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Development Document for Effluent Limitations Guidelines and Standards for the Leather Tanning and Finishing

Final

Point Source Category

DEVELOPMENT DOCUMENT

for

EFFLUENT LIMITATIONS GUIDELINES NEW SOURCE PERFORMANCE STANDARDS

and

PRETREATMENT STANDARDS

for the

LEATHER TANNING AND FINISHING POINT SOURCE CATEGORY

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ABSTRACT

This document presents the findings of an extensive study of the leather tanning industry for the purpose of developing effluent limitations for existing point sources, standards of performance for new sources, and pretreatment standards for existing and new sources to implement Sections 301, 304, 306, and 307 of the Clean Water Act. The study covers 158 facilities in SIC major group 3100 Leather and Leather products, and specifically in subgroup SIC 3111, leather tanning and finishing.

Effluent limitations guidelines are set forth for the degree of effluent reduction attainable through the application of the best practicable control technology currently available (BPT), and the best available technology economically achievable (BAT) and the best conventional technology pollutant control technology (BCT) which must be achieved by existing point sources by July 1, 1984. Standards of performance for new sources (NSPS) set forth the degree of effluent reduction that is achievable through the applications of the best available demonstrated control technology, processes, operating methods or other alternatives. Pretreatment standards for existing and new sources (PSES and PSNS) set forth the degree of effluent reduction that must be achieved in order to prevent the discharge of pollutants that pass through, interfere with, or are otherwise incompatible with the operation of POTWs.

BPT regulations are based on biological treatment, specifically high solids extended aeration activated sludge. The regulations for BAT and BCT are existing to existing BPT for toxic, nonconventional and conventional pollutants. NSPS are based on the same effluent treatment technology as BPT with reduced water use. PSES and PSNS for the nonconventional pollutant sulfides is based on catalytic sulfide oxidation. For the nonconventional pollutant chromium, PSES and PSNS, are based coagulation-sedimentation of combined waste streams.

Supporting data, rationale, and methods for development of the effluent limitation guidelines and standards are contained in this document.

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SECTION I

EXECUTIVE SUMMARY

The promulgated effluent limitations guidelines for existing sources, standards of performance for new sources and pretreatment standards for new and existing sources were described in the Federal Register for November 23, 1982 (47 FR 52848-52878). A summary of that Federal Register notice follows.

A. SUBCATEGORIZATION

The leather tanning and finishing industry 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 or Pulp, Non-Chrome Tan, Retan-Wet Finish
4. Retan-Wet Finish-Sides
5. No Beamhouse
6. Through-The-Blue
7. Shearling
8. Pigskin
9. Retan-Wet Finish-Splits

The subcategorization scheme from previous rulemaking was reviewed, taking into account all available information. Factors such as age, size of plant, location, raw material, process employed, products and waste treatability were considered in reviewing the adequacy of the original subcategorization scheme.

Upon further review of the industry and in response to public comment, EPA has established two additional subcategories, pigskins (subcategory 8) and retan-wet finish-splits (subcategory 9). In the 1979 proposal, the processing of pigskins was included in subcategory 1. However, the nature of pigskin is different from that of cattlehide (the predominant raw material in subcategory 1), and the subprocesses utilized to produce finished leather are different. Given proper water conservation and recycle and reuse techniques, the processing of pigskins results in different water use and pollutant loads from the processing of cattlehides. Accordingly, a separate subcategory, pigskins (subcategory 8), was required. In the 1979 proposal, the retanning and wet finishing of splits was included in subcategory 4. However, a split is a different raw material than grain sides, and the subprocesses utilized to produce finished leather are different. Given proper water conservation and reuse and recycle techniques, the retan-wet finishing of splits results in different water use and pollutant loads from the processing of grain sides. Accordingly, a separate subcategory, retan-wet finish-splits (subcategory 9), was added.

The two primary subcategorization factors, the nature of the raw materials and the subprocesses required to produce a product, effect the volume of water required for processing. Therefore, the Agency has calculated typical water use ratios (gallons of water per pound of raw material processed) for each subcategory.

In 1979, the Agency proposed to use an average subcategory value, based upon individual data points, in order to determine water use for each subcategory. In response to commenters' concerns over the highly variable nature of the data, the Agency, in its June 2, 1982 notice of availability, applied a different methodology. First, EPA computed the arithmetic mean of every facility's data. Subcategory water use was then determined by using the median value of the mean plant values for each subcategory. The Agency believes that this methodology provides the most reasonable measurement of typical water use for each subcategory. This method gives equal weight to each facility's data, and provides a better estimate of central tendency since the median is less sensitive to extreme values in the data than the mean.

B. EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS

The promulgated regulation establishes effluent limitations and standards to control specific toxic, nonconventional, and conventional pollutants for all nine subcategories in the leather tanning and finishing category. The BPT, BCT, and BAT mass based effluent limitations were derived using the median water ratios identified for each subcategory. Reduced water use was not used in deriving BAT mass based effluent limitations because BAT OPTION 1 included BPT in-plant and end-of-pipe technology. Water use reduction was incorporated into mass based effluent limitations for the two BAT options which were not selected. PSES are concentration based rather than mass based, and therefore median water use ratios were not a part of PSES. Reduced flow ratios for new sources in eight of the nine subcategories, were established by the Agency. A reduced water use ratio was not identified in subcategory 7 because representative and varifiable data was available from only one plant. New sources can select very efficient processing methods and equipment which achieve further water use reductions identified for the eight subcategories. The Agency looked at all plants below the median and chose the flow ratio for the plant which demonstrated the most efficient processing methods available to new sources. At least one plant in every subcategory has demonstrated these new source flow ratios. These new source water use ratios were used in deriving the mass based NSPS effluent limitations. However, as for PSES, these water use ratios were not used for the concentration based PSNS limitations.

BPT

Best practicable control technology currently available (BPT) effluent limitations are established for all subcategories. The technology basis of the BPT limitations is biological treatment, specifically high solids extended aeration activated sludge. They included mass based limitations (kg/kkg or lb/1,000 lb of raw material) for one toxic pollutant (total chromium), and four conventional pollutants BOD_5, TSS, Oil and Grease, and pH). These BPT mass limitations are derived utilizing subcategory median water use ratios and BPT effluent concentrations described later in appropriate sections of this document. The BPT effluent limitations are presented in Table VIII-1.

BCT and BAT

BCT and BAT limitations also are established for all nine subcategories in the leather tanning and finishing point source category. The technology basis of and mass based effluent limitations for BCT and BAT are the same as the promulgated BPT limitations. The BCT effluent limitations control four conventional pollutants (BOD_5, TSS, Oil and Grease, and pH.). The BAT limitations control one toxic pollutant, total chromium. These limitations are equal to BPT and are shown in Table VIII-1.

NSPS

NSPS are mass based and are established for all nine subcategories and control one toxic pollutant (total chromium), and four conventional pollutants (BOD_5, TSS, Oil and Grease, and pH). NSPS are based on the same technology and effluent concentrations and the same variability factors as BAT, but the mass based limitations for NSPS are different from those for BAT because the NSPS limitations are based on reduced water use. These limitations are given in Table XI-1.

PSES and PSNS

Finally, this regulation establishes categorical pretreatment standards for one toxic pollutant, total chromium, for all subcategories. These standards are concentration based and applied to existing and new source indirect dischargers. The categorical pretreatment standards for total chromium contained in this regulation do not apply to indirect dischargers in subcategory 1 processing less than 275 hides per day, in subcategory 3 processing less than 350 hides per day, or in subcategory 9 processing less than 3600 splits per day. Categorical pretreatment standards also are established for the control of sulfides in subcategories 1, 2, 3, 6, and 8 where unhairing operations are included. However, this regulation includes a provision which allows POTWs to certify that discharge of sulfide from a particular facility does not interfere with its treatment works. If this certification is made and EPA determines that the submission is adequate, it will publish a notice in the Federal Register identifying those facilities to which the sulfide pretreatment standard would not apply. These standards are presented in Table XII-1.

SECTION II

INTRODUCTION

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). On June 2, 1982 (see 47 FR 23958), EPA announced the availability of supplementary materials and an analysis of how these materials might influence final rulemaking. On November 23, 1982, EPA promulgated final effluent limitations guidelines, standards of performance, and pretreatment standards under the Clean Water Act of 1977 (Public Law 95-217). This document presents EPA's study of the industry, incorporates information collected since the regulations were proposed, and explains the technical rationale for the promulgated regulations.

A. PURPOSE AND AUTHORITY

The Federal Water Pollution Control Act Amendments of 1972 (the Act) established a comprehensive program to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters" (Section 101(a)). The Act required existing industrial dischargers to achieve by July 1, 1977 "effluent limitations requiring the application of the best practicable control technology currently available" (BPT), Section 301(b)(1)(A), and by July 1, 1983 "effluent limitations requiring the application of the best available technology economically achievable (BAT) which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants," 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; 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 Act authorized the setting of requirements for direct dischargers on a case-by-case basis, Congress intended that, for the most part, control requirements be based on regulations promulgated by the Administrator of EPA. Section 304(b) of the Act required the Administrator to promulgate regulations that set 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 industrial 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 specified in the Act. In 1976, EPA was sued by several environmental groups, and in settlement of the 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 BAT effluent limitations guidelines, pretreatment standards, and new source performance standards applicable to 65 "priority" pollutants and classes of pollutants for 21 major industries. See Natural Resources Defense Council, Inc. v. Train, 8 ERC 2120 (D.D.C. 1976), modified 12 ERC 1833 (D.D.C. 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 through plant site runoff, spills or leaks, sludge or waste disposal, and drainage from raw material storage associated with, or ancillary to, the manufacturing or treatment processes.

In response to the Clean Water Act of 1977 and the EPA-Natural Resources Defense Council (NRDC) Settlement Agreement, EPA began the evaluation of 65 classes of pollutants declared toxic under Section 307(a) of the Act. These groups and classes of pollutants, potentially including thousands of specific compounds, were eventually lengthened to a list of 129 priority pollutants (Table II-I), all of which were considered in developing the proposed BAT limitations, new source performance standards, and pretreatment standards for new and existing sources. In 1980, the Agency removed three toxic pollutants from this list, as follows: 50. Dichlorodiflouromethane; 49. Trichloroflouromethane; and 18. Bis(2-Chloroethyl) ether.

In addition to 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). Section 304(b)(4)(B) sets forth the factors considered in assessing BCT for an industry, including the relationship between the costs of attaining a reduction in effluents and the effluent reduction benefits, and a comparison of the cost and level of reduction of conventional pollutants by publicly owned treatment works (POTWs) and industrial sources. 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 by July 1, 1984, whichever is later, but not later than July 1, 1987.

The purpose of the promulgated regulations is to provide effluent limitations guidelines for BPT, BAT, and BCT, and to establish new source performance standards (NSPS), pretreatment standards for existing sources (PSES), and pretreatment standards for new sources (PSNS).

B. PRIOR EPA REGULATIONS

EPA promulgated BPT, BAT, NSPS, and PSNS for the Leather Tanning and Finishing Point Source Category on April 9, 1974 (39 FR 12958; 40 CFR Part 425, Subparts A-F). Several industry members challenged these regulations in the United States Court of Appeals for the Fourth Circuit. The Court left BAT and PSNS undisturbed, but remanded the BPT and NSPS regulations for several reasons (see Tanners' Council of America vs. Train, 540 F.2d 1188 4th Cir. 1976). EPA promulgated pretreatment standards for existing sources (PSES) within the Leather Tanning and Finishing Point Source Category on March 23, 1977 (42 FR 15696; 40 CRF Part 425, Subparts A-G). PSES regulations were not challenged and currently are in effect.

TABLE II-I

LIST OF TOXIC POLLUTANTS

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
18. †bis(2-chloroethyl) ether
19. 2-chloroethyl vinyl ether (mixed)
*chlorinated naphthalene

20. 2-chloronaphthalene
*chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)

21. 2,4,6-trichlorophenol
22. para-chloro meta-cresol
23. *2-chlorophenol
24. *2-chlorophenol

*dichlorobenzenes

25. 1,2-dichlorobenzene
26. 1,3-dichlorobenzene
27. 1,4-dichlorobenzene

TABLE II-1 (continued)

*dichlorobenzidine

28. 3,3'-dichlorobenzidine

*dichloroethylenes (1,1-dichloroethylene and 1,2-trans-dichloroethylene)

29. 1,1-dichloroethylene
30. 1,2-trans-dichloroethylene
31. *2,4-dichlorophenol

*dichloropropane and dichloropropene

32. 1,2-dichloropropane
33. 1,2-dichloropropylene (1,2-dichloropropene)
34. *2,4-dimethylphenol

*dinitrotoluene

35. 2,4-dinitrotoluene
36. 2,6-dinitrotoluene
37. *1,2-diphenylhydrazine
38. *ethylbenzene
39. *fluoranthene

*haloethers (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

*halomethanes (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

TABLE II-1 (continued)

52. *hexachlorobutadiene
53. *hexachlorocyclopentadiene
54. *isophorone
55. *naphthalene
56. *nitrobenzene

*nitrophenols (including 2,4-dinitrophenol and dinitrocresol)

57. 2-nitrophenol
58. 4-nitrophenol
59. 2,4-dinitrophenol
60. 4,6-dinitro-o-cresol

*nitrosamines

61. N-nitrosodimethylamine
62. N-nitrosodiphenylamine
63. N-nitrosodi-n-propylamine
64. *pentachlorophenol
65. *phenol

*phthalate esters

66. bis(2-ethylhexyl) phthalate
67. butyl benzyl phthalate
68. di-n-butyl phthalate
69. di-n-octyl phthalate
70. diethyl phthalate
71. dimethyl phthalate

*polynuclear aromatic hydrocarbons

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

TABLE II-1 (continued)

84. pyrene
85. *tetrachloroethylene
86. *toluene
87. *trichloroethylene
88. *vinyl chloride (chloroethylene)

pesticides and metabolites

89. *aldrin
90. *dieldrin
91. *chlordane (technical mixture and metabolites)

DDT and metabolites

92. 4,4'-DDT
93. 4,4'-DDE (p,p'-DDX)
94. 4,4'-DDD(p,p'-TDE)

endosulfan and metabolites

95. a-endolsufan-Alpha
96. b-endosulfan-Beta
97. endosulfan sulfate

endrin and metabolites

98. endrin
99. endrin aldehyde

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

TABLE II-1 (continued)

<u>*polychlorinated biphenyls</u> (PCBs)

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)
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.

† These three compounds are no longer listed as toxic pollutants. (45 FR 46103 and 45 FR 60942)

**This compound was specifically listed in the consent decree; however, due to its extreme toxicity laboratories did not acquire an analytical standard for this compound.

On July 2, 1979 (44 FR 38746), EPA proposed BPT, BAT, BCT, NSPS, PSNS, and PSES regulations. EPA accepted comments on the proposed regulations until April 10, 1980. In their comments on the proposed regulations, the leather tanning industry claimed that the data and other supporting record material relied upon by EPA in proposing these regulations contained a large number of errors. The Agency has responded by not only completely reviewing the entire data base and all documentation supporting this rulemaking, but also by conducting a program to acquire supplemental data during the comment period.

On June 2, 1982, (47 FR 23958), the Agency made available for public review technical and economic data and related documentation received after proposal of the regulations. EPA requested comments on these supplementary record materials and on the Agency's preliminary analysis of how these materials might influence final rulemaking.

The promulgated regulations described in this document include: new BPT and NSPS regulations, intended to replace the remanded regulations; revised BAT, PSES, and PSNS regulations which supersede existing BAT, PSES, and PSNS regulations; and new BCT regulations.

C. OVERVIEW 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. That part of the industry covered by this regulation is the subgroup SIC 3111, leather tanning and finishing. Nine distinct combinations of raw materials and leather processing operations have been identified as appropriate for subcategorizing the industry based on the type and conditions of raw material received, as well as on the major groups of subprocesses used. One hundred and fifty-eight facilities are operating within these nine subcategories.

Though several tanneries are divisions of larger corporations, small, closely-held family operations typify the industry. About 30 percent of the surveyed population employ less than 50 people, and 50 percent are housed in facilities over 50 years old.

Data on effluent discharges from most tanneries is limited due to the unsystematic or intermittent record keeping in a majority of facilities. Since only 17 facilities discharge directly to surface waters, only 11 percent of the industry is required to sample and analyze waste streams regularly under the NPDES program. The remainder of the industry (141 facilities) discharges to publicly owned treatment works (POTWs). Reporting practices vary depending on the particular municipality involved.

D. SUMMARY OF METHODOLOGY

EPA first sought to obtain a broad and accurate understanding of the leather tanning industry and to evaluate industry wastewater characteristics and treatment practices. This involved collecting information on both plant operating procedures and wastewater characteristics. EPA was able to identify the sources of wastewater, in terms of both volume and pollutant loading, to major steps in the manufacturing process. EPA then studied the effect that differences in manufacturing processes, plant age, size, geographical location, raw materials, final products, and other factors have on wastewater characteristics. Based on this assessment, EPA was able to determine whether certain segments of the industry required separate effluent limitations and standards. The result of this assessment is the final subcategorization scheme described in Section IV of this document. EPA then identified the pollutant parameters which would be considered for regulation.

Next, EPA identified several distinct control and treatment technologies, including both in-plant and end-of-pipe technologies, which are either in use or applicable to 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 also were considered. In addition, EPA considered the nonwater quality environmental impacts of these technologies, including impacts on air quality, solid waste generation, water supply, energy requirements, and the costs of meeting the regulations.

Costs were estimated by the Agency for each control and treatment technology. Unit cost curves were developed through the use of conventional engineering analysis fully considering leather tanning and finishing wastewater characteristics. EPA then derived unit process costs for model plants. The characteristics of these model plants were defined to facilitate the economic analysis of the impact of these technologies. Characteristic production and flow values applied to each treatment process unit cost curve (e.g., primary coagulation-sedimentation, activated sludge, multimedia filtration) resulted in unit process costs. These unit process costs were then added in a building-block approach to yield the total cost for each treatment technology option. After confirming the validity of this methodology by comparing EPA cost estimates to treatment system costs supplied by the industry, the Agency evaluated the economic impacts of each applicable treatment level.

After considering these factors - described more fully in subsequent sections - EPA identified various control and treatment technologies as BPT, BCT, BAT, PSES, PSNS, and NSPS. The 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. The actual technology chosen by any plant to achieve the applicable effluent limitations and standards specified in the regulations remains the discretion of that plant.

The effluent limitations for BPT, BCT, BAT, and NSPS are expressed as mass limitations (lbs/1000 lbs or kg/kkg of raw material, except for pH) and are calculated by multiplying three values: (1) long term average effluent concentration (mg/l) for each regulated pollutant determined from analysis of control technology performance data, (2) wastewater flow ratio (gal/lb or l/kg) derived for each subcategory, and (3) an appropriate variability factor (e.g., maximum month or maximum day). This basic calculation was performed for each regulated pollutant for each subcategory of the industry. Effluent limitations for PSES and PSNS are expressed as maximum allowable concentrations in milligrams per liter (mg/l).

E. DATA AND INFORMATION GATHERING PROGRAM

The collection, review and evaluation of the existing information, which served as the basis for the 1974 Development Document, was the initial major task performed. This task provided the starting point for subsequent activities and established the extent of effort that was to be required in each of the other tasks. Two major data collection efforts were conducted subsequently to provide information and data for this document. The first effort was conducted from 1976 to 1977, the second from 1979 to 1980. At the beginning of each of the efforts, the Agency and the Tanners' Council of America (TCA) agreed that the authority of Section 308 of the Act would not be used to gather technical information, except as a last resort to obtain critical or proprietary information. The following describes the activities performed under each of the efforts.

1. Data Collection

1976 - 1977

The initial task was to mail one-page surveys to approximately 300 tanneries, finishers, and sales offices. There were 116 responses to this survey. This survey served to identify the tanneries which had usable information and data, and to obtain summary industry profile data. These tanneries were subsequently mailed questionnaires requesting detailed information and wastewater data for the facility. Eighty-nine tanneries responded to this questionnaire. In response to the Clean Water Act of 1977 and the EPA - NRDC Settlement Agreement, a second detailed questionnaire was mailed to assess and evaluate toxic pollutants. EPA mailed questionnaires to the 188 tanneries in operation at that time (1976-77). Forty-six questionnaires were returned.

During this effort EPA also conducted an economic survey of the industry under the authority of Section 308 of the Act. The use of data collection authority under Section 308 was necessary because the economic information needed for the economic impact analysis would not have been provided voluntarily. Questionnaires requesting production costs, balance and income data sheets, and costs for existing pollution abatement systems were mailed to the 188 domestic tanneries known to be operating at the time. Sixteen of the eighteen direct dischargers and 120 of the 170 indirect dischargers responded to this request.

The information gathered in this effort provided a broad base for understanding the leather tanning and finishing industry. Consideration of this information revealed areas in which clarification, stricter definition, and additional information were needed. EPA also recognized that the industry's in-place treatment technologies and production levels had changed somewhat in the intervening years since the regulations were promulgated in 1974. For these reasons, EPA determined that further efforts were required to obtain an updated and more usable data base.

In their comments on the 1979 proposed regulations, the leather tanning industry claimed that the data and other supporting record material relied upon by EPA in proposing these regulations contained a large number of errors.

The Agency responded to this comment by completely reviewing the entire data base and all documentation supporting this rulemaking. All historical data points were examined for background documentation, accuracy, and applicability. In its review of the data base, the Agency corrected errors relating to previously reported data, including production levels, water use ratios, and technology costs. Review of these data revealed several problems:

a. Many tanneries did not report production and/or wastewater flow. Pollutant concentrations could therefore not be converted to mass loadings or related to production levels (i.e., kilograms of pollutant per thousand kilograms of raw material).

b. The manner in which production was reported varied from tannery to tannery; some reported conventional weights and others reported weight after fleshing, brine curing, and/or trimming. The problems were even greater with tanneries using blue stock as the raw material because the weight of grain sides and splits which enter retanning and wet finishing vary according to the degree of intervening trimming, shaving, or further splitting.

c. The majority of the tanneries reported data for wastewater after some form of treatment. These data could not be used in determining the raw waste loads generated by the industry.

d. Some of the tanneries which submitted data either had minor process variations within the major group(s) of subprocesses or performed a combination of two or more of the standard manufacturing sequences representing two or more subcategories. The data from these plants could not be compared with data from the remainder of the industry because the water use and pollutant load data would not be accurate for any one subcategory.

1979-1980

EPA therefore conducted a second effort to acquire data during the comment period on the proposed regulation. A large part of this program involved 56 detailed information request mailings developed in cooperation with and distributed by the Tanners' Council of America. This questionnaire was distributed to the 56 tanneries which had responded to earlier detailed questionnaires. To minimize the administrative burden on individual tanners, specific information already on file with EPA was provided on the new questionnaire. Tanners were asked to verify the reported information and update or correct it if necessary. Of the 56 tanneries to which questionnaires were distributed, nine had closed. Forty returned questionnaires (Table II-2). Substantial efforts were made to improve the response to this information request, including follow-up correspondence and telephone contacts with non-respondents and multiple postponements of the deadline for receiving responses. Once returned, questionnaires were reviewed to ensure that the questions had been interpreted and answered correctly. These questionnaires also were reviewed separately by the Tanners' Council of America, and any errors or discrepancies in tanners' responses were reported to the Agency. In the majority of cases, tanners were contacted by telephone and asked to clarify any information that obviously was erroneous or appeared ambiguous or suspect.

Included with the detailed questionnaire was a request that tanneries provide information about the potential sources of toxic pollutants. Very few tanners were able to identify specific toxic pollutants that were present in their effluent, and even fewer attempted to identify the sources of toxic pollutants. Thirty-eight plants, however, provided lists of all chemicals used in their processes. These lists were compiled and were used in determining the potential for discharge of toxic pollutants from tanneries.

EPA also requested that tanneries supply any available wastewater data for the period January 1976 to September 1979. Many tanners supplied additional data in response to this request, but very little data were obtained for raw wastewater characteristics. A final follow-up letter, focusing entirely on the need for raw wastewater data and the proper means for reporting data, was sent to 35 tanneries. The TCA also contacted these tanneries and urged them to provide any available data. Twenty-seven tanneries responded to this mailing; 18 provided new data.

Before any data were included in the final data base, they were checked according to the following criteria:

a. For a plant's data to be included in the data base utilized to characterize water use and waste loads for any subcategory, at least 80 percent of the plant's production must be in one subcategory, or data for each processing operation representing a separate subcategory at a plant must be for a segregated and measurable wastewater stream. Mixed subcategory plants which did not meet this criteria were not included in the data base because water use ratios and pollutant loads derived from these plants would not be accurate for a single subcategory.

b. The location at which the wastewater was sampled (i.e., before or after treatment and type of treatment) and the sampling technique (grab, composite, flow proportional) must be reported so that the data could be used properly to characterize raw waste and the performance of various treatment system components.

TABLE II-2

QUESTIONNAIRE DISTRIBUTION SUMMARY (1979)

Plants Receiving Questionnaires

56 plants total

Discharge Status

55 indirect dischargers (46 + 9 closed)
1 direct discharger

Subcategory Status

23 plants in hair pulp, chrome tan, retan-wet finish subcategory
4 plants in hair save, chrome tan, retan-wet finish subcategory
8 plants in hair save or pulp, non-chrome tan, retan-wet finish subcategory
5 plants in retan-wet finish (grain side) subcategory
9 plants in no beamhouse subcategory
1 plant in through-the-blue subcategory
1 plant in shearling subcategory
0 plants in pigskin subcategory
4 plants in retan-wet finish (splits) subcategory
1 plant not subcategorizable

Plants Responding to Questionnaire

9 plants had closed

40 operating plants responded

Discharge Status

39 indirect dischargers
1 direct discharger

Subcategory Status

16 plants in hair pulp, chrome tan, retan-wet finish subcategory
4 plants in hair save, chrome tan, retan-wet finish subcategory
6 plants in hair save or pulp, non-chrome tan, retan-wet finish subcategory
4 plants in retan-wet finish (grain side) subcategory
5 plants in no beamhouse subcategory
1 plant in through-the-blue subcategory
1 plant in shearling subcategory
0 plants in pigskin subcategory
3 plants in retan-wet finish (splits) subcategory

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c. Production and flow values must be reported for the days of sampling. Average or estimated values were used only with the approval of the individual tannery and upon verification of the data source and validity of the estimates or averages to prevent use of erroneous data.

d. Production data (in pounds) must be reported on the basis specified for each type of raw material to allow flow and waste characteristics to be normalized to production (gallons/pound of raw material; pounds of pollutant/ 1000 pounds of raw material) for each subcategory.

2. Plant Visits

1976-1977

Prior to the proposal of regulations in 1979, EPA's representatives visited 50 tanneries. During these field visits, EPA collected information on plant processing operations, sites, wastewater treatment practices, and management concerns and attitudes. Twenty-two of these tanneries also were sampled.

1979-1980

After proposal of the regulations, EPA's representatives visited 43 tanneries, including all direct dischargers. During these visits, EPA collected information on plant operations, sites, practices, equipment and processes, and in-place wastewater treatment facilities and their operation. EPA also requested that these plants provide financial information on a confidential basis to be used in updating the economic profile of the industry. Twenty-eight of the 43 tanneries provided the requested financial information. A detailed trip report was prepared to document observations at each of the 43 plants visited (Table II-3). Wastewater samples for subsequent toxic pollutant analyses were collected concurrently during ten of the 43 data collection visits.

In their comments on the proposed regulations, management at urban tanneries expressed the concern that the availability and cost of land required for the construction of wastewater pretreatment facilities for indirect dischargers might pose significant problems. In response to concerns over space availability, the 56 detailed questionnaires distributed in 1979 requested information about the land in the vicinity of the plant which might be used for wastewater treatment facilities. EPA's representatives also visited during 1980 43 additional tanneries in urban areas (Chicago, IL, Milwaukee, WI, Johnstown-Gloversville, NY, and Salem-Peabody, MA) to assess the extent of problems posed by space limitations. Neither EPA nor the industry have found that land availability was a problem for any of the direct dischargers.

3. Wastewater Sampling and Analysis

EPA also conducted a plant sampling program which included laboratory analysis for the 129 toxic pollutants and for certain conventional and nonconventional pollutants. This program consisted of:

1976-1977

One plant from each of the subcategories was sampled starting in late 1976 and early 1977. The purpose of this sampling was to determine which of the 129 toxic pollutants were present in tannery effluents (Screening Program).

Sixteen representative plants and two POTWs were sampled to determine actual quantities of toxic pollutants (Verification Program). The distribution of these two phases of plant sampling is summarized in Table II-4.

1979-1980

In 1979 and 1980, ten representative plants (and two POTWs associated with two of these plants) were sampled to determine actual quantities of toxic pollutants in selected waste streams. The samples were analyzed in accordance with toxic pollutant analytical protocol developed by EPA. The plants sampled in this program are listed in Table II-5.

4. Other Data Sources

Although individual tanneries provided the bulk of information on file with EPA, some data also were obtained during both efforts from the sources described below.

a. EPA contacted 50 municipalities to collect information on city ordinance wastewater limitations, reasons for limitations, wastewater problems related to tannery discharges, and plans for dealing with the problems.

b. NPDES permit data and background information on a number of tanneries were obtained from EPA regional offices. Permits provided limited information on the tannery, wastewater treatment facilities, discharge standards, and schedules for compliance being set at the time.

TABLE II-3

ADDITIONAL TANNERY DATA SUMMARY (1979-80)

Data Collection Visits

43	total plants
22	indirect dischargers
21	direct dischargers (one plant closed, one plant burned and will not reopen, and one plant tied into a POTW)
2	POTWs
17	plants in hair pulp, chrome tan, retan-wet finish subcategory
2	plants in hair save, chrome tan, retan-wet finish subcategory
8	plants in hair save or pulp, non-chrome tan, retan-wet finish subcategory
5	plants in retan-wet finish (sides) subcategory
3	plants in no beamhouse subcategory
4	plants in through-the-blue subcategory
3	plants in shearling subcategory
1	plant in pigskin subcategory
0	plants in retan-wet finish (splits) subcategory

Land Availability Assessments

64	total plants (indirect dischargers)
27	plants in hair pulp, chrome tan, retan-wet finish subcategory
3	plants in hair save, chrome tan, retan-wet finish subcategory
4	plants in hair save or pulp, non-chrome tan, retan-wet finish subcategory
6	plants in retan-wet finish (sides) subcategory
13	plants in no beamhouse subcategory
4	plants in through-the-blue subcategory
0	plants in shearling subcategory
0	plants in pigskin subcategory
7	plants in retan-wet finish (splits) subcategory

TABLE II-4

TOXIC POLLUTANT SAMPLING (1976 to 1977)

12	plants - direct discharge	
10	plants - indirect discharge	
2	POTWs	
	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 or pulp, non-chrome tan, retan-wet finish subcategory
	3	plants in retan-wet finish subcategory
	3	plants in no beamhouse subcategory
	1	plant in through-the-blue subcategory
	2	plants in shearling subcategory

Note: Some of these plants were sampled more than once.

TABLE II-5

TOXIC POLLUTANT SAMPLING (1979 to 1980)

10	plants total	
	6	direct dischargers
	4	indirect dischargers
	2	POTWs
	3	plants in hair pulp, chrome tan, retan-wet finish subcategory
	1	plant in hair save, chrome tan, retan-wet finish subcategory
	1	plant in hair save or pulp, non-chrome tan, retan-wet finish subcategory
	1	plant in retan-wet finish (sides) subcategory
	1	plant in through-the-blue subcategory
	1	plant in shearling subcategory
	2	plants in pigskin subcategory
	1	plant in retan-wet finish (splits) subcategory, (associated with one of the subcategory 1 plant listed above)

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

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

SECTION III

DESCRIPTION OF THE INDUSTRY

A. INDUSTRY PROFILE

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into leather. The three types of major hides and skins used most often to manufacture leather are cattlehides, sheepskins, and pigskins. Smaller quantities of hides and skins of horses, goats, deer, elk, calves, and other animals are also tanned in the United States each year. In recent years, the federal government has encouraged the tanning of pigskins. At the present time only a small percentage of the pigskins produced in the United States are made into leather. Table III-1 provides a summary of the types of raw materials used by the leather tanning industry in the United States. Typical weights of the various raw materials are given in Table III-2.

There are currently 158 tanneries producing leather in the United States. These tanneries are located primarily in five general areas: the Northeast, the Mid-Atlantic states, the Midwest, the Southeast, and the Pacific Coast (see Table III-3). Most of the tanneries are family-owned, closely-held corporations, although a few are divisions of large conglomerates. Approximately 30 percent of these plants have 50 or fewer employees and wastewater volumes typically less than 100,000 gallons per day. Nearly half of the plants are more than 50 years old in terms of the physical structures which house the leathermaking operations. Less than 10 percent of the plants have been built in the last ten years.

Although the equipment used in some plants may be relatively modern, the typical processing techniques have not changed for many years. A few plants - usually the larger ones - use modern processing methods and equipment, including reuse of process water and recovery/reuse of certain process chemicals. However, some small plants which utilize more traditional processing methods and equipment have demonstrated good housekeeping and water conservation techniques.

Local wastewater pretreatment standards or limited land availability have caused the relocation of certain tanning operations. Several tanneries have moved beamhouse and tanyard operations, which produce high pollutant loadings, to areas where local POTWs have sufficient capacity to handle their wastewater, or where a wastewater treatment system can be readily implemented. Relocation of beamhouse and tanyard operations

TABLE III-1

RAW MATERIALS SUMMARY[1]

Subcategory	Raw Material	Preprocessed Condition
1	Cattlehide	Fresh
		Salted
		Brine cured
		Brine cured-prefleshed
		Prefleshed
		Pickled
	Deer, Elk, Moose	Fresh
		Salted
		Dried
2	Cattlehide	Fresh
		Salted
		Brine cured
		Brine cured-prefleshed
	Calfskin	Salted
3	Cattlehide	Salted
		Brine cured
		Brine cured-prefleshed
		Prefleshed
	Calfskin	Salted
4	Cattlehide	Through-the-blue
	Pigskin	Through-the-blue
5	Cattlehide	Pickled
		Limed Split
	Sheepskin	Pickled
		Brine cured-prefleshed
	Lamb, Goat, Kid, Skiver	Pickled
6	Cattlehide	Fresh
		Prefleshed
		Salted
		Brine cured-prefleshed
7	Shearling	Fresh
		Wet salted
		Salt dried
8	Pigskin	Brine cured
9	Cattlehide	Blue splits

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[1] Based on responses to industry questionnaire.

TABLE III-2

TYPICAL WEIGHTS OF RAW MATERIALS

Subcategory	Unit Weight* (lbs)
1	54
2	51
3	60
4	11
5	2
6	58
7	12
8	19
9	4

*Either hide, skin, split, side, or similar depending upon subcategory or raw material

(Through-The-Blue; subcategory 6) also has occurred generally in locations close to the source of raw materials (hides or skins).

Beginning in the mid-60's and continuing until 1973, the leather tanning and finishing industry in the U.S. experienced a steady decline in the number of plants, production volumes and profits. This reduction stabilized during the 1974-76 period and through early 1977. In late 1977 and continuing through 1979, the industry's financial situation again deteriorated. In 1980, production volume stabilized and improved slightly and profitability improved. From mid-1980 to the present, the industry again has experienced a decline in production and profit. The industry continually faces international competition for a fixed hide supply and consumer markets. The U.S. shoe industry, a primary customer of the tanning industry, has declined sharply in face of increasing foreign competition. The above data are presented in Table III-4.

B. STANDARD MANUFACTURING PROCESSES

Animal skin is composed of outer and inner (epidermal and dermal) layers, and it is the inner (dermal) layer which is made into leather. This dermal layer consists mainly of the protein callogen. Tanning is essentially the reaction of collagen fibers with tannins, chromium, alum, or other tanning agents, that help stabilize, or preserve, the skin and make it useful.

TABLE III-3

TANNERIES OPERATING IN THE UNITED STATES AS OF SEPTEMBER 1982

	Number (Direct Dischargers)
Arizona	1
California	9
Colorado	4
Delaware	1
Florida	2
Georgia	1
Iowa	3 (1)
Illinois	7
Indiana	2 (1)
Kentucky	3 (1)
Massachusetts	31
Maryland	1 (1)
Maine	7 (1)
Michigan	3
Minnesota	5
Missouri	2
North Carolina	1
Nebraska	1
New Hampshire	5 (2)
New Jersey	5
New York	24 (1)
Ohio	1
Oregon	3
Pennsylvania	6 (4)
Tennessee	7 (3)
Texas	4
Utah	1
Vermont	1 (1)
Washington	1
Wisconsin	15
West Virginia	1 (1)
TOTAL	158 (17)

There are three major groups of subprocesses (beamhouse, tanyard, and retan and wet finish) which are required to make finished leather. For the purpose of this study, EPA defines a manufacturing process group as a single step in the complete manufacturing operation where additional steps may result in

TABLE III-4

PRODUCTION AND MARKETING TRENDS IN THE LEATHER TANNING AND FINISHING INDUSTRY

Year	Total Tanning Industry Production(1)	Total Industry Value of Shipments(2)	Cattle Hides Net Exports(2)	Leather Imports(2)	Exports(2)
	(1,000 Equiv. Hides)	($1,000,000)	(1,000 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	1,060	17,292	138,795	66,706
1973	21,062	1,082	16,177	127,381	82,914
1974	19,988	1,076	17,924	124,513	102,116
1975	21,894	1,092	20,329	87,953	140,497
1976	23,526	1,326	24,318	180,502	139,265
1977	21,528	1,456	23,569	155,934	149,787
1978	20,199	1,580	24,101	222,006	184,160
1979	18,170	1,803	23,073	284,348	250,420
1980	17,600	1,900	18,640	217,306	271,944
1981	19,189	2,181	18,701	354,035	275,332

Source: (1) Tanners' Council of America, Inc.
(2) U.S. Department of Commerce

different waste volumes and pollutant loads. A process group can consist of one or a series of subprocesses. In any defined process, subprocesses generally remain the same.

(1) Beamhouse operations - hides or skins are washed and soaked and the attached hair removed. Washing and soaking generate large quantities of wastewater which contain dirt, manure, salt (chlorides and other dissolved solids) and other foreign material. Solvent degreasing (usually only for sheepskins and pigskins) generates animal fat and related waste material from the skins, plus spent detergents or solvents. When solvent degreasing is performed, most plants utilize a solvent recovery system. Detergents can be of any polar form (anionic, cationic, or nonionic) depending upon the type of hide or skin to be degreased. Unhairing is performed in an alkaline medium by either the hair save or the hair burn (pulp) methods. The hair save process utilizes mechanical removal of chemically loosened hair. Many plants dispose of this hair in a landfill, although some allow the hair to enter the wastewater. The hair burn process dissolves the hair completely. This process is the single most significant source of proteinaceous organic and inorganic (lime) pollutants characterized by high pH (range of 10 to 12), and substantial amounts of BOD_5, TSS, sulfides, alkalinity, and nitrogen. Beamhouse processes (washing through unhairing) typically generate up to 75 percent of the waste load from a complete tannery.

(2) Tanyard process - tanning agent reacts with and stabilizes the proteinaceous matter in the hides or skins. Deliming and bating are performed in an acid medium and produce additional inorganic calcium salts, small additional amounts of proteinaceous hair and waste hide substance, as well as large quantities of ammonia. Pickling generates a highly acid waste stream (pH of 2.5 to 3.5) which also contains salt. Tanning is accomplished primarily by trivalent chromium salts, or by vegetable tannins in extracts derived from special types of tree bark. Spent chromium tanning liquors contain high concentrations of trivalent chromium in acid (pH of 2.5 to 3.5) solution with low concentrations of BOD_5 and TSS, and elevated temperature. Blowdown to maintain vegetable tanning liquor quality is highly colored, and also contains significant amounts of BOD_5, COD, and dissolved solids.

