND	

* ND = Not detected

[1] concentrations in ug/l

TABLE 7A Cont'd

Toxic Pollutant	Subcategory 2: Hair Save, Chrome Tan, Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	2	2	2876	252-5500
total phenol	2	2	1920	440-3400
2,4-dichlorophenol	2	1	114	
2,4-dimethylphenol	2		ND	
2,4,6-trichlorophenol	2	1	4800	
pentachlorophenol	2	1	6200	
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	2	1	32	
dimethyl phthalate	2		ND	
diethyl phthalate	2		ND	
di-n-butyl phthalate	2		ND	
butyl benzyl phthalate	2		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	2		ND	
isophorone	2		ND	
fluorene	2		ND	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	2		ND	
acenaphthene	2		ND	
chrysene	2		ND	
fluoranthene	2	1	2	
naphthalene	2	1	49	
phenanthrene/anthracene	2	1	56	
pyrene	2	1	1	
Pesticides & PCB's				
alpha and beta BHC	2		ND	
chlordane	2		ND	
Inorganics				
cyanide	2	2	35	20-50
chromium	2	2	90500	31000-150000
copper	2	2	56	55-57
lead	2	2	700	100-1300
nickel	2	2	22	5-40
zinc	2	2	315	240-400

Lesser variations occur for the classical parameters, such as BOD5 and suspended solids. Table 8 presents these values along with the waste loads for chromium and phenols; Table 8A summarizes the presence of other toxic pollutants and their respective levels for Subcategory Three tanneries.

Subcategory Four

The tanneries in this industry segment limit their operations to retanning and wet finishing hides or splits which have been unhaired and tanned. The absence of the beamhouse process results in lower organic and sulfide loadings for this subcategory. Since retanning may use chrome, however, the total chromium levels in the plant effluents are significant.

Tables 9 and 9A characterize the tannery wastewaters for classical and toxic pollutants.

Subcategory Five

Subcategory Five tanneries consist only of tanyard and retan-wet finish operations with no beamhouse. Since unhairing operations are absent from these tanneries, the raw waste loads, including BOD5, suspended solids and sulfide, are less than those for Subcategories One, Two, and Three. Tanyard operations increase classical pollutant levels beyond those typical for strictly retan-wet finish facilities. Tables 10 and 10A present the average values for classical and toxic pollutants in No Beamhouse tanneries.

Subcategory Six

Hair removal and chrome tanning of cattlehides are the basic operations of Subcategory Six tanneries. Relatively high organic loads, as well as the nitrogen and sulfide contents, reflect beamhouse operations; total chromium levels result from chrome tanning procedures. Average raw waste loads for the major parameters are presented in Table 11. Table 11A identifies the toxic pollutants and their respective concentrations.

Subcategory Seven

Tanneries in this subcategory tan and wet finish sheepskins with wool intact. Subprocessing operations eliminate the need for a beamhouse; however, the amount of foreign matter which must be removed from the wool creates higher organic waste loads than those of No Beamhouse tanneries. The absence of grease recovery during the degreasing step is responsible for the higher oil and grease loads. Chrome tanning is prevalent for shearling processing and results in significant levels of total chromium in the untreated wastewater.

Table 8

Raw Waste Characteristics for Subcategory 3
Hair Save, NonChrome Tan, Retan - Wet Finish

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	16	234	0.206 - 38.521	4.0
BOD5				
mg/l	10	48	1.00 - 7,770	1180
lb/1000 lb	10	48	0.03 - 203	39.2
TSS				
mg/l	10	55	28.0 - 8210	1680
lb/1000 lb	10	55	0.767 - 362	56.1
COD				
mg/l	7	40	1080 - 75000	5120
lb/1000 lb	7	40	28.6 - 2,220	170.9
Oil & Grease				
mb/l	8	32	2.00 - 1340	339
lb/1000 lb	8	32	0.016 - 40.5	11.3
Total Cr				
mg/l	7	30	0.250 - 111	11
lb/1000 lb	7	30	0.008 - 3.939	0.38
Sulfide				
mg/l	7	29	0.100 - 328	68
lb/1000 lb	7	29	0.004 - 11.6	2.26
TKN				
mg/l	6	21	130 - 1,200	202
lb/1000 lb	6	21	1.94 - 49.7	6.75
Ammonia				
mg/l	5	20	23 - 680	90
lb/1000 lb	5	20	0.433 - 10.5	3.0
Phenol				
mg.l	5	16	0.280 - 100	1.2
lb/1000 lb	5	16	0.004 - 0.786	0.04

TABLE 8A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

Toxic Pollutant	Subcategory 3: Hair Pulp, Nonchrome Tan, Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range [1]
Volatile Organics				
benzene	4	3	10	10-10
1,2-dichloroethane	4		ND*	
1,1,1-trichloroethane	4		ND	
1,1,2,2-tetrachloroethane	4	1	10	
chloroform	4	1	24	
dichloromethane	4	3	138	10-25
1,2-trans-dichloroethene	4		ND	
trichloroethene	4		ND	
tetrachloroethene	4	1	23	
toluene	4	4	12	10-15
1,1-dichloroethane	4		ND	
bromodichloromethane	4	1	10	
trichlorofluoromethane	4		ND	
ethylbenzene	4	3	58	10-120
1,1,2-trichloroethane	4		ND	
chlorobenzene	4		ND	
Semi-Volatile Organics - Amines				
n-nitrosodiphenylamine	4		ND	
benzidine	4		ND	
1,2-diphenylhydrazine	4		ND	
3,3′-dichlorobenzidine	4		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	4		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	4	3	126	49-204
1,3-dichlorobenzene	4		ND	
1,4-dichlorobenzene	4	3	20	19-20
1,2,4-trichlorobenzene	4		ND	
hexachlorobenzene	4		ND	
2-chloronaphthalene	4		ND	

* ND = Not detected

[1] concentrations in ug/l

TABLE 8A Cont'd

Toxic Pollutant	Subcategory 3: Hair Pulp, Nonchrome Tan, Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	4	4	9050	51-25000
total phenol	4	4	2435	280-5420
2,4-dichlorophenol	4		ND	
2,4-dimethylphenol	4		ND	
2,4,6-trichlorophenol	4	2	915	130-1700
pentachlorophenol	4	2	1455	10-2900
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	4		ND	
dimethyl phthalate	4		ND	
diethyl phthalate	4	1	Present	
di-n-butyl phthalate	4	1	Present	
butyl benzyl phthalate	4		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	4		ND	
isophorone	4		ND	
fluorene	4		ND	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	4		ND	
acenaphthene	4		ND	
chrysene	4		ND	
fluoranthene	4		ND	
naphthalene	4	3	32	6-59
phenanthrene/anthracene	4	1	8	
pyrene	4		ND	
Pesticides & PCB's				
alpha and beta BHC	4		ND	
chlordane	4		ND	
Inorganics				
cyanide	3	2	80	60-100
chromium	4	4	5132	430-10000
copper	4	4	380	100-740
lead	4	4	138	100-200
nickel	4	4	61	40-95
zinc	4	4	490	300-700

Table 9

Raw Waste Characteristics for Subcategory 4
Retan - Wet Finish

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	8	68	0.622 - 2.580	1.7
BOD5				
mg/l	3	30	201 - 1600	776
lb/1000 lb	3	30	1.90 - 24.2	11.0
TSS				
mg/l	3	28	96.0 - 7440	818
lb/1000 lb	3	28	0.908 - 82.8	11.6
COD				
mg/l	3	9	1200 - 4800	3120
lb/1000 lb	3	9	32.3 - 76.0	44.2
Oil & Grease				
mg/l	3	29	57.5 - 854	272
lb/1000 lb	3	29	0.544 - 12.4	3.85
Total Cr.				
mg/l	3	24	1.60 - 381	53
lb/1000 lb	3	24	0.045 - 5.50	0.75
Sulfide				
mg/l	3	7	0.160 - 2.40	1.1
lb/1000 lb	3	7	0.003 - 0.680	0.015
TKN				
mg/l	3	9	110 - 480	212
lb/1000 lb	3	9	1.87 - 7.60	3.0
Ammonia				
mg/l	3	9	58.0 - 160	109
lb/1000 lb	3	9	0.868 - 4.50	1.55
Phenol				
mg/l	3	8	0.233 - 17.0	3.9
lb/1000 lb	3	8	0.003 - 0.289	0.055

TABLE 9A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

Toxic Pollutant	Subcategory 4: Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration [1]	Concentration Range [1]
Volatile Organics				
benzene	3	2	10	
1,2-dichloroethane	3		ND*	
1,1,1-trichloroethane	3		ND	
1,1,2,2-tetrachloroethane	3		ND	
chloroform	3	2	10	10-10
dichloromethane	3	2	10	10-10
1,2-trans-dichloroethene	3		ND	
trichloroethene	3		ND	
tetrachloroethene	3		ND	
toluene	3	3	10	10-11
1,1-dichloroethane	3		ND	
bromodichloromethane	3		ND	
trichlorofluoromethane	3		ND	
ethylbenzene	3	3	80	10-150
1,1,2-trichloroethane	3		ND	
chlorobenzene	3		ND	
Semi-Volatile Organics - Amines				
n-nitrosodiphenylamine	3	1	247	
benzidine	3		ND	
1,2-diphenylhydrazine	3		ND	
3,3′-dichlorobenzidine	3		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	3		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	3		ND	
1,3-dichlorobenzene	3		ND	
1,4-dichlorobenzene	3		ND	
1,2,4-trichlorobenzene	3		ND	
hexachlorobenzene	3		ND	
2-chloronaphthalene	3		ND	

* ND = Not detected

[1] concentrations in ug/l

TABLE 9A Cont'd

Toxic Pollutant	Subcategory 4: Retan - Wet Finish			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	3	2	3200	3200
total phenol	3	3	3038	233-5280
2,4-dichlorophenol	3		ND	
2,4-dimethylphenol	3		ND	
2,4,6-trichlorophenol	3	2	573	573
pentachlorophenol	3		ND	
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	3		ND	
dimethyl phthalate	3		ND	
diethyl phthalate	3	1	Present	
di-n-butyl phthalate	3	1	Present	
butyl benzyl phthalate	3		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	3		ND	
isophorone	3		ND	
fluorene	3		ND	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	3		ND	
acenaphthene	3	1	Present	
chrysene	3		ND	
fluoranthene	3		ND	
naphthalene	3	1	Present	
phenanthrene/anthracene	3	2	120	106-133
pyrene	3		ND	
Pesticides & PCB's				
alpha and beta BHC	3		ND	
chlordane	3		ND	
Inorganics				
cyanide	2	1	30	
chromium	3	3	89000	16000-130000
copper	3	3	250	160-330
lead	3	3	1300	100-3500
nickel	3	3	45	6-100
zinc	3	3	198	150-280

Table 10

Raw Waste Characteristics for Subcategory 5
No Beamhouse

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	13	268	0.672 - 177	3.3
BOD5				
mg/l	10	127	20 - 19,800	1000
lb/1000 lb	10	127	3.57 - 924	27.6
TSS				
mg/l	10	124	124 - 37,400	632
lb/1000 lb	10	124	12.10 - 7,010	17.4
COD				
mg/l	7	64	140 - 37,900	1700
lb/1000 lb	7	64	12.3 - 29,200	46.8
Oil & Grease				
mg/l	7	32	85.2 - 1160	343
lb/1000 lb	7	32	1.26 - 894	9.45
Total Cr.				
mg/l	8	66	2.80 - 1900	68
lb/1000 lb	8	66	0.072 - 17.2	1.86
Sulfide				
mg/l	5	13	0.090 - 6.40	3.2
lb/1000 lb	5	13	0.001 - 0.267	0.089
TKN				
mg/l	4	12	22.0 - 160	168
lb/1000 lb	4	12	0.823 - 11.9	4.63
Ammonia				
mg/l	5	22	6.20 - 99.0	36
lb/1000 lb	5	22	0.060 - 5.02	1.00
Phenol				
mg/l	4	20	0.112 - 9.90	1.2
lb/1000 lb	4	20	0.003 - 0.705	0.034

TABLE 10A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

Toxic Pollutant	Subcategory 5: No Beamhouse			
	Number of Samples	Number of Times Detected	Mean Concentration [1]	Concentration Range [1]
Volatile Organics				
benzene	3	2	80	10-150
1,2-dichloroethane	3		ND *	
1,1,1-trichloroethane	3		ND	
1,1,2,2-tetrachloroethane	3		ND	
chloroform	3	3	10	2-18
dichloromethane	3	1	10	
1,2-trans-dichloroethene	3		ND	
trichloroethene	3	1	10	
tetrachloroethene	3	1	40	
toluene	3	2	80	10-150
1,1-dichloroethane	3		ND	
bromodichloromethane	3	1	10	
trichlorofluoromethane	3		ND	
ethylbenzene	3	2	80	10-150
1,1,2-trichloroethane	3		ND	
chlorobenzene	3		ND	
Semi-Volatile Organics - Amines				
n-nitrosodiphenylamine	3		ND	
benzidine	3		ND	
1,2-diphenylhydrazine	3		ND	
3,3'-dichlorobenzidine	3		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	3		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	3	1	36	
1,3-dichlorobenzene	3		ND	
1,4-dichlorobenzene	3	1	13	
1,2,4-trichlorobenzene	3		ND	
hexachlorobenzene	3		ND	
2-chloronaphthalene	3		ND	

[1] concentrations in ug/l

* ND = Not Detected

TABLE 10A Cont'd

Toxic Pollutant	Subcategory 5: No Beamhouse			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	3	1	6200	
total phenol	3	3	4630	390-9500
2,4-dichlorophenol	3		ND	
2,4-dimethylphenol	3		ND	
2,4,6-trichlorophenol	3	3	3270	2400-4200
pentachlorophenol	3	2	3550	3400-3700
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	3		ND	
dimethyl phthalate	3		ND	
diethyl phthalate	3		ND	
di-n-butyl phthalate	3		ND	
butyl benzyl phthalate	3		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	3		ND	
isophorone	3		ND	
fluorene	3		ND	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	3		ND	
acenaphthene	3		ND	
chrysene	3		ND	
fluoranthene	3		ND	
naphthalene	3	2	27	5-49
phenanthrene/anthracene	3	2	122	111-133
pyrene	3		ND	
Pesticides & PCB's				
alpha and beta BHC	3		ND	
chlordane	3		ND	
Inorganics				
cyanide	3		ND	
chromium	3	3	74000	16000-170000
copper	3	3	187	140-260
lead	3	3	787	60-1600
nickel	3	3	15	6-30
zinc	3	3	1045	96-2600

Table 11

Raw Waste Characteristics for Subcategory 6
Through - The - Blue

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	2	49	2.00 - 3.61	2.7
BOD5				
mg/l	2	8	1310 - 11,000	2460
lb/1000 lb	2	8	21.9 - 234	51.3
TSS				
mg/l	2	8	1,220 - 14,500	3870
lb/1000 lb	2	8	27.1 - 307	80.7
COD				
mg/l	1	5	10,500 - 32,900	6400
lb/1000 lb	1	5	223 - 669	133.4
Oil & Grease				
mg/l	2	9	67.0 - 6,170	556
lb/1000 lb	2	9	1.42 - 177	11.6
Total Cr.				
mg/l	1	4	233 - 397	104
lb/1000 lb	1	4	4.95 - 8.43	2.16
Sulfide				
mg/l	1	4	137 - 680	118
lb/1000 lb	1	4	2.91 - 14.4	2.46
TKN				
mg/l	1	5	960 - 1780	460
lb/1000 lb	1	5	20.4 - 37.8	9.6
Ammonia				
mg/l	1	4	382 - 613	120
lb/1000 lb	1	4	8.12 - 13.02	2.5
Phenol				
mg/l	1	1	9.60	1.5
lb/1000 lb	1	1	0.204	0.03*

*Estimate

TABLE 11A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

PRIORITY POLLUTANT	Subcategory 6: Through-The-Blue			
	Number of Samples	Number of Times Detected	Mean Concentration[1]	Concentration Range
Volatile Organics			*	
benzene	1		ND	
1,2-dichloroethane	1		ND	
1,1,1-trichloroethane	1	1	Present	
1,1,2,2-tetrachloroethane	1		ND	
chloroform	1	1	Present	
dichloromethane	1	1	Present	
1,2-trans-dichloroethene	1		ND	
trichloroethene	1		ND	
tetrachloroethene	1		ND	
toluene	1	1	Present	
1,1-dichloroethane	1		ND	
bromodichloromethane	1		ND	
trichlorofluoromethane	1		ND	
ethylbenzene	1	1	Present	
1,1,2-trichloroethane	1		ND	
chlorobenzene	1		ND	
Semi-Volatile Organics - Amines				
n-nitrosodiphenylamine	1		ND	
benzidine	1		ND	
1,2-diphenylhydrazine	1		ND	
3,3'-dichlorobenzidine	1		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	1		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	1	1	ND	
1,3-dichlorobenzene	1		Present	
1,4-dichlorobenzene	1	1	Present	
1,2,4-trichlorobenzene	1		ND	
hexachlorobenzene	1		ND	
2-chloronaphthalene	1		Present	

* ND = Not Detected

[1] concentrations in ug/l

TABLE 11A Cont'd

Toxic Pollutant	Subcategory 6: Through-The-Blue			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	1	1	Present	
total phenol	1	1	8480	
2,4-dichlorophenol	1		ND	
2,4-dimethylphenol	1	1	Present	
2,4,6-trichlorophenol	1	1	Present	
pentachlorophenol	1		ND	
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	1		ND	
dimethyl phthalate	1		ND	
diethyl phthalate	1		ND	
di-n-butyl phthalate	1		ND	
butyl benzyl phthalate	1		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	1		ND	
isophorone	1		ND	
fluorene	1	1	Present	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	1	1	Present	
acenaphthene	1		ND	
chrysene	1		ND	
fluoranthene	1		ND	
naphthalene	1	1	Present	
phenanthrene/anthracene	1	1	Present	
pyrene	1		ND	
Pesticides & PCB's				
alpha and beta BHC	1		ND	
chlordane	1		Present	
Inorganics				
cyanide	0		ND	
chromium	1	1	550000	
copper	1	1	100	
lead	1	1	28	
nickel	1	1	160	
zinc	1	1	980	

Table 12

Raw Waste Characteristics for Subcategory 7
Shearlings

Parameter	Number of Plants	Number of Data Points	Range of Individual Data Points	Geometric Mean
Gal/lb	4	100	2.31 - 22.1	13.9
BOD5				
mg/l	3	24	100 - 3,920	349
lb/1000 lb	3	24	6.90 - 445	40.5
TSS				
mg/l	3	25	118 - 7650	388
lb/1000 lb	3	25	13.4 - 869	45
COD				
mg/l	3	19	370 - 31,500	914
lb/1000 lb	3	19	22.6 - 3,580	106
Oil & Grease				
mg/l	3	12	56.0 - 1,210	144
lb/1000 lb	3	12	2.52 - 137	16.7
Total Cr.				
mg/l	3	16	0.020 - 140	12.9
lb/1000 lb	3	16	0.002 - 14.4	1.5
Sulfide				
mg/l	2	10	0.080 - 68.0	0.2
lb/1000 lb	2	10	0.008 - 0.903	0.08
TKN				
mg/l	2	7	39.0 - 750	53
lb/1000 lb	2	7	0.704 - 7.701	6.2
Ammonia				
mg/l	2	7	08.70 - 35.0	13
lb/1000 lb	2	7	0.146 - 3.59	1.54
Phenol				
mg/l	2	10	0.143 - 110	0.3
lb/1000 lb	2	10	0.002 - 11.3	0.03

TABLE 12A

TOXIC POLLUTANT CHARACTERISTICS OF RAW WASTEWATER

Toxic Pollutant	Subcategory 7: Shearlings			
	Number of Samples	Number of Times Detected	Mean Concentration [1]	Concentration Range
Volatile Organics				
benzene	2	2	8	5-10
1,2-dichloroethane	2		ND *	
1,1,1-trichloroethane	2		ND	
1,1,2,2-tetrachloroethane	2	1	18	
chloroform	2	2	16	12-20
dichloromethane	2	2	177	14-340
1,2-trans-dichloroethene	2		ND	
trichloroethene	2		ND	
tetrachloroethene	2		ND	
toluene	2	2	10	9-10
1,1-dichloroethane	2		ND	
bromodichloromethane	2		ND	
trichlorofluoromethane	2		ND	
ethylbenzene	2		ND	
1,1,2-trichloroethane	2		ND	
chlorobenzene	2		ND	
Semi-Volatile Organics - Amines				
n-nitrosodiphenylamine	2		ND	
benzidine	2		ND	
1,2-diphenylhydrazine	2		ND	
3,3′-dichlorobenzidine	2		ND	
Semi-Volatile Organics - Ethers				
bis(2-chloroisopropyl)ether	2		ND	
Semi-Volatile Organics - Chlorinated Hydrocarbons				
1,2-dichlorobenzene	2	1	61	
1,3-dichlorobenzene	2		ND	
1,4-dichlorobenzene	2	2	20	19-20
1,2,4-trichlorobenzene	2		ND	
hexachlorobenzene	2		ND	
2-chloronaphthalene	2		ND	

* ND = Not Detected

[1] concentrations in ug/l

TABLE 12A Cont'd

Toxic Pollutant	Subcategory 7: Shearling			
	Number of Samples	Number of Times Detected	Mean Concentration	Concentration Range
Semi-Volatile Organics - Phenols				
phenol	2	1	91	
total phenol	2	2	515	180-850
2,4-dichlorophenol	2		ND	
2,4-dimethylphenol	2		ND	
2,4,6-trichlorophenol	2		ND	
pentachlorophenol	2	1	400	
Semi-Volatile Organics - Phthalates				
bis(2-ethylhexyl)phthalate	2	1	93	
dimethyl phthalate	2		ND	
diethyl phthalate	2		ND	
di-n-butyl phthalate	2		ND	
butyl benzyl phthalate	2		ND	
Semi-Volatile Organics - Miscellaneous				
nitrobenzene	2		ND	
isophorone	2		ND	
fluorene	2		ND	
Semi-Volatile Organics - Polynuclear Aromatics				
acenaphthylene	2		ND	
acenaphthene	2		ND	
chrysene	2		ND	
fluoranthene	2		ND	
naphthalene	2	2	26	
phenanthrene/anthracene	2	1	36	
pyrene	2		ND	
Pesticides & PCB's				
alpha and beta BHC	2		ND	
chlordane	2		ND	
Inorganics				
cyanide	2	2	10	10-10
chromium	2	2	36500	2000-53000
copper	2	2	78	35-120
lead	2	2	75	70-80
nickel	2	2	24	20-27
zinc	2	2	345	190-500

Tables 12 and 12A summarize the classical and toxic pollutants found at shearling tanneries.

SUMMARY

The flow of wastewater per unit production has consistently decreased within the leather tanning industry since data was first collected and reported. For example, an industry study which served as guidance for the Refuse Act of 1899 Permit Program showed that average flow for a plant in the current Subcategory One (Hair Pulp/Chrome Tan/Retan-Wet Finish) was 73 litres/kg of hide (8.8 gallons/lb). The technical evaluation which served as the basis for the promulgated effluent limitations guidelines (March 1974) indicated that average wastewater flow for the same industry segment was 53 litres/kg (6.4 gallons/lb) of hide. This updated study of the industry reveals that the average wastewater flow for Subcategory One is 38 litres/kg (4.6 gallons/lb) of hide.

An assessment of wastewater data supplied by various tanneries indicates that flows well below the subcategory means are achievable for all subcategories. In support of this finding is the fact that individual plants in each subcategory already operate below the mean flows, as indicated by Table 13.

TABLE 13

SUMMARY OF SUBCATEGORY FLOWS

Subcategory	Total Number of Plants Reporting Flow	Average Flow litres/kg (gal./lb)	Total Number Operating Below Average Flow
1	31	38 (4.6)	16
2	12	46 (5.5)	6
3	16	33 (4.0)	8
4	8	14 (1.7)	4
5	14	28 (3.3)	7
6	2	23 (2.7)	1
7	3	116 (13.9)	2

Section VII presents a number of feasible water conservation techniques which reduce flow. Further flow reductions may be possible with the development of innovative conservation measures, spurred by increasing treatment costs.

To address the potential variations of raw waste loads with time of year, data available for specific years at each tannery were separated into winter and summer periods. The parameters considered for the

Table 14 COMPARISON OF WINTER/SUMMER RAW WASTE CHARACTERISTICS

Subcategory	FLOW		POLLUTANT PARAMETERS, kg/1000 kg (Same as LB/1000 LB) WINTER AVE./SUMMER AVE.				
	cu. m/Kg	gal/lb	BOD_5	TSS	O&G	TOT. CR.	SULFIDE
1	0.037/0.037	4.497/4.401	63.0/56.7	137.5/102.8	28.20/269.04	2.88/3.71	1.891/2.863
2	0.045/0.060	5.437/7.145	56.8/47.4	127.2/94.2	11.97/22.95	1.82/2.41	2.756/2.428
3	0.018/0.030	2.170/3.654	36.7/44.6	64.8/60.1	0.02/19.73	0.87/0.44	1.128/2.996
4	0.016/0.020	2.000/2.450	21.9/57.4	71.9/120	8.28/71.1	---/6.27	---/7.600
5	0.015/0.012	1.787/1.450	8.4/11.7	12.3/9.8	6.56/4.04	1.45/0.90	---/0.005
6	0.029/0.026	3.505/3.093	135.1/65.3	284.7/341.1	65.90/183.89	3.38/1.66	---/0.030
7	0.093/0.105	11.215/12.695	99.9/58.4	141.0/91.3	81.14/30.64	0.72/4.03	---/0.049

Table 15

Hourly Raw Waste Data for a Single Cattlehide Tannery (Subcategory 1)

Tannery No. 237 Data Taken 9/1-2/76

Time	Flow (mg)	BOD5 (ppm)	Suspended Solids (ppm)	Chromium Total (ppm)	TKN (ppm)	pH	Oil and Grease (ppm)
7 - 8 a.m.	.0592	6190	6300	116	1133	12.22	770
8 - 9 a.m.	.0523	1620	2260	36.8	333	9.48	170
9 - 10 a.m.	.0443	1320	1420	21.0	196	8.80	280
10 - 11 a.m.	.0581	1650	2080	20.2	324	9.50	160
11 - 12 noon	.0506	1370	2120	24.8	227	11.60	320
12 - 1 p.m.	.0460	1550	1920	14.5	249	11.81	230
1 - 2 p.m.	.0505	1080	760	17.2	222	9.44	270
2 - 3 p.m.	.0526	1660	1740	13.0	204	10.36	350
3 - 4 p.m.	.0347	1030	260	16.5	151	7.09	130
4 - 5 p.m.	.0337	644	180	76.5	49	7.25	160
5 - 6 p.m.	.0347	748	620	26.5	67	6.57	230
6 - 7 p.m.	.0250	862	240	81.0	58	6.43	266
7 - 8 p.m.	.0303	662	60	34.1	37	6.89	58
8 - 9 p.m.	.0201	954	1580	76.2	125	11.83	214
9 - 10 p.m.	.0241	1420	1220	236	141	6.16	1200
10 - 11 p.m.	.0221	430	240	81.5	39	6.83	192
11 - 12 Midnight	.0224	439	480	122	60	6.60	110
12 - 1 a.m.	.0243	100	60	19.3	20	7.70	34
1 - 2 a.m.	.0230	4140	7020	65.5	787	12.52	1900
2 - 3 a.m.	.0248	2210	2720	201	232	9.56	1100
3 - 4 a.m.	.0352	1690	1460	17.3	187	10.90	326
4 - 5 a.m.	.0439	2370	4400	53.2	520	12.30	635
5 - 6 a.m.	.0448	2600	6040	51.5	1378	12.34	1380
6 - 7 a.m.	.0648	3950	3820	113	920	11.95	1200

seven subcategories include flow, BOD_5, suspended solids, oil and grease, total chromium, and sulfide. Data for the untreated wastewaters represent combined streams after screening or equalization, if such treatment was in place. Where appropriate flow or production information was not supplied, it was computer assigned, based on best available information and trends for the individual plant, to generate loadings per unit production. Table 14 shows the comparison of winter and summer waste characteristics for the individual subcategories. Table 15 shows the changes in flow and waste characteristics that occur at a single tannery during one day.

Of the 129 toxic pollutants of interest, Table 16 indicates that 37 have been identified in the raw wastewaters of the leather tanning and finishing industry. Table 16 shows the number of different toxic pollutants that were detected in the raw wastewater of the plants sampled in each subcategory.

TABLE 16

NUMBER OF DIFFERENT TOXIC POLLUTANTS
DETECTED PER SUBCATEGORY

Industry	Subcategory						
Total	1	2	3	4	5	6	7
46	33	23	24	20	22	22	19

From Table 16, it is apparent that the number of different toxic pollutants detected is significantly higher for those plants which have beamhouse operations and employ the hair pulp process. The number of constituents present in the wastewaters of the remaining subcategories fall within a very small range, although the specific pollutants vary with the type of manufacturing process employed.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

WASTEWATER PARAMETERS OF SIGNIFICANCE

A thorough analysis of the literature, industry data and sampling data obtained from this study and EPA permit data demonstrates that the following wastewater parameters are of significance in the leather tanning and finishing industry:

Conventional and Nonconventional Pollutant Parameters

- Biochemical Oxygen Demand (5-day, 20 degrees C., BOD_5)
- Chemical Oxygen Demand
- Oil and Grease
- Sulfide
- Total Suspended Solids (TSS)
- Nitrogen Content (Ammonia Nitrogen and Total Kjeldahl Nitrogen)
- pH and Alkalinity
- Total Dissolved Solids
- Chlorides
- Total Volatile Solids
- Nitrates and Nitrites
- Fecal Coliforms

Toxic Pollutants

- Organics
  - Volatile
  - Semi-Volatile
    - Basic/Neutral Fraction
    - Acidic Fraction
- Inorganics
  - Cyanide
  - Metals

CONVENTIONAL AND NONCONVENTIONAL POLLUTANT PARAMETERS

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is the quantity of oxygen required for the biological and chemical oxidation of waterborn substances under ambient or test conditions. Material which may contribute to the BOD include: carbonaceous organic materials usable as a food source by aerobic organisms; oxidizable nitrogen derived from nitrites, ammonia, and organic nitrogen compounds which serve as food for specific bacteria; and certain chemically oxidizable materials such as ferrous iron, sulfides, sulfite, etc., which will react with dissolved oxygen

or which are metabolized by bacteria. In most leather tannery wastewaters, the BOD derives principally from organic materials, such as dissolved or "pulped" hair and other extraneous hide substances, and from ammonia which is derived from residual bating chemicals and from hydrolytic deamination of proteinaceous hair and hide substance.

The BOD of a waste adversely affects the dissolved oxygen resources of a body of water by reducing the oxygen available to fish, plant life, and other aquatic species. It is possible to reach conditions which totally exhaust the dissolved oxygen in the water, resulting in anaerobic conditions and the production of undesirable gases such as hydrogen sulfide and methane. The reduction of dissolved oxygen can be detrimental to fish populations, fish growth rate, and organisms used as fish food. A total lack of oxygen due to excessive BOD can result in the death of all aerobic aquatic inhabitants in the affected area.

Water with a high BOD indicates the presence of decomposing organic matter and associated increased bacterial concentrations that degrade its quality and potential uses. High BOD increases algal concentrations and blooms; these result from decaying organic matter and form the basis of algal populations.

The BOD_5 (5-day BOD) test is used widely to estimate the oxygen requirements of discharged domestic and industrial wastes. Complete biochemical oxidation of a given waste may require a period of incubation too long for practical analytical test purposes. For this reason, the 5-day period has been accepted as standard, and the test results have been designated as BOD_5. Specific chemical test methods are not readily available for measuring the quantity of many degradable substances and their reaction products. In such cases, testing relies on the collective parameter, BOD_5. This procedure measures the weight of dissolved oxygen utilized by microorganisms as they oxidize or transform the gross mixture of chemical compounds in the wastewater. The biochemical reactions involved in the oxidation of carbon compounds are related to the period of incubation. The 5-day BOD normally measures only 60 to 80 percent of the carbonaceous biochemical oxygen demand of the sample, and for many purposes this is a reasonable parameter. Additionally, it can be used to estimate the gross quantity of oxidizable organic matter.

Some treated wastewaters result from treatment systems designed to remove ammonia through the nitrification process. In some cases, the nitrifying bacteria present can exert an additional non-carbonaceous, nitrogenous oxygen demand (NOD), within the prescribed 5-day incubation period. In these instances, special inhibitors are added to standard dilution waters to ensure the measurement only of carbonaceous organic matter. Ultimate BOD, which is measured after a 20-day incubation period, tests for aggregate measurement of both carbonaceous and nitrogenous oxygen demand when nitrification inhibitors are not added to standard dilution waters. Ultimate BOD

can also be useful in estimating the total dissolved oxygen demand of wastewaters discharged to very long receiving streams with long residence periods.

Chemical Oxygen Demand (COD)

Chemical oxygen demand is a purely chemical oxidation test devised as an alternate method of estimating the total oxygen demand of a wastewater. Since the method relies on the oxidation-reduction system of chemical analyses, rather than on biological factors, it is more precise, accurate, and rapid than the BOD test. The COD test estimates the total oxygen demand (ultimate) required to oxidize the compounds in a wastewater. It is based on the fact that organic compounds, with a few exceptions, can be oxidized by strong chemical oxidizing agents under acid conditions with the assistance of certain inorganic catalysts.

The COD test measures those pollutants resistant to biological oxidation in addition to the ones measured by the BOD_5 test. COD is therefore a more inclusive measure of oxygen demand than is BOD_5 and results in higher oxygen demand values than the BOD_5 test.

The compounds which are more resistant to biological oxidation are becoming of greater and greater concern, not only becuase of their slow but continuing oxygen demand on the resources of the receiving water, but also because of their potential health effects on aquatic and human life. Many of these compounds have been found to have carcinogenic, mutagenic, and similar adverse effects, either singly or in combination. Concern about these compounds has increased as a result of demonstrations that their long life in receiving waters--the result of a slow biochemical oxidation rate--allows them to contaminate downstream water intakes. The commonly used systems of water purification are not effective in removing these types of materials, and disinfection (such as chlorination) may convert them into even more hazardous materials.

Tannery wastewaters contribute to high COD concentrations and include such constituents as extraneous hide substance, complex organic and inorganic process chemicals, dyes, and vegetable tannins.

Oil and Grease

Because of the nature of the material processed, oil and grease occur often in the leather tanning wastewater streams. They result from the degreasing process used in some tanneries and from the oils used directly in the leather processing, especially fatliquoring. Most of these oil and grease materials are animal or vegetable based and therefore amenable to removal through biological treatment. Some tanneries us a very small amount of mineral based oil; this also enters the waste stream, although presumably in very small quantities. It is a more refractory material than are the other kinds of oil and

therefore must be removed primarily by physical-chemical waste treatment processes. These compounds can settle or float and may exist as solids or liquids. Even in small quantities oil and grease cause troublesome taste and odor problems. They produce scum lines on water treatment basin walls and other containers and adversely affect fish and water fowl. Oil emulsions may adhere to the gills of fish, causing suffocation, and may taint the flesh of fish that were exposed to waste oil. Oil deposits in the bottom sediments of water can serve to inhibit normal benthic growth. Oil and grease exhibit an oxygen demand.

Oil and grease levels which are toxic to aquatic organisms vary greatly, depending on the type of pollutant and the species susceptibility. In addition, the presence of oil in water can increase the toxicity of other substances discharged into the receiving bodies of water.

Sulfide

A significant portion of alkaline sulfides contained in tannery wastewater converts to hydrogen sulfide at a pH below 8.0, resulting in the release of this gas to the atmosphere. This gas is odorous, and can damage property through paint discoloration. In sewers, hydrogen sulfide can oxidize to sulfuric acid, causing "crown" corrosion and corrosion of equipment in POTW. This gas can also be lethal to operation and maintenance personnel in sewers, and at POTW headworks, primary treatment, and sludge dewatering facilities. This is particularly significant as a hazard in sewer maintenance. Careless mixing of acid and sulfide containing alkaline streams can also be catastrophic within both tanneries and sewers. Sulfide compounds are used extensively in the beamhouse for the unhairing process, and thus are found in tannery effluent.

Sulfides impose immediate and very high dissolved oxygen demand in activated sludge aeration basins, which can result in odor problems during summer months when there are concurrent periods of very rapid bacterial oxygen uptake.

Total Suspended Solids (TSS)

Suspended solids include both organic and inorganic materials. The inorganic compounds include sand, silt, clay, and toxic metals. The organic fraction includes such materials as grease, oil, animal and vegetable waste products, and adsorbed toxic organic pollutants. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. Solids may be suspended in water for a time and then settle to the bed of the stream or lake. They may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension they increase the turbidity of the water, reduce light penetration, and impair the photosynthetic activity of aquatic plants.

Aside from any toxic effect attributable to substances leached out by water, suspended solids may kill fish and shellfish by causing abrasive injuries, by clogging gills and respiratory passages screening out light, and by promoting and maintaining the development of noxious conditions through oxygen depletion. Suspended solids also reduce the recreational value of the water.

Some of the solids generated within a tannery, such as hair or scraps, are removed readily by fine screening; other solids settle readily in clarifiers. When not removed, these solids can foul or plug pipes, pumps, and other mechanical equipment.

Nitrogen Content (Ammonia Nitrogen and Total Kjeldahl Nitrogen)

Ammonia (NH_3). Ammonia in surface and ground waters results from decomposing nitrogenous organic matter. It is one of the constituents of the complex nitrogen cycle. Ammonia exists in its non-ionized form only at higher pH levels and is most toxic in this state. The lower the pH, the more ionized ammonia is formed, and the more its toxicity decreases. Ammonia can exist in several chemical combinations including ammonium chloride and other salts. Ionized ammonia is generated by spent bating liquors in a tannery.

Evidence exists that ammonia exerts a toxic effect on all aquatic life depending upon the pH, dissolved oxygen level, and the total ammonia concentration in the water.

Total Kjeldahl Nitrogen (TKN). Total Kjeldahl nitrogen is ammonia nitrogen plus organic nitrogen in wastewater. Organic nitrogen is derived primarily from dissolved or pulped proteinaceous hair removed from hides. Hydrolysis of this organic nitrogen during biological treatment yields another significant source of ammonia. Hence, TKN measures the major nitrogen impact upon a waste treatment plant or stream and is an important measure of the potential environmental impact of tannery wastewater.

pH and Alkalinity

pH. Although not a specific pollutant, pH is related to the acidity or alkalinity of a wastewater stream. It is not a linear or direct measure of either; however, it may properly be used to control both excess acidity and excess alkalinity in water. The term pH describes the hydrogen ion--hydroxyl ion balance in water. Technically, pH is the hydrogen ion concentration or activity present in a given solution. pH numbers are the negative logarithm of the hydrogen ion concentration. A pH of 7 generally indicates neutrality or a balance between free hydrogen and free hydroxyl ions. Solutions with a pH above 7 indicate that the solution is alkaline, while a pH below 7 indicates that the solution is acidic.

Knowledge of the pH of water or wastewater aids in determining measures necessary for corrosion control, pollution control, and disinfection. To protect POTW from corrosion, pH levels of wastewaters entering the sewerage system must remain above 5. Waters with a pH below 6.0 corrode waterworks structures, distribution lines, and household plumbing fixtures. This corrosion can add such constituents to drinking water as iron, copper, zinc, cadmium, and lead. Low pH waters not only tend to dissolve metals from structures and fixtures but also tend to redissolve or leach metals from sludges and bottom sediments. The hydrogen ion concentration also can affect the taste of water; at a low pH, water tastes "sour."

Extremes of pH or rapid pH changes can stress or kill aquatic life. Even moderate changes from "acceptable" pH limits can harm some species. Changes in water pH increase the relative toxicity* to aquatic life of many materials. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The toxicity of ammonia similarly is a function of pH. The bactericidal effect of chlorine in most cases lessens as the pH increases, and it is economically advantageous to keep the pH close to 7.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Problems of hydrogen sulfide gas evolution and poor trivalent chromium removal can be magnified by wastewater pH values below 6.0. On the other hand, unusually high pH (for instance 11.0) can cause significant loss of active biomass in biological treatment systems, especially activated sludge.

Alkalinity. Alkalinity is defined as the ability of water to neutralize hydrogen ions. It is usually expressed as the calcium carbonate equivalent of the hydrogen ions neutralized.

Alkalinity commonly results from the presence of carbonates, bicarbonates, hydroxides, and to a lesser extent, borates, silicates, phosphates and organic substances. Because of the nature of the chemicals causing alkalinity and the buffering capacity of carbon dioxide in water, very high pH values seldom appear in natural waters.

Excess alkalinity as exhibited in a high pH value may make water corrosive to certain metals, detrimental to most natural organic materials, and toxic to living organisms.

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*The term toxic or toxicity is used herein in the normal scientific sense of the word, not the legal.

Leather tanning and finishing plants which include beamhouse (unhairing) operations will invariably have excess alkalinity due to the presence of large quantities of lime. This alkalinity provides buffering capacity to prevent unacceptably low pH, and enhances precipitation of many heavy metals, such as trivalent chromium, found in tannery and other industrial wastewaters.

Total Dissolved Solids (TDS)

Tannery wastes are high in dissolved solids, the majority of which are sodium chloride and calcium sulfate. Sodium chloride comes principally from desalting from the raw hides by washing and from salt added in the pickling operation. Calcium sulfate can come from several tannery operations, but principally comes from the reaction of residual ammonium sulfate and sulfuric acid with lime used in the unhairing process. Dissolved solids are particularly important in considering recycle systems; they also have potential impact on stream life and water treatment processes.

Chlorides (Cl)

The preponderant fraction of tannery dissolved solids is chlorides. Used in conjuction with total dissolved solids, this parameter indicates percentages of other dissolved solids. Chloride content is important for water reuse considerations.

Total Volatile Solids (TVS)

Total volatile solids (TVS) is an approximate measure of the organic fraction of wastewater. It is primarily useful in analyzing the potential for biological treatment of the waste. A high percentage of volatile solids to total solids in the waste indicates that properly designed conventional treatment processes may be effective in pollution control.

Nitrates (NO3) and Nitrites (NO2)

Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria.

EPA considers nitrates to be among the objectionable components of mineralized waters. Excess nitrates irritates the gastrointestinal tract, causing diarrhea and diuresis. Methemoglobinemia, a condition characterized by dyanosis and resulting in infant and animal deaths, can be caused by high nitrate concentrations in drinking waters. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit.

Fecal Coliforms

The presence in water of fecal coliforms, which originate from the intestinal tract of warm-blooded animals, indicates the potential presence of pathogenic bacteria and viruses.

The presence of fecal coliforms in water suggests fecal pollution, i.e., recent and possibly dangerous fecal contamination. When the fecal coliform count exceeds 2,000 per 100 ml there is a high correlation with increased numbers of both pathogenic viruses and bacteria.

Many microorganisms, pathogenic to humans and animals, may be carried in surface water, particularly that derived from effluent sources from municipal and industrial wastes. The diseases associated with bacteria include bacillary and amoebic dysentery, *Salmonella* gastroenteritis, typhoid and paratyphoid fevers, leptospirosis, chlorea, vibriosis and infectious hepatitis.

Fecal contamination is present in leather tanning wastewater because many hides are received with animal manure and dirt embedded in them. Secondary biological treatment can destroy large quantities of these organisms, but disinfection may be necessary where receiving streams are classified for use as drinking water supplies.

TOXIC POLLUTANTS

The 129 toxic pollutants are divided into three major groups: organics, pesticides and PCB's, and inorganics. Toxic pollutants detected in leather tannery wastes are discussed on the basis of these three groups.

Table 17 presents information on the molecular structure, number of plants where identified, concentration range in the wastewater, and, wherever possible, a brief description of leather tannery uses of these compounds.

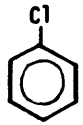
Organic Toxic Pollutants

A significant number of the organic toxic pollutants appeared in tannery wastewaters at concentrations of 1 ppb or higher. Organics are classified by the physical-chemical properties which permit specific analytic schemes for the analysis of these materials. The organic toxic pollutants include compounds in a volatile fraction, a basic or neutral fraction, and an acidic fraction.

Volatile Fraction. Table 17 summarizes the volatile organic toxic pollutants identified in tannery wastewaters. Frequency of identification and concentration ranges for these compounds also are summarized along with information on common usages. Eighteen volatile organic pollutants were found at least once in the sampled effluents.

Table 17
Characteristics of Pollutants Detected During the Sampling Program

Volatile Organics

Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations *	Uses	Treatability
Benzene		9 5 3	Raw waste-water Primary Secondary	trace - > 100 trace - 10 trace	General Solvent manufacture of dyes	Moderate Carbon adsorption. Highly amenable to biochemical oxidation in well-operated activated sludge treatment systems. Steam stripping accompanied by biochemical oxidation or carbon adsorption recommended.
Bromodichloromethane	$CHBrCl_2$	2	Raw waste-water	trace		Steam stripping, moderate carbon adsorption.
Chlorobenzene		2 3 1	Raw waste-water Primary Secondary	trace - 28 trace - 26 trace	Solvent Chemical intermediate for manufacture of phenol, aniline	Moderately biodegradable Moderate Carbon adsorption Steam stripping, oil-water separation, and/or filtration recommended
Chloroethane	C_2H_5Cl	1	Primary	N.G.	refrigerant, solvent	Steam stipping, probably possesses intermediate level of biodegradability.

* - concentrations expressed in ug/l
N.G. - only presence detected, not concentration
trace - compounds detected in only trace amounts, generally less than 10 ug/l

Table 17 (Contd.)

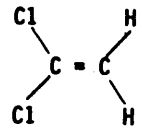
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
1,2-Dichloroethane	$CH_2Cl - CH_2Cl$	1 1	Raw waste-water Primary	28 48	Solvent for fats, waxes; intermediate in manufacture of organic chemicals	Steam stripping, moderately biodegradable, moderate activated carbon adsorption
1,1-Dichloroethene		1	Raw waste-water	20	Internal plasticizer in fibers and plastics manufacturing	Steam stripping
Dichloromethane (Methylene Chloride)	CH_2Cl_2	10 4 3	Raw waste-water Primary Secondary	trace - 340 17 - 220 trace	Common solvent - found in insecticides; degreasing and cleaning liquid	Steam stripping very poor carbon adsorption
Ethylbenzene		11 7 5	Raw waste-water Primary Secondary	trace - 120 13 - >100 trace - 12	Manufacture of styrene	Steam stripping, oil-water separation, biochemical oxidation, and/or carbon adsorption
1,1,2,2 - Tetrachloroethane	$CHCl_2 - CHCl_2$	2 1 1	Raw waste-water Primary Secondary	trace - 18 trace trace	Solvent for fats, oils, insecticide formulations	Steam stripping, not biochemically oxidizable, moderate carbon adsorption, steam stripping, carbon adsorption and filtration recommended

Table 17 (Contd.)

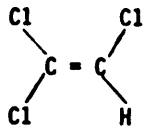
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
1,1,1-Trichloroethane	$CCl_3 - CH_3$	4 2	Raw waste-water Primary	trace - 10 11 - 11	Solvent and degreasing agent; solvent carrier for water and stain repellant compounds; strong solvent action on organics, especially oils, greases, waxes, fats, and tars; can be blended with other solvents to reduce their flammabilty or to provide added solvent properties	Steam stripping, not biodegradable, moderately adsorbed on activated carbon
1,1,2-Trichloroethane (Vinyl Trichloride)	$CHCl_2 - CH_2Cl$	1	Raw waste-water	trace	General solvent for fats, waxes	Steam stripping, followed by activated carbon adsorption recommended
Trichloroethene (Trichloroethylene)		4 4	Raw waste-water Primary	trace - 20 trace - >100	Solvent in vapor degreasing applications; solvent for fats, oils, waxes, resins; drycleaning	Steam stripping; not biochemically oxidizable; poor carbon adsorption
Trichlorofluoromethane	CCl_3F	1	Primary	trace	Is a Freon® used in aerosals, as a refrigerant, in air conditioning	Steam stripping; carbon adsorption properties moderately good
Trichloromethane (chloroform)	$CHCl_3$	4 3 4	Raw waste-water Primary Secondary	trace - 41 15 - 52 trace	General solvent; refrigerant; cleaning agent; solvent for fats, oils, rubber	Steam stripping

Table 17 (Contd.)

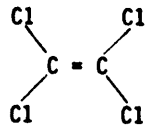
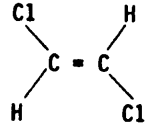
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
1,1,2,2-Tetrachloroethene (Tetrachloroethylene)		4 4 1	Raw wastewater Primary Secondary	23 - 100 11 - 31 N.G.	General solvent degreasing	Steam stripping, oil-water separation and filtration provide fair means of removal; moderate carbon adsorption expected; Not expected to be biochemically oxidizable to any worthwhile extent
Tetrachloromethane (Carbon Tetrachloride)	CCl_4	2 2 1	Raw waste water Primary Secondary	trace - 73 70 - 70 21	Solvent, chemical intermediate, solvent for oils fats, waxes, insecticide	Steam stripping, moderate carbon adsorption filtration
Toluene (Methylbenzene)		13 6 3	Raw waste water Primary Secondary	trace - >>100 15 - 100 trace - 50	General solvent	Steam stripping, oil-water separation filtration excellent biochemical oxidation
trans-1,2-Dichloroethene		3 2 1	Raw wastewater Primary Secondary	trace - 30 18-20 N.G.	Solvent for fats, phenol, general organic solvent, refrigerant, intermediate in organic chemical manufacturing	Steam stripping

Table 17 (Contd.)

Base/Neutral Organics

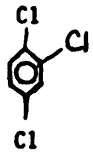
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
1,3-Dichlorobenzene		2	Raw waste-water	12		Good carbon adsorption, moderately amenable to steam stripping, oil-water separation, and filtration
1,2-Dichlorobenzene		6 7 6	Raw waste-water Primary	49 - 255 14 - 215 trace - 69	Solvent for waxes, gums; de-greasing agent for leather; in-secticide intermediate in manufacture of dyes - masks odors of decaying flesh	Moderately amenable to steam stripping, oil-water separation, and filtration good carbon adsorption
1,4-Dichlorobenzene		9 5 5	Raw waste-water Primary Secondary	13 - 60 2.4 - 99 trace - 69	Manufacture of pesticides; insecticidal fumigant con-trolling para-sites; and moth-proofing wool on sheepskins	Oil-water separation, filtration, biochemical oxidation and/or carbon adsorption
1,2,4-Trichlorobenzene		1	Raw waste water	1.8	dye carrier, heat transfer fluid, intermedi-ate to herbicide manufacture, insecticide against termites	Oil-water separation, filtration, and carbon adsorption good biodegradability

Table 17 (Contd.)

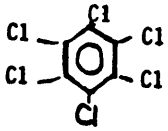
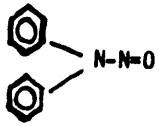
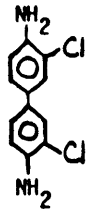
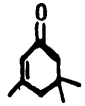
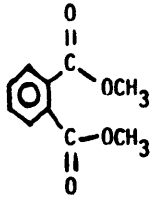
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
1,2,-Diphenylhydrazine (hydrazobenzene)		1 1	Primary Secondary	18 1.8	Special reagent in chemical laboratory operation	Filtration followed by carbon adsorption
Nitrobenzene		1 1	Raw waste-water Primary	425 29	Solvent, dye preparation used extensively for preparation of dye intermediates	Not biochemically oxidizable, but readily adsorbed by activated carbon. Filtration, followed by carbon adsorption recommended
Benzidine (Biphenyl-4,4-diamino)		1 2	Raw waste-water Secondary	27 1.6-17	Dye industry	Good adsorption and biochemical oxidation under alkaline conditions. Filtration recommended as primary step.
Hexachlorobenzene (Perchlorobenzene)		1	Secondary	0.5	Fungicide in dye manufacture	Oil-water separation, followed by clay filtration and activated carbon
n-Nitrosodiphenylamine (Nitrous diphenylamide)		1 2 1	Raw waste-water Primary Secondary	247 14-36 9.5	Manufacture of vulcanized rubber, dye stuffs, insectides, fungicides, solvents	Highly conducive to filtration and carbon adsorption

Table 17 (Contd.)

Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
3,3-Dichlorobenzidine (Biphenyl - 3,3-dichloro 4,4-diamino)		1	Secondary	1.8	Intermediate in manufacture of azo dyes	Excellent oil-water separation, filtration and carbon adsorption; biodegrades at slower rate than benzidine because of halogen substitution
Isophorone (3,5,5-trimethyl - 2-cyclohexen-1-one)		2	Secondary	1.5 - 5.4	Solvent or co-solvent for finishes, lacquers, polyvinyl & cellulose resins, pesticides, herbicides, fats, oils, gums	Oil-water separation, filtration and carbon adsorption
Dimethyl phthalate (1,2-Benzenedicarboxylic acid, dimethyl ester, phthalic acid dimethyl ester)		1 2	Raw wastewater Primary	118 77	lubricant, insect repellant, plasticizer	filtration, biochemical oxidation and carbon adsorption

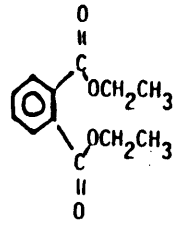
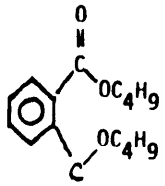
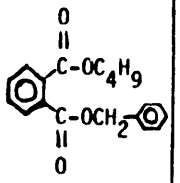
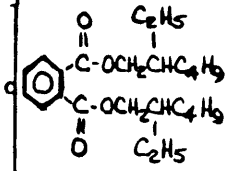
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
Diethylphthalate		2 2 1	Raw waste-water Primary Secondary	N.G. N.G. N.G.	lubricant pesticide plasticizer	Filtration, biochemical oxidation and carbon adsorption recommended
Di-n - butyl phthalate		2 2 2	Raw waste-water Primary Secondary	N.G 2.8 N.G.	insect repellant for impregnation in clothing - used in lubricants as plasticizer	moderate biochemical oxidizability - very good carbon adsorption, filtration recommended as preliminary step
Butyl benzyl phthalate		2	Primary	1.6 - 3.9	pesticides, lubricant, plasticizer	highly adsorbed by activated carbon, oil-water separation, followed by filtration, biochemical oxidation and carbon adsorption recommended; expected to be moderately biodegradable
BIS-(2-ethylhexyl) phthalate (1,2-Benzenedicarboxylic acid bis(2-ethylhexyl) ester)		3 6 7	Raw waste-water Primary Secondary	32 - 93 5 - 29 20 - 34	synthetic lubricants, pesticides, plasticizers	Outstanding carbon adsorption characteristics, poor biochemical oxidizability, - oil-water separation, followed by filtration and adsorption recommended

Table 17 (Contd.)
Base/Neutral Organics
(Polynuclear Aromatics)

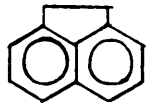
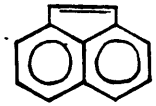
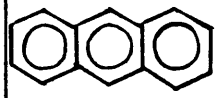
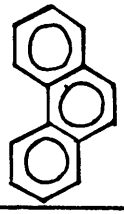
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
Acenaphthene (Naphthylene-ethylene)		2	Raw waste-water	32	Dye intermediate, Insecticide, fungicide	Readily treated by oil-water separation, followed by filtration and, if necessary, carbon adsorption
Acenaphthylene		2	Raw waste water	16	Dyes, plastics, insecticide and fungicide manufacturing.	Oil-water separation, filtration, and if necessary, carbon adsorption.
Anthracene (Paranaphthalene Anthracin green oil)		9 4 7	Raw waste-water Primary Secondary	6.6 - 133 trace - 9.1 trace - 7.3	Manufacture of anthraquinone and alizarin dyes	Oil-water separation, filtration, and carbon adsorption if necessary
Phenanthrene		9 4 7	Raw waste-water Primary Secondary	6.6 - 133 trace - 9.1 trace - 7.3	Dyes	Oil-water separation, filtration, and possibly activated carbon adsorption.

Table 17 (Contd.)

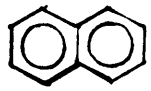
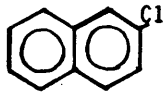
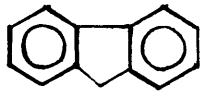
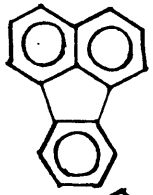
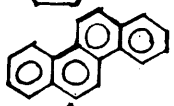
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
Napthalene		14 7 6	Raw waste-water Primary Secondary	5.2 - 757 11 - 158 2.3 - 65	Intermediate in production of dyes, solvents, insecticides; moth repellant	Strong candidate for removal by biochemical oxidation and/or carbon adsorption. Recommend oil-water separation, filtration then oxidation or adsorption.
2-Chloronaphthalene		1 1	KRaw waste-water Primary	NG 56	Manufacture of phenol, aniline heat transfer medium, solvent for paints, used in dying operations.	Oil-water separation and filtration, good carbon adsorption, moderately biodegradable.
Fluorene (2,3-Benzindene, 2,2-Methylene biphenyl, Diphenylene methane)		1 1	Raw waste-water Secondary	NG 2.8	Manufacture of resins, insectides, and dyes	Oil-water separation followed by filtration and, if necessary, carbon adsorption.
Fluoranthene (1,2-Benzacenaphthene)		2 1 2	Raw waste-water Primary Secondary	0.3 - 1.6 12 trace		Oil-water separation, filtration, and carbon adsorption
Chrysene (1,2-Benzophenanthrene)		2	Secondary	0.5 - 3.5		Oil-water separation followed by filtration
Pyrene (Benzo-d,e,f-phenanthrene)		2 1 2	Raw waste water Secondary	0.4 - 6.2 6.5 trace		Oil-water separation followed by filtration

Table 17 (Contd.)
Acidic Organics

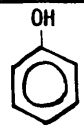
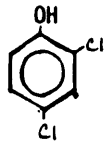
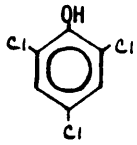
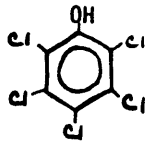
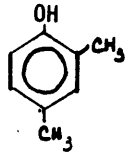
Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
Phenol (Carbolic acid, Hydroxybenzene)		16 10 7	Raw waste-water Primary Secondary	91- ~25,000 403 -8500 12 -1400	General disinfectant, either in solution or mixed with slaked lime dyes; manufacture of resin.	Very readily biochemically oxidizes, adsorbed on carbon moderately well, treatability known to consist of solvent extraction followed by carbon adsorption and/or biochemical oxidation. Appears that a well-run biochemical treatment facility, such as one containing powdered carbon, fluidized bed, or employing O_2 instead of air could treat wastewater containing phenol to low levels.
2,4-Dichlorophenol		2 2 2	Raw waste- PRIMARY SECONDARY	114 82 121 -126	Used in manufacture of herbicides, germicides, moth proofing.	Good candidate for removal by biochemical oxidation and/or carbon adsorption. Filtration, biochemical oxidation, and/or carbon adsorption recommended.

Table 17 (Contd.)

Name of Compound	Compound Structure/Formula	Number of times found	Waste Stream	Concentrations	Uses	Treatability
2,4,6-Trichlorophenol		13 8 9	Raw waste-water Primary Secondary	86 - 5,900 17 - ~10,500 trace - 4300	Intermediate in synthesis of dyes, pigments, pesticides; fungicide, bactericide, preservative.	Good carbon adsorption, moderately biodegradable filtration, oxidation, adsorption recommended.
Pentachlorophenol		7 5 9	Raw waste-water Primary Secondary	trace - 6200 trace - 9500 12 - ~1700	Insecticide, herbicide, waterproofing	Oil-water separation, filtration, and/or carbon adsorption recommended. All these processes must be performed at properly acidified conditions because of the acidic nature of the compound; appears to have biochemical oxidization capability with properly long-term acclimated biota.
2,4-Dimethylphenol		1 1	Raw waste-water Primary	N.G. N.G.	Manufacture of pesticides and surfactants; manufacture of resins, dyes; no direct application, but widely used intermediate.	Readily removable by carbon adsorption, moderately removable by biochemical oxidation. Solvent extraction recommended before either of those steps.

Of these 18, benzene, dichloromethane, ethylbenzene, toluene, and trichloromethane appeared most frequently and in concentrations ranging up to 100 ppb. With the exception of chlorobenzene, the remaining volatile compounds were halogenated short-chain alkanes and alkenes. The majority of these compounds are typically used as solvents.

Benzene appeared in raw effluents in levels ranging up to 100 ppb, in concentrations up to 10 ppb in primary effluents, and in concentrations below 10 ppb in secondary effluents. Tanneries have used benzene as a general solvent; it is also present as a contaminant in other solvents such as toluene. Benzene is used also in dye manufacturing and in pesticides registered for use on cattle.

The EPA recommended water quality criterion to protect freshwater aquatic life from the toxic effects of benzene is 3,100 μg/l as a 24 hour average, and the concentration should never exceed 7,000 μg/l. For saltwater aquatic life the 24 hour average and maximum permissible concentrations are 920 μg/l and 2,100 μg/l, respectively.[5]

Benzene is suspected of being a human carcinogen. Studies, for example, of the effect of benzene vapors on humans indicate a relationship between chronic benzene poisoning and a high incidence of leukemia.[6] As there is no recognized safe concentration for a human carcinogen, for the maximum protection of human health from the potential carcinogenic effect of benezene exposure through ingestion of water and contaminated aquatic organisms, the recommended ambient water concentration is zero.[5]

Bromodichloromethane was identified in the raw effluents of two tanneries. The EPA recommended water quality criterion to protect human health from the toxic properties of bromodichloromethane ingested through water is 2 μg/l.

Chlorobenzene appeared in in raw, primary, and secondary effluents. Its primary use is as an organic solvent, but it functions as a chemical intermediate in the manufacture of phenol and aniline. The threshold concentration of chlorobenze in water for detecting both odor and taste is 20 μg/l. At pH levels of 3 and below chlorobenzene takes up aqueous chlorine to form higher chlorinated benzene rings.

Chloroethane was detected in one tannery's wastewater which had undergone primary treatment. It is used primarily as a solvent or refrigerant. 1,2 - Dichloroethane was detected in the raw wastewater and primary effluent of one plant.

Dichloromethane, also known as methylene chloride, was found in the raw, primary, and secondary effluents of a number of plants. It is a common solvent, found, for example, in insecticides, and is used also as a degreasing and cleaning liquid.

The recommended criterion to protect freshwater aquatic life is 4,000 μg/l as a 24 hour average; the concentration should not exceed 9,000 μg/l at any time. The recommended 24 hour average concentration to protect saltwater aquatic life is 1,900 μg/l, and the maximum concentration is 4,400 μg/l. For the protection of human health from the toxic properties of methylene chlroide ingested through water, the recommended ambient water quality criterion is 2 μg/l.[7]

EPA identified ethylbenzene in tannery effluents 23 times, more than any other volatile organic pollutant. Concentrations were as high as 120 ppb in raw wastewater and as high as 12 ppb in water that had received secondary treatment.

Exposure to ethylbenzene has been shown to adversely affect both aquatic and human life. The compound can affect fish by direct toxic action and by imparting a taste to fish flesh. For the protection of human health from the toxic properties of ethylbenzene ingested through water, the recommended ambient water quality criterion is 1,100 μg/l.[7]

1,1,2,2 - Tetrachloroethane appeared in raw, primary, and secondary effluents. It is employed in insecticide formulations and as a solvent for fats and oils.

Tetrachloroethylene has been reported to be a liver carcinogen in mice; other studies indicate that human exposure over a period of several months to several years can cause liver cirrhosis and hepatitis.[8] Tetrachloroethylene is a suspected human carcinogen. To ensure the maximum protection of human health from the potential carcinogenic effect of exposure to this compound through ingestion of contaminated aquatic organisms and water, the EPA recommended ambient water concentration is zero. The recommended water quality criterion to protect freshwater aquatic life is 310 μg/l as a 24 hour average, and 700 μg/l as the maximum permissible concentration. For saltwater aquatic life the cirterion is 79 μg/l as a 24 hour average, and the concentration should never exceed 180 μg/l.[5]

Tetrachloromethane, commonly known as carbon tetrachloride, is used as a solvent for fats, oils, and waxes, as an insecticide, and as a chemical intermediate. Toxicological data show that rats and mice exposed to carbon tetrachloride incur liver and kidney damage, biochemical changes in liver function, neurological damage, and liver cancer. It is well documented that carbon tetrachloride is toxic to humans. Poisoning symptoms include nausea, abdominal pain, liver enlargement, and renal failure.[9]

Carbon tetrachloride has been shown to be a carcinogen in laboratory animals and is a suspected human carcinogen. As there is no recognized safe concentration for a human carcinogen, EPA has recommended that for the maximum protection of human health, the ambient water concentration of carbon tetrachloride equal zero. To

protect freshwater and saltwater aquatic life, the recommended 24 hour average concentration is 620 μg/l and 2,000 μg/l, respectively; with recommended maximum concentrations of 1,400 μg/l and 4,600 μg/l, respectively.[5]

Toluene, a common general organic solvent, appeared in concentrations varying from trace to more than 100 ppb in raw wastewater. In secondary treatment waters the highest concentration was 50 ppb.

A study using mice showed that toluene is a central nervous system depressant that can cause behavioral changes as well as loss of consciousness and death at high concentrations.[10] Human exposure to toluene for a 2-year period has led to cerebellar disease and impaired liver function.[10] The recommended water quality criterion to protect freshwater aquatic life is 2,300 μg/l as a 24 hour average; the concentration should not exceed 5,200 μg/l at any time. The 24 hour average and maximum concentrations to protect saltwater aquatic life are 100 μg/l and 230 μg/l, respectively.[7]

Trans - 1,2 - dichloroethylene appeared in raw, primary, and secondary effluents. The compound is a general organic solvent and a solvent for fats and phenol. The EPA recommended water quality criterion to protect freshwater aquatic life is 620 μg/l as a 24 hour average and 1,400 μg/l as a maximum permissible concentration.[5]

1,1,1 - Trichloroethane was found in raw and primary effluents. Its primary use is as a solvent and degreasing agent; trichloroethane acts as a solvent carrier for water and stain repellant compounds, it exhibits strong solvent action on organics, especially oils, greases, waves, and tars; and it blends with other solvents to reduce their flammability or provide added solvent properties.

1,1,2 - Trichloroethane, also known as vinyl trichloride, was identified in the raw wastewater from one tannery. It is also a general solvent for fats and waxes.

Trichloroethylene, another solvent for fats, oils, waxes and resins, was identified several times in raw and primary effluents. Studies indicate that exposure to the compound increases the incidence of hepatocellular carcinoma in mice.[11] The compound also acts as a central nervous system depressant in humans. Symptoms of trichloroethylene poisoning include dizziness, headaches, and respiratory tract irritation. Severe intoxication can be fatal, and exposure to high levels can lead to cardiac arrhythmia, pulmonary edema, and renal and hepatic dysfunction.[11]

Trichlorofluoromethane was detected in a trace amount in the primary treatment effluent of one tannery. It is used in aerosals, as a refrigerant, and in air conditioning.

Trichloromethane, commonly known as chloroform, appeared in the raw, primary, and secondary effluents of several tanneries. It is a general solvent, refrigerant, and cleaning agent, and it is registered for pesticide use on cattle. Lab tests show chloroform to be toxic to organisms at various levels of the food chain; in higher organisms it exhibits both temporary and lasting effects. Several studies indicate that chloroform is carcinogenic to rats and mice.[12] Human exposure to chloroform can lead to liver damage, hepatic and renal damage, and depression of the central nervous system.[12]

The recommended 24 hour average and maximum concentrations to protect freshwater aquatic life from the toxic effect of chloroform are 500 μg/l and 1,200 μg/l, respectively. The recommended water quality criterion to protect saltwater aquatic life is 620 μg/l as a 24 hour average, with a maximum concentration of 1,400 μg/l. For the maximum protection of human health from the potential carcinogenic effects of exposure to chloroform, the recommended ambient water concentration is zero.[5]

Basic/Neutral Fraction. Among the basic/neutral organic priority pollutants, dichlorobenzenes, naphthalene, and the polynuclear aromatics phenanthrene/anthracene were the most often identified. Phenanthrene and anthracene co-elute from gas chromatograh (GC) analytical equipment and exhibit very similar mass spectra so that their identifications represent either 1 compound or some combination of both compounds. The basic/neutral compounds typically are used in the manufacture of various dyes and in pesticide formulations.

1,2 - Dichlorobenzene and its isomer 1,4- dichlorobenzene were among the most common of the basic neutral compounds found in tanning effluents. Tanneries use 1,2-Dichlorobenzene in a number of processes. It is a solvent for waxes and gums, a degreasing agent for leather, an insecticide, an intermediate in dye manufacture, and a mask for various odors. 1,2- and 1,4-dichlorobenzene were identified as major contaminant chemicals in a hide curing product used by tanneries and their hide suppliers. 1,4-Dichlorobenzene is used in the manufacture of pesticides, as an insecticidal fumigant in controlling parasites, and in mothproofing wool on sheepskins.

Unlike the other dichlorobenzenes, 1,3-dichlorobenzene was detected only twice in raw wastewaters.

Bioconcentration studies of the dichlorobenzenes in the bluegill indicate that 1,3-dichlorobenzene concentrates by a factor of 66, while 1,4-dichlorobenzene concentrates by a factor of 60.[13]

For 1,2-dichlorobenzene, the criterion to protect freshwater aquatic life is 44 μg/l as a 24 hour average, and the concentration should not exceed 99 μg/l at any time. For 1,3-dichlorobenzene, the recommended 24 hour average and maximum concentrations are 310 μg/l and 700 μg/l, respectively. The criterion to protect freshwater aquatic life from

the toxic effects of 1,4-dichlorobenzene are 190 μg/l as a 24 hour average concentration, with a maximum concentration of 440 μg/l.[5]

The criterion to protect saltwater aquatic life from the toxic effects of 1,2-dichlorobenzene is 15 μg/l as a 24 hour average concentration; the concentration should not exceed 34 μg/l at any time. For 1,3-dichlorobenzene, the recommended criterion is 22 μg/l as a 24 hour average and 49 μg/l as a maximum permissible concentration. For 1,4-dichlorobenzene, the recommended 24 hour average and maximum concentrations are 15 μg/l and 34 μg/l, respectively.[5]

For the protection of human health from the toxic properties of all isomers of dichlorobenzene combined ingested through water and contaminated aquatic organisms, the ambient water criterion is determined to be 230 μg/l total dichlorobenzene.[5]

1,2,4 - Trichlorobenzene appeared in the raw wastewater of one plant in a concentration of 1.8 ppb. It is commonly used as a dye carrier, a heat transfer fluid, an intermediate in herbicide manufacture, and as an insecticide against termites. The compound resists physical and chemical degradation and accumlates in fatty tissues.