(3) Retanning and wet finishing processes - further tanning is done with chemical agents such as syntans, dyes, lubricants, and various finishes. Retanning, coloring, and fatliquoring generate additional quantities of trivalent chromium, vegetable tannins, synthetic tannins, natural and synthetic sulfonated oils, and spent acid dyes, all relatively low in BOD_5 and TSS, higher in

COD, in fairly large volumes which occasionally are highly colored, and at elevated temperature. Relatively small quantities of low strength wastewater are produced by drying and other finishing operations (pasting frame washing, rewet conditioning, vacuum dryer cooling water, wet scrubbers for buffing dust, spray booth wash down, etc.).

Most tanneries perform the entire tanning process, from beamhouse through wet finishing operations. A smaller number of tanneries, which generally have relatively large capacities, perform only beamhouse and tanyard operations to produce "wet blue" stock. The "wet blue" hides they produce are bought by tanneries which retan and finish the leather for specific uses. A number of tanneries purchase hides or skins that either do not require a complete beamhouse process (such as pigskins) or which have previously gone through beamhouse operations (such as pickled sheepskins or pickled cattlehides). A small number of tanneries produce specialized types of products such as chamois leather, lace leather, hair-on leather for industrial use, or mechanical cushions for pianos.

Some tanneries perform part or all of their work on a contract basis. Skins are supplied to these tanneries and tanned to the customer's specifications.

The leather manufactured by domestic tanners is used to produce shoes, garments, upholstery, luggage, gloves, handbags, sporting goods, and a variety of other products.

Water is essential to leathermaking and is used in virtually all manufacturing processes. Several tanners reported that the quality of process water is a significant factor in determining the characteristics of the leather produced. Various chemical preservatives, biocides, dyes, 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 III-1.

The discussion and description of tanning processes which follows focuses on the three major hide and skin types produced in the United States: cattlehides, sheepskins, and pigskins. The processes and subprocesses discussed represent those most typical of the industry.

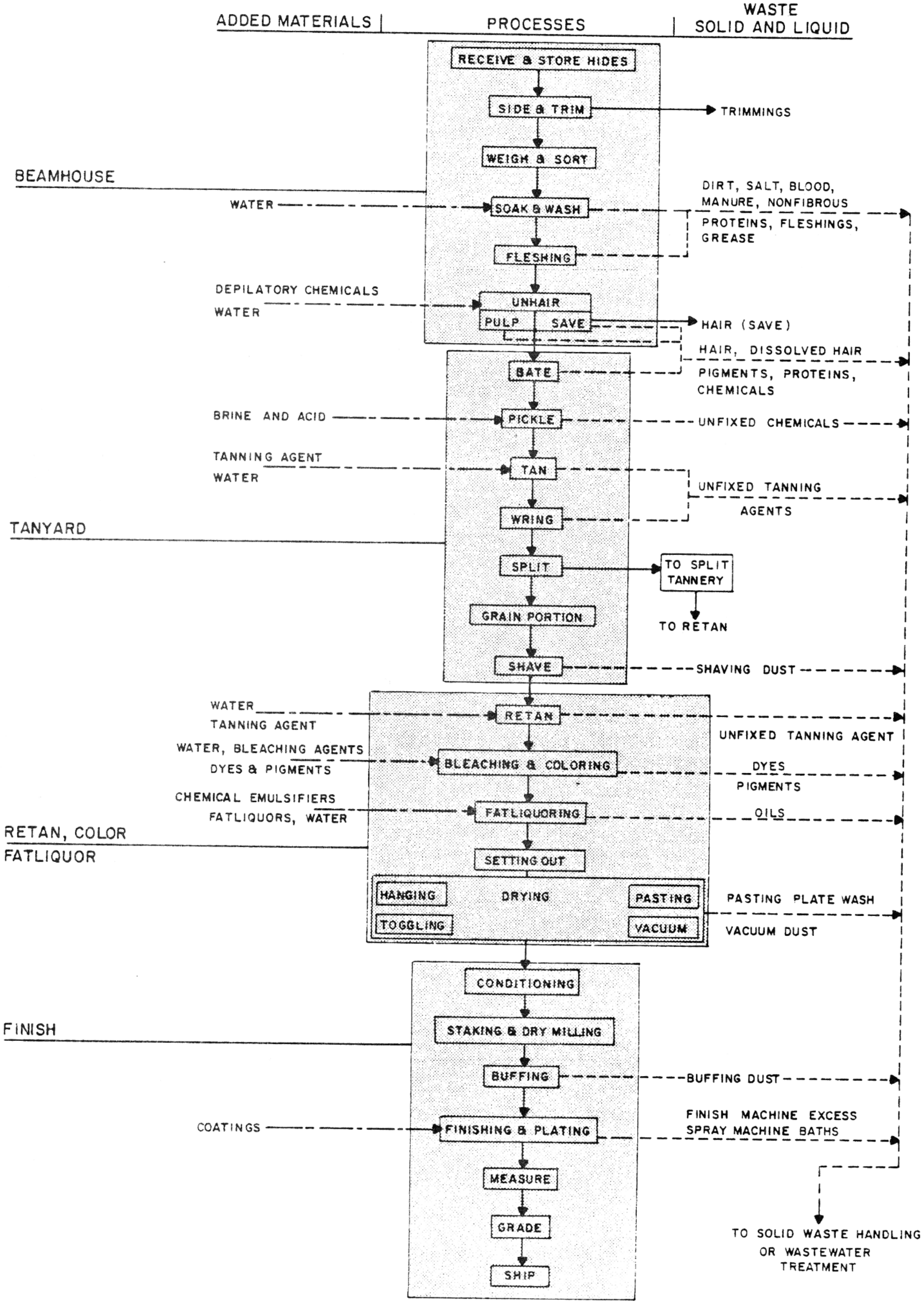

FIGURE III-1 PRODUCT AND WASTEWATER FLOW FOR GENERALIZED LEATHER TANNING AND FINISHING PLANTS

CATTLEHIDE TANNERY PROCESSES

Most of the following process description of a typical cattlehide tannery was developed from descriptive texts, and from industry questionnaires and plant visit reports.

Receiving and Storage. Nearly all cattlehides received at tanneries are either green salted or brine-cured, although brine-cured hides are predominant. In the few 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 trimming and grading, green hides are cured (green salted) 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 five to six 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 adequately cured, 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 and size and method of shipments.

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, typically in a "raceway", for two to 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 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. The use of brine-cured hides has increased in recent years because the brining process takes less time than green salt curing. The method is preferred by both packers and hide curing establishments that do not want a large inventory of hides. The brining process also produces cleaner hides, which are more attractive to the tanners.

Normally, the tannery stores the cured hides in a large, cool, well-ventilated area, which helps maintain the moisture content.

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 subprocesses in the beamhouse: 1) side and trim; 2) soak and wash; 3) fleshing; and 4) unhairing.

1) Side and Trim - The typical first step in preparing hides for processing is to trim off the heads, long shanks, and other areas along the perimeter 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. Hides that are to be made into upholstery leather remain whole throughout the tanning process. Trimmings are often collected and shipped to glue factories or other by-product manufacturers.

2) Soak and Wash - The hides soak in vats (with or without paddles), drums, or hide processors (concrete mixers with special linings) for eight to 20 hours to restore the moisture that has been lost during the curing process. They gradually absorb water and become softer and cleaner. Washing removes dirt, salt, blood, manure, and non-fibrous proteins. There may be some variation in the quantity of such waste materials, depending on the time of year and the source of hides. Depending on the type of leather to be produced, additional washes (rinses) may also follow several subprocesses, including unhairing, bating, tanning, and coloring. Hides or skins may also be rinsed before they are colored.

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

Many hides, particularly brine-cured hides, are fleshed at packing plants or at separate hide processing facilities. Removing flesh before liming is referred to as green fleshing; removal after liming is called lime fleshing. In any case, fleshings (i.e., the removed matter) are normally recovered and sold to plants for rendering or conversion to glue. Properly handled, this operation contributes very little liquid or solid waste. If fleshings are rendered on-site, the resulting waste stream (stick liquor) contributes a small but extremely concentrated waste load.

4) Unhairing - Hair removal is facilitated by three dehairing (depilatory) chemicals: calcium hydroxide, sodium sulfhydrate, and sodium sulfide. 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, drums, or hide processors containing water and the depilatory chemicals. The concentration of chemicals, the water temperature, and the amount of agitation directly affect the rate at which hair is removed. In a pulp or burn unhairing operation, concentrated chemicals and high temperatures dissolve all the hair within a few hours. If the hair is to be 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 on the nature of the hides being processed and the final products desired.

The number of tanneries using the hair save process has been declining steadily over the past several years. A few tanneries now use a hybrid hair removal process, which combines 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 washing, baling, and marketing the hair exceeds its worth. 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 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 tanning. Tanyard processes include bating, pickling, tanning, wringing, splitting, and shaving.

1) Bating - Bating is a two-step process that consists 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 from 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 decrease the pH of the hides 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 hide, 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 used, the temperature, and the reaction time are critical. Commercial processes vary in length from a few hours to overnight, depending on the hides being handled. When bating has been completed, the hides are washed thoroughly and all of the substances that have been loosened or dissolved are removed.

2) Pickling - Pickling prepares the hides to accept the tanning agents by providing the acid environment essential for chromium 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 enhances the separation of collagen protein fibers, which facilitates further complexing of the hide by the tanning agent. 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 hides can remain in this state for extended periods of time.

3) 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 the raw material's 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 United States are trivalent chromium and vegetable tannins, extracted primarily from specific tree barks. Alum, syntans, formaldehyde, gluteraldehyde, and heavy oils are other tanning agents.

Vegetable tanning is a very old 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 is usually performed 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 by the majority of leather users. Chromium tanning also takes place in a shorter period of time (four to six hours) than vegetable tanning.

The chemical state of the tanning agent and the condition of the hides are important with regard to the thorough penetration of the chromium into the hide. The addition of sodium bicarbonate and formic acid (masking agent) increases the affinity of the separated collagen protein fibers for the chromium.

The older and more traditional method of chromium tanning, known as the "two-bath" method, entails the use of hexavalent chromium, which can be very toxic. The hexavalent chromium 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. The reduced chromium then complexes the proteins.

Very few tanners continue to use the "two-bath" method. The dangers of handling hexavalent chromium and the reduced processing time and chemical costs realized by 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 is done primarily because hexavalent chromium is less expensive than trivalent chromium in some areas. The danger of toxic hexavalent chromium spills exists even where workmen exercise care, although certain tanneries have minimized these occurrences by implementing improved in-plant management practices.

4) Wringing - Blue hides are prepared for splitting by wringing excess moisture from them. 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 that produces finished leather products. Plants in the through-the-blue segment of the industry have no wet processing operations beyond this point.

5) Splitting and Shaving - Splitting adjusts the thickness of the tanned hide to the requirements of the finished products. Hide thickness varies, depending partly on the age of the animal and whether the animal was range fed or fattened at a feedlot. Different parts of the skin will also have various thicknesses. Splitting yields a grain portion of uniform thickness and a split (or flesh) side. The split layer can be processed separately at the same facility or sold to split tanneries for manufacturing suede types of leather.

Shaving removes any remaining fleshy matter from the flesh 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 thickness or weight (ounces per square foot) specifications.

Retan, Color, Fatliquor, and Finishing Processes.

To give the tanned hide special or desired characteristics, a tannery may employ further processing steps including retanning, bleaching, coloring, fatliquoring, and finishing.

1) Retanning - Most tanners have neither the equipment nor the low-cost labor to support multiple beamhouse and tanyard formulas for various finished leather products. Most hides are therefore

subject to identical processing through the "wet blue" state. The primary function of retanning is to impart certain characteristics which are lacking in the leather after the initial tanning step. The more common retanning agents are chromium, vegetable extracts, and syntans. Other agents, such as zirconium and gluteraldehyde, are used for very small quantities of leather. Retanning usually takes place in a drum during a one- or two-hour period.

Vegetable extracts help to minimize any variation that may exist between different parts of the chromium-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 chromium tannage, syntans are used in making white or pastel shades of leather.

2) 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.

3) 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 controlled by varying pH, which affects the affinity of the dye for the leather fibers.

4) 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. Firmness of the finished product can be controlled by varying the amount of oil used in this process.

Fatliquors are predominantly 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.

5) Finishing - The finishing process includes all of the operations performed on the hide after fatliquoring. Generally, trimmings and buffing dust collected during these processing

steps are disposed of as solid wastes; however, buffing dust may also enter the plant's liquid waste stream. Finishing steps include setting out, drying, conditioning, staking, dry milling, buffing, finishing, and plating.

a) Setting out smooths and stretches the skin and removes excess moisture.

b) Drying may be done in one of four ways:

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

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

   iii) pasting, in which the skins are pasted onto vertical plates that are then placed in a drying oven; and

   iv) vacuum drying, in which hides are smoothed out on a heated steel plate and covered by a perforated belt or a clothcovered steel plate. A vacuum is then used to extract water from the leather.

The first three drying processes require four to seven hours per skin while 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, except for certain leather types.

c) 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.

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

e) Dry milling tumbles the hides in a large drum to mechanically flex and soften the leather.

f) Buffing smooths or "corrects" irregularities in the grain surface by mechanical abrasion.

g) Water-base or solvent-base finishing may be applied to the leather, depending on the type of hide and intended use. Various finishes provide abrasion and stain resistance and enhance color. Solvent-based coatings are used only for special high-luster finishes because they are difficult to handle and pose a fire hazard.

h) Plating, which smooths the surface of the coating materials and bonds them firmly to the grain, is the final processing step. 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 inspected for temper, uniformity of color, thickness, and surface defects.

SHEEPSKIN TANNERY PROCESSES

The processes used to produce leather from sheepskins are generally the same as those for cattlehides, except that the beamhouse process is usually omitted. In addition, sheepskins require degreasing prior to tanning. The processes and subprocesses which distinguish sheepskin tanning from cattlehide tanning are described below.

Tanyard Processes.

U.S. tanneries receive sheepskins from both domestic and foreign suppliers. Imported skins generally arrive pickled (i.e., 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 woolpullery before the skins are pickled. Skins which are completely processed with the wool intact are referred to as shearlings and are cured in a salt brine only.

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

Skins are removed from the storage bundles and are inspected and fleshed. Though sheepskins are usually fleshed after they have been washed and soaked, tanneries which receive fleshed sheepskins will usually reflesh after tanning. Sheepskins are fleshed on the same type of machine as are cattlehides. The skins are carried through rollers and across 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 is recovered from those skins that have had the wool removed and is converted into by-products. When solvent degreasing is employed, the solvent is generally recovered and reused.

Because of the attached wool, shearlings require substantially more water in the soaking and washing operations. Grease recovery is not a conventional practice for shearling tanneries. Skins may be pickled in a process similar to that described for cattlehides.

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

Sheepskins are retanned much like cattlehides. Skins are colored in drums containing dye solutions, generally made up of synthetic dyes. Shearlings are sometimes bleached before being colored. Fatliquoring, which replaces the natural oils lost in the tanning process, takes place in the same drum as does coloring. It, too, is similar to cattlehide fatliquoring.

A number of operations follow the 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 discharged to the process waste stream.

PIGSKIN TANNERY PROCESSES

Degreasing pigskins is an essential part of pigskin tanning, which is slightly different from cattlehide tanning. The major processes required for pigskin tanning are described below.

Beamhouse Processes.

Tanneries usually receive pigskins in 40 to 50 pound bundles. Nearly all the skins are fresh or frozen, though some are refrigerated. Frozen skins are sometimes delivered in paper bags. Skins are generally kept refrigerated until tanning. Most pigskins have the majority of external hair removed at the packinghouse.

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 temperature suitable 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 of the constituents occurs. This allows decanting and discharge of the water fraction to the plant's sewer. The solvent and grease mixture is sent from the tanks to a stripping column, which recovers the solvent for reuse. Grease is then isolated for sale 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 either by decanting or by skimming the grease from the top of the tanks. The skins are then placed in drums with a lime slurry and sulfide sharpeners. This step removes the remaining embedded portion of the hair from the skins. Removal of the remaining hair "stubble" requires essentially a complete hair burn process as used in a cattlehide tannery.

Tanyard Processes

The bating operation is similar to that used in cattlehide tanning and occurs in the same drums used for liming.

As in the cattlehide tanning, the skins are placed in an acid bath for pickling to prevent precipitation of chromium salts and to facilitate tanning. The constituents required for this process are added to the same drums used for bating and liming.

Pigskins may be either chromium tanned or vegetable tanned. The major pigskin tanner in the United States, however, uses the chromium tanning process exclusively. Chrome tanning is conducted in the same drums used for liming, bating, and pickling. Pigskins are immersed in a solution of chromium sulfate and tanned completely in this operation, eliminating any need for a retan operation.

After being tanned, the skins are tumble dried, split, and shaved to 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 processed further.

Color, Fatliquor, and Finishing Processes.

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. Fatliquoring is also quite similar to cattlehide and sheepskin fatliquoring, as are the subsequent dry subprocesses.

SECTION IV

INDUSTRY SUBCATEGORIZATION

A. 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 homogeneous groups or subcategories. EPA found that the most significant factors for subcategorizing the leather tanning and finishing industry were the types of raw materials processed and the manufacturing processes employed. Analysis of all available data indicated that these two factors resulted in different water use and pollutant loads which require different sizes and costs of model pretreatment and complete treatment systems, and result in different rates of mass discharge [kg/kkg (lb/1,000 lb)] for treated effluents. Final product mix was found to be related incidentally to the subcategories established after consideration of raw materials and manufacturing processes employed.

The raw material of the leather tanning industry is the hide or skin type. The type of raw material received by the facility determines the major groups of subprocesses required to manufacture finished or partially processed (e.g. "wet blue" grain sides or splits) leather. For example, some tanneries process previously unhaired and tanned hides or skins, thus eliminating the need for beamhouse and tanyard operations. Other significant manufacturing process considerations include the tanning agent utilized (chromium versus vegetable or other nonchromium) 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 raw material, and process.

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

1. raw material
    a. cattlehide,
    b. grain sides,
    c. split,

    d. pickled sheepskin,
    e. shearling,
    f. pigskin;
2. manufacturing processes
    a. beamhouse operations,
    b. tanning process (chromium, vegetable, alum),
    c. finishing operations (including retanning);
3. final products
4. plant size
5. plant age
6. plant location and inherent climate
7. wastewater characteristics and treatability
8. engineering aspects of the application of various treatment technologies
9. non-water quality impacts
10. economic impacts.

EPA has determined that raw material and manufacturing process necessary to produce typical mixes of final products are the significant factors in subcategorizing the leather tanning and finishing point source category. The original development document (1974) grouped tanneries into six subcategories. The subcategorization proposed in 1979 included seven subcategories, with the shearling subcategory added to the six promulgated in 1974. Nine subcategories have been developed for the regulations as promulgated on November 23, 1982, and presented in Table IV-1.

The nine subcategories are defined below.

1. Hair Pulp/Chrome Tan/Retan-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 trivalent chromium and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, garments, upholstery, and gloves and lining material.

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 trivalent chromium and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, handbags, garments and gloves.

3. Hair Save or Pulp/Non-chrome Retan/Retan-Wet Finish - facilities which process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving, or loosening and mechanically removing the hair; tanning primarily with vegetable tannins, although other chemicals may be used such as alum,

syntans, oils, or others; and retanning and wet finishing. Primary uses for the final products of this subcategory include sole leather, lace, harness, and saddle leather, mechanical strap and skirting leather, and sporting good leathers (basketballs, footballs, softballs, baseballs, etc).

TABLE IV-1

SUBCATEGORY COMPARISON BY PRINCIPAL PROCESSES

Revised Subcategory	EPA Development Document July 1979 Subcategory
1. Hair Pulp, Chrome Tan, Retan-Wet Finish	1
2. Hair Save, Chrome Tan, Retan-Wet Finish	2
3. Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish	3
4. Retan-Wet Finish (Sides)	4
5. No Beamhouse	5
6. Through-the-Blue	6
7. Shearling	7
8. Pigskin	1,5
9. Retan-Wet Finish (Splits)	4

4. Retan/Wet Finish (Sides) - facilities which process previously unhaired and tanned "wet blue" grain sides into finished leather through retanning with trivalent chromium, syntans, vegetable tannins, or other tanning agents, coloring with dyes, and wet finishing processes including fatliquoring, drying (especially pasting frame or vacuum), and mechanical conditioning. Primary uses for the final products of this subcategory include shoe uppers, garments, and personal goods.

5. No Beamhouse - facilities which process previously unhaired and pickled cattlehides, sheepskins, or pigskins into finished leather by tanning with trivalent chromium or other agents, then

retanning and wet finishing. Primary uses for the final products of this subcategory include garments, shoe uppers, gloves and lining material.

6. Through-the-Blue - facilities which process raw or cured cattle or cattle-like hides only through the "wet-blue" tanned state by chemically dissolving or loosening the hair and tanning with trivalent chromium. No retanning or wet finishing is performed. The "wet blue" stock produced by this subcategory is subjected to further processing by plants in subcategory 4 (grain sides) and plants in subcategory 9 (splits).

7. Shearling - facilities which process raw or cured sheep or sheep-like skins with hair intact into finished leather by tanning with trivalent chromium or other agents, retanning, and wet finishing. Primary uses for hair on sheepskins (shearling) of this subcategory include hospital products, wool lined suede coats and similar garments or specialty footwear, and seat covers.

8. Pigskin - facilities which process raw or cured pigskins into finished leather by chemically dissolving the hair and tanning with trivalent chromium, then retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers and gloves.

9. Retan/Wet Finish (Splits) - facilities which process previously unhaired and tanned splits into finished leather through retanning and wet finishing processes that include coloring, fatliquoring, and mechanical conditioning. Primary uses for the final products of this subcategory include sueded leathers for garments, shoe uppers, gloves, and other specialty or personal goods.

B. RATIONALE FOR SUBCATEGORIZATION

1. Raw Material

The hide or skin type received by a tannery and the state of preprocessing of these hides or skins imposes specific processes on the manufacture of leather products. Hides or skins which have been unhaired previously and acid preserved ("pickled") do not require beamhouse operations. Hides or skins which have been tanned with chromium and are in the "wet blue" state do not require either unhairing or tanning; only retanning and wet finishing are required to produce finished leather (subcategory 4 -- retan-wet finish-sides; subcategory 9-- retan-wet finish-splits). Some plants do not produce finished leather, but rather produce blue stock (grain sides and splits) which are sold to another firm or shipped to another plant owned by the same company for retanning and wet finishing into "crust" leather (subcategory 6--through-the-blue). In all of these cases, the wastewater volumes and pollutant loads generated vary because of the differences in processing required for these different raw materials. This relationship between raw material and manufacturing process establishes hide or skin type as a basis for industry subcategorization.

The presence and length of hair on the hides or skins being tanned is another factor that has bearing on the manufacturing processes employed and the resulting water use and pollutant loads. Removing hair (beamhouse subprocesses) increases most pollutant parameters, such as biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solids (TSS), total Kjeldahl nitrogen (TKN), and sulfides. The proposed industry subcategorization in 1979 separated shearling tanning from the other no beamhouse operations because of the nature of the raw material. Preparation for tanning of sheepskins with the wool intact (shearlings) requires significantly more washing than is required for pickled sheepskins or cattlehides without hair. This results in higher flows and waste loads for shearling operations than for pickled sheepskins (included in subcategory 5--no beamhouse), and therefore warrants a distinct subcategory for shearlings. In the regulation promulgated in 1974, pigskins originally were included in the no beamhouse subcategory. However, in the 1979 proposal pigskin processing was moved to subcategory 1 because of the use of the unhairing process necessary to remove the short hair stubble. The June 2, 1982 notice of availability (47 FR 23958) separated retanning and wet finishing into two subcategories because of the different raw waste loads and water use associated with the retanning of grain sides versus splits. Pigskins (subcategory 8) also were separated from subcategory 1 and a separate subcategory was established because of differences in water use and pollutant loads resulting from production requirements for this raw material.

Table IV-2 presents data regarding variation in wasteloads attributable to processing of winter hides and summer hides. The industry has contended in the past that processing of heavier manure laden and longer haired winter hides increases the difficulty of wastewater treatability, and therefore should be considered as a factor in subcategorization. It can be seen from the table that normalized raw waste loads (kg/kkg) are generally lower during winter months than during summer months.

TABLE IV-2

COMPARISON OF SUMMER/WINTER RAW WASTELOADS FROM A SUBCATEGORY ONE TANNERY

Parameter	Average Raw Wasteload (kg/kkg) Summer	Winter
TSS	99.68	92.26
BOD_5	88.77	78.12
COD	206.96	183.68
Sulfide	4.55	3.79
TKN	8.93	9.80
NH_3	4.16	3.58

Therefore processing of winter hides does not contribute to increased wastewater pollutant loads and treatment system operational difficulty during winter months.

For the purpose of subcategorizing tanneries, three basic hide/skin types are important:

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

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

3. Pig or pig-like skins have short hair or are hairless and are also relatively light. This group includes only skins which have little hair, yet typically require unhairing operations.

Further separation of subcategory 5 (no beamhouse) according to raw materials (sheepskins versus cattlehides) was not warranted because the difference in median water use of pickled sheepskins (6.6 gal/lb or 55.1 l/kg) versus pickled cattlehides (5.5 gal/lb or 45.9 l/kg) was not significant compared to the median water use for the combined subcategory (5.8 gal/lb or 48.4 l/kg). Water use ratios for this subcategory are displayed in Table IV-3.

TABLE IV-3

EFFECT OF SUBDIVIDING SUBCATEGORY FIVE INTO TWO SUBCATEGORIES

Tannery Number	Complete Subcategory Data Base Water Use Ratio (gal/lb(ℓ/kg))	Tanneries Processing Pickled Cowhide Water Use Ratio (gal/lb(ℓ/kg))	Tanneries Processing Pickled Sheepskins Water Use Ratio (gal/lb(ℓ/kg))
88	3.5 (29.2)	-	3.5 (29.2)
700	3.8 (31.7)	-	3.8 (31.7)
285	3.8 (31.7)	3.8 (31.7)	-
51	4.0 (33.4)	-	4.0 (33.4)
75	5.5 (45.9)	5.5 (45.9)	-
615	5.6 (46.7)	-	5.6 (46.7)
92	5.8 (48.4)	-	5.8 (48.4)
380	6.6 (55.1)	6.6 (55.1)	-
556	7.4 (61.8)	-	7.4 (61.8)
522	7.8 (65.1)	-	7.8 (65.1)
319	8.5 (70.9)	-	8.5 (70.9)
169	11.0 (91.8)	-	11.0 (91.8)
220	13.5 (113)	-	13.5 (113)
Median Water Use Ratio	5.8 (48.4)	5.5 (45.9)	6.6 (55.1)

2. Manufacturing Processes

a. Beamhouse Operations. Beamhouse operations have a significant bearing on subcategorization. At tanneries that have a beamhouse, unhairing operations typically contribute high raw waste flows and loadings. The specific unhairing process (i.e., either hair pulp or hair save) also affects beamhouse waste characteristics and loadings, since hair dissolving (or pulping) generates higher total wastewater flows and pollutant loads than hair saving. Therefore, EPA has subcategorized the leather tanning industry to reflect the presence (subcategories 1, 2, 3, 6, 8) or absence (subcategories 4, 5, 7, 9) of beamhouse operations and variations of beamhouse operations (subcategories 1 and 2):

i. Hair pulp. Hair is chemically dissolved from the hide/skin using lime and sulfides/sulfhydrates and enters the liquid waste stream. Resulting wastewaters are very high in pH (10-12) containing high concentrations of dissolved hair (organic protein) and sulfides.

ii. Hair save. Hair (or wool) is chemically softened and removed mechanically. The major portion of the hair is removed as a solid, which allows hair to be segregated from the liquid waste stream. Residual roots and fragments may enter the waste stream. Industry trends favor the hair pulp process, primarily because the hair save process requires more time and labor, and therefore higher production costs than the hair pulp process. Moreover, the cost of washing and baling removed hair for sale as a byproduct is no longer offset by the price it brings. In some areas, no hair by product market exists at all and landfilling is necessary.

iii. No beamhouse. Hides or skins received with the hair already removed do not require beamhouse operations, and the tannery does not generate the beamhouse-type high pH waste loads that are heavily laden with proteinaceous organic matter and sulfides. Raw materials that require little or no hair removal, such as pickled sheepskins, pickled cattlehides, and shearlings, are included in this group.

b. Tanning Process. The volume and pollutant load of the wastewater from this process depends mostly on the tanning agent used. Tanners in the United States use many different agents, including trivalent chromium, vegetable tannins, alum, and synthetic tannins (syntans). Chromium tanning is used for more than 80 percent of the leathers produced. Vegetable tanning dominates the balance of leathers produced. Non-chromium tanning methods, primarily vegetable tanning, generate highly colored waste streams, but flows and waste loads are slightly less than those from chromium tanning operations. Facilities that only retan and finish previously tanned hides require separate consideration because their waste stream contains reduced mass of residual tanning compounds, such as chromium.

The presence or absence and type of tanning processes used influence the flow, waste characteristics, and pollutant loadings for each tannery's waste stream. EPA has taken into account different tanning processes and has subcategorized the industry accordingly:

i. Chromium tanning. At least 80 percent of all leather tanned is chromium tanned. Subcategory numbers 1, 2, 5, 6, 7, and 8 utilize tanning with trivalent chromium. Chromium levels in tanning wastewater can vary. This results from some facilities' use of setting agents to increase the chromium uptake ("exhaustion") in the hide substance. Generally a 60 to 70 percent uptake level is now typical of the industry but it can be as high as 95 percent or above.

ii. Non-chromium tanning. Less than 20 percent of the total tannage is not chromium tanned. The primary non-chromium tanning agent is vegetable tannins (primarily extracts from specific types of tree bark); of lesser importance are alum, synthetic agents ("syntans"), oil, and others.

iii. Previously tanned. No tanning is performed when the plant receives fully tanned hides which require only retanning and finishing.

c. Retanning and Wet Finishing Operations. The presence or absence of retanning and wet finishing is significant for industry subcategorization. Taken together these subprocesses, primarily including retanning (chromium, syntans, vegetable, others), dying or coloring (aniline and other synthetic organic dyestuffs), fatliquoring (natural oil replenishment for lubrication primarily by synthetic sulfonated oils), drying, buffing (mechanical grain correction as necessary), and finishing (primarily water based coatings, but some solvent based, applied in spray booths), contribute significantly to the total waste stream of tanneries with or without a beamhouse, most importantly to total water use. At tanneries with no beamhouse, retanning and wet finishing operations have a considerable impact on total waste flows and pollutant loadings.

Some tanneries restrict processing to the retanning and wet finishing of hides, skins, or splits received in the tanned state (subcategories 4 and 9). These facilities' water usage and raw waste loadings are considerably less than those at more complex tanneries, which unhair and tan hides.

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

3. Manufacturing Subprocesses

The Agency has attempted throughout the rulemaking process for this industry to develop subcategories based on the subprocesses (e.g. bating, pickling, etc.) which comprise each of the three major groups of subprocess (beamhouse, tanyard, retan-wet finish). However, the data available for this industry do not permit this approach to subcategorization because subprocess wastewaters at most plants are dumped onto open floors, thus not permitting accurate measurement of volumes of wastewaters generated. These subprocesses also are batch in nature and would require prohibitive sampling and analytical expense for most plants to generate a statistically meaningful amount of data for each subprocess. Further, once these wastewaters have been dumped, they travel through combined sewers at most plants, thus further complicating the development of accurate flow and pollutant load data for each subprocess. Finally, in order to complete subprocess mass balances detailed raw material mass inventories for each subprocess are required; such data typically does not exist except for processing chemical needs. Therefore, the Agency's subcategorization methodology has been based on the major groups of subprocesses because available data indicates that subcategorization based on subprocess groups is appropriate.

4. Final Products

The typical mixes of final products within subcategories are well defined, and have been identified above for each subcategory. Final product variations within subcategories do occur, but they are relatively minor in their influence on water use and waste load generation because the major groups of subprocesses required to produce them are the same. The day to day variations in processing needed to produce these mixes of final products is represented in the variability of individual water use data points over the long term at individual plants and when aggregated represent the total range of water use within each subcategory. In response to comments criticizing the Agency's failure to subcategorize by final products the Agency evaluated further separations within subcategories by finite product groupings, but these separations were not found to be needed. For example, in response to comments, subcategory 1 was further separated into three trial subcategories, plants which produced leather for upholstery, garments, and shoe uppers (Table IV-4). The resulting differences in median water use for shoe uppers as compared with the median water use for subcategory 1 were not significant (6.4 vs 6.5 gal./lb or 53.4 vs 54.2 l/kg), and only marginally different for upholstery versus the subcategory median water use (5.4 vs 6.5 gal/lb or 45.1 vs 54.2 l/kg). The categorization for garment and glove leather did show a significant difference in median water use (3.8 vs 6.5 gal/lb or 31.7 vs 54.2 l/kg). A separation was not made because only four out of 28 plants were included in this final product group and these four plants would have been able to meet the selected flow ratios. The Agency also categorized subcategory 3 into two categories: shoe sole leather (vegetable tanned), and other nonchromium mineral tanned products (Table IV-5). The resulting median water use ratios for these trial subcategories were essentially identical to the subcategory 3 median water use ratio (sole leather - 4.9 vs 4.9 gal/lb (40.9 l/kg) i.e., no change; mineral tanned products 4.8 vs 4.9 gal/lb (40.1 vs 40.9 l/kg). Further discussion of water use is presented in Section V of this Development Document.

The quality of final products is related both to quantitative and qualitative measures. Quantitative measures include standard tests utilized in industry laboratories by tanners and their customers (e.g. - shoe manufacturers) to determine leather properties germane to their intended use. For example, determinations of the percent of chromium content by weight (e.g., 3.3 percent), the "boil" test, and other tests of mechanical properties, provide standardized bases for determining whether final leather products are acceptable for their intended use. Detailed data on leather quality variation as measured by these tests has not been supplied by the industry and therefore correlation with variation of water use has not been possible. The qualitative measures of final product quality, such as the "feel" of leathers, are important but subjective and variable in nature and cannot be quantified. Therefore, any attempt to relate subcategorization and resulting differences in water use quantitatively to the feel or appearance of leather would be difficult if not impossible. Moreover, there have been no data made available to the Agency to make such correlations which would permit further subcategory separations. The data utilized by the Agency does, however, represent a variety of commercially salable leather products and associated qualities separated into nine well defined groups of raw materials, processing methods, and final product mixes.

TABLE IV-4

EFFECT OF REMOVING SELECTED TANNERY SUBGROUPS FROM SUBCATEGORY ONE

Number of Plant	Complete Subcategory 1 Data Base Water Use Ratio (gal/lb (ℓ/kg))	Upholstery Leather Subgroup Water Use Ratio (gal/lb (ℓ/kg))	Subcategory 1 without Upholstery Subgroup Water Use Ratio (gal/lb (ℓ/kg))	Garment and Glove Subgroup Water Use Ratio (gal/lb (ℓ/kg))	Subcategory 1 without Garment and Glove Subgroup Water Use Ratio (gal/lb (ℓ/kg))	Shoe Uppers Subgroup Water Use Ratio (gal/lb (ℓ/kg))	Subcategory 1 without Shoe Uppers Subgroup Water Use Ratio (gal/lb (ℓ/kg))	Hide Processors used Water Use Ratio (gal/lb (ℓ/kg))	No Hide Processors Water Use Ratio (gal/lb (ℓ/kg))
248	3.0 (25.0)	-	3.0 (25.0)	-	3.0 (25.0)	3.0 (25.0)	-	*	*
383	3.1 (25.9)	-	3.1 (25.9)	3.1 (25.9)	-	-	3.1 (25.9)	-	3.1 (25.9)
520	3.2 (26.7)	-	3.2 (26.7)	3.2 (26.7)	-	-	3.2 (26.7)	*	*
274	3.8 (31.7)	3.8 (31.7)	-	-	3.8 (31.7)	-	3.8 (31.7)	-	3.8 (31.7)
246	4.3 (35.9)	-	4.3 (35.9)	4.3 (35.9)	-	-	4.3 (35.9)	-	4.3 (35.9)
525	4.5 (37.6)	4.5 (37.6)	-	-	4.5 (37.6)	-	4.5 (37.6)	-	4.5 (37.6)
438	5.4 (45.1)	-	5.4 (45.1)	5.4 (45.1)	-	-	5.4 (45.1)	-	5.4 (45.1)
245	5.4 (45.1)	-	5.4 (45.1)	-	5.4 (45.1)	5.4 (45.1)	-	*	*
80	5.5 (45.9)	-	5.5 (45.9)	-	5.5 (45.9)	5.5 (45.9)	-	-	5.5 (45.9)
237	5.7 (47.6)	-	5.7 (47.6)	-	5.7 (47.6)	5.7 (47.6)	-	5.7 (47.6)	-
235	6.0 (50.1)	-	6.0 (50.1)	-	6.0 (50.1)	6.0 (50.1)	-	6.0 (50.1)	-
425	6.1 (50.9)	-	6.1 (50.9)	-	6.1 (50.9)	-	6.1 (50.9)	6.1 (50.9)	-
262	6.2 (51.7)	6.2 (51.7)	-	-	6.2 (51.7)	-	6.2 (51.7)	-	6.2 (51.7)
206	6.4 (53.4)	-	6.4 (53.4)	-	6.4 (53.4)	-	6.4 (53.4)	-	6.4 (53.4)
13	6.5 (54.2)	-	6.5 (54.2)	-	6.5 (54.2)	6.5 (54.2)	-	6.5 (54.2)	-
103	6.8 (56.8)	-	6.8 (56.8)	-	6.8 (56.8)	6.8 (56.8)	-	*	*
431	7.0 (58.4)	-	7.0 (58.4)	-	7.0 (58.4)	7.0 (58.4)	-	7.0 (58.4)	-
626**	7.5 (62.6)	-	7.5 (62.6)	-	7.5 (62.6)	-	7.5 (62.6)	*	*
6**	7.6 (63.4)	-	7.6 (63.4)	-	7.6 (63.4)	-	7.6 (63.4)	*	*
432	7.8 (65.1)	-	7.8 (65.1)	-	7.8 (65.1)	-	7.8 (65.1)	-	7.8 (65.1)
632**	7.9 (65.9)	-	7.9 (65.9)	-	7.9 (65.9)	-	7.9 (65.9)	*	*
231	8.9 (74.3)	8.9 (74.3)	-	-	8.9 (74.3)	-	8.9 (74.3)	8.9 (74.3)	-
31	8.9 (74.3)	-	8.9 (74.3)	-	8.9 (74.3)	8.9 (74.3)	-	-	8.9 (74.3)
58	9.7 (81.0)	-	9.7 (81.0)	-	9.7 (81.0)	9.7 (81.0)	-	-	9.7 (81.0)
37185	9.9 (82.6)	-	9.9 (82.6)	-	9.9 (82.6)	-	9.9 (82.6)	-	9.9 (82.6)
57	10.5 (87.6)	-	10.5 (87.6)	-	10.5 (87.6)	-	10.5 (87.6)	-	10.5 (87.6)
409	10.7 (89.3)	-	10.7 (89.3)	-	10.7 (89.3)	10.7 (89.3)	-	-	10.7 (89.3)
87	11.5 (96.0)	-	11.5 (96.0)	-	11.5 (96.0)	-	11.5 (96.0)	11.5(96.0)	-
Median Water Use Ratio	6.5 (54.2)	5.4 (45.1)	6.7 (55.9)	3.8 (31.7)	6.9 (57.6)	6.5 (54.2)	6.4 (53.4)	6.5 (54.2)	6.3 (52.6)

*Specific information on use of hide processors not available.

**Detailed product data not available for these tanneries.

TABLE IV-5

EFFECT OF SUBDIVIDING SUBCATEGORY THREE INTO TWO SUBCATEGORIES

Number of Plant	Complete Subcategory Data Base Water Use Ratio (gal/lb(ℓ/kg))	Tanners using Vegetable Tanning Agents Water Use Ratio (gal/lb(ℓ/kg))	Tanners Using Other Non-chrome Tanning Agents Water Use Ratio (gal/lb(ℓ/kg))	Hide Processors Used Water Use Ratio (gal/lb(ℓ/kg))	No Hide Processors Water Use Ratio (gal/lb(ℓ/kg))
385	2.3 (19.2)	2.3 (19.2)	-	-	2.3 (19.2)
415	3.0 (25.0)	3.0 (25.0)	-	-	3.0 (25.0)
47	3.1 (25.9)	-	3.1 (25.9)	-	3.1 (25.9)
397	4.2 (35.1)	4.2 (35.1)	-	4.2 (35.1)	-
46	4.8 (40.1)	4.8 (40.1)	-	-	4.8 (40.1)
186	4.8 (40.1)	-	4.8 (40.1)	4.8 (40.1)	-
388	4.9 (40.9)	4.9 (40.9)	-	4.9 (40.9)	-
399	4.9 (40.9)	4.9 (40.9)	-	-	4.9 (40.9)
404	7.7 (64.3)	-	7.7 (64.3)	-	7.7 (64.3)
239	7.9 (65.9)	7.9 (65.9)	-	7.9 (65.9)	-
24	8.2 (68.4)	8.2 (68.4)	-	8.2 (68.4)	-
376	9.6 (80.1)	9.6 (80.1)	-	-	9.6 (80.1)
Median Water Use Ratio	4.9 (40.9)	4.9 (40.9)	4.8 (40.1)	4.9 (40.9)	4.8 (40.1)

5. Wastewater Characteristics and Treatability

To assess the subcategorization of the leather tanning industry with respect to wastewater characteristics and treatability, the Agency reviewed information from various sources. A substantial amount of data were available for "classical" pollutant parameters (biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and total suspended solids (TSS)), and lesser amounts of data for oil and grease, chromium (total), sulfide, TKN, and ammonia. Information on other toxic pollutants was limited essentially to data generated during the course of this study. The final effluent data after application of BPT technology (discussed in Section VIII) for flow, BOD_5, TSS, sulfide, and chromium supports the updated industry subcategorization set forth above. The same treatment technologies, including equalization, primary coagulation-sedimentation, and secondary biological treatment in the form of high solids extended aeration activated sludge, are capable of treating the raw wastewaters associated with the various industry segments. The preliminary treatment technologies and their design vary with subcategory by presence or absence of beamhouse operations and tanyard operations. 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 and alteration of primary clarifier sizes, and hydraulic detention time and aeration capacity for activated sludge aeration basins. There is, however, no need to further subcategorize industry operations in terms of wastewater treatability since the same final effluent concentrations can be achieved by plants in all subcategories. The mass limitations (kg/kkg) will vary according to subcategory since they are dependent on water use (l/kkg).

The principal raw wastewater (not treated effluent, as noted above) characteristics considered for subcategorization were: 1) five-day biochemical oxygen demand (BOD_5) expressed in kilograms (kg) per thousand kilograms (kkg) of hide, or pounds (lb) per thousand pounds (1,000 lb); and 2) flow in liters per kg (gallons/lb) of hide. Although BOD_5 is associated with all tannery wastewater, it is present at different concentrations or loadings depending on the nature of the raw material and the manufacturing processes employed. Mass of BOD_5 per unit of unprocessed hide weight reflects many factors, including: 1) type of hide or skin processed (e.g., pickled sheepskin versus shearling; retanning and wet finishing grain sides versus splits); and 2) presence of any of the three major groups of subprocesses (beamhouse, tanyard, retan-wet finish) in the operation. For example, a "full line" cattlehide tannery [subcategory 1] generates a different mass (kg/kkg of raw material) of BOD_5 than a through-the-blue tannery [subcategory 6] or a plant which employs only retanning and wet finishing [subcategories 4 and 9].

Water use was found to vary in a manner similar to BOD_5. Raw materials result in different median water uses. For example, the processing of shearlings (subcategory 7) uses 9.4 gal/lb (78 l/kg) which is substantially more than the processing of pickled sheepskins (5.8 gal/lb or 48 l/kg). Likewise the processing of cattlehides into finished leather (subcategory 1) requires 6.5 gal/lb (54 l/kg) while the processing of pigskins (subcategory 8) requires only 5.0 gal/lb (42 l/kg). The groups of subprocesses employed also result in different water use ratios. For instance, a retan-wet finish (splits) tannery uses only 3.0 gal/lb (25 l/kg) while a hair pulp/ chrome tan/retan-wet finish tannery uses 6.5 gal/lb (54 l/kg). Similarly a tannery with only beamhouse and tanyard operations (through-the-blue) use 2.1 gal/lb (18 l/kg). The differences in water use and raw waste characteristics are detailed in Section V of this document. These differences in raw wastewater BOD_5 and water use have been accounted for by the subcategorization scheme because they are related to raw materials and processing methods and therefore they do not require further subcategorization.

Total suspended solids (TSS) data reinforce the conclusions derived from BOD_5 and flow data. If hides are being unhaired, TSS loads will be noticeably higher than at tanneries which do no unhairing. Another parameter, chemical oxygen demand (COD), is also much higher where beamhouse operations are present. Because these differences in TSS and COD found in raw wastewater are related to differences in raw materials and processes used, further subcategorization based on these pollutants is not necessary.

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 "chromium" and "non-chromium" processes in the subcategorization. The amount of chromium in raw wastewaters indicates whether a plant operates both tanning and retanning processes, or merely retans partially processed stock. Very low chromium concentrations and highly colored (typically brown) wastewaters are indicative of vegetable tanning. Sulfides originate from chemicals used in the beamhouse and from residues of these chemicals in the hides. The amount of sulfide present in the wastewater depends on the presence and type of unhairing process used. Sulfide concentrations are higher for hair pulp than for hair save.

Both chromium and sulfide levels can be controlled by in-plant measures and efficient treatment processes. Generally, the type of in-plant controls found in a plant depend on the pollutant levels in the process stream. In the case of chromium 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, plants in all subcategories can use the same end-of-pipe technologies for effluent treatment. Therefore, because both chromium and sulfide are related to raw materials and process employed neither chromium nor sulfide were found to be factors requiring further or different subcategorization.

In evaluating effluent discharges for subcategorization, EPA considered several other waste load parameters, including nitrites and nitrates, total Kjeldahl nitrogen (TKN), ammonia, total dissolved solids, total volatile solids, oil and grease, chlorides, total alkalinity, phenols, and fecal coliform. In each case, available 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. However, in the case of TKN and ammonia, the presence of high concentrations of these pollutants does influence the design and increase the cost of nitrification technology.

Toxic pollutants were found in the wastewaters at a majority of the sampled plants. Therefore, at least one toxic pollutant from each analytical grouping (acid extractible organics; base-neutral extractible organics) or pollutant type (metals, organics) is likely to be present in wastewater from plants in most subcategories. However, the number of pollutants found per subcategory varies. The Agency found a total of 52 of the 129 toxic priority pollutants in untreated tannery wastewaters. The number present per subcategory varied from 35 for subcategory 3 tanneries to eight for tanneries in subcategory 9. (See Tables V-24 and V-25 in Section V). Twenty-six toxic priority pollutants were detected in the intake process water used by tanneries. Chromium is the single priority pollutant whose levels in untreated wastewater followed a definite concentration and mass loading pattern. This finding substantiates the subcategorization scheme that distinguishes among plants that tan with chromium and those that do not.

EPA found no other discernible pattern in the concentration of the toxic pollutants discharged in all subcategories. Because the presence of toxic constituents varied among individual subcategories with no discernible pattern, their presence and treatability do not appear to be a factor in subcategorization.

6. Size and Age

EPA defines the size of a tannery as the number or weight of hides and skins processed in a day. Most subcategories contain plants of various sizes. The ratio of flows and raw pollutant loadings per unit of production remains reasonably constant, independent of plant size. The Agency found no other factors which coincide with plant size to be relevent for subcategorizing the industry. Figure IV-1 shows flow ratio vs plant size.

A plant's age had no bearing on its operations or wastewater generation. The physical structures for most plants are quite old, but even the new 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.

Figure IV-2 shows flow ratio vs. plant age.

7. Location

There was no discernible relationship between plant location and raw waste loadings, nor do a tannery's location and source of raw material necessarily coincide. Figure IV-3 shows flow ratio (water usage) vs. location. Hides and skins are usually purchased for specific product applications. With rare exceptions, the location of a plant and its source of raw material are unrelated.

Climate, directly related to geographical location, also does not influence the processing activities of tanneries in the nine subcategories. For a given raw material, the selection of processing steps remains the same. Water use and raw waste loads are not affected by climate, since they depend primarily on the type of hide or skin processed and on manufacturing processes employed to produce the typical mix of final products. Furthermore, the Agency found that climate does not affect the treatability of wastewaters and achievable final effluent concentrations. Climate does, however, have some bearing on the design, equipment selection, and, especially the operating requirements of treatment systems. For example, in selecting aeration equipment for activated sludge aeration basins (see Appendix A), floating surface aerators were not selected for plants in northern climates because they can freeze and become inoperative. In these cases, submerged static tube aerators were selected because their function is not affected by ambient air temperature.

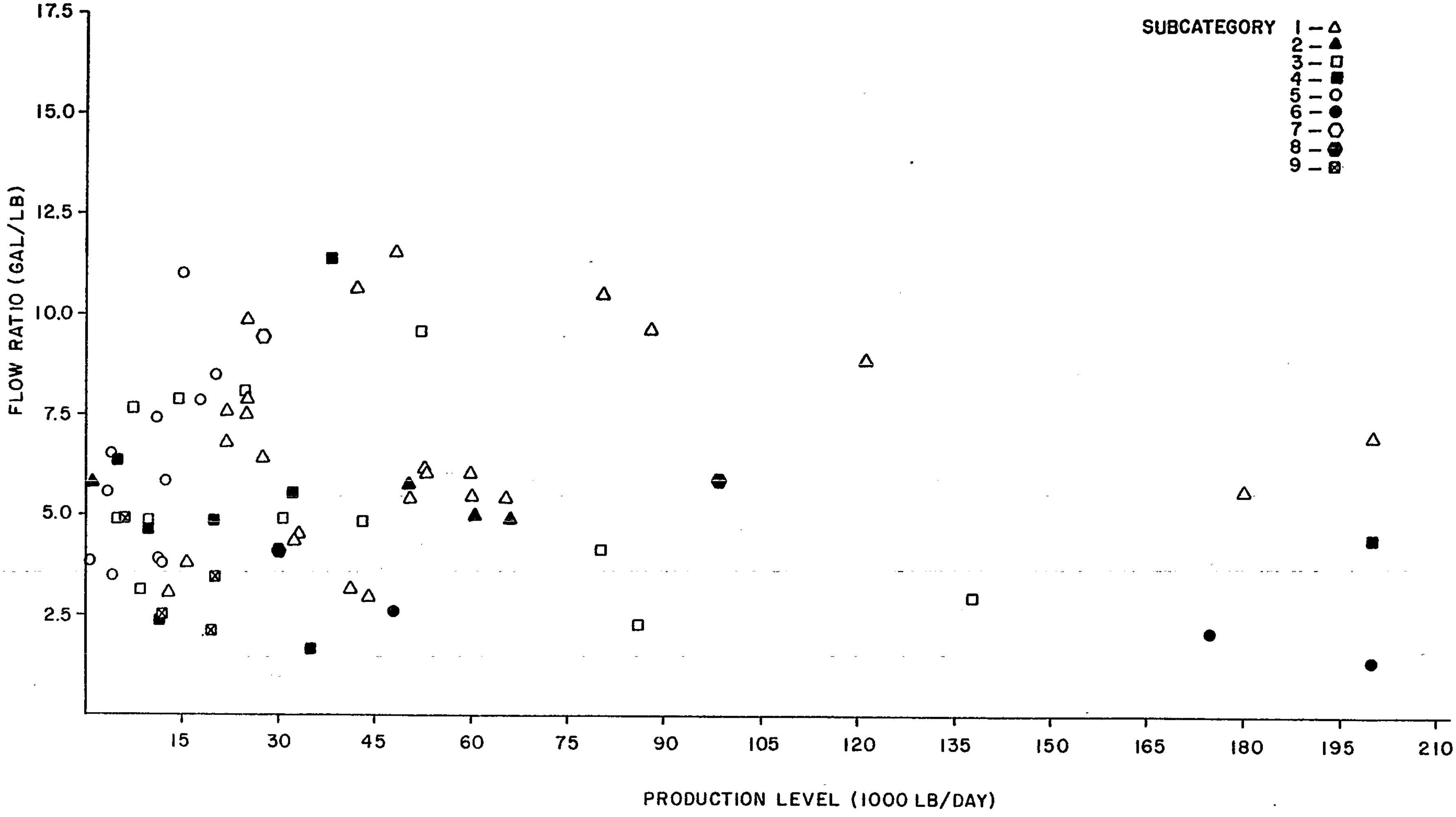

FIGURE IV-1 FLOW RATIO VS PRODUCTION LEVEL

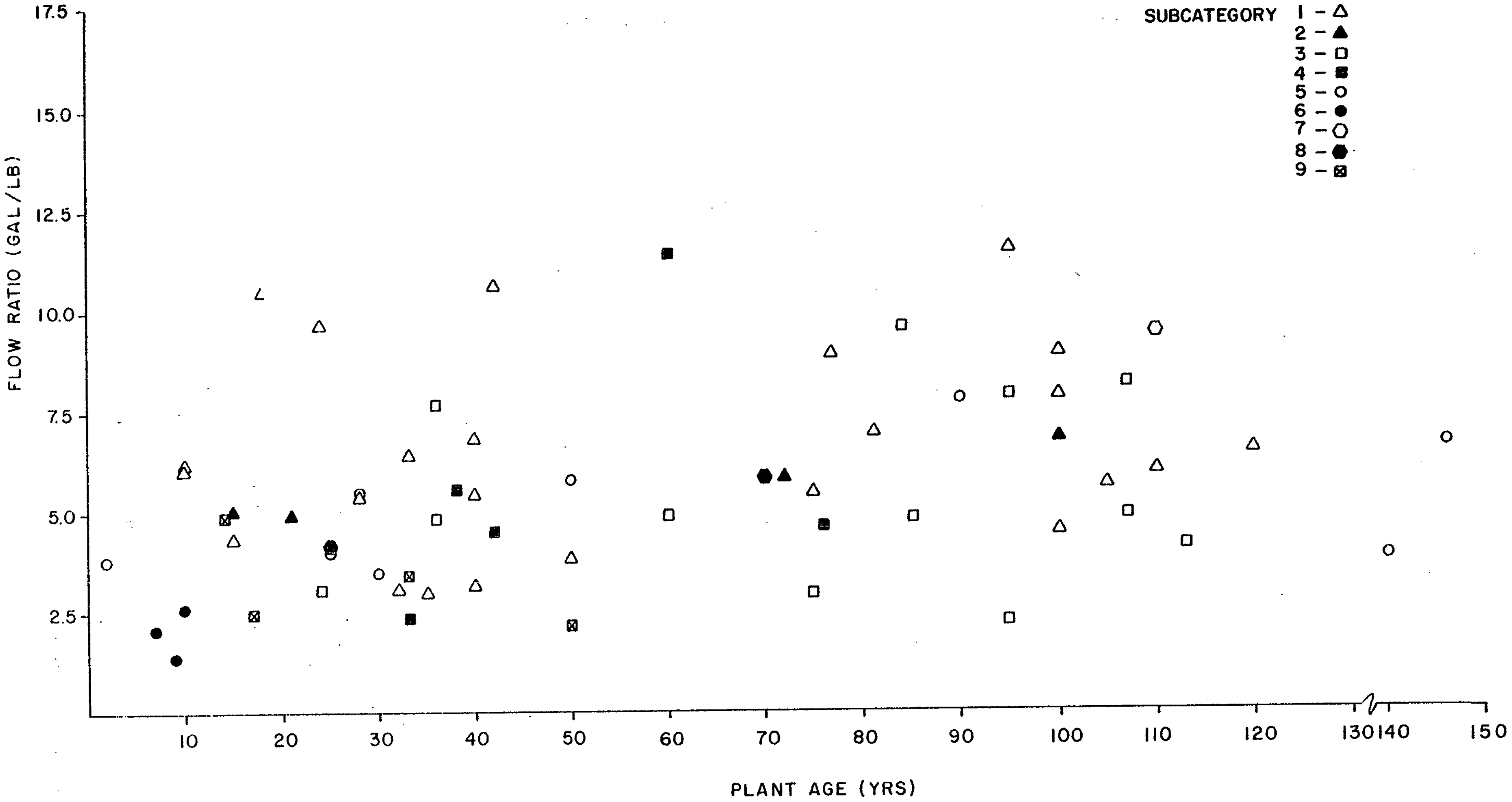

FIGURE IV-2 FLOW RATIO VS PLANT AGE

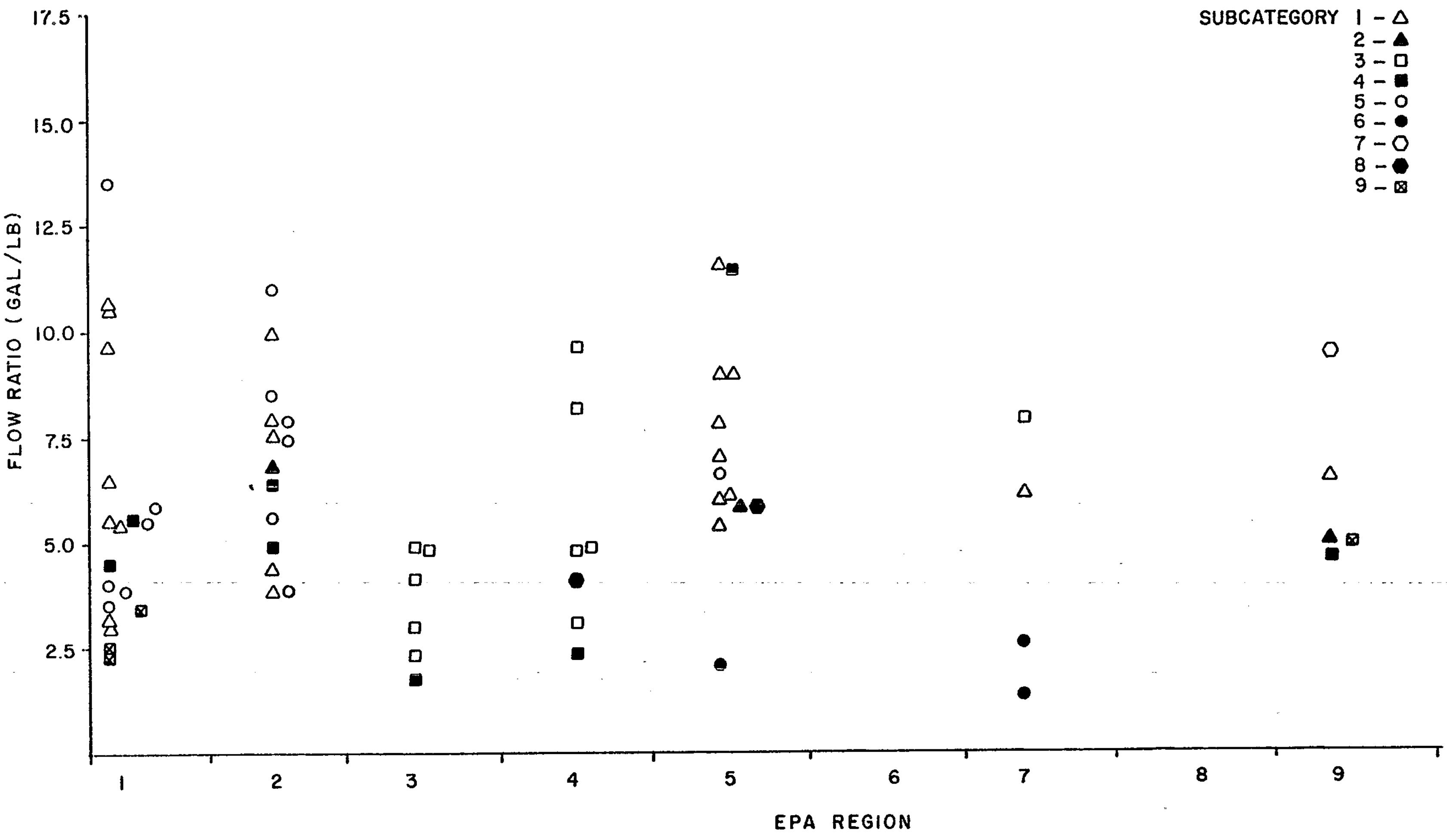

FIGURE IV-3 FLOW RATIO VS EPA REGION

Climate does not affect the treatability of pollutants in extended aeration-activated sludge systems, assuming the systems have been designed carefully and are operated and maintained diligently. In fact, certain treatment facilities operating in the most severe northern climates have been selected as model systems for the leather tanning industry (see Section VII), though these plants can be expected to incur somewhat higher costs to ensure consistent operation during winter months. Where appropriate, these factors have been considered in the types of treatment system components selected such as submerged static aeration equipment, heated buildings to house pumps, electrical control equipment, and sludge dewatering equipment (i.e., filter presses), and their costs. Therefore, further subcategorization of the leather tanning industry based on climate is not warranted.

8. Economic Impact

In order to evaluate the potential impacts, economic model plants were developed to represent model plants according to industry subcategory, size and type of discharge (direct or indirect). The plants with direct discharge were analyzed individually for closures and production and employment effects. The major decision criteria for plant closure are based on net present values (NPV) and cash flows. Further detailed discussion of this analysis and the underlying methodology are presented in the Economic Impact Analysis of Effluent Limitations and Standards for the Leather Tanning and Finishing Industry.

The results of the economic analysis projected that 9-12 of 18 small plants in subcategories 1, 3, and 9 may close rather than incur the costs of chromium control required by PSES. Six small plants in subcategory 1 which process less than 175 hides/day, three small plants in subcategory 3 which process less than 350 hides/day, and nine small plants in subcategory 9 which process less than 3600 splits/day have been exempted from the chromium pretreatment standards.

No further separations in the nine subcategories were found to be necessary based upon economic impact.

SECTION V

WATER USE AND WASTE CHARACTERISTICS

A. PURPOSE

The purpose of this section is to describe the sources, volumes, and characteristics of wastewaters in the leather tanning and finishing industry. The raw wastewater data base consists of 32,141 data points for 76 plants during the period of 1974 to 1980. Data from the original study were used only where full documentation was provided from the original study.

B. GENERAL METHODOLOGY

With the cooperation of the Tanners' Council of America (TCA), the Agency conducted several data gathering efforts from 1974 to 1980 to obtain water use and wastewater data. The most intensive and detailed effort was conducted from 1979 to 1980. Through the use of questionnaires, plant visits, and sampling visits, the Agency attempted to collect as much information as was available concerning water use and wastewater characterization for the industry. Other sources such as state and local agencies also were contacted in order to obtain additional information.

Once collected, the data were reviewed to insure its validity for use. Sampling procedures and analyses were checked to ascertain that approved methods were used, sampling locations and time periods were confirmed (if necessary), abnormally high or low data points were verified by contacting the individual tannery.

In addition to the raw wastewater data review of the manufacturing operations, each individual tannery was analyzed. Each tannery was reviewed to ensure that: 1) the production operations were typical of those for a tannery in that subcategory; 2) the raw material input was reported on the appropriate basis, and 3) no additional operations (i.e., mixed subcategories, minor process variations) were being conducted at the tannery to impact the data. The Agency also requested detailed information on the employment of water conservation techniques, water reuse, and chemical reuse at the tannery. These additional efforts undertaken during the quality review of the wastewater data are addressed in more detail in Section II of this document.

In reviewing the industry data base, EPA has observed a discrepancies between the data reported by tanners and that gathered by EPA. Some of this discrepancy may be the result of differences in production processes and scheduling resulting in widely variable wastewater discharge patterns during the course of a processing day (or days) as well as sampling procedures, analytical techniques, and reporting errors. EPA has attempted to ascertain the causes of variability and minimize this occurrence by requiring documentation for each data set used. Remaining variability in water use and pollutant loads has been accounted for by subcategorization according to differences in raw materials and processing methods.

Once the water use and pollutant data for raw wastewaters were determined to be valid and accurate, it could be compiled and analyzed to calculate representative water use ratios (gal/lb or l/kg) and pollutant loads (lb/1000 lb, or kg/kkg) for each subcategory. To characterize the wasteloads and water usage from a specific facility, the average value of each pollutant parameter and water use was calculated from the data provided. By calculating the average (mean) value of the long term water use and pollutant loads, specific facility factors such as day to day variability in raw materials and processing methods are taken into consideration. Therefore, the values calculated provide a representation of the actual wasteloads from that tannery on a long term basis.

The data from each facility were then grouped according to the subcategorization scheme of the industry as presented in the previous section. Review of the data indicated that because of the range of individual data points from plant to plant, the use of a mean value did not represent the subcategory in an equitable manner. In addition, a few plants provided large numbers of water use and pollutant concentration data points, while most plants provided relatively few data points. Thus, subcategory means based on individual data points would be biased by those plants which supplied large numbers of data points, even though these data and the processing operations they represent may be no more valid or typical of a subcategory than a limited number of data points from other plants. To avoid this inequity and to determine pollutant values that best portray the data in each subcategory, the median value of the individual <u>plant means</u> (not individual data points for each plant) was determined. The median value is the point in the data distribution at which half the plant mean values are above and half the plant mean values are below. By using this approach, individual data points that are unusually high or low, while still being valid data, do not have a disproportionate influence on water use ratios and pollutant loads representing each subcategory.

By using the above approach and methodology, the Agency was able to develop a verifiable and accurate data base from which representative water use and wasteloads could be calculated for each of the subcategories in the industry.

The data which represent each subcategory were normalized to production level (e.g., liters per kilogram or kilograms per 1,000 kilograms (kg/kkg) of hides skins, sides, or splits processed). With the exception of subcategories 4 and 9, all production data used to calculate water use ratios and pollutant loads were based on the weight of hides as received. This is a reasonable basis for developing raw material related water use and pollutant loads because weight as received varies insignificantly from the raw material weight which enters wet processing. Production levels for subcategories 4 and 9 are defined as the weight of hides entering the initial wet process (i.e. after splitting and/or trimming) because "wet-blue" grain sides and (especially) splits are subjected to varying degrees of shaving, trimming, and resplitting before entering wet process. Many subcategory 4 facilities receive through-the-blue sides, split and retan the grain side, and resell the split to other facilities (subcategory 9) which complete the finishing. Thus, no water is consumed in subcategory 4 in processing the split portion of the hide that is resold and therefore additional allowances in calculating mass based effluent limitations would not be warranted.

C. WATER USAGE

1. Background

As noted in the beginning of this section the Agency found differences in water use among plants within the leather tanning and finishing industry. These differences are primarily attributable to the raw materials processed and the processing methods used. From an examination and analysis of all available flow and pollutant data, the Agency has determined that there is a direct relationship between the primary subcategorization factors of raw materials and groups of subprocesses utilized and water use and pollutant loadings. Accordingly, the Agency has developed water use ratios for each subcategory which are achievable for each plant within that subcategory.

Figure III-1 presented previously in Section III is a generic sequence of subprocesses associated with tannery operations. This illustration indicates the origin of the liquid and solid waste streams from each process as well as the primary physical contaminants in each waste stream. As shown in Figure III-1, the major usages of water within a tannery are for:

1. soaking, washing, and unhairing of unprocessed hides;

2. tanning and retanning with chromium, vegetable, alum or other agents;
3. preparing bleach, dye, or pigment solutions which impart the desired color to the final product; and
4. cleaning and washdown of process equipment and areas.

The processing operations are further described in Section III of this document. The usages of water as they apply to a specific subcategory are described qualitatively below. The contribution to total plant water use by subprocesses employed within each subcategory are described, where data were available, as approximations or ranges to provide comparisons among subprocesses and groups of subprocesses. No further quantitative use of these data has been attempted or intended.

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

Tanneries in this subcategory process primarily brine-cured or green salted cattlehides into finished leather. A description of water use for individual subprocesses typically employed follows.

Soak and Wash. The purpose of this operation is to remove salt, restore the moisture content of the hides, and remove material such as dirt and manure. Brine-cured hides are soaked and washed simply to remove salt, but manure and dirt, as well as salt, must be removed from green-salted hides. The quantity of manure and dirt varies with the season of the year and the origin of the hide. However, this variation was not found to be a factor relating to raw materials which requires further subcategorization or to differences in wastewater treatability by season of the year. Furthermore, the Agency does not have data correlating water usage with the seasonal variation in the state of the raw material. Industry data estimate the wastewater volume from this subprocess to be about 20 percent of the total wastewater flow.

Fleshing. If fleshing is not done previously, it follows the soak and wash operation. Fleshings are generally isolated as a solid waste. When handled properly, this operation contributes only a small amount of wastewater.

Unhairing. The hair-pulp process involves soaking the hides in an aqueous solution of lime and sharpeners (e.g., sodium sulfide and sodium sulfhydrate). This process reportedly contributes 20 to 40 percent of the tannery's total wastewater flow.

Bating and Pickling. During bating, the pH is adjusted to reduce the lime and other alkaline chemical content and prepare the hide to receive the bate. Enzymes (bate) are then added to peptize the collagen fibers and remove protein degradation products.

Hides are prepared for tanning by pickling (i.e., soaking in a solution of sulfuric acid and salt). The salt is added to minimize acid swelling of the hide. Bate and pickle wastewater volumes were reported as a combined total, ranging from nine to 50 percent of plant flow and averaging 26 percent.

Tanning. The tanning step converts the raw collagen fibers of the hide into a stable non-putrescible product. Hides are tanned in an acidic, aqueous solution of trivalent chromium. In many instances, the tanning solution may be reused. This results in a relatively small wastewater volume. At this stage in the chromium tanning process, the hide is characteristically blue in color and may either be further processed or sold to plants which retan and wet finish (subcategories 4 and 9).

Retanning, Coloring, and Fatliquoring. After the tanned hides are split, these three processes are carried out sequentially, usually in the same drum. Relatively high volumes of wastewater emerge from these processes. Generally these solutions cannot be recycled due to their high color. Because of the highly variable nature of these processing steps, wastewater flow varies from 12 to 30 percent of a facility's total flow.

Drying. The drying processes chosen by the tanner also can affect wastewater volumes, although this is a minor source. Four basic operations are currently used: hanging, toggling, pasting and vacuum drying. Of these methods, pasting may generate significant wastewater volumes and pollutant loadings, both from the pasting material make-up and the need to wash any excess paste from the dried leather. Wastewater from this process is dilute and may be recycled, as reportedly practiced by some tanners. Moreover, the overall contribution of water use for drying is small.

Finishing. Finishing operations are basically dry processes with little or no wastewater discharge. Generally, water use is limited to wetting of hides to facilitate handling and cleanup operations.

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 1. In the hair save unhairing operation, the hair is loosened and later removed by machine. The depilatory chemicals used are the same as those used in hair pulping, but are present in lower concentrations such that the hair is not dissolved.

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 either handled as solid wastes or may enter the plant sewer.

Although the hair save process has historically resulted in higher water use, current trends in the industry do not emphasize the recovery of hair for resale and therefore, hair save is not frequently used. The hair washing subprocess is not practiced uniformly in this subcategory.

Subcategory Three (Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish)

The principal difference between this subcategory and subcategory 1 or 2 is the tanning operation. Cattlehides leaving the beamhouse, with hair removed either by the hair save process or hair pulp process, are bated and pickled in a similar manner, but are tanned with non-chromium agents. Vegetable tannins accomplish the major portion of non-chromium tanning; alum, zirconium, or other metal salts, as well as syntans, gluteraldehyde, and formaldehyde also are used. Process solutions are recycled in many cases because these tanning agents are so expensive.

Portions of the solution which enter the waste stream generally result from drag-out or planned blow-down to maintain the concentration of tanning agent and prevent build up of undesirable impurities in the solution. The semi-batch approach to vegetable tanning yields flows that are lower than those for chromium tanning (subcategory 2).

Subcategory Four (Retan-Wet Finish-Sides)

Tanneries in this subcategory receive previously tanned hides ("blue stock") from a subcategory 6 (Through-The-Blue) tannery which are then split by the receiving tannery prior to retanning and finishing. The split portion may be sold without further processing; therefore no further water use attributable to split processing would be necessary. Water use is based on the weight of the blue grain side leather placed into wet processing, not the total side weight prior to splitting.

Either chromium, 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 1.

Subcategory Five (No Beamhouse)

This subcategory primarily includes plants that tan unhaired and pickled sheepskins. Tanneries in this subcategory also may receive pickled and unhaired cattlehides, which are then tanned and wet-finished in ways outlined for the preceding subcategories.

Unhaired, pickled sheepskins require fleshing if they have not been fleshed previously. Previously fleshed skins usually require refleshing after tanning.

Grease removal is necessary for sheepskins and follows the soak and wash step. Using the same drums, degreasing is performed by: 1) hot water with detergent, or 2) solvent addition. With either method, the grease, which has some commercial value, is separated and recovered as a by-product.

Sheepskins may be tanned with chromium or vegetable tannins, although the majority of tanneries use chromium. Tanned sheepskins are retanned in a manner similar to cattlehides. The wet finishing operations for sheepskins are the same as those described for subcategory 1.

Elimination of the beamhouse results in lower average flow per unit of production than is typical for subcategory 1.

Subcategory Six (Through-the-Blue)

Facilities in subcategory 6 process raw or cured cattlehides through the blue tanned stage. The remaining steps are performed by other tanneries in subcategories 4 and/or 9.

Hair from the hides may be saved but usually is pulped. Following bating and pickling, the unhaired hides are chromium tanned to the blue stage.

Subcategory Seven (Shearling)

Included in this subcategory are 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 tanning, the skins are soaked and washed to remove 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 5, but grease recovery is not normally practiced by shearling tanneries.

Unlike unhaired sheepskins, shearling hides are pickled before they are tanned, in a manner similar to that used for cattlehide processing. These skins do not, however, require liming and bating. Tanning may be accomplished with either chromium or vegetable tannins, although chromium is generally preferred. The retanning and wet finishing steps for shearlings are similar to those used for cattlehides, but additional work is required on the hair, such as clipping and carding, both of which are essentially dry processes.

Because shearling hides are processed with the hair intact, average water consumption is substantially higher than that observed for tanneries in subcategory 5, which employ essentially the same processing steps.

Subcategory Eight (Pigskin)

Pigskin tanneries process skins in much the same manner as cattlehide tanneries do, except that the beamhouse process may be modified, depending on the type of skin received and the amount of hair stubble which must be removed. Scalded pigskins usually do not require the same use of unhairing chemicals as pigskins received hair on. Skin degreasing is a necessary additional process, and the grease is usually recovered as a by-product. Liming, bating, and pickling are similar to cattlehide processing, but the conventional tanning step results in a fully tanned skin, eliminating the need for retanning. Finishing operations are, again, similar to those used in cattlehide processing.

Subcategory Nine (Retan-Wet Finish-Splits)

Tanneries in this subcategory receive previously tanned (through-the-blue) split sides. Although tannery operations are similar to those used in processing the grain side portion of the hide (subcategory 4), the split side requires less process water because the split has an open fiber structure which facilitates penetration of water borne processing chemcials.

2. Flow Ratio Determinations

The data base for water use was developed primarily from information supplied by the industry. Table V-1 presents a summary of the response by plants to the Agency's request for data. This data base consists of 3126 individual data points some of which represent annual averages.

As shown in Table V-1, although nearly 75 percent of the industry responded with water use data, only 65 percent of that data was found to be usable. In selecting a facility's data to be used for the development of median, reduced, and new source subcategory flow ratios, great care was taken not only to verify the data itself but also to review the raw materials and processing operations of that facility to insure that it met the subcategory definition. In addition, the data base underwent review by the industry trade association (TCA) and individual plant personnel, which resulted in further refinement.

As described previously in Section IV of this Development Document the Agency subcategorized the industry based on raw materials and processes used. Attempts to further separate these nine subcategories based on other factors, most importantly final products, were found to be unnecessary because the resulting product specific median water use ratios were not significantly different from the subcategory medians from which they were separated. Each subcategory had a predominant mix of final products incidental to the raw materials and processing methods used in each subcategory.

The Agency concluded that for purposes of calculating mass based BPT effluent limitations and the cost of BPT control technology, a flow ratio which best represented the central tendency of each subcategory was the median value of the individual plant means. The median flow ratio is that value at which half of the individual plant means are higher and half are lower. The Agency has used the median water use ratios because they were achieved by at least half the plants in each subcategory. Median water use ratios for each subcategory and the numbers of plants achieving those ratios are presented in Tables V-2 and V-3. A discussion of the median statistic was presented previously under General Methodology in this Section of the Development Document. These subcategory median flow ratios are achievable because plants within subcategories, which use the same raw materials and groups of subprocesses as used by all plants represented within the specific subcategory, exhibit water use ratios throughout the range of water use, high and low, for the subcategory. Similarly, it must be noted that the dominant final products, incidental to these raw materials and processes used, also were found to be distributed throughout the range of water use, high and low, for the subcategory. Therefore, the Agency concluded that the remaining factor which determined the range of water use within subcategories was the extent to which plants have implemented water conservation practices. Plants which use more

TABLE V-I
SUMMARY OF PLANTS SUBMITTING DATA

Subcategory	Total Number of Plants(1)	Total Number of Plants Submitting Data(2)	Plants Used in Data Base	
			Number of Plants	Percent of Total
1	58	44	28	48
2	7	7	4	57
3	13	17	12	67
4	20	15	8	40
5	24	19	13	54
6	12	5	3	25
7	8	3	1	13
8	2	2	2	100
9	14	6	4	29
TOTALS	158	118	75	47

(1) Number of plants in current operation.

(2) Includes valid data from some plants that have closed; note specifically Subcategory 3.

water than the median water use ratios can implement available water conservation techniques which are not capital intensive in order to achieve these median water use ratios.

The Agency is aware of instances where within a particular subcategory plants utilize processing equipment (which requires substantial capital investment) which can be operated to use very little water but do not operate the equipment in such a manner. This was found to be especially true for hide processors. Hide processors (modified cement mixers) are utilized by a number of plants in the industry, ranging from use in only one subprocess (e.g., inital soaking) at some plants to a majority of subprocesses at other plants. These hide processors provide the physical means for recycling process water and chemicals, as well as affording labor saving opportunities. However, the water use ratios exhibited by plants which use them also were found throughout the range of water use, high and low, for the subcategory where data were available.

As noted in Section IV of this Document, and in response to comments, the Agency could not relate product quality to the amount of water used. Quantitative data on product quality (i.e., "feel" of leathers, or physical properties of leathers) were not available from the industry, and probably would not be possible to obtain. However, it can be said that all plants for which water use data were available in each subcategory produced leathers of commercially salable quality regardless of high or low water use.

In developing more stringent BAT control technologies for existing sources, the Agency incorporated in-plant controls to reduce water use in developing technology OPTIONS II and III. Since plants that meet the reduced water use ratios within each subcategory were found to use the same raw materials and major groups of subprocesses as plants which exhibited higher water use ratios, the Agency believes that reduced water use ratios are achievable for all plants within the subcategories. As a starting point for calculating reduced water use, the Agency identified the median water use ratio for the lower 50 percent of the plant means in each subcategory. The raw materials and processing methods represented by plants with water use ratios equal to or less than this lower median value were reviewed to ensure that they were representative of those employed by all plants in the subcategory. Minor subprocess variations may lead to either slightly higher or lower water usage. Accordingly, in determining reduced water use ratios, the Agency generally has not considered plants with minor subprocess variations. For example, see the discussion in subcategory 3 below. However, the Agency believes that it is appropriate to consider these plants

TABLE V-2

RANGE OF FLOW DATA

Subcategory	Number of Tanneries	Median Water Use Ratio (gal/lb(l/kg))	Number of Data Points*	Range of Water Use Ratios (gal/lb(l/kg))	Range of Flows (mgd(m^3/day))
1	28	6.5 (54.2)	474	3.0-11.5 (25.0-96.0)	0.04 -1.42 (151-5,380)
2	4	5.8 (48.4)	187	4.9- 6.8 (40.9-56.8)	0.007-0.365 (26-1,380)
3	12	4.9 (40.9)	1,304	2.3- 9.6 (19.2-80.1)	0.03 -0.5 (114-1,890)
4	8	4.8 (40.1)	405	1.7-11.4 (14.2-95.1)	0.014 -0.63 (53-2,380)
5	13	5.8 (48.4)	88	3.5-13.5 (29.2-113)	0.0007-0.14 (3-530)
6	3	2.1 (17.5)	43	1.4- 2.6 (11.7-21.7)	0.048 -0.175 (182-662)
7	1	9.4 (78.5)	64	9.4 (78.5)	0.27 -0.36 (1,020-1,360)
8	2	5.0 (41.7)	548	4.1- 5.8 (34.2-48.4)	0.06 -0.49 (227-1,850)
9	4	3.0 (25.0)	13	2.2- 4.9 (18.4-40.1)	0.027 -0.071 (102-269)

* some single data points represent annual averages

in developing median water use ratios because they are still representative of the subcategory as a whole.