Hexachlorobenzene was identified in the secondary effluent of one plant. The compound is used as a fungicide and in dye manufacturing. Extremely resistant to photochemical degradation, it also degrades slowly in the soil. Hexachlorobenzene bioaccumulates in fatty tissue.

N - nitrosodiphenylamine was the only nitrosamine identified in tannery effluents. As a class, nitrosamines often are carcinogenic; they have produced cancer in mammals via all routes of exposure and in essentially all vital organs. The nature of toxic response is related to the chemical characteristics of the particular compound administered. The site of activity depends upon the compound, age and species of animal, dosage level, route of administration, and rate of exposure.[14] Toxicological evidence on N-nitrosodiphenylamine is such that the compound is considered a potential human carcinogen. For this reason, to insure the maximum protection of human health from the potential carcinogenic effects of exposure to the compound, the recommended ambient water concentration is zero.[5] Nitrosamines persist in soil, sewage, and water. They are characteristically photosensitive; exposure of ultraviolet (UV) light split the nitroso group with release of nitrite and secondary amines. They are characteristically stable under alkaline conditions; in acids they undergo photodecomposition. N-nitrosodiphenylamine is used in the manufacture of insecticides, rubber, dyes, and solvents.

1,2-Diphenylhydrazine, also known as hydrazobenzene, was detected in the primary and secondary effluent of one tannery. It did not appear in the plant's raw wastewater. The compound is primarily a special reagent in chemical laboratory operations. There is little information available regarding the fate and effects of 1,2-

diphenylhydrazine in the environment, but in one study, 22 percent of rats injected with the compound developed tumors.[15] For the maximum protection of human health from the potential carcinogenic effects of exposure to 1,2-diphenylhydrazine, the ambient water concentration should equal zero. The recommended criterion to protect freshwater aquatic life is 17 μg/l as a 24 hour average concentration and 38 μg/l as a maximum concentration.[7]

Nitrobenzene was detected in the raw and primary effluent of one tannery. The concentration decreased from 425 ppb in raw wastewater to 29 ppb in the primary effluent. Nitrobenzene is used extensively for the preparation of dye intermediates and as a solvent. The recommended 24 hour average and maximum concentrations to protect freshwater aquatic life are 480 μg/l and 1,100 μg/l, respectively. To protect saltwater aquatic life, the 24 hour average criterion is 53 μg/l; the maximum concentration is 120 μg/l. For the prevention of adverse effects due to organoleptic properties of nitrobenzene in water, the criterion is 30 μg/l.

Benzidine (4,4-diamino-biphenyl), like other aromatic amines, results from the reduction of azo dyes in wastes by hydrogen sulfide or sulfur dioxide already present in water. It is also used directly in the dye industry. Benzidine undergoes relatively rapid decay in lakewater. A suspected human carcinogen, exposure to benzidine has been linked to an increased incidence of bladder tumors.[16]

3,3'-Dichlorobenzidine (3,3'-dichloro-4,4'-diaminobiphenyl), an intermediate in the manufacture of azo dyes, was detected in the secondary effluent of one tannery The compound has been demonstrated to be carcinogenic in non-human mammals under controlled test conditions. Exposure can lead to the development of various sarcomas and adenocarcinomas.[17] For the optimum protection of human health from the potential carcinogenic effects of exposure to dichlorobenzidine, the ambient water concentration should be zero.[7]

Isophorone was found in the secondary effluents of two tanneries. Isophorone acts as a solvent or cosolvent for finishes, lacquers, resins, pesticides, herbicides, fats, oils, and gums. The recommended 24 hour average and maximum water quality criterion for the protection of freshwater aquatic life is 2,100 μg/l and 4,700 μg/l, respectively. For the protection of saltwater aquatic life the 24 hour average concentration is 97 μg/l and the maximum concentration is 220 μg/l. To protect human health from the toxic properties of isophorone ingested through water, the recommended criterion is 460 μg/l.[7] Studies indicate that human exposure to concentrations of 10 to 25 ppm for a 15-minute period results in eye, nose, and throat irritations.[18]

Several phthalate esters, including dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, butyl benzyl phthalate, and bis-(2-ethylhexyl) phthalate, were identified in tannery wastewater at concentrations up to 200 ppb. Phthalate esters are used extensively

as plasticizers and, to a lesser extent, in pesticides and lubricants in vacuum pumps.

Phthalate esters can harm aquatic and terrestrial organisms at low concentrations. The compounds exhibit teratogenic and mutagenic effects under certain laboratory conditions. Of the fish species tested, the rainbow trout was the least sensitive and the bluegill the most sensitive to di-n-butyl phthalate. A cray fish species tested was the least sensitive and a freshwater zooplankton the most sensitive of all species tested.[4]

High levels of phthalate concentration from water and reproductive impairment in certain species are suggestive of potential environmental damage. The presence of these compounds in water affects the growth and reproduction essential for maintenance of animal populations.

As a means of protecting human health from the toxic properties of phthalene esters ingested through water and contaminated aquatic organisms, the recommended ambient water criteria for dimethyl phthalate and diethyl phthalate are 160 μg/l and 60 μg/l, respectively.

Among the basic/neutral compounds identified in various tannery effluents were ten polynuclear aromatic hydrocarbons (PNA's). Naphthalene, phenanthrene, and anthracene were among the most frequent basic/neutral compounds identified and were detected at levels ranging from trace to more than 750 ppb. The remaining polynuclear aromatics - acenaphthene, acenaphthylene, 2-chloronaphthalene, fluorene, fluoranthene, chrysene, and pyrene - were present frequently and usually at low concentrations. Polynuclear aromatics generally are used as intermediates in dye manufacture and in pesticides.

On the basis of present studies, the evidence is not clear whether individual polynuclear aromatics produce toxicity or carcinogenicity in man; however, coal tars, pitch, and other materials known to be carcinogenic to man contain many of the PNA's that produce cancer in animals.

The effects of naphthalene poisoning on humans have been studied. Naphthalene poisoning can cause convulsions and hematologic changes.[19] Reports also indicate that workers exposed to naphthalene for extensive periods of time are likely to develop malignant tumors.[19]

Naphthalene bioconcentrates in aquatic organisms and reduces or interferes with microbial growth. It also reduces photosynthetic rates in algae. Naphthalene accumulates in sediments by a factor as great as up to two in the concentration in overlying water and can be degraded by microorganisms to 1,2-dehydro-1,2-dihydroxynaphthalene and ultimately to carbon dioxide and water.

A combination of fluoranthene and benz(a) pyrene produced tumors in 98 percent of the mice tested, which was more than double the number of tumors produced in the benz(a) pyrene control animals.[20]

For fluoranthene the water quality criterion to protect freshwater aquatic life is 250 μg/l as a 24 hour average, and the concentration should not exceed 560 μg/l at any time. The 24 hour average and maximum concentrations to protect saltwater aquatic life are 0.30 μg/l and 0.69 μg/l, respectively. For the protection of human health from the toxic properties of fluoranthene exposure through water, the ambient water quality criterion should equal 200 μg/l.[5] For acenaphthene the criterion to protect freshwater aquatic life is 110 μg/l and 240 μg/l as 24 hour average and maximum concentrations, respectively. For saltwater aquatic life the 24 hour average and maximum concentrations are 7.5 μg/l and 17 μg/l, respectively. The ambient water criterion for the protection of human health is 20 μg/l.[7] For the protection of human health from the toxic properties of naphthalene ingested through contaminated aquatic organisms and water, the recommended ambient water criterion is 143 μg/l.[7]

Acidic Fraction. Among the acidic fraction of the organic toxic pollutants, phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, and a variety of substituted phenols, including 2,4,6-trichlorophenol and pentachlorophenol, were identified most frequently, at levels often exceeding 1 ppm in raw wastewaters. These compounds are typically used to extend raw material storage life and in bactericide, fungicide, and insecticide formulations. 2,4,5-trichlorophenol is a known major constituent of a biocide used by leather tanners. Other sources which contribute to the significant levels of phenols in raw wastewaters include synthetic and natural vegetable tannins and dye carriers. Chlorination of such waters can produce odoriferous and objectionable tasting chlorophenols which may include o-chlorophenol, p-chlorophenol, 2,6-dichlorophenol, and 2,4-dichlorophenol.

Although described in the technical literature simply as phenols, the phenol waste category can include a wide range of similar chemical compounds. In terms of pollution control, reported concentrations of phenols are the result of a standard methodology which measures a general group of similar compounds rather than specific identification of the single compound, phenol (hydroxybenzene).

Phenol was identified 33 times in tannery effluents, more than any other acidic organic pollutant. Phenolic compounds can affect freshwater fishes adversely by direct toxicity to fish and fish-food organisms, by lowering the amount of available oxygen because of the high oxygen demand of compounds, and by tainting fish flesh. The toxicity of phenol towards fish increases as the dissolved oxygen level is diminished, as the temperature is raised, and as the hardness is lessened. Phenol appears to act as a nerve poison, causing too much blood to get to the gills and to the heart cavity.[21]

Mixed phenolic substances are especially troublesome in imparting taste to fish flesh. Monochlorophenols produce a bad taste in fish far below lethal or toxic doses. Threshold concentrations for taste or odor in chlorinated water supplies have been reported as low as 0.0003 mg/l.[21]

The human ingestion of a concentrated phenol solution results in severe pain, renal irritation, shock, and possibly death.

Various environmental conditions will increase the toxicity of phenol. Lower dissolved oxygen concentrations, increased salinity, and increased temperature all enhance the toxicity of phenol. The recommended water quality criterion to protect freshwater aquatic life is 600 μg/l as a 24 hour average, and the concentration should not exceed 3,400 μg/l at any time.[7]

Although 2,4-dichlorophenol (DCP) appears to be less toxic than the higher chlorinated phenols, it has demonstrated toxicity to certain microorganisms, plants, and aquatic species and has demonstrated teratogenicity in nonhuman mammals.[22] Fourteen percent of crayfish exposed to 1 mg/l DCP over a 10-day period died. When the concentration was increased to 5 mg/l the mortality rate increased to 34 percent within 24 hours and 100% within 1 week. At 10 mg/l the mortality rate was 78 percent within 24 hours and 100 percent within 48 hours.[22] The compound has also been shown to have tumor producing action in mice.[22] The EPA recommended water quality criterion to protect freshwater aquatic life from tainting is 0.4 μg/l as a 24 hour average concentration; the concentration should not exceed 110 μg/l at any time. To prevent adverse effects to human health due to organoleptic properties of 2.4 dichlorophenol in water, the recommended criterion is 0.5 μg/l.[5]

2,4,6-trichlorophenol, like phenol, is an intermediate in the synthesis of dyes. This compound can also be an impurity of 2,4,5 trichlorophenol which is a registered biocide used extensively in this industry. It was found in high concentrations in raw wastewaters, and in some cases high concentrations in final effluents. In a study of genetic activity using an <u>in vitro</u> mammalian spot test with mice, 2,4,6-trichlorophenol exhibited definite, although weak, mutagenic activity.[23] The recommended 24 hour average and maximum concentrations to protect freshwater aquatic life are 52 μg/l and 150 μg/l, respectively. To protect human health from adverse effects of 2,4,6-trichlorophenol, the recommended criterion is 100 μg/l.[7]

2,4-dimethylphenol has also been shown to have a tumor promoting action in mice.[24] For 2,4-dimethyl phenol, the recommended criterion to protect freshwater aquatic life is 38 μg/l as a 24 hour average the concentration should never exceed 86 μg/l.[5]

Pentachlorophenol is a registered and widely used biocide in the leather industry. It was found in high concentrations in raw

wastewaters and in final effluents. Several bioassays have shown that pentachlorophenol is lethal to various species of aquatic life at a concentration of approximately 200 μg/l. The lethal concentration for species tested ranged from 195 μg/l for the brown shrimp to 220 μg/l for the gold fish.[25] The recommended 24 hour average and maximum concentrations to protect freshwater aquatic life are 6.2 μg/l and 14 μg/l, respectively. To protect saltwater aquatic life the 24 hour average concentration is recommended to not exceed 3.7 μg/l; at no time should the pentachlorophenol concentration exceed 8.5 μg/l.[5]

A study of genetic activity demonstrated that pentachlorophenol exhibited weak but definite mutagenic activity.[25] In nonhuman mammals the sublethal effects of pentachlorophenol poisoning include pathological and histopathological changes in the kidneys, liver, spleen, lungs, and brain.[25] In humans, the results of pentachlorophenol poisoning can range from elevated blood pressure and rapid respiration to coma and death.[25] For the protection of human health the ambient water concentration should be no greater than 140 μg/l.[5]

Pentachlorophenol is highly persistent in soils. Reports have indicated that the compound can persist in moist soil for at least a 12-month period.[25]

Inorganic Priority Pollutants

Several of the inorganic toxic pollutants were found in tannery wastewaters at levels of 1 ppb or more. Prominent among these is chromium which is used in the tanning process. The other inorganic toxic pollutants found in tannery wastewater and discussed herein are copper, nickel, lead, zinc, and cyanide.

Total Chromium (CrT)

Chromium compounds are used extensively throughout the leather tanning industry, and chromium is the most prevalent toxic pollutant found in wastewaters in this industry. Almost all compounds are used in the trivalent form; use of hexavalent chromium in the "two-bath" tanning process is nearly obsolete. The prevalent chromium form found in the wastewaters is trivalent chromium, although hexavalent compounds may also occur in waste streams primarily from spillage. It is not possible, however, to determine the distribution accurately, for current analytical procedures for chromium cannot always differentiate between the valence states.

Chromium in its various valence states is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date. The toxicity of chromium salts to fish and

other aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially those of hard water. Studies show that trivalent chromium is more toxic to fish of some types than is hexavalent chromium. Other studies show opposite effects. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium; it also inhibits the growth of algae. Therefore, both hexavalent and trivalent chromium must be considered potentially harmful to particular fish or organisms.

Fish appear to be relatively tolerant of chromium, but some aquatic invertebrates are quite sensitive. Toxicity varies with species, chromium oxidation state, and pH.

Chromium concentration factors in marine organisms have been reported to be 1,600 in benthic algae, 2,300 in phytoplankton, 1,900 in zooplankton, and 440 in molluscan soft parts.[26]

The chemistry of chromium is very complex, especially in untreated raw wastewaters where interferences from complexing mechanisms, such as chelation by organic matter and dissolution due to presence of carbonates, can cause deviation from predicted behavior in treatment systems. Disposal of sludges containing very high trivalent chromium concentrations can potentially cause problems in uncontrollable landfills. Incineration, or similar destructive oxidation processes can produce hexavalent chromium, which in turn is potentially more toxic than trivalent chromium under certain circumstances. In other cases where high rates of chrome sludge application are used, distinct growth inhibition and plant tissue uptake have been noted. Therefore, the use of agricultural land for tannery or POTW sludge disposal should not be generally adopted in light of the potential for long-term accumulation and toxicity in soils and plant tissue.

Copper. Copper oxides and sulfates are used for pesticides, fungicides, and certain metallized dyes. The toxicity of copper to aquatic life is dependent on the alkalinity of the water, as the copper ion is complexed by anions present, which in turn affect toxicity. At lower alkalinity copper is generally more toxic to aquatic life. Other factors affecting toxicity include pH, organic compounds, and the species tested. Relatively high concentrations of copper may be tolerated by adult fish for short periods of time; the critical effect of copper appears to be its higher toxicity to young or juvenile fish.

In most natural fresh waters in the United States, copper concentrations below 0.025 mg/l as copper evidently are not rapidly fatal for most common fish species. In acute tests copper sulfate in soft water was toxic to rainbow trout at 0.06 mg/l copper. In very hard water the toxic concentration was 0.6 mg/l copper. In general the salmonids are very sensitive and the sunfishes are less sensitive to copper.[4]

Copper appears in all soils, and its concentration ranges from 10 to 80 ppm. In soils, copper occurs in association with hydrous oxides of manganese and iron and also as soluble and insoluble complexes with organic matter. Keeney and Walsh (1975) found that the extractable copper content of sludge-treated soil decreased with time, which suggests that a reversion of copper to less soluble forms.[27]

Copper is essential to the growth of plants, and the normal range of concentrations in plant tissue is from 5 to 20 ppm. Copper concentrations in plants normally do not build up to high levels when toxicity occurs. For example, the concentrations of copper in snapbean leaves and pods was less than 50 and 20 ppm, respectively, under conditions of severe copper toxicity. Even under conditions of copper toxicity, most of the excess copper accumulates in plant tissues. Copper toxicity may develop in plants from application of sewage sludge if the concentration of copper in the sludge is relatively high.

The recommended criterion to protect saltwater aquatic life is 0.79 μg/l and 18 μg/l as 24 hour average and maximum concentrations, respectively.[7]

Nickel. Studies of the toxicity of nickel to aquatic life indicate that tolerances vary widely and are influenced by species, pH synergistic effects, and other factors.

Available data indicate that: (1) nickel in water is toxic to plant life at concentrations as low as 100 μg/l; (2) nickel adversely affects reproduction of a freshwater crustacean at concentrations as low as 0.095 mg/l; (3) nickel concentrations as low as 0.31 mg/l can kill marine clam larvae; and (4) nickel seriously affects reproduction of freshwater minnow at concentrations as low as 0.73 mg/l and the reproduction of Daphnia at 53 μg/l.[28]

In nonhuman mammals nickel acts to inhibit insulin release, depress growth, and reduce cholesterol.[28] A high incidence of cancer of the lung and nose has been reported in humans engaged in the refining of nickel.[28]

Lead. Salmonids and freshwater zooplankton are the organisms most sensitive to lead. 1 mg/l was lethal for trout, while 0.03 mg/l impaired reproductivity in a zooplankton, both in soft water. The highest no-effect level on survival, growth, and reproduction was about 0.012 mg/l.[29] In general, the salmonids are most sensitive to lead in soft water, but the influence of pH and other factors on the solubility and form of the lead have a strong effect on the concentration at which acute toxicities are demonstrated.[4]

In humans lead poisoning can cause congestion of the lungs, liver, spleen, and kidneys.[29] Lead has also caused the formation of tumors in rats and mice.[29]

To protect human health from the toxic properties of lead the recommended ambient water criterion for lead is 50 μg/l.[5]

Zinc. Toxic concentrations of zinc compounds cause adverse changes in the morphology and physiology of fish. Acutely toxic concentrations induce cellular breakdown of the gills, and possibly the clogging of the gills with mucous. Chronically toxic concentrations of zinc compounds, in contrast, cause general enfeeblement and widespread histological changes to many organs, but not to gills. Growth and maturation are retarded. In general, salmonids are most sensitive to elemental zinc in soft water; the rainbow trout is the most sensitive in hard waters. In tests with several heavy metals, the immature aquatic insects seem to be less sensitive than many tested fish. Although available data is sparse on the effects of zinc in the marine environment, zinc accumulates in some species, and marine animals contain zinc in the range of 6 to 1,500 mg/kg. Toxicities of zinc in nutrient solutions have been demonstrated for a number of plants.[4]

Cyanide. Cyanide is one of the simplest and most readily formed organic molecules. Cyanide and its compounds are almost universally present where life and industry are found. Besides its importance in a number of manufacturing processes, cyanides occur in many plants and animals as short term metabolic intermediates. Cyanide is found in certain acid dyes used in the leather industry, such as blue and green; possibly, it is found also in vegetable tannins.

In addition to the simple hydrocyanic acid (HCN), the alkali metal salts, such as potassium cyanide (KCN) and sodium cyanide (NaCN), are commonly occurring forms and sources of cyanide. The latter compounds dissolved readily in water; HCN formation is pH-dependent. A significant fraction of the cyanide exists as HCN molecules up to a pH of approximately 8, and the fraction increases rapidly as the pH of the solution decreases. When these simple salts dissociate in aqueous solution, the cyanide ion combines with the hydrogen ion to form hydrocyanic acid, which is toxic to aquatic life.

The cyanide ion combines with numerous heavy metal ions to form metallocyanide complexes. The stability of these anions is highly variable. Those formed with zinc and cadmium are not stable; dissociation and production of hydrocyanic acid in near neutral or acidic environments is rapid. In turn, some of the metallocyanide anions are extremely stable. Cobaltocyanide is difficult to destroy with highly destructive acid distillation in a laboratory. The iron cyanides are also very stable but exhibit the phenomenon of photodecomposition, and in the presence of sunlight the material dissociates to release the cyanide ion, thus affecting toxicity.

Cyanide toxicity is essentially an inhibition of oxygen metabolism, i.e., rendering the tissues incapable of exchanging oxygen. The cyanogen compounds are true noncumulative protoplasmic poisons since they arrest the activity of all forms of animal life. Cyanide shows a

very specific type of toxic action. It inhibits the cytochrome oxidase system which facilitates electron transfer from reduced metabolites to molecular oxygen. It does this by combining with the reactive ferric ions of the catalyst molecule.

The persistence of cyanide in water is highly variable. This variability depends upon the chemical form of cyanide in the water, the concentration of cyanide, and the nature of other constituents. Cyanide may be destroyed by strong oxidizing agents such as permanganates and chlorine. Chlorine is commonly used to oxidize strong cyanide solutions to produce carbon dioxide and nitrogen; if the reaction is not carried through to completion, cyanogen chloride may remain as a residual. This material is also toxic. If the pH of the receiving waterway is acidic and the stream is well aerated, gaseous hydrogen cyanide may evolve from the waterway to the atmosphere. At low concentrations and with acclimated microflora, cyanide may be decomposed by microorganisms in both anaerobic and aerobic environments or waste treatment systems.

A review of the pertinent literature concluded that free cyanide concentrations ranging from 50 to 100 ug/l as cyanide have proven eventually fatal to many sensitive fish; levels much above 200 ug/l probably are rapidly fatal to most fish species. Among the species studied were brook trout (*Salvelinus fontinalis*), brown trout (*Salmo trutta*), smallmouth bass (*Micropterus dolomieu*), bluegill (*Lepomis machrochirus*), and fathead minnows (*Pimephales promelas*).

Some information on chronic or sublethal effects of cyanide is also available. Among the findings were: increased intestinal secretions in the fish, *Cichlasoma bimaculatum*, at concentrations as low as 20 ug/l and reduced swimming capability at concentrations of 40 ug/l. Exposure to cyanide concentrations as low as 10 ug/l reduced the swimming ability or endurance of brook trout, *Salvelinus fontinalis*. Growth, or food conversion efficiency of coho salmon, *Oncorhynchus Kisutch*, decreased at hydrogen cyanide concentrations of 20 ug/l. Small freshwater fish of the family *Cichlidae* exposed to a cyanide concentration of 15 ug/l lost weight more rapidly than the control fish in water free from cyanide.

To protect freshwater aquatic life the recommended water quality criterion is 1.4 μg/l as a 24 hour average concentration; the maximum concentration should not exceed 38 μg/l at any time. The criterion to protect human health from the toxic properties of cyanide ingested through water and contaminated aquatic organisms is 0.2 mg.CN^-/l.[7]

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

TRODUCTION

is section describes waste treatment technology currently in use and ailable for use in the leather tanning and finishing industry. Two neral approaches to pollutant reduction are in-plant process ntrols and end-of-pipe effluent treatment systems. End-of-pipe eatment approaches include: (1) preliminary treatment and primary eatment; (2) secondary treatment; and (3) advanced waste treatment.

e term pretreatment as used in the proposed regulations is defined include in-plant controls (Level 1), preliminary treatment of gregated streams (Level 2), and primary treatment of combined reams by coagulation-sedimentation (Level 3). These technologies e intended to precede either separate industrial "secondary" ological treatment by direct dischargers, or discharge to a publicly ned treatment works (POTW). It is necessary to reduce shock loads, otect the biological system, remove the suspended solids that resist eatment, remove heavy metals (including chromium which would render TW sludges unacceptable for agricultural use), prevent damage to wer lines, and reduce health and life hazards in sewerage intenance.

econdary" treatment, typically a biological treatment process, is tended for use in this industry to remove biodegradable organic terial subsequent to pretreatment as defined above. A major duction of BOD5, suspended solids, phenols, some related phenolic mpounds, and certain other toxic organic pollutants is accomplished "secondary" treatment, as well as a significant degree of trification.

lvanced waste treatment, typically following primary and secondary eatment processes, includes technologies which remove residuals of ispended solids, heavy metals, and dissolved organic compounds, and oduce an effluent of high clarity and very low conventional, nconventional, and toxic pollutant content.

irrent Practices

irrent practices in the tanning industry range from no treatment of istewater to several types of "secondary" treatment. Because POTWs ovide secondary treatment, effluent quality requirements for idirect dischargers to municipal sewer systems are less stringent ian for tanneries that discharge directly to surface waters. A irvey of 89 wet-process tanners indicates that 12 percent of the idirect dischargers have no pretreatment, whereas all direct ischargers surveyed have at least primary treatment and some form of econdary treatment, which may still need upgrading to meet either or

both BPT and BAT limitations. With increasing numbers of stat imposing more stringent water quality limitations in NPDES permits f POTW's, there is a trend toward some pretreatment by all tanners.

The information collection forms and questionnaires, site visits, a sampling visits of wet processors have provided a profile of curre control practices in the leather tanning industry. Most tanne discharge to municipal treatment plants. These indirect discharge comprise 170 tannery operations, or about 90 percent of the industr Of these dischargers, 88 percent provide preliminary treatment, on fifth of the treatment operations consisting of coarse screening onl The remaining 12 percent do not provide preliminary treatment. No of the indirect dischargers provide secondary treatment.

Eighteen plants (about 10 percent of the industry) discharge the wastewater directly to surface waters. All 18 provide some type c secondary treatment, five using activated sludge treatment and t other 13 using lagoons or other treatment methods.

One plant, now closed, operated a physical-chemical treatment system.

Waste Control and Treatment Considerations

The pollutants found in leather tanning and finishing wastewate differ little from those in wastewaters of many other industries a can be treated by conventional methods for suspended solids reductio oil and grease removal, pH control, and BOD_5 reduction. Specifi constituents peculiar to certain tanning processes, such as the toxi pollutants chromium and phenol, and the nonconventional pollutant sulfide, TKN, and ammonia can be removed with available treatme methods currently practiced by the industry.

Tannery waste treatment cannot overlook the interrelationship of t different media (i.e. air, water, and land) for pollutant discharge for example, coagulation-sedimentation and sludge dewatering produce waste product for land disposal. If a chromium tanning process i used, this waste will contain large quantities of trivalent chromium and care must be exercised in managing the waste disposal to preve leachate contamination of ground or surface waters. The practice o chromium reuse or recovery within the plant should reduce the chromiu content of the sludge.

Tannery wastes can create or contribute to the following problems fo POTW's and separate industrial wastewater treatment facilities:

1. discharge of significant concentrations and mass of toxic pollutants:
2. large pieces of scrap hide and leather clogging or fouling operating equipment;
3. excessive quantities of hair and other small screenable solids;

4. highly acidic or alkaline waste streams;
5. wastewater flow surges;
6. excessive loadings of suspended and settleable solids and BOD_5, consistently or in surges;
7. odors, facilities corrosion, very high dissolved oxygen demand in biological treatment system aeration basins, and hazardous gas generation from sulfide bearing wastes
8. a problem with disposal of sludges containing chrome; and
9. pass through of ammonia nitrogen.

ıch of the problems outlined can be reduced significantly or liminated by applying pretreatment technology in leather tanneries. ine screening effectively removes hair, fibers, and scrap material :om wastewater and is available in many different configurations, ɔme of which are particularly effective on tannery type wastes. :reening equipment also must be installed, operated, and maintained roperly to function well.

ıste streams from specific processes in tanneries can be highly :idic or alkaline. If such streams are discharged without pH ljustment or mixing with a different neutralizing stream, the waste tream may create problems within the sewer or at the treatment plant. pH control mechanism of holding and mixing various wastes or of irectly adjusting the pH of the waste is easily implemented as a retreatment technology.

low and waste loading surges, which can be particularly disruptive to iological treatment systems employed by POTWs, can be minimized by qualizing the rate of flow or waste loading discharge. If space imitations at a tannery preclude an equalization tank, discharge cheduling, as practiced by at least one tannery, can reduce the agnitude of these surges.

atch basins, wet wells, and other preliminary treatment facilities hat provide a retention time and space for solids separation from the aste stream can be very effective if properly designed and aintained. Such a facility requires regular maintenance in order to perate consistently and effectively.

he potential problems in disposing of municipal sludge that contains hromium can be alleviated by chromium removed by tanneries. In this anner, a smaller quantity of sludge containing a higher concentration f chrome is more easily disposed of in a controlled environment. hrome recovery and reuse technology is available and in use by the ndustry. This substantially reduces the chrome content of the waste tream and of sludges generated in treatment of these wastes.

n its evaluation of available treatment technologies, EPA has ttempted to do the following:

1. Identify methods of substantially improving the currently typical "poor" performance of most tannery wastewater treatment systems.

2. Present information on recycle, recovery, and/or reuse technologies as viable, cost effective, established, and reliable options for pollution control.

3. Describe the performance of in-place preliminary treatment and secondary treatment technologies on the toxic pollutants found in tannery wastewaters.

4. Present information on the effectiveness of advanced waste treatment technologies on pollutants as 1) demonstrated in use, 2) transferable from a related use or experimental work, or 3) thought to be effective based on a knowledge of chemical process technology and of the similarity of behavior of chemicals of similar molecular size and structure.

This discussion groups the pollution control technologies by the point of application: in-plant, preliminary treatment, and end-of-pipe. The distinction between the first two may blur in some instances; but the focus of the first is on in-plant waste control, whereas the second group of technologies typically involves waste treatment and pollution control preparatory to discharge into a municipal sewer or into an industrial secondary treatment system. Each treatment approach is discussed with a description of equipment, examples of systems currently being used, and reduction levels expected.

IN-PLANT CONTROL TECHNOLOGY - LEVEL 1

Appraisals of plant waste production must first investigate the manufacturing cycle for any modifications which can reduce the waste flow and the concentration of waste constituents. Particular emphasis rests on reducing those factors which pose problems in treatment of the total waste stream. In some instances, reuse or recovery of materials from process solutions can produce economies which will at least partially offset costs.

Process changes and waste stream segregation are two methods of pollutant reduction and/or control essential to achieving acceptable effluent quality. Information from 46 questionnaires from tanneries provides useful information on practices being considered and implemented in this regard and the reasons for the tanner's decisions.

The following steps can often reduce pollutants and the costs of waste treatment:

1. process changes;

2. substitution of process ingredients;

3. water conservation and reuse;

4. repair and replacement of leaky or faulty equipment;

5. installation of automatic monitoring devices to detect abnormal quantities of selected constituents in waste effluents;

6. recovery and reuse of process chemicals; and

7. in-plant treatment to remove a specific waste constituent.

Process Changes

Process changes have been difficult to make in this industry because of the diverse tanning methods employed. While tanning operations traditionally employed the batch system, it is possible that more of the chemical applications as well as the washing and rinsing could be handled more efficiently on a counter-current continuous flow basis. This would achieve maximum utilization of all active ingredients, leaving only concentrated wastes of small volumes for treatment and disposal. Substitution of effluents from one process for make-up water in another generally is feasible at some points within a tannery. Before tanneries can make this change however, they must establish the quantity and pollutant content of water required for each operation.

Substitution of Process Ingredients

Chemical ingredients of low pollution potential for those which are problem pollutants often can be used to advantage in industrial processes. Difficulties caused by high concentrations of contaminants in spent tan liquors from vegetable tanning processes have been lessened through recovery and reuse of those spent liquors in segregated, concentrated waste streams, and through the use of synthetic tanning agents (syntans). A number of process chemical substitution opportunities exist; some of these opportunities are discussed later in this section.

Water Conservation and Reuse

A tannery survey of water needs will help to reduce the volume of wastes because water usage generally exceeds the quantity needed. Some methods of water conservation are listed below:

1. Encourage employees to implement any potential water saving practices. Eliminate the constantly running hoses observed in (a few)

tanneries (one practice requiring employee participation).

2. Examine tanning formulas to determine if floats can be reduced. Use of hide processors and other specially designed vessels has permitted use of lower float volumes.

3. Limit or eliminate some washing and rinsing operations.

   a. Use batch rinses, or alternatively, use the counter-current flow technique.

   b. Use preset meters or timers to limit total flow.

4. Use of wash waters and rinses for process solution makeup.

5. Use of equipment such as hide processors, pumpable drums (rather than floor dumping), float storage tanks, and other reuse equipment.

6. Recirculation of non-contact cooling water, such as for vacuum driers.

Tannery no. 397 has undertaken a comprehensive water conservatic program. Through implementation of this program, total water use ha decreased by nearly 50 percent. Installation of hide processors fc washing the incoming hides has reduced water use in this process by 7 percent. Reuse of process water in the liming operations has achieve a savings of 25 percent. Installation of paddle vats and recirculating flume arrangement following the unhairing operation ha reduced water use for washing 80 percent. Further savings hav resulted from recirculation of hair wash water by installation of fine screen for solids removal. A vegetable tanning recycle ar reclaim system using evaporators has reduced water use for thi process 65 percent. The results of such major water conservatic measures indicated that a comprehensive water conservation program ca substantially reduce water use.

In recent years, the hide processor (modified concrete mixer) ha proven to be an extremely effective means of reducing water use and a increasing number of them are in use. They are most widely used fo washing the incoming hides and for beamhouse operations in hair pul processes. A summary explaining the utilization of the hide processo in reducing tanning effluent is given by Larsen.[29]

en hide processors are used in the beamhouse operation, water use .rough deliming will be about 8.35 l/kg of hide (1 gal/lb of hide). .nnery 444, which uses hide processors for all operations from the .w product through chrome tanning or "blue" stage, has indicated that .ter use is from 12.5 to 16.7 l/kg of hide (1.5 to 2.0 gal/lb of .de).[30] Some tanneries use hide processors in the retan, color, and .tliquor operations.

ıere are also reports of water reuse from one process to another. .nnery no. 24 uses the same water for washing following their ıodified pickle" operation and their vegetable tanning operation.[30] ıere are also some indications that retan operations can use spent .quors from the vegetable tanning process. Tannery no. 144 indicates ;e of bate wastewater for alum tanning make-up water.[30] Tannery no. 35 plans to recirculate approximately 20,000 gallons per day of :eatment plant final effluent water for use in the delime wash which ›llows the hair pulp process and for wash water following the bate :ocess.[30]

ıe Institute for Leather and Shoe Research (TNO), of the Netherlands, ctensively researched water reuse. The water consumption in upper ɜather tanneries including rinsing processes appears to be 70 to 100 'kg hide and in sole leather tanneries 50 to 60 l/kg hide.[31] The :udy indicated that 80 to 90 percent of effluent volume comes from insing before and after the different wet tannery operations. ırough measurement of the electrical conductivity of wash waters it ıs found that the conductivity decreases very rapidly after a short ime; after that, the decrease is small in proportion to the amount of ıter used. It appears, therefore, that either shortening the rinsing ime substantially or replacing the rinsing by washing will save a ɔnsiderable amount of water.

ıble 18 presents a comparison of procedures for continuous rinsing ıd batch washing. The batch washing procedure reduces the water ɔnsumption to one-fifth of that in the standard procedure (a eduction of 80 percent).[31] It was shown that process time can be ɔnsiderably reduced also if the hides are not too dry. Differences ı leather quality were very small except for the distinctly tighter rain obtained with the new procedure.

Table 18. Soaking of Wet Salted Prefleshed Hides With Continuous Rinsing and Batch Washing

Standard Procedure	New Procedure
Rinse continuously 1/4-hour	Wash 1/4-hour with 250 percent water at 25°C
Drain.	Stop for 1-1/2 hours
Add 250 percent water at 18 degrees C.	Wash 1/4-hour (same water).
Drum 5 min/hour for 7 hrs. Drain.	Drain.
Add 250 percent water at 18°C.	
Rest overnight (15 hours).	
Total time--24 hours	Total time--2-1/2 hours.
Water consumption: 12.5 l/kg hide	Water consumption: 2.5 l/kg hide

Many tanneries in Australia have recently economized in the use water, particularly by eliminating waste in washing and by the use lower floats. However, lessened water use tends to increase t suspended solids and BOD concentrations in the wastewater stream.[32]

German literature has reported that "previously about 75 percent the total amount of water was used for rinsing operations and as result, and also as a consequence of working with long floats, t water consumption in upper leather manufacturer was somewhere betwe 140 and 200 l/kg of salted hide. When rinsing is replaced by bat washing the amount of water can be reduced. Short floats in t tannery operations lead to reduction in process time and a faster a more uniform uptake of chemicals, without the danger of a loose grai In this way the total amount of water use can be reduced to 35 to l/kg hide."[32]

French and British research institutes support the replacement rinsing by batch washing.[32] In Great Britain, tanneries a considering the reuse of liquors either directly or after biologic treatment, e.g., waste liming liquors for soaking and t refortification of pickle baths, with their reuse for up to thr months.[32]

Based on a total plant consumption basis, Perkowski indicated that some German tanneries water use was reduced from 200 l/kg of raw hi

processed to as low as 40 l/kg while employing various reduction and reuse procedures.[33] Work was also done on the following to reduce the quantity of pollutants entering the wastewater stream:

1 Brushing off adhering salt from the salted hides before soaking;

3. Removing lime sludge; the lime can be used in agriculture or can be burnt in a kiln to recover quicklime (a possible lime recovery scheme).[32]

P.J. Van Vlimmeren, at the Institute for Leather and Shoe Research (TNO) in Holland, has investigated water recovery and reuse schemes within tannery processes. He reports that when unhairing is possible in the first or second soaking liquor (i.e., in a salt solution), 70 to 80 percent of the organic pollutants and nearly all the preservation salt can be collected in about 5 l/kg of raw hide processed. "For example, a tannery which was using 14.3 litres water/kg hide in soaking to reduce the salt content of the hide to 2 percent could obtain the same salt content by washings with altogether 4.2 litres water, i.e., a reduction of about 70 percent."[32]

Water use reduction and the associated changes in pollutant loading were reported as follows for a U.S. tannery (No. 431) studying the effects of in-plant process changes:

> "Hide processors were installed and the traditional hair-save methods of leather production were replaced by a 'straight through' hair-burn process in which soaking, unhairing, bating, pickling and tanning is accomplished within a single processing unit. Besides eliminating numerous hide handling steps, this process change effected a 50 percent reduction in beamhouse-tanyard effluent volume from an average 107 gallons per side to 54 gallons per side. While much of this water was eventually restored as 'sewer-flushes,' an overall 38 percent reduction in 1970 effluent volumes has been observed, primarily due to an intensive water conservation campaign. Consistent with a 50 percent reduction in lime usage, the pH was lowered from 11.0 to 9.8 with a corresponding 31 percent reduction in fixed suspended solids."[34]

Other tanneries reporting on their extensive and intensive wastewater reduction program indicated that, typically, the first 50 percent reduction was achieved primarily by educating all employees on water conservation practices and management emphasis on constant use of such practices. Water reuse within specific processes in the tannery is the second thrust of this wastewater reduction program. Reuse technologies tend to involve simple, widely used equipment such as cooling towers, filters, separators, decanters or holding tanks. The cost of purchase and installation is rapidly recovered by reduced

water and chemicals use, lower sewer charges or less obviously by reduced loading of a tannery's own treatment system.

A concomitant of water use reduction may be an increase in a pollutant concentration in pretreated discharges to municipal systems. Most municipal ordinances regulating discharges to a sewer specify concentration limits. A joint understanding of the actual municipal requirements at a specific sewer inlet and of the likely consequences of a water reduction program in a tannery would be a vital first step to an informed decision by both a municipality and a tannery on controlling wastewater volume, pollutant concentration, and/or pollutant loading.

Repair and Replacement of Faulty Equipment

Industrial waste problems are often complicated or intensified by the fact that faulty or obsolete process equipment remains in service without proper repair or replacement. Operating personnel also can increase waste disposal problems because large quantities of usable materials often are lost through careless or accidental spills or through excessive drainage of liquids from hides as they are transferred from one process to another. Emphasizing the importance of eliminating these sources of wastes often simplifies waste disposal problems.

Automatic Monitoring Devices

No waste reduction and elimination program can be complete without adequate control measures. Automatic monitoring equipment for detecting abnormal levels of selected constituents closely guards against the failure of established precautionary measures. For example, abnormal and accidental concurrent discharges of concentrated highly alkaline lime-sulfide unhairing liquors and highly acid chromium tanning or pickle liquors are immediately detectable by pH meters and alarms installed on the effluent lines from these processes. In addition to indicating loss of materials, automatic sensing devices also can operate recovery equipment.

Recovery and Reuse of Process Chemicals

The most efficient method of eliminating pollutants from tannery wastes and of reducing the volume of effluent is through reuse of water and chemical agents and through recovery of materials which are normally wasted.

Reuse or reduction of process solutions or recovery of process chemicals are demonstrated methods of waste constituent reduction. A detailed summary of methods available to reduce waste constituents by process adjustments is given by Williams-Wynn.[35]

A number of vegetable tanneries are using recycle systems to reduce the amounts of tan liquor discharged into the waste streams. The Liritan process employs such a technique by counter-current flow of tannage in relation to the hides. In most cases, some blowdown is necessary to prevent the build-up of contaminants in the tanning solution. One tannery recovers this blowdown tan liquor, concentrates it in a triple effect evaporator and sells the concentrated liquor. Other tanneries use this blowdown liquor in retanning operations.

Reuse or recovery of chrome tan liquors also exists but not to the same extent as vegetable tanning. Hauck[36] has summarized methods for recovery and reuse of spent chrome tanning solutions. During World War II, the reuse of chrome tan liquor was common practice because of the scarcity of chromium salts.

Tannery no. 279 studied the reuse of chrome tanning solutions. These tests showed that the chrome liquors could be reused for periods of up to six weeks without reduction of leather quality.[30] The spent tan liquor in this study was settled and sludge was drawn off the bottom of the holding tank. The clarified solution was brought to the required concentration with chromium salts, sulfuric acid, and sodium chloride. Because of the sludge drawoff, this was not a complete recycle system; however, a substantial portion was recycled and only a small amount wasted.

This same study also examined the feasibility of recycling of the unhairing solutions. Tests on recycling of the unhairing solutions were performed on three separate occasions. The longest recycle time was two weeks. The study concluded, however, that since the concentration of waste material in the solution leveled off after a few days, the solution conceivably could be reused indefinitely. The spent liquor was drained and settled in much the same manner as the chrome tan liquor. After removing the sludge from the bottom of the tank, 65 percent of the original volume remained. About 50 percent of the sulfhydrate and the lime needed for the next run was available in that portion retained for reuse. After two weeks of use, the solution had no objectionable odor and the amount of ammonia coming off was not considered substantial.

Tannery no. 253, a shearling tannery, has been able to reuse its chrome tan solution up to five times.[30]

The same tannery has reused its pickle liquor up to five times. This is accomplished through refortification of pickle liquors by the addition of chemicals prior to adding another load of hides.

Tannery no. 388 reports reusing retan liquors.[30] Tannery no. 385 reports reusing the finishing oils.[30] Many tanneries report recycling their pasting frame water, either wholly or partially.

Stream Segregation

In-Plant Treatment. Stream segregation is not an in-plant treatmen technology, per se. It is, in reality, a critical first step t implement most in-plant technologies available to tanneries. It i the physical separation or segregation of at least the two majo wastewater streams in a tannery. One stream originates in th beamhouse, is highly alkaline, and contains a substantial organic loa of dissolved and suspended hair. The other stream originates in th tanyard, is acidic, and has a chrome content of measurable level.

These two major and substantially different wastewater streams can b most effectively pretreated as separate streams rather than in combined state. These two major streams are the specific proces waste streams which respond more completely and cost effectively t separate treatment.

Based upon information from tanneries no. 237 and 431, EPA develope proportionate raw waste load flows and pollutant loads from th beamhouse, and from the tanning, retanning, and wet finishin operations. The values for the various wastewater parameters including flow, are presented in Table 19.

Table 19

Proportioned Flows and Pollutant Loads for Beamhouse and Tanyard/Retan/Wet Finish Operations

Parameter	Beamhouse	Tanyard/Retan/Wet Finish
Flow	40%	60%
BOD_5	65	35
COD	56	44
TSS	69	31
Oil and Grease	49	51
TKN	46	54
Ammonia	0	100
Chromium	0	100

The isolation of the specific process waste streams or the segregatio of the two major streams can be accomplished by a variety of physica means such as the following:

1. Pump-out mechanism on the drum, wheel, vat, or other processing equipment connected to a specific holding or treatment tank or vessel by piping;

2. Collection of wastewater discharged from a hide processing vessel directly into a holding or treatment tank or container;

3. Separate below-grade sewers;

4. Separate above-grade sewers; and

5. Flow direction control diverters in grate-covered floor troughs.

Control of Specific Waste Constituents

Lime Reduction. Lime used in unhairing liquors is responsible for the alkalinity of the final effluent. Insoluble calcium compounds simply add to the sludge quantity. Though the pH of the mixed effluent has to be sufficiently high to precipitate chromium salts, it is desirable to reduce the amount of lime to a minimum. Experiments at the Institute TNO by P.J. Van Vlimmeren "have shown that an amount of 4 percent hydrated lime (on salted weight) is an optimum level with regard to the quality of the leather."[31]

"Because lime has a limited solubility, it is generally regarded as a 'safe' alkali for use in unhairing. Consequently, tanners are tempted to use a considerable excess of this material--far more than is needed to satisfy the alkali-binding capacity of the skin collagen and to keep the liquor saturated with lime." So reports D.A. Williams-Wynn of the Leather Industries Research Institute (South Africa) in a report concerning various operable concentrations of lime liquors. The study points out that, "the disposal of this excess of lime, most of it undissolved but not easily settled, especially in the presence of soluble protein, is a problem with which tanners constantly grapple, yet they persist in using a large excess."[35]

Their "experiments have shown that the amount of lime needed for effective unhairing is less than is required to saturate the protein, so there is certainly no justification for any undissolved lime to be present in beamhouse liquors."[35]

Table 20 lists the values for insoluble calcium hydroxide in effluent from 6-day hair-saving pit liming processes in which the lime offer was progressively reduced. The table is reproduced from William-Wynn's published study.[35]

Table 20. Analysis of Lime Liquors

Lime Offered	Insoluble $Ca(OH)_2$ in Lime Liquors	Lime Unused
4 percent	0.43 percent	53.5 percent
3 percent	0.22 percent	36.6 percent
2 percent	0.01 percent	3.5 percent
1 percent	Nil	Nil

"Unhairing was effective even at the lowest level of the lime recorded in the table. One percent of lime was not adequate when sodium sulfhydrate was used, but two percent was satisfactory and an amount under two percent seems to be the optimum. The temperature was 20°C, the float 500 percent, and sulfide varied between 0.1 and 0.4 percent. The values are means of four determinations averaged over the four sulfide concentrations."[35]

"In a hair-burning, drum-unhairing process in which the sulfide offer was much greater, the amount of lime needed to make satisfactory upper leather was about 0.5 percent with 3 percent of sodium sulfide, and about 1 percent with sodium sulfhydrate. In each case the amounts of undissolved lime in the lime liquors were less than 0.2 percent $Ca(OH)_2$. On 250 percent float this means that less than 10 percent of the lime offered remained undissolved in an 18 hour process, and the absolute quantity was negligible and would not contribute to the sludge problem."[35]

Recycle of Unhairing Liquor. Results of small-scale trials on recycling of lime-sulfide unhairing liquors were reported by Money and Adminis[37] in which the liquors have been recycled up to 27 times without deterioration in leather quality. Different soak methods were compared to determine which did not cause a build-up of salt in the liquor that would affect the swelling and unhairing. Matched-side trials were conducted comparing:

1. conventional unhairing and unhairing with lime recycle after solids removal;
2. conventional unhairing and unhairing with lime recycle and no solids removal; and
3. unhairing using lime recycle with solids and unhairing using lime recycle without solids.

None of the trials produced inferior quality leather. Fats were found to accumulate in recycled lime liquors when the solids were not removed. Advantages stated by the authors are the improved effluent quality and the savings in water use. The work has been extended to large-scale tannery trials.

The following summary is quoted from Money and Adminis' research:

> "It has been shown that lime-sulphide unhairing liquors can be recycled more than 20 times, perhaps indefinitely. The only treatments necessary before re-use are temperature adjustment and replenishment with lime, sulphide and water, preferably as washings from the previous unhairing. For 20 cycles the average consumptions based on greenhide weight were 1.5% lime, 2.2% sodium sulphide and 40-55% water; the higher water usage occurred when solids were removed before each use, a procedure which has advantages. Salted hides can be unhaired satisfactorily in re-used liquors if they first have an adequate soak to reduce their salt content. Recycling of lime liquors has no apparent effect on leather quality or yield even though, when compared with conventional unhairing, it results in a decrease in hide swelling and an uptake of proteins of their degradation products. This method could be developed as a no-effluent system of unhairing if liquors can be cycled indefinitely or, after a certain number of cycles, can be utilized as a source of protein. Even if the liquors are discharged after 20 uses there can be overall a 20-fold reduction in effluent sulphide, seven-fold reduction in effluent lime and protein, and a five-fold reduction (80 percent) in the amount of water used. If wash liquors from the previous unhairings are used to replenish the float, as is recommended, the fresh-water consumption could also be reduced 20-fold (95 percent)."[37]

Obviously it is simpler to leave the solids in the liquor. However, if they are removed after each use (or several uses) there is no problem with fat accumulation, the protein recovery is greater, and the hides are cleaner after unhairing. Vibrating and rotating screens and other systems for removing the solids from the liquor are being investigated. It is an advantage to be able to remove the hair debris and fats without removing all the insoluble lime. The present work has shown that only a small proportion of the lime liquor protein is lost as volatile products, but substantial amounts of the protein or its degradation products are taken up and retained by the hide. It is estimated that a hide unhaired in a recycled liquor would contain more protein, approximately 1 percent of the green hide weight, than it would if unhaired in a fresh lime liquor. This extra protein could be beneficial by adding substance to the leather, and it could affect the feel of the resultant leather; but in the matched-side trials no differences have been detected in the final leather.

Most existing beamhouses would have to be modified for recycling of lime liquors, and the facilities necessary will be similar to those for recycling chrome liquors. Rapid and effective drainage of the liquor can be achieved by using a drum with a perforated false bottom covering a drainage valve, or a hide processor or cement mixer. Provision of a storage tank capable of holding the daily output of lime liquors plus washings would be preferable; but it may be possible

to pump liquor directly from one drum to another. A pit unhairi system would be ideally suited to recycling, although floats a amounts of reagent would differ from those given for drum liming.

A sulfide reuse system has been installed and used by tannery no. 2 (subcategory one - Hair Pulp/Chrome Tan/Retan-Wet Finish). Th system has achieved a reduction in sulfide-containing wastewater fr 27,000 gpd to 10,000 gpd.

This reuse scheme was developed by an Italian engineering fi (Idronova) and operates with sedimentation and filtering equipme used by the European wine industry. The system operates as follows:

1. The unhairing float from the hide processors is pumped to enclosed holding tank at 12 gpm. From there it is pumped a rate of 20 gpm to a hydrodynamic sedimentator whi facilitates solids settling and filtration of the flo during gravity flow. Pumps provide circulation and si reduction to reduce large solids to about 1/4 inch size.

2. Solids are settled out using gravity and centrifugal for with the solids being drawn out the bottom of the unit in a solids container for disposal. Oil, grease and oth floating material are skimmed off the top of the solids bo

3. The supernatant sulfide liquor flows close to the top of t separation chamber, where it is drawn off. The reclaim liquors flow by gravity to two large storage tanks. Fr these tanks the reclaimed liquors are pumped back to t hide processor. Some sludge build-up occurs in the storage tanks, but it is subsequently discharged a disposed of as solid waste.

4. The tanks are closed and vented outside the the building prevent any build-up of sulfide in the building. T storage tanks are also provided with mixers.

<u>Enzyme Unhairing for Hair-Save Operations</u>. Prerequisites for a hair-saving method are: it must unhair easily and mechanically, wi removal of fine hair (if possible without reliming); it must economical, not time-consuming; it must be suited to mechanized a automated production processes; and it must give good leather qualit Hair-saving processes require more labor than hair-burn processes, a tanners will not incur additional costs unless there is a profit fr the proceeds of the hair and a cost savings in wastewater treatmen Present trends in the industry are definitely toward the hair-bu process.

Frendrup and Larsson[38] made a detailed study of the effects of vario depilatory methods on the characteristics of the residual waste They found that when hair was loosened chemically and remov

mechanically, the total nitrogen content of the unhairing wastes averaged 1.2 g/l. When the hair was destroyed completely by chemical means (hair-pulping or burning), the total nitrogen content ranged from 5 to 7 g/l. In addition, an appreciable reduction in oxygen demand, and in quantities of sulfides and sludge was observed with hair-saving methods. Hair containment and housekeeping practices are significant influences on these results.

Enzyme unhairing is one of the hair-saving methods known at the present time. Based on a considerable amount of work by the TNO Institute, this method reportedly could be developed for use in the production of sole leather, but for upper leather some difficulties in connection with the feel of the leather still must be overcome. A combination of the Liritan vegetable-tan process and enzyme unhairing (for sole leather) was also investigated at TNO.[31] The latter combination of the two developments reduced pollution by vegetable tannage to only 10 percent of that from traditional methods, according to TNO.

Sulfide Removal. *In situ* sulfide oxidation in the drum or paddle with the hides has been investigated and is in use. TNO Institute investigated[31] this method of oxidizing sulfides in the lime liquors during and after the liming process. It was found that a vigorous movement of the liquor and a free air supply are very important. In the alkaline medium the manganese catalyst converts into insoluble manganous hydroxide. Flotation of the hydroxide by hair remnants or foam must be prevented to retain the catalytic activity. When the oxidation of sulfides is combined with the liming operation the latter is started in the usual way, either in a paddle or in a drum. After complete removal of the hair, a small amount of manganous sulfate, e.g., 200 g/cubic meter (m^3), is added and paddling or drumming is continued for some additional time. Using hair-burn liming procedures and the lowest sulfide concentrations necessary for complete unhairing and the production of good quality leather, over 95 percent of the residual sulfides could be removed by oxidation within three hours. This additional drumming had little effect on the appearance and physical properties of the leather produced in this way. Tannery No. 245 is using this method of *in situ* sulfide oxidation as standard practice.

The TNO technique of *in situ* sulfide oxidation in combination with a sulfide liquor reuse system reduced the sulfide content of the wastewater discharged to POTW from 118 mg/l to about 2 mg/l concurrent with a reduction in wastewater volume.

Chrome Reduction. Tanyard wastewater is generally acidic and, because of the chrome content, is toxic to some organisms. The acidic nature of the waste stream can be neutralized by mixing with the beamhouse wastes that are alkaline or by pH adjustment with chemicals. The chrome content can be reduced by using one of a number of technologies. One technique is to increase the uptake of chrome by

the leather in tanning. A second is to reuse chrome liquors, as is, in some part of the beamhouse, tanyard, or retan process without first recovering the chrome from the solution. A third way is to precipitate the chrome with an alkaline chemical, producing a chrome sludge either for disposal or for chrome recovery. The alkaline chemical source can be beamhouse waters, fresh lime, or bases such as caustic soda or soda ash.

Aside from their application as methods of reducing the chrome content in tannery wastewater some of these methods have been used in the past as chrome conservation methods. During World War II, chrome supplies were cut off and tanners were able to reduce their chrome use 20 percent.[39] Under current conditions of increasing chrome prices and reduced imports, an economic incentive exists for tanneries to introduce these methods of chrome conservation, which will improve the wastewater quality as well. In fact, several tanneries have already started chrome recovery and reuse programs.

Increasing the uptake of chrome is an effective method of reducing chrome in the wastewater and conserving chrome. Chrome fixation can be increased by increasing the chrome concentration, increasing the temperature, adjusting the concentration of neutral salts to the minimum required to prevent swelling of the hides, increasing the basicity of the chrome waste slightly, and adjusting the pH of the tanning liquor during the tanning process. Some of these methods may affect the quality of the leather.[39] After World War II, tanners went back to the older methods. The efficiency of chrome use is now about 70 percent.[36]

Reuse of chrome liquors without first removing the chrome has been extensively studied recently and is practiced in some tanneries. From the literature it appears that the most common technique in chrome liquor reuse is to fortify the liquor with acid and salts and use the forfified liquor in the pickling process. The chrome introduced into the pickling liquor gives a pretannage.

Scroggie and others in Australia did a series of studies on reuse of spent chrome tanning liquors for pickling. In the fourth part[40] of the studies the spent chrome liquor was used to make up the pickling acid added to the hides right after the bate. The hides were obtained from five different Australian tanneries. Scroggie obtained more than 5 percent uptake of chrome as Cr_2O_3 on a dry weight basis. This chrome was distributed in a normal fashion throughout the hide. He reused the chrome 12 times over the course of several months and noted that the concentration of neutral salts reached steady state in about 3 to 4 cycles. He recommended that "the liquors can apparently then be used indefinitely (with occasional screening, etc., as necessary)."[40]

In further studies[41], Scroggie ran actual plant tests at an Australian tannery which used hide processors for the tanning process. He found

that a savings of about 25 percent could be realized on tanning reagents in Australian tanneries. A second run of 18 successive cycles over the course of several months again revealed that neutral salt concentration reached steady state after three or four cycles. Scroggie also thought that hide processors were better than drums for this sort of recycle process because the lime and bate liquors can be readily removed as needed minimizing volume build-up and problems with pH. It is also possible to pump spent chrome liquor out below the level of the oil layer and to pump the sludge out of the bottom of the hide processors to get a clean recycle stream. It is possible to remove about 95 percent of the spent chrome liquor from the processors. There is about 20 percent savings of chrome, complete savings of neutral salts, and no increase in dissolved protein. Scroggie also indicates it is possible to modify a tanning drum for reuse to get similar results. Scroggie further reported that:

> "Throughout the entire process the 're-cycled' leather was at least comparable with corresponding leather from the normal production. On removal from chrome-tanning, the leather showed no difference in general appearance, grain quality, or 'feel' and there was no grain 'draw', chrome 'blotching' or veininess apparent; random cross-sections showed a complete chrome penetration in all cases. These observations were confirmed by the tannery personnel who carried out a complete assessment of the finished leather. They reported that there was no difference in the subjective properties of the 're-cycled' leather when compared with normal production leather of the same type. Neither was any difference detected between 're-cycled' and control sides in Lastometer load or distension, or in Cr_2O_3 content or ash weight of the finished leather."[41]

And he concluded that:

> "A method is now available for the re-cycling of chrome liquors which can be fitted into current production schedules in tanneries and which has been shown to produce leather of comparable quality to that produced by conventional processing."[41]

In the sixth part of his studies[42], Scroggie reported on a series of full-scale tannery tests of chrome recycling. He stated that the common chrome uptake of 70 to 80 percent is a consequence of the law of mass action--reaction rate depends on chrome concentration--rather than any inactivation of the chrome complexes thereby requiring an intermediate reactivation before reuse. Thus, direct reuse is an effective technique. He found that the solid commercial chrome preparations were better than the liquid forms because there was no accumulation of excess chrome liquor to be disposed.

Hide processors have the best drainage characteristics for recycling chrome, but they should be lined to prevent corrosion. Two collection

tanks for the chrome liquor are necessary. Lime-sulfide unhairing solution recycling is desirable but not necessary for effective chrome recycling. In several of these tests the quality of the leather decreased. This was traced to a slight acidic swelling of the hide. Scroggie lists several advantages of chrome reuse. The first is that the possibility of shock loading on the secondary biological system is reduced. The second is that the required amounts of sodium chloride and sodium sulfate are reduced. The third is that there is a saving of 20 to 25 percent of the associated cost for the process in Australian tanneries. The other three advantages of chrome recycling which he cites are:

> "(iv) With proper control, leather of at least comparable quality to conventionally tanned leather can be produced while there are indications that leather quality can be improved in some respects.
>
> "(v) Recycling is considered to be superior to the alternative method practiced in some overseas countries of chromium precipitation and recovery as it is more convenient to use and is less costly. It is also considered to provide a more complete solution to the problem than that provided by attempts to improve the uptake of chromium, for example, by the use of very low floats or more highly reactive chromium reagents.
>
> "(vi) The possibilities for economic utilization of tannery sludges are extended by the exclusion of chromium which is precipitated in such sludges by the common method of mixing of all tannery processing effluents for treatment."

Ward, Slabbert and Shuttleworth have described tests of chrome reuse and recovery in South Africa.[43] The sulfate reached steady state after four cycles. Chrome analyses and other precautions are recommended. France[44] studied the use of organic acids for pickling and later studied recycling of spent chrome/organic acid liquor to the pickling process. He tested his method at several tanneries and found little difference in the properties of the leather produced by his method and conventional processes. He obtained faster tanning and better exhaustion with his method. He tried recycling of the liquors for even greater efficiency and possible economic advantages. He advises against reusing the wring liquor because of its fat content. He also advises pumping the spent chrome liquor about 2 feet below the oil scum and above the sludge level. He found that less chrome could be charged and all of it used. About half as much time was required for his process as the conventional pickle plus tan processes require. With a low float, the pickle may even be eliminated in some cases. His process requires no added salts because the low float results in more concentrated liquors. About 10 to 11 percent of the recycle stream consists of soluble salts at steady state. The cost of the organic acids, a mixture of formic and acetic acids, is higher than sulfuric acid. The same amounts are used, but faster processing is

possible and savings in other chemicals can cut overall costs. He mentions that this process is already in use but does not mention where. The additional equipment required for this process is one tank, one pump, and some piping; investment could be low for this reason.

Pierce and Thorstensen have published an account of the chrome reuse at tannery no. 245.[45] Hide processors are used at this tannery. The spent chrome liquors are collected in a tank large enough to hold six tannages. Oil and grease are skimmed to prevent darkening of the blue stock, and the liquor is used for pickle make-up. Sulfates and other salts build up at first but eventually level off. There is more spent chrome liquor available than is required for pickle. When the excess completely fills the tank it is precipitated with soda ash and sodium hydroxide for reuse. This does not decrease the amount of chrome used in the tanning process, but with the reuse of chrome in the pickling, there is increased uptake without additional chrome being bought. Pierce and Thorstensen note that the system saves money and that the chrome released to the sewer typically is 1.6 mg/l (as Cr), based on an effluent flow of 600,000 gallons per day.

Tannery no. 233 is reusing chrome. The chrome liquor is collected. They skim grease and remove the suspended solids. Then they use the clear chrome liquor without grease or fibers as a pretan. If the grease is not removed there can be a color problem. Previously they precipitated chrome with beamhouse waste from a pigskin unhairing operation or sold spent chrome. A concentration of 2 mg/l of chromium has been achieved in the total discharge to the municipal sewer.

Precipitation of chrome for recovery was practiced in World War II. Hauck has published a paper outlining the methods in use then and known now. Precipitation may be accomplished by beamhouse wastes, by fresh lime, or by bases whose sulfates are soluble, such as caustic soda or soda ash.[36] The chrome precipitate may be disposed of or recovered for use in the process. Hauck recommends using a base whose sulfate is soluble for the precipitation. In this case the chrome precipitate may be washed to remove the sulfate before the chrome is recovered. This prevents build-up of salts. He finds that fresh lime is not as good because the calcium sulfate whch is formed cannot be washed out. He recommends using beamhouse waste for the precipitation only if the chrome is to be disposed of instead of recovered. For reuse the chrome precipitate is redissolved in sulfuric acid, the chrome solution is analyzed, the basicity and salt concentrations are adjusted and it is ready for reuse.

An article in Leather and Shoes describes chrome precipitation with a proprietary buffer mix.[46] The supernatant chrome concentration reportedly can be lowered to about 0.1 ppm average (range 0.06 to 0.5 ppm) with this product.

A new process for chrome precipitation uses sulfides. This process, called "Sulfex", avoids the problem of the possible evolution of hydrogen sulfide by using only a small amount of soluble sulfide in equilibrium with an excess amount of nearly insoluble iron sulfide. The leftover iron sulfide is filtered out with the precipitate. This process appears to be useful for removing small amounts of chrome remaining in the wastewater after the bulk of the chrome has been precipitated. It does not appear to be suitable for bulk precipitation of chrome.[47 48]

A full-scale tannery test of chrome precipitation and reuse was conducted at tannery no. 431.[34] During this test only part of the chrome liquor was collected for precipitation. The entire liquid contents of the hide processors used for chrome tanning were collected in a tank at the end of the tanning process. None of the chrome liquor from retan or chrome-containing liquors from operations such as wringing was collected. About two-thirds of the chrome was collected and about one-third was not. The collecting tank could hold the contents of two hide processors at once. Alkali and polyelectrolyte were added. Soda ash and lime were the alkalis tested to determine which was the more cost-effective. The precipitated chrome sludge was thickened to about half its original volume, then further thickened on a vacuum filter. The chrome sludge cake was conveyed to another tank and dissolved in sulfuric acid. A cyclone separated the insoluble calcium sulfate from the dissolved chrome and the chrome solution was then stored for reuse. This precipitation process recovered between 98.0 and 99.9 percent of the chrome from the liquor. When lime was used to precipitate the chrome, some of the chrome ended up in the calcium sulfate sludge which was to be landfilled. In this case about 86 percent of the chrome was recovered in usable form. The effluent from the chrome recovery system contained about 2 mg/l of chrome. Because only part of the chrome was treated, however, the reduction of the total chromium in the effluent was 37 to 40 percent. Collecting more of the chrome would result in a greater reduction of the total chromium even if the treatment efficiency was not as high. EPA's pretreatment standards and effluent limitations assume a chromium recovery system (precipitation, solids separation, redissolution, and reuse) which captures the tan and blue wringing liquors.

This discussion has not described certain advanced treatment methods for removing chrome from wastewater streams. Reverse osmosis, ion exchange, and electrodialysis can recover metallic ions from solutions, but chromium, especially under acidic conditions, is incompatible with many materials used in these procedures. Fouling by proteins also could be a severe problem.

Tannery no. 431 demonstrated chrome recovery. Based upon the recovery system demonstrated by that study, EPA assumed the use of a similar chromium recovery system which collected waste tanning liquors and wastewater from blue-wringing which together comprise approximately 80 percent of the total mass of chromium discharged by a tannery. As

noted by data from tannery no. 431, over 98 percent of this chromium is assumed by EPA to be recoverable.

Ammonia Nitrogen Reduction. The nitrogen loadings in the raw waste of a hair-burn process have been reported as follows:

1. The average TKN loading for subcategory one (hair pulp, chrome tan, retan-wet finish) is 11.7 kg/kkg and the average ammonia nitrogen loading is 5.5 kg/kkg hide.[49]

2. An EPA sponsored tannery study reports 15.7 kg/kkg of hide of TKN, and the 4.6 kg/kkg of hide for ammonia nitrogen, in which the bating operation is totally responsible for the latter.[34]

These loadings indicate that the elimination of nitrogen-containing deliming chemicals during the bating process would significantly reduce the ammonia nitrogen and TKN in the effluent.

Koopman of TNO has analyzed residual liquors for nitrogen in a paper on deliming with magnesium sulfate.[50] The standard procedure (deliming with 3 to 3.5 percent ammonium sulfate) produces a total nitrogen content of 7 kg/kkg of hides; in comparison the test procedure (7 percent magnesium sulfate) results in a total nitrogen content of 0.62 kg/kkg of hides. Koopman also indicates a total addition of 7.4 kg/kkg of ammonia sulfate, which is 0.4 kg more than the residual. He attributes this loss to some of the nitrogen from the ammonium sulfate escaping in the form of NH_3 gas during deliming.

Koopman elaborates in his paper[50] on alternative deliming media as follows:

"The purpose of deliming is partially or completely to neutralize the bases present in the hide without giving rise to acid swelling. In this process, the lime must also be partially removed in order to prevent the formation of spots.

"The deliming media in use in leather preparation may be divided into four groups: namely, ammonium salts, strong deliming acids, weak deliming acids, and deliming with magnesium sulfate.

"1. Ammonium Salts

"In the deliming of cowhides, use is made preponderantly of ammonium sulfate and ammonium chloride, alone or in combination with acid. The combined action of ammonium salt plus acid depends on the principle that the ammonia, which the lime in the hide frees from the ammonium salt, is again converted to the ammonium salt by the reaction with the added acid. Ammonium salts of organic acids are used as well, frequently with addition of organic acids with the same acid residue as from the ammonium

salt. Thus buffer solutions are created, which have the property that they can be used to neutralize reasonable quantities of lye without danger of excessive pH, which might give rise to acid swelling.

"The use of ammonium salts in the deliming of cowhides confers the following advantages:

1. Deliming can be accomplished rapidly.

2. No acid swelling can occur during deliming.

3. Alkali swelling is largely eliminated.

4. The most frequently used ammonium salts (sulfate and chloride) are inexpensive.

"2. Strong Deliming Acids

"In addition to strong inorganic acids like hydrochloric and sulfuric acid, a number of organic acids must be included in this category, such as formic acid, acetic acid, lactic acid, and aromatic sulfonic acid. Strong deliming acids, such as hydrochloric and sulfuric, are cheap. They are in general use as preliminary deliming agents, achieving a superficial deliming. Because of the fact that with these strong acids the pH during the deliming can fall very rapidly, there is always the danger that acid swelling will set in the delimed outer layers of the hide before the acid has had time to penetrate deeper into the hide and delime the deeper layers. The somewhat milder lactic and formic acids can be safely used, adding them in installments and checking the pH of the deliming liquor and the hide. Because of the slow course of the deliming, these acids are used principally in the deliming of thin skins (goat, sheep, calf), and not for cowhide. Disadvantages associated with the use of organic acids are their high price, together with the resulting higher COD content of the wastewater.

" Weak Deliming Acids

"These do not directly displace the lime bound to the hide. After neutralization of the lime that is still present in the capillaries, the balance between chemically bound and free lime is shifted, the free lime is neutralized, and so on. This process takes place very slowly, so that these acids can penetrate into the interior of the hide and provide uniform deliming. The most important agents of this group are boric acid, and sodium bisulfite. Boric acid yields leather with a handsome grain, and is partly on that account regarded as one of the best deliming agents. Its relatively high price and the slowness of the deliming process will stand in the way of its

general adoption in the manufacture of cowhide. Because of the low acidity of boric acid, a substantial excess is required in order to obtain complete neutralization of phenolphthalein. Sodium bisulfite is more frequently used as a deliming agent than boric acid. Commercially, it is available mostly in anhydrous form as sodium metabisulfite, $Na_2S_2O_5$, in aqueous solution yielding the weak acid bisulfite $NaHSO_3$. During deliming, sodium bisulfite is converted to calcium sulfite, which is not easily soluble in water, but the solubility can be increased by addition to the deliming liquor of an excess of sodium bisulfite, thus avoiding possible spotting. Deliming with bisulfite has the disadvantage that in an acid medium the rather aggressive sulfur dioxide can escape.[50]

"4. Deliming with Magnesium Sulfate

"The fact that ammonium sulfate and chloride give very rapid deliming of cowhide led Koopman and the other researchers to the idea that this property might also be possessed by magnesium salts, in this case the sulfate (epsom salt) and the chloride. The OH- ions from the pelt are bound in a similar manner without danger of acid swelling according to the following equation:

$$Mg^{+2} + 2OH^- = Mg(OH)_2$$

"The chemical reactions for deliming with ammonium sulfate and hydrochloric acid are:

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NH_4OH$$

$$2NH_4OH + HCl = 2NH_4Cl + 2H_2O$$

and for deliming with magnesium sulfate and hydrochloric acid:

$$MgSO_4 + Ca(OH)_2 = CaSO_4 + Mg(OH)_2$$

$$Mg(OH)_2 + 2HCl = MgCl_2 + 2H_20$$

"It is apparent that in addition to the precipitation of $CaSO_4$ in the hide, there is now also a precipitation of $Mg(OH)_2$. Alkali swelling is largely obviated, the $Mg(OH)_2$ precipitate is converted into a soluble magnesium salt. Apparently all the $Mg(OH)_2$ still present in the hide after deliming is converted back to a soluble magnesium salt during the pickling. An incidental advantage of magnesium sulfate and chloride is that they are two very cheap products.

"When deliming was carried out with magnesium salts plus acid, instead of ammonium sulfate plus acid, the researchers found:

1. The visual characteristics of the leather were not adversely affected.

2. The most important physical characteristics were affected not at all or very slightly.

3. The nitrogen (TKN) content of the wastewater was significantly reduced.

4. The total processing time was not affected.

"In addition, with the same final pH after chrome tanning, followed by the same processing methods, the ash content of the leather in both cases would be equal."

Koopman states that commercial deliming products can be used for deliming light leathers (thin hides); however, for deliming of thicker leathers, the producers recommend only the products containing nitrogen compounds in the form of ammonia or amine. Koopman describes some of the factors or conditions which determine the required amount of a particular deliming agent:

1. The alkalinity of the hide, which is connected with the method of liming;

2. The degree of deliming desired;

3. The course of the rinsing processes after the liming and preceding the deliming;

4. The thickness of the hide;

5. The time at which mechanical operations, such as fleshing and splitting, are performed, with or without removal of lime adhering to the flesh side;

6. The desired deliming time.

Koopman concludes his research with the following remarks:

"It has been found that in the deliming of leather, magnesium sulfate shows definite promise as a replacement for ammonium sulfate. Magnesium sulfate does not have a deleterious effect on the quality of the leather, either as regards visual characteristics or as regards the principal strength and stretch characteristics. Like ammonium sulfate, magnesium sulfate permits complete and rapid deliming and acid swelling does not occur during the deliming.

"Magnesium sulfate (Epsom salts) is a cheap deliming agent; as compared with ammonium sulfate, the quality of the effluent water

is distinctly improved by its use. The replacement of ammonium sulfate by magnesium sulfate in deliming can, under specified conditions, lead to a definite reduction in the estimated purification costs.

"Tests on a semi-industrial scale using magnesium sulfate as the deliming agent have given, in all respects, favorable results. It would be a logical continuation to now increase the scale, and conduct one or more practical industrial-scale tests. In addition to magnesium sulfate, the use of magnesium chloride, which is also cheap, might merit consideration."[50]

This information suggests that deliming with epsom salts should realize a 67 percent reduction in the ammonia content of the total tannery effluent. This percent reduction was based upon engineering analysis of data from plant no. 431 (Table 19) on the amount of aqueous ammonia which would be removed from the segregated tanning, retanning, wet finishing waste stream by complete removal of ammonia from deliming. Since ammonia is also measured as TKN, a concurrent reduction of TKN is achieved.

Summary of Industry Efforts to Implement In-Plant Controls

Table 21 lists some feasible in-plant process change methods and indicates the number of tanneries which have considered and decided either positively or negatively to implement these in-plant changes. Sulfide substitution and elimination of bating were widely considered but the tanners found no solution which, in their experience, did not interfere with leather quality. Fourteen tanners considered a substitute for ammonium sulfate and one tannery (no. 397) has used magnesium sulfate in deliming with a considerable reduction in nitrogen waste load.

As indicated in the table, opinion is almost equally divided on the use of hide processors and also almost equally divided on lime and unhair liquor reuse. Some tanners state that the leather produced in hide processors is of poorer quality, while others state that the leather is of better quality and the hide processors improve in-plant control. Some tanners think that hide processors are more economical because less labor is required and lower water use results. Others object to the cost of installation and problems of maintenance.

In lime and unhair liquor reuse the question focuses on labor and materials savings, lower waste load and questionable leather quality. Several of the responses recorded on Table 21 in the negative column included comments which indicated that decisions are still pending and that further studies are being conducted.

Decisions on protein recovery apparently depend on the economic situation of each tannery. The important question involves the volume, quality, and the market for recoverable protein. Reuse or

TABLE 21 IN PLANT PROCESS CHANGES INDICATED ON QUESTIONNAIRE FROM TOTAL OF 46 LEATHER TANNERIES

PROCESS CHANGE METHODS	NUMBER OF PLANTS WHICH CONSIDERED BUT DECIDED AGAINST PROCESS CHANGES	NUMBER OF PLANTS WHICH ARE OR WILL BE IMPLEMENTING PROCESS CHANGES
Sulfide substitute in unhairing	17	0
Ammonium sulfate substitute in deliming	12	2
Eliminate the bating step	12	0
Use of hide processors	14	13
Wash/soak water reuse	15	7
Lime liquor reuse	12	13
Unhairing liquor reuse	8	10
Protein recovery	6	3
Spent chrome liquor reuse	19	10
Liritan vegetable tan process	5	5
Recovery of spent vegetable tan liquor	3	8
Process or equipment wash water reuse	8	13
Cooling water reuse	4	14
Other	0	5

recovery of tan liquors is generally an economic question with most decisions indicated on that basis. From the questionnaires it also appears that wash water and cooling water reuse is usually implemented if convenient and if the tanner perceives some real benefit from such an investment.

Table 22 lists the more commonly used waste stream segregation methods and the number of tanneries reporting the use of these methods. Of the 46 plants whose input was included on the table, nearly half indicate using one or more of the listed beamhouse or tanyard waste segregation methods. Nearly half also indicate using one or more of the waste stream segregation methods for specific tannery processes. Tanners generally concede the value of segregating certain process streams for reuse of process liquor, for process chemical recovery, and for more efficient treatment of final wastewater. However, it is also apparent that stream segregation must be tailored to the individual tannery situation. Some tanners do not consider their facilities readily adaptable to such renovations due to either limited space or the type of construction employed in the original building. Floor and sewer construction methods are also mentioned as being particular problems.

It is quite evident that many of these in-plant technologies are well established and that a different cost situation (e.g., the cost of ammonia removal by treatment versus elimination by substituting chemicals) will motivate tanners to further implement these pollution control methods. As the cost of processing chemicals and POTW cost recovery and operating charges increase, the cost-effectiveness for many of these in-plant control technologies will also become more attractive. Chrome recovery is an excellent example of the cost of processing chemicals making recovery economically attractive as well as environmentally sound.

END-OF-PIPE TREATMENT

Preliminary Treatment - LEVEL 2

The need for preliminary treatment or pretreatment is based on the following factors:

1. Removal of toxic pollutants found to pass inadequately treated through a POTW.

2. Removal of causes of treatment system upset or hazards and of collection system obstructions or potentially damaging materials.

3. Stringent water quality criteria imposed upon POTW in NPDES permits.

4. Reduction of load to secondary treatment units.

TABLE 22 WASTE STREAM SEGREGATION IN LEATHER TANNERIES AS REPORTED IN QUESTIONNAIRES FROM 46 PLANTS

METHOD OF WASTE STREAM SEGREGATION	NUMBER OF TANNERS WHO INDICATED USE OF SPECIFIC BEAMHOUSE AND TANYARD WASTE SEGREGATION METHODS	NUMBER OF TANNERS WHO INDICATED USE OF SPECIFIC PROCESS WASTE STREAM SEGREGATION METHODS
Total number of plants reporting use of one or more of the following methods	20	20
Below grade separate sewers or piping	16	9
Above grade separate sewers or piping	10	9
Diverters	13	8
Collection trough	10	10
Concentric bearings	4	-
Isolate specific process steps	-	9
Collect specific wastewater	-	13
Other	3	5

5. Sludge disposal criteria.

Tannery effluents exhibit a wide range of pollutants and pollutant concentrations. Suspended solids vary from 300 to 14,000 mg/l with an average of 2,000-3,000 mg/l.[30 51] The BOD_5 of tannery effluents can vary from 150 mg/l to 3,000 mg/l, with an average of 1,000 to 2,000 mg/l.[30] Grease concentrations in tannery waste can be as high as 850 mg/l. Sulfide and chromium concentrations also show a wide variation in raw wastes. Normal concentrations of lime and chromium salts do not appear to damage the system; short-term high concentrations could be detrimental to biological activity. High alkalinity and corresponding high pH are caused by lime discharges from beamhouse operations. Such discharges normally are intermittent. Trivalent chrome is used extensively as a tanning agent and hexavalent chrome may appear in trace amounts. Trivalent chromium salts are soluble in acid and neutral solutions. For wastewaters with pH in the range of 8.0 to 10.0, trivalent chromium hydroxides are highly insoluble, in the range of 0.5 mg/l or less, and will precipitate readily in primary clarifiers.

Preliminary treatment operations consist of one or combinations of the following operations and processes:

1. screening;
2. equalization;
3. sulfide oxidation;
4. carbonation of beamhouse wastewaters; and/or
5. ammonia nitrogen removal.

Screening. Fine screening removes hair particles, wool, fleshings, hide trimmings, and other large-scale particulates. While reducing undesirable wastewater constituents, screening contributes to the volume of solid waste which must be disposed. The highly putrescible wastes are commonly disposed of on-site or at remote landfill operations.

Screening equipment includes coarse screens (bar screens) and fine screens, either permanently mounted or rotating with self-cleaning mechanisms. An example is the three-slope static screen made of specially curved wires using the Coanda or wall attachment phenomenon to withdraw the fluid from the under layer of a slurry which is stratified by controlled velocity over the screen. This method has been found to be highly effective in handling slurries containing fatty or sticky fibrous suspended matter[53] and is in use in the leather tanning industry.

The principal function of screening is to remove objectionable material which has a potential for damaging plant equipment and clogging pumps or sewers. To date, much of the screening employed in this industry has not been effective due to poorly operated screens, or screens with openings that were too large, or both. This has

resulted in continuing operational problems, such as clogging of pumps, binding of clarifier sludge rakes, and so on. Therefore effective fine screening is essential in all cases.

Equalization. Equalization of waste streams is important in pretreatment facilities. The batch nature of tannery operations creates wide fluctuations in waste flows and waste strengths. Such variations can be difficult to handle and may result in over- or under-design of the preliminary and secondary treatment units. The volume and strength of waste liquors vary depending on process formulations and scheduling of tannery operations. Alkaline wastes are associated with beamhouse operations, while acid discharges arise from the tanyard. In order to produce optimum results in subsequent treatment operations, the equalization of flow, strength, and pH of strong liquors may be necessary. Although some oxidation may occur, no removal of waste constituents is normally reported for equalization. Equalization basins provide storage capacity for hydraulic balance. Auxiliary equipment must provide for mixing and maintaining aerobic conditions. Detention times should be determined based upon the wastewater generation patterns of the tannery and the requirements of the secondary treatment facility. Typically these patterns run in 24-hour cycles. In addition, most tanneries do not operate more than 5.5 or 6 days per week. Where a POTW does not receive sufficient wastewater to maintain an active biomass in a activated sludge plant, additional hydraulic equalization capacity may be necessary to carry the plant until the tannery resumes production. Basins can be monitored through pH and flow measurement.

An equalization tank or basin is usually fairly large and is most economical at low ratios of height to surface area; size is mainly subject to the fact that effective biological treatment requires retention of wastewater heat. Tanneries with insufficient space for such a tank have another option. This option, in use by at least one tannery, is to schedule wastewater dumps from the tanning facilities according to a wastewater discharge schedule that is designed to smooth the hydraulic loading on the POTW. When scheduling of dumps is combined with equalization tankage providing less than 24 hour detention time, significant improvement in the performance of subsequent treatment processes is obtained.

Sulfide Oxidation. Sulfides in the beamhouse waste constitute a potential problem because they will release hydrogen sulfide if mixed with wastes which can reduce the pH of the sulfide-bearing waste.

The removal of sulfides is not accomplished with plain sedimentation. Sulfides are more satisfactorily removed through oxidation. Various methods for oxidizing sulfides include:

1. air oxidation;
2. direct chemical oxidation;[54]
3. catalytic air oxidation.[54 55 56]

Air oxidation with diffusers provides some removal, but only with excessive aeration times.

Direct chemical oxidation with ammonium persulfate and ozone was studied by Eye and Clement.[54] Ammonium persulfate produced low removals. Ozone was most effective; however, the expense of ozone-generating facilities and developing contact equipment negated further study.[54]

Studies by Chen and Morris[56] revealed that many metallic salts are effective catalysts when compressed air at high temperatures is utilized. Manganous sulfate was the most effective catalyst in the more alkaline solutions at near-ambient temperatures. Nickel, cobalt, and manganous ions also are effective, and potassium permanganate is predicted to work well.[56] Their best formulations achieve complete removal with contact times as short as 15 minutes.

Kessic and Thomsom[57] obtained 95 to 97 percent oxidation of sulfides at contact times of approximately 20 minutes using manganous ion as the catalyst. These solutions were very dilute and achieved residual sulfide levels between 0.3 and 1.0 mg/l. In two studies, Ueno[58 59] obtained between 92 and 100 percent sulfide oxidation using high temperatures, great excesses of air and many different catalyst systems. Among those found to give good results were ferric sulfate, ferric chloride, activated carbon, carbon black, ammonium peroxydisulfate, and hydroquinone.

Eye and Clement[54] found that potassium permanganate plus air, ozone, or manganous sulfate plus air could remove sulfides completely with contact times between 3 and 30 minutes. In this study a first-stage (continuous) flow reactor removed 80 percent of the sulfide, and a second-stage batch reactor removed the rest. An actual tannery waste required 1.5 hours of treatment with potassium permanganate and air. Bailey[55] and Eye[54] further describe the effectiveness of the metallic catalysts. In a laboratory study[54], potassium permanganate was the most effective agent, with manganous sulfate also proving effective. Although the relative costs for the two catalysts favor manganous sulfate, the available space and capital costs for the two different systems will determine which catalyst is the best for a given situation. Optimum results were obtained with a manganese to sulfide weight ratio of 0.15. Pretreatment facilities employing catalytic oxidation should approach 100 percent removal of sulfides.

Available information indicates that the catalytic oxidation process can be designed to remove all dissolved sulfides. However, residual sulfur forms, which are chemically bound to organic matter in the wastewater and therefore not removed by this catalytic oxidation process, can be subsequently redissolved in significant quantities. This reappearance of sulfide could easily occur in a long sewer collection system. Further, alternative sulfide control systems, such as spent liquor reuse, will remove the majority of sulfides, but will

not completely remove sulfides without the addition of catalytic oxidation. Sulfide recovery has been demonstrated at full scale at plant no 444.

Once received in secondary treatment facilities, sulfides are largely removed. However, in order to minimize dangers of potential hydrogen sulfide release and to eliminate the immediate oxygen demand exerted in subsequent biological processes, a catalytic oxidation process is necessary for tanneries with sulfide-bearing wastes.

Catalytic sulfide oxidation can achieve complete removal (not detected) of sulfide. Sulfide liquor reuse or sulfide recovery (as in Tannery No. 444) would assist in removal and provide economic return; however, it is generally considered an optional measure to achievement of complete removal of sulfides.

Carbonation of Beamhouse Waste Stream. Carbonation is effective in the treatment of alkaline wastes. In this process, carbon dioxide reacts with lime to form calcium carbonate, which has a solubility of only 25 to 50 mg/l. The crystalline structure of the carbonate nucleus provides an effective surface for adsorption of organic matter. Suspended solids and BOD_5 are both reduced. Inorganic suspended solids in the form of calcium carbonate are significantly reduced and thus reduce excessive alkalinity, which in turn reduce mixing requirements in activated sludge aeration basins and secondary sludge production and dewatering requirements.

Four U.S. tanneries (numbers 60, 24, 58, 397) have operated flue gas or carbon dioxide carbonation. This technology is used instead of a strong acid, such as sulfuric acid, to reduce the pH of the highly alkaline waste streams from the beamhouse operations. Such pH reduction can be done for a variety of reasons, such as to precipitate excess lime, to neutralize the waste stream, and to provide sufficient pH reduction to allow a substantial degree of protein precipitation. Substantial operating cost savings can be realized by exchanging the cost of acid for the cost of electrical power to operate the carbonation system, primarily the blower.

Stack gas containing 8 to 12 percent carbon dioxide, obtained from any fuel combustion process, can be used. Introduction of gas into the waste stream requires a suitable diffuser system and reaction vessel, and continuous operation of the boilers.

Table 26 indicates removals of suspended solids and BOD_5 for carbonation in conjunction with coagulation to remove dissolved proteins and excess lime. The BOD_5 removals range from 65 to 92 percent, while suspended solids reductions from 79 to 99 percent are recorded.

Field data from tannery no. 24 indicate high reductions in suspended solids, BOD_5, and total alkalinity. Estimated flows from the

cattlehide vegetable tannery were 1,700 m^3/day (0.45 mgd). Primary clarifier overflow rates were about 20.4 m^3/day/m^2 (500 gpd/ft^2) for a chemical system utilizing flue gas carbonation and a combination of iron salts and polymers. (Sulfuric acid was also used to assist pH control). Table 23 presents the removals which were indicated[60]:

Table 23

Performance of Flue Gas Carbonation and Chemical Coagulation

Pollutant Paramater	Influent (mg/l)	Effluent (mg/l)	% Removal
Suspended Solids	2,110	100	95
BOD_5	1,660	270	84
Total Alkalinity (as $CaCO_3$)	640	0	100

Carbonation is attractive for tannery pretreatment facilities, where carbon dioxide is available at the cost of piping from the plant boilers. Removals are high, under proper operating conditions, for suspended solids and BOD_5.

In some instances, pH control is a necessary adjunct to equalization for effective removal of chromium, prevention of sulfide gas evolution, and enhancement of the protein/lime precipitation process. Normally, this has been accomplished by feeding sulfuric acid, lime or sodium hydroxide to lower or raise pH as required. This requires chemical feeding equipment with a pH sensing and control system. Pumping equipment also may be required where tankage or gravity flow constraints exist.

To reduce COD, BOD, nitrogen, dissolved solids, and suspended solids from the beamhouse waste stream, various methods of protein recovery have been successfully demonstrated in tannery unhairing wastes. A typical spent unhairing liquid from a hide processor run contains about 8,000 to 9,000 mg/l of TKN, most of which is contributed by the denatured hide proteins. Likewise, the total volatile solids concentration of 51,000 mg/l (of which 30,000 mg/l are volatile suspended solids and 21,000 mg/l are volatile dissolved solids) reflects the extremely high protein decomposition.

Happich, et al.,[61] demonstrated that a recovery scheme employing: removal of suspended solids by gravity sedimentation, screening, centrifugation and/or filtration; removal of soluble inorganic compounds by dialysis or ultrafiltration; acidification with acetic acid to pH 5.0 and 3.8; and washing and drying; yields a protein fraction of 90 to 92 percent purity. These results were obtained from lime sulfide hair pulping effluent samples from five unidentified

side-leather tanneries which use the high-sulfide, hair pulping process. First, catalytic oxidation of the sulfide liquor removed the sulfides; this was followed by acidification. Acid precipitation to a pH of 4.0 gave the best yield. Sulfuric acid has also been used to precipitate the proteins, as have chrome or pickle liquors. However, care must be taken to avoid the toxic effects of chromium in the protein sources, if the by-product is intended for the feed industry.

Happich reported that approximately 30 percent of the COD (37 percent of BOD_5) present in the untreated hair-burn waste was separated in the solids fraction after a two-stage centrifugation. Another 31.5 percent of the COD (34.9 percent of the BOD_5) ultrafiltration transferred to the filtrate, and 38.5 percent of the COD (28.1 percent of the BOD_5) was actually removed with the protein. According to Happich, effluent COD decreased by 70 percent and 65 percent of the protein in the effluent was recovered. The product could be purified to 90 percent protein by reprecipitation. The amino acid composition did not differ significantly from the protein recovered from un-oxidized lime-sulfide unhairing effluent.

Happich noted that the recovered protein contained the hair. He concluded, however, that the recovered hair protein was low in most of the amino acids found in whole egg protein and would require some supplementation for subsequent use as feed (typically for chickens). Once properly supplemented, autoclaved cattle-hair has proven to be a satisfactory source of protein for feed formulations. If no market for feed formulas exists near a tannery, however, the protein sludge may be dewatered on a gravel bed filter and sold as fertilizer or taken to a landfill site for disposal.

Van Meer experimentally tested segregation of specific process streams for reuse or treatment.[62] Wastewater volume and COD and nitrogen loading were substantially reduced, the former to 3-4 l/kg hide and COD and nitrogen from this source by 89 and 90 percent, respectively. This method carries out the unhairing in the first soaking liquor or in a separate short float. The initial wastewater treatment consists of catalytic oxidation of the sulfides with manganese sulfate and aeration. This is followed by acidification with sulfuric acid and sodium chloride to pH 4.0 and precipitation of the proteins. The resulting sludge is then either dried on a gravel bed or filtered from the effluent in a sand filter. The recovered sludge can be used as a fertilizer or feed source. The COD and TKN in the combined soaking, unhairing and wash liquors after acidification, were reportedly reduced 84 and 86 percent, respectively.

A leather tannery waste management study[34] conducted under an EPA grant in tannery no. 431 reported on experiments in the recovery of crude protein from unhairing liquors:

> "To determine the degree of effluent reduction possible through protein recovery from manganese catalyzed, air-oxidized unhairing

wastes, a sample of oxidized waste from an early...paddle aeration run was sent to the U.S. Department of Agriculture Eastern Regional Research Center in Philadelphia for protein recovery by a modified treatment scheme. Precipitation by acidification of the sample to pH 4.2 yielded a tan color protein of 80% purity.

"Another bench-scale experiment was conducted...to further define the conditions for optimum precipitation of protein and subsequent reduction of contaminant levels.

"Concentrated hair-burn liquor was air-oxidized using manganese sulfate as the catalyst, at a $Mn^{++}/S^{=}$ ratio of 0.15. After oxidation, the liquor contained approximately 160,000 mg/l of total solids, of which 58,400 mg/l was suspended solids.

"Varying levels of concentrated H_2SO_4...were added to eighteen 500 ml aliquots of the oxidized waste. The samples were mixed using a Phipps and Bird laboratory stirrer for 5 minutes at 100 rpm followed by 5 minutes of "slow" mixing at 50 rpm. After settling for 60 minutes, the supernatant liquids were decanted and analyzed for pH, total solids and suspended solids. The pH's, which varied from 0.3 to 9.4, were consistently higher than the expected values. This is most likely due to the times elapsed in the precipitation runs contrasted to the 10-15 minutes required for the original titration. While there is no apparent relationship between supernatant pH and suspended solids (supernatant suspended solids concentrations were consistently within the 280-630 mg/l range except at pH 9.4 where a markedly increased level of 1,670 mg/l was observed) the optimum for reduction of total solids (was found to be)...within the 0.9 to 5.0 pH range.

"The volumes of the resultant sludges varied from 300 ml to 475 ml with the minimum lying within the 1.0 to 3.9 pH range. Fortunately, this range of minimum sludge volume is also within the optimum range for precipitation of protein.

"At pH 3.2, the supernatant analyzed at 100,200 mg/l of total solids (minimum observed for 18 runs) and 401 mg/l of suspended solids. Thus, approximately 75% of the total solids and 99.7% of the suspended solids present in the original, air-oxidized waste sample were transferred to the 300 ml sludge fraction after precipitation and settling.

"Undoubtedly, further sludge dewatering will be required to concentrate those solids which occupied 60% of the original sample volume. Since a portion of the sludge (which contained approximately 80% moisture) dewatered readily by gravity on a 18-mesh screen, dewatering methods recommended for further investigation include gravity screening and sand bed filtration.

Lab-scale attempts at vacuum filtration failed to generate a firm cake indicating that conventional rotary vacuum drum filtration is not a feasible alternative. As indicated (previously) these concentrated hair-burn liquors comprise only a small fraction of the total wastewater flow (i.e., approximately 11,700 gal hair-burn liquor vs approximately 1.5 million gal total daily flow), yet contribute substantially to pollutant loadings. Therefore, it appears from these results that precipitation of crude protein from oxidized unhairing wastes can effect significant reductions in total plant loadings provided adequate methods of sludge dewatering and disposal can be demonstrated."

The effectiveness of flue gas carbonation of beamhouse waste streams is optimal when the pH is lowered to the isoelectric point. When limited to only the introduction of flue gas, the treatment effectiveness of this process will not be as great since the operating pH of the process is higher than the isoelectric point. Removal efficiencies were conservatively selected to represent expected performance in this industry, as follows: BOD_5 - 60 percent, where removals as high as 84 percent were noted; TSS - 65 percent, where removals higher than 95 percent were noted; COD - 60 percent, where removals of as high as 90 percent or more were noted; oil and grease - 70 percent, based upon estimates of removal by plain sedimentation and grease skimming without coagulation aids by flue gas or other chemicals (see Table 25); and TKN - 65 percent, where removals as high as 90 percent were noted.

Ammonia Nitrogen Reduction. Ammonia is difficult to remove from tannery wastewaters. Biological systems which remove BOD have not been effective in removing ammonia. For this level of treatment, EPA considered several alternatives for removing ammonia from deliming wastes by physical-chemical treatment processes. The ammonia introduced into the tannery wastewater stream by the deliming process ranges from 67 to 90 percent of all the ammonia in the raw waste. Thus, substitution for ammonia or treatment of this ammonia containing stream will greatly reduce the final ammonia content of the total wastewater effluent.

These processes assure that the primary ammonia containing stream is segregated and the ammonia removed before it is combined with other waste streams. The segregated ammonia containing stream has a higher concentration of ammonia than a combined stream, and it is therefore easier to treat by physical-chemical methods. The methods considered were:

1. water evaporation followed by crystallization or precipitation of ammonium sulfate;
2. distillation of ammonia;
3. precipitation of ammonia as calcium ammonium phosphate;

4. precipitation of ammonium sulfate by addition of ethanol;

5. reverse osmosis; and

6. ion exchange.

No tannery now uses these methods for treating ammonia wastes. Several of them are technologies used in other industries while others should work because of known chemical principles. Use of alternate deliming agents has been discussed in the In-Plant Control portion of this Section.

Evaporation/Crystallization

Evaporation plus precipitation is a well-known technology and is used to prepare many solid chemical products from aqueous and organic solutions. This technique evaporates water from the deliming waste until the ammonium sulfate concentrates approximately at the saturation value. The ammonium sulfate is then crystallized by cooling the solution and removing an additional small amount of water by applying a vacuum. One disadvantage of this process is that relatively large amounts of water must be evaporated. For example, if the segregated stream contains 1 percent ammonium sulfate, then the concentration of this stream to the saturation point of about 50 percent requires evaporation of about 98 percent of the stream. The evaporated water will contain about 0.2 percent ammonium sulfate if the evaporation occurs at about 95°C. Thus, the percent of the ammonium sulfate removed will range from 60 percent if the original concentration was 0.5 percent to 90 percent if the original concentration was 2 percent. Energy costs are a significant limit on this process.

Distillation

Distillation is well-known and widely practiced. If one component of a mixture has a higher vapor pressure than the others at a certain temperature then boiling the mixture at this temperature will concentrate the more volatile component in the vapor phase. Addition of a strong base to deliming waste will convert most of the ammonium sulfate to free ammonia, which is much more volatile than water. At 25°C ammonia is so much more volatile than water that removal of 90 percent of the ammonia requires evaporating only 8.5 percent of the water; removal of 99 percent of the ammonia requires evaporating only 16.3 percent of the water. It is important to distill at the lowest possible temperature because the relative volatility of ammonia compared to water decreases as the temperature increases. A disadvantage and serious limitation in this method is that the ammonia cannot be economically recovered after distillation and must be vented

into the atmosphere, causing unacceptable odor and consequent air pollution problmes.

Precipitation with Phosphate

The fact that calcium ammonium sulfate is insoluble in water is the basis for predicting the possibility of precipitating ammonia with phosphoric acid if the proper amount of lime is present. The insolubility of the calcium ammonium sulfate salt causes difficulties in the production of the fertilizer ammonium phosphate. It is possible that excess lime would cause an increase in the cost of this process. Calcium phosphate is not very soluble in water and would precipitate from solutions containing lime and phosphoric acid. It may thus be necessary to precipitate excess lime by flue gas carbonation before attempting to remove the ammonia with phosphoric acid.

Precipitation with Ethanol

Ammonium sulfate is insoluble in solutions of ethanol and water if the ethanol concentration is more than approximately 90 percent. Thus, it is possible to predict that ammonium sulfate can be precipitated from water by adding nine parts by weight of ethanol to each part of ammonium sulfate solution. The cost of ethanol, however, precludes further consideration.

Reverse Osmosis

Reverse osmosis can concentrate aqueous solutions of salts. A cellulose acetate membrane suitable for producing fresh water from seawater or brackish water would be suitable also for concentrating aqueous ammonium sulfate. Free ammonia would probably go through such a membrane. Pressure requirements are the main limitation on how much the ammonium sulfate solution can be concentrated. Concentration to even 5 percent would require the use of several hundred psi. Fouling could also be a serious problem. Cost and process limitations preclude this from further consideration.

Ion Exchange

Ion exchange has been used to remove small amounts of impurities from water. To remove ammonium ion, exchange with an acid is necessary. Suitable resins exist, but again fouling could be a serious problem which, along with cost, minimizes the potential for application of this process.

Table 24 Performance of Plain Sedimentation

System	Suspended Solids			BOD			Remarks	Reference
	Inf. mg/l	Eff. mg/l	Removal %	Inf. mg/l	Eff. mg/l	Removal %		
Lagoon	---	---	80-90	---	---	80-90	Fill and draw basins with 24-hour capacity.	110, 111
Sedimentation tanks, mechanical sludge facilities	900	130	86	380	146	63	Pretreatment of vegetable tan liquors. Detention time 9-15 hours.	112
Sedimentation tanks	1,200	370	69	---	---	---	Detention time 2 hours	63
Sedimentation tanks	1,184	680	43	1,046	537	48	Continuous flow (pilot)	113
Sedimentation tanks	1,880	461	67	1,285	873	30	Fill and draw (pilot)	113

Primary Treatment

Plain Sedimentation. Plain sedimentation is concerned with the removal of non-flocculating discrete particles and flotable low-density materials such as grease and scum. Tannery wastes have high concentrations of both suspended solids and grease. As shown in Table 24, suspended solids reductions can range from approximately 40 to 90 percent, while reductions in BOD_5 can range from 30 to 60 percent. Much of the suspended material removed is in the form of insoluble lime which produces a voluminous and heavy sludge. Although grease removals are not indicated, high removals are expected with surface skimmers installed in clarifiers.

Sutherland cites the operation of full-scale plain sedimentation units.[63] Sedimentation reduced the suspended solids content of a side leather tannery by 69 percent, from 1,200 mg/l to 370 mg/l. sedimentation.

Laboratory experiments by Sproul, et al.[64] utilizing beamhouse and chrome liquors showed that plain sedimentation at an overflow rate of 24.5 $m^3/day/m^2$ (600 gpd/ft^2) gave average removals of about 22 percent of suspended solids and 35 percent of BOD_5. Pilot scale experiments by Sproul, et al.[64] show that equalization of plant flows followed by plain sedimentation gave suspended solids and BOD_5 removals up to 99 and 50 percent, respectively. Chrome liquors in excess of 1 percent of the total flow proved to be an effective coagulant for composite wastes containing 2,000 mg/l suspended solids. Overflow rates of 14.3 $m^3/day/m^2$ (350 gpd/ft^2) produced a 2 percent underflow concentration.

Field operations at tannery no. 237 tend to confirm these removals.[30] The primary units consist of two circular clarifiers with overflow rates of 18.8 $m^3/day/m^2$ (460 gpd/ft^2) at an average flow of 3,030 m^3/day (0.8 mgd). No equalization facilities are provided other than mixing in a pump wet well. Cattlehide processing during the sampling period averaged 81,700 kg (180,000 lb) green-salted and brine-cured hides per day for hair pulp beamhouse operations followed by chrome tan and finishing. The following average removals resulted.[30]

Table 25

Pollutant Removals by Plain Sedimentation at Tannery No. 237

Paramater	Influent (mg/l)	Effluent (mg/l)	% Removal
Suspended Solids	3,125	945	70
BOD_5	2,108	1,150	45
Total Chromium	51	24	53
Total Alkalinity (as $CaCO_3$)	980	718	27
Grease	490	57	90

Suspended solids and BOD_5 removals were 70 percent and 45 percent, respectively. A low chromium removal of approximately 50 percent occurred. Higher removals would result if a pH of 8.5 or greater were maintained (using equalization or chemical addition) in the primary clarifiers. If sodium alkali is contributing to the high pH, a pH of 10-10.5 may be needed for best removal. Theoretically, all chrome should precipitate as chromic hydroxide; however, a very small residue is expected. Although chrome removal from the wastewater is desirable, it does create a sludge problem if proper disposal precautions are not taken. Total alkalinity was reduced 27 percent, reflecting sedimentation of suspended lime. Grease removal was 90 percent.

Coagulation-Sedimentation. Chemical addition prior to sedimentation of combined wastewater streams has further increased the removal efficiencies of primary clarifiers. This is a key step in removal of insoluble toxic pollutants, most importantly chromium. Chemical coagulation results in higher removals of suspended solids, BOD_5, sulfides, chrome, and alkalinity through flocculation of colloidal particles. Alum, lime, iron salts, and polymers have exhibited satisfactory results. Table 26 indicated that suspended solids removals from 50 to above 98 percent and BOD_5 reductions of approximately 50 to 99 percent are achieved.

Chemical coagulation followed by sedimentation has been applied at a plant using the chrome tanning process.[64] Raw wastewater analyses indicate concentrations of BOD_5 at 2,500 mg/l and suspended solids of about 2,530 mg/l. The results drawn from the laboratory-scale investigation were shown in Table 26. Other chemical coagulation results were as follows:

1. Use of an anionic polymer at a concentration of 1 mg/l resulted in a reduction of about 84 percent in suspended solids and 60 percent in BOD_5.

2. Adjustment of the waste to pH 9.0 with sulfuric acid and subsequent settling gave average removals for suspended solids and BOD_5 of 90 and 67 percent, respectively.

3. Use of ferric chloride at a concentration of 600 mg/l produced average removals of 60 and 65 percent, respectively, for suspended solids and BOD_5.

4. Ferric chloride coagulation was less effective in removal of suspended solids than was adjustment to the same pH with sulfuric acid.

5. Ferric chloride removes dissolved sulfides, but chemical costs are high.

Table 26 Performance of Coagulation-Sedimentation

System	Coagulants	Suspended Solids			BOD			Remarks	References
		Inf. mg/l	Eff. mg/l	Removal %	Inf. mg/l	Eff. mg/l	Removal %		
Coagulation-Sedimentation									
Plain Sedimentation, Coagulation, Sedimentation	Alum	1,550	68	96	--	--	90*	Adjustment of pH water H_2SO_4	114
Aeration, Coagulation, Sedimentation	Alum	2,500	850	66	3,800	1,030	73	A pilot study with presettling of a portion of the raw waste with adjustment of pH to 5.5. Mixing aerated raw waste with presettled supernatant indicated 93% color removal.	66
Coagulation, Sedimentation	Lime	918	469	49	1,001	476	52	Continuous flow with lime concentrations of 1,490 mg/l.	113
Coagulation, Sedimentation	Lime	1,980	497	75	1,630	823	49	Fill and draw with lime concentrations of 1,700 mg/l.	113
Coagulation, Sedimentation	Lime	3,135	110	95	1,437	619	57	Adjustment of pH with beamhouse liquors. Overflow rate, 25.9 cu m/day/sq m (635 gal/day/sq ft).	115
Coagulation, Sedimentation	Iron Salts	--	--	High	--	--	High	Ferric chloride added at concentrations of 2,000-5,000 mg/l.	117
Coagulation, Sedimentation	Polymer	5,200**	500**	90	--	--	--	Full-scale operation on beamhouse wastes with anionic polymer addition of 10 mg/l. Overflow rates at 65 cu m/day/sq m (1,600 gpd/sq ft).	116
Carbonation									
Equalization, 2-stage Carbonation, Coagulation Sedimentation	Lime	--	--	--	13,400	1,140	92	A pilot study with equalization of flow, carbonation with flue gas to 6.4-6.7 pH. Coagulation with lime followed by 3-hour sedimentation. Effluent is then subjected to a second stage process similar to the first. A 99% reduction in color resulted.	67
Carbonation, Coagulation, Sedimentation	Iron Salts	6,190	58	99	2,180	325	85	A pilot study with carbonation of beamhouse wastes to a pH of 6.0 followed by coagulation with ferric chloride (300-500 mg/l). Treatment produced a flow which settled quickly.	67
Coagulation, Sedimentation	Alum Poly-electrolyte	516	220	57	445	92	79	Full-scale electrophoresis unit.	30
Sedimentation, Grease Flotation	Alum Poly-electrolyte	3,108	1,103	65	14,118	345	98	Full-scale rectangular sedimentation followed by circular.	30
Sedimentation, Carbonation	None	1,766	731	59	2,166	1,238	43	Full-scale four-hour detention.	30

* Oxygen Demand
** Order of Magnitude Values.

6. Coagulation with alum at concentrations less than 500 mg/l after adjusting to a pH of 6.5 reduced the BOD_5 by 90 percent and suspended solids from 45 to 57 percent. Alum concentrations higher than 500 mg/l created a floc that would not settle.

7. Buffing dust resulting from finishing tanned hides was not found to be an effective coagulant.

In general, polymer addition produced a rapid formation of floc, minimizing the need for flocculating equipment. Without pH adjustment, polymers produced consistently higher removals than other coagulants tested.

Sulfides appearing in the pretreatment influent are not completely removed in chemical units. Inconsistent removals are indicated in the literature by researchers.[54 64 65] With pH adjustment to 8.0, an upper limit on sulfide removal may be 90 percent.[64] Sulfide removal reduces oxygen demand and averts hydrogen sulfide problems.

Chromium will precipitate as a hydroxide most effectively at a pH of approximately 8.5. A 90-percent removal in a laboratory study by Sproul, et al.[64] occurred at a pH of 8.0.

In pilot plant coagulation and sedimentation operations described by Howalt and Cavett[66] and also by Riffenburg and Allison[67] 93 and 99 percent removals of color were observed, respectively.

A thesis by Hagan[68], investigated color removal through coagulation and precipitation. In coagulation, inter-particle attraction created by suitable polymer develops a large floc that tends to settle at an optimum pH. Hagan also reported that the common-ion effect assisted in precipitation removal. The basis of this contention is that the high hydroxyl ion concentration at high pH reduces the solubility of color vectors such as digallic acid, which contains hydroxyl functional groups. Addition of coagulants and pH control at this point further increase the relative efficiency. Laboratory results on a vegetable tannery waste indicate high color removals (94 percent) through a combination of chemical precipitation and coagulation with calcium hydroxide and an anionic polymer.[60] The efficiency is dependent on pH control around 12. Many low removal may have resulted from inefficient control of the physical-chemical operations, which require operator attention to be successful.

Based upon the above performance data, the following removals are considered achievable with the implementation of carefully operated coagulation-sedimentation: BOD_5 - 60 percent, where removals as high as 85 percent were noted; TSS - 60 percent, where removals as high as 99 percent were noted. As noted in Table 26, removal efficiencies greater than 90 percent have been noted but not used because of dissimilarities in technology such as the use of two stage systems and use of very high chemical dosages of costly chemicals, such as 5000

mg/l ferric chloride. More conservative efficiencies were chosen since most efficiencies noted were in this range and should be more consistently achievable. COD - 65 percent, a slightly increased removal rate selected by comparison to flue gas carbonation because coagulation in this application can be expected to be somewhat more effective in removing refractory components; oil and grease - 70 percent, expected to be as effective than was plain sedimentation (Table 25 - 90 percent) but the removal efficiency conservatively chosen; and total chromium to a residual of 2 mg/l, because chromium hydroxide is a highly insoluble precipitate, with chromium solubility of less than 0.5 mg/l with a pH of 8.5. This concentration is made more achievable by in-plant chromium recovery which reduces the amount of chromium which must be removed by this treatment process. Plant no. 245 reported concentrations of 1.6 mg/l in combined discharge to a POTW with chromium reuse, and plant no. 233 reported concentrations of 2 mg/l in discharge to a POTW after chromium recovery and coagulation-sedimentation.

"Secondary" Biological Treatment - LEVEL 4

As mentioned previously, preliminary treatment and primary treatment do not remove all of the organic material in a wastewater stream. Most of the BOD_5 and suspended solids can be removed by biological processes which oxidize the organic materials. "Secondary" treatment is also very important to control of toxic pollutants for this industry. Many different systems are known for the biological oxidation of wastewater. In these systems bacterial respiration is the primary method of oxidizing organic substances present in the wastewater. This results in a substantial reduction of the effluent BOD. The higher level of treatment generally includes one or more biological unit processes following primary treatment. Secondary biological treatment technology includes activated sludge, various kinds of lagoons, and trickling filters. Selection of one of these biological treatment systems is influenced by factors such as wastewater constituents, effluent requirements, climatic conditions, site constraints, operating characteristics, and economics. It has been repeatedly observed in tanneries and other industrial operations that waste treatment systems achieve the design effluent quality only if: (1) the design is correct for the wastewater characteristics; (2) the system is not overloaded, (i.e., pollutant and hydraulic loading not more than 100 percent of design specifications); and (3) all components of the system receive regular and necessary maintenance.

Trickling Filter Process. Very few tanneries and some POTW's use trickling filter systems for biological waste treatment. Reasonably high pollutant removal efficiencies are technically possible, yet the positive control needed for high strength waste treatment has not been generally demonstrated.

A trickling filter is an aerobic biological unit. Wastewater constituents are brought in contact with a microorganism mass

developed on the surface of the filter media. To achieve high removals from tannery effluents, toxicity and excessive organic loads must be avoided. Lime deposition on filters also has, in some instances, retarded biological activity. Also, the high strength of tannery wastes requires the provision of a large surface area. Although recirculation and improvements in filter media may reduce overall area needs, waste load reduction may not be consistent throughout the year to meet the demands of future effluent limitations requirements. Temperature is critical in operation. High heat losses can occur in the spray distribution system and across the bed media, yielding low efficiencies. Populations of nitrifying organisms will be suppressed by continual dosing of the system with carbonaceous organic material.

Two tanneries in the southeast have indicated that they are using a trickling filter or trickling filter-like system as one component in their secondary treatment system. Tannery no. 400 uses a rock media filter as the first stage in a two-stage biological system. This tannery does not have an unhairing step. The purchased hides have been previously unhaired and prefleshed. The tannery is a vegetable tannery using the "Liritan" process. Data on the reduction of BOD_5 and suspended solids across the trickling filter is not available.

Another southeastern tannery (no. 24) also uses a trickling filter as the first stage in a two-stage biological system. Operational data reported in 1972 indicated that the plastic media filter was ineffective, with removals of less than 30 percent BOD_5 and suspended solids. Kinman[69] reported improved operation of the overall system by cleaning the media and increasing the air supply to the filter. Confirming data obtained in a recent field survey at Tannery no. 24 indicate that the trickling filter (oxidation tower), including secondary clarification, has the combined performance characteristics displayed in Table 27.

Table 27

Performance Characteristics of Trickling Filter Treatment for Tannery Wastewaters

Pollutant Parameter	Influent to Trickling Filter (mg/liter)	Effluent From Clarifier (mg/liter)	Removal (percent)
BOD_5	270	62	77
Suspended Solids	110	45	59
COD	--	240	--
Total Kjeldahl Nitrogen (as N)	--	210	--
Ammonia Nitrogen (as N)	--	60	--

The flow to the filter was approximately 4,000 m^3/day (1 mgd) including a 50 percent recycle of the secondary clarifier effluent. The BOD_5 and suspended solids effluent concentrations surpass typical secondary treatment system effluents from tanneries. Further reduction in BOD_5 and suspended solids may not be possible due to the colloidal characteristics of the suspended material and the relatively high overflow rate of 37 m^3/day/m^2 (800 gpd/ft^2) in the secondary clarifier.

Trickling filters have limited application in the treatment of high strength tannery wastes. System upsets are common due to organic overload and climatic conditions. Existing filters may be incorporated into systems for treatment prior to a second stage biological system.

Lagoons. Lagoons, also referred to as oxidation ponds or stabilization ponds, have been used for tannery treatment where land is available and where land values are low enough to make lagoon systems an economical alternative to activated sludge. Lagoons serve two purposes: equalization and the provision of a desirable environment for biological activity. In a large lagoon with a long retention time, primary and secondary clarification may be eliminated. Sludge accumulation, however, can reduce the efficiency to the point where it becomes necessary to construct a new lagoon or dredge the old one.

There are three types of lagoons based on the biological environment that exists for the stabilization of organic wastes. These types are:

1. Aerobic Lagoon--Biological stabilization in the presence of oxygen. Included in this category are aerated lagoons which incorporate mechanical methods (i.e., stirring, spraying, or bubbling) to increase the dissolved oxygen content in the lagoon.

2. Anaerobic Lagoon--Biological stabilization in the absence of free oxygen.

3. Aerobic/Anaerobic Lagoon--A stratified lagoon where aerobic activity predominates near the surface and anaerobic activity takes place near the bottom of the lagoon.

In a field demonstration at a tannery in Virginia, Parker investigated aerobic and aerobic/anaerobic treatment of vegetable tanning wastes.[70] The system load was varied by increasing the flow causing the lagoon to go from aerobic conditions to aerobic/anaerobic and finally to predominately anaerobic. With adequate retention time, denitrification, as indicated by reduction of Kjeldahl nitrogen, occurs in aerobic lagoons and the aerobic zone of aerobic/anaerobic lagoons. Parker reports TKN removal of 67 percent in the aerobic lagoon. Nitrification-denitrification is possible in multi-stage

systems. The aerobic lagoon is followed by anaerobic treatment in another lagoon to reduce the nitrate to nitrogen gas, which then enters the atmosphere.

Thirteen tanneries surveyed presently treat their waste with lagoons, either as pretreatment, major method, or finishing step to some other system. Several tanneries indicated that lagoons are only a temporary treatment while other more efficient systems are planned or being built. Eleven of the thirteen tanners use mechanical aeration of their aerobic or aerobic/anaerobic lagoons. Aeration increases dissolved oxygen content and thereby reduces retention time or lagoon size, which saves on land requirements. Four tanners have aerobic/anaerobic lagoons while three others are equipped with multi-stage aerobic and anaerobic lagoons. Nearly all (85 percent) provide screening of wastewater and 38 percent are using plain sedimentation or coagulation-sedimentation as a primary treatment before discharging into lagoons. Several tanners reported adding phosphoric acid to provide an adequate nutrient balance for effective biological activity.

A major disadvantage of using aerobic lagoons to treat tannery wastes is the decrease of efficiency during the winter months, especially in the northern states. In addition, ice cover can inhibit aerobic conditions. A northeastern tannery (no. 401) reported the data in Table 28, which exemplifies the seasonal variation in effluent quality from their lagoon system:

Table 28

Aerobic Lagoon Performance as a Function of Season

Pollutant Paramter	Summer and Fall (mg/liter)	Winter and Spring (mg/liter)
BOD_5	15	98
COD	176	398
TSS	19	85
Cr	0.7	3.5
Grease	26	43
TKN	39	65
Sulfide	0.2	0.8

This data typifies the shortcoming of aerated or aerobic lagoons for treating leather tanning wastewater. The extensive surface area for heat dissipation and the low solids (microbial population) content of the lagoons precludes consistently good effluent quality during winter months.

Anaerobic lagoons are usually covered to retain the heat so they are less affected by low ambient temperatures. A scum layer of grease may

accumulate on the surface to reduce heat loss and ensure anaerobic conditions. Polyvinyl chloride, Hypalon™, and Styrofoam™ have been used to cover anaerobic lagoons to retain heat, control odor, and in a few cases to attempt collection of methane gas. For optimum performance and to reduce odor production, the pH of anaerobic lagoons should be kept between 7.0 and 8.5. Anaerobic lagoons are used by the tanning industry as one part of a system and not as the sole treatment method.

Under the proper biological conditions, i.e., pH control, sufficient nutrients, etc., and with long retention times (usually requiring large amounts of land in relation to plant size), lagoons can provide consistent effluent quality in warmer climates. Land values and availability dictate whether lagoons are more economical than alternate treatment systems. In colder climates winter operation can never approach summer treatment efficiency, unless they utilize costly covers, or the system has sufficient storage capacity to hold several months discharge.

Activated Sludge Systems. The activated sludge process is one of the most controllable and flexible of all secondary treatment systems. It is applicable to almost all treatment situations and plays a very important role in this industry for treatment of toxic pollutants. With proper design and operation, high organic removals are possible. Designs based on solids retention time (SRT) afford optimum residence time for solids with minimal hydraulic retention. However, pilot studies are required to establish appropriate design parameters defining the relative rate of biological growth and decay with a given wastewater.

Basically, the activated sludge process consists of: mixing of returned activated sludge with the waste to be treated; aeration and separation of the activated sludge from the mixed liquor; and disposal of the excess sludge. Activated sludge is typically preceded by some form of primary treatment, especially in tannery applications. Variation in pretreatment may include the use of equalization, sulfide oxidation, chrome precipitation, sedimentation or clarification, and some form of screening.

Based on the influent and effluent data from samples collected and analyzed during this program, BOD_5 removal varied from 89 to 98 percent for activated sludge systems. Suspended solids removal ranged from 90 to 98 percent. BOD_5 measurements of filtered samples indicated the significance of solids removal and hence the importance of the size and design parameters for the final clarifier. Successful operation of the activated sludge treatment system depends on a number of factors such as: continuity and uniformity of feed by means of equalization, whether provided by a separate equalization tank or by the design of the aeration basin, maintenance of nutrient balance and high mixed liquor solids in the aeration basin, and final

clarification designed for very low overflow rates for removal of suspended solids.

Tannery no. 237 in Minnesota has initiated full activated sludge operations for an estimated 3,600 m^3/day (0.95 mgd) flow from a chrome tanning, hair pulp facility with finishing operations. The project was partially financed through an Environmental Protection Agency grant. The system at Tannery No. 237 uses screening, plain sedimentation, activated sludge, final clarification and sludge filtering.

The combined tannery flows are screened, then pumped to dual plain sedimentation basins. The 12-m (40-ft) diameter clarifiers are equipped with surface skimmers. Four concrete lined lagoons are used as activated sludge aeration basins. Each lagoon has a capacity of 3,875 m^3 (1 mil. gal.) at 1.8 m (6 ft) operating depth, which may vary in operation. Three lagoons are operated in parallel and the fourth lagoon functions as a sludge digestor. An aeration capacity of 60 hp per lagoon was installed. Return sludge design permits recycle to each lagoon as well as ahead of the primary clarifiers. Aeration and digestion are followed by final sedimentation in two 12-m (40-ft) diameter clarifiers. The effluent is chlorinated prior to discharge to a nearby watercourse. Primary sludge and waste activated sludge are dewatered in a pressure filter and landfilled on-site. Automatic samplers permit monitoring of individual treatment units to ensure better operational control.

Data for this activated sludge system at plant no. 237 shows more than 90 percent removal of BOD_5 in the summer months and 90 percent removal of suspended solids (final effluent BOD_5 concentrations ranged from as low as 8 mg/l to as high as 489 mg/l); BOD_5 and suspended solids removal decrease somewhat in the winter. Wintertime removal efficiencies are: BOD_5--89 percent; suspended solids--88 percent. EPA believes that these results do not accurately reflect the achievable final effluent concentrations (i.e., BOD_5 and TSS) of activated sludge systems since a number of design and operational factors contributed to poor performance, such as lack of equalization, very shallow aeration basins with inadequate mixing, under designed secondary clarifiers, frequent changes in experimental mode of operation, presence of significant quantities of sulfides from primary treatment, and other factors.

EPA evaluated a full-scale activated sludge plant in a Kentucky tannery (No. 47) in a two-week study. This tannery is a cattlehide tannery with pulp hair beamhouse operations and alum tanning with some chrome and vegetable tanning. At the time of the study, flow was 61 m^3/day (0.016 mgd). The treatment system consists of screening, primary clarification, extended aeration activated sludge, and secondary clarification. Primary treatment includes a rotating, coarse screen followed by fine screening and 24-hour equalization. Overflow rates of 13.6 and 13.4 $m^3/day/m^2$ (290 and 285 gpd/ft^2) were

observed in primary and secondary clarifiers, respectively. Hydraulic detention time averaged 1.6 days in the aeration basin.

Additional data from sixty months of operation indicate long-term average effluent performance in the range of 60 mg/l of BOD_5 and 95 mg/l of TSS. Variability showed no seasonal influence, but rather the influence of equipment failures or shock waste loads. This is especially significant since all system equipment is located in a flood plain and is therefore above ground and exposed to the elements, thus exacerbating the potential for temperature influence.

An activated sludge facility in New York (tannery no. 320) is presently treating effluent from a save hair beamhouse, chrome tan, finishing, and rendering operations. Total wastewater from these processes is about 1500 m^3/day (0.4 mgd). Combined flows are screened prior to equalization. The equalization basin had a 24-hour capacity in 1974. The unclarified discharge from the equalization basin is directed to an aeration basin with approximately 12-hour detention with an organic load to the basin of about 3600 kg per day per 1000 m^3 (220 lb BOD_5/day/1,000 ft^3). The final clarifier has an overflow rate of 24 to 28 m^3/day/m^2 (500 to 600 gpd/ft^2).

An organic removal of 80 percent produced an effluent BOD_5 concentration of 343 mg/l and suspended solids reductions of 92 percent. Effluent suspended solids concentrations of 190 mg/litre reflect ineffective solids capture in the final clarifier. The pH of the effluent is 8.0 to 8.5. The most interesting aspects of these treatment operations are the high pH of waste entering the aeration basin and the high mixed liquor suspended solids concentration maintained in the aeration basin. In many cases, a pH above 11.0 is seen as potentially toxic to biological activity. However, carbon dioxide derived from organism respiration is adequate to reduce the pH to about 8.0, at which point biological stabilization occurs. Since primary clarification is not provided, all suspended solids in the tannery waste go directly to the aeration basin. All solids capture must, therefore, occur in the final clarifier. The most important fact to note is that from the start of operation, the treatment plant was overloaded compared to the design of the system. Further, some difficulty in solids capture in the final clarifier was experienced. In spite of the very high effluent concentrations, variability and upsets were not related to winter conditions.

Removals of 89 percent for BOD_5 and 90 percent for suspended solids were observed during a sampling visit for toxic pollutants at plant no. 320. However at the time samples were taken the skimmer in the clarifier was not working properly and was by actually stirring up the water, it was decreasing the removal efficiency. Furthermore, no chemicals were in use except lime and ferric chloride as sludge dewatering filter aids.

A related biological treatment technology is the oxidation ditch. The oxidation ditch is essentially a modified form of the activated sludge system. Applications of this process on domestic waste treatment are numerous in Europe. A full-scale installation at Oisterwijk, Netherlands, has successfully treated chrome tannery wastes since 1973. This system is called the Carrousel system. In tannery treatment, the wastes were directed to an oval ditch or "race track" for aeration. Separate equalization facilities were not required since the ditch provides excellent equalization. An adjustable immersion dish aerator operates in a localized and limited volume of the channel and imparts oxygen to the wastewater and regulates the velocity of flow in the channel. The effluent is clarified prior to discharge with the sludge returning to the aeration zone. The oxidation ditch operates in the extended aeration mode (one day hydraulic detention or greater) and at high mixed liquor solids. The resulting food-to-microorganism (F/M) ratio is very low. At these low F/M ratios (0.05), long detention time, and high sludge age, endogenous respiration minimizes the amount of waste sludge.

Data for the first year operation of the Carrousel system on leather tanning waste at a hydraulic load of 1800 m^3/day is summarized in Table 29.

Table 29

Carrousel System Performance for Leather Tanning Wastewater

Pollutant Parameter	Raw	Secondary Effluent	Percent Removal
BOD_5	1100	20	98
COD	3390	249	93
Cr	19.5	0.27	99
Total N	408	270	34
NH_4-N	264	248	5

This fully-operational European Carrousel treated the flow from a side leather tannery using 25,060 kg per day of green-salted hides (55,200 lb/day). The tanning process produced 1800 m^3/day (0.475 mgd) of wastewater from pulp hair, chrome tan, and finishing operations. Hydraulic detention time in the oxidation ditch varied from 2 to 3 days, and the rate of activated sludge return was estimated at 75 percent. Production of secondary sludge was about 0.3 kg (lb) dry solids per kg (lb) BOD_5 applied, or 0.55 kg (lb) dry solids per kg (lb) BOD_5 without primary sedimentation. The organic load on the ditch varied from 23.5 to 48.2 kg BOD_5 per day (51.8 to 106.2 lb BOD_5 per day). The oxygen supplied was about 1.75 times the average requirement, however. This was sufficient for peak demands. High removals of BOD_5 (98 percent) and COD (88 percent) result at the low F/M ratio.

Sulfides were completely oxidized with the aeration supplied and chrome precipitation was highly effective, with concentrations below 1 mg/l observed in the effluent. Nitrification was sporadic, with some denitrification through the liberation of nitrogen gas.

High removals of BOD, COD, suspended solids, chromium and detergents resulted from the operation of the Carrousel tannery waste treatment facility. Efficiency did not decrease during the winter months.

This same system was recently installed at a shearling tannery (no. 253) in New England. This Carrousel system treats 300,000 gallons per day of primary effluent. During a very cold period (even for New England) from December 1976 through February 1977, average influent and effluent BOD_5 concentrations were 341 mg/l and 8 mg/l, respectively. Ammonia concentrations in the influent and effluent were 32 mg/l and 8 mg/l, respectively. This indicates that this activated sludge system produced better results than the Netherlands application, including demonstration of nonsensitivity to winter temperatures in removing carbonaceous oxygen demand (BOD_5) and nitrogenous oxygen demand (ammonia) by nitrification. This system, like the activated sludge system at tannery no. 320, operated at high mixed liquor suspended solids (6,000 - 15,000 mg/l).

These results have been further corroborated by a POTW in New England treating greater than 90 percent of its waste load from tannery no. 50. This POTW is a high rate (F/M greater than 0.1) short hydraulic detention time (approx. 12 hrs.) activated sludge system. During the first year of operation (1976), final effluent quality was poor due an extended acclimation period and to lack of familiarity with the operational idiocyncracies of the plant. After operational procedures were refined, effluent BOD_5 concentrations improved dramatically, from an average range of 102-393 mg/l to a range of 49-67 mg/l. In fact during the very cold winter months of 1976-1977, effluent BOD_5 quality improved to 34 to 45 mg/l. Since that time tannery flow has increased well beyond the design limits for extended periods of time, but better operating skills have maintained average BOD_5 effluent quality below 80 mg/l. Therefore, the basic feasibility of the activated sludge process and the importance of diligent operation have been firmly demonstrated.

Activated sludge systems, including various modifications, have been and can be effective in organic reductions to low BOD_5 concentrations even under low temperature conditions. Removals of suspended solids prior to final effluent discharge and maintenance of a large quantity of active biomass in the aeration basin, especially during winter months to compensate for lower rates of organism activity, appear to be dependent on conservative design and diligent operation of the final clarifier.

Based on the discussion above, treatment of process wastewaters by a high solids, low F/M, extended aeration activated sludge system is

appropriate for the leather tanning industry. The performance of primary coagulation-sedimentation followed by activated sludge biological treatment has been established primarily by plant no. 47, as noted in Section IX of this document. The long-term performance (annual average) for this plant is BOD_5 - 60 mg/l, and TSS - 95 mg/l. With the addition of in-plant control and preliminary treatment (i.e., chromium recovery, ammonia substitution, catalytic sulfide oxidation, flue gas carbonation of segregated beamhouse wastewaters, and water conservation/reuse), the Agency believes that this long-term performance is improved primarily due to longer hydraulic detention times and reduced pollutant loads. Additional rationale is presented in Section X. The Agency has conservatively estimated the achievable long-term concentrations in the effluent from this secondary biological process as follows: BOD_5 - 40 mg/l; TSS - 60 mg/l; total chromium - 1 mg/l; oil and grease - 14 mg/l; TKN - 30 mg/l; ammonia - 10 mg/l; and phenol - 0.25 mg/l. For residual COD an effluent concentration of 250 mg/l was determined from a ratio of COD to BOD_5 developed from biological treatment data during an EPA study.[71] This relationship is displayed in Figure 3. For BOD_5 concentrations below 160 mg/l the plot approximates a straight line. Achievable COD concentrations for technologies which generate effluent BOD_5 concentrations below this value have been determined using the BOD_5 concentration and Figure 3.

Rotating Biological Contactor. The rotating biological contactor (RBC) consists of a series of closely spaced flat parallel disks which are rotated while partially immersed in wastewaters being treated. A biological growth covering the surface of the disk adsorbs dissolved organic matter present in the wastewater. As the biomass on the disk builds up, excess slime is sloughed off periodically and is settled out in sedimentation tanks. The rotation of the disk carries a thin film of wastewater into the air where it adsorbs the oxygen necessary for the aerobic biological activity of the biomass. The disk rotation also promotes thorough mixing and contact between the biomass and the wastewaters. In many ways the RBC system is a compact version of a trickling filter. In the trickling filter, the wastewaters flow over the media and thus over the microbial flora; in the RBC system, the flora is passed through the wastewater.

The system can be staged to enhance overall waste load reduction. Organisms on the disks selectively develop in each stage and are thus particularly adapted to the composition of the waste in that stage. The first stages might be used for removal of dissolved organic matter, while the latter stages might be adapted to nitrification of ammonia.

The RBC system was developed independently in Europe and the United States about 1955 for the treatment of domestic waste, but found application only in Europe, where there are an estimated 1,000 domestic installations.[72] The use of the RBC for the treatment of industrial wastes in the U.S. has been under evaluation for some time.

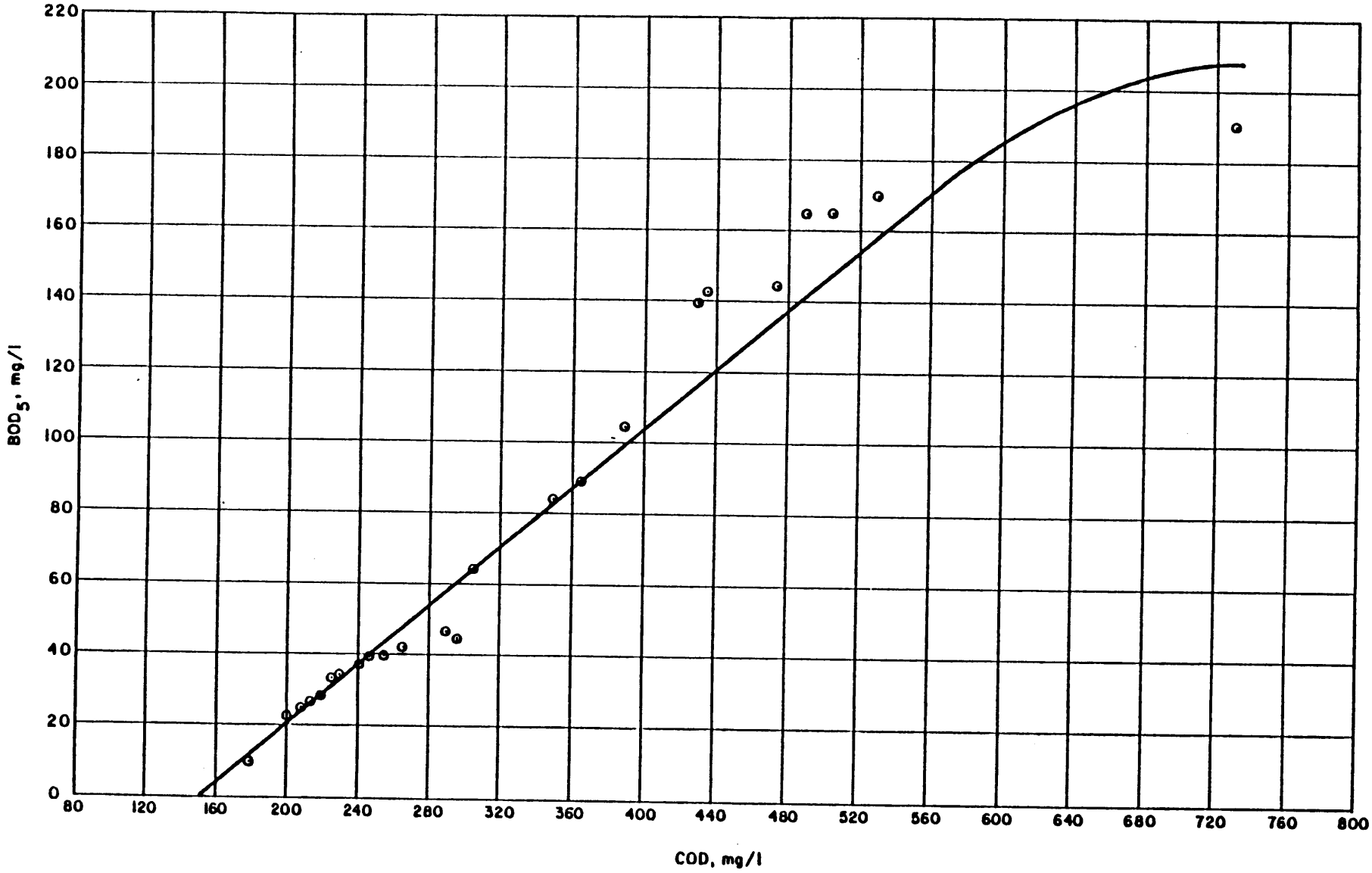


Figure 3. COD to BOD5 Ratio in Tannery Secondary Effluents

Source: Reference # 71 (Figures 65 & 69)

Bench scale tests have been made on tannery wastewater. Other pilot scale results on meat packing waste showed a BOD_5 effluent concentration of approximately 25 mg/l.[73]

Data from one of the suppliers of RBC systems indicate ammonia removal of greater than 90 percent by nitrification in a multistage unit.[73] Four to eight disk stages with maximum hydraulic loadings of 61 l/day/m^2 (1.5 gpd/ft^2) of disk area are considered normal for ammonia removal with final ammonia concentrations as low as 2.0 mg/l or less.[74]

Rotating biological contactors with secondary clarifiers could be used as a substitute for an entire aerobic system. The number of stages required depend on the desired degree of treatment and the influent strength. More typical applications of the rotating biological contactors, however, may be for polishing the effluent from biological processes, nitrification of effluents, and as pretreatment prior to discharging wastes to a municipal system. A BOD_5 reduction of 98 percent is reportedly achievable with a four-stage RBC.[72]

The major advantages of the RBC system, as indicated by the suppliers of this equipment, are its relatively low first cost; the ability to stage to achieve dissolved organic matter reduction with the potential for removal of ammonia by nitrification; and its resistance to hydraulic shock loads. Disadvantages are that the system should be housed in cold climates to maintain high removal efficiencies and to control odors. Although this system has demonstrated its durability and reliability for domestic wastes in Europe, its use on several industrial wastes in the United States has not yet established a high degree of confidence in this technology.[73]

Nitrogen Control. Nitrogen control is provided through the process of nitrification-denitrification, as described below.

Nitrification.

Nitrification is the biological conversion of nitrogen in organic or inorganic compounds from a more reduced to a more oxidized state. In the field of water pollution control, nitrification usually is referred to as the process in which ammonia as ammonium ion is oxidized to nitrite and nitrate sequentially. When aeration systems are used to treat an industrial wastewater, some nitrification can be expected to occur naturally, thus reducing the quantity of ammonia requiring further removal.

Adequate process design and operating control are necessary for consistent results. Factors that affect the nitrification process include concentration of nitrifying organisms, temperature, pH, detention time, dissolved oxygen concentration, and the concentration of any inhibiting compounds.[74]

Nitrifying organisms are aerobic and adequate dissolved oxygen (DO) in the aeration system is necessary. DO concentrations should be above 1 to 2 mg/l to assure consistent nitrification. Nitrification is affected by the temperature of the system. Available information provides conflicting data on the systems' performance at low temperatures. Although detailed studies are lacking,it should be possible to achieve nitrification at low temperatures and compensate for slower nitrifying organism growth rates by maintaining a longer solids detention time and hence larger nitrifying active mass in the system.[76]

The optimum pH for nitrification of municipal sewage has been set between 7.5 and 8.5. Nitrification can proceed at low pH levels, but at less than optimum rates. During nitrification, hydrogen ions are produced and the pH decreases, the magnitude of the decrease being related to the buffering capacity of the system.

The removal of nitrogen compounds from a tannery waste stream is important because these compounds: exhibit an oxygen demand similar to that of BOD; provide nutrients for plant organisms in the receiving water body, increasing eutrophication rates; and may present a significant hazard to aquatic organisms.

Biological oxidation of organic and ammonia nitrogen to nitrites and nitrates is accomplished by only two bacteria types, nitrosomonas, which convert ammonia and organic nitrogen to nitrites, and nitrobacter, which convert nitrites to nitrates. The growth conditions necessary for these bacteria can be supplied by conventional secondary activated sludge systems, although longer detention times are required, generally resulting in larger systems for BOD control, especially at low operating temperatures.

Very little data exists on nitrification toxicity effects. Sulfides under BPT conditions should be reduced to a concentration of 1 mg/l, a level below concern for either nitrifying bacteria. Chromium, which is reduced to a level of 2 mg/l after chromium recovery and combined primary treatment, is of potential concern since one source[77] lists chromium toxicity at levels of 0.25 mg/l. While actual test data is limited, the acclimatization of organisms should tend to mitigate any problem with chrome toxicity. Removal of phenol and other potentially toxic organic chemicals in the primary and first stage along with the acclimatization of the organisms of activated sludge to the tannery wastes should permit effective nitrification.