The Agency concluded that water conservation techniques which are not capital intensive can be used to achieve these reduced water use ratios. However, in developing costs for control technology options (BAT OPTIONS II and III and PSES TECHNOLOGY OPTIONS I, II, and III), the Agency included costs for stream segregation which is necessary for end-of-pipe pretreatment technology, such as sulfide oxidation for beamhouse wastewaters, and chromium removal from tanyard and retan-wet finish wastewaters by coagulation-sedimentation. Stream segregation includes piping and pumps to capture wastewaters from processing vessels for transport to these pretreatment technologies. This same equipment can serve to provide the opportunity to recycle and reuse wastewaters, thus contributing to reduced water use at existing facilities. Evaluation of the water use data indicated that reduced water use ratios, below overall subcategory medians, could be achieved in seven of the nine subcategories. These ratios and the numbers of plants achieving these are presented in Table V-3. There were two subcategories for which reduced water use ratios were not identified because limitations in existing data prevented the use of engineering judgment to identify feasible water use reduction achievable by existing sources without data from operating plants to support these judgments. Reduced water use was not used in deriving BAT mass based effluent limitations because the selected option (OPTION 1) was BPT which was based on median water use.

The Agency has used reduced water use ratios to calculate the costs of PSES instead of median water use ratios. Since the Agency has promulgated concentration based pretreatment standards, the amount of water used at any plant is not germane to the achievability of PSES. However, the Agency has used reduced water use ratios to calculate the costs of PSES. These costs were based on the assumption that no pretreatment technology was in place. Also when designing and building new treatment facilities it is sound engineering practice and economically necessary to minimize the costs of the facility. Therefore, the Agency used reduced water use achievable by existing sources because the Agency believes that the cost of the pretreatment technology can be minimized by first reducing to the maximum extent feasible the volume of wastewater to be treated.

New facilities generally have a distinct advantage over existing facilities in regard to water use reduction and conservation. By emphasizing these items in the design and layout of a new facility, a tanner has more opportunity and flexibility than does an existing tanner. Therefore, it is reasonable that new

TABLE V-3

SUBCATEGORY FLOW RATIOS

Subcategory	Water Use Ratio Median (gal/lb(ℓ/kg))	Water Use Ratio Reduced (gal/lb(ℓ/kg))	Water Use Ratio New Source (gal/lb(ℓkg))	No. of Tanneries Currently Meeting Median Ratio	No. of Tanneries Currently Meeting Reduced Ratio	No. of Tanneries Currently Meeting New Source Ratio	No. of Tanneries In Data Base
1	6.5 (54.2)	5.4 (45.1)	4.3 (35.9)	15	8	5	28
2	5.8 (48.4)	5.0 (41.7)	4.9 (40.9)	3	2	1	4
3	4.9 (40.9)	4.8 (40.1)	4.2 (35.1)	8	6	4	12
4	4.8 (40.1)	4.6 (38.4)	4.5 (37.6)	4	4	3	8
5	5.8 (48.4)	4.0 (33.4)	3.8 (31.7)	7	4	3	13
6	2.1 (17.5)	1.4 (11.7)	1.4 (11.7)	2	1	1	3
7	9.4 (78.5)	9.4 (78.5)	9.4 (78.5)	1	1	1	1
8	5.0 (41.7)	5.0 (41.7)	4.1 (34.2)	1	1	1	2
9	3.0 (25.0)	2.5 (20.9)	2.5 (20.9)	2	2	2	4

facilities can achieve further reductions in water use than can existing facilities.

To establish realistic and achievable new source flow ratios, the Agency identified the median value from those facilities that are currently meeting or bettering the reduced flow ratio identified by the methodology described above. Plants in eight of the nine subcategories used less water than the water use ratios identified for new sources by employing process equipment and techniques which together allow the processing of raw materials with substantial reductions in water use. For three of the eight subcategories, no further reductions beyond the reduced water use ratios identified for existing sources were determined to be feasible. In these three subcategories limitations of existing data prevented the Agency's use of engineering judgment to identify feasible further water use reductions achievable by new source without data from operating plants to support these judgments.

Tanneries which were covered by two or more subcategories have the same opportunities for implementation of available flow reduction techniques (batch rinses, spent liquor reuse, etc.) as do single subcategory tanneries because flow reduction capability is not constrained by the processing of more than one type of raw material within a plant. One tannery covered by subcategories 2 and 7 exhibited a water use ratio approximately equal to the ratio for subcategory 2 (5.8 gal/lb or 48.4 l/kg) even though 17 percent of its production was covered by subcategory 7 (9.4 gal/lb or 78.5 l/kg).

In summary, the water use ratios developed by the methodology described above have been utilized as follows: 1) subcategory median water use ratios were used for BPT, BAT, and BCT mass limitations (see Sections VIII, IX, and X for discussion) and for the cost of these technologies; 2) reduced water use ratios for existing sources were used for BAT Technology OPTIONS II and III, and for the cost of PSES TECHNOLOGY OPTIONS I, II, and III (see Section XII and Appendix A); and 3) reduced water use ratios for new sources were used for mass limitations and costs for NSPS (see Appendix A and Section XI), and for costs for PSNS TECHNOLOGY OPTIONS I, II, and III (see Appendix A and Section XII).

3. Subcategory Analysis

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

Water use data from 28 plants were utilized for this subcategory. Table V-4 lists each of the plants in ascending order of water use. The raw material, processing operations, and the incidental final product(s) are also presented on this table. The median water use ratio for this subcategory is 6.5 gallons per pound (gal/lb) or 54.2 l/kg.

As may be seen in Table V-4, the raw materials and groups of subprocesses used within the subcategory are the same (i.e., cattlehides; hair pulp, chromium tan, retan-wet finish). The incidental mix of uses for the final products is well defined, dominated by shoe uppers, garments, upholstery, and gloves and lining material. Plants using the same raw materials and performing the same operations were found to exhibit both high and low water ratios. For example, Tannery No. 87 and Tannery No. 248 both pulp hair, chromium tan, and retan-wet finish brine cured, pre-fleshed cattlehides into leather used mainly for shoe uppers, plus other leather goods, yet Tannery No. 87 uses 3.8 times more water per pound of raw material than does Tannery No. 248. The Agency believes that the difference between water use for these plants is accounted for by water conservation techniques and that the subcategory median flow ratio is achievable by plants operating above this subcategory median if water conservation measures are utilized.

The existing source reduced flow ratio for subcategory 1 (5.4 gal/lb or 45.1 l/kg) is achieved by eight of the 28 plants in the data base. See Table V-3. Again, the Agency reviewed the raw materials and processing methods used by these eight plants to determine whether any factor caused these plants to exhibit lower flow ratios. No relationship was evident. These eight plants have demonstrated a seven percent reduction in water use while producing finished leather of commercially salable quality.

The new source flow ratio for this subcategory is 4.3 gal/lb (35.9 l/kg) This is reduction of 33 percent below the subcategory median flow ratio (6.5 gal/lb or 54.2 l/kg) and is being achieved by five out of 28 plants which together employ the same raw materials and processing methods to produce leathers used in the same mix of predominant final products (shoe uppers, garments, upholstery) represented in this subcategory. Unique processing methods and equipment or variations are not known to be used by these five existing plants. Therefore, since these five existing sources achieved these water use ratios by processing methods common to the subcategory, new sources also can be expected to achieve these water use ratios. The Agency's control technology costs for new sources include costs for stream segregation which includes equipment that also can be used to recycle and reuse wastewaters and thereby contribute to achievement of these water use ratios.

TABLE V-4

WATER USE RATIO DATA BASE
RAW MATERIAL AND PRODUCT MIX

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
		SUBCATEGORY 1		
248	3.0 (25.0)	100% BCPF Cattlehide	80% Shoe Uppers 20% Handbag, Luggage, Belts	
383	3.1 (25.9)	40% Fresh Cattlehide 35% GS Cattlehide 15% GS Deerskin 10% GS Elkhide	Garment & Glove Shoe Linings & Orthopedic Leather	
520	3.2 (26.7)	100% GS Cattlehide	100% Garment - Sold in the crust	
274	3.8 (31.7)	100% BCPF Cattlehide	33% Garment 67% Upholstery	
246	4.3 (35.9)	92% PF Cattlehide 6% GS Moose & Elkhide 2% Pickled Sheep & Goatskin	80% Glove 10% Garment 5% Shoe 5% Specialty	
525	4.5 (37.6)	80% BCPF Cattlehide 20% GS Cattlehide	100% Upholstery	
438	5.4 (45.1)	64% BCPF Cattlehide 23% BCPF Sowskins 8% GS Cattlehide 5% GS Deer & Elkhide	94% Glove 5% Lining 1% Orthopedic Shoe Uppers	
245	5.4 (45.1)	50% GS Cattlehide 50% Fresh Cattlehide	80% Shoe Uppers & Linings 20% Purse & Handbag	
80	5.5 (45.9)	60% GS Cattlehide 30% BCPF Cattlehide 10% BC Cattlehide	50% Military Shoe Leather 35% Upper Leather 15% Lining Leather	
237	5.7 (47.6)	50% GS Cattlehide 50% BC Cattlehide	95% Military Shoe Uppers 5% Other	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
235	6.0 (50.1)	80% PF Trimmed Cattlehide 20% GS or BC Cattlehide	80% Shoe Uppers 20% Military Shoe Uppers	
425	6.1 (50.9)	100% BCPF Cattlehide	30% Moccasin & Boot 20% Shoe Lining 35% Crusted Lining 15% Miscellaneous	
262	6.2 (51.7)	100% GSPF Cattlehide	100% Upholstery	
206	6.4 (53.4)	100% BCPF Cattlehide	60% Shoe Uppers 20% Lining 20% Garment	
13	6.5 (54.2)	100% BCPF Cattlehide	85% Shoe Uppers 15% Handbag,etc.	
103	6.8 (56.8)	100% GS Cattlehide	80% Shoe Uppers 20% Accessory	
431	7.0 (58.4)	99% BCPF Cattlehide 1% BC Cattlehide	96% Shoe Uppers 4% Miscellaneous	
626	7.5 (62.6)	Cattlehide	Shoes, Personal Leather, Garment Glove	
6	7.6 (63.4)	Cattlehide	Bag, Case, Strap, Garment, Glove	
432	7.8 (65.1)	90% BCPF Cattlehide 10% GSPF Cattlehide	40% Garment 30% Shoe Uppers 30% Specialty	
632	7.9 (65.9)	Mostly Deerskin	***	
231	8.9 (74.3)	100% GS Cattlehide	75% Upholstery 12.5% Shoe Uppers 12.5% Specialty	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
31	8.9 (74.3)	94% BCPF Cattlehide 6% Blue Cattlehide	95% Shoe Uppers 5% Waist Belt	
58	9.7 (81.0)	100% BCPF Cattlehide	100% Shoe Uppers	
37185	9.9 (82.6)	50% BC Cattlehide 45% Goatskin 5% Sheepskin	25% Boot 20% Glove 40% Suede 5% Military 5% Smooth Grain 5% Sunken Grain	
57	10.5 (87.6)	100% BCPF Cattlehide	70% Shoe Uppers 10% Garment 10% Handbag 10% Upholstery	
409	10.7 (89.3)	52% BCPF Cattlehide 36% GS Cattlehide 12% Pickled Sheepskin	84% Shoe Uppers 8% Suede Sheep Garment 5% Garment 3% Grain Sheep Garment	
87	11.5 (96.0)	100% BCPF Cattlehide	70% Shoe Uppers 19% Leather Goods 6% Belt 5% Shoe Linings	
SUBCATEGORY 2				
7	4.9 (40.9)	17% Salted Shearlings 83% Fresh Cattlehide	Cattlehide 80% Shoe Uppers 10% Handbag 10% Miscellaneous Sheepskin 100% Shearlings	
8	5.0 (41.7)	90% GS Cattlehide 10% Fresh Cattlehide	85% Shoe Uppers 10% Handbag 5% Belt	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
236	5.8 (48.7)	100% GS or BC Deerskin	100% Glove or Garment	
320	6.8 (56.8)	75% GS Cattlehide 25% BCPF Cattlehide	100% Shoe Uppers 50% Splits Finished 50% Splits Sold Blue	
SUBCATEGORY 3				
385	2.3 (19.2)	100% BCPF Cattlehide	66% Sole Leather 33% Rough Shoulders 1% Strap Sides	No bating No retan
415	3.0 (25.0)	100% BCPF Cattlehide	40% Sole Leather 35% Strap Shoulders 10% Rough Shoulders 10% Strap Bellies 5% Pickled Bellies	No retan for majority
47	3.1 (25.9)	93% BC or GS Cattlehide 7% GS Calfskin	75% Alum Lace 25% Chrome Latigo	Extensive reuse of tanning liquors
397	4.2 (35.1)	100% BCPF Cattlehide	42% Sole Leather 42% Curried Leather 16% Pickled Bellies	
46	4.8 (40.1)	100% BCPF Cattlehide	65% Sole Leather 35% Specialty	
186	4.8 (40.1)	95% BCPF Cattlehide 5% PF Cattlehide	95% Lace Leather 5% Hard Rawhide	
388	4.9 (40.9)	98% BCPF Cattlehide 2% Blue Splits	98% Basketball & Football Leather 2% Miscellaneous	
399	4.9 (40.9)	100% BCPF Cattlehide	80% Veg. Tan Saddle, Strap, Harness 15% Chrome & Veg. Retan Lace 5% Alum Lace	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
404	7.7 (64.3)	43% BC Cattlehide 52% Blue Cattlehide 5% Horsehide	50% Baseball 40% Softball 5% Orthopedic Glove 5% Garment	
239	7.9 (65.9)	100% BCPF Cattlehide	66% Veg. Tan Strap 29% Veg. Tan Skirting 5% Alum Latigo	
24	8.2 (68.4)	100% BCPF Cattlehide	84% Strap 9% Skirting 6% Latigo 1% Miscellaneous	
376	9.6 (80.1)	100% BCPF Cattlehide	80% Sole Leather 20% Industrial Leather	
		SUBCATEGORY 4		
389	1.7 (14.2)	100% Cattlehide	34% Shoe Uppers & Lining 33% Belts 33% Purse, Handbag	No color or fat liquor
404	2.4 (20.0)	43% BC Cattlehide 52% Blue Cattlehide 5% Horsehide	50% Baseball 40% Softball 5% Orthopedic Glove 5% Garment	Operates beamhouse for portion of operation
50	4.5 (37.6)	100% Blue Cattlehide	70% Shoe Uppers 15% Handbag & Belt 10% Personal Leather Goods 5% Military	
3	4.6 (38.4)	100% Blue Cattlehide	80% Shoe Uppers 15% Lace & Latigo 5% Sole & Mechanical	
4937	4.9 (40.9)	100% Blue Cattlehide	Garment Leather	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
224	5.6 (46.7)	100% Blue Cattlehide	100% Shoe Uppers	
625	6.4 (53.4)	100% Blue Cattlehide	***	
191	11.4 (95.1)	100% Blue Cattlehide	50% Shoe Uppers 30% Export Leather 20% Personal Leather Goods	
			SUBCATEGORY 5	
88	3.5 (29.2)	100% Pickled/BC Sheepskins	100% Lining Leather	No retan
700	3.8 (31.7)	100% Pickled Sheepskin	Garment Leather	
285	3.8 (31.7)	100% Limed Split Single Bend Cattlehide	100% Soft Suede	No retan, formaldehyde tanning
51	4.0 (33.4)	100% Pickled/Wet Blue Sheepskin	45% Garment 49% Lining & Novelty 6% Hat	
75	5.5 (45.9)	100% Pickled Cow Bellies	70% Work Glove 30% Shoe Lining	
615	5.6 (46.7)	75% Pickled Sheepskin 25% Stained Sheepskin	***	
92	5.8 (48.4)	41% Pickled Lambskin 32% Pickled Sheepskin 15% Pickled Skivers 12% Pickled Chamois Fleshes	60% Garment 40% Shoe Uppers	
380	6.6 (55.1)	100% Pickled Cattlehide	Belts, Dog Collars, Harness, Arch Supports, & Special Equipment	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
556	7.4 (61.8)	Pickled Sheepskin Blue Cattlehide	***	
522	7.8 (65.1)	95% Pickled Sheepskin 5% Pickled Goatskin	70% Garment 30% Glove	
319	8.5 (70.9)	***	***	
169	11.0 (91.8)	Pickled Sheepskin, Cattlehide, Deerskin	***	
220	13.5 (113)	Pickled Sheepskin	Government Leather	
		SUBCATEGORY 6		
444	1.4 (11.7)	93% BCPF Cattlehide 7% PF Cattlehide	100% Blue Sides	
559	2.1 (17.5)	100% BCPF Cattlehide	100% Wet Blue	
502	2.6 (21.7)	100% BCPF Cattlehide	100% Wet Blue	
		SUBCATEGORY 7		
500	9.4 (78.5)	80% GS Wool Sheepskin 20% Salt Dried Sheepskins	90% Garment Shearling Suede 10% Seat Covers, Bed Pads, Blue Skins	
		SUBCATEGORY 8		
185	4.1 (34.2)	85% BC or GS Pigskin 15% Pickled Cow Bellies	95% Work Glove 5% Boot Lining	
233	5.8 (48.4)	85% GS, Unhaired, Pigskin 15% GS, Hair-on Pigskin	70% Shoe Uppers 25% Glove Lining 5% Garment	

TABLE V-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Process Variations
		SUBCATEGORY 9		
507	2.2 (18.4)	95% Blue Split Cattlehide 5% Blue Pigskins	100% Suede	
97	2.5 (20.9)	100% Blue Split Cattlehide	95% Shoe Uppers 5% Lining, Garment, Other	
116	3.4 (28.4)	90% Blue Split Cattlehide 10% Blue Pigskins	100% Suede	
501	4.9 (40.9)	100% Blue Split Cattlehide	30% Shoe Uppers, Linings 30% Glove 15% Garment 25% Specialty	

GSPF	Green salted-prefleshed
BCPF	Brine cured-prefleshed
GS	Green salted
PF	Prefleshed
BC	Brine cured
***	No specific data provided

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

Water use data was provided by four of seven facilities in this subcategory. See Tables V-1 and V-4. All four of these plants operate hair save beamhouse operations, chromium tan, and retan-wet finish. Tannery No. 7 also processes shearlings as 17 percent of its production. Since the processing of shearlings is included in subcategory 7 and uses almost twice as much water as do plants in subcategory 2, the Agency excluded this plant from its data base for determining median water use. The median water use of these four plants is 5.4 gal/lb (45.1 l/kg). However, because Tannery No. 7 also processes shearlings, the median of the remaining three plants, 5.8 gal/lb (48.4 l/kg), was used for the subcategory. The reduced flow ratio for existing sources, 5.0 gal/lb (41.7 l/kg), represented a reduction of 14 percent. This water use ratio was even achieved by Tannery No. 7 despite its processing of shearlings which should require substantially more water use. Accordingly the Agency believes that this flow ratio is achievable by all plants within the subcategory. The ability of Tannery No. 7 to reduce flows to 4.9 gal/lb (40.9 l/kg) while processing shearlings supports the Agency's conclusion. This leads to the selection of 4.9 gal/lb (40.9 l/kg) as the new source flow ratio, a further reduction of only two percent below the reduced water use ratio for existing sources, and 16 percent below the median.

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

Twelve plants were utilized in determining flow ratios for subcategory 3 as listed in Table V-4. Both hair save and hair pulp operations are included since the primary process related factor in this subcategory was the use of non-chromium tanning (primarily vegetable tanning). Retan-wet finish operations also are represented in this subcategory. Due to minor processing variations from the subprocesses included in the major groups noted in Table V-4 which in these cases may have contributed to a lower water use, Tannery Nos. 385, 415 and 47 were not utilized as the basis for flow reduction although their flow ratios all were lower than the median. The Agency believes that this is a conservative approach because the major groups of subprocesses and the raw materials utilized are the same and accordingly, these plants should have been able to meet the reduced flow ratios even if data from Tannery Nos. 385, 415 and 47 were utilized. The Agency, however, utilized this conservative approach to ensure that the water flow ratios would be more easily achievable by all plants within the subcategory. Other process factors (e.g. vegetable tannage versus other non-chromium mineral tannages and use of equipment such as hide processors) were investigated, but no significant relationship to water use was found. See Table IV-5 for tabular display of these trial separations and the resulting median water use ratios. The median water use ratio for this subcategory was 4.9 gal/lb (40.9 l/kg). Eight (including those three plants not in the analysis) of the 12 plants in this subcategory currently achieved the median flow ratio. The four plants above the median included three vegetable tanners and one mineral non-chromium tanner. Tannery No. 376 employs the same raw materials and processes as plants operating at or below the median water use ratio but has a flow of 9.6 gal/lb (80.1 l/kg). The Agency believes that with proper water conservation techniques, this tannery and the other plants above the median can achieve the median ratio for the subcategory. In this subcategory, only minor reduction in water use for existing sources was identified (4.8 gal/lb or 40.1 l/kg) after review of those plants considered (excluding Tannery Nos. 385,415, and 47 as noted above). Similarly, modest reduction to 4.2 gal/lb or 35.1 l/kg (14 percent lower than the median) was determined to be achievable by new sources as demonstrated by Tannery No. 397 (and the three plants excluded) using raw materials and groups of subprocesses typical of the subcategory.

Subcategory Four - (Retan-Wet Finish (sides))

Particular attention was paid to the weight basis for subcategory 4, because the weight of raw material entering the first wet process (i.e., split and shaved) is usually less than the weight as received. Table V-4 lists all of the plants in the data base used to develop median water use for this subcategory. Eight plants provided water use data. However, two plants, Tannery Nos. 389 and 404, were not used in the development of reduced flow ratios due to minor variations in processing operations which in one case should have contributed to higher water use. For example, Tannery No. 389 reported no coloring or fatliquoring subprocesses which may have contributed to a marginally lower water use. Tannery No. 404 operates a beamhouse and tanyard for a portion of its production which requires more water than for retan-wet finishing. Separate and verified water use data were available for segregated wastewater streams from the retan-wet finishing operations and from the complete unhairing-tanning-retan-wet finishing operations. Even with these differences, Tannery No. 404 was among the lowest water users in this subcategory. The resulting median flow is 4.8 gal/lb (40.1 l/kg). The available data demonstrated little additional flow reduction; the reduced flow ratio is 4.6 gal/lb (38.4 l/kg). Due to the distribution of data, one half of the plants in the data base already achieve the reduced flow ratio. The new source flow ratio, 4.5 gal/lb (37.6 l/kg), was achieved by Tannery No. 5000 using the same raw materials (blue grain sides) and processes (retan-wet finish) as the other plants in the subcategory.

Subcategory Five - (No Beamhouse)

Plants in the no beamhouse subcategory process both pickled cowhide and pickled sheepskins. Thirteen facilities (see Table V-4) provided usable data. All 13 plants used two major groups of subprocesses, tanyard and retan-wet finishing. Processing of cattlehides at three plants was distributed above and below the median water use ratio, as was the processing of sheepskins at ten plants. Accordingly, the Agency believes that the median water use can be achieved for plants processing either of the raw materials. The median water use ratio for the subcategory was 5.8 gal/lb (48.4 l/kg). Both the highest (13.5 gal/lb or 113 l/kg) and the lowest (3.5 gal/lb or 29.2 l/kg) water use ratios were exhibited by sheepskin processes. In determining reduced water use, three of the thirteen plants with minor process variations were not considered. The reduced water use for existing sources 4.0 gal/lb (33.4 l/kg), was achieved by two sheepskin tanners and one cattlehide tanner. The new source water ratio, 3.8 gal/lb (31.7 l/kg), was achieved by one sheepskin and one cattlehide tanner. These water use ratios are achievable because at least two existing plants using the same raw materials and the same processes have demonstrated these ratios.

Subcategory Six - (Through-the-Blue)

Only three plants provided usable data in subcategory 6 (see Table V-4). All plants used the same raw materials and groups of subprocesses (hair pulp, chromium tan) and little variance in flow ratio was found. All plants were also noted to be fairly new. A median flow ratio of 2.1 gal/lb (17.5 l/kg) was determined. Both the reduced and the new source flow ratios are 1.4 gal/lb (11.7 l/kg). No additional flow reduction for new sources was considered appropriate because this ratio already is low.

Subcategory Seven - (Shearling)

Only one plant submitted usable data in this subcategory although eight are known to be operating. The water use ratio for this plant, 9.4 gal.lb (78.5 l/kg), was used for all purposes without reduction. The raw material (shearlings) and groups of subprocesses (chromium tan, retan-wet finish) used by this plant were found to be typical of all other plants in the subcategory for which information was available. No achievable water use reduction was projected because data from other plants were not available to confirm engineering projections.

Subcategory Eight - (Pigskin)

Only two facilities (see Table V-4) are known to be operating with the majority of production, i.e., 80%, in subcategory 8. Although one facility is considerably larger, size has not demonstrated a significant effect on water use in this industry. Therefore the two plants were evaluated equally, resulting in a median flow ratio of 5.0 gal/lb (41.7 l/kg). With only two plants, a reduced water use ratio for existing sources was not identified. The new source flow ratio, 4.1 gal/lb (34.2 l/kg), was considered achievable because Tannery No. 185 achieved that water use.

Subcategory Nine - (Retan-Wet Finish (Splits))

Four plants which process blue splits by retan-wet finish were found to have provided usable data (see Table V-4). As in subcategory 4, particular attention was paid to basing the flow ratio on the material weight placed into the first wet process rather than the received weight. All plants had consistent processing steps and were used in developing the median water use ratio of 3.0 gal/lb (25.0 l/kg). This median water use ratio was achieved by two of the four plants. The reduced water use ratio for existing sources was selected to be the same as for new sources, 2.5 gal/lb (20.9 l/kg),, a reduction of 20 percent. This ratio was achieved by two of four plants for which data were available. Further reduction for new sources was not projected because data from other plants in the subcategory were not available to confirm such a projection.

D. WASTE CHARACTERISTICS

The characteristics of untreated wastewaters presented in the following tables 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. Raw wastes as presented here are the total plant effluent prior to any treatment other than screening or flow equalization. Thus, raw waste characteristics may reflect the reduction in pollutant load achieved by screening, which is usually minimal.

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

Depending on its origin, a waste stream may contain 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 (TSS), oil and grease, total chromium, ammonia, and sulfide. Information regarding other classical pollutant parameters, including solids and nutrients, is also available from selected sources.

Relating (normalizing) wastewater volumes and pollutant parameters to production is one way of gaining perspective on the waste generated by tannery operations. Water use and pollutant loadings have been related to production (defined as the weight of hides/skins processed) for the purpose of normalizing the data. The production level for a given plant, in terms of hide/skin weight processed per operating day, was used directly wherever possible. In some cases it was computed from the number and average weight of hides reported by the tannery during the period of record if daily hide weight data were not available. This approach was used 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 (e.g., green-salted, brine-cured, fresh), and the variable amounts of extraneous matter attached to the hides contributed to variations in the weight of raw material processed. These factors also can influence the waste flows and loadings. Therefore, daily data were used wherever possible to fully reflect the variations. As discussed previously, wastewater flow is generally presented as the ratio of total volume of wastewater generated to production level per operating day (gallons per pound or liters per kilogram). Other wastewater characteristics (classical pollutants) are expressed in terms of pollutant mass per 1,000 units of production. The weight of raw material as received is essentially the same as the weight of raw material entering wet processing in seven subcategories because very little trimming occurs. In subcategories 4 and 9, the weight entering wet processing can be substantially less than the weight as received depending upon the degree of trimming, shaving, and splitting.

Raw waste loadings are presented for each subcategory in the following tables. The Agency calculated "classical" pollutant loadings from concentrations in milligrams per liter (mg/l), wastewater volume in gallons per day (gpd), and production levels as 1,000 lb units of incoming raw material, with the exception of subcategories 4 and 9, as described previously. The data base for these parameters has been assembled primarily from historical data submitted by plants in the industry, supplemented by data gathered from governmental sources, EPA toxic pollutant sampling visits, and plant visits.

Data concerning total chromium levels are presented in both conventional and toxic pollutant tables representing analysis by the diphenyl carbazide (wet chemistry) and atomic adsorption spectrophotometer (AA) methods, respectively. Historically, the wet chemistry method has been used, resulting in considerably more data. Thus, until a larger data base for AA analysis has been developed, the wet chemistry results represent the basis for wastewater characterization.

EPA representatives collected data regarding toxic pollutants through sampling programs described previously (Section II). With the exception of chromium (which has been monitored for some time in this industry), the analytical results represent a limited but valid data base for toxic pollutants present in leather tanning and finishing wastewaters. The toxic pollutant data acquired by EPA indicate clearly the presence of toxic constituents in the waste streams. However, a mass relationship between toxic pollutant levels and production is unclear at this time (with the exception of chromium). To some extent, the presence of specific constituents is related to or identifies the manufacturing process employed.

The Agency sampled a cross-section of the leather tanning industry to determine the presence and levels of toxic pollutants, as noted previously in Tables II-4 and II-5. Table V-5 lists the processes, raw material, and finished product uses for each of the 27 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 amounts in other chemicals. The most heavily used toxic pollutant in leather tanning is chromium, but others used in significant amounts and found in wastewaters 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);

TABLE V-5

PLANT CHARACTERISTICS OF TANNERIES SAMPLED FOR TOXIC POLLUTANTS

Subcategory	Tannery Process (See Key Below) (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Hide--Materials	Finished Product	Location	Demographic Information: Age in Years (1979)	Demographic Information: Average Number of Employees
1	X			X		X	X	X	X	Cattle--green salted; brine cured	Shoe upper	Minnesota	104	400
1	X			X		X	X	X	X	Cattle--green salted; brine cured	Shoe upper, garment patent	Maine	21	600
1	X		X	X		X	X	X	X	Cattle--fresh, sheepskin shearling	Shoe upper, miscellaneous	California	102	200
1	X			X			X	X	X	Cattle--green salted, brine cured	Upholstery, bags	Maryland	3	280
1	X			X		X	X	X	X	Cattle--green salted	Shoe upper, bags	New Hampshire	27	200
1	X	X		X		X	X	X	X	Cattle--brine cured	Shoe upper, bags	Tennessee	30	260
1	X			X		X	X	X	X	Cattle--fresh and brine cured	Shoe upper	California	122	375
1	X			X		X	X	X	X	Cattle--green salted	Garment, shoe upper	Maine	39	450
2		X		X		X	X	X		Cattle--brine cured	Shoe upper, bags	New Hampshire	56	50
2		X		X		X	X	X	X	Cattle--green salted, brine cured	Shoe upper	New York	102	300
3		X		X	X	X	X	X	X	Cattle--brine cured	Sole, waistbelt	Virginia	52	250
3	X				X**		X	X	X	Steers, cows, calves--brine cured	Alum lace leather	Kentucky	112	32
3		X			X			X	X	Steers, cows, calves--brine cured	Sole, curried leather	Pennsylvania	*	220
3		X			X	X	X	X	X	Steer	Sole leather	West Virginia	*	*
4						X	X	X	X	Thru-the-blue sides	Shoe upper, bag, belt	Maine	42	400
4						X	X	X	X	Thru-the-blue cattle, pig, buffalo	Shoe upper, bag,	New Hampshire	25	60
5				X		X	X	X	X	Pickled lambskins	Garment	Maine	18	93
5				X		X	X	X	X	Pickled sheepskins & lambskins	Garment and shoe lining	Massachusetts	83	130
5				X	X			X	X	Pickled cow bellies	Shoe lining, work gloves	Massachusetts	25	55
6	X			X						Cattle--brine cured	Thru-the-blue tanned sides	Missouri	8	100
6	X			X						Cattle--brine cured	Thru-the-blue	Iowa	10	40
7				X	X		X	X		Wet salted shearlings	Garment	New Hampshire	77	135
7				X		X	X	X		Salted shearlings	Garment	California	110	250
8	X			X		X	X	X	X	Pig--green salted	Shoe upper, glove	Michigan	70	300
8	X			X		X	X	X	X	Pig--brine cured	Work glove	Tennessee	25	60
9						X	X	X	X	Thru-the-blue splits	Garment, glove, shoe	Maine	39	45
9						X	X	X	X	Splits--tanned	Shoe upper	Massachusetts	17	35

(1) Hair-Pulp (2) Hair-Save (3) Wool Pull (4) Chrome Tan (5) Vegetable Tan (6) Retan (7) Color (8) Fatliquor (9) Finish

*Data not available
**Alum tannage

4. hexachloroethane, ethylbenzene and toluene solvents;

5. 2,4,6-trichlorophenol (a biocide);

6. biocides based on cresol; and

7. heavy metals (organo-metallic dyes).

Metals, including zinc, lead, nickel, copper, typically originate in organo-metallic dyes. Cyanide is also found in dyes, and probably in natural tannins as well. Although efforts were made to establish a list of toxic compounds found in tannery process chemicals, many tanners do not know the specific ingredients of the chemical formulations they are using. Additionally, many suppliers do not know the basic chemical ingredients or purposes for which their products are used in tanneries. These observations are particularly true for chemicals used in only 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 formulations are viewed by the tanner in functional terms only and not as chemicals reacting in a predictable manner.

As in water use, the levels and types of pollutants discharged in raw wastewaters by a plant are a function of its specific manufacturing processes. Each subcategory is discussed below.

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

The primary constituents of the soak and wash waste stream are BOD_5, COD, suspended solids, and dissolved solids. For a cattlehide tannery, in which soak and wash precedes hair pulping and chromium tanning, BOD_5 and suspended solids represent significant contributions to the total waste load. Because the incoming hides are generally either brine-cured or green-salted, the salt must also be removed in preparation for unhairing. This removal results in relatively high total solids values.

Fleshing of the hides follows the soak and wash process. Fleshings are generally isolated as a solid waste, and, when handled properly, do not contribute significantly to the total waste load.

The liming and unhairing process is one of the principal contributors of pollutants to the plant's 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 come from spent unhairing liquors. However, depending on the specific processes and formulations, some potentially significant amounts may carry over into spent tanning and retanning liquors.

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 but the ammonia content generally constitutes two-thirds of the total. The pickling step which follows bating generates relatively low levels of pollutants including BOD_5, suspended solids, and nitrogen.

The wastewater generated from chromium tanning is significant because it is the major source of chromium. However, the volume of this waste stream, as well as 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). Use of high temperatures in retanning maximizes chromium uptake, thereby reducing chromium discharge to the total waste stream.

Because subcategory 1 represents the largest portion of the leather tanning industry, considerably more data were available for characterizing its wastewaters than for any other subcategory, particularly for classical parameters. Table V-6 summarizes the classical parameters, including flow, which were employed to characterize the raw waste loads associated with this industry segment. The values for flow and selected waste constituents of primary significance represent both subcategory mean and median values for comparison purposes; flow values are shown in gallons of wastewater per pound of raw material processed and liters per kilogram (l/kg) while values for waste constituents are shown in kilograms per 1,000 kilograms of hide processed (kg/kkg) as well as milligrams per liter (mg/l). Table V-7 summarizes the toxic pollutants present in subcategory 1 raw wastewaters; constituents are characterized by pollutant type, number of positive analytical results, and pollutant concentration range.

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

The principal difference between subcategories 1 and 2 is the method of removing hair from cattlehides. Even though more water is used when hair is removed and washed by machine, the median water use ratio for this subcategory was found to be lower (5.8 gal/lb vs. 6.5 gal/lb or 48.4 vs 54.2 l/kg) than for subcategory 1. The waste loads associated with the hair-save process were found to vary, higher for some parameters (e.g., TSS) and lower for some parameters (e.g., Oil and Grease), from those for hair-pulp operations. The proteinaceous hair does not dissolve totally in the lower strength unhairing solution in the hair-save process. The total sulfide content was found to be correspondingly lower (1.94 kg/kkg vs 2.86 kg/kkg) for this subcategory. Current industry trends in this subcategory do not emphasize separation of the hair from the waste stream, since there is little economic incentive to wash and bale the hair for sale as a by-product. Thus, the partially dissolved hair is discharged and is reflected in part in the higher TSS load (264 kg/kkg vs 102 kg/kkg). The remaining tannery operations essentially are the same as subcategory 1, contributing similar additional waste loads.

Tables V-8 and V-9 summarize the raw wastewater characteristics for subcategory 2 in terms of classical parameters and toxic pollutants, respectively.

Subcategory Three - (Hair Pulp or Save/Non-chrome Tan/Retan-Wet Finish)

The tanning of cattlehides by agents other than chromium distinguishes this segment from subcategory 2. The most significant difference between the raw waste loads of the two subcategories occurs in the total chromium content. The use of tanning agents other than chromium (e.g., metal salts, syntans, formaldehyde and alum) reduces the average chromium concentration to a low level. The small amount of chromium present in the effluent from tanneries in subcategory 3, compared to subcategories 1 and 2, generally originates in the retanning operations, which may require chromium salts to impart the desired characteristics in the finished leather. Concentrations similar to those found in subcategories 1 and 2 occur for the classical parameters, BOD_5 and suspended solids. Table V-10 presents these values; Table V-11 summarizes toxic pollutants and their levels found in waste streams of subcategory 3 tanneries.

Subcategory Four - (Retan-Wet Finish (sides))

The tanneries in this industry segment limit their operations to retanning and wet finishing hides (blue stock) which have been unhaired and tanned elsewhere. The absence of the beamhouse process results in lower organic and sulfide loadings for this subcategory than for subcategories 1, 2, and 3. Since retanning

TABLE V-6

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY ONE

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	1,184	1,078	16	1,429	121 - 15,167
	(kg/kkg)	53.72	63.47	15	119	1.38 - 166.60
COD	(mg/l)	3,078	3,569	11	1,268	108 - 41,600
	(kg/kkg)	186.70	187.58	10	80	2.92 - 456.02
Total Suspended Solids	(mg/l)	1,582	1,913	17	1,485	142.2 - 19,939
	(kg/kkg)	102.12	104.00	16	165	0.31 - 469.77
Volatile Suspended Solids	(mg/l)	1,654	1,664	4	1,298	24 - 12,015
	(kg/kkg)	98.13	90.35	4	53	1.46 - 161.90
Oil & Grease	(mg/l)	493	990	13	51	224 - 6,834
	(kg/kkg)	27.54	57.80	13	51	10.28 - 417.19
Total Kjeldahl Nitrogen	(mg/l)	200	204	12	336	0.25 - 626
	(kg/kkg)	12.06	12.05	11	46	0.59 - 30.41
Ammonia	(mg/l)	69	63	12	1,298	4 - 182
	(kg/kkg)	3.86	3.85	11	6	0.086 - 12.71
Sulfide	(mg/l)	59	64	9	1,306	1.3 - 272
	(kg/kkg)	2.86	3.35	9	110	0.06 - 11.75
Total Chromium	(mg/l)	47	79	13	153	1.00 - 647.00
	(kg/kkg)	2.75	4.76	12	76	.038 - 43.697
Cyanide	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Phenol	(mg/l)	1.74	1.52	3	7	0.14 - 2.9
	(kg/kkg)	0.13	0.11	3	7	0.01 - 0.19
Total Organic Carbon	(mg/l)	1,243	1,243	1	1	1,243
	(kg/kkg)	44.09	44.09	1	1	44.09
Flow Ratio	(gal/lb)	6.5	6.83	28	-	-
	(l/kg)	54	57	28	-	-

TABLE V-7

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER
SUBCATEGORY ONE

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	1	1	1	1,100	1,100	1,100
Chromium	1	1	1	160,000	160,000	160,000
Copper	1	1	1	50	50	50
Nickel	1	1	1	60	60	60
Zinc	1	1	1	500	500	500
Acenaphthene	1	1	1	32	32	32
Benzidine	1	1	1	27	27	27
2,4,6-Trichlorophenol	1	1	1	880	880	880
1,2-Dichlorobenzene	1	1	1	255	255	255
1,4-Dichlorobenzene	1	1	1	54	54	54
1,2-<u>Trans</u>-dichloroethylene	1	1	1	30	30	30
Ethylbenzene	1	1	1	88	88	88
Naphthalene	1	1	1	24	24	24
Nitrobenzene	1	1	1	425	425	425
Phenol	1	1	1	4,400	4,400	4,400
Bis(2-ethylhexyl)phthalate	1	1	1	51	51	51
Dimethyl Phthalate	1	1	1	118	118	118
Acenaphthylene	1	1	1	16	16	16
Tetrachloroethylene	1	1	1	100	100	100
Toluene	1	1	1	100	100	100
Trichloroethylene	1	1	1	20	20	20
Asbestos	1	1	1	(*)	(*)	(*)

(*) Screening level only - chrysotile asbestos detected.

TABLE V-8

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY TWO

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	1,241	1,364	3	129	238 - 4,740
	(kg/kkg)	53.19	67.31	3	28	14.59 - 224.37
COD	(mg/l)	3,357	3,357	2	9	1,710 - 5,331
	(kg/kkg)	160.88	160.88	2	6	62.53 - 252.35
Total Suspended Solids	(mg/l)	4,853	3,793	3	879	320 - 23,370
	(kg/kkg)	264.28	198.72	3	120	24.16 - 655.71
Volatile Suspended Solids	(mg/l)	1,293	1,293	2	16	560 - 3,950
	(kg/kkg)	62.50	62.50	2	7	20.48 - 101.77
Oil & Grease	(mg/l)	306	306	2	10	64 - 580
	(kg/kkg)	13.07	13.07	2	6	4.28 - 30.66
Total Kjeldahl Nitrogen	(mg/l)	274	274	2	120	101 - 543
	(kg/kkg)	12.76	12.76	2	19	7.90 - 24.81
Ammonia	(mg/l)	90	90	2	9	82 - 170
	(kg/kkg)	4.07	4.07	2	9	3.00 - 4.21
Sulfide	(mg/l)	36	36	1	6	14 - 83
	(kg/kkg)	1.94	1.94	1	3	1.47 - 4.71
Total Chromium	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Cyanide	(mg/l)	0.01	0.01	1	3	0.01
	(kg/kkg)	0.001	0.001	1	3	0.001
Phenol	(mg/l)	4.56	4.56	1	3	1.26 - 7.92
	(kg/kkg)	0.24	0.24	1	3	0.06 - 0.45
Total Organic Carbon	(mg/l)	1,243	1,243	1	3	1,060 - 1,590
	(kg/kkg)	64.83	64.83	1	3	56.436 - 75.264
Flow Ratio	(gal/lb)	5.80	5.30	4	-	-
	(l/kg)	48	44	4	-	-

TABLE V-9

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER
SUBCATEGORY TWO

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	1	4	4	15,600	1,210	2,360.0
Chromium	1	4	4	150,000	66,800	113,050.0
Copper	1	4	4	79	55	67.5
Nickel	1	4	4	80	40	70.0
Zinc	1	4	4	3,640	400	977.5
Benzene	1	2	4	5	3	4.0
1,2,4-Trichlorobenzene	1	1	4	1	1	1.0
1,1,1-Trichloroethane	1	3	4	5	2	4.0
1,1,2-Trichloroethane	1	2	4	3	3	3.0
Chloroform	1	1	4	7	7	7.0
1,2-Dichlorobenzene	1	2	4	135	77	106.0
1,4-Dichlorobenzene	1	3	4	32	11	17.0
2,4-Dimethylphenol	1	1	4	7	7	7.0
Ethylbenzene	1	4	4	3,080	100	834.0
Fluoranthene	1	1	4	1.6	1.6	1.6
Methylene Chloride	1	3	4	15	5	6.0
Naphthalene	1	2	4	33	21	27.0
N-Nitrosodiphenylamine	1	1	4	8	8	8.0
Phenol	1	2	4	5,500	1,117	3,308.5
Bis(2-ethylhexyl)phthalate	1	3	4	235	32	100.0
Di-N-Butyl Phthalate	1	1	4	1	1	1.0
Acenaphthylene	1	1	4	5	5	5.0
Pyrene	1	1	4	0.4	0.4	0.4
Toluene	1	4	4	310	100	204.0
Trichloroethylene	1	1	4	3	3	3.0
Asbestos	1	1	4	3	3	3.0

(*) Screening level only - chrysotile asbestos detected.

TABLE V-10

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY THREE

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	2,210	2,127	6	506	100 - 4,490
	(kg/kkg)	54.63	63.14	6	410	1.83 - 151.11
COD	(mg/l)	7,746	7,668	5	354	350 - 64,000
	(kg/kkg)	271.66	266.73	5	267	18.88 - 1,741.21
Total Suspended Solids	(mg/l)	3,462	3,306	5	1,028	44 - 10,420
	(kg/kkg)	81.55	96.71	5	834	1.13 - 530.66
Volatile Suspended Solids	(mg/l)	2,386	2,386	2	9	1,644 - 4,180
	(kg/kkg)	61.85	61.85	2	8	26.01 - 140.21
Oil & Grease	(mg/l)	491	463	3	18	9.8 - 931
	(kg/kkg)	14.10	17.32	3	18	0.31 - 39.17
Total Kjeldahl Nitrogen	(mg/l)	462	456	5	28	53.8 - 913
	(kg/kkg)	12.81	13.58	5	28	1.62 - 36.92
Ammonia	(mg/l)	135	180	5	30	42 - 680
	(kg/kkg)	4.48	4.86	5	30	0.87 - 16.29
Sulfide	(mg/l)	92	100	3	15	2.4 - 328
	(kg/kkg)	2.17	3.43	3	15	.017 - 13.77
Total Chromium	(mg/l)	1.04	2.16	4	17	0.6 - 9.0
	(kg/kkg)	0.04	0.06	4	17	.003 - 0.262
Cyanide	(mg/l)	0.36	0.36	2	7	0.01 - 0.78
	(kg/kkg)	0.02	0.02	2	4	0.028 - 0.031
Phenol	(mg/l)	6.55	9.59	3	13	0.4 - 21.6
	(kg/kkg)	0.26	0.39	3	13	0.01 - 0.91
Total Organic Carbon	(mg/l)	382	382	1	3	350 - 415
	(kg/kkg)	11.20	11.20	1	3	10.52 - 11.67
Flow Ratio	(gal/lb)	4.90	5.45	12	-	-
	(l/kg)	41	45	12	-	-

TABLE V-11

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER SUBCATEGORY THREE

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	2	4	5	400	80	100
Chromium	2	5	5	115,000	3,700	28,000
Copper	2	5	5	200	100	160
Nickel	2	5	5	350	50	120
Zinc	2	5	5	830	460	685
Mercury	1	3	5	0.30	0.20	0.20
Benzene	1	3	5	1.00	0.80	0.80
Chlorobenzene	1	2	5	0.20	0.20	0.20
1,2,4-Trichlorobenzene	1	2	5	3.00	2.10	2.55
2-Chloronaphthalene	1	1	5	1.20	1.20	1.20
2,4,6-Trichlorophenol	2	5	5	1,700	15	71
Chloroform	1	1	5	24	24	24
1,2-Dichlorobenzene	2	3	5	304	49	204
1,3-Dichlorobenzene	1	2	5	3.20	3	3.10
1,4-Dichlorobenzene	2	3	5	40	19	20
2,4-Dichlorophenol	1	3	5	71	12	23
Ethylbenzene	1	4	5	43	15	17.50
Fluoranthene	1	2	5	4.70	1.00	2.85
Methylene Chloride	1	4	5	265	12	18.50
Naphthalene	2	2	5	59	28	43.50
4-Nitrophenol	1	2	5	23,041	4,053	13,547
N-Nitrosodiphenylamine	1	1	5	3.60	3.60	3.60
Pentachlorophenol	1	4	5	2,900	200	579
Phenol	2	5	5	25,000	51	338
Bis(2-ethylhexyl)phthalate	1	1	5	9.80	9.80	9.80
Di-N-Butyl Phthalate	1	2	5	4.90	1.00	2.95
Diethyl Phthalate	1	1	5	4.50	4.50	4.50
Fluorene	1	2	5	3.50	1.00	2.25
Pyrene	1	2	5	5.20	1.00	3.10
Tetrachloroethylene	1	4	5	78	18	27.50
Toluene	2	4	5	15	3.00	3.50
Trichloroethylene	1	2	5	0.30	0.20	2.50
Anthracene/Phenanthrene	1	3	5	7.60	3.00	6.80

TABLE V-12

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY FOUR

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	404	456	3	53	120 - 879
	(kg/kkg)	25.00	29.25	3	40	5.28 - 55.47
COD	(mg/l)	6,204	6,204	2	9	398.4 - 25,111
	(kg/kkg)	299.96	299.96	2	8	6.79 - 1,334.14
Total Suspended Solids	(mg/l)	1,132	886	3	53	46 - 1,680
	(kg/kkg)	62.76	51.01	3	40	1.52 - 91.21
Volatile Suspended Solids	(mg/l)	700	700	1	6	460 - 870
	(kg/kkg)	23.24	23.24	1	5	15.19 - 31.01
Oil & Grease	(mg/l)	86	153	3	15	15 - 642.4
	(kg/kkg)	8.68	6.76	3	14	1.64 - 13.74
Total Kjeldahl Nitrogen	(mg/l)	69	95	3	16	4.3 - 285
	(kg/kkg)	2.03	3.83	3	15	0.274 - 15.1
Ammonia	(mg/l)	45	50	3	16	1 - 203
	(kg/kkg)	1.51	1.79	3	15	0.033 - 3.99
Sulfide	(mg/l)	0.51	0.51	2	8	0.1 - 1.15
	(kg/kkg)	0.11	0.11	2	8	0.009 - 0.141
Total Chromium	(mg/l)	36	30	3	47	2.5 - 93.41
	(kg/kkg)	1.88	1.86	3	35	.083- 9.695
Cyanide	(mg/l)	0.01	0.01	1	6	0.1
	(kg/kkg)	-	-	1	-	-
Phenol	(mg/l)	4.64	4.64	2	13	0.07 - 24.07
	(kg/kkg)	0.24	0.24	2	12	0.002 - 0.57
Total Organic	(mg/l)	907	907	1	6	405 - 1,400
Carbon	(kg/kkg)	29.88	29.88	1	5	20.46 - 39.62
Flow Ratio	(gal/lb)	4.8	5.2	8	-	-
	(l/kg)	40	43	8	-	-

TABLE V-13

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER SUBCATEGORY FOUR

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/I) Maximum	Minimum	Median
Lead	1	6	7	1,900	470	1,000
Chromium	1	6	7	71,000	32,400	50,750
Copper	1	6	7	700	220	495
Nickel	1	4	7	130	110	120
Zinc	1	6	7	480	120	185
Mercury	1	1	7	0.32	0.32	0.32
Benzene	1	1	7	26.0	26.0	26.0
1,1,1-Trichloroethane	1	1	7	1.00	1.00	1.00
2,4,6-Trichlorophenol	1	2	7	4.00	2.00	3.00
Parachlorometa Cresol	1	3	7	5.00	3.00	3.00
Chloroform	1	6	7	34.0	4.00	14.00
1,2-Dichlorobenzene	1	4	7	22.0	9.00	12.00
1,2-Trans-dichloroethylene	1	6	7	15.0	3.00	7.00
2,4-Dichlorophenol	1	2	7	2.00	1.00	1.50
2,4-Dimethylphenol	1	6	7	146	45.0	98.0
Ethylbenzene	1	6	7	345	74.0	255
Naphthalene	1	6	7	3,230	326	1,480
4-Nitrophenol	1	6	7	2,700	64.0	910
Pentachlorophenol	1	6	7	400	38.0	240
Phenol	1	6	7	5,460	1,500	2,070
Bis(2-ethylhexyl)phthalate	1	6	7	180	28.0	81.5
Di-N-Butyl Phthalate	1	2	7	2.00	2.00	2.00
Diethyl Phthalate	1	1	7	2.00	2.00	2.00
Tetrachloroethylene	1	6	7	237	9.00	85.0
Toluene	1	6	7	630	86.0	113.5
Trichloroethylene	1	6	7	15.0	2.00	4.5
Asbestos	1	1	1	(*)	(*)	(*)

(*) Screening Level only - chrysotile asbestos detected

TABLE V-14

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY FIVE

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	1,550	1,550	2	6	156 - 4,060
	(kg/kkg)	39.16	39.16	1	3	10.49 - 69.03
COD	(mg/l)	8,374	8,374	2	6	1,232 - 26,950
	(kg/kkg)	145.64	145.64	1	3	93.13 - 235.59
Total Suspended Solids	(mg/l)	714	714	2	6	260 - 1,490
	(kg/kkg)	49.17	49.17	1	3	17.49 - 98.27
Volatile Suspended Solids	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Oil & Grease	(mg/l)	702	702	1	1	702
	(kg/kkg)	86.26	86.26	1	1	86.23
Total Kjeldahl Nitrogen	(mg/l)	86	86	2	6	42.6 - 218
	(kg/kkg)	4.95	4.95	1	3	3.03 - 8.60
Ammonia	(mg/l)	47	47	2	6	21 - 110
	(kg/kkg)	2.09	2.09	1	3	1.41 - 3.07
Sulfide	(mg/l)	0.10	0.10	1	2	0.1
	(kg/kkg)	0.01	0.01	1	2	0.008 - 0.012
Total Chromium	(mg/l)	21	21	2	6	14.60 - 30.00
	(kg/kkg)	2.21	2.21	1	3	1.17 - 3.69
Cyanide	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Phenol	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Total Organic Carbon	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Flow Ratio	(gal/lb)	5.80	6.67	13	-	-
	(l/kg)	48	56	13	-	-

TABLE V-15

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER SUBCATEGORY FIVE

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	3	3	3	1,600	300	700
Chromium	3	3	3	170,000	16,000	16,000
Copper	3	3	3	260	140	250
Nickel	3	3	3	30.0	6.00	6.00
Zinc	3	3	3	2,600	96.0	150
Benzene	1	1	3	100	100	100
2,4,6-Trichlorophenol	3	3	3	4,200	573	3,200
Chloroform	1	1	3	18.0	18.0	18.0
1,2-Dichlorobenzene	1	1	3	36.0	36.0	36.0
1,4-Dichlorobenzene	1	1	3	13.0	13.0	13.0
Ethylbenzene	2	2	3	100	100	100
Naphthalene	1	1	3	5.20	5.20	5.20
Pentachlorophenol	2	2	3	3,700	3,400	3,550
Phenol	2	2	3	6,200	3,200	4,700
Tetrachloroethylene	1	1	3	40.0	40.0	40.0
Toluene	2	2	3	100	11.0	55.5
Anthracene/Phenanthrene	1	1	3	133	133	133

TABLE V-16

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY SIX

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	5,892	5,892	2	7	2,020 - 11,000
	(kg/kkg)	130.25	130.25	2	7	49.47 - 233.48
COD	(mg/l)	13,602	13,602	2	7	5,610 - 32,900
	(kg/kkg)	302.35	302.35	2	7	137.39 - 698.42
Total Suspended Solids	(mg/l)	8,629	8,629	2	7	4,560 - 14,460
	(kg/kkg)	200.40	200.40	2	7	116.67 - 306.92
Volatile Suspended Solids	(mg/l)	8,186	8,186	2	4	2,650 - 12,540
	(kg/kkg)	183.34	183.34	2	4	64.9 - 266.17
Oil & Grease	(mg/l)	740	740	2	7	67 - 1,290
	(kg/kkg)	17.32	17.32	2	7	1.42 - 27.39
Total Kjeldahl Nitrogen	(mg/l)	894	894	2	7	385 - 1,740
	(kg/kkg)	20.29	20.29	2	7	9.43 - 36.93
Ammonia	(mg/l)	292	292	2	7	25.2 - 613
	(kg/kkg)	6.35	6.35	2	7	0.69 - 13.01
Sulfide	(mg/l)	358	358	1	4	137 - 680
	(kg/kkg)	7.59	7.59	1	4	2.91 - 14.44
Total Chromium	(mg/l)	295	295	1	4	233.0 - 397.0
	(kg/kkg)	6.26	6.26	1	4	4.496 - 8.428
Cyanide	(mg/l)	0.01	0.01	1	3	0.01
	(kg/kkg)	-	-	1	3	-
Phenol	(mg/l)	5.01	5.01	2	4	0.3 - 9.6
	(kg/kkg)	0.11	0.11	2	4	0.007 - 0.204
Total Organic Carbon	(mg/l)	2,913	2,913	1	3	1,620 - 3,920
	(kg/kkg)	75.06	75.06	1	3	41.93 - 96.0
Flow Ratio	(gal/lb)	2.10	2.03	3	-	-
	(l/kg)	18	17	3	-	-

TABLE V-17

TOXIC POLLUTNATS DETECTED IN RAW WASTEWATER
SUBCATEGORY SIX

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Cadmium	1	2	3	36.0	25.0	30.5
Chromium	1	3	3	396,000	178,400	185,400
Copper	1	3	3	150	66.0	110
Nickel	1	3	3	225	140	180
Zinc	1	3	3	915	660	820
Mercury	1	1	3	1.10	1.10	1.10
1,1,1-Trichloroethane	1	1	3	5.00	5.00	5.00
2,4,6-Trichlorophenol	1	1	3	5.00	5.00	5.00
1,2-Dichlorobenzene	1	2	3	200	140	170
1,3-Dichlorobenzene	1	2	3	29.0	20.0	24.5
1,4-Dichlorobenzene	1	1	3	51.0	51.0	51.0
2,4-Dichlorophenol	1	3	3	5.00	5.00	5.00
2,4-Dimethylphenol	1	1	3	5.00	5.00	5.00
Naphthalene	1	3	3	26.0	15.0	21.0
2-Nitrophenol	1	3	3	5.00	5.00	5.00
4-Nitrophenol	1	1	3	5.00	5.00	5.00
Pentachlorophenol	1	3	3	30.0	18.0	29.0
Phenol	1	2	3	200	120	160
Bis(2-ethylhexyl)phthalate	1	3	3	780	5.00	24.0
Asbestos	1	1	1	(*)	(*)	(*)

(*) Screening Level only - chrysotile asbestos detected

TABLE V-18

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY SEVEN

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	556	556	1	55	180 - 1,200
	(kg/kkg)	56.97	56.97	1	55	12.79 - 171.87
COD	(mg/l)	1,770	1,770	1	50	499 - 2,760
	(kg/kkg)	184.56	184.56	1	50	42.36 - 880.13
Total Suspended Solids	(mg/l)	762	762	1	61	157 - 3,262
	(kg/kkg)	77.68	77.68	1	61	14.81 - 362.59
Volatile Suspended Solids	(mg/l)	460	460	1	3	392 - 564
	(kg/kkg)	46.93	46.93	1	3	40.0 - 57.54
Oil & Grease	(mg/l)	163	163	1	43	15.9 - 366
	(kg/kkg)	15.33	15.33	1	43	1.47 - 30.51
Total Kjeldahl Nitrogen	(mg/l)	46	46	1	11	19.58 - 66
	(kg/kkg)	4.01	4.01	1	11	1.89 - 6.73
Ammonia	(mg/l)	16	16	1	11	5.88 - 26
	(kg/kkg)	1.39	1.39	1	11	0.57 - 2.25
Sulfide	(mg/l)	5.27	5.27	1	3	4.4 - 6.8
	(kg/kkg)	0.54	0.54	1	3	0.45 - 0.69
Total Chromium	(mg/l)	64	64	1	34	7.0 - 147.0
	(kg/kkg)	7.4	7.4	1	34	.93 - 16.97
Cyanide	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Phenol	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Total Organic Carbon	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Flow Ratio	(gal/lb)	9.4	9.4	1	-	-
	(l/kg)	78	78	1	-	-

TABLE V-19

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER
SUBCATEGORY SEVEN

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	1	1	5	80	80	80
Beryllium	1	1	5	0.25	0.25	0.25
Cadmium	1	1	5	2.00	2.00	2.00
Chromium	1	4	5	56,000	42,000	53,000
Copper	1	4	5	140	110	120
Nickel	1	4	5	120	27.0	110
Zinc	1	4	5	500	290	425
Mercury	1	4	5	26.0	0.20	2.10
Benzene	1	1	5	5.00	5.00	5.00
1,2-Dichloroethane	1	1	5	63.0	63.0	63.0
1,1,2,2-Tetrachloroethane	1	1	5	18.0	18.0	18.0
Chloroform	1	1	5	12.0	12.0	12.0
1,4-Dichlorobenzene	1	1	5	20.0	20.0	20.0
1,2-*Trans*-dichloroethylene	1	2	5	31.0	28.0	29.5
Methylene Chloride	1	1	5	14.0	14.0	14.0
Naphthalene	1	1	5	35.0	35.0	35.0
Nitrobenzene	1	1	5	10.0	10.0	10.0
Pentachlorophenol	1	2	5	1,250	400	825
Phenol	1	3	5	91.0	10.0	10.0
Bis(2-ethylhexyl)phthalate	1	1	5	93.0	93.0	93.0
Toluene	1	1	5	9.00	9.00	9.0
Trichloroethylene	1	2	5	42.0	20.0	31.0
Anthracene/Phenanthrene	1	1	5	36.0	36.0	36.0

TABLE V-20

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY EIGHT

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	3,402	3,402	2	331	1,148 - 7,457
	(kg/kkg)	115.16	115.16	2	306	28.58 - 711.53
COD	(mg/l)	4,919	4,919	2	6	3,420 - 6,311
	(kg/kkg)	201.63	201.63	2	6	89.25 - 452.87
Total Suspended Solids	(mg/l)	5,156	5,156	2	496	1,494 - 40,555
	(kg/kkg)	181.31	181.31	2	456	22.49 - 2,033.73
Volatile Suspended Solids	(mg/l)	3,922	3,922	2	495	598.2 - 39,338.4
	(kg/kkg)	144.69	144.69	2	455	17.54 - 1,650.37
Oil & Grease	(mg/l)	1,632	1,632	2	5	219 - 4,266
	(kg/kkg)	64.02	64.02	2	5	5.16 - 220.04
Total Kjeldahl Nitrogen	(mg/l)	116	116	2	4	90 - 200
	(kg/kkg)	5.70	5.70	2	4	1.54 - 13.64
Ammonia	(mg/l)	54	54	2	6	22 - 90
	(kg/kkg)	2.60	2.60	2	6	0.43 - 6.28
Sulfide	(mg/l)	263	263	1	277	1 - 1,000
	(kg/kkg)	12.15	12.15	1	257	0.031 - 61.43
Total Chromium	(mg/l)	89	89	1	207	20.2 - 270.8
	(kg/kkg)	4.40	4.40	1	195	0.790 - 57.80
Cyanide	(mg/l)	0.01	0.01	1	3	0.01
	(kg/kkg)	0.001	0.001	1	3	0.001
Phenol	(mg/l)	1.10	1.10	2	6	0.1 - 3.23
	(kg/kkg)	0.03	0.03	2	6	0.001 - 0.076
Total Organic Carbon	(mg/l)	1,396	1,396	2	4	950 - 1,495
	(kg/kkg)	61.88	61.88	2	4	35.21 - 125.52
Flow Ratio	(gal/lb)	5.00	5.00	2	-	-
	(l/kg)	42	42	2	-	-

TABLE V-21

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER SUBCATEGORY EIGHT

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	1	1	3	105	105	105
Chromium	1	3	3	112,000	40,800	42,300
Copper	1	3	3	204	56.0	200
Nickel	1	3	3	43.0	38.0	40.0
Zinc	1	3	3	210	156	174
Benzene	1	3	3	2.00	1.00	2.0
1,1,1-Trichloroethane	1	3	3	129	66.0	89.0
Chloroform	1	3	3	5.00	3.00	3.00
1,1-Dichloroethylene	1	2	3	4.00	3.00	3.50
2,4-Dichlorophenol	1	3	3	6.00	2.00	3.00
2,4-Dimethylphenol	1	1	3	1.00	1.00	1.00
Ethylbenzene	1	3	3	81.0	31.0	43.0
Methylene Chloride	1	3	3	241	165	180
4-Nitrophenol	1	3	3	1,415	297	607
N-Nitrosodiphenylamine	1	2	3	1.00	1.00	1.00
Pentachlorophenol	1	3	3	201	5.00	46.0
Phenol	1	3	3	447	236	257
Bis(2-ethylhexyl)phthalate	1	3	3	17.0	11.0	15.0
Di-N-butyl Phthalate	1	3	3	22.0	11.0	13.0
Tetrachloroethylene	1	2	3	2.00	1.00	1.50
Toluene	1	3	3	12.0	6.00	7.00

TABLE V-22

RAW WASTEWATER CHARACTERISTICS
SUBCATEGORY NINE

Parameter		Median	Mean	Number of Plants	Number of Individual Observations	Range of Individual Values
BOD_5	(mg/l)	864	864	1	9	376 - 1,600
	(kg/kkg)	16.91	16.91	1	9	7.34 - 33.38
COD	(mg/l)	3,833	3,833	1	3	2,900 - 4,800
	(kg/kkg)	42.61	42.61	1	3	32.23 - 53.36
Total Suspended Solids	(mg/l)	1,232	1,232	2	10	222.1 - 7,440
	(kg/kkg)	23.85	23.85	2	10	5.99 - 82.73
Volatile Suspended Solids	(mg/l)	2,852	2,852	1	3	985 - 5,170
	(kg/kkg)	31.70	31.70	1	3	10.95 - 57.47
Oil & Grease	(mg/l)	678	678	2	11	140 - 1,047
	(kg/kkg)	19.30	19.30	2	11	2.00 - 31.51
Total Kjeldahl Nitrogen	(mg/l)	353	353	1	3	260 - 480
	(kg/kkg)	3.93	3.93	1	3	2.89 - 5.34
Ammonia	(mg/l)	149	149	2	4	78 - 207
	(kg/kkg)	3.62	3.62	2	4	0.87 - 6.23
Sulfide	(mg/l)	1.70	1.70	2	4	1.4 - 2.4
	(kg/kkg)	0.03	0.03	2	4	0.02 - 0.04
Total Chromium	(mg/l)	37	37	2	8	20.0 - 47.4
	(kg/kkg)	1.07	1.07	2	8	0.567 - 1.344
Cyanide	(mg/l)	-	-	-	-	-
	(kg/kkg)	-	-	-	-	-
Total	(mg/l)	0.16	0.16	1	1	0.16
Phenol	(kg/kkg)	0.01	0.01	1	1	0.01
Total Organic	(mg/l)	-	-	-	-	-
Carbon	(kg/kkg)	-	-	-	-	-
Flow Ratio	(gal/lb)	3.00	3.25	4	-	-
	(l/kg)	25	27	4	-	-

TABLE V-23

TOXIC POLLUTANTS DETECTED IN RAW WASTEWATER
SUBCATEGORY NINE

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	2	5	5	590	100	200
Chromium	2	5	5	120,000	1,470	8,900
Copper	2	5	5	360	62	150
Nickel	2	5	5	30	20	20
Zinc	2	5	5	4,000	94	165
Cadmium	1	4	5	20	20	20
Mercury	1	4	5	0.6	0.3	0.3
N-Nitrosodiphenylamine	1	1	5	247	247	247
Anthracene/Phenanthrene	2	2	5	106	4	55
Benzene	1	4	5	92	5	5
2,4,6-Trichlorophenol	1	1	5	3	3	3
2,4-dimethylphenol	1	2	5	41	1	21
Ethylbenzene	1	4	5	99	22	67
Methylene Chloride	1	4	5	33	13	23
Naphthalene	1	4	5	183	39	115
Pentachlorophenol	1	3	5	151	2	33
Phenol	1	3	5	109	32	88
Bis(2-ethylexyl)phthalate	1	3	5	109	9	26
Di-n-butyl phthalate	1	2	5	4	1	2.5
Diethyl phthalate	1	1	5	1	1	1
Tetrachloroethylene	1	2	5	1	1	1
Toluene	1	4	5	23	6	13.5

may involve chromium, the total chromium level in the plant's effluent is significant but lower than for a plant which includes tanyard operations (1.88 kg/kkg vs. 2.75 kg/kkg for subcategory 1).

Tables V-12 and V-13 characterize the tannery wastewaters for classical and toxic pollutants, respectively.

Subcategory Five - (No Beamhouse)

Subcategory 5 tanneries have only tanyard and retan-wet finish operations, with no beamhouse. Since unhairing operations are absent from these tanneries, the raw waste loads, including BOD_5, suspended solids, and sulfide, are less than those for subcategories 1, 2, and 3. Tanyard operations increase classical pollutant levels beyond those typical for strictly retan-wet-finish facilities. Tables V-14 and V-15 present the mean, median, and range of values for classical and toxic pollutants in "no beamhouse" tanneries.

Subcategory Six - (Through-the-Blue)

The major operations of subcategory 6 tanneries involve hair removal and chromium tanning of cattlehides to produce blue stock for subsequent retan-wet finishing at other plants. Relatively high organic loads, as well as the nitrogen and sulfide contents, come from beamhouse operations; total chromium levels result from chromium tanning processes. Characteristic raw waste loads for the classical parameters are presented in Table V-16. Table V-17 identifies the toxic pollutants detected and the range of concentrations.

Subcategory Seven - (Shearling)

Tanneries in this subcategory tan and wet finish sheepskins with wool intact. Although there is no need for a beamhouse, the amount of foreign matter which must be removed from the wool creates organic waste loads higher than those created by "no beamhouse" tanneries. The absence of grease recovery during the degreasing step usually results in higher oil and grease loads. Chrome tanning is prevalent for shearling processing and results in significant levels of total chromium in the untreated wastewater.

Tables V-18 and V-19 summarize the classical and toxic pollutants found at shearling tanneries.

Subcategory Eight - (Pigskin)

An additional subcategory for pigskin tanneries has been established since the previous document was published (July 1979). While the processing steps are very similar to those in subcategory 1 tanneries, less water is used, while higher pollutant loads are generated, thus substantiating a separate subcategory (based on differences in raw materials) for pigskin tanneries. A significant factor is that pigskins require unhairing, depending on the skin received, and degreasing. These aspects of pigskin tannery processes (i.e.,) can alter raw wastewater characteristics markedly (e.g., BOD_5, TSS, Oil and Grease, Sulfide). Additionally, the conventional tanyard operation results in a fully tanned skin, unlike cattlehide processing, which eliminates the need for a retanning step. Representative parameter concentrations and waste loads are presented in Tables V-20 and V-21.

Subcategory Nine - (Retan-Wet Finish (splits))

Originally a part of subcategory 4 in the proposed regulations, tanneries which retan and wet-finish only splits use substantially less water than other retan-wet finish facilities, although process operations are the same. Therefore, data for these facilities are presented separately in Tables V-22 and V-23.

TABLE V-24

NUMBER OF DIFFERENT TOXIC POLLUTANTS
DETECTED PER SUBCATEGORY

	Subcategory								
Industry Total	1	2	3	4	5	6	7	8	9
52	23	27	35	28	18	21	25	22	8

Of the 126 toxic pollutants Table V-24 indicates that 52 have been identified in the raw wastewaters of the leather tanning and finishing industry. Table V-24 also shows the number of different toxic pollutants that were detected in the raw wastewater of the plants sampled in each subcategory.

From Table V-24, it is apparent that the number of different toxic pollutants detected in the wastewaters falls within a fairly small range (with the exception of subcategory 9), although the specific pollutants vary with the type of manufacturing process employed.

It should also be noted that 13 toxic pollutants were detected in the raw process (intake) water used by the tanneries sampled, as detailed in Table V-25.

TABLE V-25

NUMBER OF DIFFERENT TOXIC POLLUTANTS DETECTED IN RAW PROCESS WATER

	Subcategory								
Industry Total	1	2	3	4	5	6	7	8	9
26	13	9	10	15	-	4	-	10	-

Although the preceeding tables have characterized the wastewater discharges of the nine subcategories, it must be recognized that the values displayed for conventional parameters result from long term observations. In reality, both flow and wastewater strength vary widely throughout each day and from day to day because leather tanning and finishing processes are batch processes. Table V-26 illustrates this for a subcategory 1 tannery. Similarly, seasonal influences alter raw wasteloads due to such factors as hide weight changes and the degree of extraneous matter which must be removed from the hide. However, as discussed in Section IV (Subcategorization), winter and summer hide weight differences did not require further separation of subcategories or warrant different effluent limitations or standards.

TABLE V-26

HOURLY RAW WASTE DATA FOR A SUBCATEGORY ONE TANNERY

Time	Flow (mg(m^3))	BOD$_5$ (mg/l)	Suspended Solids (mg/l)	Chromium Total (mg/l)	TKN (mg/l)	pH (s.u.)	Oil and Grease (mg/l)
7 - 8 a.m.	.0592(224)	6,190	6,300	116	1,333	12.22	770
8 - 9 a.m.	.0523(198)	1,60	2,260	36.8	333	9.48	170
9 - 10 a.m.	.0443(167)	1,320	1,420	21.0	196	8.80	280
10 - 11 a.m.	.0581(220)	1,650	2,080	20.2	324	9.50	160
11 - 12 a.m.	.0506(192)	1,370	2,120	24.8	227	11.60	320
12 - 1 p.m.	.0460(174)	1,550	1,920	14.5	249	11.81	230
1 - 2 p.m.	.0505(191)	1,080	760	17.2	222	9.44	270
2 - 3 p.m.	.0526(199)	1,660	1,740	13.0	204	10.36	350
3 - 4 p.m.	.0347(131)	1,030	260	16.5	151	7.09	130
4 - 5 p.m.	.0337(128)	644	180	76.5	49	7.25	160
5 - 6 p.m.	.0347(131)	748	620	26.5	67	6.57	230
6 - 7 p.m.	.0250(95)	862	240	81.0	58	6.43	266
7 - 8 p.m.	.0303(115)	662	60	34.1	37	6.89	58
8 - 9 p.m.	.0201(76)	954	1,580	76.2	125	11.83	214
9 - 10 p.m.	.0241(91)	1,420	1,220	236	141	6.16	1,200
10 - 11 p.m.	.0221(84)	430	240	81.5	39	6.83	192
11 - 12 p.m.	.0224(85)	439	480	122	60	6.60	110
12 - 1 a.m.	.0243(92)	100	60	19.3	20	7.70	34
1 - 2 a.m.	.0230(87)	4,140	7,020	65.5	787	12.52	1,900
2 - 3 a.m.	.0248(94)	2,210	2,720	201	232	9.56	1,100
3 - 4 a.m.	.0352(133)	1,690	1,460	17.3	187	10.90	326
4 - 5 a.m.	.0439(166)	2,370	4,400	53.2	520	12.30	635
5 - 6 a.m.	.0448(170)	2,600	6,040	51.5	1,378	12.34	1,380
6 - 7 a.m.	.0648(245)	3,950	3,820	113	920	11.95	1,200

Data Taken 9/1-2/76

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

A. 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

B. 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_5 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_5 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_5 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 and potentially toxic 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 because 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 use 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 can produce scum lines on water treatment basin walls and other containers, block sewer collection pipes, and adversely affect fish and waterfowl. 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 ("rotten eggs"), and can damage property through paint discoloration. In sewers, hydrogen sulfide can be oxidized by aerobic bacteria to sulfuric acid resulting in "crown" corrosion and corrosion of equipment in POTWs. Hydrogen sulfide gas also can 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. Unfortunately, this hazard is so common that incidents involving hydrogen sulfide are frequently understated or not reported. Hydrogen sulfide gas, while explosive at concentrations of 4.3 to 46 percent volume in air, is lethal to humans at much lower concentrations, typically 0.2 percent volume in air (2000 ppm). Acute poisoning occurs at levels of about 0.1 percent. Evolution of hydrogen sulfide gas is pH dependent. Sulfides in water solution exist as several species. At pH 7, 50 percent of the sulfide present exists as hydrogen sulfide; at pH 6 about 90 percent is hydrogen sulfide. At pH 7 and 20°C, 1 mg/l dissolved hydrogen sulfide in water is in equilibrum with about 275 ppm hydrogen sulfide in the surrounding air. Careless mixing of acid and sulfide containing alkaline streams can 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. The actual hazardous potential is site specific. Well aerated, free flowing sewers at neutral to high pH generally will not experience hydrogen sulfide problems unless slug loadings are discharged into them. Conversely, acidic, stagnant areas resulting from discontinuities ("low spots") in the hydraulic profile of sewers are likely to evolve the gas.

Sulfides also 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 in a tannery primarily by spent bating liquors and by breakdown of organic proteins (dissolved hair and dermal matter).

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 a measure of the ammonia nitrogen plus organic nitrogen in wastewater. Organic nitrogen (as measured approximately by TKN minus ammonia) is derived primarily from dissolved or pulped proteinaceous hair removed from hides. Biological deamination and 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, in addition to ammonia, of the potential environmental impact of nitrogen contained in tannery wastewater.

Phenols(Total). "Total Phenols" is a nonconventional pollutant parameter. Total phenols is the result of analysis using the 4-AAP (4-aminoantipyrene) method. This analytical procedure measures the color development of reaction products between 4-AAP and some phenols. The results are reported as phenol. Thus "total phenol" is not total phenols because many phenols (notably pentachlorophenol) do not react. Also, since each reacting phenol contributes to the color development to a different degree, and each phenol has a molecular weight different from others and from phenol itself, analyses of several mixtures containing the same total concentration in mg/l of several phenols will give different numbers depending on the proportions in the particular mixture.

Despite these limitations of the analytical method, total phenols is a useful parameter when the mix of phenols is relatively constant and an inexpensive monitoring method is desired. In any given plant or even in an industry subcategory, monitoring of "total phenols" provides an indication of the concentration of this group of priority pollutants as well as those phenols not selected as priority pollutants. A further advantage is that the method is widely used in water quality determinations. Phenols were identified 24 times in raw wastewaters, more than any other acid fraction pollutant.

In an EPA survey of 103 POTWs the concentration of "total phenols" ranged from 0.0001 mg/l to 0.176 mg/l in the influent, with a median concentration of 0.016 mg/l. Analysis of effluents from 22 of these same POTWs which had biological treatment meeting secondary treatment performance levels showed "total phenols" concentrations ranging from 0 mg/l to 0.203 mg/l with a median of 0.007. Removals were 64 to 100 percent with a median of 78 percent.

It must be recognized, however, that six of the eleven priority pollutant phenols could be present in high concentrations and not be detected. Conversely, it is possible, but not probable, to have a high "total phenol" concentration without any phenol itself or any of the ten other priority pollutant phenols present. A characterization (GC/MS) of the phenol mixture to be monitored to establish constancy of composition by a statistically valid surrogate relationship will allow "total phenols" to be used with confidence.

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 indicates 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 POTWs from corrosion, pH levels of wastewaters entering the sewerage system must remain above 6.

Waters with a pH below 6 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 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. On the other hand, unusually high pH (for instance 11) 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 or low 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 of 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 in the waste indicates that properly designed conventional treatment processes may be effective in pollution control.

Nitrates (NO_3) and Nitrites (NO_2)

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 cyanosis 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 coliform bacteria, 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, cholera, 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.