Nitrification rates are reported to be dependent on temperature. One reference[78] states that proper nitrification occurs only at temperatures of at least 12 to 15°C. One successful application of nitrification has been demonstrated at a rendering plant in Ohio. This is a conventional activated sludge system which uses two consecutive aeration tanks in series prior to secondary clarificatin and multi-media filtration. The system operates at a temperature of

at least 55°F (12.8°C) even on the coldest days by virtue of the high raw wastewater discharge temperature associated with the rendering process, estimated at 90°F (32°C); and on extremely cold days, by covering the tops of the aeration tanks with boards. Tanneries discharge raw wastewater at temperatures approximating 70°F (21°C) in winter, and thus the expectation would be that lower temperatures may occur in a tannery nitrification system. Heat addition is also possible as an alternative but would increase operating expense unless waste heat recovery (such as stack gas heat) were employed. Only during the coldest time of the year in the northern locations should temperature maintenance be of concern.

To operate successfully, nitrifying bacteria must have proper pH conditions (7.5 to 8.2) and nutrients (such as calcium, magnesium, phosphorus, copper, and iron).[78] These requirements, if not present in tannery wastewaters, will have to be provided by chemical addition. Only pH control and phosphorus addition are expected to be needed for normal tannery wastewaters.

Physical-Chemical Processes - LEVEL 4A

Chappel Process. The Chappel process is a patented physical-chemical process for treating wastewater streams. The basis for this process is the assumption that all waste streams contain components which flocculate or settle in the proper environment. The process consists of dividing the wastewater stream into two equal parts, treating one part with the acid solution (mineral acids, aluminum sulfate, and oxidizing chemicals) and the other with the alkaline solution (sodium hydroxide, forms of dissolved aluminum, and oxidizing chemicals), and then reuniting the divided waste streams. Some flocculation and solids formation takes place when the acid solution and the alkaline solution are added to the separated parts of the waste stream. Additional flocculation and solids formation takes place when the two parts of the wastewater stream are reunited. The reunited wastewater stream flows into a series of two or more settling tanks. The wastewater and sludge entering each of the tanks is initially agitated and allowed to settle. Supernatant and sludge are pumped counter-current through the series of settling tanks. Agitation in each tank mixes settled sludge with the wastewater. According to Chappel, the sludge aids the flocculation and settling of pollutants in the wastewater stream. The wastewater stream from the final settling tank is passed through a sand or multi-media filter and discharged to the receiving waters. Some of the sludge from the first settling tank is recycled to aid flocculation and sedimentation and the remainder is removed for disposal. It has been indicated that this sludge has no oxygen demand and is sterile; however, it may require dewatering.

The Chappel process was used to treat less than 100,000 gallons per day of wastewater from a retan facility (no. 247). In this installation, there were nine settling tanks (existing idle tankage used in part), and only 25 percent of the effluent is passed through a

rudimentary sand filter. The other 75 percent is discharged directly to the receiving river. It is particularly noteworthy that this system was housed within the tannery itself. This is very important to plants which have very limited adjacent land available for installation of equipment.

The effluent quality from this installation far surpassed state permit requirements. This process is highly effective in removing pollutants from tannery no. 247 wastewater, as shown in Table 30. It is obvious that this application of physical-chemical treatment was highly effective in removing toxic pollutants (see also Table 36, Section X) including chromium, and conventional and nonconventional pollutants.

Table 30

Treatment of Wastewater with Chappel Process at Tannery No. 247

Pollutant Parameter	Typical Influent Value (mg/l)	Typical Effluent Value (mg/l)
BOD_5	700 - 800	3 - 10
COD	1200 - 2700	20 - 40
TSS	300 - 800	6 - 11
TKN	120 - 270	3 - 6
NH_3	60 - 160	1 - 3
O&G	110 - 280	4 - 9
Cr	16	less than 0.1

Process effectiveness has been tested in treating tannery wastes from three other tanneries. Results are summarized in Table 31.

Table 31

Performance Summary of the Chappel Process Treating Tannery Wastewaters

Pollutant Parameter	Influent Value (mg/l)	Effluent Value (mg/l)
Tannery No. 57		
BOD_5	1800	5 - 70
Sulfide	70	0.1
Tannery No. 409		
Chromium	20	0.1
Sulfide	1.8	0
Tannery No. 213		
Chromium	40	0.1
Sulfide	1	0.2

Wastewaters with significantly higher BOD_5 may require a modification of the process to obtain effective treatment. The modification consists of operating two systems in series; the first removes the bulk of the pollutants, while the second "polishes" the wastewater. This process is also being used to treat a paper mill waste, although data is not currently available.

On a long-term basis, the Agency conservatively estimates that this physical-chemical treatment system will produce the same effluent concentrations as can be produced by a PAC upgraded (Level 5) and multi-media filtered (Level 6) activated sludge system. Both the physical-chemical (Level 4A) and biological treatment (Level 4) systems are preceded by in-plant control (Level 1), preliminary treatment (Level 2), and primary treatment (Level 3), which will produce pretreated effluent concentrations similar to or lower than those listed in Table 30 as "Typical Influent" at plant no. 247. The long-term treated effluent performance (concentrations-mg/l) is conservatively estimated by EPA to be somewhat higher than represented in Table 30 because the available data from plant no. 247 was not for a sufficient length of time to estimate effluent variability. The estimated concentrations are as follows: BOD_5 - 14 mg/l; TSS - 16 mg/l; COD - 180 mg/l; oil and grease - 6 mg/l; total chromium - 0.33 mg/l; TKN - 15 mg/l; ammonia - 5 mg/l; and phenol - 0.1 mg/l.

Color Removal. Vegetable extracts and syntans used in the production of leather comprise only a small percentage of the total waste volume, however, spent vegetable tanning solution can be responsible for a major portion of the organic content and most of the color agents in a total wastewater discharge.

Several factors relating to the chemical structure of the color agents were considered significant in efforts to reduce color by Nemerow.[79]

Tomlinson, et. al.[80] conducted laboratory investigations with mimosa (wattle) extract with lesser amounts of quebracho and chestnut bark extracts. Two commercial syntans, Orotan TV (a phenolic syntan) and Leukanol D-48 (an acid or naphthalene syntan), were also used in the blend. A small amount of sodium bisulfite was added to accelerate the adsorption of tannin by the hide protein collagen. These six ingredients, mixed in the proper proportions with water amounting to about 75 percent of the total weight of the solution, constituted the stock tanning solution.

During the course of the investigations, the following treatment techniques for the removal of color were evaluated: oxidation with sodium hypochlorite, use of lime or alum, and coagulation with organic polymers.

Color removal from the vegetable tanning solution was achieved under the treatment conditions developed in the course of the research. The treatment scheme, as described in Tomlinson and applied to an actual tannery, would involve the following sequential steps:

1. Segregation of the spent vegetable tanning liquor.

2. Addition of sulfuric acid to reduce the pH of the solution below 3.0.

3. Addition of a predetermined dosage of a preselected cationic organic polyelectrolyte and, at the same time, continued addition of sulfuric acid to maintain the pH below 3.0.

4. Slow mixing to provide sufficient contact time for maximum color removal.

5. Sedimentation for approximately 30 minutes.

6. Decantation of the treated supernatant, at a regulated rate, to the remainder of the waste flow from the tannery for further treatment, if needed.

7. Withdrawal of the sludge for further dewatering, if required, and disposal.

Tomlinson summarizes his study as follows:

> "A commercially available cationic polymer was used successfully for color removal in the research. The optimum dosage was on the order of 30 mg/l. (This procedure resulted in a reduction in color of more than 90 percent). Concurrent with the excellent

color removal, significant reductions were observed in the COD (50 to 60 percent) and suspended solids (85 to 90 percent).

"Sludge amounting to approximately 30 percent of the original volume of the tanning solution is produced as a result of the need to remove the color and reduce the other pollutants. It was shown in this research that the sludge resulting from coagulation at a pH of approximately 2.5 to 3.0 settled better and had greatly improved dewatering characteristics compared with sludges resulting from treatment at higher pH levels.

"The economic feasibility (of this technology) would depend on the characteristics of the waste, the effluent requirements, and the cost of achieving them by other methods. For a given real situation, complete laboratory studies would have to be made with various polyelectrolytes to determine the combination of polyelectrolyte, dosage, pH, mixing time, flocculation time and settling time that would produce the desired results at least cost. Because characteristics of tanning solutions vary, it is to be expected that optimum treatment combinations would also vary."

Upgrading Biological Treatment with Activated Carbon - LEVEL 5

The use of activated carbon in treating industrial wastewaters has been generally successful depending on the application, the soundness of engineering, the degree of proper operation and maintenance, and the performance criteria established for the system. According to Cheremisinoff[81] "adsorption studies indicate that most of the EPA-proposed dissolved organic toxic chemicals can be removed from the water by activated carbon (and) other similar chemical contaminants (aromatic, nonpolar, high molecular weight), such as OSHA-defined carcinogens and the chemicals under examination by EPA for inclusion on the toxic substances list are also predicted to be adsorable from wastewater by activated carbon."

Cheremisinoff explains further:

"Adsorption makes possible the purification of wastewater streams containing only small amounts of impurities that would be difficult to clean by other means and at an attainable cost. Carbon is the most versatile of the solid adsorbents and finds the widest application in both air and water pollution control. The use of activated carbon for removal of organic compounds from air and water streams has a long history of successful use, being one of the most efficient organic removal processes available.

"The ability of activated carbon to adsorb material either from gases or from liquids stems from its highly porous structure. Each particle consists of a vast network of interconnecting pores of a variety of sizes. The highly porous structure results in a

very large surface area, providing many sites upon which adsorption of molecules can take place. Normally, adsorption on activated carbon is the result of physical attraction of molecules to the carbon surface by van der Waals forces. As a rule, molecules with higher molecular weights experience greater forces of attraction than materials of lower molecular weights. Hence, activated carbons, aside from the effects of molecular screening due to the sizes of the pores, have a preference for higher molecular weight substances.

"When a granule of activated carbon is placed in contact with a mixture of gases, the higher molecular weights are preferentially attracted to the carbon where they are adsorbed. When a granule of activated carbon is placed in contact with a liquid mixture, there is a similar tendency for higher molecular weight substances to be adsorbed. However, in the liquid systems the situation is more complicated. In liquid systems, activated carbon tends to have a preference not only for substances which are of higher molecular weight but also for those substances that are non-polar in nature. Thus, there is a particular affinity for the adsorption of non-polar organic molecules from polar solvents such as water.

"The forces of attraction between the carbon and adsorbate molecules are greater for adsorbate molecules which are similar in size to the carbon pores. The most tenacious adsorption takes place when the pores are barely large enough to admit the adsorbate molecules. The smaller the pores with respect to the molecules, the greater the forces of attraction. The pores cannot be so small, however, that the adsorbate molecules find it difficult to enter, or the adsorptive capacity for those molecules will be greatly reduced. Although the effects are not completely understood, it is known that the presence of elements other than carbon can have a considerable influence on a carbon's adsorptive capabilities. Particularly important is oxygen, which can exist in a variety of chemically combined conditions with the surface carbon atoms. These oxygen groups appear to increase the affinity of the carbon for polar compounds and decrease its selectivity for non-polar compounds.

"Carbon adsorption systems are of two types-regenerative and nonregenerative. For operations in which daily carbon requirements are large or under constant use, granular carbons offer the advantage of established methods of regeneration which greatly reduce carbon replacement costs. Powdered carbons offer advantages in applications where the daily carbon requirements may not be large enough to warrant installation and operation of on-site regenerative equipment. It is also possible that some specific adsorptive capacity may be available in certain types of powdered carbon."[81]

Powdered carbon is mixed directly with the liquid to be treated. This 'slurry' is then agitated to allow proper contact. Finally, the spent carbon, carrying the adsorbed impurities, is filtered or settled out. In practice, a multiple-stage, counter-current process is commonly used to make the most efficient use of the carbon's capacity.

A relatively new application of powdered activated carbon (PAC) is being tested and evaluated in combined carbon-biological systems, because of the ability of activated carbon to improve the performance of biological systems. This concept is now undergoing extensive testing, using powdered carbon material in activated sludge systems.[82] The carbon is metered into the system with the influent at a concentration normally less than 100 mg/l. It is recirculated and purged along with the biological solids at a rate which maintains an equilibrium concentration of 1000-2000 mg/l. Since the powdered carbon is added directly to the activated sludge process, this eliminates the need for carbon-adsorption beds or columns.

Powdered carbon may provide some of the following benefits when added to activated sludge systems:

1. improved toxic pollutant removals;
2. improved organic pollutant removals, including BOD, COD, and TOC;
3. more uniform operation and effluent quality, particularly during periods of widely varying organic and hydraulic loads;
4. decreased effluent solids and thicker sludges resulting in reduced sludge handling costs;
5. adsorption of organics, such as detergents, oils and dyes that are refractory to the biological system;
6. protection of the biological system from toxic waste components;
7. more effective removal of phosphorus and nitrogen;
8. increased effective plant capacity at little or no additional capital investment;
9. savings on operating costs resulting from reduced defoamer, coagulant and power requirements; and
10. greater treatment flexibility than other methods since carbon dosages can be varied to match waste strengths and flow rates.

Powdered carbon improves treatment in the activated sludge process because of its adsorptive and physical properties. Carbon adsorbs the pollutants and oxygen, localizing them for bacterial attack. Because the aerobic reaction is dependent upon the concentration of the reactant, this localizing effect serves to drive the reaction further towards completion, resulting in improved BOD removal.[83] Many pollutants that are not biologically degraded in a conventional activated sludge system would be degraded if they were in contact with the biomass for a longer period of time. When adsorbed by the carbon, these molecules settle into the sludge. Contact time is thereby extended from hours to days. This results in lower effluent COD and TOC.

High density powdered carbons improve solids removal in secondary clarifiers. This results in lower effluent suspended solids and also a reduction in BOD. Under high organic load conditions which normally would lead to sludge bulking, the dense carbon will act as a weighting agent keeping the sludge in the system. A doubling of sludge volume indexes in systems where carbon addition is practiced is not uncommon. Both the use of greater sludge mass and the extended retention of slowly degraded compounds by the carbon give more time for the compound to be biologically stabilized. When dispersed biofloc results due to low organic loads, carbon serves as a seed for floc formation, preventing loss of solids under these conditions. Phosphorus and nitrogen removals are reportedly enhanced.

Powdered carbon can be added at any convenient point in the activated sludge process to get it into the reaction section. It is not necessary to add carbon continuously in most cases. Batch addition at any time of day is generally satisfactory. A dense, easily wetted carbon can be added dry or slurried with water. In fact, the very nature of the slurried carbon in a solution provides extremely intimate and thorough contact between the carbon particles and the solution being treated--more so than with granular carbon treatment. Chemical coagulants can be added along with the carbon to provide simultaneous removal of colloidal organics.

The effectiveness of powdered carbon as an additive to improve activated sludge treatment has been demonstrated in a variety of industrial applications and at POTWs. These improved operating properties of activated sludge as demonstrated in other applications covers wastewaters with similar characteristics. For example, both leather tanning and petroleum refining wastewaters are pretreated prior to biological treatment and PAC addition. Pretreated wastewater in both industries also contain toxic pollutants. Therefore, it is EPA's belief that PAC addition is transferable because of the exact duplication of the technology as used in other industries to wastewaters that are similar; and that the performance of this technology is also transferable.

This type of treatment has gained acceptance in the last four years and is currently an essential part of treatment at 60 to 80 plants. These plants range in size from 10,000-gpd package units located along the Alaska pipeline to a fully integrated 40-mgd powdered activated carbon treatment system (PACT).[84]

The PACT process involves a continuous addition of powdered activated carbon to the aeration tank. Buildup in the aeration tank occurs (a function of the sludge retention time), providing a substantial reservoir of carbon in the system. The continuous addition of fresh carbon to the aeration tank allows the process to adsorb nonbiological organic matter present in the wastewaters, thereby providing a degree of advanced treatment concomitant with normal secondary treatment. A recent study[85] indicated that powdered activated carbon addition to activated sludge systems provides exceptional resistance to shock-loading by trichlorophenol, presumably due to the large reservoir of carbon carried in the MLSS. Trichlorophenols occur in most tannery wastewaters at concentrations ranging up to about 10 ppm in the raw wastewater. A study[86] completed on organic-chemical wastewater indicated that the PACT system was economically preferable in achieving the desired effluent quality to columnar, granular and activated-carbon systems, both preceding and following activated sludge.

Data pertaining to effectiveness of the PAC treatment system in removing toxic pollutants indicates good performance for many organic constituents. Removal in excess of 95 percent for total phenol was observed through the treatment system, producing an effluent concentration of less than 0.02 mg/l.[87]

The addition of PAC to an activated sludge system was investigated on a pilot scale to improve the treatment of petroleum refinery wastewater. It was found that "effective removal of oil and colloidal solids in the pretreatment step is necessary for successful operation." In addition, cost effectiveness was achieved by "operating at a very high sludge age and a low carbon dose." The higher sludge age did not result in the deterioration of settling characteristics. A decrease in effluent variability was noted which was attributed to enhanced nitrification at low temperatures and dampening effects of increased hydraulic loading to the activated sludge plant. In addition to effective removal of ammonia (less than 1 mg/l), PAC addition was responsible for reductions of 65 percent for soluble organic carbon and 95 percent for phenolics with a residual concentration of less than 0.02 mg/l.[86]

A similar study was conducted by another refinery which was interested in improving conventional activated sludge systems. Accomplished with pilot plant units, increased sludge age (from 10 to about 50 days) in combination with powdered carbon addition was found to be a potential alternative to installing costly granular activated carbon columns to treat secondary effluent. With good pretreatment, upgraded activated

sludge proved effective in reducing ammonia, oil and grease, and phenols to median levels of less than 4.0, 5.0 and 0.1 mg/l, respectively.[88]

In the poultry processing industry, addition of powdered carbon at a southern commercial poultry processing plant improved effluent quality and process control.[89] A full-scale evaluation of powdered carbon treatment began in August 1974. In this plant, two activated sludge units treat an average of 400,000 gallons during a 10-hour working day. The poultry waste passes through air flotation treatment prior to activated sludge treatment. Polymer is continuously fed to secondary clarifiers to improve solids settling. Sludge solids are removed periodically (every 3-4 weeks) and transported to drying beds.

The variable flow in this system, attributable to normal processing operations, caused frequent sludge bulking, high effluent solids, and variable effluent quality prior to use of powdered activated carbon. Three aerobic lagoons were required for further organic removal. Prior to carbon addition, the activated sludge effluent averaged 35 ppm suspended solids, 70 ppm oil, 7 ppm BOD_5, and 24 ppm ammonia-nitrogen.

During the monitored period, influent to the activated sludge system averaged 254 ppm BOD_5, 95 ppm oil, and 129 ppm suspended solids. Dissolved oxygen levels of 8-11 ppm were maintained in the activated sludge aeration basins. Powdered carbon was maintained in the aeration basins at an equilibrium level of 1,000-1,200 ppm. This required a daily addition of 10-15 ppm based on influent to make up the carbon lost during sludge wasting. After carbon addition, variability diminished and overall quality improved. Average effluent solids decreased 60 percent to 12 ppm, BOD_5 decreased 57 percent to 3 ppm, oil decreased 70 percent to 21 ppm, and nitrogen decreased 83 percent to 4 ppm. Assuming that the influent analysis made during the control period is typical of normal plant operation, the overall reduction in BOD_5 was 99 percent; oil, 77 percent; and suspended solids, 91 percent.

The basis for estimating the performance of activated sludge with PAC addition started with the long-term performance of activated sludge as previously described under "Secondary" Biological Treatment - Level 4, preceded by in-plant control (Level 1), preliminary treatment (Level 2), and primary treatment (Level 3). The range of removal efficiencies and final effluent concentrations after PAC addition in the above referenced applications served to guide EPA's estimates of removals in this case. As summarized in Table 32, EPA estimates that biologically stablized leather tanning effluents can be upgraded by about 50 percent for BOD and 60 percent for TSS. This nominal level was chosen because the pilot and full scale studies were performed on biologically stabilized wastewater in other industries where the characteristics of the tested effluent was similar to treated leather tanning wastes.

PAC upgraded biological treatment will yield the following concentrations: BOD_5 - 20 mg/l, or approximately 50 percent removal where 60 percent removal or more has been reported; TSS - 25 mg/l, or approximately 60 percent removed where similar removals but substantially lower effluent concentrations were achieved; COD - 195 mg/l, as developed by the COD to BOD_5 relationship (see Figure 3); oil and grease - 10 mg/l, or approximately 50 percent removal where effluent concentrations as low as 5 mg/l were reported; (total) chromium - 0.5 mg/l, or approximately 50 percent removal estimated somewhat less than TSS removal due to residual TSS and fine, insoluble chromium which may carry over from secondary clarifiers; TKN - 20 mg/l and ammonia - 5 mg/l, or approximately 50 percent reduction where greater removals and effluent concentrations as low as 4 mg/l were reported, and where nitrification without PAC addition at plant no. 253 has produced ammonia concentrations very close to these concentrations; and phenol - 0.1 mg/l, which is a concentration achieved by this technology in the petroleum refining industry.

A full-scale demonstration of this technology is now underway at tannery no. 253 and additional data will be reviewed by EPA.

Table 32

Incremental Increase in Summary of Performance of Activated Sludge by Powdered Activated Carbon Addition [86 87 88 89]

Parameter	Demonstrated Incremental Increase in Efficiency (percent)	Effluent Conc. (mg/l)	Estimated Increase in Efficiency (percent)	Estimated Conc. (mg/l)
BOD_5	57	3	50	14
TSS	60	12	60	16
Oil and Grease	70	5	50	6
Ammonia	83	4	50	5
Phenol	95	0.1	60	0.1

Table 33

Summary of Multi-Media Filtration Performance [119]

Parameter	Range of Incremental Increase in Performance (percent)	Effluent Conc. (mg/l)	Estimated Increase in Performance (percent)	Estimated Effluent Conc. (mg/l)
BOD_5	50	6	30	14
TSS	45 - 77	5	35	16

Multi-Media Filtration - LEVEL 6

With the exception of gravity sedimentation, deep-bed filtration is the most widely used unit process for liquid-solids separation. Deep-bed filters have been employed in systems for phosphorous removal from secondary effluents, and in physical-chemical systems for the treatment of raw wastewater.

Filtration has been applied in a wide variety of municipal and industrial applications. In most cases, filtration is used for separation of residual suspended solids after biological treatment.[103 105 118 119] Filtration is also being used in the leather tanning industry for separation of residual biological and inert solids which may include PAC with adsorbed toxic organic compounds and insoluble heavy metals such as chromium. Therefore, EPA believes that multi-media filtration technology is transferable, and that the same range of performance demonstrated in other applications is also transferable to the leather tanning industry.

Waste containing suspended solids passes through a filter containing granular material resulting in the capture of suspended solids in the bed. Eventually, the pressure drop through the bed becomes excessive or the ability of the bed to remove suspended solids is impaired. The filtration cycle ceases and the bed is backwashed prior to its return to service. In an ideal filter, the size of the particles should decrease uniformly in the direction of flow. This condition is partially achieved with the use of a multi-media deep bed filter. This type of filter uses materials with different densities ranging from large size particles with the lowest densities at the top of the filter and small particles with the highest densities at the bottom of the filter. With this arrangement, the filter has a large storage capacity for suspended solids, and is able to remain in operation for longer periods of time. Influent solids should be limited to about 100 mg/l to avoid too frequent backwashing. Effluent suspended solids are normally less than 10 mg/l.[118] Filtration can also accomplish removal of free oil, and to a limited degree, emulsified oil. Where

concurrent removal of suspended solids is necessary, filtration can be effective.

A summary of the typical performance of several applications of filtration applied on activated sludge and other biologically stabilized effluents is given in Table 33. From these data, EPA finds that a reasonable estimate of achievable performance by filtration is 30 percent removal of BOD_5 and 35 percent removal of TSS. For purposes of applying this technology to PAC upgraded effluent quality (Level 5), the following conservative long-term performance is achievable with multi-media filtration of upgraded activated sludge effluent: BOD_5 - 14 mg/l, or approximately 30 percent removal; TSS - 16 mg/l, or approximately 35 percent removal; oil and grease - 6 mg/l, or approximately 40 percent removal.

A lower removal efficiency for TSS (35 percent) than noted in the literature was considered appropriate because of the low operating range of long term average effluent concentration in this industry (less than 20 mg/l), and the very fine solids which must be separated. A somewhat lesser efficiency for BOD_5 removal (30 percent) was conservatively estimated because of the low operating range of concentration (less than 20 mg/l) and for lack of more extensive data. Oil and grease removal efficiency was estimated to be approximately 40 percent because residual oil and grease after biolgocial treatment is likely to be associated with suspended solids, and thus removed at an efficiency comparable to TSS. Other effluent concentrations were estimated as follows: COD - 180 mg/l, as developed by the COD to BOD_5 relationship (see Figure 3); TKN - 15 mg/l, or approximately 25 percent removal due to removal of residual insoluble proteinaceous TKN with TSS; ammonia - 5 mg/l, or no change since filtration does not enhance nitrification; (total) chromium - 0.33 mg/l, or approximately 35 percent removal which is the same as the anticipated removal of TSS; (total) phenol - 0.1 mg/l, or no change since phenol is removed by biological treatment and none occurs in filtration. These values were chosen as representative of the performance to be expected on similar biologically stablized leather tanning wastewater where the residual biological solids, inert PAC particles and oil and grease are amenable to physical separation.

Granular Activated Carbon Columns - LEVEL 7

The properties outlined during the discussion of powdered activated carbon are also pertinent to granular activated carbon (GAC). Rather than being mixed in a slurry, granular carbon is packed in beds or columns. The water to be treated is then either filtered down or forced up through the beds. In this manner, each successive layer of carbon acts to remove impurities, with maximum adsorption taking place in the early stages of contact and less and less taking place as the gradually purified solution continues on until (if the bed is sufficiently deep) all adsorbable organic impurities are removed. In

some cases, suspended matter (via filtration by the carbon) as well as dissolved pollutants (via adsorption) can be removed simultaneously.[91] As noted by Cheremisinoff[81], carbon adsorption has a wide range of applicability to wastewaters with residual dissolved organic compounds of high molecular weight (i.e., chlorinated phenols) which must be removed. For this reason, EPA believes that GAC are transferable to application in this industry.

Minor[82] describes the benefits of activated carbon treatment as follows:

> "The properties of many organic chemicals complicate conventional biological treatment. Activated carbon can be an attractive alternative. It offers the following advantages over biological systems for many wastes:
>
> 1. insensitivity to toxics (and will in fact remove most toxic organics);
> 2. less sensitivity to temperatures;
> 3. less time required for start-up;
> 4. higher removal of BOD, COD, and TOC for many (but not all) wastes; and
> 5. effectiveness in streams with high dissolved solids.
>
> "Since it can be regenerated and entrainment into the wastewater can easily be prevented by screens, the granular carbon has been chosen over powdered carbon in the majority of applications. The technology for evaluating the applicability of granular activated carbon and the ability to design commercial systems from pilot data are well established.
>
> "The ability of activated carbon to be regenerated for economical reuse is a distinct advantage. Both powdered and granular carbons are capable of being regenerated by existing technology. Granular activated carbon is regenerated thermally at temperatures of 1600-1800°F. Due to the high hardness and resistance to attrition of coal-base granular carbon, system losses of 5-8 percent per cycle are commonly experienced. Powdered activated carbon is also regenerated thermally at 1600-1800°F. applications."[91]

However, a major inhibition to the widespread use of granular activated carbon has been the high capital cost of installing thermal regeneration facilities in small installations. A possible solution to this problem has been developed by a major chemical company whereby customers can lease carbon adsorption systems at a guaranteed monthly charge. The company assumes the responsibility for regeneration at central facilities.

As mentioned previously, granular carbon has been chosen over powdered carbon in the majority of full-scale industrial applications. Adsorption equipment consists of adsorbers or columns holding the granular activated carbon beds through which wastewater flows. They can be designed for pressure or gravity flow to achieve the desired contact time of the water and carbon. Suspended solids and space considerations are also a factor in adsorber configuration. When suspended solids are present, they will be filtered out on the carbon bed. This dual purpose of carbon beds can be usefully employed as long as the adsorbers are designed to accommodate backwashing and bed cleaning procedures, such as air scour and/or surface wash.

Performance criteria for the application of activated carbon columns should be developed from continuous on-line pilot scale (or larger) apparatus for any complex wastewater. Because of the waste-specific nature of adsorption, an approach to evaluating activated carbon performance from on-site investigations has been developed.[92] Although the published document is directed towards the organic chemicals and plastics industry, the general approach can be applied to most wastewaters including those generated by leather tanners.

The effectiveness of granular carbon adsorption in treating industrial waste was reviewed by D. G. Hager.[93] Examples of TOC, color, and phenol removal were demonstrated for 107 different industrial sources. Fifteen plants have operated for two years, meeting the adsorption design objectives. In addition to the wastewater survey conducted by Hager, a selected number of adsorption isotherm tests were conducted on synthetic samples of water containing toxic chemicals as defined by EPA. Other data in the literature[94] [95] [96] [97] suggest that carbon adsorption should be an effective treatment method for organics similar to the designated toxic chemicals, including a wide range of organophosphorus compounds, and polycyclic aromatic hydrocarbons.

Based on the adsorption isotherm test results in the initial 1973 survey[93], several plants elected to follow up with pilot studies. Fifteen plants installed adsorption systems; the results of these studies are summarized in Table 34. In those cases where the TOC effluent appears high, the carbon is being used to remove chemicals prior to conventional biological treatment. These are chemicals that are toxic in nature and would have a tendency to inhibit or destroy the biological activity of the system. The data also reveal that in every case some form of pretreatment, such as equalization, pH adjustment or filtration, was used prior to carbon adsorption. All rely on off-site reactivation of the carbon where both rotary kilns as well as multihearth furnaces are employed.

To achieve advanced treatment of secondary effluent from an organic chemical manufacturing complex, granular activated carbon columns following trimedia filtration were selected based on extensive pilot plant data.[98] The in-place biological treatment system was operating

Table 34 Adsorption Treatment Systems

Waste	Flow 1,000 gal/day	Pretreatment	Contact Time min.	Influent	Effluent	Percent Removal
Phenol	50	Settling, Equalization, Mixed Media Filtration	165	200	0.1	+ 99
Surfactant	50	Equalization	165	300	5	98
Chlorinated Hydrocarbons	1,000	Equalization	8	4	0.05	99
Organic Intermediates	20	Equalization, Filtration	412	4,000	1,000	75
Phenol	200	Equalization	41	600	100	83
Surfactant	15	Clarification	550	6,000	1,000	83
Herbicide	20	pH Adjustment	412	10,000	100	99
Terpene	72	Equalization	120	1,200	300	75
Phenol	350	Biological, Mixed Media Filtration	24	800	0.05	+ 99
Dispersed and Dissolved Dyes	150	Equalization, pH Adjustment, Diatomaceous Earth Filtration	55	High Color	100 AMPHA	
Benzene	150	pH Adjustment	55	1,500	30	98
Phenol	150	Sand Filtration, Settling	55	1,200	1.0	+ 99
Phenol	500	Biological Settling, Multi Media Filtration	33	80	1.0	87
Herbicide	300	Settling, Filtration	55	1,500	150	90
Chlorinated Aromatic	6	Chemical/Reduction	1,375	6,000	3,000	50

effectively in removing BOD, COD and TOC from the complex wastewaters; however, the removal of color, odor and toxic constituents was necessary. In addition, suspended solids required further reduction.

At another chemical manufacturing plant, the effluent from a coagulation-sedimentation step is fed directly to the carbon columns for removal of organic impurities. Most notable is the reduction of phenol which consistently over several years averaged better than 99 percent.[99] Spent carbon is directed to a reactivation furnace for regeneration.

Filtration of the effluent from biological treatment systems prior to introduction into carbon columns is an accepted practice to minimize clogging of the columns. Application of carbon columns in this industry is after filtration (Level 6) and upgraded activated sludge biological treatment (Level 5). Granular activated carbon columns should yield residual concentrations for the significant pollutant paramters as follows: BOD_5 - 6 mg/l; TSS - 3 mg/l; COD - 165 mg/l; oil and grease - 2 mg/l; total chromium - 0.25 mg/l; TKN - 14 mg/l; ammonia - 5 mg/l; and phenol - 0.1 mg/l. All of these effluent concentrations are estimates based upon literature data, with the exception of: (total) chromium - 0.25 mg/l, or approximately 25 percent removal attributable to removal of residual TSS, to approach the limits of chromium solubility.

Membrane Technology

General Various membrane processes that are finding interest in pollution control applications as end-of-pipe treatment and for in-plant recovery systems are ultrafiltration, reverse osmosis, and electrodialysis. Although these processes are available for producing a concentrated solution from a relatively dilute feed, each process tends to occupy a specific region of application due to economic as well as technological considerations.

In contrast to the membrane processes of reverse osmosis or ultrafiltration, however, electrodialysis employs the removal of the solute (with some small amount of accompanying water) from solution rather than the removal of the solvent. Another major distinction is that only ionic species are removed. The fact that only ionized salts will be removed allows for the simultaneous separation of these substances from any neutral or un-ionized organic matter that may be present. Although these features are similar to ion exchange, the advantage is that in electrodialysis the process is continuous, with nothing to be regenerated, hence no chemical additions are required.[100] The process finds usefulness in treating brackish waters, removing dissolved inorganics in 750-7500 mg/l concentrations, and in some by-product recovery schemes. The necessary equipment is usually compact, and proven plant scale performance exists, both in municipal and industrial applications.

Electrodialysis Ionic components of a solution are separated through the use of semipermeable ion-selective membranes in the electrodialysis process. In water a salt dissolves to produce positively charged anions. If an electrical field is placed across the solution, the cations migrate toward the negatively charged cathode while the anions migrate in the opposite direction toward the positively charged anode. Cation-exchange membranes are permeable almost exclusively to cations, while anion exchange membranes similarly pass only anions. Because of the alternate spacing of cation and anion permeable membranes in the electric field, compartments of concentrated and dilute solutions (salts) are formed. The compartments into which the feed was introduced become the dilution side and the streams exiting from these compartments is referred to as the dilution stream (any organic matter present will remain in this stream). The stream issuing from the concentrate compartments is the brine.

In commercial practice the basic appratus for electrodialysis is a stack of rectangular membranes terminated on each end by an electrode. Flow of the process streams is contained and directed by spacers that alternate with the membranes. The assembly of membranes, spaces, and electrodes is held in compression by a pair of end plates. The apparatus thus resembles a plant-and-frame filter press. Ancillary apparatus, including power supply, pumps, and piping, is conventional except that plastic components are used wherever possible to avoid stray electrical currents and the introduction of metal ions into the process streams.

Since unwanted side-reactions of hydrogen gas and alkali formation take place at the cathode while chlorine and acid form at the anode, these two compartments must be provided with separate flush streams.

Although electrodialysis is not a new process and has, in fact, been used in laboratories since the early 1900's, it was not until after World War II that practical synthetic ion-exchange membranes were developed. Initially, the principal use for electrodialysis outside the laboratory was for brackish water desalination. The first attempt at commercializing electrodialysis was made in the twenties by a German company. This venture was unsuccessful, in part, because of the low level of technological development.

Most of the stable membranes today, however, are based on copolymers of divinyl-benzene-styrene with ion-exchange groups. The cation membranes are mostly of the sulfonic type, while the anion membranes are of the quarternary ammonium type and are usually reinforced with plastic fibers. Newer membranes of perfluorosulfonic acid polymers that have improved stability and chemical resistance are also available.

Most membranes permit operation up to 50 degrees C, although membrane development activity is attempting to raise that limit. The ability of the different types of membranes to withstand pH extremes varies considerably. For example, some are stable in acid environments ranging from 5 to 35 percent H_2SO_4 and from 4 percent up to concentrated HCl. On the alkaline side, some membranes cannot be used at all, while others are claimed to be stable in 50 percent NaOH. Almost all of the electrodialysis membranes are quite sensitive to oxidizing solutions. Some permit short duration exposure to 1 ppm chlorine while needing less than 0.1 ppm for long-term operations.

Fouling of the membranes is the primary disadvantage of the system. This may occur through scaling (the chemical precipitation of salts), which is caused by exceeding solubility limits. Suspended organic matter also needs to be removed down to 50-100 microns. The physical configuration of the electrodialysis stack affects its susceptibility to solids fouling. Iron and manganese should be limited to 0.2 ppm combined. Trivalent ions, such as aluminum and phosphate, may cause increased electrical resistance. Some organic matter, including ionic surfactants (MBAS), and tannic, fulvic, and humic acids, as well as butyrate and larger esters, can cause membrane blockage. To reduce membrane fouling, activated carbon pretreatment, possibly preceded by chemical precipitation and some form of multi-media filtration, may be necessary.

Other limitations to this process are the high initial costs, requirement for skilled labor, high energy costs, need for membrane cleaning and replacement, sophisticated equipment and instrumentation, and the production of excess brine waters.

The principal action of electrodialysis--to concentrate ionic materials--enables consideration of systems which accomplish the following separations: to reduce the volume of brine waste streams; to recover inorganic salts; to remove inorganic salts from waste streams to facilitate further treatment; to separate and recover ionic materials from complex aqueous solutions containing neutral organics; and to concentrate acids.

In the metals industries, electrodialysis can be used to recover metals from plating waste streams.[101] Substantial disposal problems exist from depleted plating baths and rinse waters. Materials such as cyanides of zinc and cadmium can be reconcentrated to bath strength and can be reduced in concentration to very low levels. A closed-loop recovery process[103] incorporating electrodialysis and ion-exchange permits complete recovery of nickel, allows reuse of the dilute stream for rinsing, and recovers the acid required for the regeneration of the ion-exchanges. Copper and chromium have also been recovered from etching processes; while a waste stream of dilute ammonium fluoride from glass etching has been successfully separated and concentrated by electrodialysis for further treatment.

Within the leather tanning and finishing industry, it may prove feasible to remove such trace inorganics as chromium, copper, lead, nickel, and zinc by the electrodialysis process. This remains to be determined, however, through pilot studies on these constitutents in tannery effluents.

Bleaching wood pulp with chlorine or hypochlorite solution yields a copious effluent stream of salty water, the disposal of which has become a significant problem in the paper industry.[104] By the use of electrodialysis, an effluent of 4000 ppm NaCl can be separated into a water stream containing 500 ppm or less of salt and a brine stream of up to 150,000 ppm. The water stream, demineralized to the purity required by the process, is recycled as wash water. The brine stream is electrolyzed in a membrane cell to sodium hydroxide solution and chlorine; these substances may be used directly, or part of each may be combined to form sodium hypochlorite solution. Thus the brine stream is also returned to the process.

By using a process similar to that described above, it may be possible to significantly reduce the total dissolved solids and chloride concentrations present in tannery wastewater. The largest portions of the dissolved solids are sodium chloride and calcium sulfate. Sodium chloride, which can be found in the range of 500-8900 ppm (depending on the category), comes principally from removal of salt or brine from the raw hides by washing and also from salt added in the pickling operation. Used in conjunction with total dissolved solids, the chloride parameter indicates percentages of other dissolved solids. Because of the substantial amount of dissolved solids/chlorides present, electrodialysis may find application in reducing these minor pollution parameters. However, this has yet to be demonstrated on any scale for tannery wastes.

Whenever an effluent stream contains an organic or inorganic ionic material, electrodialysis offers a possible method for recovery, separation, segregation, or concentration of that material, provided adequate pretreatment requirements are consistently achieved. Of paramount importance, of course, is the avoidance of membrane fouling, either by scaling or suspended solids, when considered for tannery applications. Other conditions such as pH fluctuations and dissolved organic solids concentrations must also be carefully controlled if electrodialysis is used in the tannery. Yet, with water recovery rates of 80-90 percent, greatly reduced disposal volumes, the independence of chemical additives and low energy requirements, electrodialysis streams may be an economically feasible means of meeting the parallel challenge of wastewater treatment and recovery through brine concentrations.

Summary of Waste Control and Treatment Technology

The preceding discussion addresses numerous technologies which can be employed in-plant or end-of-pipe to minimize the quantity of

pollutants discharged by tanneries to POTW's or surface waters. These technologies are pertinent to the leather tanning industry because they (1) reflect current practices of the industry, (2) were evaluated during demonstration studies conducted by the industry, or (3) will control or remove selected pollutants. In instances where the control of specific constituents is a primary concern, technology transfer was necessary. An example of this approach is the upgrading of secondary biological treatment with PAC addition. To control toxic organic compounds and heavy metals, EPA assessed this technology from information developed by the organic chemicals and petroleum refining industries and then applied it to leather tanning effluents.

Applicable technologies for the leather tanning industry and their performance were determined upon the best available information. As can be seen from Figures 4 through 8, segregation of the waste streams from the beamhouse and tanyard operations is an integral part of comprehensive waste management for the industry. For subcategories with beamhouse operations, the segregated waste stream will be subjected to sulfide oxidation and flue gas carbonation. Ammonia substitution in the bating process and chrome recovery and reuse are applicable to the tanyard processes. The effluents resulting from these measures, which are defined as Levels 1 and 2, are then combined for equalization followed by coagulation-sedimentation (Level 3). A schematic of the appropriate end-of-pipe treatment technologies, including Level 3, is provided in Figure 9.

The effectiveness of the selected technology scheme which includes in-plant controls and end-of-pipe treatment is summarized in Table 35. For each level of technology through Level 3 (coagulation-sedimentation), long-term performance is shown in terms of percent removal for the selected parameters. Effectiveness for Levels 4 through 7 in removing pollutants is expressed as residual effluent concentrations over a long term.

TOXIC POLLUTANT REDUCTIONS

The list of 129 toxic pollutants is divided into four groups of chemicals: volatile organics, semi-volatile organics, inorganics (primarily metals), and pesticides and PCB's. The first group is primarily composed of chemicals that readily vaporize at ambient conditions. Common solvents such as benzene, toluene and carbon tetrachloride are typical chemicals in this group. Removal of these chemicals from wastewater would occur any time the wastewater is not confined in a completely enclosed container such as a pipe or a full tank. The removal rate is substantially increased by introducing turbulence in the wastewater from any source such as a mixer, an aerator or in cascading flow in a treatment device. The removal of these chemicals as a vapor results in a discharge to the atmosphere.

The second group of chemicals, the semi-volatile organics, includes higher molecular weight organics such as phenol and the substituted

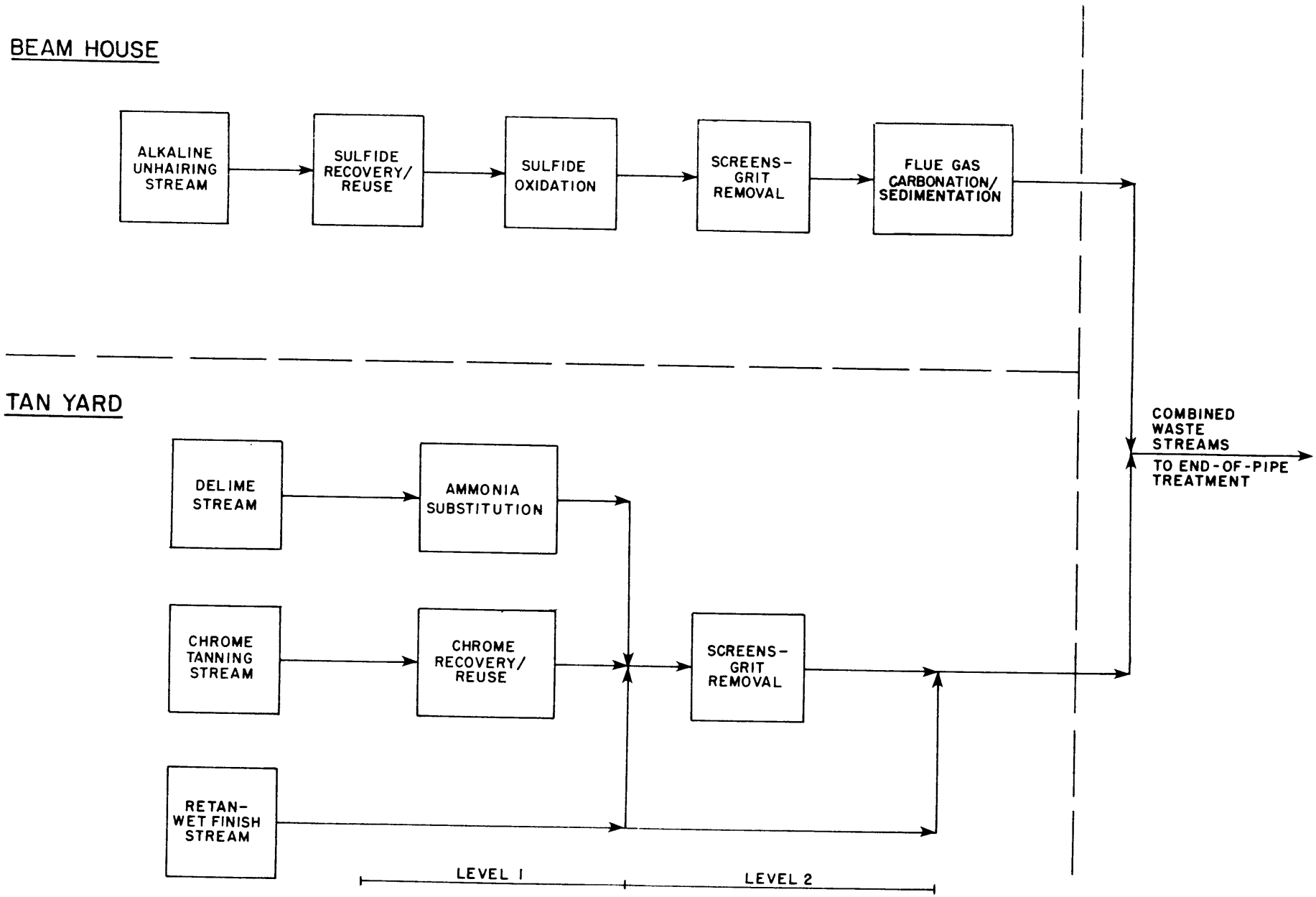


Figure 4. Technology Schematic for In-Plant Control and Preliminary Treatment (Subcategories 1 and 2)

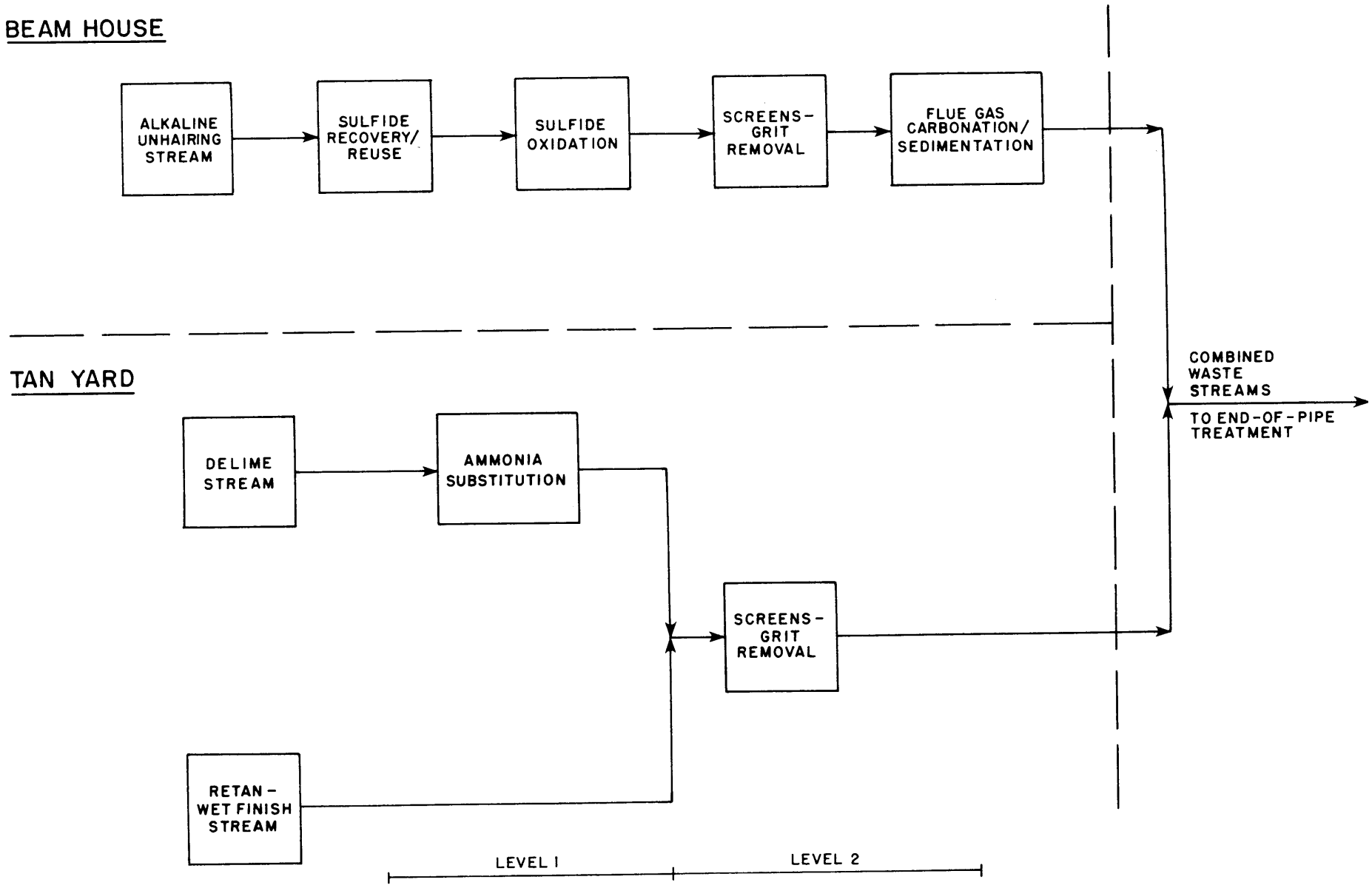


Figure 5. Technology Schematic for In-Plant Control and Preliminary Treatment (Subcategory 3)

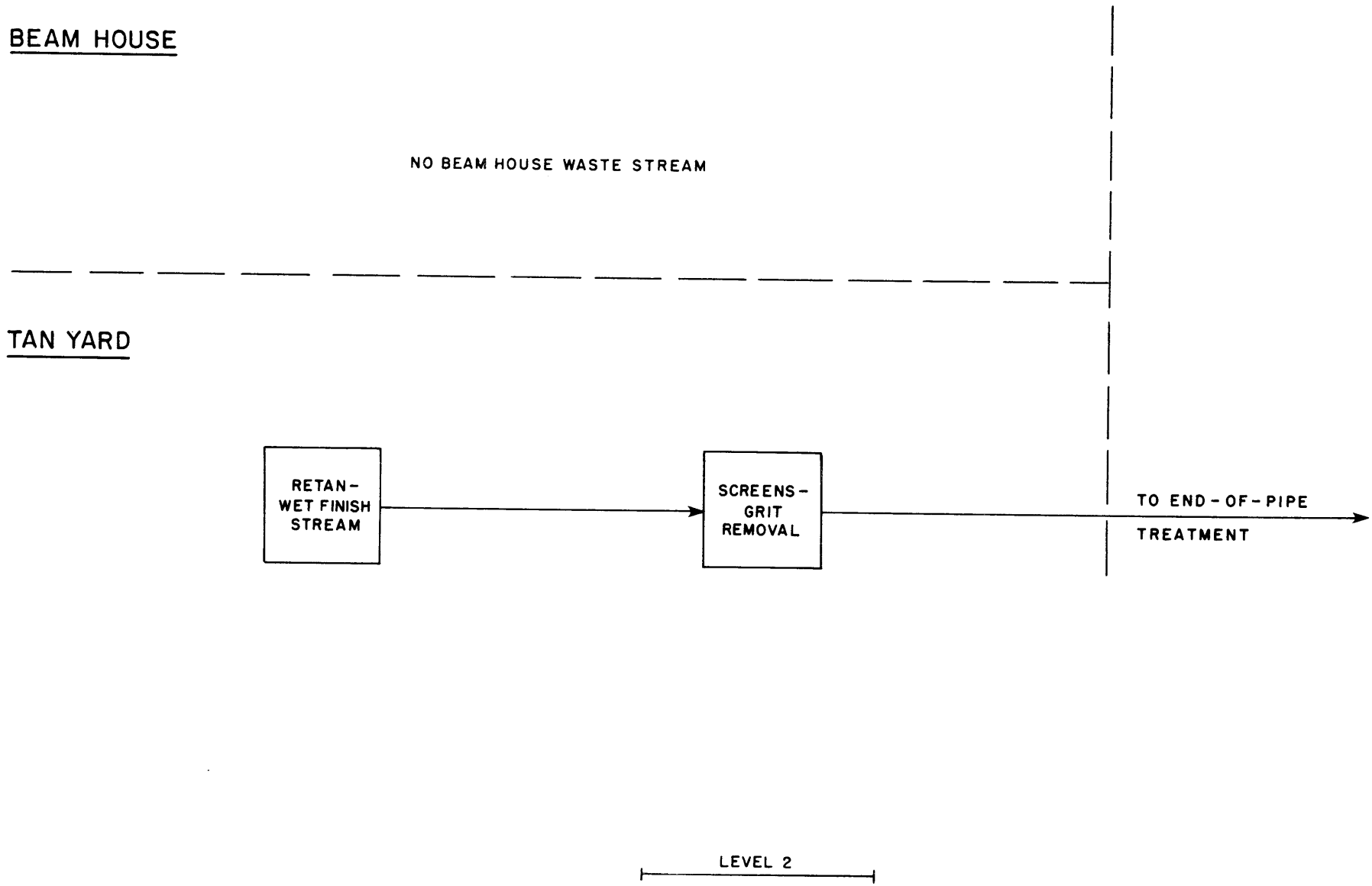


Figure 6. Technology Schematic for In-Plant Control (Subcategory 4)

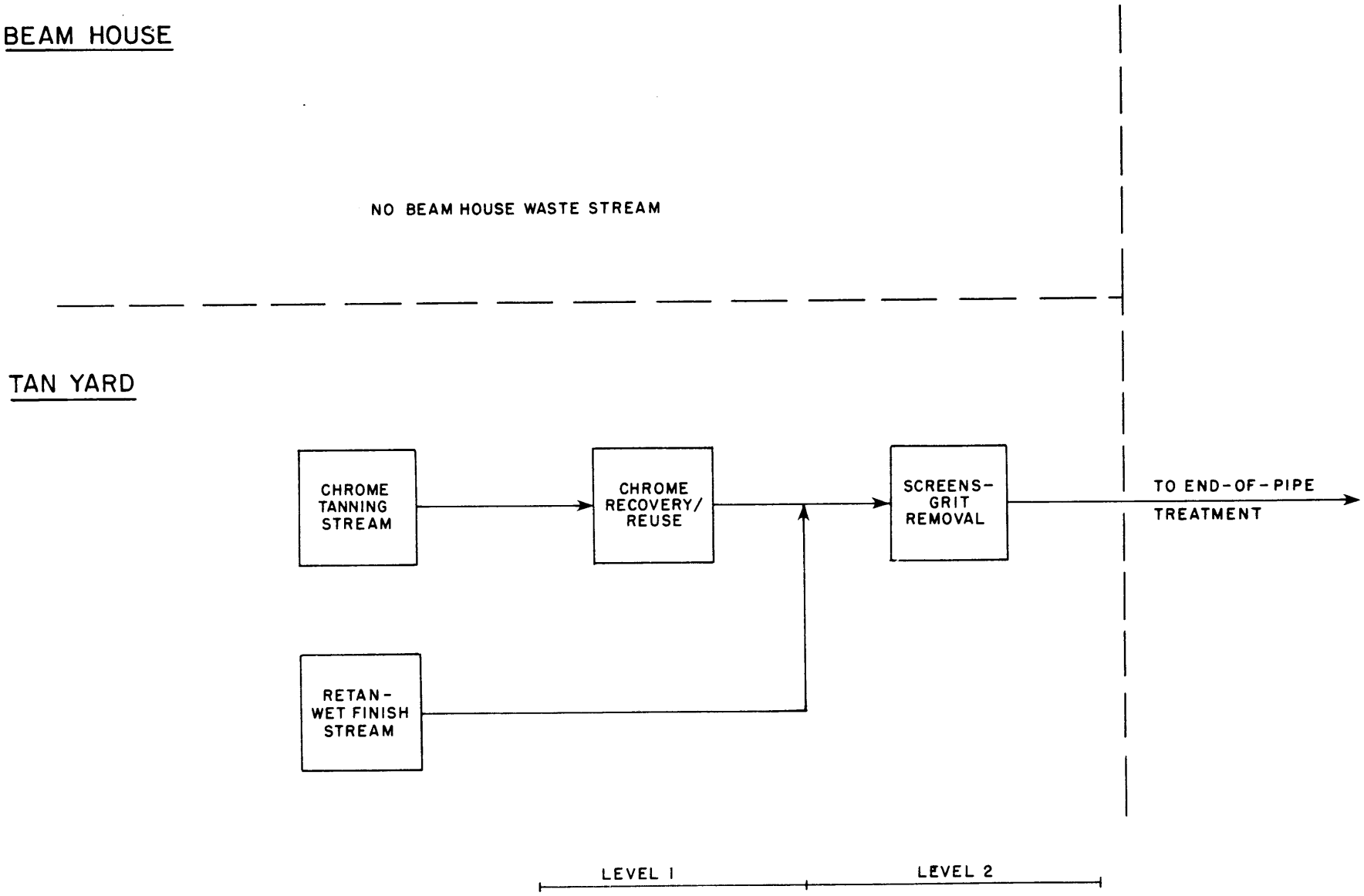


Figure 7. Technology Schematic for In-Plant Control (Subcategories 5 and 7)

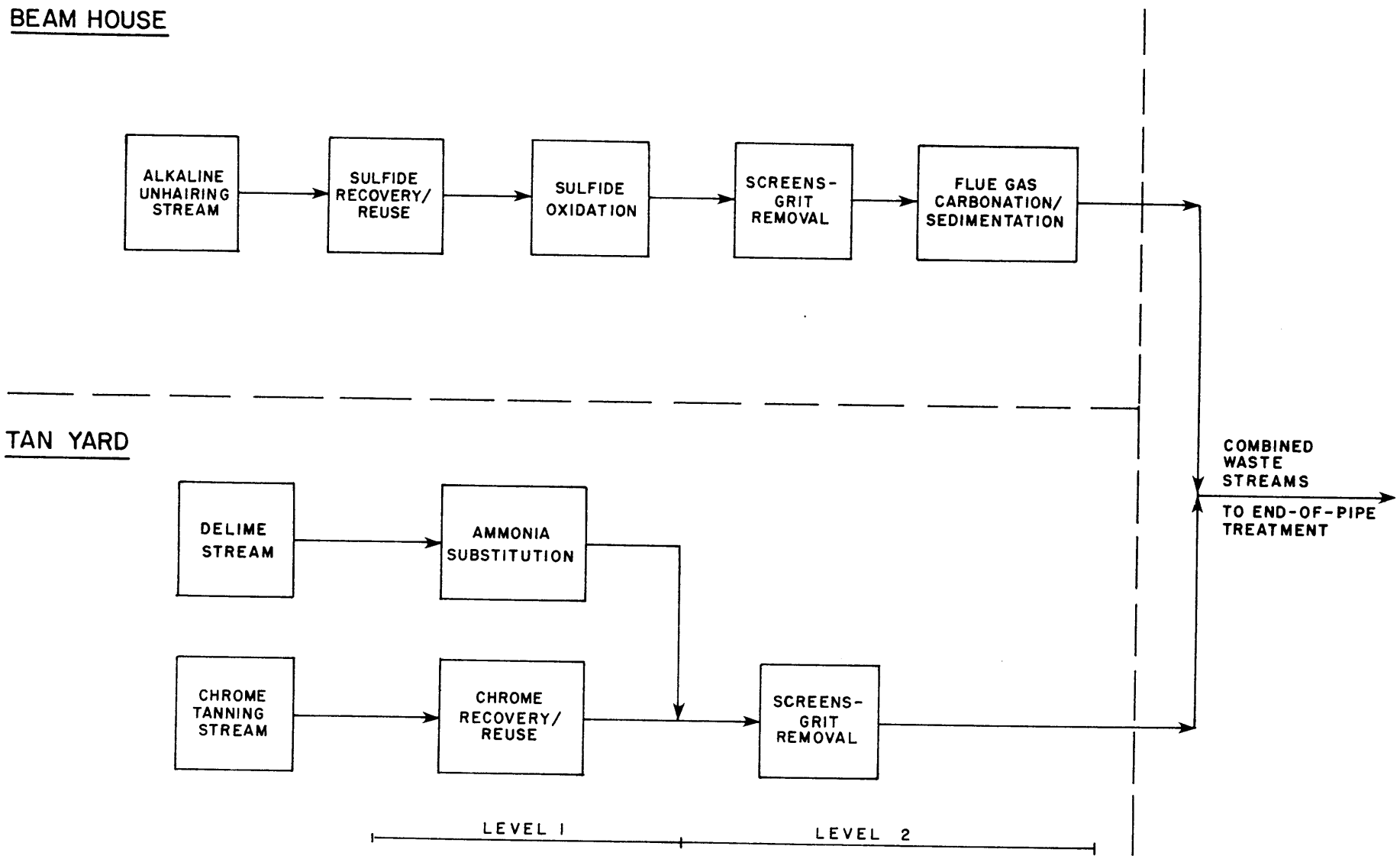


Figure 8. Technology Schematic for In-Plant Control and Preliminary Treatment (Subcategory 6)

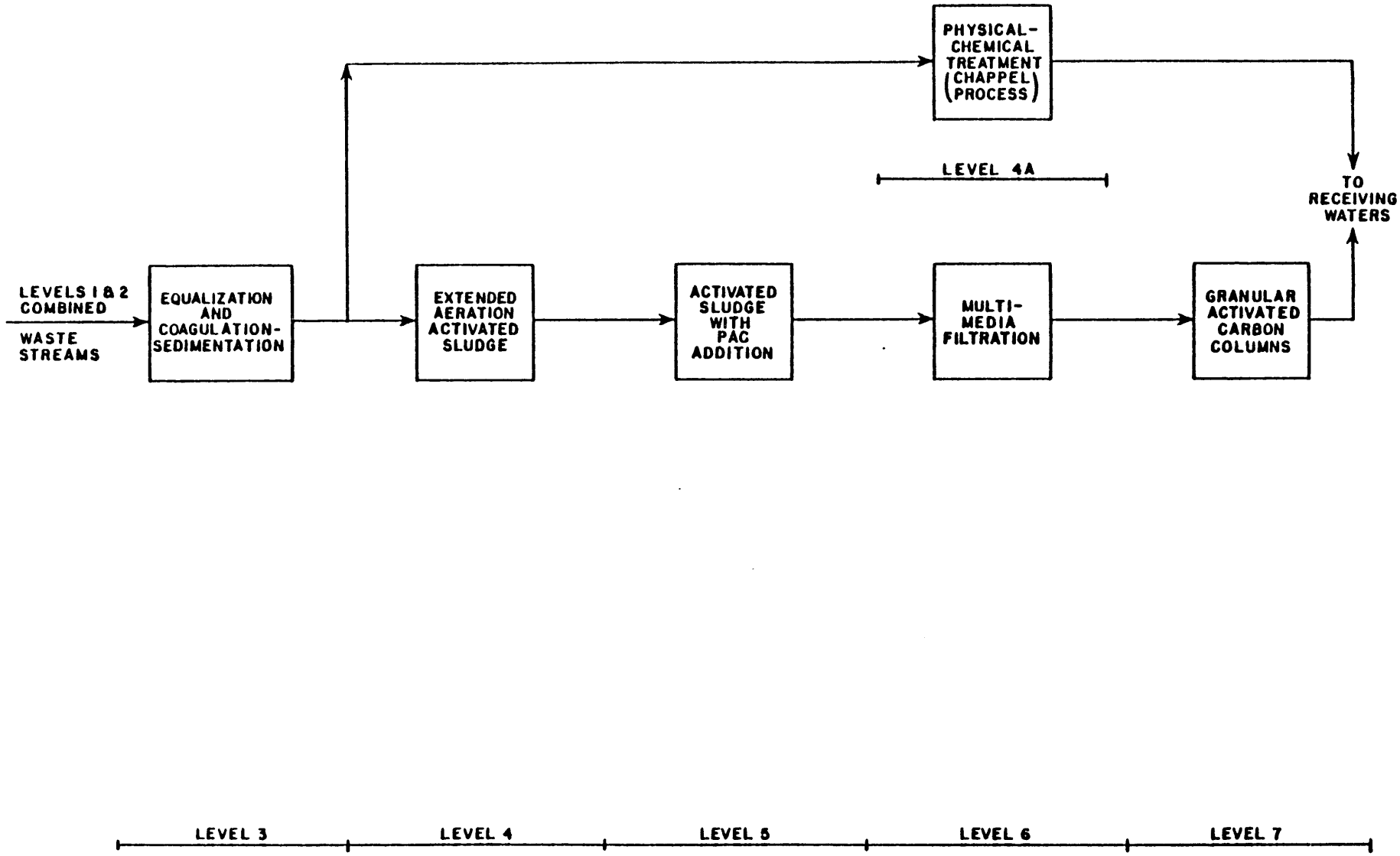


Figure 9. Technology Schematic for End-of-Pipe Wastewater Treatment for all Subcategories

Table 35

Summary of Effectiveness of Candidate Technologies

POLLUTANT PARAMETER	WASTE STREAM SEGREGATION (%)		PERCENT REMOVALS FOR TREATMENT LEVELS 1 & 2		PERCENT REMOVALS FOR COMBINED WASTE STREAMS	RESIDUAL CONCENTRATIONS AFTER TREATMENT LEVEL (mg/l)			
	BEAMHOUSE	TANYARD	BEAMHOUSE	TANYARD	TREATMENT LEVEL 3 (Coagulation-Sedimentation)	LEVEL 4 (Biol. Treat)	LEVEL 5 (PAC)	LEVEL 6 (MMF)	LEVEL 7 (Carbon Col.)
Flow	40	60	---	---	---	---	---	---	---
BOD_5	65	35	60	0.0	60	40	20	14	6
TSS	69	31	65	0.0	60	60	25	16	3
COD	56	44	60	0.0	65	250	195	180	165
Oil & Grease	49	51	70	0.0	70	14	10	6	2
Total Chromium	0.0	100	0.0	80	to 2 ppm	1	0.5	0.33	0.25
Sulfide	100	0.0	100	0.0	---	---	---	---	---
TKN	46	54	65	*	0.0	40	20	15	14
Ammonia	0.0	100	0.0	67	0.0	10	5	5	5
Phenol	0.0	100	0.0	0.0	0.0	0.25	0.1	0.1	0.1

* reduction of 67% of the ammonia content

phenolics that are used as hide and leather preservatives. Removal of some of these compounds from wastewater is known to occur in a number of ways, such as oil-water separation by skimming in sedimentation tanks, and biological treatment by activated sludge. For other chemicals in the group, no determination of an effective technology to remove them has been made or reported. Secondary biological treatment removes phenol.

Physical-chemical mechanisms such as adsorption of the chemicals on settleable and suspended solids or entrainment or reaction with additives or reaction products in precipitation, coagulation, and/or sedimentation has been demonstrated to be effective in toxic pollutant removal.

The inorganic toxic pollutants are the metals plus cyanide. Chromium is listed as one of these pollutants and is in widespread use in the tanning industry. Specific processes to control, recover, or remove chromium have been described previously in this section. Treatment by physical-chemical means is the primary removal mechanism for metals removal. Cyanide removal has not been specifically applied in this industry as it has been in the electroplating industry.

Pesticides and PCB's comprise the fourth group of toxic pollutants. Physical-chemical methods, especially adsorption, are reportedly effective in removing pesticides from wastewaters. Similar technology is being installed to remove PCB's from wastewater by a plant that previously manufactured PCB's.

The effectiveness of various end-of-pipe treatment systems in removing toxic pollutants from leather tannery wastewater is indicated in Table 36. These results originate from the field sampling and laboratory analysis of wastewater from 22 tanneries and two POTW's with a large proportion of tannery wastewater to treat.

In Table 36, the notation ND indicates that the compound was not detected with the analytical procedure prescribed for that specific sample. Sometimes ND notations in the "INF" (influent) column are followed by indications of presence of the compound in the "EFF" (effluent) column. The determination of toxic pollutants at low-level concentrations is a question of detection of the compounds, with the analytical methodology not the absolute determinant of presence or absence of the compounds. A compound not detected may be present, but at a very low concentration. To analyze some influent samples it became necessary to dilute them to a considerable extent and thereby reduce the concentration. In some cases, this dilution reduced the concentration of a compound to a level below the detection limit. This prevented identification and quantification in the specific sample and waste stream that it came from. This produced the influent ND notations in the table for some compounds followed by reported presence in the effluent stream.

Table 36

TOXIC POLLUTANT TREATMENT EFFECTIVENESS FROM THREE DAY TOXICS SAMPLING PROGRAM
(Concentrations: Toxic Pollutants - ug/l, Regulated Pollutants - mg/l)

Type of Treatment				Activated Sludge or Extended Aeration												Aerated Lagoon(s)			Physical-Chemical		
Subcategory	7*			2			2			3*			*			1			4+		
Plant	253			248			320			47			Berwick POTW			184			247		
Sample Point	IN	EFF	%	IN	EFF	%	IN	EFF	%	IN	EFF	%	IN	EFF	%	IN	EFF	%	IN	EFF	%
Toxic Pollutant																					
Volatile Organics																					
benzene	5	ND	100	ND	ND	—	tr	tr	—	tr	tr	—	tr	ND	100	tr	tr	—	tr	tr	—
1,1,2,2-tetrachloroethane	18	ND	100	ND	ND	—	ND	ND	—	tr	ND	100	ND	ND	—	ND	ND	—	ND	ND	—
chloroform	12	10	16	41	tr	98	tr	ND	100	ND	ND	—	11	10	9	ND	ND	—	tr	tr	—
toluene	9	ND	100	tr	tr	—	>100	tr	99	tr	tr	—	>100	tr	99	>100	tr	99	11	tr	99
Semi-volatile Organics																					
1,2-dichlorobenzene	ND	ND	—	215	69	68	ND	tr	—	49	ND	100	ND	ND	—	255	ND	100	ND	ND	—
1,4-dichlorobenzene	20	ND	100	99	21	79	ND	tr	—	19	ND	100	ND	ND	—	54	ND	100	ND	ND	—
phenol	91	ND	100	480	435	9	5500	1400	75	845	ND	100	8500	ND	100	4400	ND	100	3200	60	98
2,4,6-trichlorophenol	ND	ND	—	10500	4300	59	ND	12	—	1700	38	98	331	5	98	880	ND	100	573	tr	99
pentachlorophenol	400	130	68	9500	3100	67	ND	12	—	2900	200	93	200	22	89	ND	ND	—	ND	ND	—
bis(2-ethylhexyl) phthalate	93	34	63	ND	ND	—	32	6	83	ND	26	—	29	4	86	51	2	96	ND	ND	—
naphthalene	35	ND	100	49	15	69	ND	2.3	—	19	ND	100	29	ND	100	24	ND	100	ND	8.5	—
phenanthrene/anthracene	36	6	83	56	tr	98	2.9	1.4	52	7.6	ND	100	6.6	0.7	89	ND	ND	—	133	7.3	95
ethylbenzene	ND	ND	—	ND	ND	—	>100	tr	99	43	tr	98	>100	tr	99	88	ND	100	>100	12	92
Pesticides and PCBs																					
$\alpha+\beta$ BHC	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—
Inorganics																					
chromium	53000	2200	96	31000	20000	35	170000	1700	99	6400	170	97	50000	3900	92	160000	1100	99	16000	< 20	99.9
copper	120	7	94	57	37	35	220	8	96	200	25	88	350	28	92	50	5	90	260	< 8	97
cyanides	10	tr	—	20	40	—	50	40	20	100	400	—	30	tr	67	60	150	—	tr	tr	—
lead	80	30	63	100	30	70	3100	60	98	100	50	50	1500	90	94	1100	80	93	300	8	97
nickel	27	19	30	5	34	—	75	30	60	60	30	50	8	5	38	60	30	50	6	4	33
zinc	500	68	86	230	140	39	2100	170	92	460	59	87	1700	280	84	500	49	90	150	61	61
Regulated Pollutants																					
BOD	1015	27	97	1241	917	26	2000	297	86	1530	49	97	933	77	92	1867	21	99	617	6.7	99
COD	2367	488	79	2557	1777	31	4033	893	87	5953	553	91	2600	430	84	5530	217	96	1900	28	99
TSS	768	108	86	1098	557	49	2252	129	94	6377	227	96	1152	114	90	2907	155	95	522	7.7	98
chromium	53000	2200	96	31000	20000	35	170000	1700	99	6400	170	97	50000	3900	92	160000	1100	99	16000	< 20	99
pH	5.2	7.7	—	11.0	10.5	—	8.4	7.6	—	8.6	7.6	—	8.6	7.5	—	8.4	6.8	—	4.3	4.4	—
TKN	49	27	45	252	186	26	287	163	43	750	277	63	130	70	46	500	105	79	183	4.4	98
NH3	11	17	—	98	60	39	150	123	18	437	236	46	82	39	52	263	64	76	113	1.5	99
oil & grease	413	25	94	171	91	47	553	17	97	247	35	86	263	20	92	720	17	98	180	15.4	91
sulfide	0.16	0.13	17	50	30	40	16	6	63	19	17	9	3.9	0.27	93	204	0.4	99	0.5	0.3	40

% - Percent Removal
tr - compound detected in only trace amounts, generally less than 10 ug/l
ND - compound not detected
* - plants achieving BPT or better in the long term
\+ - plant now closed

The trace "tr" designation was used to indicate the identification of the presence of a compound but with insufficient quantity (generally less than 10 ug/l for organic compounds) to quantify its presence.

The results in this table suggest a number of conclusions, as follows:

1. Volatile organics are largely removed in any type treatment system that is in use in the leather tanning industry, except for some degree of persistence of chloroform. The uniformity of removal is probably due to the volatility and resulting ease of stripping these compounds from solution. It also appears that this occurs regardless of treatment effectiveness on any other pollutant parameters whether conventional, nonconventional, or toxic.

2. Semivolatile organics also receive some degree of removal by all waste treatment systems in use. Those systems that are most effective in removing the conventional and nonconventional pollutants (BOD_5, TSS, etc.) also seem to be most effective on semivolatiles.

3. Metals comprise the inorganic group of toxic pollutants and include chromium. All of the treatment systems remove the metals to some extent; and performance on the metals seems to correlate with removal of conventional and nonconventional pollutants, most importantly TSS. The most effective treatment system on metals is the physical-chemical system.

4. The fate of the toxic pollutants removed from the wastewater was not determined. However, EPA believes it is highly probable that a substantial percentage of the pollutants removed are removed with the solids separated from the wastewater.

5. In general, effective waste treatment for the toxic pollutants seems to correlate well with effective removal of the conventional and nonconventional pollutants. If the treatment system does well on the latter, then it will do well in removing the toxic pollutants.

SLUDGE HANDLING AND DISPOSAL

A major part of tannery waste treatment involves the handling and disposal of the semi-solid sludges obtained from liquid treatment processes. The most predominant methods of ultimate disposal of tannery waste sludges include sludge lagoons, landfills, dumps, and spreading on the land.

Some attempts have been made to dewater sludges prior to ultimate disposal, with varying success. The three principal dewatering techniques include centrifugation, vacuum filtration, and pressure filtration. Centrifuges have appeared to meet with less success than vacuum filters or pressure filters.

Reducing the moisture content of sludge by spreading on drying beds has also been successful in some areas. This is particularly attractive to smaller facilities where land area is available.

One of the principal difficulties with tannery waste is the chromium content in sludges and the potential toxic impact of this metal on the environment. In testing a heat-treated alkaline sludge, it has been indicated that some of the trivalent chromium may be oxidized to the hexavalent form. Apparently, the trivalent chromium is converted through the high temperature, high pressure, high pH, and the oxidizing environment of the heat treatment process.

Chromium reuse reduces the levels of chromium in the sludge. Disposal of sludge containing these lower residual quantities of chromium in a sanitary landfill will reduce environmental problems.

Prior to dewatering in mechanical equipment, sludge is normally conditioned by use of ferric salts, lime, polymers, or a combination of these. The quantity and type of chemicals required are dependent upon characteristics of the sludge being handled.

Dewatering with mechanical equipment such as centrifuges generally can produce a cake containing 15 to 30 percent dry solids. Plate and frame filter presses have been found to produce cakes of 40 to 50 percent dry solids. The higher capital cost of filter presses may be quickly offset by lower hauling and disposal costs where landfills are located great distances from the tannery or the POTW.

Some sludge is disposed of on the land, taking advantage of its lime content for agricultural purposes. One disadvantage of this type of disposal practice is the potential toxic effects of chromium or other constituents on plants, groundwater, and surface water supplies.

Lagoons for dewatering have some limited uses. In humid areas where rainfall approximates or exceeds evaporation, such application is not satisfactory.

Use of lagoons, drying beds, landfills, and landspreading all require key attention to the environmental impacts. Particularly important is the leaching of potential toxic or organic materials to the groundwater supplies or surface waters. Proper controls must be taken to ensure that these conditions will not develop.

SECTION VIII

COST, ENERGY, AND NON-WATER QUALITY ASPECTS

Plant sizes and related production rates have been selected for purposes of economic impact analysis. Five typical "model" plants were selected in Subcategories One and Two; three model plants were selected in Subcategories Three and Seven; four model plants in Subcategory Five; and two model plants in Subcategories Four and Six.

CAPITAL COST ASSUMPTIONS

EPA calculated the waste treatment system capital costs based on the plant production, wastewater flow, and related pollutant load data for typical "model" plants in each subcategory. Capital costs for specific treatment system components largely depend on the wastewater flow or hydraulic load.

The actual component cost estimates are based on unit cost curves. The following assumptions are reflected in the capital costs:

1. Costs are expressed in December 31, 1977, dollars.

2. Expected accuracy for these conceptual-type estimates is plus or minus 40 percent.

3. Engineering costs are not included in cost estimates. However, most states require that design plans and specifications be prepared by a registered professional engineer in accordance with applicable codes.

4. Construction work to be performed by outside contractor using union labor and no work to be done by in-plant labor or maintenance personnel (except stream segregation work). The construction contractor's overhead and profit are included in the cost estimates.

5. No land acquisition cost is included.

EPA believes that the capital cost estimates in this report may be higher than the actual cost that tanneries will incur in installing the suggested technology. For example, a pollution control consultant to the industry reported that to his knowledge none of the tanneries for which he was consulting had used an outside contractor to build waste treatment facilities, but that the facilities at each tannery had been built with in-house labor. This would represent a substantial cost savings. There are numerous other investment cost reductions available to the resourceful tannery in design, construction, and operation of treatment ктechnology. These reductions cannot be accurately defined or predicted, nor is the

effect of them included in the cost data. The intent of this cost information is to present maximum expected costs of wastewater treatment technology suggested for the industry.

ANNUAL COST ASSUMPTIONS

The components of total annual cost are capital cost, depreciation, and operating and maintenance costs, the latter including manpower, chemical, and power costs. The cost of capital is estimated to be 9 percent of the investment cost. This cost is an estimate of the weighted average of the cost of equity and of debt financing throughout the industry. The depreciation component of annual cost was estimated on a straight-line basis, with no salvage value and an assumed-year life for all capital investment costs.

The rate for tannery labor manhours was set at $5.00 per hour plus 50 percent for burden, supervision, etc., based on information from the industry. The electrical power cost was estimated to be 2.5 cents per kilowatt-hour (kWh). The operating year was assumed to be 260 days per year in all cost calculations to account for the variable numbers of days per week of operation reported by the industry. The operating year used for the wastewater treatment plant was 365 days per year. Operation and maintenance costs are based on December 31, 1977 dollars.

CAPITAL AND OPERATION AND MAINTENANCE COST CURVES

Using the assumptions stated above, total installed costs were developed by the technical contractors based upon: 1) the design factors presented in Section VII of this document for each unit treatment process, and 2) updated cost information for equipment and material, labor, chemicals, and energy. Costs were developed for each of the treatment technologies described in Section VII. The capital cost curves were obtained by plotting the total installed costs against wastewater flow rate. The annual operation and maintenance costs were computed by totaling the manpower, maintenance, chemical and electrical power costs. This total was compared to average flow rate in the operation and maintenance cost curves. Cost curves were generated for eight wastewater treatment levels (as introduced in Section VII), stream segregation, and sludge dewatering. The rationale, design basis, and items included in each of the cost curves are described in the following sections.

Stream Segregation - Level 1

Because of different in-plant treatment requirements for the beamhouse and tanyard wastewaters, the flows from these sources have to be physically separated until after Level 2 in-plant treatment. The segregation of the beamhouse and tanyard wastewaters involves modifications to processing wheels, piping from the wheels to a sump,

and installation of the sump system for each of the two waste streams. The piping and sump pumps have been sized to simultaneously handle the flow from two wheels.

The number of processing wheels that require modification was determined by dividing the plant production in hides per day by 270. The cost of modifying each wheel was computed to be $5,000. The first cost of the sump pumps and the sump pit was calculated at $28,000, regardless of the plant production rate. The installed cost of the piping, fittings, valves, and pipe hangers was computed for each of the tannery sizes considered. The total installed cost for steam segregation, including piping, pumps, and modifications, is plotted versus average flow rate in Figure 10.

The operation and maintenance costs associated with stream segregation were computed using the following criteria:

1. Maintenance - 20 percent of installed cost of piping, processing drum modifications and sump pump.

2. Operation - 60 horsepower-hours per processing drum per day. Figure 11 shows the annual operation and maintenance costs for stream segregation for the range of flow rates considered.

Stream segregation applies to subcategory numbers 1, 2, 3, 6, and 7.

Sulfide Oxidation - Level 1

The recommended in-plant process changes include the recovery and reuse of the chemicals contained in the unhairing liquors. The recovery and reuse of the unhairing liquors removes most of the sulfide content of the beamhouse waste stream. The remaining residual sulfide concentration must be completely removed prior to discharge to the end-of-pipe treatment plant to eliminate the possibilities of corrosion and the health problems associated with hydrogen κsulfide gas generation. The residual sulfide concentration in the unhairing waste can be removed by utilization of the sulfide oxidation process.

The recommended sulfide oxidation process includes two holding tanks, a pump, blower, and chemical feeding equipment. The spent unhairing wastewater is pumped into the storage tanks, the magnesium sulfate is added, and the air for oxidation is supplied by the blower. The design criteria for each of the components included is as follows:

1. Holding tanks (each) = 75 percent of daily flow of unhairing wastewater;

2. blower = 0.22 cfm/lb (0.014 m^3/min/kg) sulfide oxidized;

3. pump = capable of draining two unhairing vats in 60 minutes;

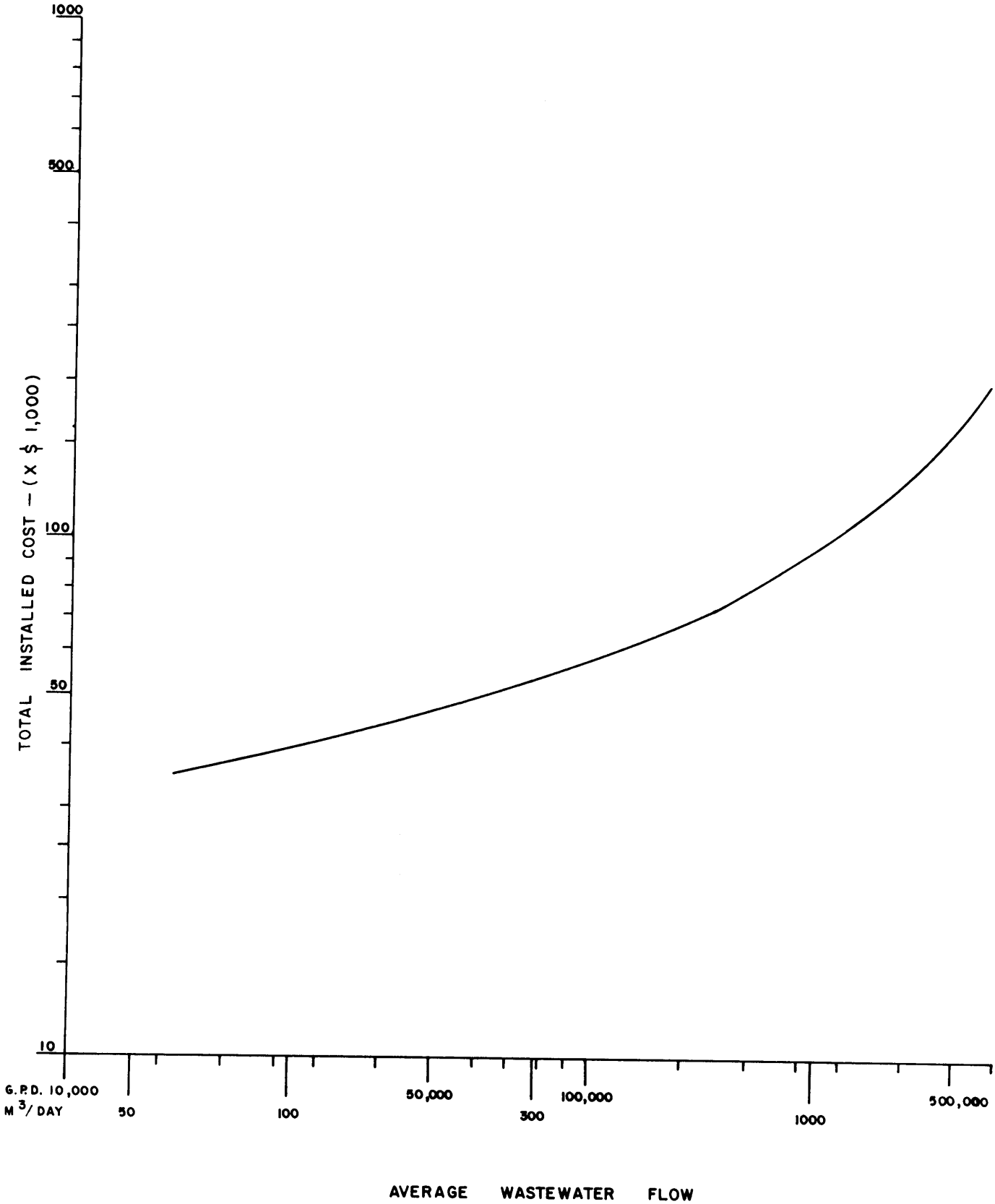


Figure 10. Capital Cost Curve for Stream Segregation

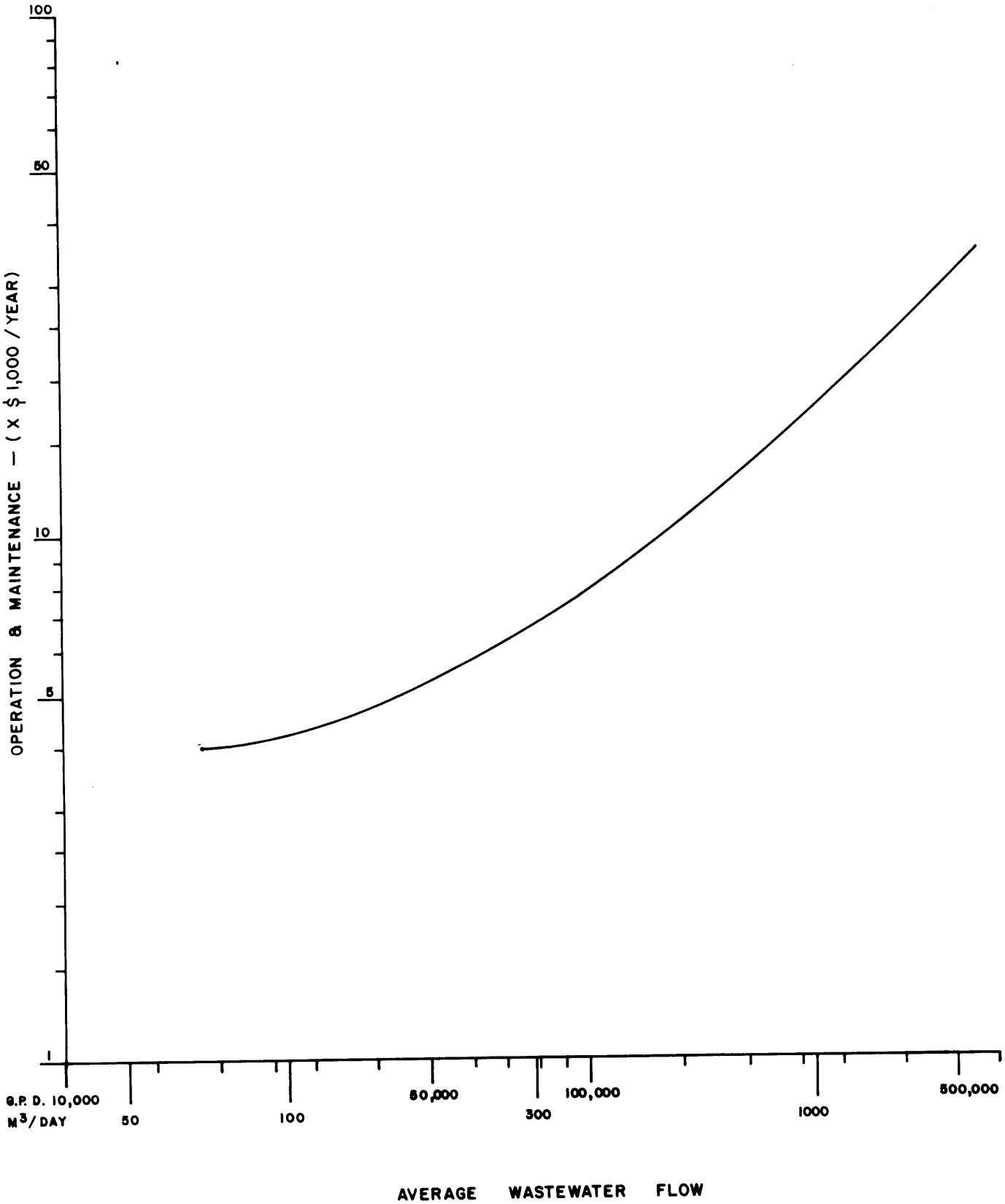


Figure 11. Operation and Maintenance Cost Curve for Stream Segregation

4. sulfide content (after recovery and reuse) = 3 pounds (kg)/1000 pounds (1000 kg) of hides processed; and

5. wastewater volume = 0.52 gallons/pound (0.0043 m^3/kg) of hide processed.

A plot of the installed cost of sulfide oxidation incorporation based on the above parameters is shown on Figure 12 as a function of the number of cattlehides processed per day of operation.

Sulfide oxidation applies to subcategory numbers 1, 2, 3, and 6.

Ammonia Substitution - Level 1

During the unhairing operation, lime and sharpeners are added to loosen or dissolve the hair attached to the hide. Bating follows the unhairing step to reduce the alkaline swelling of the hides and to reduce the pH of the solution prior to the tanning operation. The pH reduction is accomplished typically by the reaction of ammonium sulfate with the residual lime to produce calcium sulfate. Most of the ammonia nitrogen in the tannery effluent wastewater is directly attributed to the deliming chemicals used in the bating process. Therefore, the elimination of the nitrogen-containing deliming chemicals used in the bating process would significantly reduce the very high ammonia and TKN content of the effluent.

The reduced ammonia content in the wastewater effluent resulting from the substitution of magnesium sulfate for ammonia sulfate eliminates the requirement for nitrogen removal processes in the end-of-pipe treatment plant. The substitution of magnesium sulfate in the bating process has no adverse effect on the quality of the finished leather. No capital expenditures are required for the changeover from ammonia to magnesium sulfate.

Treatment Level 1 includes both residual sulfide oxidation from the spent unhairing liquor and the substitution of magnesium for ammonia in the bating process. The capital costs for sulfide oxidation have been already described and presented in Figure 12. The operation and maintenance for treatment Level 1 includes the chemical cost for magnesium sulfate used for sulfide removal, the increased chemical cost for ammonia substitution, operating manpower, and electrical cost for running the blower and pump for sulfide oxidation. Figure 13 shows the operation and maintenance cost curve for sulfide oxidation and ammonia substitution in bating.

Ammonia substitution applies to subcategory numbers 1, 2, 3, and 6.

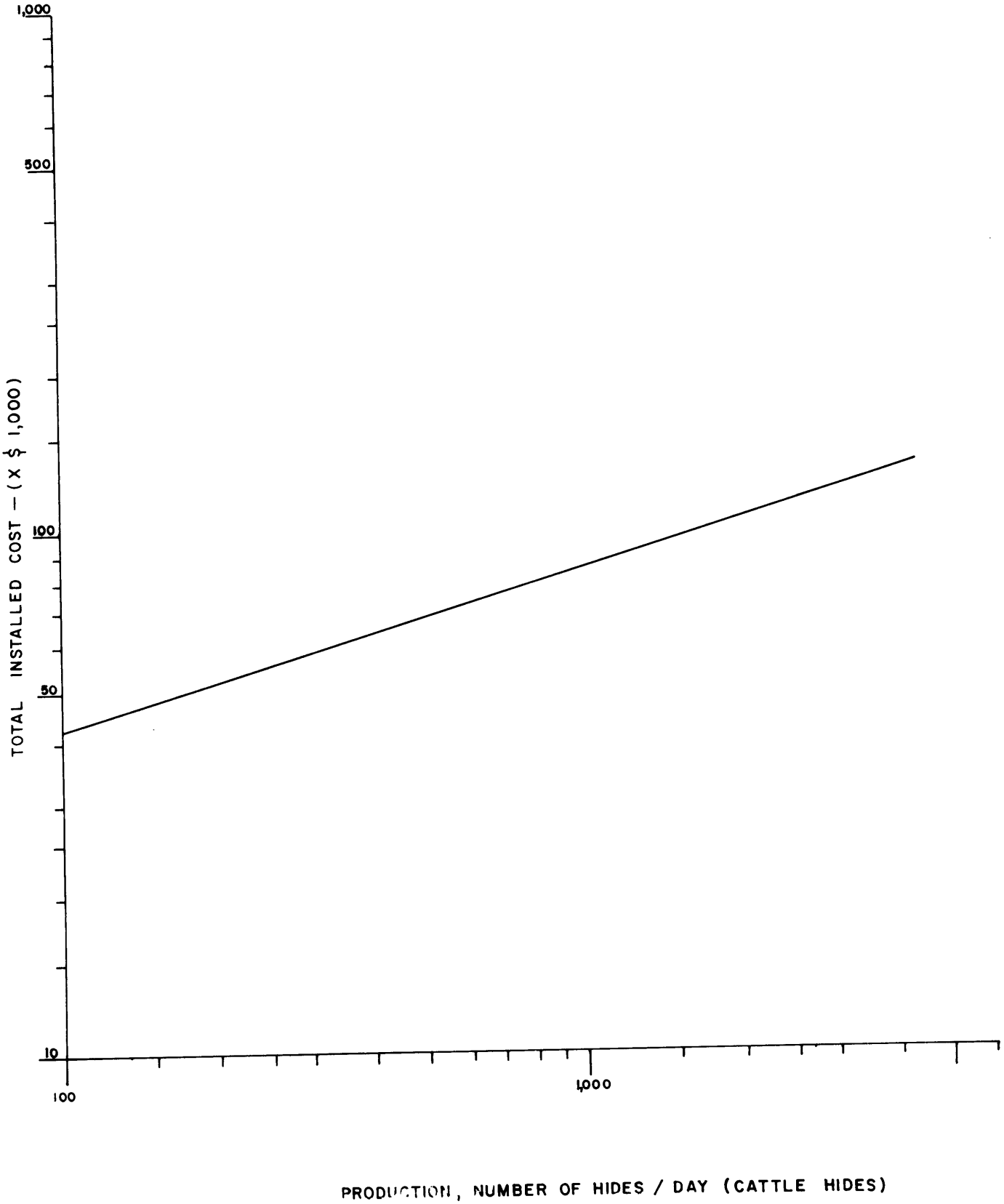


Figure 12. Capital Cost Curve for Sulfide Oxidation

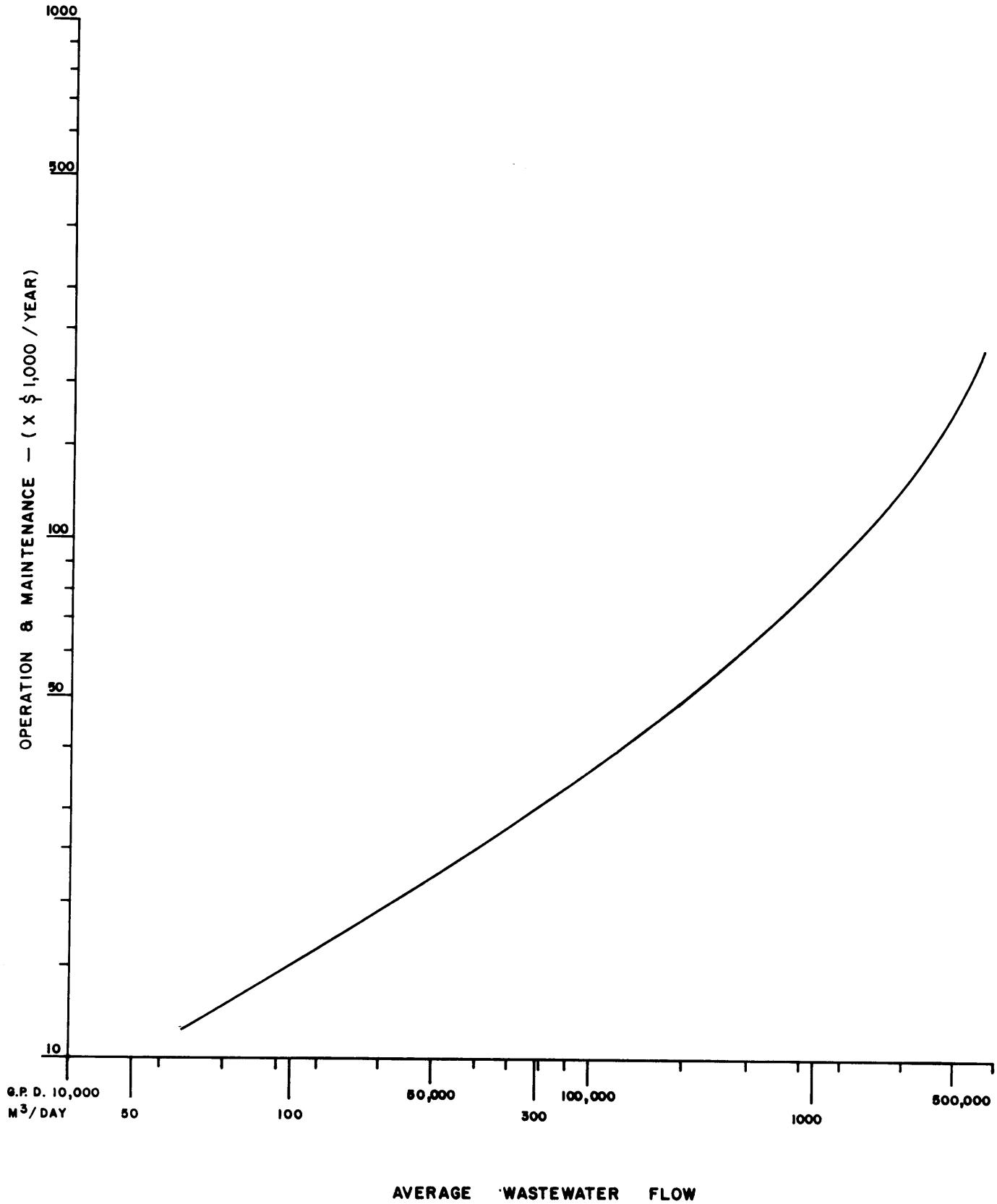


Figure 13. Operation and Maintenance Cost Curve for Sulfide Oxidation and Ammonia Substitution

Flue Gas Carbonation/Sedimentation - Level 2

Flue gas carbonation is the final in-plant wastewater treatment step for the beamhouse wastewater prior to the equalization basin. Flue gas carbonation consists of blowing flue gas from a boiler into the beamhouse wastewater prior to a clarifier. The lime and protein particles that are precipitated in the clarifier will be withdrawn by a sludge pump for resale as a by-product or be dewatered for handling as solids waste.

The capital cost for flue gas carbonation includes the flue gas handling equipment, sludge pump, and circular clarifier. The installed cost of the flue gas handling equipment required for carbonation, blower, piping, and diffuser is shown graphically on Figure 14. The volume of beamhouse wastewater was conservatively estimated to be 75 percent of the total wastewater flow from the tannery for cost estimating purposes. The clarifier sizing is based on a hydraulic overflow rate of 400 gpd/ft^2 (16.3 m^3/d/m^2). Figure 15 shows the flue gas carbonation clarifier capital cost, plotted against beamhouse flow rate.

The operation and maintenance (O&M) cost for the flue gas handling blower and piping was computed at 20 percent of the capital cost plus the electrical power cost for the blower. The O&M costs for the clarifier and sludge pump were calculated using 2 manhours of labor per day, 5 percent of the capital cost, and the electrical power required for the clarifier drive and the pump motors. The operation and maintenance cost curve for flue gas carbonation/sedimentation is shown in Figure 16.

Flue gas carbonation/sedimentation applies to subcategory numbers 1, 2, 3, and 6.

Equalization and Coagulation-Sedimentation - Level 3

Following flue gas carbonation the wastewaters from the beamhouse and tanyard combine and enter the equalization tank. The equalization tank smooths out pH swings during tank dumps, equalizes surges in flow rate, and stores wastewater for use by the succeeding treatment units during weekends and plant shutdowns.

Figure 17 is a graph of the capital cost of the equalization capital cost against the total average design wastewater volume. The installed cost of equalization is based upon a detention time of 36 hours; a steel tank on concrete slab; and a mixer size of 0.1 hp/1,000 gallons (26.4 hp/1,000 m^3).

The operation and maintenance cost for equalization is equal to the electrical energy required for the connected horsepower of the mixer, operating 24 hours per day, 365 days per year.

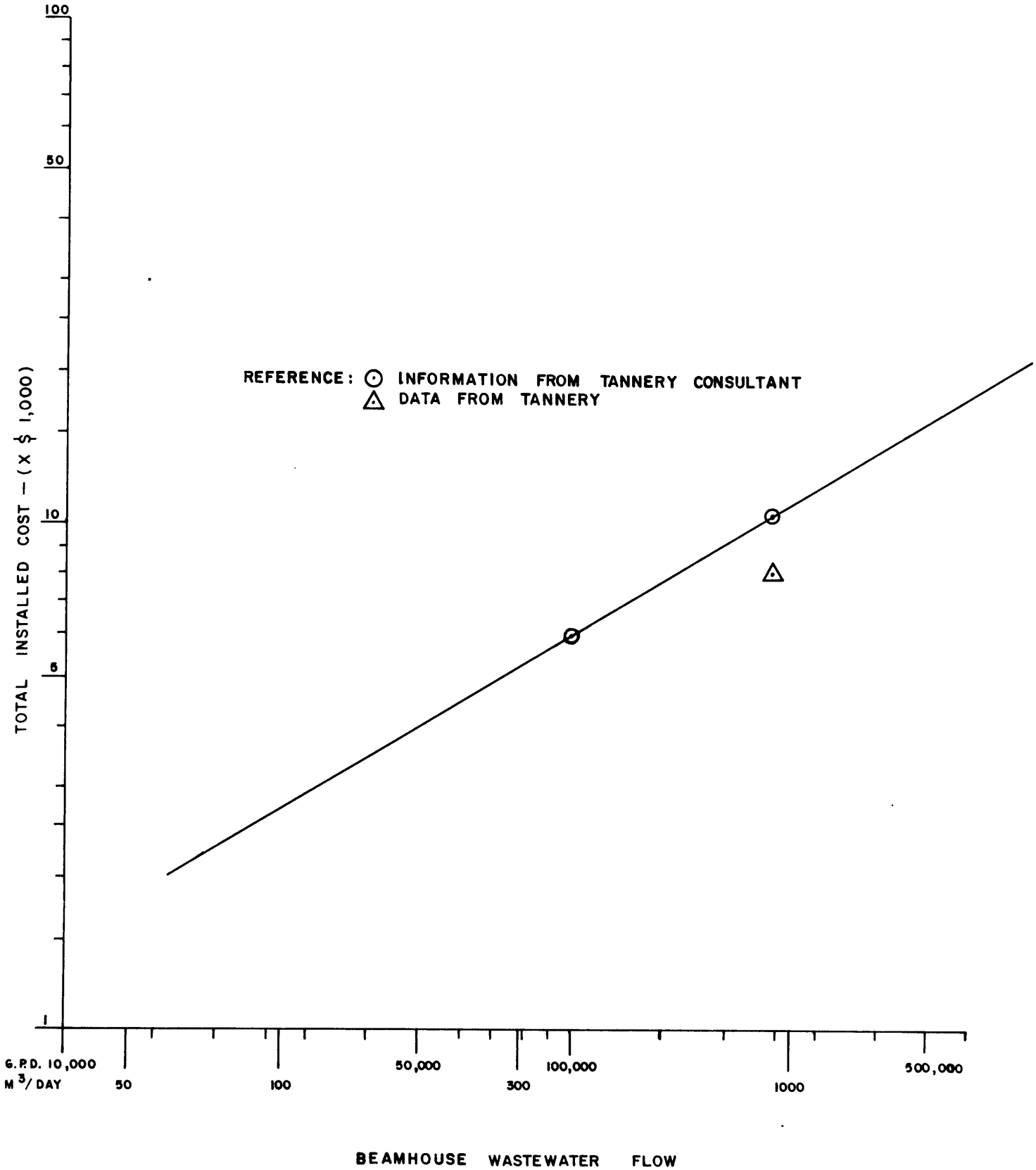


Figure 14. Capital Cost Curve for Flue Gas Handling Equipment

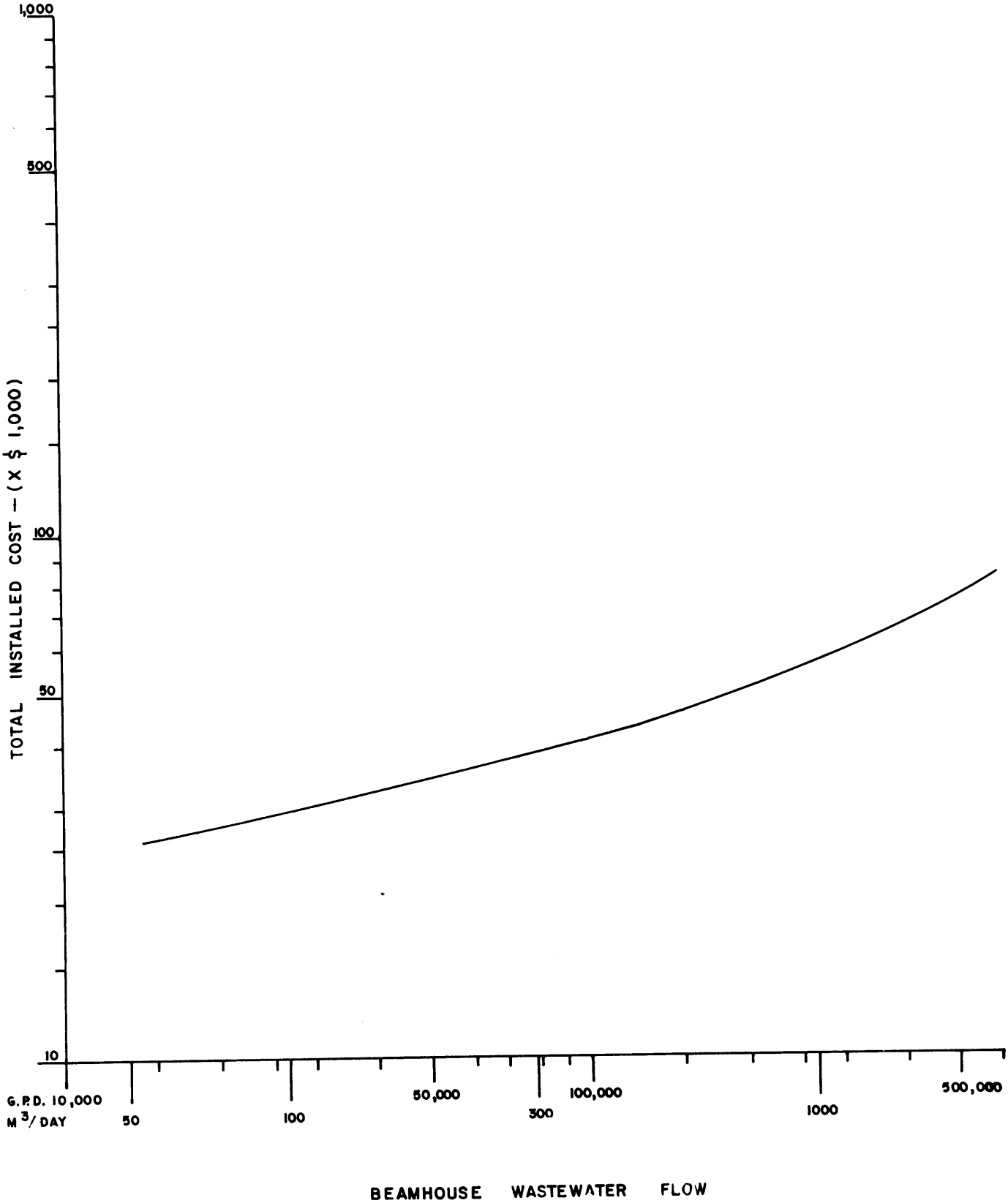


Figure 15. Capital Cost Curve for Flue Gas Carbonation Clarifier

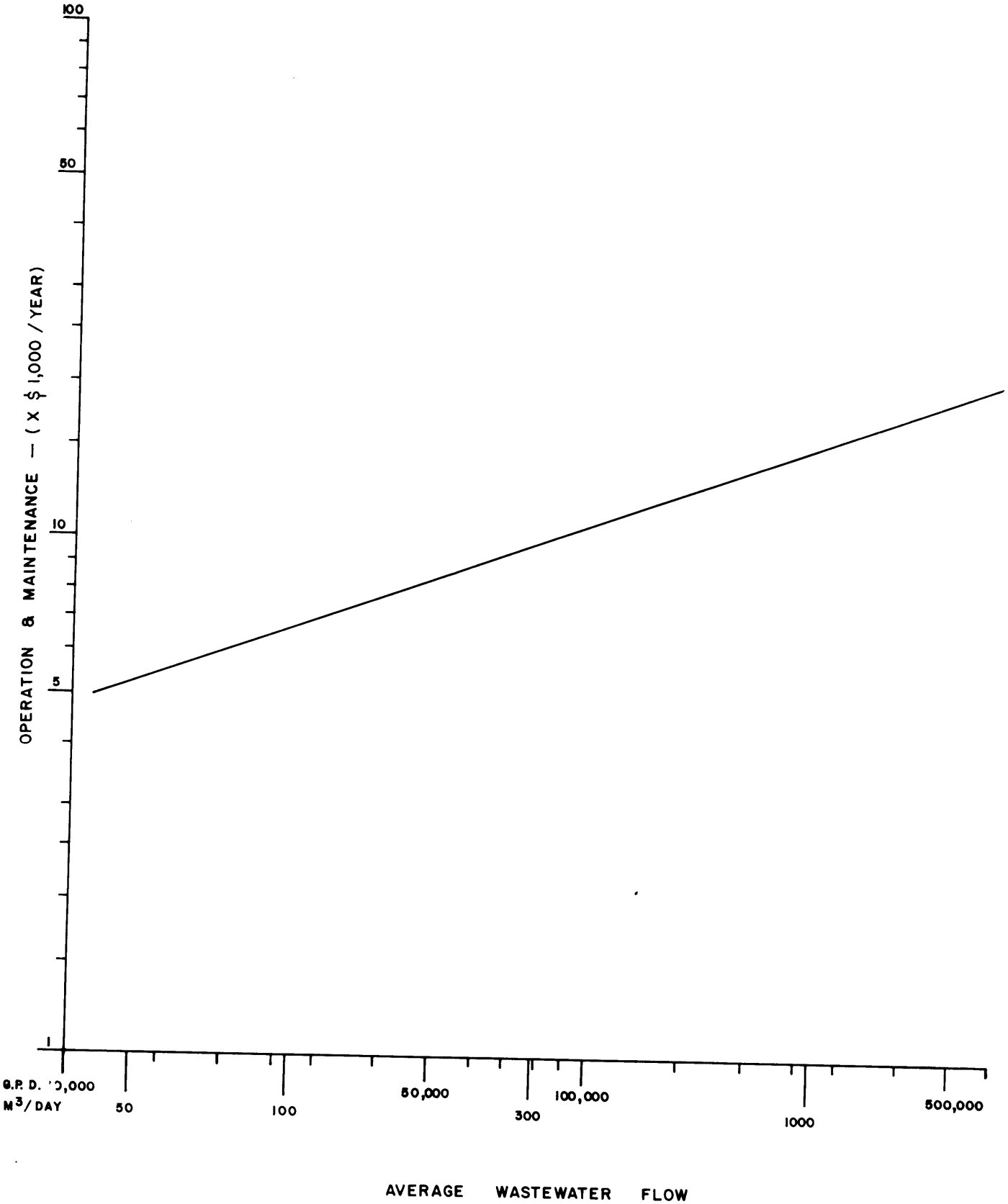


Figure 16. Operation and Maintenance Cost Curve for Flue Gas Carbonation

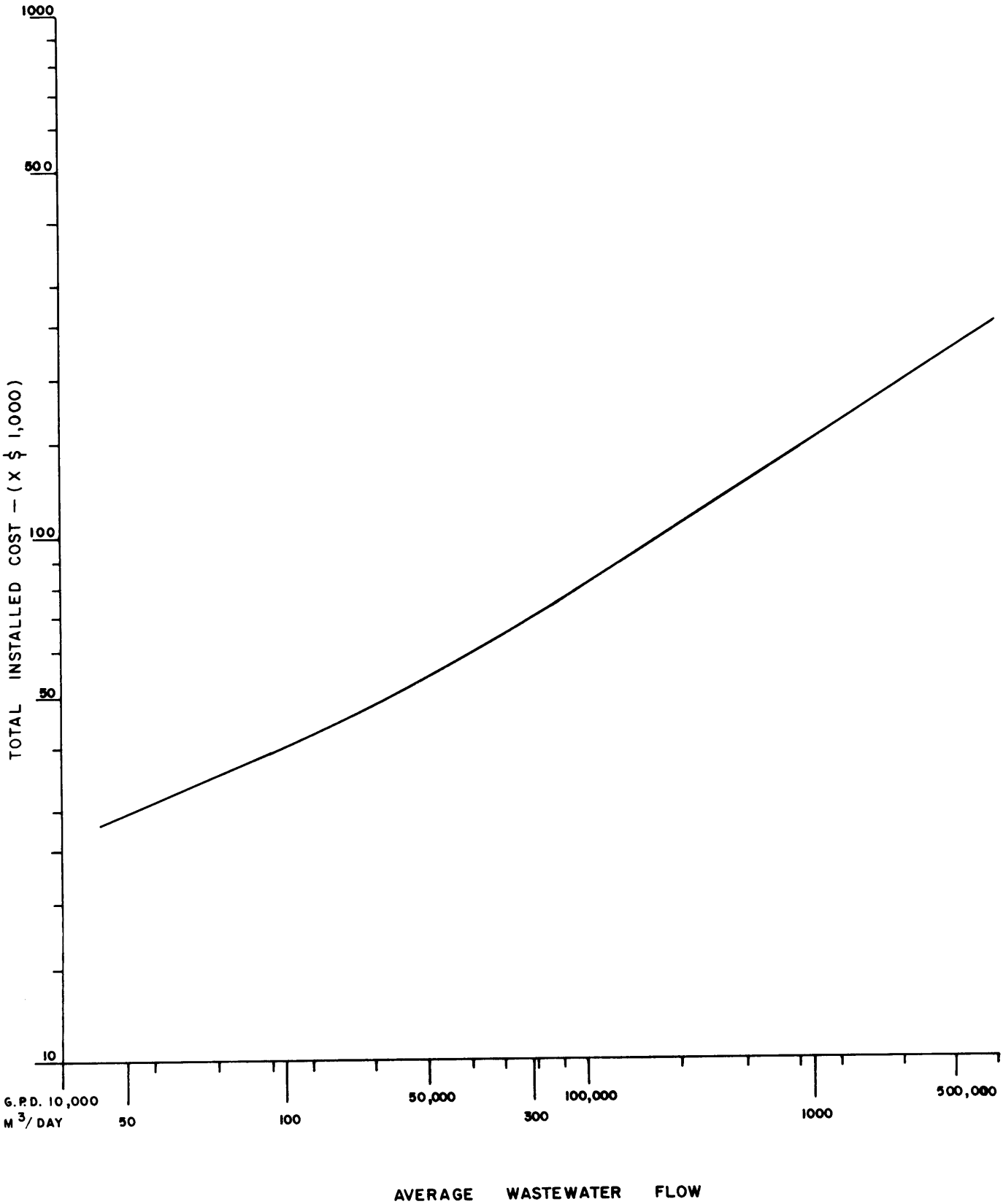


Figure 17. Capital Cost Curve for Equalization

The equalized flow enters the primary clarifier where lime and polymer will be added to enhance the coagulation and sedimentation of the solids in the wastewater. Included in the capital cost is the solids-contact type primary clarifier, chemical storage and feed equipment, and foundation. The hydraulic overflow rate used to size the clarifier was 700 gpd/ft^2 (28.7 m^3/d/m^2). Figure 18 is the capital cost curve for the complete coagulation-sedimentation unit.

The operation and maintenance cost for coagulation-sedimentation was determined by adding the cost of the coagulation chemicals to the cost for annual manhour requirements. The annual manhour requirements for operation and maintenance labor are shown in Figure 19.

Treatment Level 3, as described in Section VII, includes both equalization and coagulation-sedimentation. The capital cost would be the additive costs obtained from Figures 17 and 18. The operation and maintenance costs for treatment Level 3 can be determined from Figure 20.

Equalization and coagulation-sedimentation of combined streams applies to all subcategories.

Secondary Biological Treatment - Level 4

Wastewater treatment Level 4, as described in Section VII, consists of the high solids, extended aeration type activated sludge process. Activated sludge secondary treatment has the following components: aeration basin, final clarifier, phosphoric acid feed system, and sludge pumps. The capital cost curve, shown as Figure 21, was computed using the following sizing basis:

aeration provided by subsurface static aerators;

aeration basin is an earthen lagoon with Hypalon lining; detention time is determined by F/M of 0.1.

final clarifier overflow rate is 150 gpd/ft^2 (6.2 m^3/d/m^2).

The operation and maintenance cost for secondary treatment is graphically shown in Figure 22. Secondary treatment O&M consists of labor, materials and supplies, and electrical power costs.

Secondary biological treatment by extended aeration activated sludge applies to all subcategories.

Upgraded Secondary Treatment with PAC Addition - Level 5

As described in Section VII on treatment technology, the pollutant removal efficiency of activated sludge (treatment Level 4) can be significantly increased by adding powdered activated carbon to the

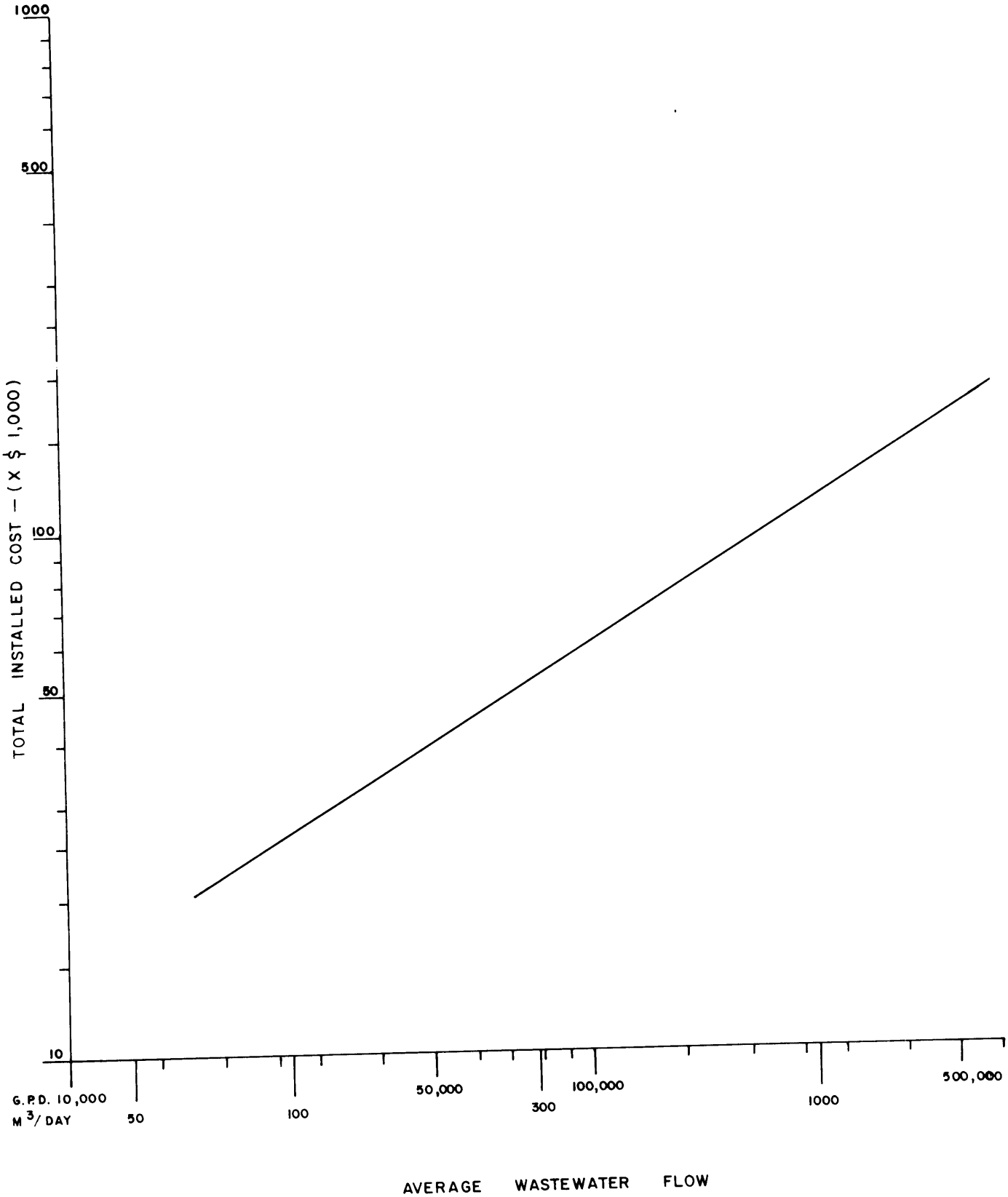


Figure 18. Capital Cost Curve for Coagulation-Sedimentation

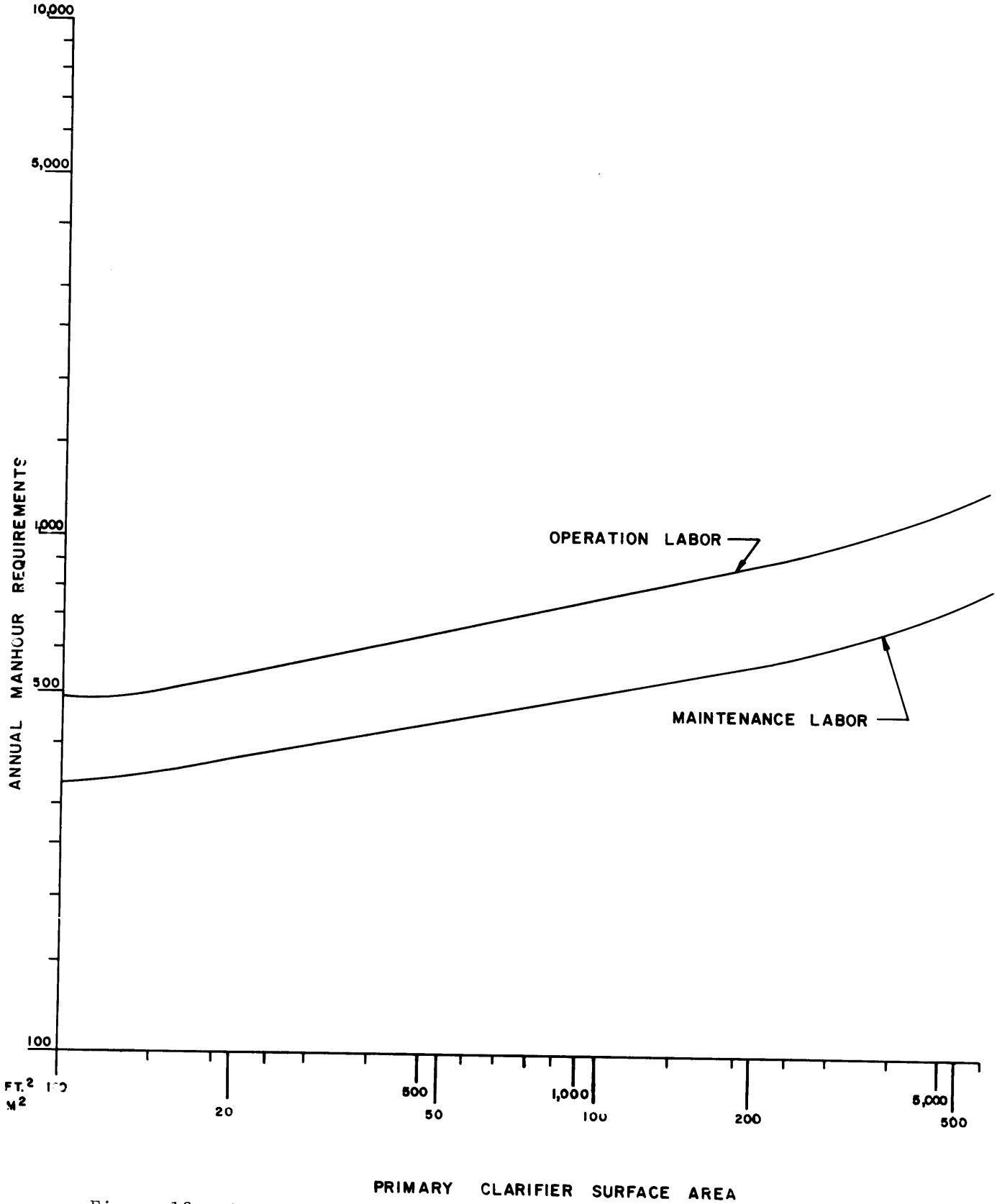


Figure 19. Annual Manhour Requirements for Coagulation-Sedimentation

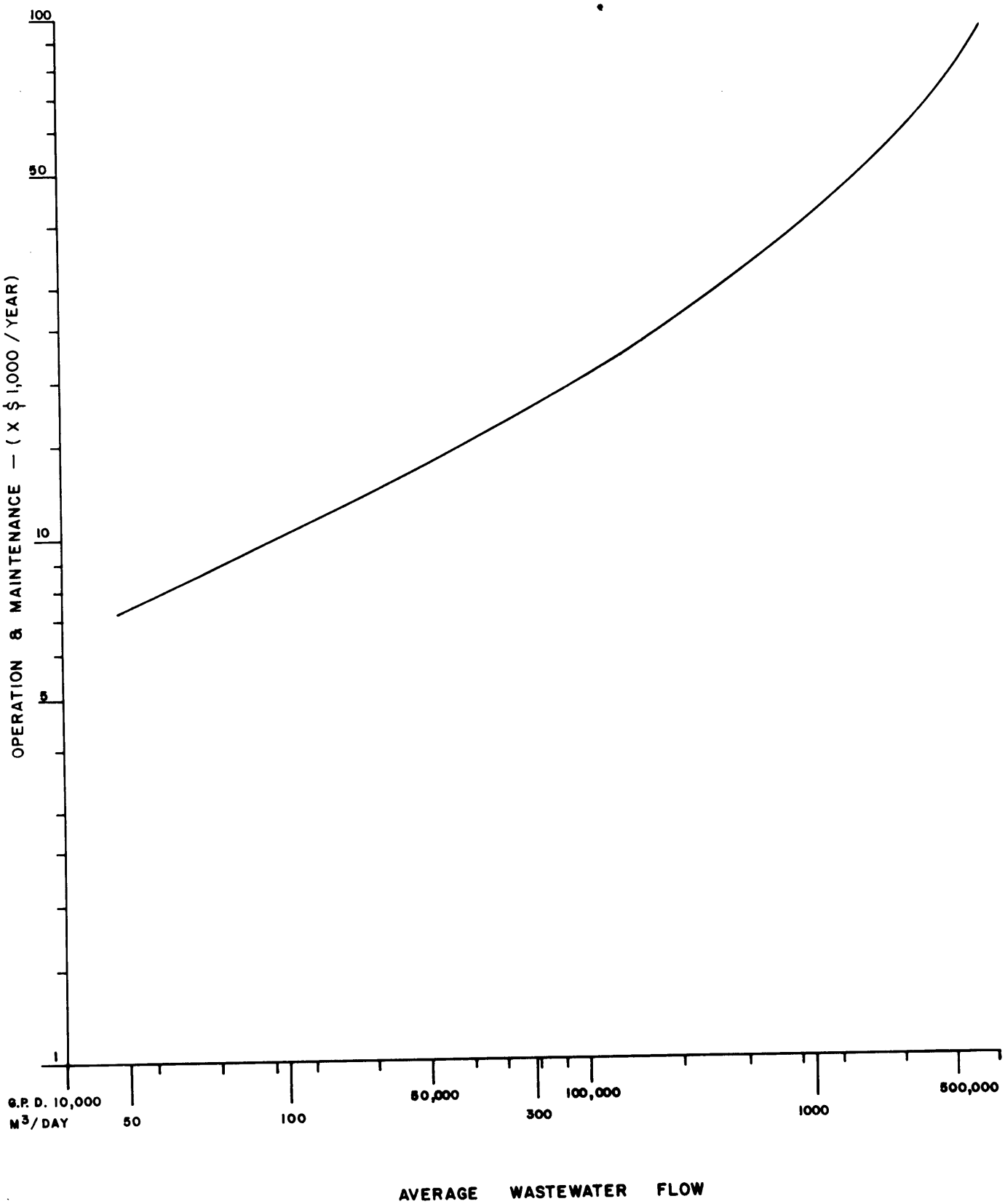


Figure 20. Operation and Maintenance Cost Curve for Equalization and Coagulation-Sedimentation

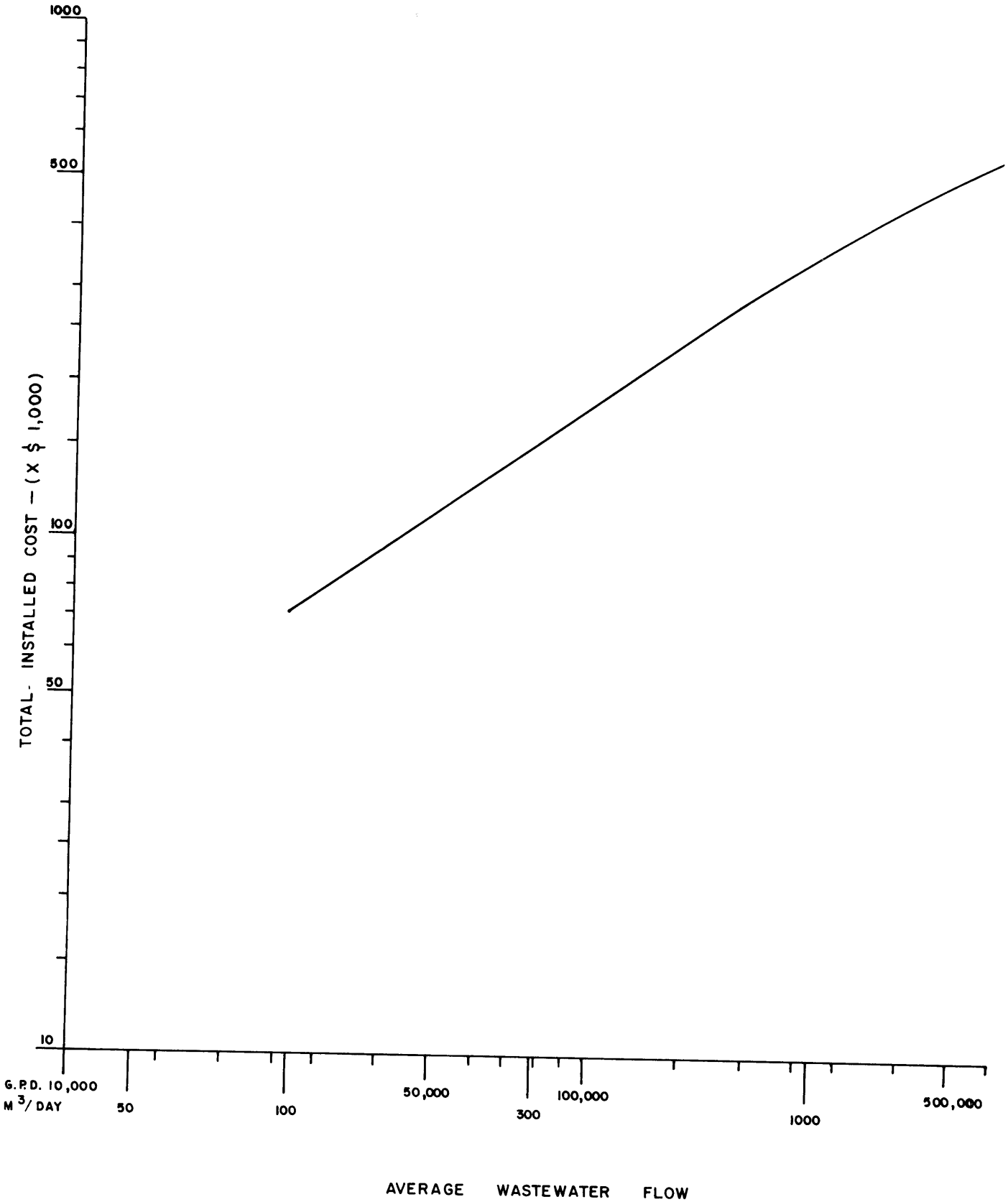


Figure 21. Capital Cost Curve for Activated Sludge Secondary Treatment

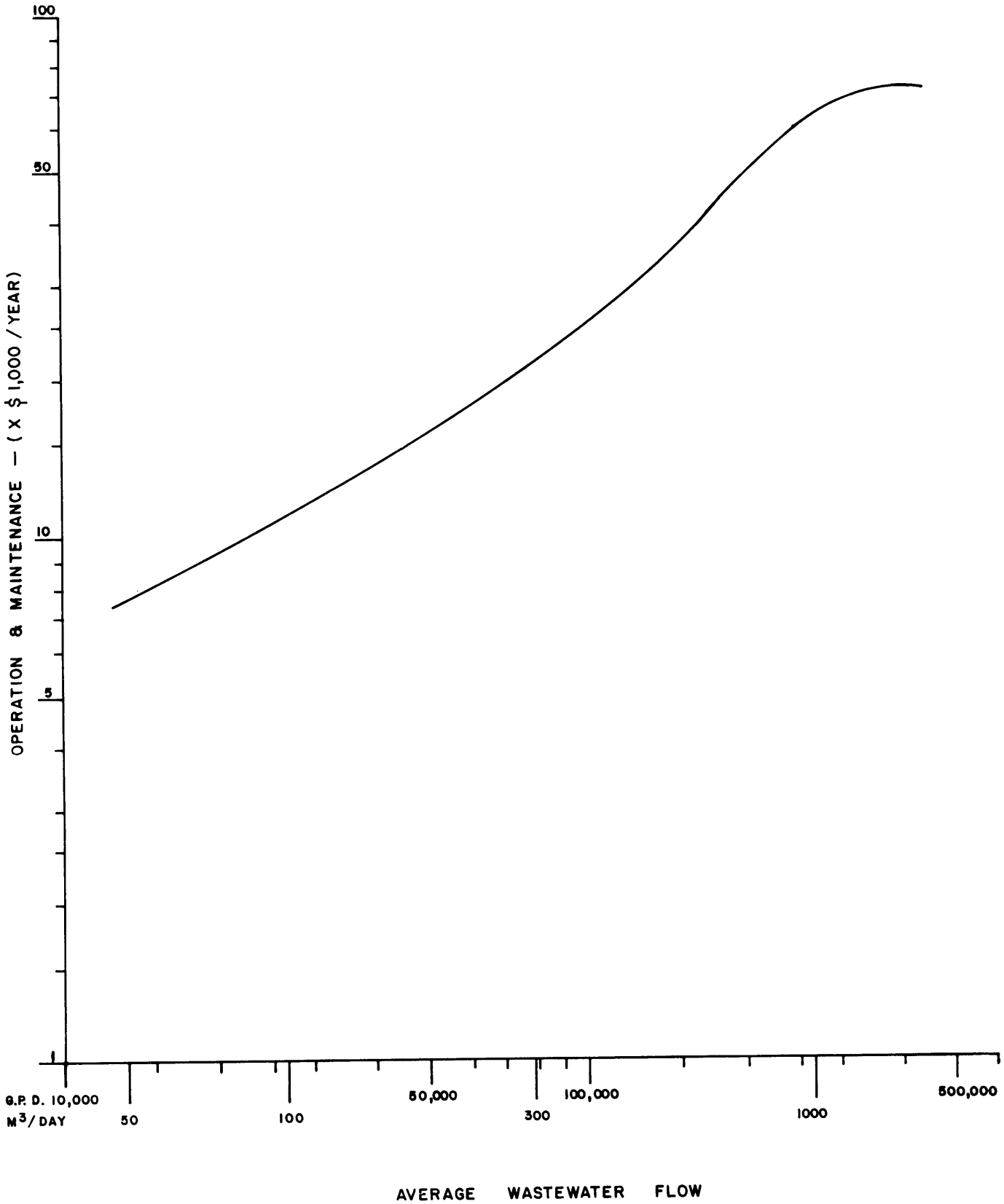


Figure 22. Operation and Maintenance Cost Curve for Activated Sludge Secondary Treatment

aeration basin. The carbon will be added manually by the bag into the aeration basin influent. Thus, the capital cost is only the cost of enough carbon to attain the desired concentration in the aeration basin, based on the following design criteria:

powdered activated carbon concentration = 1800 ppm;

cost of new carbon (no regeneration) = $0.30/lb ($0.66/kg);

sludge age = 30 days; and

number of complete carbon replacements = 12 per year.

The operation and maintenance costs were equal to the annual cost of replacing the activated carbon lost in the wasted activated sludge. Figure 23 shows the relationship of annual operation and maintenance costs for carbon replacement versus wastewater volume.

PAC addition to activated sludge applies to all subcategories.

Multi-media Filtration - Level 6

Multimedia filtration follows upgraded activated sludge in the treatment scheme and is defined as treatment Level 6. The capital cost of multi-media filtration includes the media, tanks, pumps, piping, valves, and installation and is shown graphically versus wastewater volume in Figure 24. The cost data shown on Figure 24 was taken from a rendering industry study incorporating multi-media filtration.[103]

The cost curve for operation and maintenance of multi-media filtration, Figure 25, is based on the following components:

Labor = 1/3 man-year for a system operating at less than 100,000 gpd (379 m^3/d) wastewater flow;

Labor = 1/2 man-year for systems handling more than 100,000 gpd (379 m^3/day);

Power = 10 hp continuous for systems handling less than 100,000 gpd (379 m^3/d);

Power = 15 hp continuous for systems rated at 100,000 to 250,000 gpd (379-948 m^3/day); and

Power = 20 hp continuous for systems handling more than 250,000 gpd (948 m^3/day).

Multi-media filtration applies to all subcategories.