C. TOXIC POLLUTANTS

The 126 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. Discussion that follows of the environmental and human health fate and effect of these toxic pollutants has been developed primarily from the November, 1980 Ambient Water Quality Criteria Documents (EPA-440/5-80 Series)[1], the November 28, 1980 Federal Register notice which summarized them[2], and a two volume report entitled Water-Related Environmental Fate of 129 Priority Pollutants.[3].

1. 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 (purgeable) fraction, a basic or neutral extractable fraction, and an acidic extractable fraction.

Volatile Fraction. Two volatile organic pollutants were found at least once in the sampled effluents. These compounds are typically used as solvents.

Methylene Chloride. Methylene chloride, also called dichloromethane (CH_2Cl_2), is a colorless liquid manufactured by chlorination of methane or methyl chloride followed by separation from the higher chlorinated methanes formed as coproducts. Methylene chloride boils at 40°C, and has a vapor pressure of 362 mm Hg at 20°C. It is slightly soluble in water (20 g/l at 20°C), and very soluble in organic solvents. U.S. annual production is about 250,000 tons. Methylene chloride is a common industrial solvent found in insecticides, metal cleaners, paint, and paint and varnish removers. It was found in the raw effluents of a number of tanneries.

Methylene chloride is not generally regarded as highly toxic to humans. Most human toxicity data are for exposure by inhalation. Inhaled methylene chloride acts as a central nervous system depressant. There is also evidence that the compound causes heart failure when large amounts are inhaled. Methylene chloride does produce mutation in tests for this effect. In addition a bioassay recognized for its extermely high sensitivity to strong and weak carcinogens produced results which were marginally significant. Thus potential carcinogenic effects of methylene chloride are not confirmed or denied, but are under continuous study. Difficulty in conduting and interpreting the test results from the low boiling point (40°C) of methylene chloride which increases the difficulty of maintaining the compound in growth media during incubation at 37°C; and from the difficulty of removing all impurities, some of which might themselves be carcinogenic. For the protection of human health from the potential concinogenic effects due to exposure to methylene chloride through ingestion of contaminated water and contaminated aquatic organisms, the ambient water concentration should be zero based on the non-threshold assumption for this chemical. However, zero level may not be attainable at the present time. Therefore, the levels which may result in incremental increase of cancer risk over the lifetime are estimated at 10^{-5}, 10^{-6} and 10^{-7}. The corresponding recommended criteria are 0.0019 mg/l, 0.00019 mg/l, and 0.000019 mg/l.

The biochemical oxidation of this compound was studied in one laboratory scale study at concentrations higher than those expected to be contained by most municipal wastewaters. After five days no degradation of methylene chloride was observed. The conclusion reached is that biological treatment produces little or no removal by degradation of methylene chloride. The high vapor pressure of methylene chloride is expected to result in volatilization of the compound from aerobic treatment steps in a POTW. It has been reported that methylene chloride inhibits anaerobic biological treatment processes. Methylene chloride that is not volatilized in the POTW is expected to pass through into the effluent. Methylene chloride was detected in treated effluents in 12 out of 40 samples ranging from 3 to 71 μg/l, with a median concentration of 20 μg/l.

Ethylbenzene. Ethylbenzene is a colorless, flammable liquid manufactured commercially from benzene and ethylene. Approximately half of the benzene used in the U.S. goes into the manufacture of more than three million tons of ethylbenzene annually. Ethylbenzene boils at 136°C and has a vapor pressure of 7 mm Hg at 20°C. It is slightly soluble in water (0.14 g/l at 15°C) and is very soluble in organic solvents. About 98 percent of the ethylbenzene produced in the U.S. goes into the production of styrene, much of which is used in the plastics and synthetic rubber industries. Ethylbenzene is a consitutent of xylene mixtures used as diluents in the paint industry, agricultural insecticide sprays, and gasoline blends. EPA also identified ethylbenzene in tannery effluents; concentrations were as high as 3080 ppb in raw wastewaters.

Although humans are exposed to ethylbenzene from a variety of sources in the environment, little information on effects of ethylbenzene in man or animals is available. Inhalation can irritate eyes, affect the respiratory tract, or cause vertigo. In laboratory animals ethylbenzene exhibited low toxicity. There are no data available on teratogenicity, mutagenicity, or carcinogenicity of ethylbenzene. Criteria are based on data derived from inhalation exposure limits. For the protection of human health from the toxic properties of ethylbenzene ingested through water and contaminated aquatic organisms, the ambient water quality criterion is 1.4 mg/l.

Laboratory scale studies of the biochemical oxidation of ethylbenzene at concentrations greater than would normally be found in municipal wastewaters have demonstrated varying degrees of degradation. In one study with phenol-acclimated seed cultures 27 percent degradation was observed in a half day at 250 mg/l ethylbenzene. Another study at unspecified conditions showed 32, 38, and 45 percent degradation after 5, 10, and 20 days, respectively. Based on these results and general observations relating molecular structure to ease of degradation, the conclusion is reached that biological treatment produces only a moderate removal of ethylbenzene by degradation. Other studies suggest that most of the ethylbenzene is removed from the aqueous stream to the sludge. The ethylbenzene contained in the sludge may volatilize. Ethylbenzene was detected in treated effluents in 11 out of 40 sampls ranging from 0.3 to 29 μg/l with a median concentration of 9 μg/l.

Basic/Neutral Fraction. Among the basic/neutral extractable organic priority toxic pollutants detected, 1,2-dichlorobenzene and bis-2(ethyl hexyl) phthalate were the most often identified. The basic/neutral compounds typically are used in the manufacture of various dyes and in pesticide formulations.

1,2-Dichlorobenzene. 1,2-Dichlorobenzene, also called ortho-dichlorobenzene, is used primarily as a solvent in the manufacture of toluene diisocyanate (a chemical used in the manufacture of plastics and foams), and as an intermediate in the synthesis of dye stuffs, herbicides, and degreasers. It is one of the most common of the base/neutral compounds found in tanning effluents. 1,2-Dichlorobenzene is produced almost entirely as a co-product of monochlorobenzene production. The total annual production of 1,2-Dichlorobenzene, and its isomer, 1,4-Dichlorobenzene, approaches 55,000 tons. 1,2-Dichlorobenzene has a relatively low vapor pressure of 1.5 mm Hg at 25°C and a boiling point of 181°C. It has a low aqueous solubility of 0.145 g/l and a moderately high affinity for lipophilic materials (log octanol/water partition coefficient of 3.38). 1,2-Dichlorobenzene has a formula of $C_6H_4Cl_2$. It is very soluble in organic solvents.

The predominant exposure pathway to humans is through the air. 1,2-Dichlorobenzene is a lipophilic compound, which is readily absorbed into the body. It can be absorbed by the lungs, gastrointestinal tract, and skin, and can subsequently be distributed by the blood to the brain, heart, lever, kidney, and bone marrow. Toxic effects of human exposure to 1,2-Dichlorobenzene include minor irrative problems (headache, nausea, weakness) and more serious blood and liver problems. There is no conclusive evidence that 1,2-Dichlorobenzene is carcinogenic; however, a collection of varied data suggests that it may be, and the compound is undergoing further testing.

For the protection of human health from the toxic properties of dichlorobenzene ingested through water and through contaminated aquatic organisms, the ambient water quality criterion for dichlorobenzenes (all isomers combined) is 0.40 mg/l. Very little information is available concerning the toxicity of 1,2-Dichlorobenzene to aquatic organisms. The lowest reported chronic toxic concentration is 2.0 mg/l.

Little information is available concerning the fate and effects of 1,2-Dichlorobenzene in treatment systems. Because of its slightly volatile nature, a portion of any 1,2-Dichlorobenzene can be expected to volatilize during wastewater aeration. Similarly, because of its moderately high affinity for organic matter, a portion can be expected to be incorporated into sludge. Based upon the limited biodegradation data available, some biodegradation may be expected, especially if treatment system biota are acclimated to 1,2-Dichlorobenzene. 1,2-Dichlorobenzene was detected in treated effluents in 18 out of 40 samples ranging from 1 to 69 μg/l with a median concentration of 7.5 μg/l.

Bis(2-ethylhexyl) phthalate. In addition to the general remarks and discussion on phthalate esters, specific information on bis(2-ethylhexyl) phthalate is provided. Little information is available about the physical properties of bis(2-ethylhexyl) phthalate. It is a liquid boiling at 387°C at 5 mm Hg and is insoluble in water. Its formula is $C_6H_4(COOC_8H_{17})_2$. This toxic pollutant constitutes about one-third of the phthalate ester production in the U.S. It is commonly referred to as dioctyl phthalate, or DOP, in the plastics industry where it is the most extensively used compound for the plasticization of polyvinyl chloride (PVC). Bis(2-ethylhexyl) phthalate has been approved by the FDA for use in plastics in contact with food. Therefore, it may be found in wastewaters coming in contact with discarded plastic food wrappers as well as the PVC films and shapes normally found in industrial plants. This toxic pollutant is also a commonly used organic diffusion pump oil, where its low vapor pressure is an advantage.

For the protection of human health from the toxic properties of bis (2-ethylhexyl) phthalate ingested through water and through contaminated aquatic organisms, the ambient water quality criterion is determined to be 15 mg/l. If contaminated aquatic organisms alone are consumed, excluding the consumption of water, the ambient water criteria is determined to be 50 mg/l.

Although the behavior of bis(2-ethylhexyl) phthalate in a POTW has not been studied, biochemical oxidation of this toxic pollutant has been studied on a laboratory scale at concentrations higher than would normally be expected in municipal wastewater and tannery wastewater. In fresh water with a non-acclimated seed culture, no biochemical oxidation was observed after 5, 10, and 20 days. However, with an acclimated seed culture, biological oxidation occured to the extents of 13, 0, 6, and 23 percent of theoretical after 5, 10, 15 and 20 days, respectively. Bis(2-ethylhexyl) phthalate concentrations were 3 to 10 mg/l. Little or no removal of bis(2-ethylhexyl) phthalate by biological treatment is expected. Bis(2-ethylhexyl) phthalate was detected in treated effluents in 23 out of 40 samples ranging from 1 to 2300 μg/l with a median concentration of 8 μg/l.

Acidic Fraction. Among the acidic fraction of the organic toxic pollutants, phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, and three substituted phenols, including 2,4,6-trichlorophenol, pentachlorophenol, and 4-nitrophenol were identified most frequently. These compounds are typically used to extend raw material storage life and in bactericide, fungicide, and insecticide formulations. Other sources which contribute to the significant levels of phenols in raw wastewaters include synthetic and natural vegetable tannins and dye carriers.

Phenol. Phenol, also called hydroxybenzene and carbolic acid, is a clear, colorless, hygroscopic, deliquescent, crystalline solid at room temperature. Its melting point is 43°C and its vapor pressure at room temperature is 0.35 mm Hg. It is very soluble in water (67 gm/l at 16°C) and can be dissolved in benzene, oils, and petroleum solids. Its formula is C_6H_5OH.

Although a small percent of the annual production of phenol is derived from coal tar as a naturally occuring product, most of the phenol is synthesized. Two of the methods are fusion of benzene sulfonate with sodium hydroxide, and oxidation of cumene followed by clevage with a catalyst. Annual production in the U.S. is in excess of one million tons. Phenol is generated during distillation of wood and the microbiological decomposition of organic matter in the mammalian intestinal tract. Phenol is used as a disinfectant, in the manufacture of resins, dyestuffs, and pharmaceuticals, and in the photo processing industry. In this discussion, phenol is the specific compound which is separated by methylene chloride extraction of an acidified sample and identified and quantified by GC/MS. Phenol also contributes to the "Total Phenols", discussed above, which are determined by the 4-AAP colorimetric method.

Phenol exhibits acute and sub-acute toxicity in humans and laboratory animals. Acute oral doses of phenol in humans cause sudden collapse and unconsciousness by its action on the central nervous system. Death occurs by respiratory arrest. Sub-acute oral doses in mammals are rapidly absorbed then quickly distributed to various organs, then cleared from the body by urinary excretion and metabolism. Long term exposure by drinking phenol contaminated water has resulted in statistically significant increase in reported cases of diarrhea, mouth sores, and burning of the mouth. In laboratory animals long term oral administration at low levels produced slight liver and kidney damage. No reports were found regarding carcinogenicity of phenol administered orally - all carcinogenicity studies were skin tests. For the protection of human health from phenol ingested through water and through contaminated aquatic organisms the concentration in water should not exceed 3.5 mg/l. Fish and other aquatic organisms demonstrated a wide range of sensitivities to phenol concentration. However, acute toxicity values were at moderate levels when compared to other organic priority pollutants.

Data have been developed on the behavior of phenol in POTWs. Phenol is biodegradable by biota present in POTWs. The ability of a POTW to treat phenol-bearing influents depends upon acclimation of the biota and the constancy of the phenol concentration. It appears that an induction period is required to build up the population of organisms which can degrade phenol. Too large a concentration will result in upset or pass through in the POTW, but the specific level causing upset depends on the immediate past history of phenol concentrations in the influent. Phenol levels as high as 200 mg/l have been treated with 95 percent removal in POTWs, but more or less continuous presence of phenol is necessary to maintain the population of microorganisms that degrade phenol. Phenol which is not degraded is expected to pass through the POTW because of its very high water solubility. However, where chlorination is practiced for disinfection, chlorination of phenol may occur. The products of that reaction may be priority pollutants. Phenol was detected in treated effluents in 22 out of 40 samples ranging from 1 to 2100 µg/l with median concentration of 15 µg/l.

EPA has developed data on influent and effluent concentrations of total phenols in a study of 103 POTWs. However, the analytical procedure was the 4-AAP method mentioned earlier and not the GC/MS method specifically for phenol. Discussion of the study, which of course includes phenol, is presented under the pollutant heading "Total Phenols."

<u>2,4,6-Trichlorophenol</u>. 2,4,6-Trichlorophenol ($Cl_3C_6H_2OH$, abbreviated here to 2,4,6-TCP) is a colorless, crystalline solid at room temperature. It is prepared by the direct chlorination of phenol. 2,4,6-TCP melts at 68°C and is slightly soluble in water (0.8 mg/l at 25°C). This phenol does not produce a color with 4-aminoantipyrene, and therefore does not contribute to the nonconventional pollutant parameter "Total Phenols." No data were found on production volumes. 2,4,6-TCP is used as a fungicide, bactericide, glue and wood preservative, and for antimildew treatment. It is probably an impurity of and found concurrently with 2,4,5-Trichlorophenol, a registered fungicide, bactericide, used by the leather tanning industry to prevent deterioration of leather. It is also used for the manufacture of 2,3,4,6-tetrachlorophenol and pentachlorophenol.

No data were found on human toxicity effects of 2,4,6-TCP. Reports of studies with laboratory animals indicate that 2,4,6-TCP produced convulsions when injected interperitoneally. Body temperature was elevated. The compound also produced inhibition of ATP production in isolated rat liver mitochondria, increased mutation rates in one strain of bacteria, and produced a genetic change in rats. No studies on teratogenicity were found. Results of a test for carcinogenicity were inconclusive. For the prevention of adverse effects due to the organoleptic properties of 2,4,6-trichlorophenol in water, the water quality criterion is 0.100 mg/l.

Studies of the biochemical oxidation of the compound have been made at laboratory scale at concentrations higher than those normally expected in municipal wastewaters and tannery wastewater. Biochemical oxidation of 2,4,6-TCP at 100 mg/l produced 23 percent degradation using a phenol adapted acclimated seed culture. Based on these results, biological treatment is expected to produce a moderate degree of degradation. Another study indicates that 2,4,6-TCP may be produced by chlorination of phenol during normal chlorination treatment. 2,4,6-trichlorophenol was detected in treated effluents in 15 out of 40 samples ranging from 1 to 4300 μg/l with a median concentration of 5 μg/l.

Pentachlorophenol. Pentachlorophenol (C_6Cl_5OH) is a white crystalline solid produced commercially by chlorination of phenol or polychlorophenols. U.S. annual production is in excess of 20,000 tons. Pentachlorophenol melts at 190°C and is slightly soluble in water (14 mg/l). Pentachlorophenol is not detected by the 4-amino antipyrene method.

Pentachlorophenol is a bactericide and fungacide and is used for preservation of wood and wood products. It is competitive with creosote in that application. It is also used as a preservative in glues, starches, and photographic papers. It is an effective algicide and herbicide. It is a registered and widely used biocide in the leather industry. It was found in high concentrations in raw wastewaters.

Although data are available on the human toxicity effects of pentachlorophenol, interpretation of data is frequently uncertain. Occupational exposure observations must be examined carefully because exposure to pentachlorophenol is frequently accompained by exposure to other wood preservatives. Additionally, experimental results and occupational exposure observations must be examined carefully to make sure that observed effects are produced by the pentachlorophenol itself and not by the by-products which usually contaminate pentachlorophenol. Acute and chronic toxic effects of pentachlorophenol in humans are similar; muscle weakness, headache, loss of appetite, abdominal pain, weight loss, and irritation of skin, eyes, and respiratory tract. Available literature indicates that pentachlorophenol does not accumulate in body tissues to any significant extent. Studies on laboratory animals of distribution of the compound in body tissues showed the highest levels of pentachlorophenol in liver, kidney, and intestine, while the lowest levels were in brain, fat, muscle, and bone. Toxic effects of pentachlorophenol in aquatic organisms are much greater at pH of 6 where this weak acid is predominantly in the undissociated form than at pH of 9 where the ionic form predominates. Similar results were observed in mammals where oral lethal doses of pentachlorophenol were lower when the compound was administered in hydrocarbon solvents (un-ionized form) than when it was administered as the sodium salt (ionized form) in water. There appear to be no significant teratogenic, mutagenic, or carcinogenic effects of pentachlorophenol. For the protection of human health from the toxic properties of pentachlorophenol ingested through water and through contaminated aquatic organisms, the ambient water quality criterion is determined to be 1.01 mg/l.

Only limited data are available for reaching conclusions about the treatability of pentachlorophenol. Pentachlorophenol has been found in the influent to POTWs. In a study of one POTW the mean removal was 59 percent over a 7 day period. Trickling filters removed 44 percent of the influent pentachlorophenol, suggesting that biological degradation occurs. The same report compared removal of pentachlorophenol of the same plant and two additional POTW on a later date and obtained values of 4.4, 19.5 and 28.6 percent removal, the last value being for the plant which was 59 percent removal in the original study. Influent concentrations of pentachloropehnol ranged from 0.0014 to 0.0046 mg/l. Other studies, including the general review of data relating molecular structure to biological oxidation, indicate that pentachlorophenol is not removed by biological treatment processes. Anaerobic digestion processes are inhibited by 0.4 mg/l pentachlorophenol.

The low water solubility and low volatility of pentachlorophenol lead to the expectation that most of the compound will remain in sludge. The effect on plants grown on land treated with pentachlorophenol - containing sludge is unpredicatable. Laboratory studies show that this compound affects crop germination at 5.4 mg/l. However, photodecomposition of pentachlorophenol occurs in sunlight. The effects of the various breakdown products which may remain in the soil was not found in the literature. Pentachlorophenol was detected in treated effluents in 22 out of 40 samples ranging from 5 to 15,000 µg/l with a median concentration of 41 µg/l.

4-Nitrophenol. 4-Nitrophenol ($NO_2C_6H_4OH$), also called paranitrophenol, is a colorless to yellowish crystalling solid manufactured commercially by hydrolysis of 4-chloro-nitrobenzene with aqueous sodium hydroxide. 4-Nitrophenol melts at 114°C. 4-Nitrophenol is slightly soluble in water (15 gl at 25°C) and soluble in organic solvents. This phenol does not react to give a color with 4-aminoantipyrene, and therefore does not contribute to the nonconventional pollutant parameter "Total Phenols." U.S. annual production is about 20,000 tons. Paranitrophenol is used to prepare phenetidine, acetaphenetidine, azo and sulfur dyes, photochemicals, and pesticides. Paranitrophenol also is a biocide required by specifications for leathers procured by the military and produced by the tanning industry.

The toxic effects of 4-nitrophenol on humans have not been extensively studied. Data from experiments with laboratory animals indicate that exposure to this compound results in methemoglobinemia (a metabolic disorder of blood), shortness of breath, and stimulation followed by depression. Other studies indicate that the compound acts directly on cell membranes, and inhibits certain enzyme systems *in vitro*. No information regarding potential teratogenicity was found. Available data indicate that this compound does not pose a mutagenic hazard to humans. Very limited data for 4-nitrophenol do not reveal potential carcinogenic effects, although the compound has been selected by the National Cancer Institute for testing under the Carcinogenic Bioassay Program. No U.S. standards for exposure to 4-nitrophenol in ambient water have been established.

Data on the treatability of 4-nitrophenol are not available. However, laboratory scale studies have been conducted at concentrations higher than those expected to be found in municipal wastewaters and tannery wastewaters. Biochemical oxidation using adapted cultures from various sources produced 95 percent degradation in three to six days in one study. Similar results were reported for other studies. Based on these data, and on general observations relating molecular structure to ease of biological oxidation, it is concluded that complete or nearly complete removal of 4-nitrophenol occurs during biological treatment. Pollutant 4-nitrophenol was detected in treated effluents in 11 out of 40 samples ranging from 5 to 1,438 µg/l with a median concentration of 105 µg/l.

2. Inorganic Priority Pollutants

Several of the inorganic toxic pollutants were found in tannery wastewaters. 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.

Hexavalent and trivalent chromium compounds have very different chemical characteristics. Hexavalent chromium is very soluble in natural water. Although it is a strong oxidizing agent in acidic solutions, hexavalent chromium is relatively stable in most natural waters. Trivalent chromium tends to form stable complexes with negatively charged organic and inorganic species and thus its solubility and toxicity vary with water quality characteristics such as hardness and alkalinity.

Information on the toxic effects of chromium to freshwater organisms is relatively extensive, but the data base for hexavalent chromium is greater than that for trivalent chromium. Hexavalent chromium has acute values ranging from 67 μg/l for a scud to 59,900 μg/l for a midge. Invertibrate species are generally more sensitive to hexavalent chromium than fish species. The chronic aquatic toxicity data base on hexavalent chromium ranging from 73 μg/l for a rainbow trout to 1,990 μg/l for a fathead minnow. The total recoverable hexavalent chromium criterion to protect freshwater aquatic life is 0.29 μg/l as a 24-hour average and the concentration should not exceed 21 μg/l at any time. Trivalent chromium acute aquatic toxicity values ranged from 3,200 μg/l for scud to 16,010 μg/l for cladoceran. The total recoverable trivalent chromium concentration which should not be exceeded at any time is hardness dependent and equal to 4,700 μg/l at 1000 mg/l at $CaCO_3$. The Ambient Water Quality Criteria documents published by EPA in November, 1980 cite trivalent chromium chronic toxicity to freshwater aquatic life at concentrations as low as 44 μg/l. However, more recent toxicity data show chronic impacts to rainbow trout at 29 μg/l. Ongoing EPA efforts to develop a chronic criteria for trivalent chromiun confirm the chronic aquatic toxicity of this pollutant.

Therefore both hexavalent and trivalent chromium must be considered potentially harmful to aquatic species.

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 chromium 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. Chromium was detected in treated effluents in 40 out of 40 samples ranging from 170 to 92,000 μg/l with a median concentration of 3,450 μg/l.

Copper. Copper is a metallic element that sometimes is found free, as the native metal, and is also found in minerals such as cuprite (Cu_2O), malechite [$CuCO_3 \bullet Cu(OH)_2$], azurite [$2CuCO_3 \bullet Cu(OH)_2$], chalcopyrite ($CuFeS_2$), and bornite (Cu_5FeS_4). Copper is obtained from these ores by smelting, leaching, and electrolysis. It is used in the plating, electrical, plumbing, and heating equipment industries, as well as in insecticides and fungicides.

Traces of copper are found in all forms of plant and animal life, and the metal is an essential trace element for nutrition. Copper is not considered to be a cumulative systemic poison for humans as it is readily excreted by the body, but it can cause symptoms of gastroenteritis, with nausea and intestinal irritations, at relatively low dosages. The limiting factor in domestic water supplies is taste. To prevent this adverse organoleptic effect of copper in water, a criterion of 1 mg/l has been established.

The toxicity of copper to aquatic organisms varies significantly, not only with the species, but also with the physical and chemical characteristics of the water, including temperature, hardness, turbidity, and carbon dioxide content. In hard water, the toxicity of copper salts may be reduced by the precipitation of copper carbonate or other insoluble compounds. The sulfates of copper and zinc, and of copper and calcium are synergistic in their toxic effect on fish. 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. Concentrations of 0.02 to 0.031 mg/l have proved fatal to some common fish species. In general the salmonoids are very sensitive and the sunfishes are less sensitive to copper. The recommended criterion to protect freshwater aquatic life is 0.0056 mg/l as a 24-hour average, and 0.012 mg/l maximum concentration at a hardness of 50 mg/l $CaCO_3$. For total recoverable copper the criterion to protect freshwater aquatic life is 5.6 x 10^{-3} mg/l as a 24-hour average. Copper salts cause undesirable color reactions in the food industry and cause pitting when deposited on some other metals such as aluminum and galvanized steel.

Irrigation water containing more than minute quantities of copper can be detrimental to certain crops. 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. Copper is essential to the life of plants, and the normal range of concentration 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 mg/kg, respectively, under conditions of severe copper toxicity. Even under conditions of copper toxicity, most of the excess copper accumulates in the roots; very little is moved to the aerial part of the plant.

Copper is not destroyed when treated by a POTW, and will either pass through to the POTW effluent or be retained in the POTW sludge. It can interfere with the POTW treatment processes and can limit the usefulness of municipal sludge. The influent concentration of copper to POTW facilities has been observed by the EPA to range from 0.01 to 1.97 mg/l, with a median concentration of 0.12 mg/l. The copper that is removed from the influent stream of a POTW is adsorbed on the sludge or appears in the sludge as the hydroxide of the metal. Bench scale pilot studies have shown that from about 25 percent to 75 percent of the copper passing through the activated sludge process remains in solution in the final effluent. Four-hour slug dosages of copper sulfate in concentrations exceeding 50 mg/l were reported to have severe effects on the removal efficiency of an unacclimated system, with the system returning to normal in about 100 hours. Slug dosages of copper in the form of copper cyanide were observed to have much more severe effects on the activated sludge system, but the total system returned to normal in 24 hours. In a recent study of 268 POTWs, the median pass-through was over 80 percent for primary plants and 40 to 50 percent for trickling filter, activated sludge, and biological treatment plants. POTW effluent concentrations of copper ranged from 0.003 to 1.8 mg/l (mean 0.126, standard deviation 0.242). Copper which does not pass through the POTW will be retained in the sludge where it will build up in concentration. The presence of excessive levels of copper in sludge may limit its use on cropland. Sewage sludge contains up to 16,000 mg/kg of copper, with 730 mg/kg as the mean value. These concentrations are significantly greater than those normally found in soil, which usually range from 18 to 80 mg/kg. Experimental data indicate that when dried sludge is spread over tillable land, the copper tends to remain in place down to the depth of tillage, except for copper which is taken up by plants grown in the soil. Recent investigation has shown that the extractable copper content of sludge-treated soil decreased with time, which suggests a reversion of copper to less soluble forms was occurring. Copper was detected in treated effluents in 22 out of 40 samples ranging from 5 to 440 μg/l with a median concentration of 34 μg/l.

Nickel. Nickel is seldom found in nature as the pure elemental metal. It is a relatively plentiful element and is widely distributed throughout the earth's crust. It occurs in marine organisms and is found in the oceans. The chief commercial ores for nickel are pentlandite [$(Fe,Ni)_9S_8$], and a lateritic ore consisting of hydrated nickel-iron-magnesium silicate. Nickel has many uses. It is used in alloys and as the pure metal. Nickel salts are used for electroplating baths.

The toxicity of nickel to man is thought to be very low, and systemic poisoning of human beings by nickel or nickel salts is almost unknown. In non-human mammals nickel acts to inhibit insulin release, depress growth, and reduce cholesterol. A high incidence of cancer of the lung and nose has been reported in humans engaged in the refining of nickel. Nickel salts can kill fish at very low concentrations. However, nickel has been found to be less toxic to some fish than copper, zinc, and iron. Nickel is present in coastal and open ocean water at concentrations in the range of 0.0001 to 0.006 mg/l although the most common values are 0.002 - 0.003 mg/l. Marine animals contain up to 0.4 mg/l and marine plants contain up to 3 mg/l. Higher nickel concentrations have been reported to cause reduction in photosynthetic activity of the giant kelp. A low concentration was found to kill oyster eggs. For the protection of human health based on the toxic properties of nickel ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 0.0134 mg/l. If contaminated aquatic organisms are consumed, excluding consumption of water, the ambient water criterion is determined to be 0.100 mg/l. Available data show that adverse effects on aquatic life occur for total recoverable nickel concentrations as low as 0.0071 mg/l as a 24-hour average. Nickel is not destroyed when treated in a POTW, but will either pass through to the POTW effluent or be retained in the POTW sludge. It can interfere with POTW treatment processes and can also limit the usefulness of municipal sludge. Nickel salts have caused inhibition of the biochemical oxidation of sewage in a POTW. In a pilot plant, slug doses of nickel significantly reduced normal treatment efficiencies for a few hours, but the plant acclimated itself somewhat to the slug dosage and appeared to achieve normal treatment efficiencies within 40 hours. It has been reported that the anaerobic digestion process is inhibited only by high concentrations of nickel, while a low concentration of nickel inhibits the nitrification process. The influent concentration of nickel to POTW facilities has been observed by the EPA to range from 0.01 to 3.19 mg/l, with a median of 0.33 mg/l. In a study of 190 POTW, nickel pass-through was greater than 90 percent for 82 percent of the primary plants. Median pass-through for trickling filter, activated sludge, and biological process plants was greater than 80 percent. POTW effuent concentrations ranged from 0.002 to 40 mg/l (mean = 0.410, standard deviation = 3.279). Nickel not passed through the POTW will be incorporated into the sludge. In a recent two-year study of eight cities, four of the cities had median nickel concentrations of over 350 mg/kg, and two were over 1,000 mg/kg. The maximum nickel concentration observed was 4,010 mg/kg.

Nickel is found in nearly all soils, plants, and waters. Nickel has no known essential function in plants. In soils, nickel typically is found in the range from 10 to 100 mg/kg. Various environmental exposures to nickel appear to correlate with increased incidence of tumors in man. For example, cancer in the maxillary antrum of snuff users may result from using plant material grown on soil high in nickel. Nickel toxicity may develop in plants from application of sewage sludge on acid soils. Nickel has caused reduction of yields for a variety of crops including oats, mustard, turnips, and cabbage. In one study nickel decreased the yields of oats significantly at 100 mg/kg. Whether nickel exerts a toxic effect on plants depends on several soil factors, the amount of nickel applied, and the contents of other metals in the sludge. Unlike copper and zinc, which are more available from inorganic sources than from sludge, nickel uptake by plants seems to be promoted by the presence of the organic matter in sludge. Soil treatments, such as liming reduce the solubility of nickel. Toxicity of nickel to plants is enhanced in acidic soils. Nickel was detected in treated effluents in 25 out of 40 samples ranging from 5 to 720 μg/l with a median concentration of 90 μg/l.

Lead. Lead is a soft, malleable, ductible, blueish-gray, metallic element, usually obtained from the mineral galena (lead sulfide, PbS), anglesite (lead sulfate, $PbSO_4$), or cerussite (lead carbonate, $PbCO_3$). Because it is usually associated with minerals of zinc, silver, copper, gold, cadmium, antimony, and arsenic, special purification methods are frequently used before and after extraction of the metal from the ore concentrate by smelting. Lead is widely used for its corrosion resistance, sound and vibration absorption, low melting point (solders), and relatively high imperviousness to various forms of radiation. Small amounts of copper, antimony and other metals can be alloyed with lead to achieve greater hardness, stiffness, or corrosion resistance than is afforded by the pure metal. Lead compounds are used in glazes and paints. About one third of U.S. lead consumption goes into storage batteries. About half of U.S. lead consumption is from secondary lead recovery. U.S. consumption of lead is in the range of one million tons annually.

Lead ingested by humans produces a variety of toxic effects including impaired reproductive ability, disturbances in blood chemistry, neurological disorders, kidney damage, and adverse cardiovascular effects. Exposure to lead in the diet results in permanent increase in lead levels in the body. Most of the lead entering the body eventually becomes localized in the bones where it accumulates. Lead is a carcinogen or cocarcinogen in some species of experimental animals. Lead is teratogenic in experimental animals. Mutangenicity data are not available for lead. For the protection of human health from the toxic properties of lead ingested through water and through contaminated aquatic organisms the ambient water criterion is 0.050 mg/l. Available data show that adverse effects on aquatic life occur at concentrations as low as 7.5×10^{-4} mg/l of total recoverable lead as a 24-hour average with a water hardness of 50 mg/l as $CaCO_3$.

Lead is not destroyed in POTW, but is passed through to the effluent or retained in the POTW sludge; it can interfere with POTW treatment processes and can limit the usefulness of POTW sludge for application to agricultural croplands. Threshold concentration for inhibition of the activated sludge process is 0.1 mg/l, and for the nitrification process is 0.5 mg/l. In a study of 214 POTW, median pass through values were over 80 percent for primary plants and over 60 percent for trickling filter, activated sludge, and biological process plants. Lead concentration in POTW effluents ranged from 0.003 to 1.8 mg/l (means = 0.106 mg/l, standard deviation = 0.222).

Application of lead-containing sludge to cropland should not lead to uptake by crops under most conditions because normally lead is strongly bound by soil. However, under the unusual conditions of low pH (less than 5.5) and low concentrations of labile phosphorus, lead solubility is increased and plants can accumulate lead. Lead was detected in treated effluents in 19 out of 40 samples ranging from 8 to 320 μg/l with a median concentration of 60μg/l.

Zinc. Zinc occurs abundantly in the earth's crust, concentrated in ores. It is readily refined into the pure, stable, silvery-white metal. In addition to its use in alloys, zinc is used as a protective coating on steel. It is applied by hot dipping (i.e. dipping the steel in molten zinc) or by electroplating.

Zinc can have an adverse effect on man and animals at high concentrations. Zinc at concentrations in excess of 5 mg/l causes an undesirable taste which persists through conventional treatment. For the prevention of adverse effects due to these organoleptic properties of zinc, concentrations in ambient water should not exceed 5 mg/l. Available data show that adverse effects on aquatic life occur at concentrations as low as 0.047 mg/l as a 24-hour average. Toxic concentrations of zinc compounds cause adverse changes in the morphology and physiology of fish. Lethal concentrations in the range of 0.1 mg/l have been reported. Acutely toxic concentrations induce cellular breakdown of the gills, and possibly the clogging of the gills with mucous. Chronically toxic concentrations of zinc compounds cause general enfeeblement and widespread histological changes to many organs, but not to gills. Abnormal swimming behavior has been reported at 0.04 mg/l. Growth and maturation are retarded by zinc. It has been observed that the effects of zinc poisoning may not become apparent immediately, so that fish removed from zinc-contaminated water may die as long as 48 hours after removal. In general, salmonoids are most sensitive to elemental zinc in soft water; the rainbow trout is the most sensitive in hard waters. A complex relationship exists between zinc concentration, dissolved zinc concentration, pH, temperature, and calcium and magnesium concentration. Prediction of harmful effects has been less than reliable and controlled studies have not been extensively documented. The major concern with zinc compounds in marine waters is not with acute lethal effects, but rather with the long-term sublethal effects of the metallic compounds and complexes. Zinc accumulates in some marine species, and marine animals contain zinc in the range of 6 to 1500 mg/kg. From the point of view of acute lethal effects, invertebrate marine animals seem to be the most sensitive organism tested. Toxicities of zinc in nutrient solutions have been demonstrated for a number of plants. A variety of fresh water plants tested manifested harmful symptoms at concentrations of 10 mg/l. Zinc sulfate has also been found to be lethal to many plants and it could impair agricultural uses of the water.

Zinc is not destroyed when treated by POTW, but will either pass through to the POTW effluent or be retained in the POTW sludge. It can interfere with treatment processes in the POTW and can also limit the usefulness of municipal sludge. In slug doses, and particularly in the presence of copper, dissolved zinc can interfere with or seriously disrupt the operation of POTW biological processes by reducing overall removal efficiencies, largely as a result of the toxicity of the metal to biological organisms. However, zinc solids in the form of hydroxides or sulfides do not appear to interfere with biological treatment processes, on the basis of available data. Such solids accumulate in the sludge. The influent concentrations of zinc to POTW facilities has been observed by the EPA to range from 0.017 to 3.91 mg/l, with a median concentration of 0.33 mg/l. Primary treatment is not efficient in removing zinc; however, the microbial floc of secondary treatment readily adsorbs zinc. In a study of 258 POTW, the median pass-through values were 70 to 88 percent for primary plants, 50 to 60 percent for trickling filter and biological process plants, and 30-40 percent for activated process plants. POTW effluent concentrations of zinc ranged from 0.003 to 3.6 mg/l (mean = 0.330, standard deviation = 0.464).

The zinc which does not pass through the POTW is retained in the sludge. The presence of zinc in sludge may limit its use on cropland. Sewage sludge contains 72 to over 30,000 mg/kg of zinc, with 3,366 mg/kg as the mean value. These concentrations are significantly greater than those normally found in soil, which range from 0 to 195 mg/kg, with 94 mg/kg being a common level. Therefore, application of sewage sludge to soil will generally increase the concentration of zinc in the soil. Zinc can be toxic to plants, depending upon soil pH. Lettuce, tomatoes, turnips, mustard, kale, and beets are especially sensitive to zinc contamination. Zinc was detected in treated effluents in 37 out of 40 samples ranging from 25 to 1,300 µg/l with a median concentration of 100 µg/l.

Cyanide. Cyanides are among the most toxic of pollutants commonly observed in industrial wastewaters. Introduction of cyanide into industrial processes is usually by dissolution of potassium cyanide (KCN) or sodium cyanide (NaCN) in process waters. However, hydrogen cyanide (HCN) formed when the above salts are dissolved in water, is probably the most acutely lethal compound. The relationship of pH to hydrogen cyanide formation is very important. As pH is lowered to below 7, more than 99 percent of the cyanide is present as HCN and less than 1 percent as cyanide ions. Thus, at neutral pH, that of most living organisms, the more toxic form of cyanide prevails. Cyanide ions combine with numerous heavy metal ions to form complexes. The complexes are in equilibrium with HCN. Thus, the stability of the metal-cyanide complex and the pH determine the concentration of HCN. Stability of the metal-cyanide anion complexes is extremely variable. Those formed with zinc, copper, and cadmium are not stable - they rapidly dissociate, with production of HCN, in near neutral or acid waters. Some of the complexes are extremely stable. Cobaltocyanide is very resistant to acid distillation in the laboratory. Iron cyanide complexes are also stable, but undergo photodecomposition to give HCN upon exposure to sunlight. Synergistic effects have been demonstrated for the metal cyanide complexes making zinc, copper, and cadmium, cyanides more toxic than an equal concentration of sodium cyanide.

The toxic mechanism of cyanide is essentially an inhibition of oxygen metabolism, i.e., rendering the tissues incapable of exchanging oxygen. The cyanogen compounds are true noncummulative protoplasmic poisons. 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. This system is the one which facilitates electron transfer from reduced metabolites to molecular oxygen. The human body can convert cyanide to a non-toxic thiocyanate and eliminate it. However, if the quantity of cyanide ingested is too great at one time, the inhibition of oxygen utilization proves fatal before the detoxifying reaction reduces the cyanide concentration to a safe level. Cyanides are more toxic to fish than to lower forms of aquatic organisms such as midge larvae, crustaceans, and mussels. Toxicity to fish is a function of chemical form and concentration, and is influenced by the rate of metabolism (temperature), the level of dissolved oxygen, and pH. In laboratory studies free cyanide concentrations ranging from 0.05 to 0.15 mg/l have been proven to be fatal to sensitive fish species including trout, bluegill, and fathead minnows. Levels above 0.2 mg/l are rapidly fatal to most fish species. Long term sublethal concentrations of cyanide as low as 0.01 mg/l have been shown to affect the ability of fish to function normally, e.g., reproduce, grow, and swim. For the protection of human health from the toxic properties of cyanide ingested through water and through contaminated aquatic organisms, the ambient water quality criterion is determined to be 0.200 mg/l. Persistance of cyanide in water is highly variable and 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 permanganate and chlorine. Chlorine is commonly used to oxidize strong cyanide solutions. Carbon dioxide and nitrogen are the products of complete oxidation. But if the reaction is not complete, the very toxic compound, cyanogen chloride, may remain in the treatment system and subsequently be released to the environment. Partial chlorination may occur as part of a POTW treatment, or during the disinfection treatment of surface water for drinking water preparation.