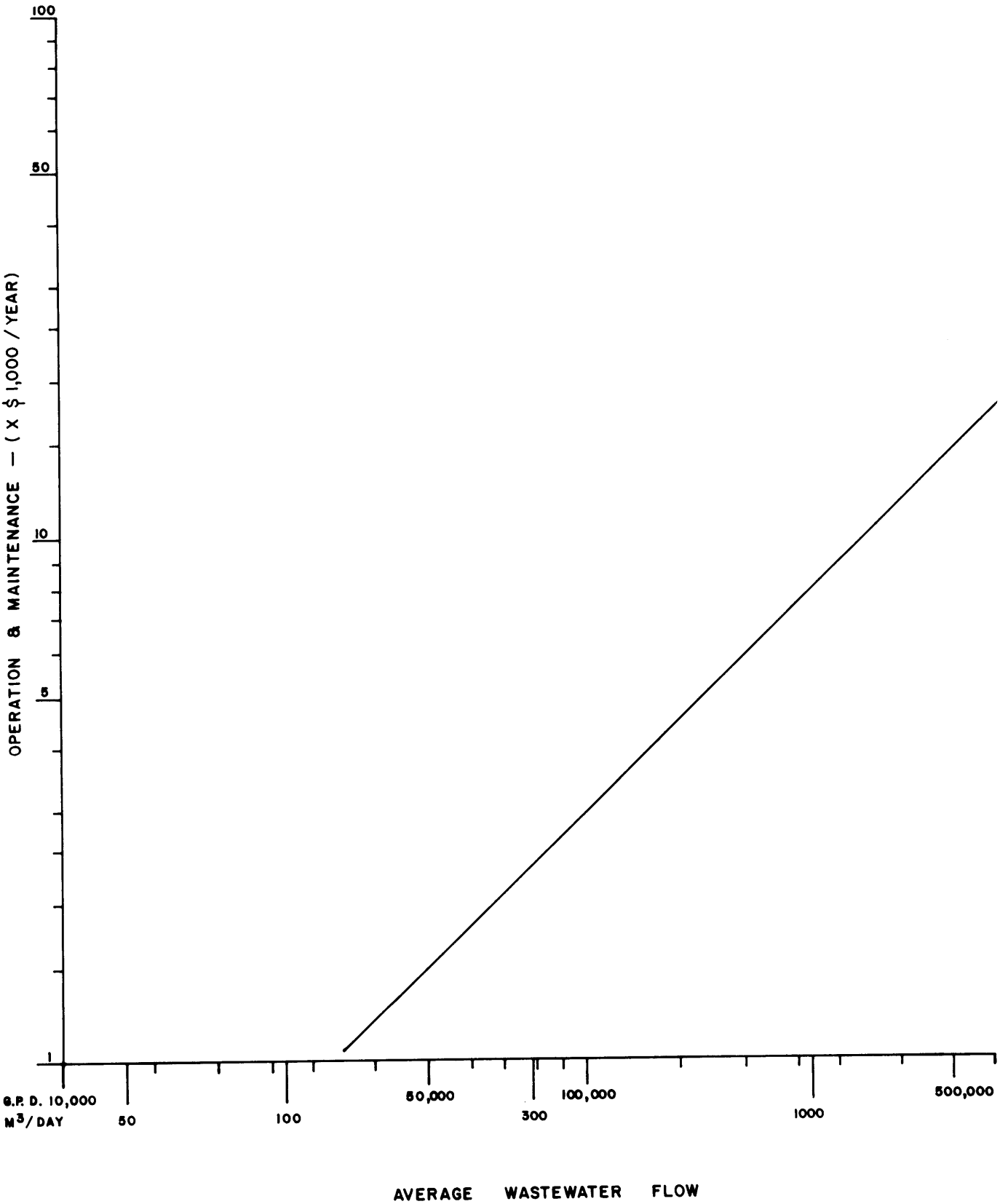


Figure 23. Operation and Maintenance Cost Curve for Upgraded Secondary Treatment

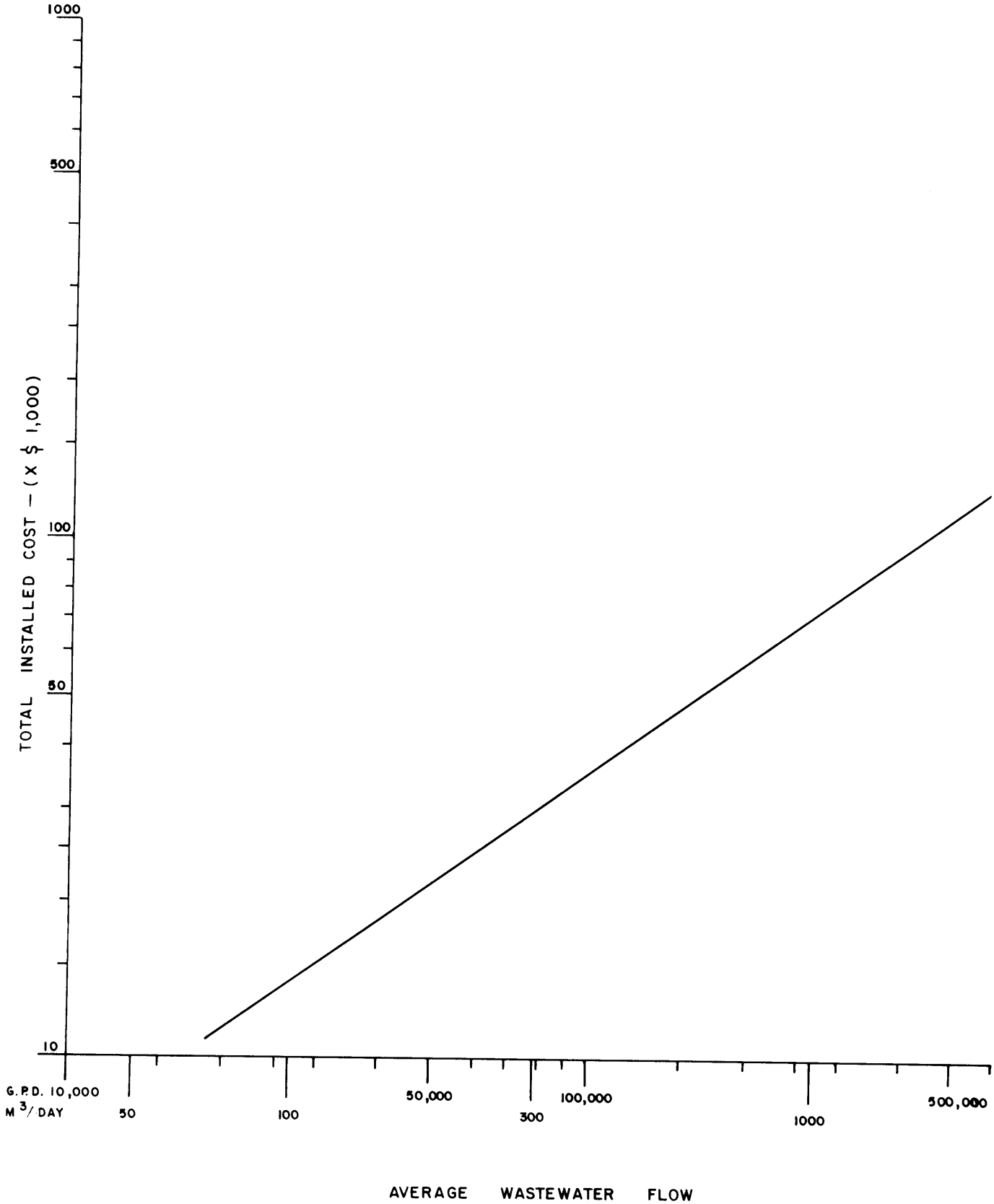


Figure 24. Capital Cost Curve for Multi-Media Filtration

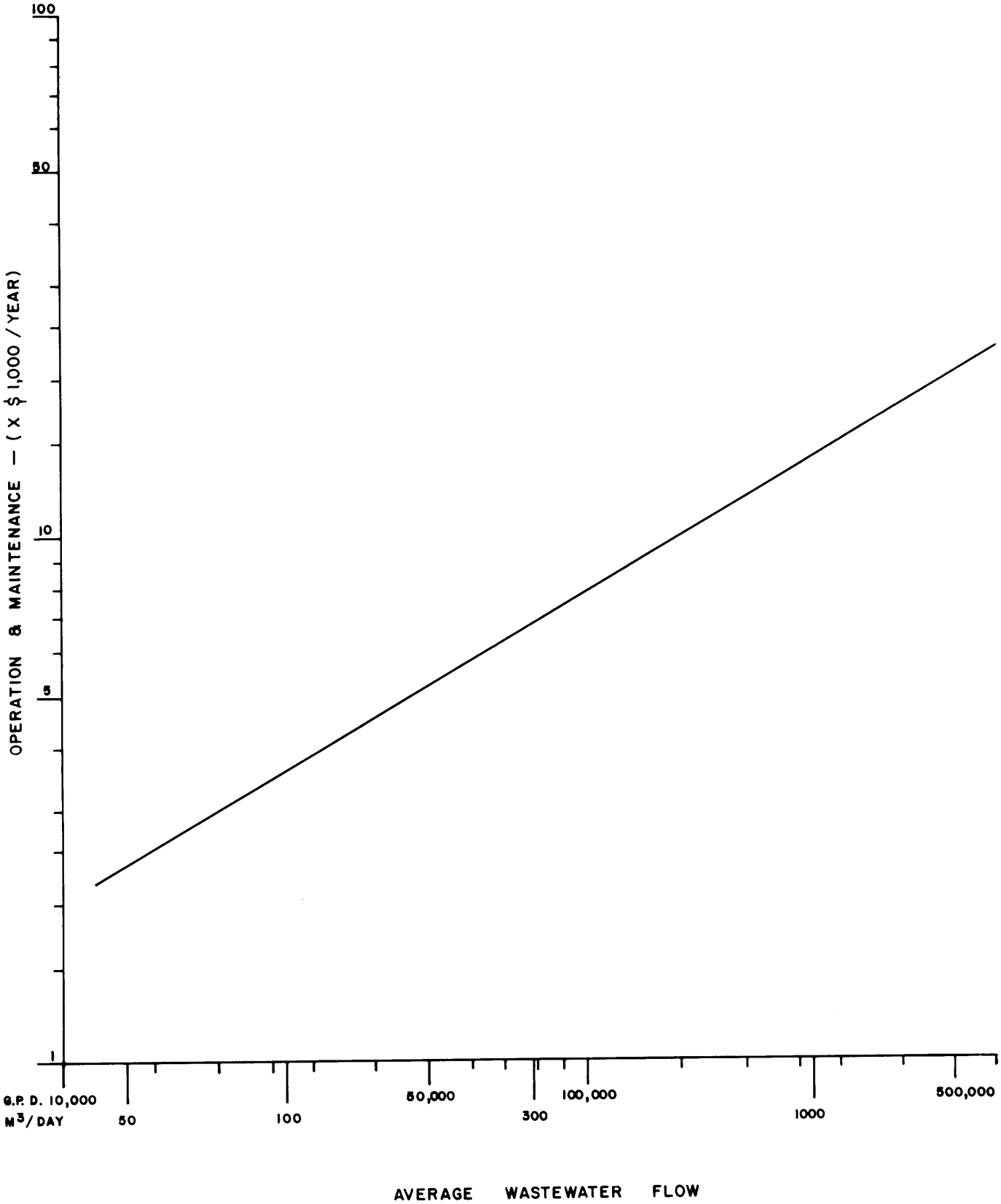


Figure 25. Operation and Maintenance Cost Curve for Multi-Media Filtration

Granular Activated Carbon Columns - Level 7

The use of granular activated carbon columns following multi-media filtration will further reduce the pollutant levels of BOD_5, TSS, COD, and oil and grease. Granular activated carbon column treatment is referred to as treatment Level 7. The capital cost for the complete activated carbon column system with two columns is shown on Figure 26. The costs used in this document for carbon columns were taken from the EPA technology transfer document for carbon adsorption.[104] The costs shown in Figure 26 are based on an empty bed contact time of 30 minutes.

The operation and maintenance costs associated with treatment Level 7 are summarized in Figure 27 based upon the following design criteria:

Carbon used = 1300 lb/mgd treated (0.16 kg/m^3);

Carbon cost = \$0.34/lb (\$0.75/kg) regenerated by outside contract; and

Manpower = 2 man-days/week

GAC columns apply to all subcategories.

Physical/Chemical Treatment - Level 4A

The Chappel process, treatment Level 4A, is a patented physical-chemical treatment process which can produce a treated effluent quality equal to secondary treatment including powdered activated carbon followed by multi-media filtration. The tannery treatment train for direct dischargers using the Chappel process consists of stream separation, in-plant process changes and treatment, equalization, primary coagulation-sedimentation and then the Chappel treatment units. The physical-chemical Chappel process consists of the following equipment:

circular steel equalization tank, 8 ft. deep, providing 1 hr detention time;

acid and alkaline chemical addition tanks;

three steel settling tanks, 8 ft. deep, each providing 6-hr detention time including sludge pumps, aerators, and agitators; and

a clarifier with a 400 gpd/ft^2 (16.4 $m^3/d/m^2$) hydraulic overflow rate.

The capital cost of the Chappel treatment process, shown graphically in Figure 28, was taken from a rendering industry study.[106] The

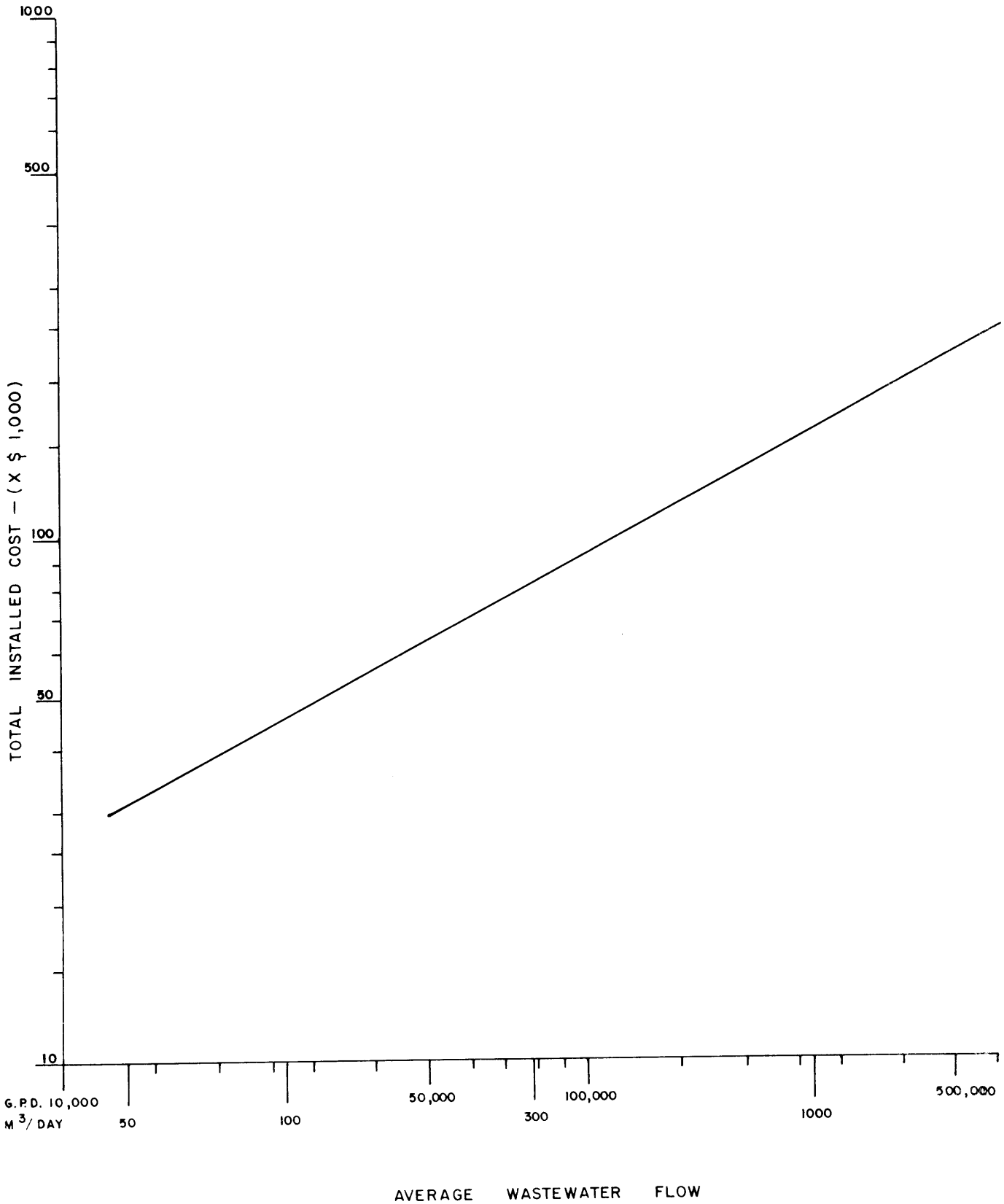


Figure 26. Capital Cost Curve for Activated Carbon Column System

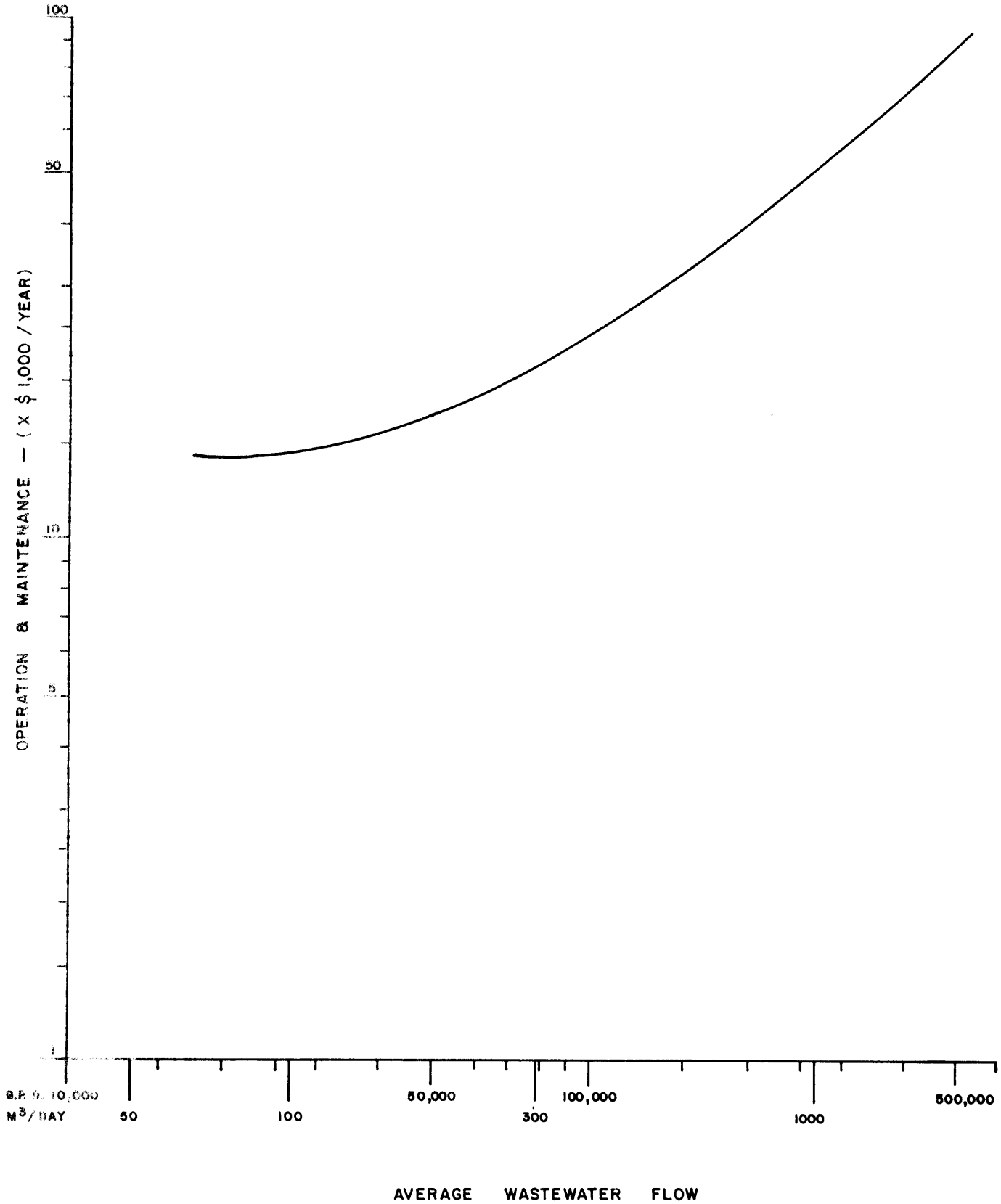


Figure 27. Operation and Maintenance Cost Curve for Activated Carbon Column System

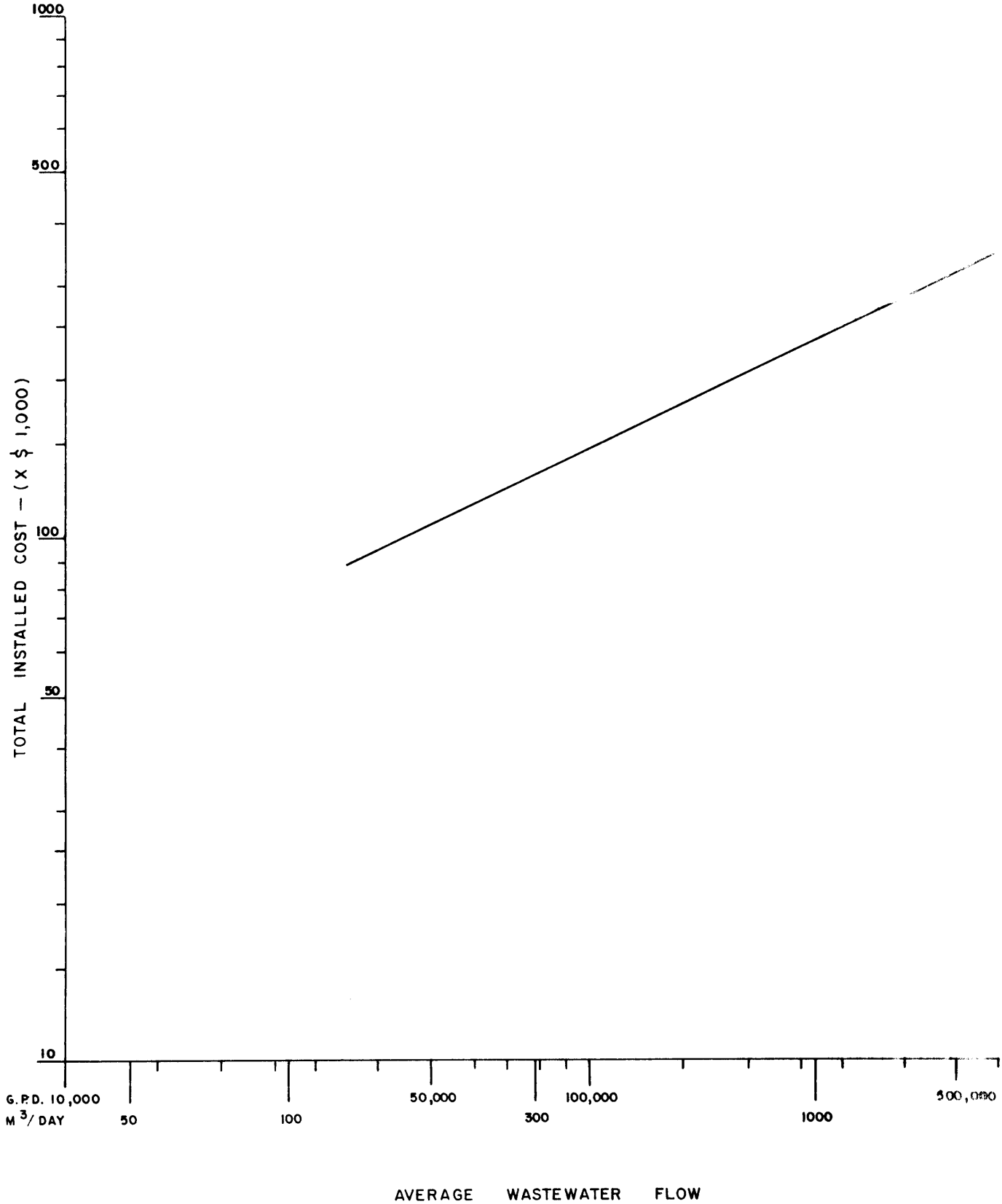


Figure 28. Capital Cost Curve for Chappel Process

equalization settling, and clarifier tanks were priced using air lift pumps at a cost of $750 per foot ($2,460 per meter) in diameter. Figure 29 is a plot of the operation and maintenance cost of the Chappel process against treated flow rate.

Sludge Dewatering

The sludge produced from the various wastewater treatment plant processes, such as coagulation-sedimentation, extended aeration activated sludge, and multi-media filtration backwash, is relatively dilute varying from 0.5 to 8 percent solids. To allow for easier handling and disposal of sludge from the wastewater treatment facility, a sludge drying or dewatering device is required. A horizontal tank leaf filter press sized to provide 700 ft^2 of filtration area per million gallons (17 mi^2/1,000 m^3) of wastewater was used as the basis for the sludge dewatering cost estimate.

The capital costs required for sludge dewatering are indicated in Figure 30. The operation and maintenance cost estimate for dewatering of the sludge is shown in Figure 31.

CAPITAL AND OPERATING COST SUMMARY

Capital costs and operation and maintenance costs have been presented for the in-plant control, preliminary treatment, and end-of-pipe technologies applicable to leather tanneries for pollution control. The levels of technology indicated correspond with those presented in Section VII of this document. The capital expenditure required to implement a pollution control program to achieve these levels of performance will depend on the type and extent of pollution control equipment in place at each tannery, and on tannery-specific cost-effectiveness trade-offs between in-plant and end-of-pipe technologies. In-plant technologies usually involve the reuse, recovery, or removal of process materials that are pollutants from specific waste streams, whereas end-of-pipe technologies are applied to the total wastewater stream to reduce the pollutant loading.

The costs for sulfide and chrome recovery are not included in the technology tabulation. Chrome and sulfide recovery or reuse processes are being installed or considered in the industry because of the strong economic incentive and favorable return on such investments. The trend in the cost and supply situation for chrome essentially mandates chrome reuse, thus eliminating chrome recovery as strictly a pollution control measure.

An increase in energy consumption will occur wherever additional wastewater treatment or processing is implemented. Substitution of raw materials with non-polluting alternatives is possible and requires no additional energy expenditure. Recovery and reuse of raw materials, instead of once-through use, will produce an overall net

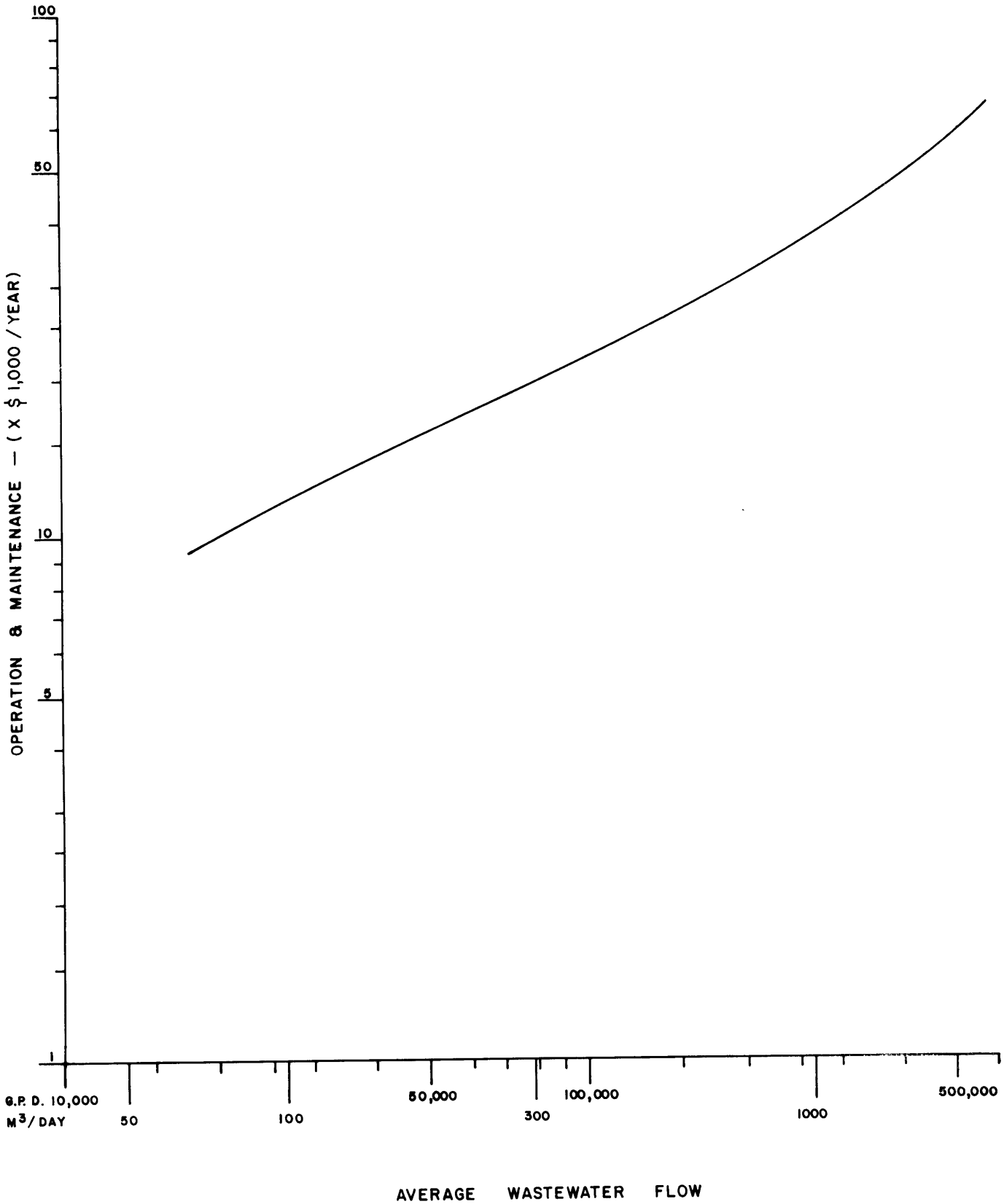


Figure 29. Operation and Maintenance Cost Curve for Chappel Process

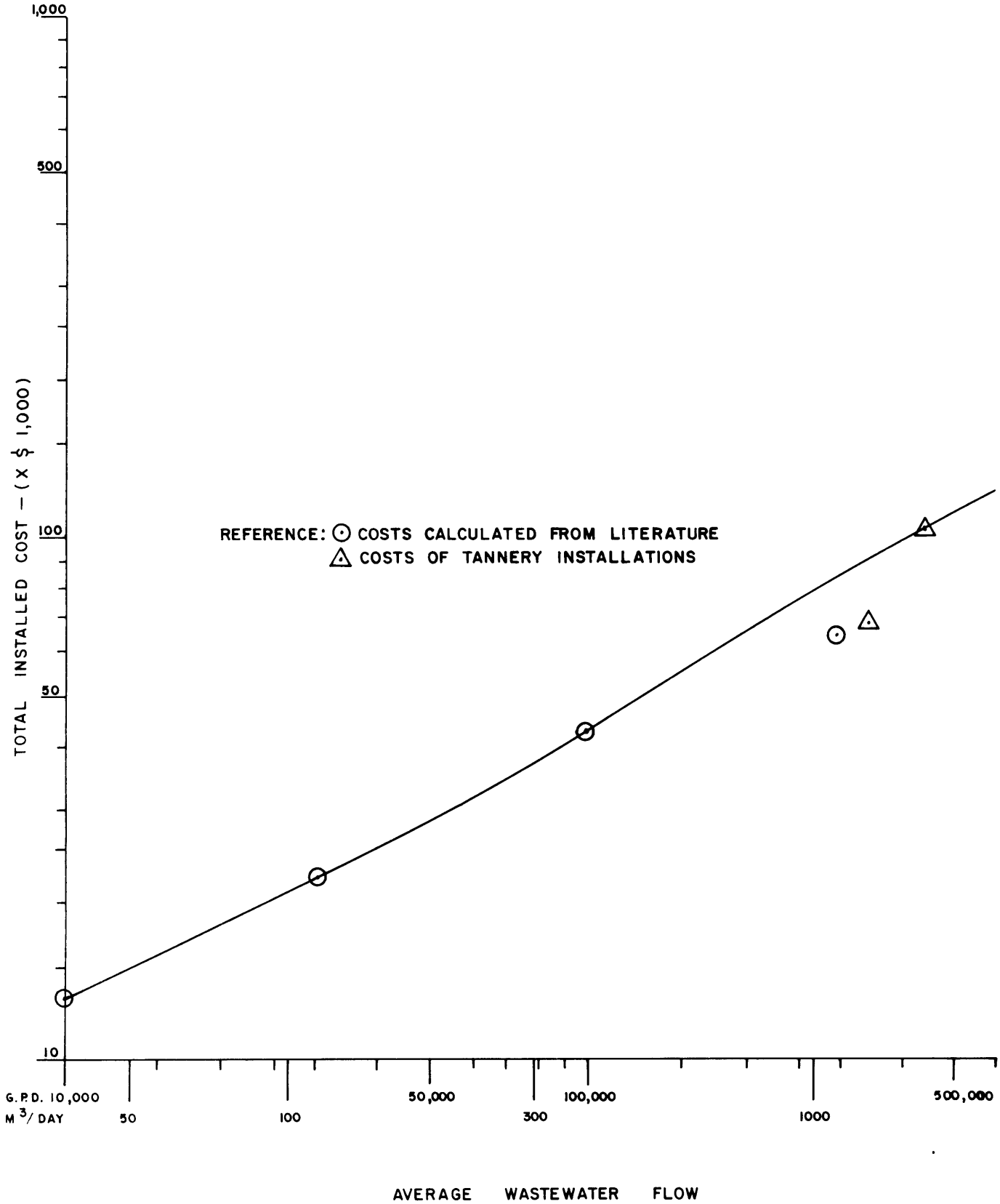


Figure 30. Capital Cost Curve for Sludge Dewatering

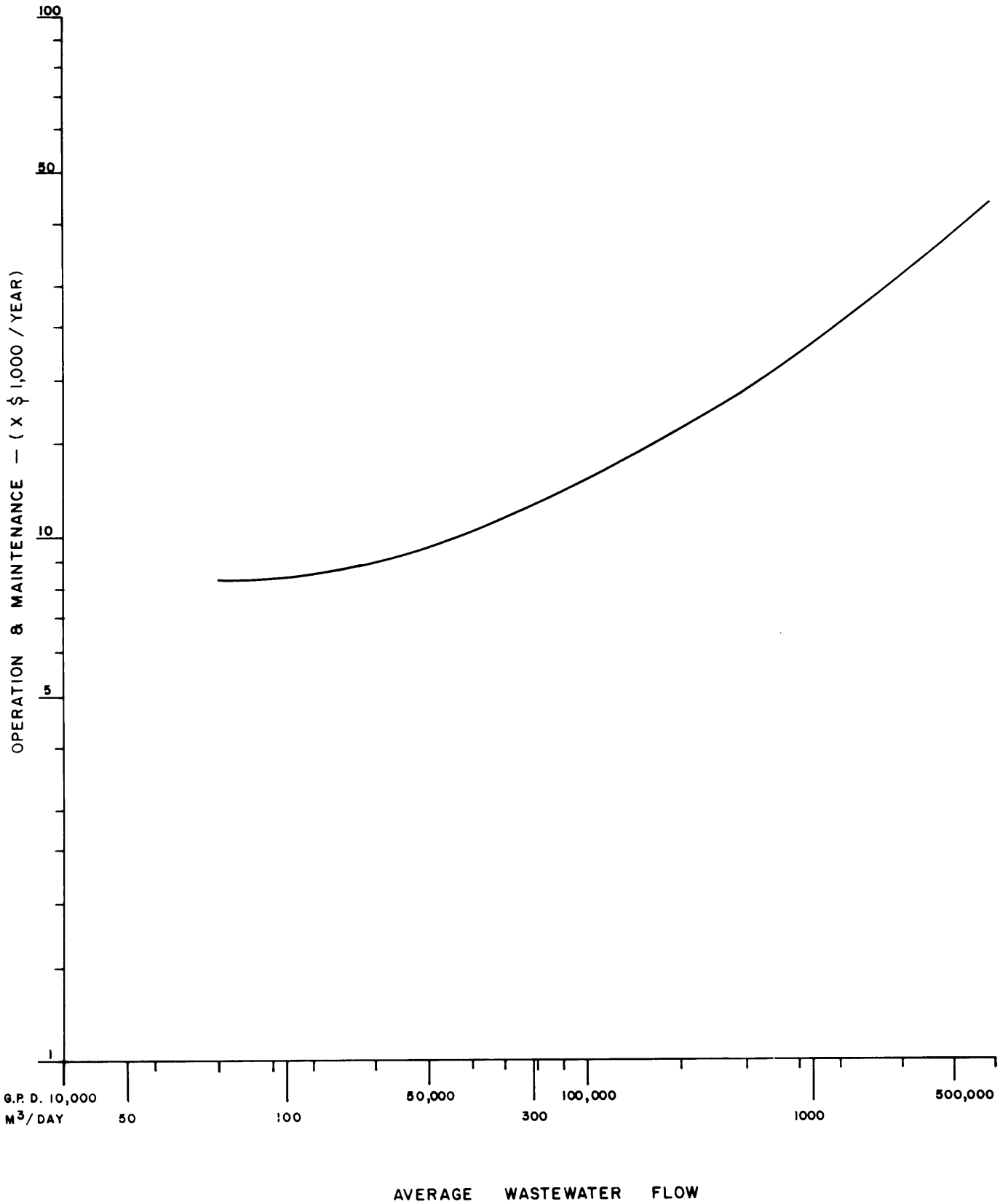


Figure 31. Operation and Maintenance Cost Curve for Sludge Dewatering

energy savings in the total economy of the industry, although energy consumption in a specific tannery may increase.

MONITORING COSTS

The estimated cost is $300 per sample for analysis of acid fraction organic pollutants and $25 per sample for each inorganic toxic pollutant based on current sampling and analytical procedures and technology. The estimated cost of analysis for all pollutants regulated by BAT (BOD_5, COD, TSS, Oil and Grease, Total Chromium, Phenol (4AAP), TKN, Ammonia and Sulfide) is approximately $100 per sample. See Section XIV - MONITORING for further details.

ENERGY REQUIREMENTS

The design of end-of-pipe wastewater treatment plant units is dependent on the performance of in-plant and pretreatment technologies for specific waste streams originating within a tannery. Reuse of process streams, recovery and reuse of chemicals, and reduction of wastewater volume are primary aspects of these technologies. Each of these reuse and reduction processes is inherently energy conserving in the production of leather and in wastewater treatment.

The removal or reduction of pollutants in any wastewater stream requires an energy expenditure. The higher levels of treatment as described in Section VII produce a higher quality effluent with lower levels of pollutants. This means a greater energy consumption than at lesser levels of performance.

NON-WATER QUALITY ASPECTS

Solid Wastes

Characteristics. Solid waste from a tannery with a wastewater pretreatment/treatment system may include any or all of the following:

1. fleshings,
2. hair,
3. hide trimmings,
4. tanned hide trim and shavings,
5. leather trimmings,
6. buffing dust,
7. leather finishing residues,
8. wastewater treatment sludges, and
9. general plant waste.

The specific types of solid waste generated by a tannery depend upon the type of processing operations conducted. The quantity of each type of waste generated depends upon the volume of production at the tannery.

Tanneries which generate fleshings and hide trimmings sometimes sell these waste materials to rendering plants, or occasionally to glue manufacturers. Since these waste materials are highly putrescible, daily collection is required. Very small tanneries which process only a few hundred hides per day often find it uneconomical to sell this waste since the by-product recovery value is exceeded by the handling and transportation costs.

Most vegetable leather tanneries and a few chrome leather tanneries remove hair from hides using a hair save operation. At a few of these tanneries, the hair is washed, dried and baled, and subsequently sold as a by-product. Most of these plants, however, merely screen out the removed hair and dispose of it in landfills. A few plants allow the hair to enter the general plant wastewater, which can result in plugging of pipes, clogging and destruction of pumps, fouling of clarifier sludge raking mechanisms and weirs, etc. Use of the hair save method is declining in favor of the hair-pulp method. As noted in Section III, however, some tanners still use a modified hair save beamhouse which produces hair that is disposed of in a landfill. At tanneries using the hair pulp method of hair removal, the hair is dissolved and becomes part of the wastewater stream.

Some chrome leather tanneries, particularly split leather tanners located in the northeastern U.S., generate large quantities of tanned hide trimmings and shavings. This waste material can be sold as a by-product. By-products are used in the manufacture of fertilizer, chrome glue, hog feed supplement, and leather board, and provide an energy source for steam production. The majority of this type of waste, however, is disposed as solid waste.

A recent industry study estimated that the total quantity of solid waste disposed in the land in 1974 was 203,000 metric tons.[106] The distribution of the total quantity of waste between the four major waste types was as follows:

Table 37

Industry Estimates for Land Disposal of Solid Wastes

Type of Waste	Quantity*	Percent of Total Waste
Wastewater treatment residues (screenings & sludge)	122,000	60
Tanned hide trimmings & shavings and leather trimmings	71,000	35
General plant waste	6,000	3
Leather finishing residues	4,000	2

*metric tons generated in 1974

Reuse and recovery with reuse are two technologies that will reduce solid waste generation in wastewater treatment plants. Alternative chemicals use may have similar results.

Pollution control applied to specific waste streams before all are combined into a single total wastewater stream may produce a solid waste, but the specific contaminants in the solids will generally be known and in the most concentrated form. Such solid wastes are most manageable in terms of proper control and disposal. Numerous small quantities of solid waste of more concentrated composition may be less economical to handle and transport, but will be much more environmentally manageable than a single, large, dilute, and multicontaminated solid waste. The latter would usually result from a waste treatment system confined exclusively to end-of-pipe technology.

The primary contaminants of solid wastes from tanneries are chromium and other heavy metals occurring in the wastewater, such as copper, lead, and zinc. Repeated reuse of the chromium containing streams and/or recovery and reuse will reduce chrome contamination of the solid wastes. The other metals originate in the raw materials or as corrosion products from the equipment in the tanneries. The former can be controlled by changing raw materials or their composition, or by eliminating the use of such raw materials. Alternative construction materials for equipment would be the best solution to the corrosion source.

Disposal Alternatives. Approximately 60 percent of the wastewater treatment residues produced come from chrome leather tanneries with primary and/or secondary wastewater treatment facilities, while 20 percent originate from chrome tanneries with secondary wastewater treatment systems. Treatment plant sludge from chrome tanneries is

normally dewatered prior to disposal. Sludge dewatering may be accomplished using gravity or mechanical means. Gravity dewatering (sequential settling) is relatively uncommon; however, sludge drying beds on the tannery plant site are used by some tanners. Mechanical sludge dewatering is normally accomplished using vacuum filters, centrifuges, or filter presses. These three mechanical dewatering techniques have all been found to be effective in producing sludge cakes ranging from 10 to 40 percent solids. There seems to be a preference for filter presses due to the drier (40 percent solids) filter cake produced.

Secondary wastewater treatment sludges from vegetable tanneries are normally dewatered in evaporative lagoons, after which the sludge is either used as a soil conditioner or disposed of in a dump or landfill.

Sewer sump sludge is composed primarily of precipitated lime and is not normally dewatered prior to disposal. Dumps and landfills are the most common disposal facilities for this waste.

The different types of solid waste disposal facilities utilized and estimates of the proportion of the total quantity of tannery solid waste going to each type of facility are shown in Table 38. As shown, nearly all tannery solid waste is disposed in landfills or dumps. Trenches, lagoons, and certified hazardous waste disposal facilities are currently used almost exclusively for sludge disposal. A small percentage of tanneries operate their own disposal sites. Tannery-owned disposal facilities are usually associated with vegetable leather tanneries and are the result of the plant's remote location or the fact that other disposal sites will not accept the solid waste. Most tannery solid waste which is land disposed contains substantial concentrations of trivalent chromium (up to several percent on a wet weight basis) and, in many cases, copper, lead, and zinc as well. For example, the "typical" concentrations of certain constituents in tannery sludge are presented in Table 39. As shown, sludge from vegetable leather tanneries is the only type which does not normally contain significant heavy metal concentrations, unless concurrent chrome tanning or retanning occurs at the same plant. The recent trend toward chrome reuse or recovery would not be reflected in this data and would suggest lower chrome concentrations in future sludges.

EPA believes that many of the toxic pollutants, especially heavy metals, are removed with the sludge. There are no data available on the fate of these pollutants or the actual distribution of these pollutants between the solid and liquid phases. These toxic pollutants would thereby become part of the solids to be disposed of from leather tanneries. No analyses were made for toxic pollutants at the time the data in Table 39 was generated, thus no additional information is currently available regarding toxic pollutants in sludges from leather tanning waste treatment. A substantial amount of

Table 38 Disposal Sites Utilized

General Category of Disposal Site	Specific Type of Disposal Site	Percent of Waste Disposed
Landfill		60
	municipal sanitary	3
	private sanitary	3
	municipal engineered*	5
	private engineered	10
	municipal converted**	20
	private converted	14
	on-site tannery	5
Dump		25
	municipal	20
	private	1
	on-site tannery	4
Trenches or lagoons		9
	municipal	4
	private	4
	on-site tannery	1
Certified***	private	6

*Engineered disposal sites which do not provide daily cover
**Dumps which have been coverted to landfills without being engineered
***Certified hazardous waste disposal facilities

Table 39 "Typical" Sludge Characteristics*

Constituent	Chrome leather tannery pretreatment/treatment sludge		Chrome leather tannery sewer sump sludge (not dewatered)	Vegetable leather tannery secondary treatment sludge (not dewatered)
	before dewatering	after dewatering		
Solids content (%)	5-10	20-30	5-15	3-6
Chromium (mg/l)	3,000-6,000	10,000-15,000	2,000-4,000	<5
Copper (mg/l)	100-150	150-200	100-200	<10
Lead (mg/l)	10-25	50-150	10-25	<5
Sulfides (mg/l)	20-50	50-150	30-60	25-50
Phenols (mg/l)	<10	<10	<10	<1

*All values are on a wet weight basis

data will become available and will be considered prior to promulgation of these regulations.

The fact that 60 percent of tannery solid wastes are waste treatment residues and that the disposal sites reportedly used include a wide variety of types suggests that the solid waste disposal practice of the industry leads to widespread dispersed deposition of toxic pollutant contaminated solids.

Disposal Site Factors. The possibility that leachate generation and subsequent contamination of ground and surface waters may occur at facilities where tannery wastes are disposed of requires that disposal sites be carefully selected. Site topography must minimize surface water flow across the site, and the soils should be able to contribute to leachate attentuation. Operational procedures should be employed which will minimize percolation of precipitation through the refuse. Leachate collection systems at landfills used for solid waste disposal are recommended to provide adequate assurance that ground and surface waters will be protected from contamination.

Leather finishing residues are the one solid waste from tanneries that may contain significant quantities of flammable organic solvents. Consequently, disposal sites which receive this type of waste must take precautions to minimize the potential fire hazard from this material.

RCRA Considerations

Regulations proposed by EPA under Section 3001 of the Resource Conservation and Recovery Act (RCRA) list leather tanning and finishing solid wastes as "hazardous." 43 FR 58946, 58959 (Dec. 18, 1978). These wastes, therefore, will be subject to rigorous handling, transportation and treatment, storage, and disposal requirements, under Sections 3002-3004 of RCRA. EPA's proposed generator standards would require generators of leather tanning wastes to meet stringent containerization, labeling and reporting requirements, and, if they dispose of wastes off-site, to prepare a manifest which will track the movement of the wastes from the generator's premises to a permitted off-site treatment, storage, or disposal facility. See 43 FR 58946, 58969 (Dec. 18, 1978). The proposed transporter regulations would require transporters of leather tanning wastes to comply with the manifest and assure that the wastes are delivered to a permitted facility. See 43 FR 18506 (April 28, 1978). Finally, the proposed treater, storer, and disposer standards would establish technical design and performance standards for leather tanning waste storage facilities, and for landfills, basins, surface impoundments, incinerators, and other facilities where such wastes would be treated or disposed, as well as security, contingency plan, employee training, recordkeeping, reporting,

inspection, monitoring and financial liability requirements for all such facilities. See 43 FR 58946, 58982 (Dec. 18, 1978).

Hide and Leather Waste Alternative Uses

The following discussion was taken from a report prepared for the Tanners Council of America (TCA), February 18, 1977.

The four use areas selected for analysis were chosen to consider as broadly as possible all categories of solid waste and also several types of initial processing (i.e., size reduction, incineration, pyrolysis and hydrolysis). The use areas selected for analysis were:

1. Incineration of blue split and finished leather waste;

2. Fiberized leather for loose building insulation;

3. Pyrolyzed leather waste to make activated carbon and by-product chemicals; and

4. Hydrolyzed leather and cattle hair to make leather and hair meals for use in animal and pet foods.

Incineration. Incineration of various leather wastes with provision for useful recovery of the released energy is a surprisingly productive use for the materials. Leather is a "clean" fuel in the sense that it contains virtually no sulfur. The heating value (dry basis) is about 80 to 90 percent as much as that for a low-sulfur Western coal.

The heating value of wet blue waste is naturally diminished somewhat by the water present, but it still amounts to about 55 to 75 percent of that for a low-sulfur Western coal. By burning the available leather waste, a blue split tannery could save nearly all the money now spent for coal or fuel oil to furnish the required process hot water. The incinerators could probably be switched over to coal without any problems when and if better uses for the waste leather were developed, making this kind of venture essentially risk-free.

In addition to the recovery of energy, incineration of chrome tanned leather waste also permits the recovery of a non-renewable resource, chromium oxide. In one case, an ash from the incineration of chrome tanned waste contained 2.23 percent hexavalent chromium. The trivalent chromium (Cr_2O_3) content of chrome tanned leather ash is known to range from 13.5 to 58.3 percent.

The incineration ash would have a minimum value of about $200 per contained ton of Cr_2O_3 on the basis of the current value of imported chromite ore. If the ash could be upgraded to a pigment grade product

(99+ percent Cr_2O_3), it could be sold for about $1 per pound as the purified pigment.

On the basis of competition with a low-sulfur Western coal at $19 to $21 per ton delivered in Chicago, blue leather waste would have an approximate value of $11.75 to $15.75 per ton (dry basis). This value takes account of the heat required to evaporate the water from the wet waste. Sale of the ash would add about $4 per ton to the realizable value of the blue leather waste by incineration, making the total realizable value by incineration in the range of $16 to $20 per ton (dry basis).

The capital cost (installed) of an incinerator handling about 1.2 tons of waste per hour would be at least $600,000. Such an installation would furnish 8,645 lb/hour (19,040 kg/hr) of steam.

"Poured" Insulation. Ground or fiberized leather waste has many attributes which make it a good candidate material for use as a loose insulation for residences and light commercial structures. It is strongly resistant to environmental degradation and surprisingly resistant to ignition, even though it can be incinerated. A study sponsored by the Tanners' Council of America found only one company in the business of producing a fiberized leather product. There was no indication of any effort to promote the material for insulation purposes.

No measurements have been made on the insulation performance of fiberized leather, but measurements of its apparent bulk density place the material in the range of granulated cork and chopped cellulosic insulation. The thermal conductivity of bulk leather is comparable to that for paper, again indicating that a fiberized leather material should perform technically much like cellulosic insulation.

The chief problems to be dealt with in developing fiberized leather as an insulation material are the cost of fiberizing and the requirement that the product be odorless. Both of these problems can likely be solved. The total costs for a fiberized leather product would probably be about $110 per ton, which would be comparable with cellulosic insulation at $240 per ton.

The market for all insulation material has grown remarkably in the last few years due to the rapid increase in the cost of all forms of energy. The growth in the use of cellulosic insulation materials has been at the rate of 34 percent compounded annually over the last few years. It is believed that in 1976 the total market for cellulosic insulation was about 300,000 tons. This may be compared with the 80,000 tons of chrome leather waste believed to be available annually in the United States.

Activated Carbon. Upon heating leather waste to a temperature of 400 degrees C, a 50 percent yield of a hard granular char could be obtained. This has been interpreted to mean that leather could be converted in about this yield to a hard, granular, activated carbon. Although there are three literature references during the last 20 years to making activated carbon from leather wastes, none of these references noted that hard granules could be obtained. This is a significant feature because hard granular activated carbon is a premium material.

Activated carbon is manufactured commercially in the United States by nine different companies. A new producer completed a semi-works plant in 1976 and plans to complete a full scale plant in 1978. Production will be based on a new proprietary one-step process in contrast with the two-step processes used by the other producers. It has been suggested that future work on the conversion of leather waste to activated carbon should be directed toward the development of a one-step process in view of the energy conservation possibilities in such an approach.

The selling prices for granular activated carbons are in the range of $0.40 to $0.50 per pound ($0.88 to $1.10 per kg). This is significantly higher than the $0.10 to $0.12 per pound ($0.22 to $0.26 per kg) prices paid for powdered activated carbons. The price of a granular carbon reflects both the absorption efficiency of the material and its resistance to attrition in use (i.e., its hardness).

Activated carbons are also used to remove: tastes and odors from potable waters; impurities and colored substances from sugar; impurities from a great variety of chemicals; and harmful or odorous substances from gaseous effluents. A small but well-known use is as a component in cigarette filters.

The energy costs for charring leather wastes and then treating the char to activate it are no doubt significant factors of unknown magnitude. Capital costs are evidently also an important factor. The volatile materials evolved in the carbonation process would at least have value as fuel. It seems likely that the ammonia given off could be advantageously recovered for use as fertilizer. The mixture of volatile organic materials also evolved might have value as chemical intermediates greater than their value as fuel.

Leather and Hair Meal for Feeds. Although both leather and hair are protein materials, neither of them is digestible as such. Hydrolysis will render each of them digestible, and both of the resulting meals have been shown to be useful supplements in diets for swine and poultry.

Hair meal is very similar in amino acid composition to feather meal, which is a well-established ingredient in poultry diets. Therefore, in respect to nutritional utility, hair meal is the full equivalent of feather meal.

In the case of ruminants (sheep and cattle), hair meal could be used to supply virtually all of the nitrogen requirements of the animals because they have no well-defined amino acid requirements. Because sheep and cattle can use nitrogen from a number of very low cost sources (urea, grass, alfalfa, etc.) it is believed that hair meal would be too expensive for inclusion in their diets.

However, there is some danger that hair meals might be contaminated with toxic substances arising from the use of chlorinated phenols as fungicides in processing the hides. This possibility must be ruled out before a specific attempt is made to market hair meal as a feedstuff component.

Animal consumption of feather meal is currently 100,000 tons annually, with ample supplies available. Hair meals would compete directly with feather meal, which sells for about $185 per ton. The cost of recovering, washing, and drying hair amounted to $120 per ton. In making hair meal, the drying would not take place until after hydrolysis, so that hair preparation would be somewhat less than $120 per ton.

The basic costs associated with the conversion of hair to a dry meal amount to about $65 per ton. The total costs ($180 per ton) are well below the present ceiling of $300 to $340 per ton set by the current selling price of feather meal. However, present protein prices are high because the 1976 soybean crop in the United States was about 20 percent below the 1975 crop and the 1976 foreign crop was also below expectations. At the same time, demand has remained strong.

Leather meal is permitted as a component in the diets of swine at a level not exceeding 1 percent. This is too small an amount to make leather meal at all attractive as a component in swine rations. However, feeding tests with broilers indicated that 6 percent leather meal in the diet afforded an economic advantage over the control diet in allowing the omission of two other ingredients (feather meal and poultry by-product meal).

Leather meal has not yet been approved for inclusion in poultry diets. An application for approval by the Food and Drug Administration was withdrawn "without prejudice" when it was discovered that highly dangerous dioxins (TCDD) were present in leather meal. While the levels of dioxins in leather meal were not established, even very small amounts are valid cause for hesitation in going ahead with the use of leather meal in animal feeds.

Dioxins are known to have been impurities in the chlorinated phenols used as fungicides in the processing of hides into leather. Recent advances in the manufacture of chlorinated phenols have led to great reductions in the amounts of dioxins contained in these fungicidal phenols. High temperature drying of hydrolyzed leather may also lead to the conversion of the small amounts of chlorinated phenols in the hides into dioxins. If this were the source of the dioxins, then the formation of dioxins might be avoided by drying the hydrolyzed leather sludge for a longer time at a lower temperature.

This use for leather meal has good economic prospects. The poultry feed market in 1975 amounted to over 26,000 tons. If all this feed were to contain 6 percent of leather meal, almost 1,600 tons of leather meal could be used in this single application annually. This is considerably less than the 80 thousand tons of chrome leather waste previously referred to as being annually available in the United States.

In view of the similarity between leather meal and meat scrap/bone meal in respect to protein quality, it seems likely that leather meal, free of dioxins, should sell at about the same price as meat scrap/bone meal. Recent price quotations show that meat scrap/bone meal (50 percent protein) sells for a little over $250 per ton. On this basis, leather meal, containing as it does about 65 percent protein, should sell for about $325 per ton. Leather meal today sells for only $102.50 to $108 per ton.

Air Pollution

The major potential source of air particulate matter from a tannery is from hide buffing operations. However, most tanneries control this by wet scrubbing. Scrubber water is generally combined with the total waste stream. Several tanneries are adding buffing dust to sludge derived from liquid waste treatment for disposal.

In addition to process sources, tannery boilers can be a source of air pollution. With proper design and maintenance of gas- and oil-fired boilers, there should be no emission problems; however, with coal-fired boilers, fly ash emissions are a problem. Fly ash emissions can be kept to a minimum with proper design and operation. Dust collection equipment may be used to further control air pollution. Wet scrubbers or electrostatic precipitators are capable of providing in excess of 98 percent removal of the fly ash. If a wet scrubber is used, the waste dust slurry can be discharged to the wastewater treatment system. Fly ash from the electrostatic precipitators can be combined with the dewatered sludge for disposal.

Sulfide is the other potential air pollutant of consequence originating from leather tannery wastes. The sulfide content of tannery wastes must be reduced and maintained at a low level for

biological treatment systems to work, to protect the health and lives of workers exposed to leather tanning wastewaters, and to minimize the potential for air pollution from any waste treatment system.

Imposition of BPT, BAT, BCT, NSPS, PSES, and PSNS will not create any substantial air pollution problems. However, small amounts of volatile organic compounds may be released to the atmosphere by aeration systems in biological treatment.

Noise

Noise levels associated with wastewater treatment and control both in-plant and at end-of-pipe are of no material significance as a specific noise source or as an increase in the ambient noise levels in leather tanning facilities.

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE--EFFLUENT LIMITATIONS GUIDELINES

GENERAL

The effluent limitations which were required to be achieved by July 1, 1977, are based on the degree of effluent reduction attainable through the application of the Best Practicable Control Technology Currently Available (BPT). The BPT technology is generally based upon the average of the best existing performances by plants of various sizes, ages and unit processes within the industry. This average is not based upon a broad range of plants within the leather tanning and finishing industry, but has been derived from performance levels achieved by exemplary plants. In industrial subcategories where present control and treatment practices are uniformly inadequate, a level of control higher than any currently in place may be required if the technology to achieve this level can be practicably applied.

BPT emphasizes not only treatment facilities at the end of manufacturing processes, but includes control technologies within the process itself, if such in-plant control technologies are considered to be normal practice within an industry.

In establishing BPT effluent limitation guidelines, EPA must consider several factors, including:

1. the manufacturing processes employed by the industry;
2. the age and size of equipment and facilities involved;
3. the engineering aspects of application of various types of control techniques;
4. the cost of achieving the effluent reduction resulting from the application of the technology; and
5. non-water quality environmental impact (including energy requirements).

The BPT regulations promulgated by EPA on April 9, 1974 (39 FR 12958) were remanded by the United States Court of Appeals in Tanners' Council of America v. Train, 540 F.2d 1188 (4th Cir. 1976). The Court held, among other things, that: 1) the Agency's basis for technology transfer from the meat packing industry to the leather tanning and finishing industry was not supported by the record, and 2) EPA's

consideration of seasonal variability in effluent concentrations and the need for cold climate adjustments was inadequate.

MANUFACTURING PROCESSES

As indicated in earlier sections, there are differences in tanning processes which result in varying raw waste characteristics. The Agency has recognized these variations by establishing seven major industry subcategories for effluent limitations.

AGE AND SIZE OF EQUIPMENT AND FACILITIES

As indicated in Section IV of this report, no significant data substantiate the claim that tannery age or size justifies different effluent limitations. Data indicate that some of the oldest and smallest tanneries currently achieve levels of treatment equivalent to those achieved by large new facilities.

BEST PRACTICABLE TECHNOLOGY (BPT)

The best practicable control technology currently available is based upon demonstrated tannery waste treatment experience and practice.

In the remanded regulations, BPT technology was defined as equalization followed by primary treatment and biological treatment; aerated lagoons were considered to be equivalent to activated sludge. The following unit operations and unit processes are defined by EPA to be the best practicable control technology currently available:

Wastewater Flow	Sludge
Level 3	Levels 3 and 4
Screening	Collection
Equalization	Dewatering
Primary Coagulation-Sedimentation	Disposal
Level 4	
Activated Sludge (High Solids Extended Aeration with Nitrification)	
Secondary Clarification	

This technology is applicable to all subcategories (see Figure 9).

Acceptable effluent quality may be achieved by various means. However, this particular arrangement is proposed because it is a practical approach to treatment and it is used successfully, in whole or in part, by several tanneries and by POTW's which receive

substantial tannery waste. It also allows a certain degree of positive control of the treatment parameters if necessary because of waste characteristics, loadings, or ambient conditions.

It must be noted that low solids aerated lagoons are not considered to be equivalent to this BPT technology since these systems perform poorly during the winter months in northern climates. Plants using these systems will be required to upgrade their treatment facilities to achieve the BPT effluent limitations on a consistent basis. Extensive data now in the record also show that, for the pollutants regulated by BPT, winter climate does not affect the performance of properly designed and operated extended aeration activated sludge systems. These systems have been demonstrated in the leather tanning and finishing industry and technology transfer from meat packing or any other industry is no longer required.

Development of the Limitations

The pollutants controlled by this revised regulation include the same pollutants controlled by the remanded BPT regulation, specifically BOD_5, TSS, oil and grease, pH, and (total) chromium. The discharge of these pollutants is controlled by mass effluent limitations (kg/kkg or lbs per 1,000 lbs of raw material). The Agency calculated the mass limitations using demonstrated effluent concentrations, average water use data for the individual subcategories (see Section V), and the appropriate variability factors to establish maximum monthly average and maximum day values. Since the mass effluent limitations are based on flow, these values vary among the subcategories.

Sixty months of operating data from the activated sludge system at tannery no. 47 has been statistically analyzed. excluding data from two brief periods of upset. Based upon this analysis, EPA established the maximum average concentrations for a 30-day period for the parameters regulated under BPT as follows: BOD_5 - 90 mg/l, and TSS - 145 mg/l. Results of analysis of operating data from the Berwick, Maine POTW (excluding data from the initial start-up and operator familiarization period and periods of upset or mechanical difficulties) serve as the basis of limitations for oil and grease - 25 mg/l, and (total) chromium -3 mg/l. The effluent concentrations listed above are the same for all subcategories, and therefore the differences in average water use (gallons/pound of hide) determine the differences in mass effluent limitations.

The 30-day maximum effluent concentrations presented above are approximately 1.5 times greater than the long-term average for these parameters, as observed at tannery no. 47. The variability analysis of this data indicated that the ratio of maximum daily concentration to maximum 30-day average concentration is approximately 2.0. This ratio was used to calculate the mass effluent limitations reflecting the maximum value for any one day. It is noteworthy that these

effluent concentrations were achieved on a year-round basis; therefore, variance for winter operation in cold climates is not necessary.

ENGINEERING ASPECTS OF CONTROL TECHNIQUE APPLICATION

The specific level of technology defined as BPT is practicable because plants in the tannery industry already practice it; other industries with high strength wastes use it also. Data from tannery no. 47 (subcategory No. 3) and the Berwick, Maine POTW, which receives wastewater from plant no. 50 in subcategory no. 4, served as the basis for the BPT effluent concentrations. Performance of the treatment system at plant no. 253 (described in Section VII) supports these limitations, since it achieves effluent levels well below those reflected by the limitations. Two vegetable tanning plants have accepted NPDES permits which require effluent concentrations virtually identical to those noted above. The Hartland, Maine POTW, which treats more than 90 percent tannery wastewater, achieves effluent concentrations which are generally lower than those noted above (Figure 32). Differences in raw waste loads among subcategories can be compensated for by properly designed coagulation-sedimentation and activated sludge units. Transfer of technology from other industries, such as meat packing, is no longer necessary to establish effluent limitations for leather tanners. For the other direct dischargers, waste control and treatment is uniformly inadequate, and requires transfer of BPT technology and performance to the remaining subcategories. Most of the existing biological treatment systems in the industry are inadequate. For example, some of the plants: (1) do not have the equipment necessary to be operated as high solids extended aeration activated sludge; (2) are overloaded activated sludge systems; (3) have simple lagoons with inadequate or no aeration facilities; (4) are poorly operated; or (5) suffer some combination or all of these inadequacies. Where possible, EPA has documented these inadequacies on a plant-by-plant basis and evaluated the equipment and costs necessary to achieve high solids nitrifying extended aeration activated sludge treatment and the BPT effluent concentrations.

As noted in the discussion in Section VII, high solids extended aeration activated sludge provides consistent performance, winter and summer. These systems <u>must</u> be <u>properly designed</u> and <u>diligently operated</u>. For tannery wastes treated with an activated sludge system, EPA developed design parameters from which cost estimates could be prepared. The estimates are intended to provide a substantial margin of extra treatment capacity and should thus represent a maximum cost figure for any tannery. Some of the important design factors are:

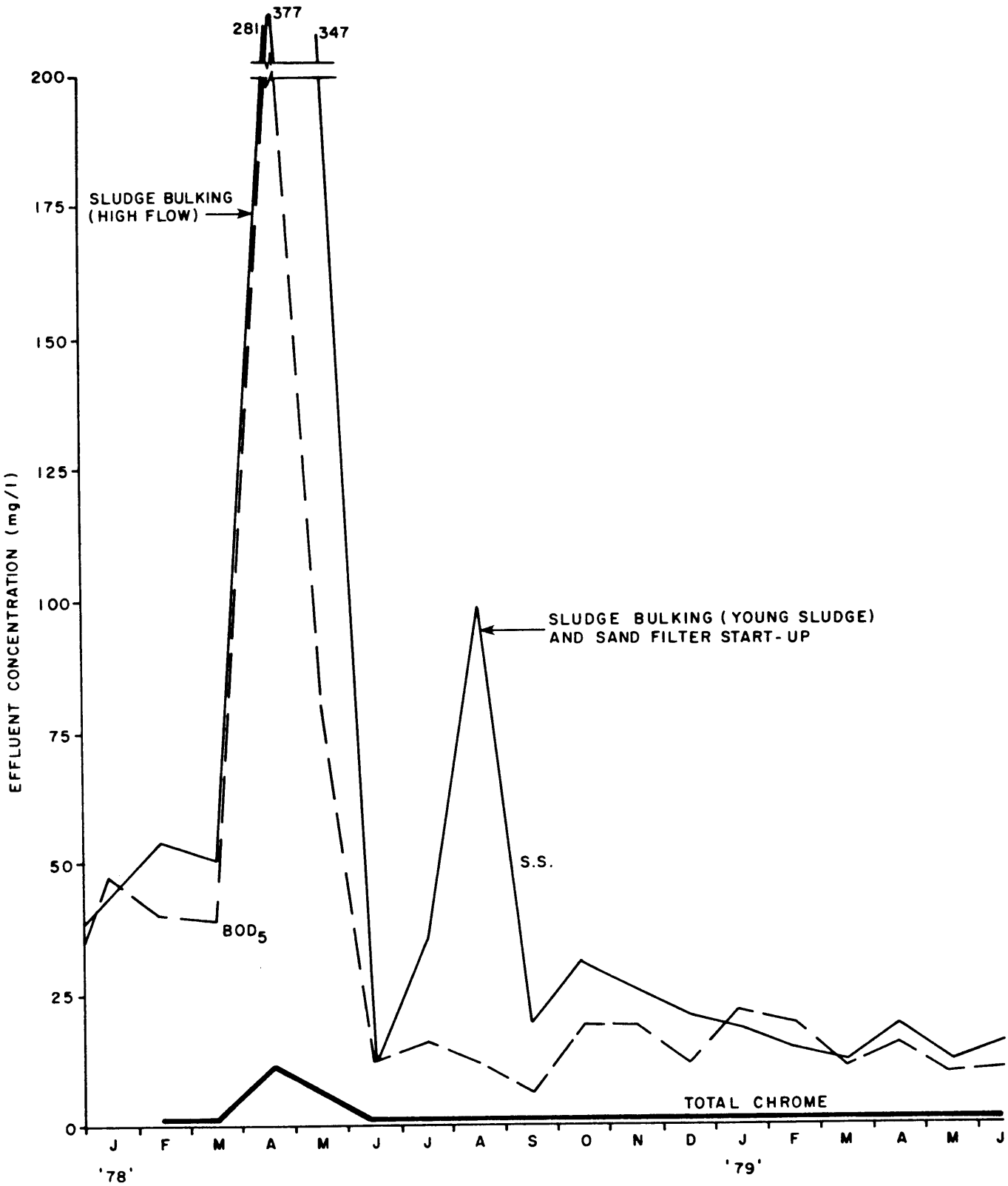


Figure 32. Average Monthly Final Effluent Concentrations of BOD5, TSS, and Chromium (Total) from an Activated Sludge System in a Northern Climate (Hartland, Maine POTW)

Equalization	Detention: 36 hours at design flow
Primary Sedimentation	Overflow Rate: 29 $m^3/d/m^2$ (700 gpd/ft^2)
Aeration Basin F/M Ratio	0.05-0.1
Mixed Liquor Suspended Solids (MLSS)	6000-10,000 mg/l
Sludge Age	20-30 days
Oxygen Delivery	2.5 kg/kg BOD_5 in influent to basin
Nutrient Balance:	Carbon: Nitrogen: Phosphorus - 100:5:1
Secondary Clarification	Overflow Rate: 8 $m^3/d/m^2$ (200 gpd/ft^2)

The importance of diligent operation has been demonstrated in at least two cases. An activated sludge system at Tannery No. 237 in Minnesota produced final effluent BOD_5 concentrations which varied from as high as 489 mg/l to as low as 8.8 mg/l, depending upon the experimental mode of operation. During the first year (1976) of operation of a POTW in New England, final effluent quality was poor due an extended acclimation period and to lack of familiarity with the operational idiocyncracies of the plant. After operational procedures were refined, effluent BOD_5 concentrations improved dramatically, from an average range of 102-393 mg/l to a range of 49-67 mg/l. During the very cold winter months of 1976-1977, in fact, effluent BOD_5 quality improved to 34 to 45 mg/l (Figures 33 and 34). Since that time tannery flow has increased well beyond the design limits for extended periods of time, but better operating skills have maintained average BOD_5 effluent quality below 80 mg/l, except for periods of operational difficulties (i.e., inoperative clarifiers, etc.). Therefore, the basic feasibility of the activated sludge process and the importance of operational control have been firmly demonstrated.

COST AND EFFLUENT REDUCTION BENEFITS

EPA expects that the total capital investment necessary to upgrade the treatment systems of the 18 direct dischargers not achieving BPT effluent limitations will be $4.5 million. Operation and maintenance costs for all of these plants will increase by $1.5 million per year. Achievement of proposed BPT effluent limitations will remove approximately 54 million pounds per year of conventional pollutants

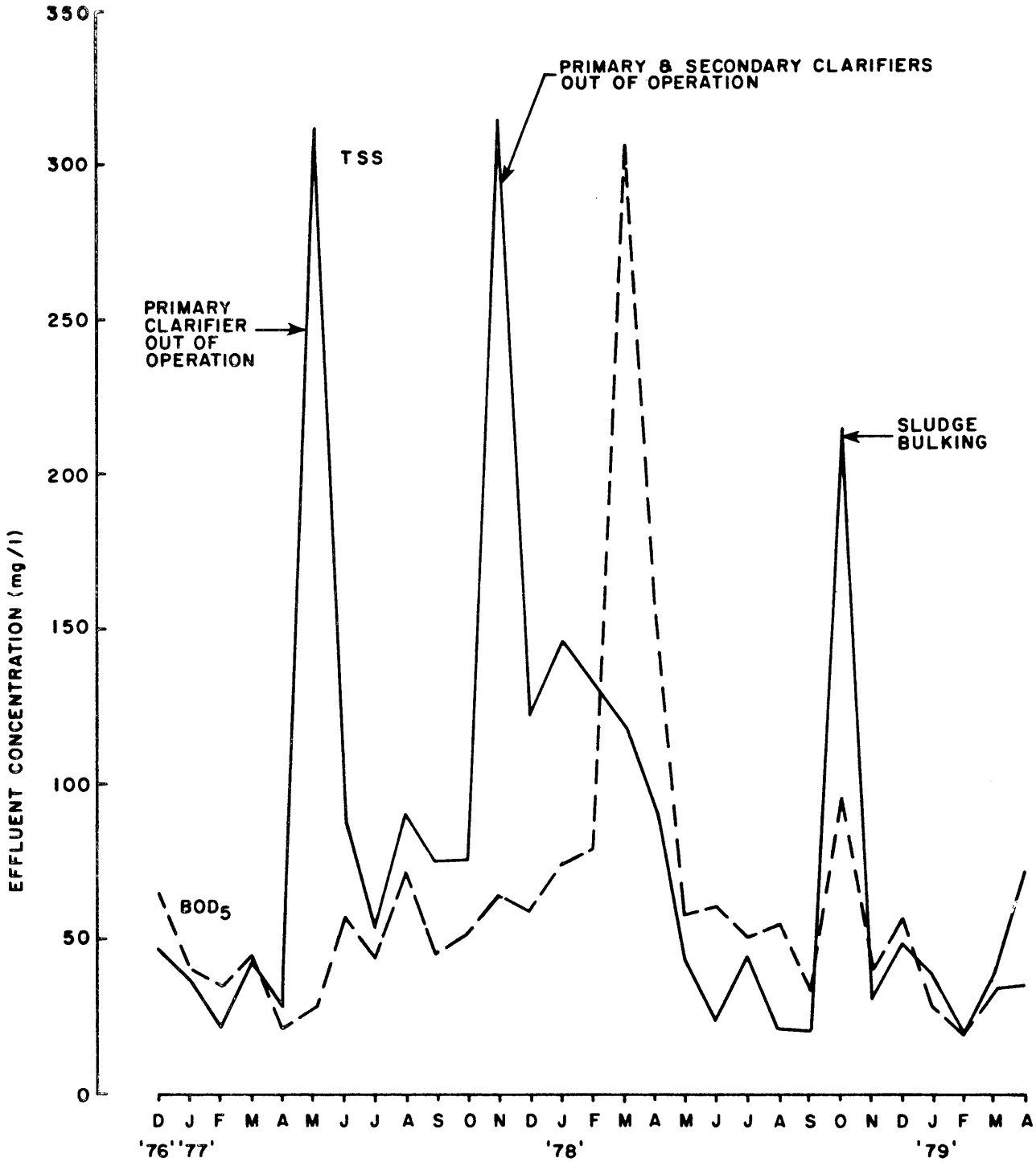


Figure 33 Average Monthly BOD_5 & TSS Effluent Concentration from an Activated Sludge System in a Northern Climate (Berwick, Maine POTW)

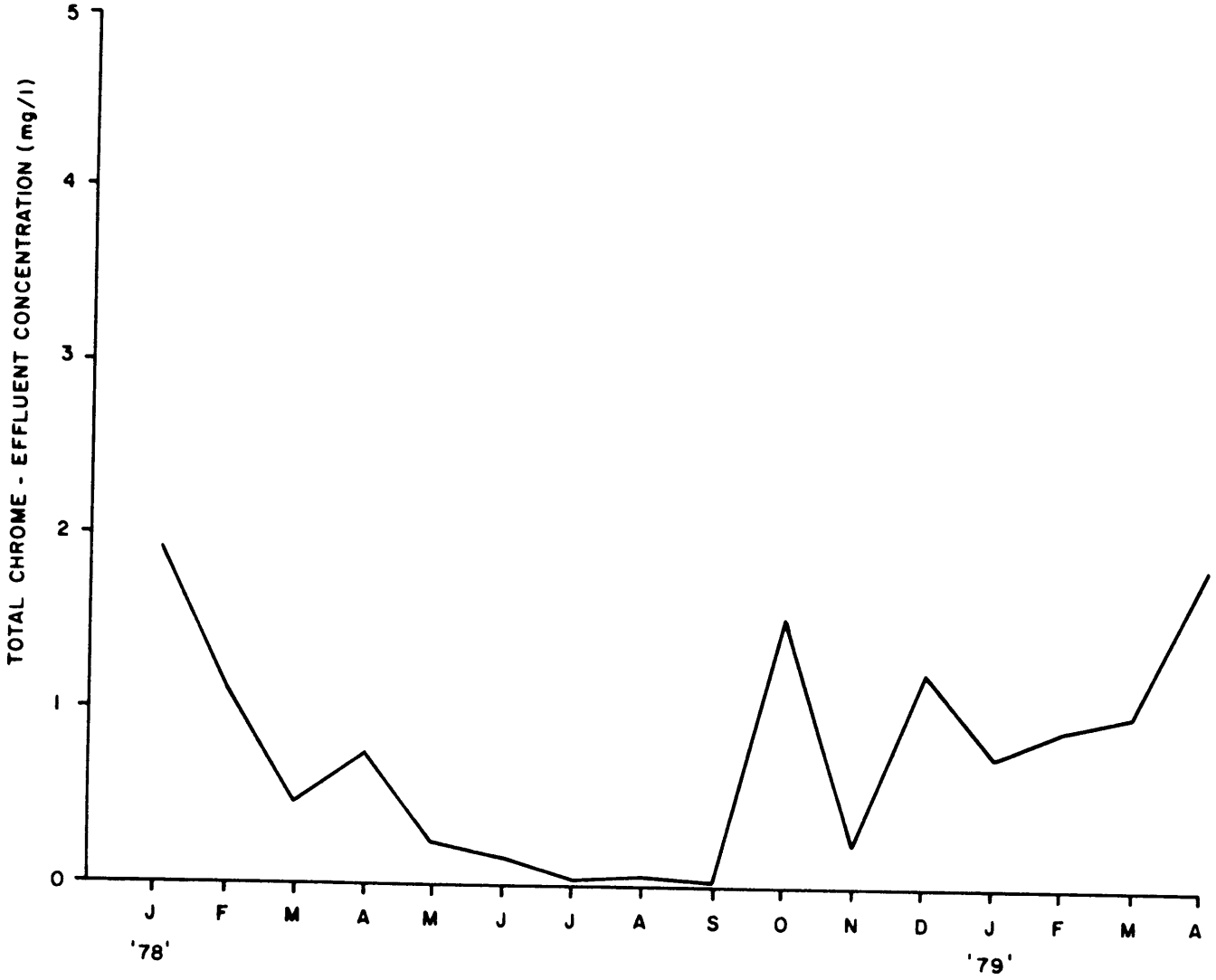


Figure 34 Average Monthly Total Chromium Effluent Concentration from an Activated Sludge System in a Northern Climate (Berwick, Maine POTW)

(BOD5, COD, TSS, and Oil and Grease), 284,000 pounds per year of chromium, 374,000 pounds per year of sulfide, 100,000 pounds per year of TKN, and significant quantities of other toxic pollutants in leather tanning and finishing wastewaters. EPA believes that these effluent reduction benefits outweigh the associated costs.

NON-WATER QUALITY ENVIRONMENTAL IMPACT

Unrecovered waste products removed from tannery discharges or from processing steps within the tannery take the form of general tannery solid wastes or waste sludges from treatment facilities. EPA estimates that the proposed BPT effluent limitations will contribute an additional 22,000 metric tons per year of solid waste in the form of sludges from upgraded wastewater treatment systems. The major non-water quality impact of these wastes is the increased burden on the land to accept their disposal. Waste trimmings and hair from hides are presently recovered as by-products. Recovery and reuse of chrome in some tanning operations will substantially reduce chrome levels in waste sludge produced by the treatment facility. In addition, this will reduce the potential release of toxic chrome due to the use of dewatered sludge at landfills. In all cases, however, dewatered sludges from chrome tanneries need separate handling at disposal sites in order to avoid any potential difficulties. Proper landfill siting and operation will minimize the impact of tannery waste disposal on the land. See Section VIII for a discussion of how RCRA will impact upon the handling and disposal of tannery solid wastes.

EPA has estimated that the energy required by a typical plant to achieve BPT effluent limitations is approximately 1 percent of the total energy consumed for production purposes. This estimate is based upon the total energy used by the industry from all fuel sources for production purposes as documented in the 1972 Census of Manufacturers. The bulk of this increased energy usage is for aeration equipment operation.

APPLICATION OF BPT EFFLUENT LIMITATIONS

1. If a tanner processes hides in more than one subcategory (e.g., cattlehides and shearlings), the effluent limitations should be prorated based on the percentage of the total hide weight being processed in each subcategory.

2. The production figure recommended for applying these limitations is the daily average production of the maximum 30 consecutive days.

BPT EFFLUENT LIMITATIONS

Based on the rationale outlined above, mass effluent limitations (kg/kkg or lb/1000 lb) for the seven subcategories established for the leather tanning industry are presented in Table 40.

Table 40

BPT EFFLUENT LIMITATIONS

Subcategory One - Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	7.0	3.5
TSS	11.2	5.6
Total Chromium	0.24	0.12
Oil and Grease	2.0	1.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Two - Hair Save/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	8.2	4.1
TSS	13.4	6.7
Total Chromium	0.28	0.14
Oil and Grease	2.2	1.1
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Three - Hair Save/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	6.0	3.0
TSS	9.6	4.8
Total Chromium	0.20	0.10
Oil and Grease	1.7	0.83
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Four - Retan-Wet Finish

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.6	1.3
TSS	4.2	2.1
Total Chromium	0.086	0.043
Oil and Grease	0.70	0.35
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Five - No Beamhouse

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	5.0	2.5
TSS	8.0	4.0
Total Chromium	0.17	0.083
Oil and Grease	1.4	0.69
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Six - Through-the-Blue

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	4.0	2.0
TSS	6.6	3.3
Total Chromium	0.14	0.068
Oil and Grease	1.1	0.56
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Seven - Shearling

Pollutant or Pollutant Property	BPT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	20.8	10.4
TSS	33.6	16.8
Total Chromium	0.70	0.35
Oil and Grease	5.8	2.9
pH	Within the range of 6.0 to 9.0 at all times.	

SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE-- EFFLUENT LIMITATIONS GUIDELINES

GENERAL

The effluent limitations which must be achieved by July 1, 1984, are not based on an average of the best performance within an industrial category. Instead, they are based on the very best economically achievable control and treatment technology employed by a point source within the industrial category or subcategory, or by another industry from which technology is readily transferable. BAT may include process changes or internal controls, even when not common industry practice.

Best available technology economically achievable (BAT) emphasizes in-process controls, as well as control or additional treatment techniques employed at the end of the production process. In developing BAT effluent limitations EPA also considered:

1. the manufacturing processes employed;
2. the age and size of the equipment and facilities involved;
3. the location of manufacturing facilities;
4. process changes;
5. the engineering aspects of the application of various types of control techniques;
6. the cost of achieving the effluent reduction resulting from application of the technology; and
7. non-water quality environmental impact (including energy requirements).

The BAT technology level considers those processes control technologies which at the pilot plant, semi-works, and other levels, have demonstrated sufficient technological performance and economic viability to justify investing in such facilities. BAT represents the highest degree of demonstrated control technology for plant-scale operation, up to and including "no discharge" of pollutants where feasible. The costs of this level of waste control are defined by top-of-the-line of current technology, subject to limitations imposed by economic and engineering feasibility. Technical risk may exist with respect to performance and certainty of costs and some

technologies may require process development and adaptation before application to a specific plant.

The statutory assessment of BAT "considers" costs, but does not require a balancing of costs against effluent reduction benefits (see Weyerhaeuser v. Costle, 11 ERC 2149 (D.C. Cir. 1978). In developing the proposed BAT, however, EPA has given substantial weight to the reasonableness of costs. The Agency has considered the volume and nature of discharges, the volume and nature of discharges expected after application of BAT, the general environmental effects of the pollutants, and the costs and economic impacts of the required pollution control levels.

Despite this expanded consideration of costs, the primary determinant of BAT is effluent reduction capability. As a result of the Clean Water Act of 1977, the achievement of BAT has become the principal national means of controlling toxic water pollution. The leather tanning industry discharges over twenty different toxic pollutants and EPA has selected among four available BAT technology options which will reduce this toxic pollution by a significant amount.

MANUFACTURING PROCESSES, AND SIZE, AGE AND LOCATION OF FACILITIES

The processes employed in different sized tanneries within each subcategory are essentially the same. Furthermore, the factors of location, age, or manufacturing processes do not affect the control technology that can be applied effectively. Facilities located in cold climates can employ the same technologies and achieve the same limitations as those in warmer climates, as verified by Figure 32.

PROCESS CHANGES

The most direct and cost-effective waste treatment approach is to prevent the entry of pollutants into the waste stream or to remove the pollutants from the source stream before dilution, contamination, or other interaction occurs in the mixing of several waste streams. Process changes--especially chemical reuse or in-plant waste stream isolation and collection for treatment--can facilitate achievement of the recommended effluent limitations. Numerous tanneries have considered such changes and have implemented them. Extensive experimental work has been conducted in the U.S. and throughout the world on various in-plant process changes to reduce water use, chemical consumption, and pollutant loading in the resulting wastewater.

IDENTIFICATION OF BAT TECHNOLOGY

BAT technology uses BPT technology as a basis for further improvements. As noted earlier, Level 3 (primary coagulation-sedimentation) and Level 4 (high solids extended aeration-activated

sludge system with nitrification) technologies are the basis for BPT effluent limitations. Additional technologies considered BAT are presented below.

In-Plant Control and Preliminary Treatment

Level 1 - Water conservation and reuse to reduce flow (all subcategories)
- Stream segregation for preliminary treatment (subcategory nos. 1, 2, 3, 6, and 7)
- Ammonia substitution in deliming (subcategory nos. 1, 2, 3, and 6)
- Chrome recovery and reuse (subcategory nos. 1, 2, 5, 6, and 7)
- Sulfide liquor reuse followed by catalytic oxidation of residual sulfide (subcategory nos. 1, 2, 3, and 6)
- Fine screening of segregated streams (all subcategories)

Level 2 - Flue gas carbonation and sedimentation for beamhouse wastewaters (subcategory nos. 1, 2, 3, and 6)

A schematic diagram of these technologies for all seven subcategories is presented in Figures 4 through 8 (Section VII). The end-of-pipe technologies which follow are applicable to all subcategories (Figure 9).

End-of-Pipe Treatment

Level 5 - Addition of powdered activated carbon (PAC) to upgrade extended aeration-activated sludge (Level 4)

Level 6 - Multimedia filtration

Level 7 - Granular activated carbon columns

Level 4A - Alternative Technology - Physical/chemical treatment

Table 41 tabulates the long term performance of BAT technologies for each subcategory, starting with raw waste loads and continuing through segregated stream in-plant control and preliminary treament, combined stream end-of-pipe primary and secondary biological treatment, and advanced waste treatment.

The Agency considers physical/chemical treatment (Level 4A in Figure 9), an alternative technology for direct dischargers, enabling them to achieve an effluent quality equal to that produced through Level 6 (multi-media filtration). This technology can be applied after Level 3 by direct dischargers. The existing biological treatment systems of direct dischargers which exhibit poor performance can be upgraded with physical/chemical treatment to achieve the desired effluent quality.

Both BPT and BAT raw waste loads are predicated on demonstrated flow reductions. The performance bases for all of the candidate technologies identified above and displayed in Table 41 were presented in appropriate technology descriptions in Section VII of this document.

DEVELOPMENT OF BAT EFFLUENT LIMITATIONS

BAT Reduced Flow

As noted in Section V of this document, process water consumption per unit of production (litres/kkg or gallons/lb) has consistently decreased within the leather tanning industry since data collection began. This trend is expected to continue with changes in manufacturing practices and greater economic incentive for reducing wastewater discharges. EPA considers reduced water use to be an important and integral part of BAT.

EPA analyzed the log-normal distribution of the wastewater flow data for each subcategory to determine the geometric mean and standard deviation. Achievable reduced flows were established by identifying flow rates which were in the range of from one-half to a full standard deviation less than the geometric mean for each of the subcategories. A limit of approximately 30 percent of flow reduction below the geometric mean was established in recognition of the fact that the total wastewater volume becomes smaller, the opportunities to achieve further flow reduction become fewer.

Reduced flow rates were derived using the procedure described above for six of the seven industry subcategories. Because of a limited data base, Subcategory Six (Through-the-Blue) required a different approach. In this case, the Agency calculated the difference in the reduced flow rates between Subcategory One and Subcategory Four to develop a representative value for through-the-blue tanneries.

The BAT flow rate computed for each subcategory was then compared to average tanneries in the same subcategory. The key criterion for establishing BAT flows is that at least one plant within the subcategory must currently meet the reduced value; where all of the plant averages exceed the computed flow rate, EPA adjusted the value to equal the lowest plant average. Adjustments were required for Subcategories Six and Seven. Table 42 summarizes the reduced flow rates employed to evaluate BAT technology.

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per l/lb per 1000 lb

PARAMETER	EXISTING AVERAGE RAW WASTE LOAD	RAW WASTE LOAD WITH REDUCED FLOWS	RAW BEAMHOUSE STREAM	RAW TANYARD STREAM	TREATED BEAMHOUSE STREAM	TREATED TANYARD STREAM	LEVEL 2 PRIMARY INFLUENT	LEVEL 3 PRIMARY EFFLUENT
Subcategory 1								
Flow (gal/#)	4.6	3.5	1.4	2.1	1.4	2.1	3.5	3.5
BOD_5	1620/62.3	2130/62.3	3470/40.5	1240/21.8	1390/16.2	1240/21.8	1300/38	520/15.2
TSS	2410/92.3	3160/92.3	5460/63.7	1630/28.6	1910/22.3	1630/28.6	1740/50.9	700/20.4
COD	4640/178	6080/178	8540/99.7	4470/78.3	3420/39.9	4470/78.3	4050/118.2	1420/41.4
O&G	400/15.4	530/15.4	640/7.5	450/7.9	200/2.3	450/7.9	350/10.2	105/3.1
Total Cr	75/2.9	99/2.9	0/0	170/2.9	---	33/.58	20/.58	2/.06
Sulfide	64/2.47	85/2.47	210/2.47	0/0	---	---	---	---
TKN	330/12.6	430/12.6	500/5.8	390/6.8	170/2.03	240/4.15	210/6.18	210/6.18
Ammonia	104/3.98	140/3.98	0	230/3.98	---	76/1.33	46/1.33	46/1.33
Phenol	1.0/.038	1.3/.038	0	2.2/.038	---	2.2/.038	1.3/.038	1.3/.038
Subcategory 2								
Flow (gal/#)	5.5	3.7	1.5	2.2	1.5	2.2	3.7	3.7
BOD_5	980/45.1	1460/45.1	2340/29.3	860/15.8	940/11.7	860/15.8	890/27.5	360/11
TSS	1920/88.3	2860/88.3	4870/60.9	1490/27.4	1700/21.3	1490/27.4	1580/48.7	630/19.5
COD	2610/119.7	3880/119.7	5360/67	2870/52.7	2140/26.8	2870/52.7	2580/79.5	900/27.8
O&G	244/11.2	363/11.2	440/5.5	310/5.7	130/1.7	310/5.7	240/7.4	71/2.2
Total Cr	31/1.4	45/1.4	0.0	76/1.4	0.0	15/.28	9/.28	2/.06
Sulfide	20/0.92	30/.92	74/.92	0.0	0.0	0.0	0.0	0.0
TKN	137/6.3	204/6.3	230/2.9	185/3.4	80/1.0	34/.62	52/1.62	52/1.62
Ammonia	90/4.15	135/4.15	0.0	230/4.15	0.0	75/1.37	44/1.37	44/1.37
Phenol	2.2/.1	3.2/.1	0.0	5.5/.10	---	5.5/.10	3.2/.10	3.2/.10

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per l/lb per 1000 lb
(Continued)

PARAMETER	LEVEL 4 SECONDARY TREATMENT	LEVEL 5 UPGRADED SECONDARY (PAC)	LEVEL 6 MMF	LEVEL 7 CARBON COL.	LEVEL 4A CHAPPEL
Subcategory 1 - Hair Pulp-Chrome Tan-Retan-Wet Finish					
Gal/lb	3.5	3.5	3.5	3.5	3.5
BOD_5	40/1.2	20/0.6	14/0.4	6/0.18	14/0.4
TSS	60/1.75	25/0.73	16/0.47	3/0.09	16/0.47
COD	250/7.3	195/5.7	180/5.3	165/4.8	180/5.3
O&G	14/0.6	10/0.3	6/0.2	2/0.06	6/0.2
Total Cr	1.0/0.03	0.5/.015	0.33/0.01	0.25/0.007	0.33/0.01
Sulfide	0/0	0/0	0/0	0/0	0/0
TKN	40/1.2	20/0.6	15/0.45	14/0.4	15/0.45
Ammonia	10/0.29	5/0.15	5/0.15	5/0.15	5/0.15
Phenol	0.25/0.008	0.1/0.003	0.1/0.003	0.1/0.003	0.1/0.003
Subcategory 2 - Hair Save-Chrome Tan-Retan-Wet Finish					
Gal/lb	3.7	3.7	3.7	3.7	3.7
BOD_5	40/1.2	20/0.6	14/0.4	6/0.18	14/0.4
TSS	60/1.8	25/0.75	16/0.5	3/0.09	16/0.5
COD	250/7.7	195/6.0	180/5.6	165/5.1	180/5.6
O&G	14/0.6	10/0.3	6/0.2	2/0.06	6/0.19
Total Cr	1.0/0.03	0.5/0.015	0.33/0.01	0.25/0.008	0.33/0.01
Sulfide	0/0	0/0	0/0	0/0	0/0
TKN	40/1.2	20/0.6	15/0.45	14/0.4	15/0.45
Ammonia	10/0.3	5/0.15	5/0.15	5/0.15	5/0.15
Phenol	0.25/0.015	0.1/0.003	0.1/0.003	0.1/0.003	0.1/0.003

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per 1/lb per 1000 lb
(Continued)

PARAMETER	EXISTING AVERAGE RAW WASTE LOAD	RAW WASTE LOAD WITH REDUCED FLOWS	RAW BEAMHOUSE STREAM	RAW TANYARD STREAM	TREATED BEAMHOUSE STREAM	TREATED TANYARD STREAM	LEVEL 2 PRIMARY INFLUENT	LEVEL 3 PRIMARY EFFLUENT
Subcategory 3								
Flow (gal/#)	4.0	2.7	1.1	1.6	1.1	1.6	2.7	2.7
BOD_5	1180/39.2	1740/39.2	2780/25.5	1030/13.7	1110/10.2	1030/13.7	1060/23.9	430/9.6
TSS	1680/56.1	2490/56.1	4220/38.7	1300/17.4	1470/13.5	1300/17.4	1370/30.9	550/12.4
COD	5120/170.9	7590/170.9	10,400/95.7	5640/75.2	4170/38.3	5640/75.2	5040/113.5	1760/39.7
O&G	340/11.3	500/11.3	600/5.5	430/5.8	180/1.70	430/5.8	330/7.5	100/2.3
Total Cr	11/.38	17/.38	---	28/.38	---	28/.38	17/.38	2/.045
Sulfide	68/2.3	100/2.3	250/2.3	---	---	---	---	---
TKN	202/6.8	300/6.8	340/3.1	280/3.7	120/1.1	130/1.7	120/2.8	120/2.8
Ammonia	90/3	133/3	---	220/3	---	75/1.0	44/1.0	44/1.0
Phenol	1.2/.04	1.8/.04	---	3/.04	---	3/.04	1.8/.04	1.8/.04
Subcategory 4								
Flow (gal/#)	1.7	1.3		1.3		1.3	1.3	1.3
BOD_5	780/11	1010/11	No	1010/11	No	1010/11	1010/11	400/4.4
TSS	820/11.6	1070/11.6		1070/11.6		1070/11.6	1070/11.6	420/4.6
COD	3120/44.2	4080/44.2	Beamhouse	4080/44.2	Beamhouse	4080/44.2	4080/44.2	1430/15.5
O&G	270/3.9	360/3.9		360/3.9		360/3.9	360/3.9	110/1.2
Total Cr	53/.75	69/.75	Waste	69/.75	Waste	69/.75	69/.75	2/.02
Sulfide	1.1/.015	1.4/.015		1.4/.015		1.4/.015	1.4/.015	---
TKN	210/3	280/3		280/3		280/3	280/3	280/3
Ammonia	110/1.55	140/1.55		140/1.55		140/1.55	140/1.55	140/1.55
Phenol	3.9/.055	5/.055		5/.055		5/.055	5/.055	5/.055

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per l/lb per 1000 lb
(Continued)

PARAMETER	LEVEL 4 SECONDARY TREATMENT	LEVEL 5 UPGRADED SECONDARY (PAC)	LEVEL 6 MMF	LEVEL 7 CARBON COL.	LEVEL 4A CHAPPEL
Subcategory 3 - Hair Save-Nonchrome Tan-Retan-Wet Finish					
Gal/lb	2.7	2.7	2.7	2.7	2.7
BOD_5	40/0.90	20/0.45	14/0.32	6/0.14	14/0.27
TSS	60/1.35	25/0.56	16/0.36	3/0.07	16/0.34
COD	250/5.6	195/4.4	180/4.1	165/3.7	180/4.1
O&G	14/0.45	10/0.22	6/0.13	2/0.045	6/0.22
Total Cr	1.0/0.022	0.5/0.012	0.33/0.007	0.25/0.006	0.33/0.007
Sulfide	0/0	0/0	0/0	0/0	0/0
TKN	40/0.90	20/0.45	15/0.34	14/0.32	10/0.22
Ammonia	10/0.23	5/0.12	5/0.12	5/0.12	5/0.11
Phenol	0.25/0.006	0.1/0.002	0.1/0.002	0.1/0.002	0.1/0.002
Subcategory 4 - Retan-Wet Finish					
Gal/lb	1.3	1.3	1.3	1.3	1.3
BOD_5	40/0.44	20/0.22	14/0.15	6/0.07	14/0.13
TSS	60/0.66	25/0.28	16/0.18	3/0.035	16/0.16
COD	250/2.7	195/2.1	180/2.0	165/1.8	180/2.0
O&G	14/0.22	10/0.11	6/0.07	2/0.022	6/0.07
Total Cr	1.0/0.011	0.5/0.006	0.33/0.004	0.25/0.003	0.33/0.004
Sulfide	0/0	0/0	0/0	0/0	0/0
TKN	40/0.44	20/0.22	15/0.16	14/0.15	10/0.11
Ammonia	10/0.11	5/0.055	5/0.055	5/0.055	5/0.055
Phenol	0.25/0.003	0.1/0.001	0.1/0.001	0.1/0.001	0.1/0.001

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per l/lb per 1000 lb
(Continued)

PARAMETER	EXISTING AVERAGE RAW WASTE LOAD	RAW WASTE LOAD WITH REDUCED FLOWS	RAW BEAMHOUSE STREAM	RAW TANYARD STREAM	TREATED BEAMHOUSE STREAM	TREATED TANYARD STREAM	LEVEL 2 PRIMARY INFLUENT	LEVEL 3 PRIMARY EFFLUENT
Subcategory 5								
Flow (gal/#)	3.3	2.3		2.3		2.3	2.3	2.3
BOD_5	1000/27.6	1440/27.6		1440/27.6		1440/27.6	1440/27.6	570/11
TSS	630/17.4	910/17.4	No	910/17.4	No	910/17.4	910/17.4	360/7
COD	1700/47	2440/47		2440/47		2440/47	2440/47	860/16.5
O&G	340/9.5	490/9.5	Beamhouse	490/9.5	Beamhouse	490/9.5	490/9.5	150/2.9
Total Cr	68/1.9	97/1.9		97/1.9		19/.37	19/.37	2/.038
Sulfide	3.2/.09	4.6/.09		4.6/.09		4.6/.09	4.6/.09	0
TKN	170/4.6	240/4.6		240/4.6		240/4.6	240/4.6	240/4.6
Ammonia	36/1	52/1		52/1		52/1	52/1	52/1
Phenol	1.2/.034	1.8/.034		1.8/.034		1.8/.034	1.8/.034	1.8/.034
Subcategory 6								
Flow (gal/#)	2.70	2.5	1.5	1.0	1.5	1.0	2.5	2.5
BOD_5	2280/51.3	2460/51.3	2660/33.3	2160/18	1060/13.3	2160/18	1500/31.3	600/12.5
TSS	3580/80.7	3870/80.7	4450/55.7	3000/25	1560/19.5	3000/25	2130/44.5	850/17.8
COD	5900/133	6400/133	5960/745	7010/58.5	2380/29.8	7010/58.5	4230/88.3	1480/30.9
O&G	520/11.6	560/11.6	460/5.7	710/5.9	140/1.7	710/5.9	360/7.6	110/2.3
Total Cr	98/2.2	104/2.2	---	260/2.2	---	52/.43	21/.43	2/.042
Sulfide	110/2.5	120/2.5	200/2.5	---	---	---	---	---
TKN	430/9.6	460/9.6	350/4.4	620/5.2	120/1.5	280/3.5	240/5.0	240/5.0
Ammonia	110/2.5	120/2.5	0	300/2.5	0	100/.8	40/.8	40/.8
Phenol	1.3/.03	1.5/.03	0	3.6/.03	0	3.6/.03	1.5/.03	1.5/.03

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per l/lb per 1000 lb
(Continued)

PARAMETER	LEVEL 4 SECONDARY TREATMENT	LEVEL 5 UPGRADED SECONDARY (PAC)	LEVEL 6 MMF	LEVEL 7 CARBON COL.	LEVEL 4A CHAPPEL
Subcategory 5 - No Beamhouse					
Gal/lb	2.3	2.3	2.3	2.3	2.3
BOD_5	40/0.77	20/0.38	14/0.27	6/0.12	14/0.27
TSS	60/1.15	25/0.48	16/0.30	3/0.06	16/0.30
COD	250/4.8	195/3.7	180/3.5	165/3.2	180/3.5
O&G	14/0.38	10/0.19	6/0.11	2/0.038	6/0.12
Total Cr	1.0/0.019	0.5/0.01	0.33/0.006	0.25/0.005	0.33/0.006
Sulfide	0/0	0/0	0/0	0/0	0/0
TKN	40/0.77	20/0.38	15/0.28	14/0.27	15/0.19
Ammonia	10/0.19	5/0.10	5/0.10	5/0.10	5/0.10
Phenol	0.25/0.005	0.1/0.002	0.1/0.002	0.1/0.002	0.1/0.002
Subcategory 6 - Thru-The-Blue					
Gal/lb	2.5	2.5	2.5	2.5	2.5
BOD_5	40/0.83	20/0.42	14/0.29	6/0.13	14/0.29
TSS	60/1.25	25/0.52	16/0.33	3/0.06	16/0.33
COD	250/5.2	195/4.1	180/3.8	165/3.4	180/3.8
O&G	14/0.42	10/0.21	6/0.13	2/0.04	6/0.13
Total Cr	1.0/0.02	0.5/0.01	0.33/0.007	0.25/0.005	0.33/0.007
Sulfide	0/0	0/0	0/0	0/0	0/0
TKN	40/0.83	20/0.42	15/0.31	14/0.29	15/0.31
Ammonia	10/0.20	5/0.10	5/0.10	5/0.10	5/0.10
Phenol	0.25/0.005	0.1/0.002	0.1/0.002	0.1/0.002	0.1/0.002

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per l/lb per 1000 lb
(Continued)

PARAMETER	EXISTING AVERAGE RAW WASTE LOAD	RAW WASTE LOAD WITH REDUCED FLOWS	RAW BEAMHOUSE STREAM	RAW TANYARD STREAM	TREATED BEAMHOUSE STREAM	TREATED TANYARD STREAM	LEVEL 2 PRIMARY INFLUENT	LEVEL 3 PRIMARY EFFLUENT
Subcategory 7								
Flow (gal/#)	13.9	11.0	6.6	4.4	No	4.4	11.0	11.0
BOD_5	350/40.5	440/40.5	480/26.3	390/14.2		390/14.2	440/40.5	180/16.2
TSS	390/45	490/45	560/31.1	380/13.9	Beamhouse	380/13.9	490/45	200/18
COD	910/106	1160/106	1080/59.4	1260/46.4		1260/59.4	1160/59.4	230/20.8
O&G	144/16.7	180/16.7	150/8.2	230/8.5	Treatment	230/8.5	180/16.7	55/5
Total Cr	12.9/1.5	16/1.5	---	40/1.5	---	8.2/.3	3.3/.3	2/.18
Sulfide	0.2/.02	0.2/.02	0.4/.02	---	0.0	---	---	---
TKN	53/6.2	68/6.2	53/2.9	90/3.3	53/2.9	90/3.3	68/6.2	68/6.2
Ammonia	13/1.5	17/1.5	---	40/1.5	---	40/1.5	17/1.5	17/1.5
Phenol	0.3/.03	0.4/.03	---	0.8/.03	---	0.8/.03	0.4/.03	.4/.03

Table 41

LEVEL OF TREATMENT - WASTE STREAM COMPOSITION, mg per 1/lb per 1000 lb
(Continued)

PARAMETER	LEVEL 4 SECONDARY TREATMENT	LEVEL 5 UPGRADED SECONDARY (PAC)	LEVEL 6 MMF	LEVEL 7 CARBON COL.	LEVEL 4A CHAPPEL
Subcategory 7 - Shearlings					
Gal/lb	11	11	11	11	11
BOD_5	40/3.7	20/1.8	14/1.3	6/0.47	14/1.3
TSS	60/5.5	25/2.3	16/1.5	3/0.24	16/1.5
COD	250/23	195/18	180/17	165/15	180/17
O&G	14/1.8	10/0.9	6/0.6	2/0.16	6/0.6
Total Cr	1.0/0.09	0.5/0.05	0.33/0.03	0.25/0.023	0.33/0.03
Sulfide	--	--	--	--	--
TKN	40/3.7	20/1.8	15/1.4	14/1.3	15/1.4
Ammonia	10/0.92	5/0.5	5/0.5	5/0.5	5/0.5
Phenol	.25/0.023	0.1/0.01	0.1/0.01	0.1/0.01	0.1/0.01

Table 42
SUMMARY OF REDUCED SUBCATEGORY FLOWS FOR BAT

Subcategory	Total Number of Plants Reporting Flow	Reduced Flow gal/lb (l/kg)	Number of Plants Operating at Reduced Flow
One	31	3.5 (29)	11
Two	12	3.7 (31)	1
Three	16	2.7 (23)	4
Four	8	1.3 (11)	2
Five	14	2.3 (19)	5
Six	2	2.5 (21)	1
Seven	3	11.0 (92)	1

Raw Waste Loads

The mean values for wastewater flow (gal/lb of raw material) and raw waste loads (kg/kkg raw material) reflect the geometric mean of the log-normal distribution for each parameter. Subcategory Six (Through-the-Blue) required a different approach because of limited information. Raw waste loads for each pollutant parameter relating to this subcategory were derived by subtracting from subcategory no. 1 raw waste loads the subcategory no. 4 raw waste loads, since through-the-blue plants are exactly the same as hair pulp, chrome tan, retan-wet finish plants (subcategory one), but without retan-wet finish operations (subcategory four).

In computing the raw waste concentrations to reflect the reduced flows, the pollutant load measured in kg/kkg remained constant. This was done because while available data for this industry does show trends in pollutant reduction, these data do not conclusively confirm that reduced water contact with the product concurrently produces reduced pollutant loads. With a constant pollutant load and a reduced flow per unit of production, the calculated pollutant concentration (mg/l) predicted by this methodology is greater for each parameter than the BPT values. The BAT raw waste characteristics are shown in the second column of Table 41, which provides a comparison with the current average subcategory waste concentration listed in the first column. These results represented the expected average raw waste characteristics used in the engineering analysis of BAT technology.

BAT Treatment Technology

EPA developed the BAT effluent limitations in building block fashion, basing pollutant control levels on BPT technology (primary treatment, secondary biological treatment). Individual unit treatment processes included as a part of in-plant control and preliminary treatment are

discussed in Section VII and are identified (above) as BAT technologies by EPA. Although plants in the industry have used individual treatment processes, the combination of all of the processes utilized for this regulation has not been demonstrated.

Starting from raw waste loads (lbs/1,000 lbs) determined for each subcategory, including proven flow reductions, the performance of each of the unit treatment processes was applied to reduce these loads in the appropriate sequence (Level 1 and 2) for the segregated waste streams. The first step in this analysis portrayed in Table 41 was to utilize industry data discussed in Section VII on the proportions of flow and pollutant loads separately attributable to beamhouse operations and tanyard, retan-wet finish operations, so that the effect of segregated stream pretreatment technologies can be subsequently established. The raw waste load flow (gal/lb) and pollutant load (lb/1,000 lb) proportions (summarized in Table 35, Section VII) were applied to BAT raw waste loads for each subcategory (labeled "Raw Waste Load With Reduced flow" in Table 41) to yield separate flow (gal/lb) and pollutant loads (lb/1,000 lb) for these two streams, and calculated concentrations (labeled "Raw Beamhouse Stream" and "Raw Tanyard Stream" in Table 41). As an example, subcategory No. 1 BAT flow is segregated between beamhouse and tanyard according to Table 35 as follows:

Beamhouse: 3.5 gal/lb x 0.4 = 1.4 gal/lb
Tanyard: 3.5 gal/lb x 0.6 = 2.1 gal/lb

Similarly, BAT raw waste load BOD_5 would be segregated as follows:

Beamhouse: 62.3 lb/1000 lb x 0.65 = 40.5 lb/1000 lb
Tanyard: 62.3 lb/1000 lb x 0.35 = 21.8 lb/1000 lb

Remaining parameters were caluclated in the same manner. The "Raw Beamhouse Stream" mass loadings were then subjected to Level 1 technology (sulfide oxidation) to completely remove sulfides and Level 2 technology (flue gas carbonation-sedimentation) to reduce excess lime and protein as noted under "Percent Removals For Treatment Levels 1 and 2 - Beamhouse" in Table 35. For the same subcategory No. 1 example, the raw beamhouse stream would be reduced by sulfide oxidation and by flue gas carbonation efficiencies to the following residuals:

BOD_5 40.5 lb/1000 lb x (1.0-0.6) = 16.2 lb/1000 lb
Sulfide: 2.47 lb/1000 lb x (1.0-1.0) = 0.0 - complete removal

Remaining parameters were calculated in the same manner. The resulting wastewater characteristics (lb/1,000 lb - calculated concentrations) are presented under "Treated Beamhouse Stream" of Table 41. Similarly, the "Raw Tanyard Stream" mass loadings were subjected to the removals of chromium recovery and ammonia substitution as discussed in Section VII and summarized in Table 35

under "Percent Removals For Treatment Levels 1 and 2 - Tanyard." Again for the subcategory No. 1 example, the raw tanyard stream chromium, ammonia, and TKN would be reduced as follows:

Chromium:	2.9 lb/1000 lb x (0.8) = 2.32 lb/1000 lb captured
	2.9 lb/1000 lb x (1-0.8) = 0.58 lb/1000 lb discharged
Ammonia:	3.98 lb/1000 lb x (1-0.67) = 1.33 lb/1000 lb discharged
	3.98-1.33 = 2.65 lb/1000 lb removed by substitution
TKN:	(6.8 - 2.65) lb/1000 lb = 4.15 lb/1000 lb

No reductions were made for other parameters. The resulting wastewater characteristics (lb/1,000 lb - calculated concentrations) are presented under "Treated Tanyard Stream" of Table 41.

The next pretreatment technology applied is coagulation-sedimentation of combined streams (Level 3) which is a part of BPT technology. Influents to combined stream pretreatment were calculated by adding the flow (gal/lb) and mass loadings (lb/1,000 lb) under "Treated Beamhouse Stream" and "Treated Tanyard Stream" to yield "Level 2 Primary Influent." For the subcategory No. 1 example, flows were added as follows:

Treated Beamhouse flow + Treated Tanyard flow = Combined flow to Level 3
1.4 gal/lb + 2.1 gal/lb = 3.5 gal/lb

Pollutant loadings were calculated as follows:

Beamhouse + Tanyard = Combined load to Level 3			
BOD_5:	16.2 lb/1000 lb	+ 21.8 lb/1000 lb	= 38 lb/1000 lb
Ammonia:	--	+ 1.33 lb/1000 lb	= 1.33 lb/1000 lb
Chromium:	--	+ 1.58 lb/1000 lb	= 0.58 lb/1000 lb
Sulfide:	0.0	+ --	= 0.0

It is noteworthy to compare the water use and pollutant mass loadings of this column of Table 41 to the first column of Table 41, "Existing Average Raw Waste Load." Application of Levels 1 and 2 technology to BPT systems, accomplish major reduction in the waste load treated by BPT technology (Level 3 and Level 4). For example, in subcategory one, flow is reduced by approximately 25 percent; BOD_5 load reduced by approximately 40 percent; TSS load reduced by approximately 45 percent; COD load reduced by approximately 75 percent; and ammonia load reduced by approximately 67 percent. It is on this basis that engineering estimates were made of the reduced long-term average treated effluent concentrations as a result of the addition of in-plant control and preliminary treatment (Levels 1 and 2) as a part of BAT technology. The starting points of these engineering estimates were the BPT effluent limitations that were based upon plant performance (see Section IX). EPA estimates conservatively that the long-term final effluent concentration for BOD_5 will be reduced from 60 m/gl to 40 mg/l; TSS will be reduced from 95 to 60, where effluent

TSS to BOD5 ratios are typically 1.5 to 1; COD concentration was determined by the relationship between COD and BOD5 (Figure 3); ammonia removal by nitrification will be improved from nil to 10 mg/l which is generally achieved by plant no. 253; TKN concentration was determined by the approximate 4:1 ratio to ammonia generally noted where data is available; chromium concentration was based upon performance of the best existing plants in this industry and also related to the improved TSS performance expected at this level; phenol concentration was estimated to be 0.25 mg/l based upon limited performance in this industry and the petroleum industry. These reductions in long term effluent concentrations, noted as "Level 4 Secondary Treatment" in Table 41 in effluent concentrations (i.e., BOD5), were not precisely calculated through use of available treatment kinetics models, but rather were estimated based upon engineering analysis of the influence of raw waste load reduction and improved operation of existing BPT technology. Among the key factors in this determination were reduced flow and resulting commensurate increases in hydraulic detention time in biological treatment, reduced mass loading of BOD and TSS, reduced ammonia loading to minimize ammonia toxicity to nitrifying bacteria, and better operator knowledgeability of treatment system control (e.g., nutrient balance, maintenance of mixed liquor solids, F/M, and sludge age in aeration, secondary clarifier sludge blankets, etc.). As reflected in Table 41, this served as the technology and effluent quality basis for BAT Option One at Level 4.

Engineering analysis established the performance of additional end-of-pipe control technologies by transferring them from related applications. For example, the addition of powdered activated carbon (PAC) to improve the performance of activated sludge biological treatment is a demonstrated technology transferred from the organic chemicals and petroleum refining industries. The effluent quality produced by Option One - Level 4 as described above served as the starting point for application of PAC technology, with resulting improved effluent quality (Table 41) being the basis for BAT Option Two - Level 5. EPA estimates conservatively that the long-term final effluent concentration for BOD5 will be reduced by 50 percent from 40 mg/l to 20 mg/l, where higher percent removals and lower effluent concentrations were reported; TSS concentration will be reduced from 60 mg/l to 25 mg/l because the effectiveness of suspended solids separation is greatly enhanced by powdered activated carbon and the resulting TSS to BOD ratio reduced; COD concentration is determined from the COD to BOD5 relationship (Figure 3); oil and grease concentration will be reduced from 14 mg/l to 10 mg/l due to PAC enhanced biological treatment which is the primary mechanism for removal of oil and grease subsequent to primary coagulation-sedimentation, and where lower effluent concentrations were reported; chromium concentration will be slightly reduced from 1 mg/l to 0.5 mg/l, due primarily to better suspended solids control and where lower concentrations have been achieved in the leather industry; ammonia concentration will be reduced from 10 mg/l to 5 mg/l where

nitrification by biological treatment is improved and where the performance of plant no. 253 approaches this concentration without the influence of PAC; TKN concentration will be reduced from 40 mg/l to 20 mg/l in keeping with the 4:1 ratio of to ammonia; and phenol will be reduced from 0.25 mg/l to 0.1 mg/l by enhanced biological treatment, with this concentration being achieved by well run biological treatment systems in the petroleum refining industry and in some cases by plants in the leather industry.

Suspended solids remaining in BAT OPTION TWO effluents were then treated through a system of multi-media filtration transferred from numerous other industrial and municipal applications. The primary treatment accomplished by multi-media filtration is control of suspended solids, including residuals of insoluble chromium. EPA estimates that TSS concentrations will be reduced by approximately 35 percent from 25 mg/l to 16 mg/l, where consistently lower effluent concentrations of 10 mg/l have been noted in other applications; chromium will be reduced by an amount similar to TSS from 0.5 mg/l to 0.33 mg/l, where effluent concentrations as low as 0.17 mg/l have been reported in the leather industry (see Table 37) without the use of filtration. The literature notes that application of filtration technology also removes BOD probably associated with TSS. EPA estimates that approximately 30 percent of the BOD_5 will be removed, from 20 mg/l to 14 mg/l. The COD concentration associated with this reduction is determined by the COD to BOD_5 relationship (see Figure 3). In concert with BOD_5 removal, a small reduction in oil and grease will be accomplished, from 10 mg/l to 6 mg/l; effluent concentrations as low as 5 mg/l have been reported. It is also estimated that a small removal of TKN concentration will occur, from 20 mg/l to 15 mg/l; this is due to the removal of residual proteinaceous solids (TSS). No further reductions are made in either ammonia or phenol because biological treatment does not occur in filtration. The resulting effluent quality (Table 41) was the basis for BAT Option Three - Level 6.

Finally, the performance of granular activated carbon (GAC) columns in pilot plant and additional limited industrial application was applied to the effluent quality resulting from BAT Option Three - Level 6, with the resulting final effluent quality (Table 41) serving as the basis for BAT Option Four - Level 7. The final effluent concentrations were based largely upon reported concentrations in other applications with similar treatment preceding GAC columns.

The mass effluent limitations presented in Table 43 for the seven subcategories are based on BAT Option Three - Level 6. EPA selected this option because it provides significant removal of the toxic pollutants of concern in the leather tanning industry (primarily phenol and substituted phenols, and chromium and other heavy metals) by in-plant control, pretreatment, and end-of-pipe treatment. Although the Act does not require a balancing of costs against BAT effluent reduction benefits, the costs of the technology options

weighed heavily in this decision (see Section IX). EPA rejected BAT OPTION FOUR because of the high costs and small incremental pollutant removals when applied to wastewater treatment in the leather tanning and finishing industry. EPA believes that the effluent limitations are conservative and are achievable through careful operation and maintenance of BAT OPTION TWO-Level 5 treatment alone. Application of multi-media filtration will ensure achievement of these effluent limitations where operation and maintenance procedures may not be optimal.

EPA considers physical/chemcial treatment technology (Level 4A) an option for direct dischargers to produce an effluent quality equal to Level 6. Direct dischargers can apply this technology after Level 3 or following biological treatment to achieve BAT effluent quality.

One plant, sampled before ceasing operation, had physical/chemical treatment in place which achieved lower effluent concentrations for all pollutant parameters (both indicator and toxic pollutants) than all of the effluent concentrations proposed by these BAT regulations. No other plant achieves all of the limitations proposed for BAT. However, at least one plant (No. 253) in New England approaches the BAT effluent limitations for the indicator pollutants, including BOD_5, TKN, and ammonia.

Data Variability

Long-term performance is the basis for all of the reductions and residual concentrations projected for the pollutant parameters listed in Table 41. Data from tanneries with treatment systems similar to that selected as BAT were subjected to variability analysis to determine an average variation coefficient for the parameters considered. Final effluent data for BOD_5 and TSS was segmented into 30 day periods and average concentrations computed. The maximum concentrations observed for any one day were compared to the highest average for a 30 day period, and a ratio of 3.5 developed. Similarly, the maximum average concentration for a thirty-day period was compared to the long term (i.e., annual) average concentration and a ratio of 1.5 developed. Variability factors specific to each pollutant could not be developed with available data so that the variability factors developed for BOD_5 and TSS taken together were generally applied to the regulated parameters.

Table 43 shows the BAT effluent limitations as mass units (lbs/1,000 lbs or kg/kkg). These values were derived by multiplying the BAT effluent concentrations in Table 41 for Level 6 by the 1.5 variability coefficient to obtain the average concentration for 30 consective days. The adjusted effluent concentrations were then multiplied by the reduced flow rate for each subcategory to obtain the BAT 30-day average mass effluent limitations. A similar procedure, using a 3.5 variability factor, generated daily maximum values. The only pollutant parameter not subjected to the variability adjustment

procedure was COD. For the BAT effluent limitations, residual COD was computed from the BOD_5 to COD relationship (Figure 3) presented in Section VII.

REGULATED POLLUTANTS

The BAT effluent limitations proposed for the leather tanning industry focus on three major groups of pollutants:

1. Non-toxic, non-conventional pollutants. The non-toxic, non-conventional pollutants limited by BAT (ans NSPS) include total Kjeldahl nitrogen (TKN), ammonia, and sulfide. As noted below, these pollutants serve as "indicator" pollutants for the removal of toxic pollutants, except for sulfides. These pollutants are subject to numerical limitations expressed in lbs per 1000 lbs of raw material.

2. Toxic pollutants. The toxic pollutants expressly controlled for direct dischargers in each subcategory are phenol and chromium, which are subject to numerical limitations expressed in lbs per 1000 lbs of raw material. Since the EPA has adopted the control of "indicator" pollutants as the basis for controlling toxic pollutants, no effluent limitations are recommended for any toxic pollutants other than chromium and phenol.

3. Indicator pollutants. The difficulties of toxic pollutant analyses have prompted EPA to propose a new method of regulating selected toxic pollutants. Historical data and inexpensive analytical methods are limited for certain toxic pollutants. Therefore, EPA is proposing numerical limitations on "indicator" pollutants for which there is substantially more data; these include BOD_5, COD, TSS, oil and grease, TKN, ammonia, (total) chromium, and (total) phenol. The data available to EPA revealed that when these indicator pollutants were controlled, the concentrations of toxic pollutants were significantly lower than when indicator pollutants were present in high concentrations. Moreover, the treatment systems existing in the industry were designed for removal of conventional and nonconventional pollutants.

EPA's consideration of "indicator" limitations was brought to the attention of Congress during the formative stages of the Clean Water Act of 1977. At that time, EPA was examining several techniques to alleviate the difficulties of lengthy and expensive analytical procedures. The proposed alternate "indicator" limitations serve that purpose. This method of toxics regulation obviates the difficulties, high costs, and delays fo monitoring and analyses that would result from limitations solely on the toxic pollutants.

Quotations recently obtained from a number of analytical laboratories indicate that the cost of each wastewater analysis for organic toxic pollutants ranges between $650 and $1,700, excluding sampling costs. Even if cost were not such a factor, the availability of laboratory

time and capability would have posed additional constraints. When this study began, a well-trained technician using the most sophisticated equipment could perform only one complete organic analysis in an 8-hr work day. Moreover, there were only about 15 commercial laboratories in the United States with sufficient capability to perform these analyses. Today there are about 50 commercial laboratories known to EPA which have the capability to perform these analyses, and the number is increasing as the demand for such capability also increases. Efficiency also has been improving.

Appendix E lists the toxic pollutants found in treated effluents at more than two tanneries and in concentrations greater than available analytical detection limits. EPA concludes that these pollutants can be effectively controlled by limitation of the indicator pollutants even though the toxics (other than phenol and chromium) are not expressly regulated by numerical limitations.

The toxic pollutants regulated by indicators include all of the volatile (purgeable) organics, some of the acid-extractable organic compounds, the base-neutral-extractable organic compounds, and the inorganic compounds. An indicator for the substituted phenolic compounds is "total phenol" as measured by the 4-aminoantipyrine method (4AAP). This method measures the simple phenol (a toxic pollutant) present, plus fractions of the specific substituted phenols such as 2,4,6 trichlorophenol and 2,4-dichlorophenol. While pentachlorophenol does not respond to this test, EPA concludes that when both 4AAP phenol and other indicator pollutants (especially COD, TKN, and ammonia) are controlled, this compound and other compounds resistant to rapid biodegradation will be controlled as well. Similarly, EPA concludes that control of zinc, lead, nickel, and copper is accomplished by a specific limitation on total chromium, and by control of TSS as an indicator pollutant.

Many of the toxic organic compounds are known to be resistant to biological treatment and are measured largely by the COD test. Control of COD is therefore an indicator for certain of the toxic organic compounds, as well as a conventional pollutant parameter of major concern. Furthermore, COD can be rapidly and reliably determined by a traditional and relatively inexpensive analytical method.

Ammonia nitrogen is an oxygen demanding non-conventional pollutant of major concern, as is TKN. In addition to measuring ammonia nitrogen, TKN measures organic proteinaceous nitrogen, a wastewater constituent which ultimately contributes to ammonia nitrogen in both treatment systems and receiving waters. The conditions necessary for treating TKN and ammonia (nitrification) in activated sludge systems are the same as those for treating many of the slowly or partially biodegradable toxic organic compounds. These non-conventional pollutants are therefore indicators for removal of toxic pollutants.

It should be noted that some of the indicator pollutants, such as BOD_5, COD, TSS and oil and grease, are classified as "conventional" pollutants under Section 304(a)(4) of the Act or proposed regulations. Where conventional pollutants serve as "indicator" pollutants for toxic pollutants, BAT limitations for these pollutants have been established to assure installation of waste treatment technology adequate for the removal of toxic pollutants. In such cases, the "indicator" limitations on conventional pollutants will be established regardless of the BCT test. Furthermore, some of the "indicators" are nonconventional pollutants. These nonconventional "indicator" pollutants will not be subject to economic and water quality modifications under Sections 301(c) and (g) of the Act. Exceptions may be justified. A specific discharger may attempt to show that his waste stream does not contain any of the toxic pollutants that a BAT effluent limitation on a conventional or non-conventional toxic "indicator" was designed to remove. If this can be shown, then a limitation on a conventional pollutant would be subject to the BCT cost test, and a limitation on a non-conventional pollutant would be subject to requests for modifications.

The Agency is also considering the possibility of establishing numerical limitations (either in concentration or mass units) for the following toxic pollutants: phenol (by GC/MS methods), 100 μg/l; 2,4,6-trichlorophenol, 50 μg/l; pentachlorophenol, 25 μg/l; lead, 250 μg/l; zinc, 250 μg/l; cyanide, 500 μg/l.

The numerical limitations under consideration for phenol (100 μg/l), 2,4,6-trichlorophenol (50 μg/l), and pentachlorophenol (25 μg/l) are based upon the structure, known chemical properties, and available treatability data for these compounds as developed by Strier.[107] These are considered to be 30 day average concentrations based upon combined activated sludge - powdered activated carbon biological treatment.[108]

The numerical limitations being considered for lead (250 μg/l), zinc (250 μg/l), and cyanide (500 μg/l) are based upon their treatability as indicated by data developed during the sampling and analysis program for this industry. Strier's limitations developed were higher[108]: lead and zinc - 500 μg/l, and cyanide - 1,000 μg/l. Strier developed these limitations utilizing data from a number of industrial sources and projecting different treatment schemes. The data now available in this industry, however, supports the lower concentrations.

Comments and additional data are welcomed on all of these toxic pollutant limitations being considered by the Agency.

ENGINEERING ASPECTS OF THE APPLICATION OF BAT

Leather tannery wastewater originates as numerous discrete discharges from processing vessels containing various chemical mixtures designed or prepared to produce a specific effect on the hide or skin in the tanning process. Each discrete discharge may represent a different mix of pollutants and thus a potentially different waste treatment situation. Some of the processes are grouped by function into beamhouse operations and tanyard operations. The wastewater from these different operations varies in pH, suspended and/or dissolved proteinaceous solids, sulfide and chromium levels. Thus, tannery wastewater discharges seem especially amenable to process-group-specific (beamhouse or tanyard) collection and treatment, with the latter designed for specific, less variable pollutant mixes and loadings.

The separate collection of wastewater from the beamhouse and tanyard operations allows waste control measures to be tailored to the characteristics of each stream. Stream segregation is considered essential to achieve the recommended BAT effluent limits for tanneries with a beamhouse and tanyard. In addition, this concept facilitates recovery and reuse of process chemicals. Numerous industry sources have expressed the same opinion with regard to effective wastewater management and control. A tannery may succeed in its wastewater treatment program without stream segregation; however, such a step is instrumental in positive and cost-effective control of sulfides, and and is a substantial aid in establishing and operating a consistent and effective treatment system.

Another method of pollutant reduction employed by the industry is to substitute alternative chemicals for those presently in use. An example of this method is the substitution of magnesium sulfate for ammonium sulfate in the deliming process to reduce the ammonia content of the wastewater.

In-plant process changes and preliminary treatment of segregated waste streams effectively reduce raw waste loads discharged to the treatment system. A substantial source of organic raw waste load, for example, is the beamhouse unhairing stream which contains dissolved hair protein. The waste load from this source can be decreased by flue gas carbonation and sedimentation, following a sulfide oxidation step; this reduces solids and BOD_5 while producing a potentially valuable protein by-product for animal feed.

The control of suspended solids depends on adequate capacity, proper design, and operation of the clarifier. The addition of mixed-media or sand filtration technology downstream from the secondary clarifier will assure compliance with the recommended BAT effluent limitations. This assumes, however, that the clarifier and the filter unit are properly designed and operated.

Cost-effective removal of oil and grease is best accomplished in preliminary treatment or end-of-pipe primary treatment with well-maintained and properly designed catch basins or clarifiers with skimmers. Industries such as leather tanning, which characteristically produce high oil and grease in their wastewater, concentrate their removal efforts in primary treatment. Moreover, "secondary" treatment technologies will work better when high oil and grease loadings are avoided. Equipment fouling and overloads to the secondary treatment system are associated with excessive influent oil and grease loading. Many toxic pollutants which are not soluble in water tend to be included in fats, oils, and greases, and therefore can be reduced by separating or skimming the floating oil and grease from primary clarifiers.

Ammonia reduction in leather tanning wastewaters has been achieved by: 1) end-of-pipe extended aeration technology; 2) physical-chemical treatment; and 3) substitution of magnesium sulfate for ammonium sulfate in the deliming process of the tanyard operations. Using magnesium sulfate directly reduces the ammonia content of tannery wastewater by 67 percent, but increases chemical cost. One vegetable tannery has indicated leather quality problems resulting from the substitution while other plants did not report problems. As substantial body of literature, highlighted in Section VII, indicates that substitution for ammonia is feasible.

Most tanneries select a chemical alternative strictly on the basis of cost. However, waste treatment cost for ammonia removal must now be included in cost considerations because of the BAT effluent limit. Reduced costs of ammonia removal support the use of an alternative to ammonium sulfate. Ammonia substitution is then justified as a part of the basis for BAT effluent limitations.

Wastewater treatment technologies recommended for achieving the BAT limitations are producing low ammonia concentrations in the effluent from leather tanneries and from industrial plants with comparable waste streams, such as rendering plants. To achieve substantial ammonia reduction, the recommended technology requires proper design and carefully controlled operation. Long-term operating data from shearling Tannery No. 253, which operates a Carrousel oxidation ditch activated sludge system (subcategory no. 7), is the basis for transfer of this nitrification technology to the remaining subcategories of the leather tanning and finishing industry. With the exception of the initial startup period, and periods of upset including April and May, 1979, this plant has produced consistently low effluent concentrations of ammonia and TKN during both summer and winter months, as shown in Figures 35 and 36.

Data from a full-scale nitrifying high solids extended aeration-activated sludge system in other subcategories is not yet available for comparison. EPA believes that with in-plant control of ammonia to reduce the higher masses (lb/1,000 lb) and concentrations

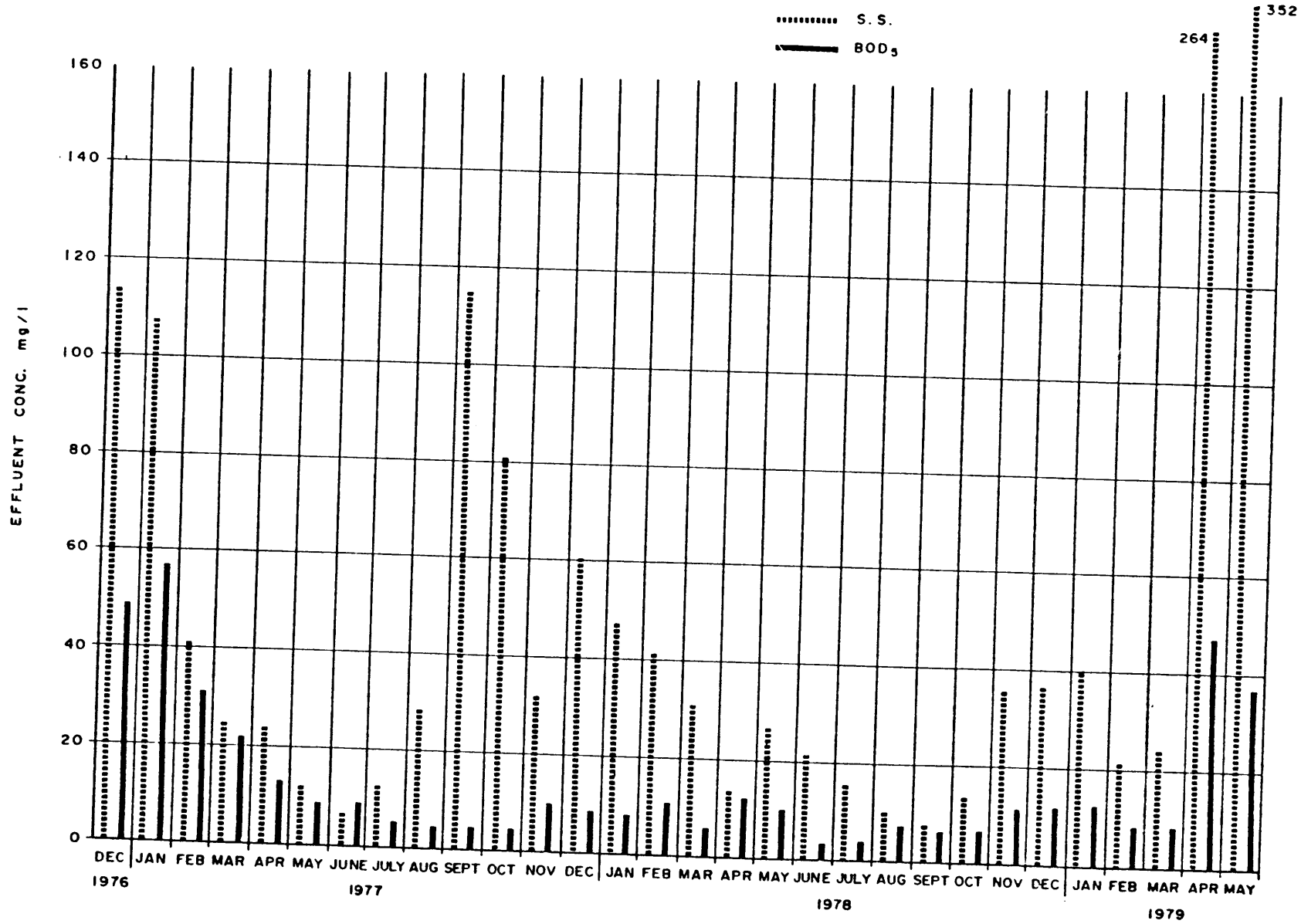


Figure 35. Average Monthly Final Effluent Concentrations of BOD5 and TSS for the Carrousel Activated Sludge System at Tannery #253

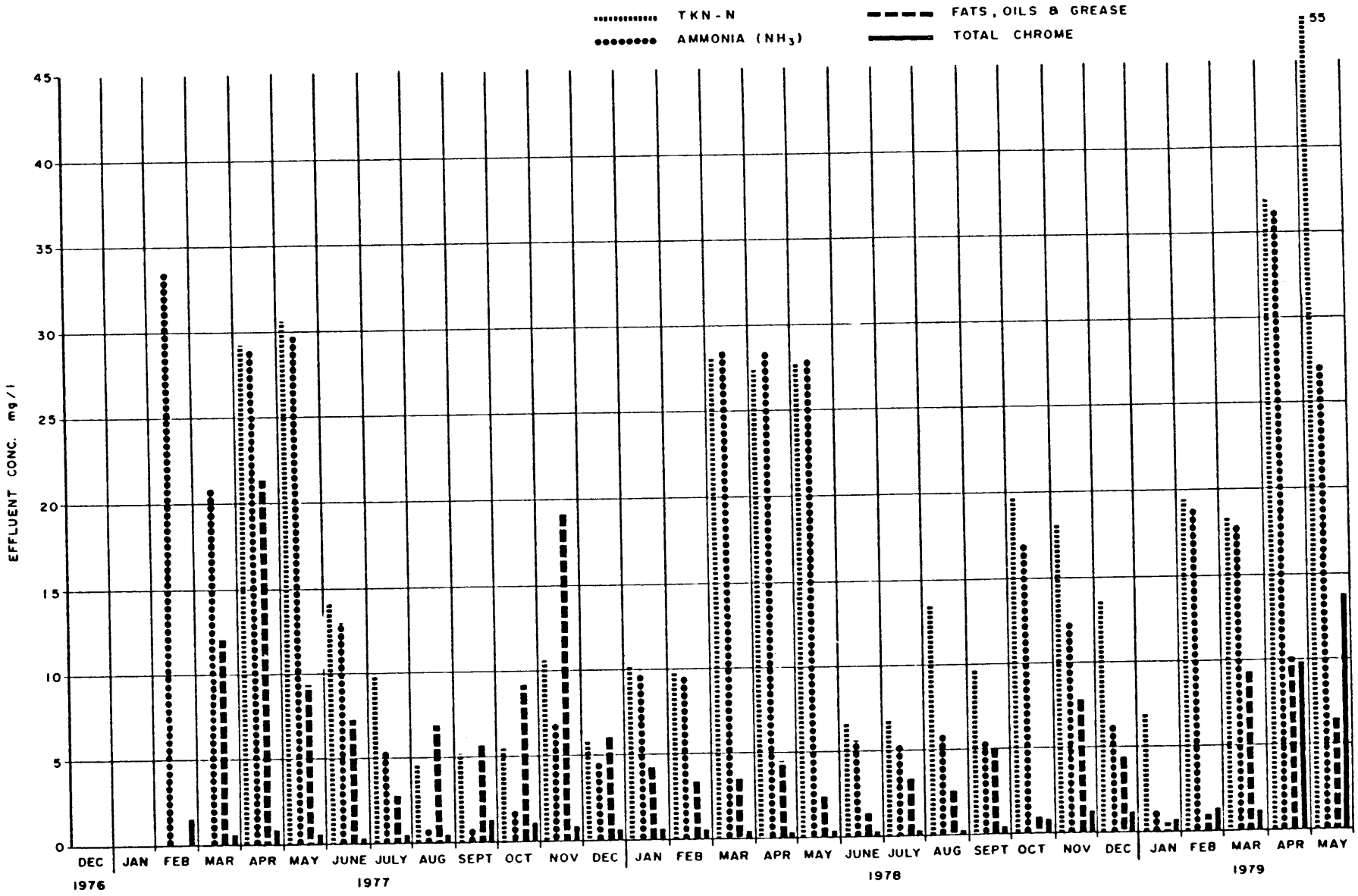


Figure 36. Average Monthly Final Effluent Concentrations of TKN, Ammonia, Oil and Grease, and Total Chromium for the Carrousel Activated Sludge System at Tannery #253

which must be treated in the other subcategories, nitrification will be equally effective. When data from full scale systems in the remaining subcategories become available, adjustments in the limitations for TKN and ammonia may be necessary.

Tannery no. 247 is a retan-wet finish (Subcategory Four) tannery which recently closed. This tannery had employed only a physical-chemical treatment system to achieve an effluent quality unequalled in the industry. A difference of almost a full order of magnitude existed between the effluent quality produced by the tannery no. 247 system and the treatment facilities at other tanneries. The physical-chemical treatment system (Level 4A), although not in use at a full-line tannery (e.g., Subcategory One, Two, or Three), seems suitable for the waste flow and pollutant characteristics typical of leather tanneries. It is amenable to direct and immediate process control, and is not subject to the inherent sensitivities of biological treatment systems.

COST AND EFFLUENT REDUCTION BENEFITS

On the assumption of reduced flow rates, EPA estimated the capital investment and operation and maintenance costs for model plants in the seven subcategories (Tables 43 and 44). The estimates were developed for the incremental levels of technology employing the appropriate cost relationships described in Section VIII of this document.