Cyanides can interfere with treatment processes in POTW, or pass through to ambient waters. At low concentrations and with acclimated microflora, cyanide may be decomposed by microorganisms in anaerobic and aerobic environments or waste treatment systems. However, data indicate that much of the cyanide introduced passes through to the POTW effluent. The mean pass-through of 14 biological plants was 71 percent. In a recent study of 41 POTW the effluent concentrations ranged from 0.002 to 100 mg/l (mean = 2.518, standard deviation = 15.6). Cyanide also enhances the toxicity of metals commonly found in POTW effluents, including the priority pollutants cadmium, zinc, and copper.

Data for Grand Rapids, Michigan, showed a significant decline in cyanide concentrations downstream from the POTW after pretreatment regulations were put in force. Concentrations fell from 0.66 mg/l before, to 0.01 mg/l after pretreatment was required. Cyanide was detected in treated effluents in 39 out of 40 samples ranging from less than 10 to 40 μg/l with a median concentration of less than 10 μg/l.

D. ANALYTICAL METHODS

Sulfides

Study of the analytical methods for determination of total sulfides has revealed both sample handling difficulties and analytical matrix interferences with the 304h method specified (iodometric titration). Two other methods were evaluated: the Association of Offical Analytical Chemists Modified Monier Williams Sulfide determination and the Society of Leather Trades Chemist's "Method for Sulfide Analysis SLM 4/2." All three methods were evaluated utilizing both a standard sodium sulfide solution and actual tannery beamhouse wastewaters. Details of this evaluatuon are presented in the Technical Record. The Modified Monier-Williams technique was determined to be limited in its detection of lower limits of sulfides as well as inherent inaccuracies due to multiple sample handling stages. Significant increases in analyst time also were noted. The iodometric technique experienced difficulties in titration endpoint determination with the highly colored samples. This difficulty could not be overcome without loss of the pretreatment precipitate (ZnS) and accompanying additional error. Method SLM

4/2, which utilized a ferricyanide titration exhibited no similar titration endpoint difficulties and could be filtered to remove excess color without loss of accuracy. As a gravimetric technique, its detection limit is linked to sample size. At 25 milliliters of sample, a commonly used sample size in this industry, the limit of detection is 6.4 mg/l. Increasing the sample size to 100 ml would result in a detection limit of 1.6 mg/l. The details of this method are presented in the technical record, in Section 425.03 of the regulation, and in Appendix D of this Document.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

A. INTRODUCTION

This section describes technology that is applicable to the control and treatment of wastewaters generated by the leather tanning and finishing industry. This section also addresses manufacturing practices that can reduce waste discharges and end-of-pipe processes designed to remove pollutants.

To describe the various treatment processes available, the Agency has divided this control and treatment technology into six groups of similar processes. They are:

- In-plant Source controls
- Preliminary Treatment Processes
- Primary Treatment Processes
- Biological Treatment Processes
- Upgraded Biological Treatment Processes
- Advanced Treatment Processes

At the end of this section, descriptions are presented of the control technology options, their components and performance, as considered by the Agency in developing BPT, BAT, BCT, NSPS, PSES, and PSNS regulations.

Specific unit treatment processes were assigned to facilitate the logical progression of each successive group toward reducing pollutant discharges and improving effluent quality. This approach is intended to clarify the benefits and associated costs of more sophisticated treatment.

1. Current Wastewater Treatment Practices

Available information indicates that 158 wet-process tanneries are currently operating in the United States. Seventeen of these facilities are "direct dischargers": i.e., after some treatment, process wastewater is discharged directly to surface waters thus requiring an NPDES permit. The remaining 141 "indirect dischargers" discharge their wastewater to publicly owned treatment works (POTWs) with or without pretreatment.

The industry profile data base, updated from the 1979 voluntary survey and plant visits during 1979 and 1980, includes information from 59 indirect dischargers and 21 direct dischargers. Three of these direct dischargers closed and one became an indirect discharger, accounting for the difference between the 21 direct dischargers in the data base and the 17 existing direct dischargers noted above.

A summary of current wastewater treatment practices at the 76 facilities in the updated data base is shown in Table VII-1.

TABLE VII-I

SUMMARY OF CURRENT WASTEWATER
TREATMENT PRACTICES

Description	Number of Tanneries[1]
Indirect Dischargers, Total	59
No pretreatment	4
Screening only	13
Primary treatment	32
Secondary treatment	4
Did not provide a response	6
Direct Dischargers, Total	17
Aerated lagoons	8
Activated sludge	4
Unaerated lagoons	2
Rotating biological contactors	2
Trickling filter -lagoon systems	1

[1] Based on response to questionnaire

2. Waste Control and Effluent Treatment Considerations

The pollutants detected in tannery wastewaters can cause or contribute to the treatment problems listed below. These potential problems must be considered in designing safe and effective wastewater treatment systems.

- Clogging of equipment by scrap hide and leather pieces;
- High loadings of hair, suspended solids, and BOD_5;
- Treatment process upset caused by flow and pollutant surges;

- Highly variable pH;
- Potential fatal hazard to human life and offensive odor resulting from release of hydrogen sulfide gas from solution;
- Discharge of significant quantities of toxic substances; and
- Disposal of sludges which may be highly putrescible and contain chromium and other heavy metals.

Appropriate pretreatment processes can alleviate or eliminate these problems. For example, fine screening can remove hair, scrap leather, and hide pieces; an equalization tank can reduce flow and pollutant surges; pH adjustment, or controlled mixing of acid and alkaline wastes, can maintain effluent pH within desired limits; and the problem of disposing of chromium-bearing treatment sludge can be reduced by recovering or more effectively utilizing chromium at its source in the tannery.

The Agency's treatment technology evaluations are intended to:

- Identify methods of improving the generally poor performance of many tannery wastewater treatment systems;
- Present information concerning efficient, effective methods of recycling and recovering tanning process ingredients; and
- Describe the efficiency with which available wastewater treatment processes remove toxic substances as well as conventional and nonconventional pollutants.

B. IN-PLANT SOURCE CONTROLS

In many cases, experience in the industrial wastewater treatment field has shown reducing waste discharges at their source is more cost effective than applying end-of-pipe processes to clean up an existing effluent problem. For this reason, "In-Plant Source Controls" is a logical starting point for a discussion of leather tanning waste control and effluent treatment technology. The following five groups of controls or manufacturing process modifications have been considered:

1. "Good housekeeping" practices

2. Stream segregation

3. Water conservation

4. Recycle or reuse of concentrated liquors

5. Process modifications, including chemical substitutions, directed at reducing or eliminating specific pollutants.

These methods are summarized based on industry supplied information in Tables VII-2 and VII-3. The Agency has observed that implementation of many water conservation and recycle/reuse technologies as discussed in this section, either singly or in varying combinations, do not alway result in overall reduction in water use. Table VII-4 summarizes the use of in-plant controls for each plant in the data base by subcategory and by increasing water use flow ratios. In many cases water savings in one group of subprocesses is offset by inefficient use of water in other subprocesses. The Agency also has observed that plants in a number of subcategories have achieved reduced water use ratios with either very few or none of the technologies which require investment. Therefore, expenditure for installation of potentially water conserving equipment or reuse/recycle technology, is not necessary to achieve either median or reduced water use ratios. However, many plants invest in modern processing equipment because worn out equipment must be replaced to maintain production capability. Other plants install waste liquor recovery and reuse or recycle and refortification systems in order to decrease the cost of production attributable to processing chemicals (e.g., chromium). As discussed previously in Section IV, Subcategorization, the Agency also has observed that potentially efficient processing methods were distributed throughout the range of water use within subcategories. As discussed previously, neither the quality of a final product nor the product itself is affected by reduced water usage within the ranges of water use ratios defined by the Agency for each subcategory. The Agency has included discussion of these technologies and their use in this industry to serve as guidance both to the industry and to regulatory authorities.

"Good Housekeeping" Practices

"Good Housekeeping" includes the following simple and inexpensive practices:

- Eliminating unnecessary uses of water, such as leaving hoses running when not needed;
- Reducing chemical spills which may result from carelessness;
- Preparing a program to control and cleanup unavoidable chemical spills;
- Repairing or replacing faulty equipment; and

TABLE VII-2

SUMMARY OF RESPONSES TO QUESTIONS CONCERNING IN-PLANT CONTROLS

In-Plant Control	No. of Plants That Considered*	No. of Plants That Attempted Operation*	No. of Plants That Decided To Implement*	No. of Plants Where Now Operating*
Water Conservation Controls				
1. Use of hide processors, turbotan, Idronova, or other processing equip.	48/65	31/65	26/65	16/69
2. Wash and soak water reuse	34/65	15/65	10/65	5/65
3. Process or equipment wash-water reuse	32/77	18/77	18/77	12/17
4. Batch rinse	38/77	26/77	22/77	21/77
5. Cooling Water Reuse	29/77	19/77	18/77	14/77
Recovery of Concentrated Liquors				
1. Sulfide Stripping and Recovery	18/38	2/38	2/38	2/38
2. Unhairing Liquor Reuse	29/56	11/56	10/56	5/56
3. Lime Liquor Reuse	34/56	11/56	8/56	4/56
4. Spent Chrome Liquor Reuse	48/65	24/65	16/65	8/65
5. Chrome Precipitation and Recovery	31/65	11/65	9/65	6/65
6. Sludge Incineration and Chrome Recovery	14/65	4/65	0/65	0/65
7. Liritan Process	12/12	9/12	7/12	6/12
8. Vegetable Tannin Recovery	12/12	7/12	7/12	3/12
Process Modifications				
1. Sulfide Substitution in Unhairing	35/56	15/56	3/56	3/56
2. Ammonia Substitution in Deliming	28/56	11/56	3/56	3/56

*The tabulated values compare the number of positive responses to the number of tanneries responding to the question.

TABLE VII-3

WASTE STREAM SEGREGATION IN LEATHER TANNERIES AS REPORTED IN QUESTIONNAIRES

METHOD OF WASTE STREAM SEGREGATION	NUMBER OF TANNERS USING SPECIFIC BEAMHOUSE AND TANYARD WASTE SEGREGATION METHODS	NUMBER OF TANNERS USING SPECIFIC PROCESS WASTE STREAM SEGREGATION METHODS
Total number of plants reporting use of one or more of the following methods	40	34
Below grade separate sewers or piping	19	11
Above grade separate sewers or piping	9	7
Diverters	16	14
Collection trough	16	14
Concentric bearings	3	-
Other	7	16

- Installing automatic monitoring devices to detect abnormal discharges of hazardous gases or polluting substances.

Often, educating employees about the benefits of reducing wastewater volume and pollutant discharges will elicit "Good Housekeeping" practices. Tanners in general, have to become more conscious of their water use. Because many tanners have a cheap, unlimited water supply they don't conserve water. In other cases, the charge for wastewater treatment imposed by POTWs has not increased sufficiently to provide economic incentive to reduce water use and pollutant loads.

Stream Segregation

The segregation of specific waste streams is the initial step that a tanner must take to implement many of the following in-plant controls. In most tanneries the wastewaters from the various processing operations are discharged into one sewer. As noted in previous sections, these waste streams have different characteristics. For example, the wastewater from the unhairing operations contains sulfides and has a high pH while the wastewater from the tanning operations contains chromium and has a low pH. Both total chromium and sulfide are pollutants of major concern in this industry and both should be removed from the tannery effluent. The pollutant distribution for the two major processing areas in a tannery are estimated on Table VII-5. By separating the beamhouse and tanyard streams, a tannery has the opportunity to treat each waste stream individually with a treatment process designed specifically for the related pollutant. Obviously, there is a cost savings since the treatment process is designed to handle a lower volume of wastewater (i.e., the clarifiers are smaller and accordingly less expensive).

In addition, each of the two major wastewater streams (beamhouse and tanyard), can be separated further for additional control measures. Examples of this in the industry are the isolation of spent solvent from the degreasing operations, the separation of the chromium bearing liquors from other wastestreams in the tanyard, separation of buffing dust scrubber water or segregating the pickling liquor. The objectives of these additional stream separations are: 1) the spent liquors can be refortified and used again 2) the spent liquors from a specific process can be used in an upstream process thus decreasing the chemical requirement for the later process (i.e. the source of the spent liquor), or 3) decreasing the size of treatment facilities for a specific contaminant such as chromium. These operations are detailed further in this section. The overall impact of stream

TABLE VII-4

WATER USE RATIO DATA BASE IN-PLANT CONTROLS

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
SUBCATEGORY 1				
248	3.0 (25.0)	100% BCPF Cattlehide	80% Shoe Uppers 20% Handbag, Luggage, Belts	E,G,T
383	3.1 (25.9)	40% Fresh Cattlehide 35% GS Cattlehide 15% GS Deerskin 10% GS Elkhide	Garment & Glove Shoe Linings & Orthopedic Leather	T
520	3.2 (26.7)	100% GS Cattlehide	100% Garment - Sold in the crust	C,D,G,Q
274	3.8 (31.7)	100% BCPF Cattlehide	33% Garment 67% Upholstery	G
246	4.3 (35.9)	92% PF Cattlehide 6% GS Moose & Elkhide 2% Pickled Sheep & Goatskin	80% Glove 10% Garment 5% Shoe 5% Specialty	***
525	4.5 (37.6)	80% BCPF Cattlehide 20% GS Cattlehide	100% Upholstery	***
438	5.4 (45.1)	64% BCPF Cattlehide 23% BCPF Sowskins 8% GS Cattlehide 5% GS Deer & Elkhide	94% Glove 5% Lining 1% Orthopedic Shoe Uppers	C
245	5.4 (45.1)	50% GS Cattlehide 50% Fresh Cattlehide	80% Shoe Uppers & Linings 20% Purse & Handbag	***
80	5.5 (45.9)	60% GS Cattlehide 30% BCPF Cattlehide 10% BC Cattlehide	50% Military Shoe Leather 35% Upper Leather 15% Lining Leather	S,T
237	5.7 (47.6)	50% GS Cattlehide 50% BC Cattlehide	95% Military Shoe Uppers 5% Other	***

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
235	6.0 (50.1)	80% PF Trimmed Cattlehide 20% GS or BC Cattlehide	80% Shoe Uppers 20% Military Shoe Uppers	E,I,J,Q,R
425	6.1 (50.9)	100% BCPF Cattlehide	30% Moccasin & Boot 20% Shoe Lining 35% Crusted Lining 15% Miscellaneous	E,I,J,Q
262	6.2 (51.7)	100% PFGS Cattlehide	100% Upholstery	J,R
206	6.4 (53.4)	100% BCPF Cattlehide	60% Shoe Uppers 20% Lining 20% Garment	***
13	6.5 (54.2)	100% BCPF Cattlehide	85% Shoe Uppers 15% Handbag,etc.	E,G,Q,T
103	6.8 (56.8)	100% GS Cattlehide	80% Shoe Uppers 20% Accessory	Q,G
431	7.0 (58.4)	99% BCPF Cattlehide 1% BC Cattlehide	96% Shoe Uppers 4% Miscellaneous	E,G,Q,R,S
626	7.5 (62.6)	***	***	***
6	7.6 (63.4)	***	***	***
432	7.8 (65.1)	90% BCPF Cattlehide 10% GSPF Cattlehide	40% Garment 30% Shoe Uppers 30% Specialty	T
632	7.9 (65.9)	Mostly Deerskin	***	***
231	8.9 (74.3)	100% GS Cattlehide	75% Upholstery 12.5% Shoe Uppers 12.5% Specialty	E,P

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
31	8.9 (74.3)	94% BCPF Cattlehide 6% Blue Cattlehide	95% Shoe Uppers 5% Waist Belt	***
58	9.7 (81.0)	100% BCPF Cattlehide	100% Shoe Uppers	G,I,J,Q,S,T
37185	9.9 (82.6)	50% BC Cattlehide 45% Goatskin 5% Sheepskin	25% Boot 20% Glove 40% Suede 5% Military 5% Smooth Grain 5% Sunken Grain	R,S,T
57	10.5 (87.6)	100% BCPF Cattlehide	70% Shoe Uppers 10% Garment 10% Handbag 10% Upholstery	J,S,T
409	10.7 (89.3)	52% BCPF Cattlehide 36% GS Cattlehide 12% Pickled Sheepskin	84% Shoe Uppers 8% Suede Sheep Garment 5% Garment 3% Grain Sheep Garment	T
87	11.5 (96.0)	100% BCPF Cattlehide	70% Shoe Uppers 19% Leather Goods 6% Belt 5% Shoe Linings	E
		SUBCATEGORY 2		
7	4.9 (40.9)	17% Salted Shearlings 83% Fresh Cattlehide	Cattlehide 80% Shoe Uppers 10% Handbag 10% Miscellaneous Sheepskin 100% Shearlings	***
8	5.0 (41.7)	90% GS Cattlehide 10% Fresh Cattlehide	85% Shoe Uppers 10% Handbag 5% Belt	S,T

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
236	5.8 (48.4)	100% GS or BC Deerskin	100% Glove or Garment	***
320	6.8 (56.8)	75% GS Cattlehide 25% BCPF Cattlehide	100% Shoe Uppers 50% Splits Finished 50% Splits Sold Blue	R,T
			SUBCATEGORY 3	
385	2.3 (19.2)	100% BCPF Cattlehide	66% Sole Leather 33% Rough Shoulders 1% Strap Sides	No bating No retan B,D,F,H,P,R
415	3.0 (25.0)	100% BCPF Cattlehide	40% Sole Leather 35% Strap Shoulders 10% Rough Shoulders 10% Strap Bellies 5% Pickled Bellies	No retan for majority F,P,Q,R
47	3.1 (25.9)	93% BC or GS Cattlehide 7% GS Calfskin	75% Alum Lace 25% Chrome Latigo	Extensive reuse of tanning liquors-H,I
397	4.2 (35.1)	100% BCPF Cattlehide	42% Sole Leather 42% Curried Leather 16% Pickled Bellies	E,G,O,P,R,S,T
46	4.8 (40.1)	100% BCPF Cattlehide	65% Sole Leather 35% Specialty	H,O,R,T
186	4.8 (40.1)	95% BCPF Cattlehide 5% PF Cattlehide	95% Lace Leather 5% Hard Rawhide	***
388	4.9 (40.9)	98% BCPF Cattlehide 2% Blue Splits	98% Basketball & Football Leather 2% Miscellaneous	E,G,H,I,P
399	4.9 (40.9)	100% BCPF Cattlehide	80% Veg. Tan Saddle, Strap, Harness 15% Chrome & Veg. Retan Lace 5% Alum Lace	T

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
404	7.7 (64.3)	43% BC Cattlehide 52% Blue Cattlehide 5% Horsehide	50% Baseball 40% Softball 5% Orthopedic Glove 5% Garment	***
239	7.9 (65.9)	100% BCPF Cattlehide	66% Veg. Tan Strap 29% Veg. Tan Skirting 5% Alum Latigo	E,G,P,T
24	8.2 (68.4)	100% BCPF Cattlehide	84% Strap 9% Skirting 6% Latigo 1% Miscellaneous	E,G,O,T
376	9.6 (80.1)	100% BCPF Cattlehide	80% Sole Leather 20% Industrial Leather	F,G,H,O,Q,T
		SUBCATEGORY 4		
389	1.7 (14.2)	100% Cattlehide	34% Shoe Uppers & Lining 33% Belts 33% Purse, Handbag	No color or fat liquor
404	2.4 (20.0)	43% BC Cattlehide 52% Blue Cattlehide 5% Horsehide	50% Baseball 40% Softball 5% Orthopedic Glove 5% Garment	Operates beamhouse for portion of operation
50	4.5 (37.6)	100% Blue Cattlehide	70% Shoe Uppers 15% Handbag & Belt 10% Personal Leather Goods 5% Military	G,R,S
3	4.6 (38.4)	100% Blue Cattlehide	80% Shoe Uppers 15% Lace & Latigo 5% Sole & Mechanical	Q,S
4937	4.9 (40.9)	100% Blue Cattlehide	Garment Leather	***

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
224	5.6 (46.7)	100% Blue Cattlehide	100% Shoe Uppers	S
625	6.4 (53.4)	100% Blue Cattlehide	***	
191	11.4 (95.1)	100% Blue Cattlehide	50% Shoe Uppers 30% Export Leather 20% Personal Leather Goods	Q
		SUBCATEGORY 5		
88	3.5 (29.2)	100% Pickled/BC Sheepskins	100% Lining Leather	No retan
700	3.8 (31.7)	100% Pickled Sheepskin	Garment Leather	G,J,T
285	3.8 (31.7)	100% Limed Split Single Bend Cattlehide	100% Soft Suede	No retan, formaldehyde tanning
51	4.0 (33.4)	100% Pickled/Wet Blue Sheepskin	45% Garment 49% Lining & Novelty 6% Hat	T
75	5.5 (45.9)	100% Pickled Cow Bellies	70% Work Glove 30% Shoe Lining	***
615	5.6 (46.7)	75% Pickled Sheepskin 25% Stained Sheepskin	***	***
92	5.8 (48.4)	41% Pickled Lambskin 32% Pickled Sheepskin 15% Pickled Skivers 12% Pickled Chamois Fleshes	60% Garment 40% Shoe Uppers	T
380	6.6 (55.1)	100% Pickled Cattlehide	Belts, Dog Collars, Harness, Arch Supports, & Special Equipment	G

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
556	7.4 (61.8)	Pickled Sheepskin Blue Cattlehide	***	***
522	7.8 (65.1)	95% Pickled Sheepskin 5% Pickled Goatskin	70% Garment 30% Glove	T
319	8.5 (70.9)	***	***	***
169	11.0 (91.8)	Pickled Sheepskin, Cattlehide, Deerskin	***	***
220	13.5 (113)	Pickled Sheepskin	Government Leather	***
		SUBCATEGORY 6		
444	1.4 (11.7)	93% BCPF Cattlehide 7% PF Cattlehide	100% Blue Sides	B,E,G,I,J,R
559	2.1 (17.5)	100% BCPF Cattlehide	100% Wet Blue	E,T
502	2.6 21.7)	100% BCPF Cattlehide	100% Wet Blue	C,F,G,J,T
		SUBCATEGORY 7		
500	9.4 (78.5)	80% GS Wool Sheepskin 20% Salt Dried Sheepskins	90% Garment Shearling Suede 10% Seat Covers, Bed Pads, Blue Skins	G,J,R
		SUBCATEGORY 8		
185	4.1 (34.2)	85% BC or GS Pigskin 15% Pickled Cow Bellies	95% Work Glove 5% Boot Lining	E,R,T
233	5.8 (48.4)	85% GS, Unhaired, Pigskin 15% GS, Hair-on Pigskin	70% Shoe Uppers 25% Glove Lining 5% Garment	G,H,P,R,S

TABLE VII-4 (continued)

Tannery Number	Water Use Ratio (gal/lb) ((ℓ/kg))	Raw Material Mix (percent)	Product Mix (percent)	Water Conservation Measures
		SUBCATEGORY 9		
507	2.2 (18.4)	95% Blue Split Cattlehide 5% Blue Pigskins	100% Suede	***
97	2.5 (20.9)	100% Blue Split Cattlehide	95% Shoe Uppers 5% Lining, Garment, Other	P
116	3.4 (28.4)	90% Blue Split Cattlehide 10% Blue Pigskins	100% Suede	***
501	4.9 (40.9)	100% Blue Split Cattlehide	30% Shoe Uppers, Linings 30% Glove 15% Garment 25% Specialty	***

BCPF	Brine cured prefleshed
GS	Green salted
PF	Prefleshed
BC	Brine cured
***	Insufficient date provided

B - Sulfide stripping and recovery
C - Ammonium sulfide substitution
D - Eliminate bating
E - Use of hide processors
F - Wash/soak water reuse
G - Batch rinse
H - Lime liquor reuse
I - Unhairing liquor reuse
J - Chrome liquor reuse
O - Liritan process
P - Vegetable tan liquor reuse
Q - Process/Equipment wash water reuse
R - Cooling water reuse
S - Automated spray booths
T - Stream segregation

segregation and subsequent treatment/reuse of waste stream is to lower water requirements and need for processing chemicals. Forty tanneries reported in the information request that they were using stream segregation in one form or the other. Stream segregation gives a tannery the opportunity to reduce the volume of wastewater generated. Forty percent of the tanneries that have some type of stream segration have water use ratios less than subcategory medians. Stream segregation was an important factor in many tanneries flow reduction and/or treatment projects (e.g. Tannery Nos. 184, 60, 248, and 444). Stream segregation is detailed further in end-of-pipe treatment technologies.

Water Conservation

Water is used in many operations in a tannery. Water is used for the make up of processing liquors (unhairing, bating, pickling, tanning, etc), hide washing and soaking operations, rinsing of hides after specific processing steps, and transportation of waste materials. The use of water in processing liquors is discussed in the following section. Many methods have been attempted both on a pilot scale and full scale to reduce the water use in these areas.

Batch rinsing in the washing, soaking and rinsing of hides is one method that has been experimented with and is also commonly used in the industry. Based on the data provided by the industry, approximately 50 percent of the industry is using some form of batch rinsing. Batch rinsing can be utilized in many ways depending on the specific tannery. One of the more common ways is the use of "closed door" rinsing. That is, instead of pumping rinse water in a rotating tanning drum with an open door (thus allowing water continually to flow out of the drum), the door is closed. In comparing the two methods, batch rinsing was found to be far more efficient[5]. Tanneries that utilize batch rinsing in the industry are Tannery Nos. 248, 397, 700, and 50.

Van Vlimmerman reported the results of several experiments which compared continuous rinsing to batch rinsing of wet salted hides[6]. In the first experiment, hides were rinsed by both methods until a desired residual salt concentration had been reached in the hide. In three different tests, the desired concentration was reached in the batch mode with 48, 67, and 71 percent less water. A second experiment compared continuous rinsing for the hide soaking process to a procedure using a single batch of water for the soak and wash. The batch rinsing process consumed only 20 percent of the water required for continuous rinsing. The differences in the quality of leather produced by each method were very slight.

Another form of batch rinsing is similar to the previous method except that it is used in the wash-soak operation. Countercurrent washing is a specific water reuse method that was reported to be used by several tanneries in the industry (Tannery No. 184). In one tannery the initial washwater is used in the make up of the unhairing liquor. Similarly another tannery is screening a portion of its plant wastewater and using it in its unhairing liquor. Another method of countercurrent use of water (Tannery No. 184) is the use of the chromium rinse waters in the make up of pickling liquor. This not only decreases water consumption but also the use of chromium in the tanning operation.

Hide processors or similar devices can save water in two ways. Hide processors provide the opportunity for lower floats and facilitate washing and waste liquor reuse. Constantin and Stockman[7] reported that replacing their tannery's paddle vats, used for beamhouse operations, and tanning drums with hide processors reduced the beamhouse and tanyard waste flows by approximately 50 percent. This equipment changeover was accompanied by a change from a hair-save process to hair-pulp mode for unhairing. In fact, Tannery No. 184 prefers hide processors because of less water usage, improved temperature control of the liquor, the use of lower floats, savings in labor costs including the ease of loading and unloading hides, and a lower energy consumption.

The collection and handling of buffing dust has an impact on the volume of water used by a tannery. Buffing dust is collected by two different means, by bag collection or wet scrubbing. Review of water use data indicated that a majority (70 percent) of those tanneries using dry bag collection had lower water use ratios than the median water use for their subcategory. The separation of buffing dust scrubber water from other process streams for recycling, separate treatment and reuse, disposal, or reuse in other processes has shown effectiveness in the industry. Of the 21 tanneries indicating separation of buffing dust scrubber water, 17 have flows lower than median flows.

Recycling buffing dust scrubber water has brought about significant water savings in some tanneries[7 8]. A screen to remove the buffing dust must be installed before the scrubber water can be reused. A buffing dust scrubber water recycling system was installed at the side leather tannery described by Constantin and Stockman, and the plant's total wastewater flow was reduced by almost 250,000 gallons per day (950 m^3/d)[7]. This was part of an overall water conservation program which included the installation of hide processors and the change to the hair-pulp process. The net effect of the program was a 38 percent reduction in water use, from approximately 2.35 mgd to 1.42 mgd (8,900 m^3/d to 5,400 m^3/d). Another tannery in subcategory 4 reduced its wastewater flow by roughly 46 percent after installing a buffing dust scrubber water recycle system[8].

Recycling cooling water rather than using single-pass systems is another way of conserving water in a tannery. Approximately one-third of the industry reported reusing cooling water. The effectiveness of this method has been demonstrated in that at least one-half of these tanneries were in the lower half (less than the median) of the distribution of water use ratios for most of the subcategories. The attractiveness of cooling water reuse depends mainly on the cost of cooling water and whether the cooling is accomplished in a contact (resulting in contamination from processing of the product) or noncontact (free from product processing contamination) manner.

Recycle or Reuse of Liquors

Process solutions, such as unhairing liquors, bating liquors, and tanning solutions, also can be reused to reduce a plant's water consumption. Generally, the primary objectives of this practice is to reduce the discharge of a particular pollutant, such as sulfide, or to conserve a costly chemical, such as chromium.

Sulfide Liquor Reuse. The hair-pulp process has been taking precedence over the traditional hair-save process in cattlehide unhairing. Hair pulping is faster and requires less labor than hair saving. Hair pulping generates greater waste loads, however, because much higher concentrations of depilatory chemicals, such as sodium sulfhydrate, are used. The pulping operation also dissolves most of the hair which is then discharged in the waste stream. In contrast, fewer chemicals are used in the hair-save process and most of the hair can be isolated from the wastewater as a solid residue which lessens both the organic and solid waste load. The pollution problems inherent in the hair-pulp process have led to the present interest in reusing the hair-burn liquor and recovering some of the constituents of the spent liquors. The methods which have been used or proposed range from simple reuse of the liquor (usually with suspended solids removal after each cycle) to treatment with a complex physical-chemical system. The physical-chemical system separates the spent unhairing liquor into four fractions, each containing a potentially recoverable waste product.

TABLE VII-5

DISTRIBUTION OF FLOWS AND POLLUTANT LOADS BEAMHOUSE AND TANYARD OPERATIONS

Pollutant Parameter and Subcategory		Pollutant Distribution Beamhouse Percent	Pollutant Distribution Tanyard Percent
Flow		40	60
BOD_5	1,2,3,8	65	35
	6	81	19
	4,5,7,9	0	100
TSS	1,2,3,8	69	31
	6	86	14
	4,5,7,9	0	100
COD	1,2,3,8	56	44
	6	86	14
	4,5,7,9	0	100
Oil & Grease	1,2,3,8	49	51
	6	71	29
	4,5,7,9	0	100
Total Chromium.	1,2,3,8	0	100
	6	0	100
	4,5,7,9	0	100
Sulfide	1,2,3,8	95	5
	6	95	5
	4,5,7,9	0	100
TKN	1,2,3,8	46	54
	6	72	28
	4,5,7,9	0	100
Ammonia	1,2,3,8	0	100
	6	0	100
	4,5,7,9	0	100
Phenol	1,2,3,8	25	75
	6	25	75
	4,5,7,9	0	100

The simplest of the hair-burn liquor reuse systems involves screening, storing, and refortifying the spent liquor before reuse. Van Tornout[9] reported the results of experiments with this type of sulfide liquor reuse system in which the liquor was reused 18 times. For the 18th cycle, eight sides (cattlehides) were tested; four were limed with the reused liquor and four with a fresh lime liquor. Only a slight difference was found in leather quality; those hides unhaired in the fresh liquor swelled more and weighed about four percent more than those unhaired with the reused liquor. The author concluded that recycling did not affect the efficiency of the process.

The potential reduction of pollutant loadings can be estimated from the lime and sulfide concentration data reported by Van Tornout[9]. The initial composition of the liquor was three percent sodium sulfide and two percent lime (based on hide weight). The residual liquors at the end of the experiment contained approximately 1.5 percent sodium sulfide and 1.2 percent lime. This information suggests that the reuse approach would reduce the discharge of sulfide by approximately 50 percent and of lime by 60 percent. The tests indicated that the liquor could have been recycled indefinitely. Van Tornout felt that screening the used liquor during each cycle was necessary to remove hide pieces and undissolved hair. In conducting his experiments, Van Turnout used a one-millimeter vibrating screen.

In another experiment, Money and Adminis[10] compared two different hair-burn liquor recycling methods. In one series of tests, a 150-mesh screen was used to remove suspended solids during each cycle; during the other series, suspended solids were not removed. Otherwise, the experimental procedure was similar to Van Tornout's: the used liquors were screened (if appropriate), refortified, heated to 30°C, and reused. In the "solids removal" tests, the sodium sulfide composition was three percent (based on green weight) and hydrated lime was two percent. For the "no solids removal" tests, four percent sodium sulfide was maintained. Both methods produced leather of acceptable quality, comparable to leather produced by the traditional procedure. No differences were found between matched sides when compared by area yields, lastometer tests, and tannery personnel. Leather tanned by chromium and vegetable tannins was produced from hides which were unhaired in liquors recycled 26 and 27 times, with and without solids removal. The resulting products were judged to be "no different (than) the normal production." Money and Adminis agreed with Van Tornout's results that leathers produced with recycled liquors swelled less and, consequently, weighed less after unhairing. However, the hides unhaired with recycled liquors retained more nitrogen than those unhaired with the usual procedure, suggesting that recycled liquors could yield a product with more substance and weight.

Money and Adminis noted differences between recycled liquors from the "solids removal" tests and "no solids removal" tests. After reaching steady-state, the liquors from the "no solids removal" tests had higher levels of nitrogen and total solids. Nitrogen, fats, hide pieces, and some lime were apparently removed as sludge by screening. Fats accumulated in the "no solids removal" system during successive cycles. The authors thought this would present a problem, particularly with unfleshed hides which have more fat than prefleshed ones.

For the "solids removal" system, the amounts of lime and sodium sulfide which had to be replenished after each cycle were 1.5 percent and 2.2 percent of hide weight, respectively. This indicates that 25 percent of the lime and 40 percent of the sulfide could be saved compared to the traditional method of discharging spent hair-burn liquors after each batch.

A Swiss company, Idronova® Huni AG, is marketing an unhairing liquor recovery system worldwide. Their process is similar to the two just described. A unique feature of the Idronova® system is the "hydrodynamic sedimentator" which removes suspended solids from the liquor. After solids are removed, the liquor is stored, adjusted to the desired strength and temperature, and reused. The estimated chemical savings and effluent discharge reductions with the Idronova® sulfide recovery system are between 50 and 70 percent for sulfide and 20 percent or more for lime. Information supplied by the manufacturer reveals that at least 25 Idronova® sulfide recovery systems have been installed in tanneries around the world[11]. Tannery No. 184 has installed an Idronova® and has reported favorable results since installation

A complete unhairing liquor reuse and recovery process has been proposed by the Eastern Regional Research Center (ERRC) of the U.S. Department of Agriculture[12]. This process separates the used unhairing liquor into four parts, respectively rich in fats, suspended lime, sodium sulfide, and protein. The first step in the process is gravity settling, intended to separate the used unhairing solution into three layers: a floating, fat-rich layer on top; a clear supernatant layer with most of the dissolved sulfide and protein in the middle; and a heavy sludge containing undissolved lime on the bottom. If much of the fat settles to the bottom with the heavy solids, a centrifuge can be added to separate fat from the lime sludge. The supernatant layer is screened, treated with carbon dioxide to reduce the pH slightly and with a polyelectrolyte to aid flocculation, then settled in a second clarifier. The underflow from this clarifier is dewatered with the same centrifuge used to dewater the lime sludge from the first clarifier. The supernatant from the second clarifier is treated with sulfuric acid, which reduces the pH to between 3.5 and 4.2, and then is pumped to a closed vacuum degasifying tower. The dissolved proteins, at or near their isoelectric point, can flocculate and settle easily within this pH range. The sulfide in the liquid is unstable because the solution is supersaturated (with respect to a normal atmosphere) with hydrogen sulfide gas. Hydrogen sulfide is driven out of solution, aided by a vacuum pump, and reabsorbed in a high pH solution of lime. The degasified liquid solution is pumped to a third clarifier where the proteins settle and hydrogen peroxide is added to oxidize the residual sulfide. The protein-rich underflow from the third clarifier is concentrated with a vacuum filter and dried. This process yields four end products: a pure sulfide solution which can be reused in preparing hair-burn liquor; a lime-rich sludge from the centrifuge which can be used for agricultural liming; a potentially marketable mixture rich in fat; and a proteinaceous material which can be used in chicken feed.

The ERRC has constructed and evaluated a pilot-scale system of their unhairing liquor treatment and recovery system. Table VII-6 shows the results of a test in which spent unhairing liquor from a paddle vat process was treated by this system.

Though the technical feasibility of the ERRC treatment system has been established, the ERRC has not yet developed accurate estimates of the cost of constructing and operating the system. Therefore, the system's economic feasibility has not yet been established.

Another sulfide recovery system, which involves stripping hydrogen sulfide at low pH and re-absorbing the gas in an alkaline solution, has been installed at a large midwestern tannery and evaluated by an EPA demonstration grant project[13]. This system treats the tannery's entire waste flow after primary clarification. The pretreated wastewater is pumped to the top of a four-level degasification tower where acid is added to reduce the pH to between 5.0 and 5.5. Each level has a tray in which the liquid depth is kept at approximately three feet. Compressed air is introduced to the tower below the bottom tray and is sparged into the wastewater on each level. The air flows upward from one level to the next, countercurrent to the downward liquid flow. Hydrogen sulfide is effectively stripped from the wastewater. The mixture of air and hydrogen sulfide gas is transferred to an absorption tower where a sodium hydroxide solution is used to re-absorb hydrogen sulfide and to recover the sulfide.

This system achieved excellent results during 1976. Sulfide removal was essentially complete when the pH in the degasifying tower was kept below 5.9. The savings generated by recovering sulfide was greater than annual operating costs of the system; the installation was profitable according to an analysis presented in the report.

TABLE VII-6

ERRC UNHAIRING LIQUOR RECOVERY SYSTEM PERFORMANCE

Parameter	Percent Reduction in Unhairing Liquor	Percent Reduction in Combined Tannery Effluent
BOD_5	86	42
COD	85	53
Sulfide	100	86
TKN	86	74
Oil & Grease	100	41

This sulfide stripping and absorption system required attentive operation and frequent maintenance. The air flow to the degasifying tower and the feed-rate of sulfide bearing wastewater had to be carefully controlled to keep the ratio of hydrogen sulfide to air well below 4.0; when the ratio exceeds this level, the air and hydrogen sulfide mixture is explosive. Proteins also clogged the air spargers in the degasification tower; the degasification tower had to be shutdown every 15 days to clean the air spargers. A new sulfide stripping and recovery system was built recently and was being tested when EPA representatives visited the tannery in January 1980. This system was designed to remove the proteins before degasification to reduce air sparger clogging.

Chrome Recovery. Chrome is found in the waste streams from chromium tanning, rinsing after chromium tanning, blue stock wringing, retanning, rinsing after retanning, coloring, fatliquoring, and drying. Three general methods have been used to reuse or recover chromium from process wastewaters: 1) isolating the spent chromium tanning solutions for reuse as "pretannage" in the pickle liquor, as chromium tanning liquor (after refortification), or as retanning solution; 2) concentrating the effluent chromium by chemical precipitation for use in formulating new chromium tanning liquors; and 3) incinerating the chromium-bearing sludges and recovering hexavalent chromium from the incinerator ash. The amount of chromium recovered varies with each of the three methods and depends on the amount of chromium sent to the recovery system and the efficiency with which chromium is recovered from the treated wastes.