With BPT (Levels 3 and 4) already in-place for the existing 18 direct dischargers, EPA estimates the additional total investment for the leather tanning industry to achieve recommended BAT effluent limitations based on Level 6 performance, to be $1.9 million. A breakdown of the incremental expenditures for initial investment and annual cost applicable to BAT Options, One, Two, Three, and Four for all direct dischargers is as follows:

Levels 1 and 2 (OPTION ONE)	Investment	975,000
	Annual	1,490,000
Level 5 (OPTION TWO)	Investment	70,000
	Annual	90,000
Level 6 (OPTION THREE)	Investment	845,000
	Annual	180,000
Level 7 (OPTION FOUR)	Investment	1,925,000
	Annual	640,000

Effluent reduction by BAT technology reduces the discharge from the leather tanning industry of conventional pollutants, non-conventional pollutants, and toxic pollutants, which are found in the wastewaters, to the required effluent concentrations. In-plant process changes that reduce wastewater volume or pollutant loading may be implemented

Table 43

CAPITAL COSTS FOR EACH LEVEL (4th QTR '77) OF TREATMENT, $1000

CATEGORY - SIZE	STREAM SEGREGATION	LEVEL 1 IN PLANT	LEVEL 2 PRETREATMENT	LEVEL 3 PRETREATMENT	LEVEL 4 SECONDARY TREATMENT	LEVEL 5 UPGRADED SECONDARY TREATMENT	LEVEL 6 AWT I	LEVEL 7 AWT II	LEVEL 4A CHAPPEL	SLUDGE DEWATERING
1-Hair Pulp-Chrome Tan-Retan-Wet Finish										
100 Hides/Day	37	42	31	54	65	1	12	39	77	19
400	53	65	46	117	166	2	30	82	144	39
900	74	83	59	187	274	3	50	124	204	61
1500	97	97	70	251	346	5	75	158	260	79
3000	150	118	89	358	475	8	118	216	350	108
2-Hair Save-Chrome Tan-Retan-Wet Finish										
100 Hides/Day	37	42	31	49	61	1	11	36	72	18
400	53	65	44	106	155	2	28	77	135	36
900	74	83	57	169	255	3	45	116	192	56
1500	97	97	68	227	321	5	68	149	244	74
3000	150	118	84	324	442	8	107	202	328	103
3-Hair Save-Nonchrome Tan-Retan-Wet Finish										
100 Hides/Day	37	43	35	65	87	1	16	49	92	23
625	63	75	51	150	221	3	39	103	175	50
1500	97	97	62	199	292	5	56	132	218	65
4-Retan-Wet Finish										
2000 Sides/Day	--	--	--	119	172	2	31	83	144	40
4250 Splits/Day	--	--	--	68	86	1	16	49	93	23
5-No Beamhouse										
1200 Skins/Day	--	--	--	37	37	1	10	26	38	13
2400	--	--	--	62	77	1	12	45	53	21
5800	--	--	--	122	172	2	15	85	80	40
5000 Hides/Day	--	--	--	205	298	5	31	135	147	66
6-Thru-The-Blue										
1500 Hides/Day	74	75	60	209	280	3	52	144	213	62
3000	97	97	80	315	407	5	92	184	298	92
7-Shearlings										
900 Skins/Day	39	--	--	116	168	2	30	82	146	39
3000	62	--	--	243	342	6	70	155	253	77
5000	78	--	--	333	450	8	110	206	333	106

Table 44

OPERATION AND MAINTENANCE COSTS FOR EACH LEVEL OF TREATMENT ($1000/YR)

CATEGORY - SIZE	STREAM SEGREGATION	LEVEL 1 IN PLANT	LEVEL 2 PRETREATMENT	LEVEL 3 PRETREATMENT	LEVEL 4 SECONDARY TREATMENT	LEVEL 5 UPGRADED SECONDARY TREATMENT	LEVEL 6 AWT I	LEVEL 7 AWT II	LEVEL 4A CHAPPEL	SLUDGE DEWATERING
1-Hair Pulp-Chrome Tan-Retan-Wet Finish										
100 Hides/Day	4.0	12.9	6.2	9.1	9.6	0.6	3.1	14.3	10.2	8.2
400	7.2	31.8	10.2	17.5	23.4	2.4	7.0	21.7	20.1	11.2
900	12.0	57.5	13.3	29.9	40.4	5.2	11.0	37.1	29.5	17.9
1500	17.2	88.2	15.7	42.4	64.7	8.2	14.4	53.8	38.6	23.5
3000	29.5	168.5	19.2	67.1	71.4	14.4	19.9	88.2	54.0	37.0
2-Hair Save-Chrome Tan-Retan-Wet Finish										
100 Hides/Day	4.0	11.9	6.1	9.0	8.9	0.6	2.9	13.6	9.8	8.2
400	7.2	29.8	9.8	16.7	21.5	2.2	6.4	20.2	19.3	11.2
900	12.0	55.5	12 5	28.3	37.0	4.6	10.1	33.8	28.5	17.9
1500	17.2	86.2	15.0	39.9	58.6	7.2	13.3	48.6	37.3	23.5
3000	29.5	166.5	18.2	62.7	64.6	12.8	18.5	79.0	52.2	37.0
3-Hair Save-Nonchrome Tan-Retan-Wet Finish										
100 Hides/Day	4.0	17.4	7.3	10.7	11.5	1.0	4.0	17.4	14.4	8.8
625	9.4	46.7	11.8	24.1	35.6	3.8	9.0	29.0	25.7	14.6
1500	17.2	95.0	13.9	33.9	49.0	6.0	11.7	40.9	32.3	20.2
4-Retan-Wet Finish										
2000 Sides/Day	--	--	--	17.7	18.2	2.4	7.1	23.1	20.2	8.3
4250 Splits/Day	--	--	--	10.7	13.5	1.0	4.0	17.3	14.5	7.2
5-No Beamhouse										
1200 Skins/Day	--	--	--	7.8	7.2	0.2	2.0	24.2	9.8	6.5
2400	--	--	--	10.4	11.0	0.8	3.5	24.2	13.7	7.2
5800	--	--	--	18.6	22.4	2.4	7.2	38.1	20.3	8.4
5000 Hides/Day	--	--	--	33.9	49.0	6.0	12.0	56.0	32.3	20.2
6-Thru-The-Blue										
1500 Hides/Day	12.0	87.2	13.6	24.1	35.6	5.6	11.4	32.2	68.1	14.6
3000	17.2	162.5	17.3	42.4	64.7	10.8	16.8	42.2	84.8	23.5
7-Shearlings										
900 Skins/Day	8.4	--	--	18.5	24.1	2.4	7.0	20.0	37.4	8.3
3000	27.2	--	--	44.7	65.4	7.6	14.0	38.4	63.2	25.8
5000	45.4	--	--	67.1	69.9	12.8	19.0	54	80.8	37

for purely economic reasons, with the added benefit of improved wastewater quality. Chrome recovery and reuse, which is approaching standard practice, is an example of such decision-making within the industry. Other process changes include sulfide reuse and recovery, and substitution for ammonia in deliming. Reduction of water use can be accomplished through conservation and recycle systems (including pasting frame wash water), and other process modifications such as those highlighted in Section VII of this document. The total mass of regulated pollutants for all direct discharges removed from BPT effluent levels by this BAT technology option would be as follows: 610,000 lbs/year of BOD_5; 2,000,000 lbs/year of COD; 1,100,000 lbs/year of TSS; 710,000 lbs/year of oil and grease; 21,000 lbs/year of chromium (total); 1,670,000 lbs/year of TKN; 620,000 lbs/year of ammonia; 5,100 lbs/year of phenol (total); and 26,000 lbs/year of sulfide. EPA estimates the total mass of toxics pollutants discharged would be as follows: 640 lbs/year of volatile organics; 800 lbs/year of base/neutral organics; 2,000 lbs/year of acid organics; and 380 lbs/year of the inorganic pollutants exclusive of chromuim.

NON-WATER QUALITY ENVIRONMENTAL IMPACT

EPA has found that a significant portion of the toxic pollutants removed from tannery wastewater remains intact in the solids that are removed from the wastewater. These solids are subsequently disposed in landfills and other disposal sites with variable controls, as indicated in Sections VII and VIII. The impact of such disposal is the primary non-water quality concern resulting from the BAT effluent limitations. EPA estimates that achievement of BAT effluent limitations will generate an additional 41,000 metric tons/year of sludges from BAT treatment technology as applied by all direct dischargers.

Energy consumption for waste treatment will increase in order to achieve the proposed limits. However, the wastewater control and management practices implemented to reduce the total flow may result in a net energy saving, compared to the energy expended to achieve BPT effluent limitations. Reduction in pumping and other operations associated with wastewater movement and control will reflect less energy use.

BAT EFFLUENT LIMITATIONS

The effluent concentrations and associated mass loadings listed in Table 41 are long-term averages. Variability has been factored into the maximum month and maximum day effluent limitations presented in Table 45.

Table 45

BAT EFFLUENT LIMITATIONS

Subcategory One - Hair Pulp, Chrome Tan, Retan-Wet Finish

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.1	0.61
COD	9.5	5.8
TSS	2.5	0.70
Oil and Grease	0.91	0.26
Total Chromium	0.053	0.015
TKN	2.3	0.66
Ammonia	0.77	0.22
Phenol	0.015	0.0043
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Two - Hair Save/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.3	0.65
COD	10.0	6.2
TSS	2.6	0.74
Oil and Grease	1.0	0.28
Total Chromium	0.053	0.015
TKN	2.4	0.69
Ammonia	0.81	0.23
Phenol	0.016	0.0046
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Three - Hair Save/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.6	0.47
COD	7.3	4.5
TSS	1.9	0.54
Oil and Grease	0.70	0.20
Total Chromium	0.039	0.011
TKN	1.8	0.51
Ammonia	0.60	0.17
Phenol	0.012	0.0034
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Four - Retan-Wet Finish

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	0.81	0.23
COD	3.5	2.2
TSS	0.91	0.26
Oil and Grease	0.35	0.10
Total Chromium	0.018	0.005
TKN	0.84	0.24
Ammonia	0.28	0.081
Phenol	0.0056	0.0016
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Five - No Beamhouse

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.4	0.40
COD	6.2	3.8
TSS	1.6	0.46
Oil and Grease	0.60	0.17
Total Chromium	0.034	0.0096
TKN	1.5	0.43
Ammonia	0.49	0.14
Phenol	0.010	0.0029
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Six - Through-the-Blue

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.5	0.44
COD	6.8	4.2
TSS	1.8	0.50
Oil and Grease	0.67	0.19
Total Chromium	0.035	0.010
TKN	1.6	0.47
Ammonia	0.56	0.16
Phenol	0.011	0.0031
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Seven - Shearling

Pollutant or Pollutant Property	BAT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	6.7	1.9
COD	29.8	18.0
TSS	7.7	2.2
Oil and Grease	2.9	0.83
Total Chromium	0.16	0.046
TKN	7.4	2.1
Ammonia	2.4	0.69
Phenol	0.049	0.014
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

SECTION XI

EFFLUENT REDUCTION ATTAINABLE BY BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY

INTRODUCTION

The 1977 amendments added section 301(b)(4)(E) to the Act, establishing "best conventional pollutant control technology" (BCT) for discharges of conventional pollutants from existing industrial point sources. Conventional pollutants are those defined in section 304(b)(4) - BOD, TSS, fecal coliform and pH - and any additional pollutants defined by the Administrator as "conventional." On July 28, 1978, EPA proposed that COD, oil and grease, and phosphorus be added to the conventional pollutant list (43 Fed. Reg. 32857).

BCT is not an additional limitation, but replaces BAT for the control of conventional pollutants. BCT requires that limitations for conventional pollutants be assessed in light of a new "cost-reasonableness" test, which involves a comparison of the cost and level of reduction of conventional pollutants from the discharge of POTW's to the cost and level of reduction of such pollutants from a class or category of industrial sources. As part of its review of BAT for certain "secondary" industries, EPA proposed methodology for this cost test. (See 43 Fed. Reg. 37570, August 23, 1978).

EPA is proposing that the conventional "indicator" pollutants, which are used as "indicators" of control for toxic pollutants, be treated as toxic pollutants. In this way, effluent limitations will be established for the conventional indicator pollutants at BAT levels, and the limitations will not have to pass the BCT cost test. When a permittee, in a specific case, can show that the waste stream does not contain any of the toxic pollutants that a conventional toxic "indicator" was designed to remove, then the BAT limitation on that conventional pollutant will no longer be treated as a limitation on a toxic pollutant. The technology identified as BAT for control of toxic pollutants also affords removal of conventional pollutants to BAT levels. As noted below, these effluent levels passed the BCT cost test, and therefore, are also designated as BCT effluent levels.

APPLICATION OF BCT METHODOLOGY

EPA applied the BCT cost test to the costs associated with the removal of conventional pollutants in the leather industry. In the first step in the analysis, EPA calculated the size of an average plant for each subcategory based upon the actual production of plants with direct discharge. No plants existed in subcategory no. 6 (through-the-blue), and the average plant size for indirect dischargers was used. Raw waste load data (Tables 6-12) for each subcategory determined the amount of wastewater and pollutant load generated by each plant for an

average of 253 production days per year. Data in Section VIII was used to develop the investment and total annualized cost of BPT, assuming no in-place technology; the cumulative costs beyond BPT for each technolgoy option were developed in the same manner. The size of each plant and the mass limitations were then used to calculate the cumulative pounds per year of BOD5 plus TSS removed by each technology option beyond BPT. The ratios of the total annualized costs to the pounds per year of BOD5 and TSS removed were than calculated for each BCT technology option, for each subcategory. The incremental cost of removing BOD5 and TSS at POTWs was then obtained from cost data published in the Federal Register (see 43 FR 37594, August 23, 1978; Table C8) by selecting the cost for the same size POTW (in million gallons per day-mgd) as the average size leather tanning treatment system for each subcategory. Table 46 summarizes the results of this cost comparison test.

Based upon these results the Agency concluded that BCT limitations based upon multi-media filtration (BAT Option Three - Level 6) are reasonable. At this treatment level, cost to pollutant reduction ratios for the seven subcategories range from $0.31 per pound of BOD5 and TSS removed (compared to POTW cost of $1.54 at 0.09 mgd) for subcategory no.4 to $0.94 per pound of BOD5 and TSS removed (compared to POTW cost of $1.28 at 0.152 mgd) for subcategory no. 3. Therefore, EPA is proposing BCT effluent limitations at the BAT Option Three - Level 6.

BCT EFFLUENT LIMITATIONS

The pollutants controlled by this regulation include the conventional pollutants designated in the Act, BOD5, TSS, and pH, and the proposed conventional pollutants COD and oil and grease. The BCT technology basis and the related effluent limitations which are presented in Table 47 are the same as outlined for the BAT regulation.

TABLE 46 SUMMARY OF COST-REASONABLENESS TEST FOR EACH BCT OPTION AND SUBCATEGORY

SUBCAT.	BPT Level 3 + 4			OPTION 1 BPT + Lev. 1 & 2			OPTION 2 Option 1 + Lev. 5			OPTION 3 Option 2 + Lev. 6			OPTION 4 Option 3 + Lev. 7			BAT-BCT Flow/POTW
	$	LBS	$/LB	$	LB	$/LB	$	LBS	$/LB	$	LBS	$/LB	$	LBS	$/LB	COST
1	202	2904	.07	88	90	0.98	98	140	.70	124	155	.80	205	170	1.21	.276/0.93
2	215	2432	.09	92	119	0.77	101	172	.59	128	187	.68	212	202	1.05	.290/0.90
3	133	1242	.11	66	61	1.08	72	88	.82	90	96	.94	143	104	1.38	.152/1.28
4	92	335	.27	-	31	-	3	47	.06	16	52	.31	54	57	.95	.09/1.54
5	49	136	.36	-	11	-	2	17	.12	9	19	.47	32	21	1.52	.032/1.75
6	312	6830	.05	84	108	.78	96	207	.46	135	235	.57	234	263	.89	.0533/.65
7	250	487	.51	38	109	.35	47	173	.27	78	193	.40	147	212	.69	.363/.81

$ - Total Annualized Cost (Interest, Depreciation, O & M), in Thousands of Dollars

LBS - Total pounds of BOD_5 + TSS removed from BPT to each BCT option

Table 47

BCT EFFLUENT LIMITATIONS

Subcategory One - Hair Pulp/Chrome Tan/Retan - Wet Finish

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.1	0.61
COD	9.5	5.8
TSS	2.5	0.70
Oil and Grease	0.91	0.26
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Two - Hair Save, Chrome Tan, Retan-Wet Finish

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.3	0.65
COD	10.0	6.2
TSS	2.6	0.74
Oil and Grease	1.0	0.28
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Three - Hair Save/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.6	0.47
COD	7.3	4.5
TSS	1.9	0.54
Oil and Grease	0.70	0.20
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Four - Retan-Wet Finish

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	0.81	0.23
COD	3.5	2.2
TSS	0.91	0.26
Oil and Grease	0.35	0.10
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Five - No Beamhouse

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD5	1.4	0.40
COD	6.2	3.8
TSS	1.6	0.46
Oil and Grease	0.60	0.17
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Six - Through-the-Blue

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD5	1.5	0.44
COD	6.8	4.2
TSS	1.8	0.50
Oil and Grease	0.67	0.19
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Seven - Shearling

Pollutant or Pollutant Property	BCT Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	6.7	1.9
COD	29.8	18.0
TSS	7.7	2.2
Oil and Grease	2.9	0.83
pH	Within the range of 6.0 to 9.0 at all times.	

SECTION XII

NEW SOURCE PERFORMANCE STANDARDS

INTRODUCTION

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology (BADT). New plants have the opportunity to design the best and most efficient leather tanning processes and wastewater treatment technologies. Therefore, Congress directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible. A major difference between NSPS and BAT is that the Act does not require evaluation of NSPS in light of the BCT cost test.

EPA has selected control and treatment technology Level 6 (including multi-media filtration) as the basis for NSPS because it provides for the maximum feasible removal of toxic pollutants of concern. The Agency rejected Level 7 (GAC columns) because EPA believes that GAC columns are too expensive and sophisticated for use in this industry. Although EPA believes that physical-chemical treatment (Level 4A) may be a viable option, it rejected this technology option because of technical and cost questions regarding its application to raw wastewaters different from those of the retan-wet finish plant (Subcategory Four) where it was installed. However, a new plant may well overcome cost and technical questions with careful design and pilot plant evaluation.

NSPS EFFLUENT LIMITATIONS

Since the control and treatment technology basis for NSPS is the same as that established for BAT (Level 6), the methodology used to develop the effluent limitations, the engineering aspects of this technology, and the numerical effluent limitations (Table 43) are also the same.

SECTION XIII

PRETREATMENT STANDARDS

GENERAL

The effluent limitations that must be achieved by new and existing sources in the leather tanning and finishing industry that discharge into a POTW are termed pretreatment standards. Section 307(b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES) to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of POTW's. The 1977 amendments to the Act also requires pretreatment for pollutants, such as heavy metals, that limit POTW sludge management alternatives, including the beneficial use of sludges on agricultural lands. The legislative history of the 1977 Act indicates that pretreatment standards are to be technology-based, analagous to the best available technology for removal of toxic pollutants. The general pretreatment regulations (40 CFR Part 403), which served as the framework for these proposed pretreatment regulations for the leather tanning and finishing industry, can be found in 43 Fed. Reg. 27736-27773 (June 26, 1978).

Consideration was also given to the following in establishing a pretreatment standard:

1. the manufacturing processes employed by the industry;
2. the age and size of the equipment and facilities involved;
3. the location of manufacturing facilities;
4. process changes;
5. the engineering aspects of the application of pretreatment technology and its relationship to POTW;
6. the cost of application of technology in relation to the effluent reduction and other benefits achieved from such application; and
7. non-water quality environmental impact (including energy requirements).

PRETREATMENT STANDARDS FOR EXISTING SOURCES (PSES)

Manufacturing Processes, and Size, Age, and Location of Facilities

The processes employed in different size tanneries within each subcategory are basically similar. Furthermore, the factors of size,

age, and processes employed do not affect the pretreatment control technology used and proposed. Hence these factors were not directly involved in determining the pretreatment standard. Also, the location of facilities was not a factor to be considered regarding pretreatment, just as described in Section IV (Industry Subcategorization).

Process Changes

As pointed out in Section VII, indirect dischargers should consider additional wastewater management and control practices to reduce wastewater volume and pollutant loadings, as well as the surcharges and capital cost recovery paid by tanneries discharging to POTW's. This reduction can be achieved by implementing the following measures:

1. Appoint a person with specific responsibility for water management. This person should have reasonable powers to enforce improvements in water and waste management and implement better housekeeping practices.

2. Determine or estimate water use and waste load strength from principal sources. Install and monitor flowmeters in all major water use areas.

3. Make all employees aware of good water management practices and encourage them to apply these practices. One practice requiring employee participation is the elimination of the constantly running hoses observed in some tanneries.

4. Recirculate non-contact cooling water, such as that from vacuum driers.

5. Segregate waste streams from each major in-plant process, i.e., beamhouse, tanyard, and retan/finishing for subsequent treatment before mixing with others.

6. Use more care in unloading, unfolding and otherwise preparing hides for processing to minimize salt entry into the sewers.

7. Collect unhairing waste stream, reduce pH to isoelectric point to precipitate dissolved protein, and recover the protein as a valuable by-product.

8. Reuse or recover active chemicals from waste streams such as the sulfide-containing stream, pickling solution, and chrome tanning solution.

9. Examine tanning formulas to determine if floats can be reduced. Use of hide processors and other specially designed vessels has lowered float volumes.

10. Provide regularly scheduled maintenance attention for screening and solid waste handling systems throughout the operating day. A backup screen may be desirable to minimize solids entry into the municipal sewer system.

Such practices are feasible and may be economically attractive through the reduction of municipal water and sewer use charges resulting from lower flows and waste loadings.

Pretreatment Technology

Candidate control technologies for pretreatment are the same as those considered as candidate BAT technologies for direct dischargers. These technologies are as follows:

Level 1 - Water conservation and reuse to reduce flow (all subcategories)
- Stream segregation for preliminary treatment (subcategory nos. 1, 2, 3, 6, and 7)
- Ammonia substitution in deliming (subcategory nos. 1, 2, 3, and 6)
- Chrome recovery and reuse (subcategory nos. 1, 2, 5, 6, and 7)
- Sulfide liquor reuse followed by catalytic oxidation of residual sulfide (subcategory nos. 1, 2, 3, and 6)
- Fine screening of segregated streams (all subcategories)

Level 2 - Flue gas carbonation and sedimentation for beamhouse wastewaters (subcategory nos. 1, 2, 3, and 6)

Level 3 - Primary coagulation-sedimentation of combined streams (applicable to all subcategories)

Performance of these levels of treatment were described in Section VII for the specific technology. Table 41, presented in Section X, indicates the performance of these technologies for tannery wastewaters. Figures 4 through 9 schematically showed the pretreatment technology identified for existing sources by subcategory.

Rationale For The Pretreatment Standard

The rationale for developing the pretreatment standards rests primarily on the concept of controlling pollutants which interfere, pass through, or are otherwise incompatible with POTW treatment systems and sludge disposal. See Section 307(b) of the Act and EPA's recently promulgated pretreatment regulations (40 CFR Part 403, 43 Fed. Reg. 27736-27773 (June 26, 1978). BOD_5, TSS, oil and grease, total chromium, sulfide, ammonia, and other toxic pollutants are present in sufficient concentrations in the raw waste from tanneries

to present POTW's with potential problems of pollutant pass-through and sludge disposal.

For this technology-based analysis, EPA has assumed the following:

1. Any joint municipal-industrial POTW which receives leather tanning and finishing wastewater has been assumed to provide primary sedimentation and secondary biological treatment including final clarification and sludge management. These facilities are assumed to be properly designed and diligently operated.

2. Analysis of pass-through and upset relating to POTW has been determined up to the point of wastewater release from control of the leather tanning and finishing plant; therefore, specific collection system circumstances may warrant consideration at the local level.

3. Local water quality constraints and unique operational or sludge disposal problems, have not been considered during this engineering analysis.

4. Strict adherence to and local enforcement of the general prohibited discharge provisions of the pretreatment regulation, and similar provisions in local ordinances, is essential to ensure that potential problems of upset and/or pass-through noted below are not permitted to occur.

Tannery wastewaters potentially can create or contribute to the following problems for a POTW:

1. potential problem with future disposal of sludges containing toxic pollutants, especially chromium;

2. odors, facilities corrosion, very high dissolved oxygen demand in aeration basins of biological treatment systems, and hazardous gas generation from sulfide-bearing wastes;

3. wide fluctuations in pH, and hydraulic and pollutant loads;

4. excessive quantities of hair and other small screenable solids;

5. high concentrations of suspended and settleable solids, BOD_5, and other pollutants; and

6. pass-through of ammonia nitrogen.

The potential problems listed above can be largely eliminated through leather tanners' strict adherence to local discharge provisions and national pretreatment regulations. Moreover, properly designed and diligently operated POTW's can suitably treat leather tanning and finishing wastewater.

The information gathered during this study indicates that the BOD_5 and TSS found in tannery wastewater are amenable to removal by properly designed and operated activated sludge secondary biological treatment systems. Operating data from four joint municipal-industrial POTW's which employ the activated sludge process to treat more than 50 percent tannery wastewater indicates that influent BOD_5 and TSS concentrations, which range from 250 mg/l to 950 mg/l and 200 mg/l to 900 mg/l, respectively, can be reduced to effluent concentrations of 10 mg/l to 65 mg/l and 11 mg/l to 75 mg/l, respectively. The broad range of influent concentrations did not indicate a sensitivity to a maximum level beyond which the wastewaters were not effectively treated. However, none of these plants consistently achieved the BOD_5 and TSS effluent concentrations which served as the basis for BAT and BCT regulations.

Chromium is removed to low effluent concentrations from wastewater in POTW's which include primary treatment and secondary biological treatment systems. Data from one municipality indicates that influent chromium (trivalent) concentrations, often greater than 100 mg/l, are reduced in the final effluent to concentrations of less than 2 mg/l. Other POTW data indicate final effluent concentrations from 1 mg/l to as little as 0.1 mg/l.

Chromium removal occurs in treatment systems, but POTW's do not monitor for chromium as extensively as they monitor for BOD_5 and TSS. Alkaline precipitation of chromium occurs readily in primary clarifiers. EPA found no evidence that chromium interferes with the performance of biological treatment systems in use as secondary treatment. Two factors influence the chrome concentration of POTW effluent: (1) dilution resulting from other wastes entering the POTW; and (2) removal occurring within the waste treatment processes. However, the presence of carbonates and improper pH can substantially impair trivalent chromium removal. Moreover, comparison of observed chromium effluent concentrations with those required by BAT effluent limitations for direct dischargers indicates that the POTW effluent may contain higher concentrations. With the bulk of the chromium removed at the individual industrial sites by pretreatment through Level 3, affected POTW's will be able to improve upon the effluent concentrations of chromium and approach the levels of chromium required by BAT. Consistent achievement of BAT chromium concentrations by the POTW is one of the criteria for eligibility for "credits" as set forth by 40 CFR Part 403.

A few municipalities have had substantial difficulty in finding acceptable sites for disposal of sludges containing large quantities

of chromium. Pretreatment through Level 3 at the industrial site will remove the bulk of the chromium, other toxic metals, and a portion of the insoluble toxic organic pollutants present, dramatically reducing the burden of these pollutants in POTW sludges. This will permit consideration of more sludge disposal alternatives, possibly including beneficial use on agricultural land. Sludge disposal considerations, such as beneficial use are the second criteria for "credits" eligibility.

Hazardous hexavalent chromium was used in only two tanneries of about 100 in the sample population. These tanneries use the older "two bath" tanning method, in which hexavalent chromium is reduced in the tanning drums. Hexavalent chromium should therefore appear only in trace amounts in the wastewater, which itself presents a chemically reducing environment due to the presence of significant amounts of organic matter. The data available tend to confirm this, although the actual presence of hexavalent chrome in tannery wastewater is difficult to accurately quantify.

Available information indicates that sulfide is removed in secondary biological treatment systems such as those employed in POTW's. However, sulfides have the potential to interfere with the operation of POTW in three significant ways:

1. Sulfides react in wastewater streams, sewers, and POTW components at a certain pH to form hydrogen sulfide, which is toxic to humans at a Threshold Limit Value of 10 ppm in air.[109] Reports occur periodically about the deaths of workers in sewers, usually caused by hydrogen sulfide poisoning. Similar reports on the deaths of a number of workers were noted in the public record during the course of this study, including workers in both U.S. and Italian tanneries where careless handling of process chemicals were at fault. These accidents also occur in the confined spaces of sewer systems and in low, protected spaces in POTW's.

2. The catalytic oxidation of hydrogen sulfide produces sulfates in wastewater which can be highly corrosive to sewers and treatment plant equipment, shortening their operating life and creating maintenance problems and downtime when the system is not able to operate as needed. Adequate control of pH to alkaline levels can minimize corrosion of operating equipment, including sludge handling, dewatering, and disposal equipment. Reappearance of variable but relatively low amounts of hydrogen sulfide has been noted after catalytic sulfide oxidation.

3. Sulfides produce hydrogen sulfide odors under fairly common conditions in waste treatment processes. People can detect these very obnoxious odors in very low concentrations in the air. Chronic odor problems from POTW's occur especially

during summer months, when rapid bacterial uptake of dissolved oxygen can cause release of unoxidized hydrogen sulfide.

A careful review of the extent of these sulfide-related problems has led EPA to conclude that national regulation is necessary. Currently available and practicable technology (catalytic oxidation) can remove most if not all dissolved sulfides. Where a tanner has segregated the sulfide-bearing beamhouse wastewater for separate catalytic oxidation, sulfide carry-over by the hides or skins into tanyard and wet finishing waste streams may require the precipitation of this residual to achieve the effluent limitation. Coagulation with ferric chloride is an approach available for controlling sulfide in tanyard and wet finishing wastewaters. However, it also is likely that sulfide will be liberated to the atmosphere during the acid-based processes including tanning. Taken together, sulfide removal technology and provision of suitable pH conditions can achieve a pretreatment standard of 0.0 mg/l (not detectable by the analtyical method for sulfide) at the point of discharge to the POTW sewer.

Effluent data from POTW's indicate that ammonia nitrogen passes through both POTW's and separate tannery wastewater treatment systems which are well designed and operated. Substitution for ammonia in the deliming process, along with beamhouse pretreatment to remove a substantial portion of the protein which ultimately contributes substantially to ammonia, should sufficiently reduce the ammonia content of leather tanning wastewaters. This should allow nitrification in POTW biological treatment systems to be more successful in controlling pass-through of this pollutant.

EPA has reviewed the proposed pH range of 6.0 to 9.0, with special regard for the control of hydrogen sulfide gas evolution and trivalent chromium removal at low values of pH. The Agency has determined that for maximum control of sulfides in gravity collection systems and POTW headworks, and for maximum removal of trivalent chromium largely in primary clarifiers, the optimum pH range is 7.0 to 10.0. Potentially dangerous evolution of sulfides can occur below a pH of 7.0, and below a pH of 6.0 potentially inadequate removal of trivalent chromium can occur. At pH greater than 10.0, the potential may exist for disruption of biological treatment systems. Therefore, the appropriate general sections of the regulation have been amended to require pH no lower than 7.0 and no higher than 10.0 for the four subcategories which include beamhouse operations, and to require pH no lower than 6.0 and no higher than 10.0 for the retan-wet finish, no beamhouse, and shearling subcategories.

Methodology Used to Develop PSES Effluent Limitations

Engineering analysis developed the PSES effluent limitations using in-plant control and primary treatment technologies in building block fashion. Within the tannery, the beamhouse and tanyard waste streams

will be segregated and subject to the appropriate in-plant controls and preliminary treatment processes (Levels 1 and 2) prior to combined end-of-pipe treatment.

Table 41 (Section X) shows the breakdown of the raw beamhouse and tanyard waste streams prior to separate control measures. The table also shows achievable long-term effluent concentrations following Level 3 treatment, (primary coagulation-sedimentation) of the combined waste streams.

EPA will use the discharge from Level 3 treatment as the basis for the PSES effluent limitations. Multiplying the Level 3 long-term average effluent concentrations by the 1.5 variability ratio described in Section X resulted in the average 30-day concentrations for each subcategory. The maximum daily concentrations for PSES are determined from the 30-day average and the maximum to mean ratio of 2.0 obtained from the variability analysis described in Section X. Based on the preceding rationale, only the total chromium, ammonia, sulfide, and pH will be regulated by the PSES effluent limitations.

Engineering Aspects of Pretreatment Technology and Relationship to Publicly Owned Treatment Works

As noted earlier in this section, the problems associated with leather tanning and finishing wastewater can be largely controlled by adherence to general pretreatment regulations (40 CFR Part 403), and to these pretreatment standards which limit chromium, ammonia, sulfide, and pH ranges for each subcategory. Chromium is being regulated directly as the most significant toxic pollutant, which interferes with POTW sludge disposal alternatives. It also serves as an indicator for other heavy metals including lead, zinc, copper, and nickel. Ammonia is being limited to reduce this load on POTW's and reduce pass-through of ammonia from POTW's to receiving streams. Sulfide is being limited because the evidence currently available indicates that sulfide odor and hazard problems are substantial.

Equalization (at least 24 hours) has been an extremely important technolgoy --especially when a tannery which is a major contributor to a POTW exhibits widely fluctuating discharge patterns (pH, flow, organic and solids loading). When significant production shut-down periods (such as two days of every week) do not allow consistent wastewater feed to high-rate, short detention time activated sludge systems, equalization is required. Lack of equalized and consistent flow results in the loss of the acclimated biological population in activated sludge, which is extremely difficult and slow to rebuild during very cold periods of POTW operation. Hydraulic surges can cause complete wash out of clarifier sludge blankets, including the chromium precipitate in primary clarifiers.

Control of pH may be a necessary adjunct to equalization for effective physical removal of chromium and to prevent hydrogen sulfide gas evolution. Plants which use large quantities of sulfides and

sulfhydrates in the unhairing process risk catastrophic accidents if pH is not controlled when segregated wastewaters are mixed. Plants which do not operate a beamhouse may need lime addition to increase pH to a level where effective biological treatment can be maintained, to minimize corrosion, and to reduce chromium residuals to a level acceptable to the POTW.

Effective fine screening (with openings in the range of 0.040 inches to remove easily separated scraps, fibers, and hair) was lacking at most leather tanning and finishing plants in the industry. Without fine screening, pipes can become clogged and pumps, clarifier sludge rakes, and other related equipment at the POTW can incur severe damage.

The Agency recognizes that many plants in urban areas will require extensive planning and judicious use of interior floor space and adjacent land to incorporate pretreatment facilities. Constraints on available interior plant floor space and adjacent land was a key decision criterion in the pretreatment technology selection process. Moreover, the selected PSES were not as stringent as EPA would have preferred due to land constraints.

In cases where a number of plants are located in close proximity to each other, combined pretreatment facilities may afford a cost-effective approach to reduce both total costs and costs to each tanner, minimize duplication of facilities at each plant, and take advantage of economics of scale. This is likely to be especially germane to sludge dewatering and transporting equipment, and to the identification, development, and use of hazardous waste disposal sites.

COST AND EFFLUENT REDUCTION BENEFITS

Approximately 170 tanneries currently discharge to POTW's, and are thus subject to pretreatment standards for existing sources. While a few of these plants have some wastewater treatment in place, the following estimated costs assume none. EPA estimates that total investment costs to meet proposed PSES will be approximately $59 million, with total annual operating costs of about $21 million, increasing current operating expenses by 3.0 percent.

EPA estimates that the total mass of regulated pollutants for all indirect dischargers removed from untreated wastewaters by this PSES technology option would be as follows: 2,300,000 lbs/year of chromium (total); 1,400,000 lbs/year of ammonia; and 1,800,000 lbs/year of sulfide. The total mass of pollutants not regulated but removed from untreated discharge levels by this PSES technology option would be as follows: 30,000,000 lbs/year of BOD_5; 88,000,000 lbs/year of COD; 46,000,000 lbs/year of TSS; 8,200,000 lbs/year of oil and grease; and 2,500,000 lbs/year of TKN. EPA estimates the total toxic pollutant discharge would be as follows: 6050 lbs/year of volatile organics; 7500 lbs/year of base/neutral organics; 18,000 lbs/year of acid

organics; and 3600 lbs/year of inorganic pollutants exclusive of chromium. EPA believes that these estimates of total annual toxic pollutant discharges are low because the effluent concentrations from POTWs are anticipated to be higher than the concentrations which underlie BAT effluent limitations.

Non-Water Quality Environmental Impact

The proposed pretreatment standard will substantially reduce the potential hazards to life and property in sewerage systems and POTW's. The potential for odor problems in the operation of the POTW from the sulfide-bearing wastewaters from tanneries also will be minimized.

EPA estimates that 37,000 metric tons per year will be generated by PSES. These sludges will contain additional toxic pollutants (up to three percent by weight of chromium) and lesser quantities of other heavy metals and organic toxic pollutants. On the other hand, EPA estimates that implementation of proposed pretreatment standards will result in POTW sludges having commensurately lesser quantities and concentrations of toxic pollutants. POTW sludges will become more amenable to a wider range of disposal alternatives, possibly including beneficial use on agricultural lands. Moreover, disposal of these vastly greater quantities of adulterated POTW sludges is significantly more difficult and costly than disposal of smaller quantities of wastes generated at individual plant sites.

Leachate generation and subsequent contamination of ground and surface waters may occur at facilities where tannery wastes are disposed. This hazard requires that disposal sites be carefully selected. Site topography must minimize surface water flow across the site, and the soils should contribute to leachate attenuation. Proper operating procedures should minimize percolation of precipitation through the refuse. Leachate collection systems at landfills used for solid waste disposal are recommended to provide adequate assurance that ground and surface waters will be protected from contamination.

PSES EFFLUENT LIMITATIONS

Table 48 lists the pretreatment standards for existing sources in each subcategory.

Table 48

PSES EFFLUENT LIMITATIONS

Subcategory One - Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	Maximum concentration for any one day	Average of daily concentrations for 30 consecutive days
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	136	68
Sulfide	0.0	0.0
pH	Within the range of 7.0 to 10.0 at all times.	

Subcategory Two - Hair Save/Chrome Tan, Retan-Wet Finish

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	138	69
Sulfide	0.0	0.0
pH	Within the range of 7.0 to 10.0 at all times.	

Subcategory Three - Hair Save, Non-Chrome Tan, Retan-Wet Finish

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	132	66
Sulfide	0.0	0.0
pH	Within the range of 7.0 to 10.0 at all times.	

Subcategory Four - Retan-Wet Finish

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	156	78
Sulfide	0.0	0.0
pH	Within the range of 6.0 to 10.0 at all times.	

Subcategory Five - No Beamhouse

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	156	78
Sulfide	0.0	0.0
pH	Within the range of 6.0 to 10.0 at all times.	

Subcategory Six - Through-the-Blue

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	120	60
Sulfide	0.0	0.0
pH	Within the range of 7.0 to 10.0 at all times.	

Subcategory Seven - Shearling

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
Total Chromium	6	3
Ammonia	52	26
Sulfide	0.0	0.0
pH	Within the range of 6.0 to 10.0 at all times.	

PRETREATMENT STANDARDS FOR NEW SOURCES (PSNS)

Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) coincidently with the adoption of NSPS. New indirect dischargers, like new direct dischargers, have the opportunity to incorporate the best available demonstrated control technologies (BADT) including process changes, in-plant controls, and end-of-pipe treatment. New plants can select and locate on a site to ensure adequate installation of the treatment system.

For pretreatment of wastewaters from new sources, candidate control technologies include the same in-plant control and end-of-pipe treatment scheme considered as candidate BAT technologies for direct dischargers. The PSNS technologies are as follows:

Level 1 - Water conservation and reuse to reduce flow
- Stream segregation for preliminary treatment
- Ammonia substitution in deliming
- Chrome recovery and reuse
- Sulfide liquor reuse followed by catalytic oxidation of residual sulfide
- Fine screening of segregated streams

Level 2 - Flue gas carbonation and sedimentation for beamhouse wastewaters

Level 3 - Equalization of combined streams followed by primary coagulation-sedimentation

Level 4A - Physical/chemical treatment (Chappel Process)

Performance and applicability of these levels of treatment were discussed above under discussion of PSES Pretreatment Technology, and in the specific technology descriptions in Sections VII and X of this document. Table 41 (Section X) indicates the performance of these technologies with respect to each of the seven subcategories.

As noted in the rationale for the pretreatment standard for existing sources, the adoption of Level 3 technology by tanneries may not permit POTW's to achieve BAT effluent limitations. Hence, pass-through of toxic pollutants and presence of toxic pollutants in sludges may still be of concern. EPA has therefore chosen to propose PSNS at the same effluent quality required either by BAT (Level 6) or BAT Level 4A (physical/chemical treatment). The candidate pretreatment technologies will encourage new plants to treat their own wastewaters, subject to NSPS, and discharge direct to navigable waters.

PSNS EFFLUENT LIMITATIONS

The general pretreatment regulations recognize that categorical pretreatment standards for conventional and nonconventional pollutants may be necessary to serve as "indicators" of toxics control (40 CFR Part 403 ,43 FR 27761, June 26, 1978). In this industry, all of the "indicator" pollutant parameters regulated by BAT are also regulated by PSNS to ensure removal of toxic pollutants. The numerical concentration limitations for all subcategories are listed in Table 49.

Table 49

PSNS EFFLUENT LIMITATIONS

Pollutant or Pollutant Property	Maximum concentration for any one day-mg/l	Average of daily concentrations for 30 consecutive days-mg/l
	milligrams per liter (mg/l)	
BOD_5	74	21
COD	325	200
TSS	84	24
Oil and Grease	32	9
Total Chromium	1.8	0.5
TKN	79	23
Ammonia	26	7.5
Phenol	0.53	0.15
Sulfide	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Equivalent mass limitations for each subcategory are as follows:

Subcategory One - Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.1	0.61
COD	9.5	5.8
TSS	2.5	0.70
Oil and Grease	0.91	0.26
Total Chromium	0.053	0.015
TKN	2.3	0.66
Ammonia	0.77	0.22
Phenol	0.015	0.0043
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Two - Hair Save/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	2.3	0.65
COD	10.0	6.2
TSS	2.6	0.74
Oil and Grease	1.0	0.28
Total Chromium	0.053	0.015
TKN	2.4	0.69
Ammonia	0.81	0.23
Phenol	0.016	0.0046
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Three - Hair Save/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.6	0.47
COD	7.3	4.5
TSS	1.9	0.54
Oil and Grease	0.70	0.20
Total Chromium	0.039	0.011
TKN	1.8	0.51
Ammonia	0.60	0.17
Phenol	0.012	0.0034
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Four - Retan-Wet Finish

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	0.81	0.23
COD	3.5	2.2
TSS	0.91	0.26
Oil and Grease	0.35	0.10
Total Chromium	0.018	0.005
TKN	0.84	0.24
Ammonia	0.28	0.081
Phenol	0.0056	0.0016
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Five - No Beamhouse

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.4	0.40
COD	6.2	3.8
TSS	1.6	0.46
Oil and Grease	0.60	0.17
Total Chromium	0.034	0.0096
TKN	1.5	0.43
Ammonia	0.49	0.14
Phenol	0.010	0.0029
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Six - Through-the-Blue

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	1.5	0.44
COD	6.8	4.2
TSS	1.8	0.50
Oil and Grease	0.67	0.19
Total Chromium	0.035	0.010
TKN	1.6	0.47
Ammonia	0.56	0.16
Phenol	0.011	0.0031
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

Subcategory Seven - Shearling

Pollutant or Pollutant Property	Effluent Limitations	
	Maximum for any one day	Average of daily values for 30 consecutive days
Mass Units - kg/kkg (or lb/1000 lb) of raw material		
BOD_5	6.7	1.9
COD	29.8	18.0
TSS	7.7	2.2
Oil and Grease	2.9	0.83
Total Chromium	0.16	0.046
TKN	7.4	2.1
Ammonia	2.4	0.69
Phenol	0.049	0.014
Sulfide (mg/l)	0.0	0.0
pH	Within the range of 6.0 to 9.0 at all times.	

SECTION XIV

MONITORING

INTRODUCTION

When required to carry out the objectives of the Act, EPA is authorized by Section 308 to require the owner or operator of a polluant discharge source to establish and maintain records, make reports, install and use monitoring equipment or methods, sample effluents and provide such other information as the Administrator may reasonably require. The authority under Section 308 has been frequently used by permit issuers to set monitoring requirements to "determine whether any person is in violation" of the requirements of a permit or other requirements of the Act (Section 308(a)(2)). Additionally, EPA has frequently sought information under Section 308 to aid in developing regulations for many industries.

In these, and perhaps other "toxics" regulations, EPA is setting monitoring requirements for direct and indirect dischargers for the purpose of "developing or assisting in the development" of future effluent limitations guidelines, pretreatment standards and standards of performance (Section 308(a)(1)). These monitoring requirements are not intended to supersede or duplicate compliance monitoring requirements set by NPDES permit authorities. A mandatory monitoring and analysis program is feasible at this time because the costs for toxic pollutant analyses have decreased and laboratory availability and efficiency have dramatically increased since the initiation of this study.

MONITORING PROGRAM

The monitoring program included in the proposed regulation will serve a number of purposes. First, the long term data generated on conventional, nonconventional and toxic pollutants will allow the Agency to review and revise, if necessary, the proposed regulations. Where data indicates that treatment technologies discharge effluent levels different from those in the regulations, adjustments will be made and the regulations amended. Second, the data collection program is designed to permit the Agency to establish express limits on specific toxics of concern (i.e., pentachlorophenol, 2,4,6-trichlorophenol, lead, etc.), or alternatively, establish statistically valid correlations among "surrogate" (now "indicator") pollutants and the toxic pollutants of concern. Selection of surrogate pollutants would allow identification of a shorter and less costly (in terms of monitoring expense) list of pollutant parameters for which plants would be required to sample and analyze. Third, these monitoring requirements will combine all major data collection activities into one reporting mechanism.

There are numerous developments and alternatives potentially available to reduce the monitoring cost for toxic pollutants in addition to the identification of surrogates (indicators) of toxic pollutants. A specific group or groups within the total list of toxic pollutants may be simplified, or the large number of samples nationwide may produce some economies of scale with automated or similar cost reduction approaches.

The proposed monitoring and analysis program would require continuous flow and pH monitoring at points of discharge to POTWs (for indirect dischargers) or discharge to receiving waters (for direct dischargers). Plants which process more than 3.1 million pounds per year of raw material will be required to collect a 24-hour composite sample once every week (in all cases during a representative period of wastewater generation, other than weekends or similar periods of minimal or no processing) and analyze for BOD_5, COD, TSS, oil and grease, chromium (total), TKN, ammonia, and sulfide. Concurrent grab samples must also be taken weekly and analyzed for phenol (total-4AAP). In addition, these plants will also be required to collect one 24-hour composite sample once quarterly (again during a representative period of wastewater generation, concurrent with a weekly sample) and analyze for a limited number of toxic pollutants, including lead, phenol (by GC/MS), 2,4,6-trichlorophenol, and pentachlorophenol. Concurrent grab samples must also be taken quarterly and analyzed for cyanide (total).

Plants which process less than 3.1 million pounds per year of raw material will be required to collect a 24-hour composite sample once every two weeks and analyze for BOD_5, COD, TSS, oil and grease, chromium (total), TKN, ammonia, and sulfide. Concurrent grab samples must also be taken once every two weeks and analyzed for phenol (total-4AAP). In addition, these plants will also be required to collect one 24-hour composite sample twice per year (concurrent with a sample taken on alternate weeks) and analyze for a limited number of toxic pollutants, including lead, phenol (by GC/MS), 2,4,6-trichlorophenol, and pentachlorophenol. Concurrent grab samples must also be taken twice per year and analyzed for cyanide (total).

All plants will be additionally required to report the total wastewater flow (gallons) discharged, the total raw material processed (both in units of 1000 pounds and numbers of hides, skins, splits, etc.), and the hourly values of flow and pH for the period of sample collection. On a case-by-case basis, EPA may request collection of additional samples of raw wastewater or wastewater at points of intermediate treatment to establish treatment efficiencies. EPA may also request on a case-by-case basis collection of duplicate samples so that cross-laboratory validation analyses can be run. Finally, the initial data reporting will include all pertinent information which qualitatively describes the treatment system sampled and

quantitatively specifies the design and operating features of all unit processes and equipment.

Monitoring requirements for direct dischargers will be effective on the issuance of a new NPDES permit or renewal or extension of an existing permit, and will remain in effect for two years from that date. Monitoring requirements for indirect dischargers will be effective three years from the date of promulgation of these regulations (or on the earlier installation of technology to meet pretreatment standards) and will remain in effect for one year. On a quarterly basis, all individual data points generated by this monitoring program must be submitted directly to the Project Officer, Leather Tanning and Finishing Industry, Effluent Guidelines Division (WH-552), EPA, 401 M St. S.W., Washington, D.C. 20460. Copies also must be submitted to NPDES authorities (direct dischargers) and affected POTWs (indirect dischargers). Where these individual data points are submitted for compliance monitoring purposes, duplicate sampling and analyses are not required.

SECTION XV

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SECTION XVI

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SECTION XVII

GLOSSARY

Aerobic

A biological process in which oxygen is used for microorganism respiration needs. Especially relating to the degradation process of waste matter in the presence of dissolved oxygen.

Anaerobic

A biological process in which chemically combined oxygen is used for microorganism respiration needs. Relating to biological degradation of waste matter in the absence of dissolved oxygen.

Back

That portion of the animal hide, especially cattlehide, consisting of the center portion of the hide along the backbone and covering the ribs, shoulders, and butt (excluding the belly).

Bating

The manufacturing step following liming and preceding pickling. The purpose of this operation is to delime the hides, reduce swelling, peptize fibers, and remove protein degradation products from the hide.

Beamhouse

That portion of the tannery where the hides are washed, limed, fleshed, and unhaired when necessary prior to the tanning process.

Belly

That portion of the hide on the underside of the animal, usually representing the thinnest part of the tannable hide.

Bend

That portion of the hide representing the entire hide cut down the backbone with the bellies and shoulders removed.

Biochemical Oxygen Demand (BOD5)

The amount of oxygen required by microorganisms while stabilizing decomposable organic matter under aerobic conditions. The level of BOD is usually measured as the demand for oxygen over a standard five-day period. Generally expressed in mg/l.

Blowdown

The amount of concentrated liquor wasted in a recycle system in order to maintain an acceptable equilibrium of contaminants in any process liquor.

Blue

The state or condition of hides subsequent to chrome tanning and prior to retanning. Hides in this stage of processing are characteristically blue in color.

Buffing

A light sanding operation applied to the grain or underside of leather and also to splits. Buffing smooths the grain surface and improves the nap of the underside of the leather.

Buffing Dust

Small pieces of leather removed in the buffing operation. Buffing dust also includes small particles of abrasive used in the operation and is of a coarse powder consistency.

Carding

Method using a wire brush to disentangle wool. One of the shearling finishing processes.

Chemical Oxygen Demand (COD)

A measure of the amount of organic matter which can be oxidized to carbon dioxide and water by a strong oxidizing agent under acidic conditions. Generally expressed in mg/l.

Chlorine Contact Tank

A detention basin designed to allow sufficient time for the diffusion and reaction of chlorine in a liquid for disinfection purposes.

Chromium (Total)

Total chromium is the sum of chromium occurring in the trivalent and hexavalent state. Expressed in mg/l as Cr.

Clarification

A physical means for the removal of suspended particles in a liquid by gravity sedimentation (settling).

Coagulant

A substance which forms a precipitate or floc when added to water. Suspended solids adhere to the large surface area of the floc, thus increasing their weight and expediting sedimentation.

Collagen

The fibrous protein material within the hide which provides the bulk of the volume of the finished leather and its rigidity.

Colloids

Microscopic suspended particles which do not settle in a standing liquid and can only be removed by coagulation or biological action.

Color

A measure of the light-absorbing capacity of a wastewater after turbidity has been removed. One unit of color is that produced by one mg/l of platinum as K_2PtCl_6.

Coloring

A process step in the tannery whereby the color of the tanned hide is changed to that of the desired marketable product by dyeing or painting.

Combination Tanned

Leathers tanned with more than one tanning agent. For example, initially chrome-tanned followed by a second tannage (called a RETAN) with vegetable materials.

Composite Sample

A series of small wastewater samples taken over a given time period and combined as one sample in order to provide a representative analysis of the average wastewater constituent levels during the sampling period.

Concrete Mixer

A term often applied to hide processors.

Conditioning

Introduces controlled amounts of moisture to the dryed leather giving it varying degrees of softness.

Corium

The layer of hide between the epidermis and the flesh. Also called the dermis.

Currying

Oil incorporation into leather in a low water system, classically used to lubricate vegetable tanned leather.

Degreasing

In pigskin and sheepskin tanneries a solvent or detergent is added to the drum containing washed hides. Grease is removed from the hides and recovered as a by-product.

Deliming

The manufacturing step in the tanyard that is intended to remove the lime from hides coming from the beamhouse.

Demineralization

The process of removing dissolved minerals from water by ion exchange, reverse osmosis, electrodialysis, or other processes.

Dermis

That part of the hide which is between the flesh and the epidermis.

Desalinization

The process of removing dissolved salts from water.

Detention (Retention)

The dwelling time of wastewater in a treatment unit.

Dewatering

The process of removing a large part of the water content of sludges.

DO

Dissolved oxygen. Measured in mg/l.

Drag-out

Loss of process chemicals and solution onto products during processing which are made up by periodic fresh addition of chemicals and solution.

Drum

A large cyclinder, usually made of wood, in which hides are placed for wet processing. The drum is rotated around its axis, which is oriented horizontally. Also called wheel.

Dry Milling

The rotating of leather in a large wooden drum with no added chemicals or water. Dry milling softens the leather.

Electrodialysis

A form of advanced waste treatment in which the dissolved ionic material is removed by means of a series of semipermeable membranes and electric current.

Embossed

A mechanical process of permanently imprinting a great variety of unique grain effects into the leather surface. Done under considerable heat and pressure.

Enzymes

Complex protein materials added to the hide in the bating step in order to remove protein degradation products that would otherwise mar hide quality.

Epidermis

The top layer of skin; animal hair is an epidermal outgrowth.

Equalization

The holding or storing of wastes having differing qualities and rates of discharge for finite periods to facilitate blending and achievement of relatively uniform characteristics.

Equivalent Hides

A statistical term used to relate the production of tanneries using various types of raw materials. An equivalent hide is represented by 3.7 sq m of surface area and is the average size for a cattlehide.

Eutrophication

The excess fertilization of receiving waters with nutrients, principally phosphates and nitrates, found in wastewater which results in excessive growth of aquatic plants.

Fatliquoring

A process by which oils and related fatty substances replace natural oils lost in the beamhouse and chrome tanning processes. Regulates the softness and pliability of the leather.

Finishing

The final processing steps performed on a tanned hide. These operations follow the retan-color-fatliquor processes, and include the many dry processes involved in converting the hide into the final tannery product.

Fleshing

The mechanical removal of flesh and fatty substances from the underside of a hide prior to tanning. In the case of sheepskin tanning, fleshing is often accomplished after the tanning process.

Float

The proper level or volume of skins or hides, chemicals, and water that is maintained in any wet process unit (vats, drums, or processors) within the tannery.

Floc

Gelatinous masses formed in liquids by the addition of coagulants, by microbiological processes, or by particle agglomeration.

Flocculation

The process of floc formation normally achieved by direct or induced slow mixing.

Flume

An open, inclined channel or conduit for conveying water or water and hides.

Grab Sample

A single sample of wastewater which will indicate only the constituent levels at the instant of collection; contrasted to a composite sample.

Multi-Media Filter

A filtration device designed to remove suspended solids from wastewater by trapping the solids in a porous medium. The multi-media filter is characterized by fill material ranging from large particles with low specific gravities to small particles with a higher specific gravity. Gradation from large to small media size is in the direction of normal flow.

Grain

The epidermal side of the tanned hide. The grain side is the smooth side of the hide where the hair is located prior to removal.

Grease

A group of substances including fats, waxes, free fatty acids, calcium and magnesium soaps, mineral oils, and certain other non-fatty materials. The grease analysis will measure both free and emulsified oils and greases. Generally expressed in mg/l.

Green Hides

Hides which may be cured but have not been tanned.

Head

That part of the hide which is cut off at the flare into the shoulder; i.e., the hide formerly covering the head of the animal.

Hide

The skin of a relatively large animal, at least the size of mature cattle.

Ion Exchange

The reciprocal transfer of ions between a solid and a solution surrounding the solid. A process used to demineralize waters.

Ionization

The process by which, at the molecular level, atoms or groups of atoms acquire a charge by the loss or gain of one or more electrons.

Isoelectric Point

The pH at which acidic ionization balances basic ionization so that an electrolyte will not migrate in an electrical field.

Liming

The operations in the beamhouse where a lime solution comes in contact with the hide. Liming in conjunction with the use of sharpeners such as sodium sulfhydrate is used to either chemically burn hair from the hide or to loosen it for easier mechanical removal. Hair burning normally utilizes higher chemical concentrations.

Nitrogen, Ammonia

A measure of the amount of nitrogen which is combined as ammonia in wastewater. Expressed in mg/l as N.

Nitrogen, Kjeldahl (Total Kjeldahl Nitrogen or TKN)

A measure of nitrogen combined in organic and ammonia form in wastewater. Expressed in mg/l as N.

Nitrogen, Nitrate

A measure of nitrogen combined as nitrate in wastewater. Expressed in mg/l as N.

Nutrient

Any material used by a living organism which serves to sustain its existence, promote growth, replace losses, and provide energy. Compounds of nitrogen, phosphorus, and other trace materials are particularly essential to sustain a healthy growth of microorganisms in biological treatment.

Outfall

The final outlet conduit or channel where wastewater or other drainage is discharged into an ocean, lake, or river.

Pack

Layers of salted hides formed at the slaughterhouse or hide curing firm (usually approximately 20 to 40 feet in area and 5 to 6 feet high).

Paddle Vat (Paddle)

A vat with a semi-submerged rotating paddle arrangement used for the mixing of water and chemicals with the hide.

pH

The reciprocal logarithm of the hydrogen ion concentration in wastewater expressed as a standard unit.

ppm

Parts per million. The expression of concentration of constituents in wastewater, determined by the ratio of the weight of constituent per million parts (by weight) of total solution. For dilute solutions, ppm is essentially equal to mg/l as a unit of concentration.

Pasting

The process step generally following the retan-color-fatliquor operations whereby the hide is attached to a smooth plate with a starch and water paste and dried in a controlled heated vessel.

Pickling

The process that follows bating whereby the hide is immersed in a brine and acid solution to bring the skin or hide to an acid condition; prevents precipitation of chromium salts on the hide.

Plating

The finishing operation where the skin or hide is "pressed" in order to make it smoother. Plating may be done with an embossing plate which imprints textured effects into the leather surface.

Polymer

An organic compound characterized by a large molecular weight. Certain polymers act as coagulants or coagulant aids. Added to the wastewater, they enhance settlement of small suspended particles. The large molecules attract the suspended matter to form a large floc.

POTW

Publicly owned treatment works, i.e., municipal waste treatment system.

Pullery

A plant where sheepskin is processed by removing the wool and then pickling before shipment to a tannery.

Pulp

Method of unhairing in which depilatory agents are used to dissolve hair entirely in a few hours.

Retanning

A second tanning process utilizing either the natural tanning materials (chromium or vegetable extracts) or synthetic tanning agents. Retanning imparts specialized properties to the leather.

Reverse Osmosis

A process whereby water is forced to pass through semipermeable membranes under high pressures. Water passing through the membrane is relatively free of dissolved solids; solids are retained in concentrated form on the feed side of the membrane and are wasted.

Sanding

A dry operation performed on the tanned and fatliquored hide in order to achieve the desired surface texture of the leather. Sanding operations include the use of abrasive or buffing wheels.

Sedimentation

Clarification (settling).

Setting Out

A multi-purpose operation which smoothes and stretches the skin while compressing and squeezing out excess moisture. Puts hides into proper condition for drying.

Sharpeners

Chemicals (such as sodium sulfide and sodium sulfhydrate) used in addition to lime to assist in the unhairing process.

Shaving

An abrasive, mechanical action used to correct errors in splitting and thus yielding a uniformly thick grain side or split.

Shavings

The waste products generated during the shaving operations. These are essentially small pieces of the tanned hide, which are approximately the size of wood shavings.

Shearling

A lamb or sheepskin tanned with the hair retained.

Shoulder

That part of the hide between the neck and the main body of the hide.

Side

One-half of a hide, produced by cutting the hide down the backbone. Normally done to facilitate processing using smaller equipment than would be required if full hides were processed.

Skin

The pelt or skin of animals smaller than mature cattle; e.g., pigskin, sheepskin, calfskin.

Skiver

The thin layer shaved or cut off the surface of finished leather, principally sheepskin.

Sludge

A concentrate in the form of a semi-liquid mass resulting from settling of suspended solids in the treatment of sewage and industrial wastes.

Split

A side which has been cut parallel to its surface to provide one large piece of leather of approximately uniform thickness and a thin, smaller piece of non-uniform thickness called a split.

Staking

Mechanically softens the leather by stretching and flexing it in every direction. Usually done on automatic machines which move leather between rapidly oscillating, overlapping fingers.

Sulfide

Ionized sulfur. Expressed in mg/l as S.

Suspended Solids (SS)

Constituents suspended in wastewater which can usually be removed by sedimentation (clarification) or filtration.

Syntan

Synthetic tanning materials, generally used in combination with vegetable, mineral, or formaldehyde tannages. Syntans are almost exclusively used in retanning rather than tanning operations.

Tanning

The chemicals derived from the leaching of bark, nuts, or other vegetable materials used in the vegetable tanning process.

Tanyard (Tanhouse)

That portion of the tannery in which the bating, pickling, and tanning are performed on the hides or skins.

Toggling

Method of drying in which skins are kept in a stretched position by means of clips called toggles. The skin is attached to a perforated frame which is slid into a drying oven.

Total Dissolved Solids (TDS)

The total amount of dissolved materials (organic and inorganic) in wastewater. Expressed in mg/l.

Total Solids (TS)

The total amount of both suspended and dissolved materials in wastewater. Expressed in mg/l.

Trimming

The removal of the ragged edges and inferior portions of hides and skins either before or after tanning. Trimming is normally accomplished by workers using knives.

Trimmings

The hide and leather scraps produced during the trimming operation.

Unhairing

The process where the hair is removed from the hide.

Volatile Solids

Solids, dissolved or suspended, which are primarily organic and during stabilization exert the significant portion of the BOD_5.

Weir

A control device placed in a channel or tank which facilitates measurement or control of the water flow.

APPENDIX A

PRIORITY POLLUTANT SAMPLING AND ANALYSIS - SCREENING AND VERIFICATION

FIELD SAMPLING PROCEDURES

The primary objective of the field sampling for priority pollutants was to produce 72-hr. composite samples from which the mean concentration of all priority pollutants at each sampling point could be estimated. Raw wastewater samples were obtained either before any treatment or following minimal pretreatment, depending on accessibility to the wastewater stream. Treated effluent samples were taken either following plant pretreatment or secondary treatment.

The sampling method employed varied depending upon the type of water being sampled for sampling at both the raw waste and pretreatment points. Automatic samplers and flow recorders were used to account for short term fluctuations in concentration. Samples were taken every 15 minutes, and a 24 hr. composite was prepared by combining the samples on the basis of relative water flows recorded during each collection period. From the 24-hr. composites aliquots were removed to satisfy the sample requirements of the basic water quality parameters. The remaining volume from the composite was used for the 72-hr composite. Blanks were collected from the water supply. Sampling requirements were not as rigorous for samples taken after secondary treatment because holdup and mixing times for activated sludge may be comparable to the 72-hr. sampling period. Either grab samples were taken 3 times a day and the entire sample retained, or an automatic sampler was employed and the collected samples were mixed for the composite.

Volatile organic samples were not taken from the sample bottles but were collected in prepared vials. At intervals during the 72-hr. sampling period grab samples were collected in a bucket. The vials were immersed in the bucket, and, while immersed, they were capped.

A number of precautions were taken to minimize potential contamination from sampler components. Teflon™ tubing was used in place of the normal vinyl tubing, the sample collection line was automatically backflushed before and after each sample collection, and the samplers were equipped with new tubing before each tannery was sampled. The tubing, sampler blank containers, and collection bottles were all washed with soapy water and rinsed several times.

The samples and blanks were kept on ice prior to shipment and shipped in insulated containers.

Analytical Method Development and Procedures

The analytical method development for the priority pollutants was performed according to chemical class. Organic priority pollutants included volatile (purgeable), base/neutral and acidic (extractable) pollutants, pesticides, and total phenols. Inorganic priority pollutants consisted of 13 elements and cyanide.

The primary method used for analysis of the volatiles, base/neutrals, and acidic organics was gas chromatography/mass spectrometry (GC/MS). To avoid interference problems an additional selectivity factor, selected ion monitoring (SIM) was adopted. A GC was employed for pesticides with limited MS confirmation.

Minor changes in the protocol were made between the screening and verification processes, but the essential methodology was the same.

Volatile Organics: The contents of the individual sample vials collected at each sampling site were combined to form the composite. An aliquot was removed, spiked with an internal standard, transferred to the purging apparatus, and purged with prepurified nitrogen onto a Tenax™ trap. The trap was thermally disorbed onto the GC column. After each mix the column was eluted into the ion source of a mass spectrometer for MS analysis.

GC/MS analysis of organic pollutants found in the wastewaters of plants sampled during the screening phase determined only the presence or absence of the pollutants rather than quantitation. A pollutant was considered identified when its base peak and second most intense peak maximized coincidentally at the retention time window of the standard with the proper relative intensities. A pollutant was considered absent when either the base peak or second most intense peak did not coincidentally maximize within the retention time window of the standard. After each GC run a reconstructed GC and a range plot were printed. Dedicated mass plots were obtained, and the data was evaluated with a composite standard.

In the verification phase analysis extracted ion current plots (EICPs) were used for identification and quantitation of the pollutants. Compound identifications were based on the coincidence of peaks in 2 EICPs with the characteristic retention time and relative intensities.

Base/neutrals: These compounds were assayed in the tannery wastewaters by extracting basified and acidified aliquots, concentrating the extracts, and analyzing them by GC/MS in the same general method as described above.

Acidic Organics: Acidic extracts were prepared from a duplicate water sample in a manner identical to the base/neutrals except that the

samples were acidified to pH 1 with HCl prior to extraction. The extracts were then analyzed by GC/MS.

Pesticides: Samples were liquid/liquid extracted and the solvent layer was run through a series of clean up procedures. The resulting extract was then injected into a gas chromatograph equipped with an electron capture detector.

Total Phenols: The samples were distilled and the distillate assayed for phenolic compounds by the 4-aminoantipyrene complexation procedure.

Metals: The priority pollutant metals were assayed by atomic adsorption spectrometry (AAS) following appropriate digestion of the sample. The digesting solutions used were HNO_3, HNO_3/HCl, $HNO_3/K_2Cr_2O_7$, and $HNO_3/HClO_4/H_2SO_4$.

Cyanide: Samples were analyzed for cyanide by a colorimetric method. Sulfides were removed before distillation.

APPENDIX B

Toxic Pollutants Not Detected In Treated Effluents

acenaphthene
acrolein
acrylonitrile
1,2,4-trichlorobenzene
1,2-dichloroethane
hexachloroethane
1,1-dichloroethane
1,1,2-trichloroethane
chloroethane
bis(chloroethyl) ether
bis(2-chloroethyl) ether
2-chloroethyl vinyl ether
2-chloronaphthalene
para-chloro-meta-cresol
2-chlorophenol
1,3-dichlorobenzene
1,1-dichloroethylene
1,2-dichloropropane
1,3-dichloropropene (*cis*- & *trans*)
2,4-dimethylphenol
2,4-dinitrotoluene
2,6-dinitrotoluene
4-chlorophenyl phenyl ether
4-bromophenyl phenyl ether
bis-(2-chloroisopropyl) ether
bis-(2-chloroethoxy) methane
methyl chloride (chloromethane)
methyl bromide (bromomethane)
bromoform (tribromomethane)
bromodichloromethane
trichlorofluoromethane
dichlorodifluoromethane
dibromochloromethane
hexachlorobutadiene
hexachlorocyclopentadiene
2-nitrophenol
4-nitrophenol
2,4-dinitrophenol
4,6-dinitro-*o*-cresol
n-nitroso-dimethylamine
n-nitroso-di-*n*-propylamine
butyl benzyl phthalate
di-n-octyl phthalate
dimethyl phthalate
1,2-benzanthracene (benzo(a)anthracene)

3,4-benzopyrene (benzo(b)pyrene)
3,4-benzofluoranthene (benzo(b)fluoranthene)
11,12-benzofluoranthene (benzo(k)fluoranthene)
acenaphthylene
1,12-benzoperylene (benzo(ghi)perylene)
1,2,5,6-dibenzanthracene (dibenzo(a,k)anthracene)
indeno (1,2,3-cd) pyrene (1,2-o-phenylene pyrene)
trichloroethylene
vinyl chloride (chloroethylene)
aldrin
dieldrin
chlordane
4,4'-DDT
4,4'-DDE (p,p'-DDX)
4,4'-DDD (p,p'-TDE)
a-endosulfan
b-endosulfan
endosulfan sulfate
endrin
endrin aldehyde
heptachlor
heptachlor epoxide
a-BHC
b-BHC
r-BHC (lindane)
s-BHC
PCB-1242 (Arochlor 1242)
PCB-1254 (Arochlor 1254)
PCB-1221 (Arochlor 1221)
PCB-1232 (Arochlor 1232)
PCB-1248 (Arochlor 1248)
PCB-1260 (Arochlor 1260)
PCB-1016 (Arochlor 1016)
toxaphene
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

APPENDIX C

Toxic Pollutants Detected In Treated Effluents At Two Plants Or Less

trans-1,2-dichloroethene
1,1,1-trichloroethane
tetrachloromethane
(carbon tetrachloride)
1,1,2,2-tetrachloroethene
1,1,2,2-tetrachloroethane
chlorobenzene
hexachlorobenzene
n-nitrosodiphenylamine
1,2-diphenylhydrazine
benzidine
3,3'-dichlorobenzidine
nitrobenzene
isophorone
fluorene
fluoranthene
pyrene
diethyl phthalate
di-*n*-butyl phthalate
chrysene
2,4-dichlorophenol

APPENDIX D

Toxic Pollutants Detected In Treated Effluents At Or Below The Limit Of Detection

benzene
phenanthrene/anthracene
beryllium
cadmium
mercury
antimony
asbestos*
arsenic
selenium
silver
thallium

*Total chrysotile fiber count

APPENDIX E

2,4,6-trichlorophenol
chloroform
1,2-dichlorobenzene
1,4-dichlorobenzene
ethylbenzene
methylene chloride (dichloromethane)
naphthalene
pentachlorophenol
phenol
bis (2-ethylhexyl) phthalate
toluene
chromium
copper
cyanide
lead
nickel
zinc

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