The distribution of chromium in the wastes from a typical hide processor run is shown in Table VII-7[7]. This study did not report sufficient data to determine the proportion of chromium discharged from the wringing and retan-wet finish operations. More recent data submitted to the Agency[14] indicate that approximately 74 percent of the tannery's raw waste chromium load results from tanning, washing, spills, and blue stock wringing; the remaining 26 percent is from retanning and finishing operations. Based on this data (along with information from Reference No.7), and on assumptions regarding chromium concentrations and volume of blue stock wringings, the chromium waste distribution in the wastewater from this tannery was estimated and is presented in Table VII-8.

Uncomplicated chromium recovery systems capture the spent tanning solutions for reuse as a pretanning agent in the pickle liquor. The spent tanning solutions are screened or filtered to remove suspended solids, then collected in one or more storage tanks. Fats and oils are allowed to float to the surface and are skimmed off. Fat must be removed to prevent irregular darkening of the leather. The clarified spent tanning solution is then pumped as needed to the pickling process. Because the volume of spent tanning liquor normally exceeds the amount that can be used in pickling, excess liquor is usually discharged to the sewer. The efficiency of this recovery technique in reducing a plant's total chromium effluent discharge is therefore limited by the percentage of spent tanning liquor that can be reused in pickling, the percentage of chromium in the spent tanning liquors, and the exhaustion of chromium offered in the pickle liquor.

One side leather tannery which employs this type of chromium recovery system was able to use approximately 50 percent of the spent tanning solution in the pickle liquor[14]. The reduction in the plant's chromium discharge was estimated at 25 to 40 percent. This tannery was able to isolate the spent chromium tanning liquors with minimal expense and equipment by scheduling

TABLE VII-7

DISTRIBUTION OF CHROMIUM IN HIDE PROCESSOR WASTEWATERS

Waste Stream	Incremental Volume (gal.(m^3))	Cumulative Volume (gal.(m^3))	Incremental Chromium Load (lbs(kg))	Cumulative Chromium Load (lbs(kg))	Cumulative Chromium Concentration (mg/l)
1. Spent Tanning Solution	900 (3.4)	900 (3.4)	47 (21)	47 (21)	6,260
2. First Wash	500 (1.9)	1,400 (5.3)	12 (5.4)	59 (26.4)	5,060
3. Second Wash	650 (2.5)	2,050 (7.8)	7 (3.2)	66 (29.6)	3,860
4. Third Wash	650 (2.5)	2,700 (10.3)	5 (2.3)	71 (31.9)	3,150
5. Fourth Wash	1,350 (5.1)	4,050 (15.4)	5 (2.3)	76 (34.2)	2,250
6. Spills	1,050 (4.0)	5,100 (19.4)	4 (11.8)	80 (36)	1,890

Source: Reference No. 7

discharges to the tan cellar drain and pumping only the spent tanning liquors to the storage vessel.

Maire[16] presented an economic analysis of a chromium recovery system that involved reusing the spent chromium liquor in the pickling operation. The analysis assumed that proper scheduling of batch discharges could isolate the spent chromium tanning liquors, as described above. Consequently, only a sump pit and pump would be required to collect the spent liquor. The capital cost for the chromium recovery system also included costs for screening and grease skimming equipment. For a 1,000 hide per day tannery, the total project cost was estimated to be $30,000 at 1977 price levels. The annual savings in chemical and energy expenses were estimated to be $51,000, assuming that 85 percent of the spent chromium liquor would be reused.

A chromium liquor reuse system with one slight variation was operated at another side leather tannery (recently closed) for several years[17]. Hide processors were used for pickling and tanning. Spent tanning liquors were screened, then collected in the storage tanks. Not all of the spent chromium liquor could be reused directly. Rather than dump the excess, one tank of spent liquor was treated as needed with soda ash and caustic soda to raise the pH to approximately ten. Chromium hydroxide precipitate was formed and settled, and the supernatant was drawn off and discharged to the sewer. The sludge was then acidified and added to the supply of spent liquor for reuse in pickling. This chromium recovery system was installed during March of 1972; at the same time that four hide processors were installed to replace some older tanning equipment.

Two EPA Region I "Industrial Waste Surveys" were conducted at the plant, one before and one after the process and equipment change. Data collected during these surveys indicate the impact of chromium recovery on the plant's wastewater discharge. Spent tanning liquor capture was very high; with the recovery system in operation, only about 20 gallons of spent liquor per processor run were lost to the sewer, compared to approximately 1,300 gallons per run with the old system (the capacities of the old drums were not stated). Between the two wastewater surveys, the plant's production increased by approximately 25 percent while the overall chromium reduction in the plant's discharge was approximately 50 percent. Another variation of the systems discussed above was developed in Australia by Davis and Scroggie[18 19 20]. The spent tanning liquor is screened and pumped to storage tanks. The appropriate amounts of concentrated mineral acid and salt are added to the spent liquor storage tanks to make up the desired pickle formula. This solution comprises the pickling solution, and the process is operated as usual.

TABLE VII-8

ESTIMATED DISTRIBUTION OF CHROMIUM IN WASTEWATER DISCHARGED FROM A SIDE LEATHER TANNERY

	Flow			Chromium		
Waste Stream	Cumulative gal/day	(m^3/d)	Cumulative Percent of Total Plant Discharge	Cumulative lbs/day	(kg/d)	Cumulative Percent of Total Plant Discharge
Spent Tanning Solution	14,400	(55)	1.0	560	(254)	41
First Wash	22,400	(85)	1.6	707	(321)	52
Second Wash	32,800	(124)	2.3	789	(358)	58
Third Wash	43,200	(164)	3.0	843	(382)	62
Fourth Wash	64,800	(245)	4.6	898	(407)	66
Spills	81,600	(309)	5.7	952	(432)	70
Blue Wringings	93,000	(352)	6.5	1,006	(456)	74
Retan-Wet Finish Total	810,000	(3066)	56.6	1,360	(617)	100

Note: The waste flows for all waste streams except blue stock wringings are as reported in Reference No. 7, pp. 70,71. The flow for blue wringings was estimated to be approximately 11,000 gallons per day (42 m^3/d), equivalent to approximately 2.5 gallons (0.009m^3) per hide multiplied by 4,350 hides/day. The cumulative percent of chromium for all wastes through blue wringings was 74 percent and the 26 percent chromium content in the retan and wet-finish fractions was given in Reference No. 17. The total chromium load in pounds per day was calculated from the production of 4,350 hides per day, the effluent load of 5.2 lbs. chromium per 1,000 lbs. (2.2kg/1,000kg) of hides processed and an assumed weight of 60 lbs (27kg) (green salted basis) per hide. The pounds of chromium per day for each waste fraction in the table were then calculated using the 74-26 percent tanyard, retan-wet finish breakdown, the calculated chromium load from blue wringing, and the percentage of chromium from each of the operations listed in Table VII-7 (which were taken from Reference No. 7).

Without draining the "spent" pickling liquor, sufficient powdered chromium or stock chromium solution and masking agent are added to the vessel to obtain the desired chromium offering and the tanning operation is conducted as usual. After basification and completion of tanning, the spent liquor is drained and pumped to the storage tank from which it is recycled continuously. This system was initially tested in a laboratory[18] using a small [2.5 foot (0.76m) diameter] drum. The tanning liquor was used for 12 tanning cycles, with all indications that it could have been recycled indefinitely.

Subsequently, full-scale tests were conducted[19] in a tannery in which hide processors were used for tanyard operations. The spent tanning liquor was used for 18 cycles before the end of the test, with all indications that the liquors could have been recycled indefinitely. In this test, the stock chromium solution was a sugar-reduced solution containing 1.1 pounds chromium oxide (Cr_2O_3) per gallon (0.13 kg/L). Because the stock chromium solution was relatively dilute, a portion of the spent tanning liquor had to be discharged during each cycle to avoid accumulating excess liquor. In practice, about 1,100 of the 1,300 gallons (4160 of the 4920 L) of spent liquor was captured for recycle at the end of each run. Chrome powder was used during the laboratory-scale tests and this problem did not occur. In both tests of chromium recycling, the consumption of chromium and masking agent was reduced by 20 to 25 percent. Considerably less salt and acid were required. In all tests, the leather produced with recycled liquors compared favorably to leather produced by conventional methods, leading the authors to state: "A method is now available for the recycling of chromium 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."

This chromium recycling method was tested by several Australian tanneries and their results were discussed in another article by Davis and Scroggie[20]. Some problems were encountered during these trials, but, for the most part, these have been largely overcome and the knowledge gained has helped in understanding the process. The most common problem experienced was caused by a "small degree of acid swelling" during the pickling or tanning steps. The acid swelling can be controlled by monitoring the specific gravity of the solution during pickling and tanning, and adding sufficient sodium chloride to maintain the desired salt concentration (and increase the specific gravity). Davis and Scroggie[20] stated that tanning vessels with good drainage are helpful when recycling chromium liquors to prevent excessive dilution of the recycled liquor. This dilution can decrease the neutral salt concentration and tends to cause swelling problems and to add extra liquor volume, which then has to be discharged. Hide processors have good drainage and are well suited to chromium recycling. In contrast, some tanning drums tend to trap some liquor between hides and do not drain well. In this case, retrofitting the drums with baffles or a similar feature may be necessary to ensure good drainage.

Another method of recycling chromium liquor involves using the reclaimed liquor as the basis for preparing the next tanning liquor. With this system, the spent pickling solution is drained from the tanning vessel and the refortified tanning solution is added. Tanning is conducted as usual and the "spent liquor" is discharged to the spent liquor recovery tank. Davis and Scroggie[21] also conducted experiments with this system at both laboratory and full-scale levels. They found that good quality leather could be produced when the specific gravity and salt concentration were maintained within the desired limits. The authors concluded this recovery system was more appropriate in combination with an equilibrated pickle process, but the system discussed in Reference Nos. 18, 19, and 20 was better suited to a rapid, non-equilibrated pickling process. The non-equilibrated pickling process was more prevalent in Australia at the time the tests were conducted.

The chromium recovery systems discussed have all been designed to recover only the chromium in the spent tanning solutions. As shown in Table VII-8, the washwaters associated with chromium tanning also contain a significant amount of waste chromium. The volume of washwater is usually so large that the chromium in the wastewater cannot be recovered in these reuse systems because the washwater has greatly diluted the spent chromium liquors and the resulting volume would be more than is needed for pickling or tanning.

To solve this problem, chromium recovery systems designed to treat the spent tanning liquors and rinse waters employ chemical precipitation to concentrate the chromium. These systems can generally recover more chromium than the direct reuse systems; however, more equipment, greater capital investment, and more sophisticated operating controls are required.

Chromium is precipitated by adjusting the pH of the chromium-bearing wastes to approximately 8.5, the minimum solubility point of chromium hydroxide. The precipitate is allowed to settle and a chromium sludge blanket is formed. The supernatant should have a very low chromium concentration (around 0.5 mg/l) if solids separation is effective. In most cases, sludge dewatering equipment is necessary to produce a solids cake, which can then be modified to produce a concentrated stock chromium solution.

Constantin and Stockman[7] conducted an extensive investigation of chromium recovery by precipitation. Four alkalines, lime, caustic soda, soda ash, and ammonium hydroxide, were compared to determine which was most effective in reducing the supernatant chromium concentration, and in producing a sludge that settles easily and can be dewatered easily. Hydrated lime was determined the most effective alkaline based on these criteria. One disadvantage with lime was that the chromium stock solution formed by acidifying the chromium hydroxide sludge cake contained a high concentration of calcium sulfate. A hydrocyclonic separator was used to prevent a build-up of calcium sulfate in the tanning liquors.

Based on preliminary experimentation, a full-scale chromium recovery system was constructed and tested. A diagram of this system is shown in Figure VII-1. The full-scale chromium recovery system was apparently designed to collect and treat only the concentrated spent tanning solution and did not have sufficient capacity to treat all washwater. In two test runs, the system was able to recover 86 and 90 percent of the chromium contained in the spent tanning liquor. More recent data[14] indicate that this system can recover approximately 83 percent of the chromium in the wastewater that is treated. Of the remaining 17 percent, approximately 11 percent is disposed of in the solid wastes and six percent is discharged to the sewer.

The most comprehensive chromium recovery system that has been proposed involves incineration of the chromium-bearing sludges and recovery of chromium from the ashes. Successful operation of the system depends on low temperature, alkaline incineration to oxidize trivalent chromium to the hexavalent state. These conditions are necessary to retain the chromium in the ash[14]. Hexavalent chromium is then recovered from the ash by a two-stage process. The first stage, in which most of the chromium is recovered, involves leaching of bichromate from the ash using a filter to separate the leachate and ash residual. Two different methods have been proposed for the second stage. The first method entails mixing the residual ash from the first stage in a reducing solution to convert the chromium from the hexavalent state to the trivalent state. The pH of the resulting solution is then adjusted to approximately 8.5 to form a precipitate of chromium hydroxide, which is recovered by using a dissolved air flotation unit. The second method involves transferring the residual ash from the first stage to a pressure filter and pumping a reducing solution through the ash cake in the filter to reduce the hexavalent chromium in the ash to insoluble chromium

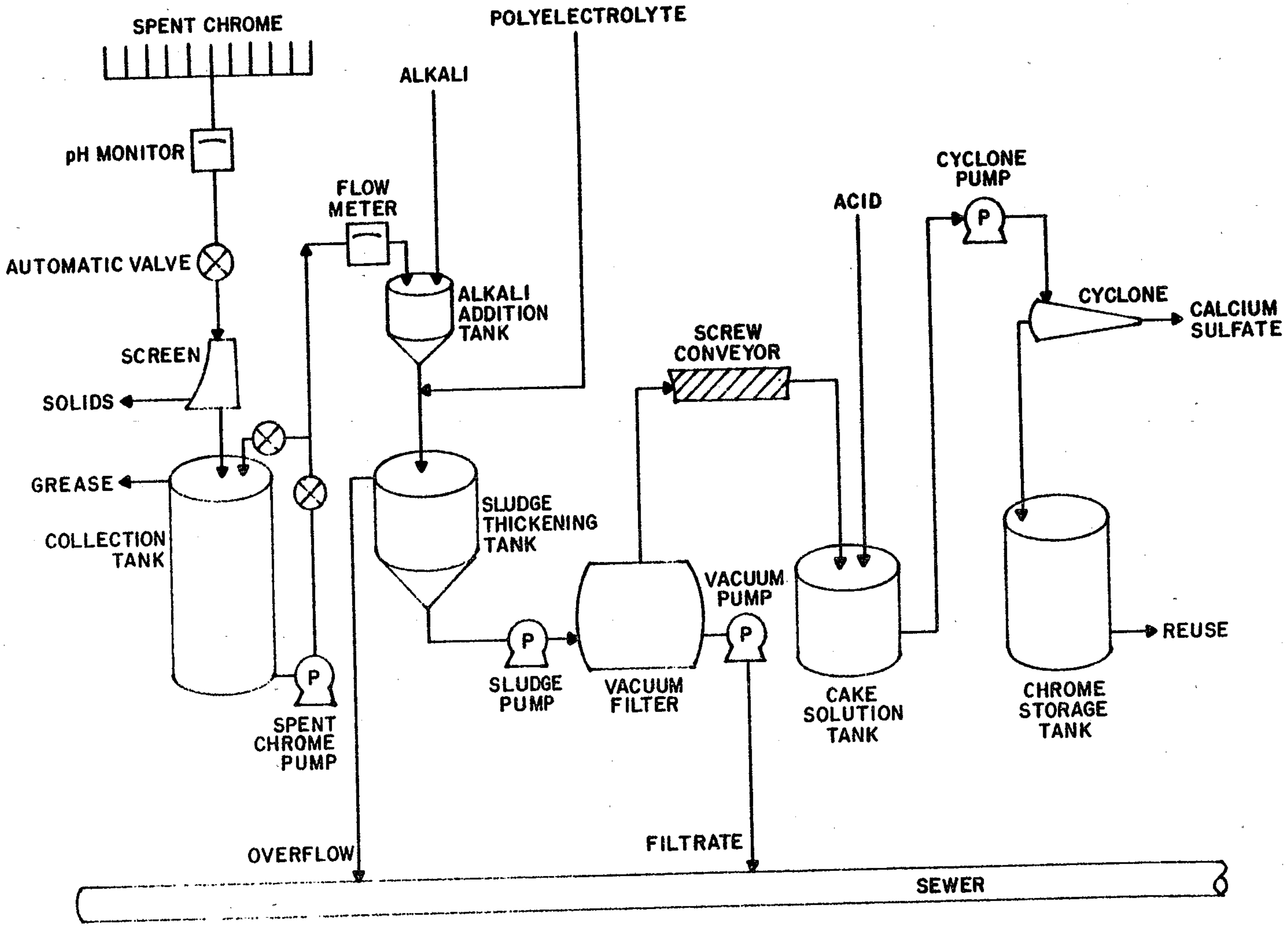


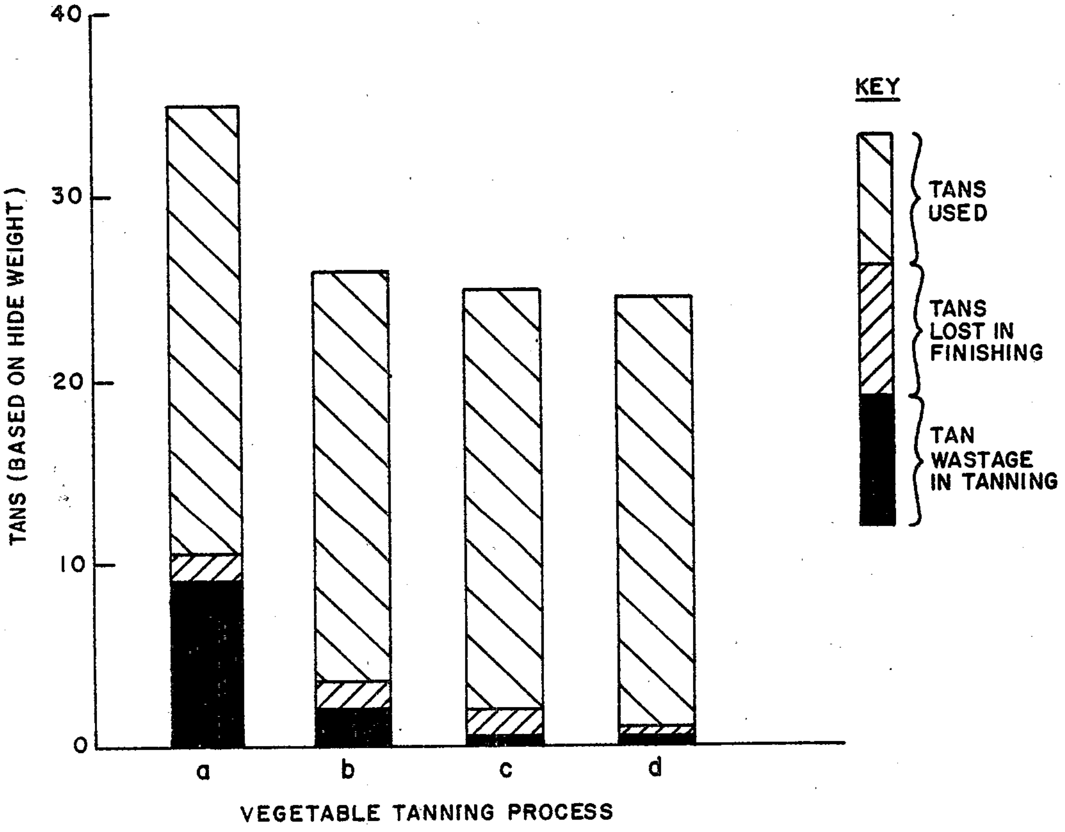
FIGURE VII-1 CHROME RECOVERY SYSTEM

oxide. The ash, excluding the chromium oxide, is then landfilled.

Because no full-scale systems of this type are currently operating, the long term operating characteristics and problems associated with continuous operation are not known. However, the system has several apparent advantages[6]: 1) almost all chromium discharged from a tannery may be recovered and eliminated from the wastewater stream; 2) scrap leather pieces and buffing dust can also be incinerated, and the chromium in them can be recovered, scraps and buffing dust are believed to contain approximately eight percent of the chromium purchased by one side leather tannery; and 3) the problem of tannery sludge disposal is reduced because the volume and weight of sludge are substantially decreased by incineration.

Vegetable Tannin Recovery. The Liritan process has enabled vegetable tanners to economize in the purchase of vegetable tannins and, at the same time, substantially reduce the amount of tannins discharged in their wastewater. A comparison of a minimal recovery, countercurrent vegetable tanning process with three modifications of the Liritan process[22] is presented in Figure VII-2. The Liritan processes depicted in this figure (processes b,c, and d) represent applications used in the United States. Process "b" employs a single color vat between the calgon pickle and the strong, recirculating tanning liquors. The color vat acts as a barrier to salt carryover from pickling into the tannery liquors. To maintain purity, tanning liquor is discharged as needed from the weakest (first) tanning vat into the coloring vat. The pretanning solution in the coloring vat is correspondingly discharged daily, or as needed, to maintain a liquid balance. The coloring vat reduces tannin wastage by allowing more extensive recirculation of the concentrated tanning liquors and by exhausting most of the tannins in the coloring vat. Process "c" employs one or two coloring vats consisting of tempering and washing liquors. The first vat is more dilute than the second; the flow through the coloring vats is countercurrent. This system allows the concentrated tanning liquors to be refortified and recirculated in a closed loop. A slight improvement over process "c" can be obtained by process "d", which alternately uses the stronger color vat as the tempering vat. System "d" in Figure VII-2 can reportedly attain a tannin exhaustion of 95 percent[22].

A U.S. vegetable tannery is operating a Liritan process similar to process "c" in Figure VII-2 and is also recovering tannins from the coloring vat overflow. The overflow is concentrated to approximately 40 percent solids in an evaporator, then



a. COUNTER CURRENT ALL PIT

b. LIRITAN WITH ONE COLOR VAT (25° Bk) DISCHARGED DAILY

c. LIRITAN WITH ONE OR TWO COLOR VATS IN A CLOSED SYSTEM

d. LIRITAN WITH ONE OR TWO COLOR VATS, WITH ONE USED AS THE TEMPERING VAT. (REFERENCE NO. 22)

FIGURE VII-2 QUANTITIES OF TANS USED AND TAN WASTAGE FOR VARIOUS VEGETABLE TANNING PROCESSES spray-dried to produce a vegetable tannin powder that is sold to chromium tanners as a retanning agent.

The Liritan process also has been used successfully in a pilot test for tanning harness and belting leather[23].

Manufacturing Process Modifications

Alternative Hide Preservation Methods. Two alternatives to the conventional hide curing techniques of salt curing and brine curing have been investigated as a means of reducing the high sodium chloride content in tannery wastewaters. The alternatives proposed in the literature are intended to preserve the untanned hides for short periods of time, usually one week or less. The proposed preservatives include refrigeration; boric acid; combinations of zinc, chlorite, or hypochlorite, and sodium pentachlorophenate; and sulfite combined with acetic acid[24]. These last two preservatives seem to be the most economical and practical and will be discussed below. Another alternative is to eliminate hide preservation altogether and process the hides immediately after they are flayed from the animal.

The short-term hide preservation technique developed and tested by the Eastern Regional Research Center (ERRC)[24 25 26] uses a 20 percent float containing one percent sodium bisulfite and one percent acetic acid. Acceptable shoe upper leather and upholstery leather have been produced from hides preserved in this manner. Hides have been successfully preserved for up to 28 days in tests; however, Bailey and Hopkins[25] recommend that hides be stored for only one week until tanners gain more experience with this technique.

Australian tanners have used sodium chlorite and sodium pentachlorophenate to preserve hides for a short time. Many of these tanners recommend using zinc chloride or calcium hypochlorite instead of sodium chlorite because sodium chlorite is a hazardous chemical[27]. Pentachlorophenate, however, is chemically similar to pentachlorophenol, which (along with zinc) is listed by EPA as a toxic pollutant.

Reduction of Lime in Unhairing Liquors. Although lime is generally not considered a pollutant, its presence in unhairing liquors should be minimized for two reasons. Excessive use of lime will generate additional amounts of sludge, since much of the calcium in lime will be removed as sludge, and will also increase the amount of acid required to neutralize the pH of the beamhouse waste stream.

Williams-Wynn[28] suggests that tanners generally use much more lime than is needed; lime use could be reduced without affecting leather quality. He reported the results of an experiment in which the lime offering in a six-day hair-save process was reduced to the point where little or no lime remained after unhairing. This corresponded to a lime offering of two percent based on hide weight. At this level, only 3.5 percent of the initial lime offering was unused. With a lime offering of four percent, 53.5 percent or the initial lime offering was unused. He concluded that a two percent lime offering was satisfactory and that the optimum was probably slightly less than two percent. For a hair-burn process in drums, the author stated that the amount of lime needed to make satisfactory upper leather was about 0.5 percent with three percent of sodium sulfide; with sodium sulphydrate, about one percent lime was satisfactory.

<u>Enzyme Unhairing for Hair-Save Operations</u>. Several requirements for any hair-save method include: an uncomplicated process, fine hair removal (if possible, without reliming); economical; sufficient hair dissolution to be suitable for mechanized and automated production processes; and fine quality leather production. Hair-save processes require more labor than hair-burn processes, and tanners will not willingly incur additional costs unless the sale of the hair is profitable or a savings in wastewater treatment costs can be realized. Industry is tending toward the hair-burn process as evidenced by the relatively small number of plants (7) still operating in subcategory 2.

Frendrup and Larsson[29] conducted a detailed study of the effects of various depilatory methods on the characteristics of the residual wastes. They found that when hair was loosened chemically and removed 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-save methods. Hair containment and good housekeeping practices significantly influence these results.

Enzyme unhairing is one of the presently known hair-save methods. According to researchers at the TNO Institute, who have done considerable work in this area, this method could be developed for use in the production of sole leather. For upper leather, some difficulties still need to be overcome. A combination of the Liritan process and enzyme unhairing (for sole leather) also was investigated at TNO[6]. Researchers at the Institute reported this combination reduced pollutant loads associated with vegetable tanning to only 10 percent of those associated with traditional methods.

In Situ Sulfide Oxidation. Oxidation of unhairing liquors with manganese (II) ion as a catalyst is a well-established process for converting sulfide to sulfate. Catalytic oxidation is employed most commonly as an end-of-pipe treatment process; however, oxidation has also been conducted in the unhairing vessel. The latter practice is termed "*in situ* sulfide oxidation." In both systems the chemistry of the process is the same, and will be discussed in more detail under preliminary treatment processes.

Van Vlimmerman[6] reported the results of *in situ* sulfide oxidation tests at the TNO Institute. Using the smallest permissable amount of sulfide that would complete unhairing and produce fine quality leather, Van Vlimmerman was able to oxidize over 95 percent of the sulfide within three hours. The dose of manganese sulfate was 200 milligrams per liter.

In situ sulfide oxidation was used at one hair-pulp chromium tannery. This tannery also had an Idronova® sulfide recovery system. After the unhairing step was completed, the unhairing liquor was pumped to the sulfide liquor storage tanks, which are part of the Idronova® system. Dry manganese sulfate and additional water were then added to the hide processor with the hides still in the processor. Mixing was continued, and finally the oxidized liquid was discharged to the sewer. Data collected during a three-day wastewater sampling survey conducted in March of 1977 indicated that the tannery's combined wastewater discharges to the POTW contained 1.8 milligrams per liter (mean of three values) of sulfide. Prior to installing the Idronova® system and using *in situ* oxidation, the sulfide concentration in the tannery's effluent was considerably higher. The mean effluent sulfide concentration, based on data from three days prior to these process changes, was 55 mg/l.

Ammonia Substitution. Ammonium sulfate is used by essentially all U.S. cattlehide tanneries in their deliming and bating processes. The ammonia used in this process generally represents a significant part of the ammonia concentration in the raw waste. The biological oxidation of ammonia to nitrate exerts an oxygen demand; removing ammonia in wastewater is therefore desirable for much the same reason as is BOD removal.

Koopman[30] proposes substituting Epsom salt (magnesium sulfate heptahydrate) for the ammonium sulfate used in deliming to reduce effluent ammonia concentrations. He conducted two matched-side tests comparing deliming with epsom salt with deliming with ammonium sulfate. During this experiment, the customary procedure for producing box leather (chromium tanned) was followed for deliming through tanning, except for substituting Epsom salt in deliming. The control group was delimed with 3.5 percent ammonium sulfate, based on hide weight, and the test group was delimed with 7.0 percent epsom salt and 0.5 percent sulfuric acid. The leather produced with the new deliming procedure compared favorably in every respect to that produced by conventional deliming. Deliming with Epsom salt reduced the ammonia content in the effluent from the deliming process by approximately 91 percent. Koopman concluded that magnesium sulfate (epsom salt) was a promising substitute for ammonium sulfate.

Officials at two U.S. tanneries have tested magnesium sulfate as a surrogate in the deliming process. Their results have been considerably less successful than Koopman's. After conducting several matched-side tests comparing Koopman's deliming method and the conventional deliming process with ammonium sulfate, Constantin[31] concluded that: "Comparable deliming was not obtained with Epsom salts even in twice the processing time." Further, the grain, texture, and durability of leather produced with epsom salt were poorer than those of leather produced with ammonium sulfate. Constantin also estimated that the cost to change to magnesium sulfate would be approximately $0.70/hide (1978 dollars).

The Koopman deliming and bating method also was evaluated at one vegetable tannery for three months[32]. Magnesium sulfate caused several problems. One problem attributed to the experimental deliming process was a loss in the hide weight; the vegetable-tanned bends weighed approximately nine percent less than those tanned in the conventional manner. Since sole leather is sold by weight, the tannery lost approximately nine percent of its revenue from sole leather sales. Another problem was that the grain of the pickled bellies, which are sold to other tanneries for further processing, was not uniform. Problems were also experienced because of a build-up of magnesium salts in the calgon pickle and the Liritan color vats. Scale formed in the vegetable tannin recovery evaporator. The hides had to remain in the calgon pickle solution for more time than normal to compensate for the neutral salt build-up in the pickling solution.

Summary

There are numerous in-plant controls that have demonstrated their effectiveness for reducing waste loads and flows in a tannery. The most commonly used methods have been detailed in this section. There are others, but because of their uniqueness or singular use in the industry they were not included in this discussion.

The 1979 questionnaire included several questions concerning in-plant waste treatment practices. For each practice the tanners were asked whether they had 1) considered implementing the practice; 2) attempted its operation; 3) implemented the practice; or 4) were currently using the practice. The ratio of the total number of "yes" responses to the relevant total number of plants for each question are listed (e.g., 13/64) in Table VII-2.

Table VII-2 shows that several water conservation practices are used widely in the industry.

Sulfide recovery and chromium recovery have been adopted by relatively few tanneries. Half of the vegetable tanneries responding to the questionnaire indicated that they were using Liritan vegetable tanning systems.

The Agency's 1979 questionnaire included questions concerning methods of stream segregation. The responses to these questions are summarized in Table VII-3. Of the plants with data included on Table VII-3, nearly half used one or more of the listed beamhouse or tanyard waste segregation methods. Nearly half also indicated using one or more of the waste stream segregation methods for specific 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, stream segregation also must be tailored to each tannery. Some tanners do not consider their facilities readily adaptable to such renovations due to limited space or building construction. Floor and sewer construction methods are also mentioned as problem areas.

Many of these in-plant technologies are evidently well-established and a different economic situation will motivate tanners to further implement these pollution control methods. As the cost of processing chemicals and user fees at the POTW increase, the cost-effectiveness of many of these in-plant control technologies will become more attractive. Chromium recovery is an excellent example of an instance where the cost of processing chemicals makes recovery economically attractive, as well as environmentally sound.

C. PRELIMINARY TREATMENT PROCESSES

This group includes all end-of-pipe treatment processes applied to segregated wastewater streams from different sections of the tannery. The two segregated streams that are considered are from the beamhouse and from the tanyard and retan-wet finish process areas.

Four general treatment processes will be considered here. The first is screening, a process applicable to both segregated streams and to the chemical recovery processes. The second process is sulfide reduction. Two options for this process, oxidation and chemical precipitation, will be discussed. The third process is protein precipitation and the fourth is reduction or removal of ammonia.

1. Screening

Wastewater is screened to remove suspended solids. Coarse screens are installed primarily to protect downstream treatment equipment from large debris such as chunks of wood, rags, or bricks. Fine screens are used to remove suspended solids such as hair, buffing dust, and scraps from fleshing and hide washing operations.

Screening is one of the most widely practiced pretreatment measures in the industry. Fifty-six of the 80 plants responding to the 1979 questionnaire used some type of screening. Fifty-four of these plants reported the details and specifications of their screens. While a significant portion of the industry has reported installation of one or more screens, observations during numerous plant visits by EPA employees and representatives revealed that whole hides or sides, large pieces of leather scrap, and other large objects often were found in wet wells or other treatment system facilities after screens. Obviously, either proper screen installation or operation, or both, were not effected. Without proper screening, sewers can be blocked, and subsequent treatment system equipment can be damaged.

A summary of screen types and sizes of screen openings, as reported in the questionnaire, is presented in Table VII-9. Some plants use more than one type or size of screen, resulting in the totals for each category exceeding the number of plants that responded to these questions.

TABLE VII-9

SUMMARY OF SCREENING DATA FROM 1979 QUESTIONNAIRE

Description of Data	No. of Plants Using Specified Equipment
Screen Opening Size	
less than 0.05" (1.27 mm)	20
0.05" (1.27 mm) to 0.25" (6.35 mm)	20
greater than 0.25" (6.35 mm)	24
Type of Screen	
Rotary	21
Static Tangential	19
Bar	10
Static	5
Vibrating	2
Other	5

2. Sulfide Reduction

Chemical oxidation and precipitation are the two methods (excluding techniques included in In-plant Controls) used extensively in the United States and Europe to reduce sulfides in tannery wastes. In the oxidation process, removed sulfide is oxidized to thiosulfate, sulfite, or sulfate in an aerobic environment. Bacteria can reduce these oxidized forms of sulfur to sulfide under anaerobic conditions. Successful sulfide oxidation requires that the treated wastewater remain aerobic. The precipitation of sulfide, usually done by adding iron salts, eliminates the possibility of the oxidized sulfur species reverting to sulfide. However, precipitation has several disadvantages: a large quantity of relatively expensive chemicals are required and more solid waste is created.

The amount of sulfide that can be removed from wastewater depends on both the percentage of the total sulfide contained in the treated waste stream and on the efficiency of the treatment process. Most of the sulfide in tannery wastes is contained in the beamhouse waste stream. Two studies have shown that the beamhouse waste stream contains approximately 99 percent of the total sulfide generated by a subcategory 1 tannery[7 33], while a third study indicated that the beamhouse stream contained only about 86 percent of the total sulfide discharge[13].

Sulfide Oxidation. The only sulfide oxidation process that has been used widely in the leather tanning industry is catalytic oxidation. The air oxidation process, using manganese (II) ion as a catalyst, was developed by The British Leather Manufacturers' Research Association and was first presented by Bailey and Humphreys[34]. The relatively simple process involves collecting the sulfide bearing wastes (usually one day's discharge) in a suitable tank, adding manganese (II) ion, and aerating the mixture.

Several researchers have conducted experiments comparing the effectiveness of different metal ions in catalyzing air oxidation of sulfides[34 35 36]. Nickel (II), cobalt (II), copper (II), manganese (VII), and manganese (II) have been found to be effective catalysts. Manganese was selected by Bailey and Humphreys because the other metals were thought to inhibit subsequent biological waste treatment.

The advantages of permanganate Mn (VII) over manganous [Mn(II] ion include permanganate's function as a chemical oxidant and as a catalyst after reduction to the plus-two oxidation state[35 36]. Permanganate has been found to be more effective than manganese (II); with equivalent concentrations of permanganate and a manganese (II) ion, the reaction rate with permanaganate is faster[36], and oxidation of sulfide wastes from a cellulose sponge manufacturing facility required only about half as much permanganate for optimum performance[37]. In spite of permanganate's performance, manganese (II) ion has been used in most full-scale applications, presumedly because it is less expensive. In the spring of 1980, the price per unit of manganese (II) purchased as manganese sulfate ($MnSO_4$) was approximately one-tenth that of potassium permanganate.

Thiosulfate is considered the primary end product of sulfide oxidation with manganese sulfate[34 37]. This implies a stoichiometric oxygen requirement of 1.0 pounds (1.0 kg) of oxygen per pound (kg) of sulfide oxidized[38]. Catalytic oxidation has also been reported to reduce the alkalinity of unhairing liquor. Van Meer reported that oxidation of spent unhairing liquor reduced the alkalinity 77 and 80 percent in two tests[39].

Bailey and Humphreys[25] conducted batch pilot tests at three different tanneries: a glove leather tannery, a side leather tannery, and a fellmongery. Based on their pilot plant results, a design aeration capacity of approximately one cfm per square foot of aeration tank area (for diffused air systems) and a catalyst dose of 100 milligrams of manganese (II) per liter were recommended for full-scale design criteria. In a later publication, Bailey announced that approximately half this dose of manganese (II) ion would be sufficient with surface aeration systems because mechanical aeration provides better dispersion of the catalyst[40].

Eye and Clement[36] experimented with batch oxidation of spent unhairing liquors using permanganate as a catalyst. The optimum dose of catalyst corresponded to a manganese to sulfide ratio of approximately 0.15. This is equivalent to 750 milligrams of manganese per liter for an initial sulfide concentration of approximately 5,000 mg/l.

Constantin and Stockman[7] conducted pilot-scale sulfide oxidation tests, which were used to develop design criteria for a full-scale system. The results from several tests demonstrated that catalyst doses with manganese to sulfide ratios of 0.05 to 0.10 were effective. The full-scale system was able to reduce the sulfide concentration from approximately 2,500 mg/l to below the detection limit of their analytical technique (about 7 mg/l) in two hours, 45 minutes. This oxidation rate is very high and may have resulted from the relatively large aeration capacity of the equipment at this installation. Each sulfide oxidation tank was equipped with a mechanical surface aerator that provided 11.5 horsepower per 1000 ft^3 (303 $kw/10^3m^3$) of wastewater treated (in a batch process).

Thorstensen[41] reported results of full-scale batch oxidation at a side leather tannery. All wastewater from the unhairing operation, which made up approximately 10 percent of the plant's total flow, was pumped to the oxidation tank. The initial sulfide concentration of approximately 230 mg/l was reduced to a non-detectable level after 5 hours. The system employed subsurface aeration equipment providing 99 cfm per 1000 ft^3, (0.99 m^3 air/m^3 min) of wastewater, or, stated in terms of tank area, 1.07 cfm per sq ft (19.6 $m^3/hr \cdot m^2$) This value is essentially equal to Bailey and Humphrey's recommendation[34 40]. Thorstensen reported using 150 pounds (68 kg) of manganese sulfate per day in approximately 30,000 gallons (114 m^3) of wastewater. Assuming 28 percent manganese by weight, this is equivalent to 162 mg/l, or a manganese to sulfide ratio of 0.72.

Information gathered from the 1979 questionnaires reveals that the sulfide oxidation systems in use across the country are quite varied. They range from systems designed to collect and treat only the concentrated unhairing liquors to ones treating the plant's entire flow. A summary of the operating parameters for those plants with sulfide oxidation is shown in Table VII-10. Table VII-11 indicates the toxic pollutants that were detected in the effluent from sulfide oxidation.

Hydrogen peroxide has also been used successfully to oxidize sulfides in tannery wastes. When the pH is above 8.0, sulfide is oxidized to sulfate. When the pH is below 8.0, sulfide is oxidized to sulfur. Because oxidation to sulfate requires almost four times more hydrogen peroxide than oxidation to sulfur, reducing the pH to below 8.0 before adding the peroxide solution is important for economic reasons. O'Neill et al.[42] described results of oxidation tests with hydrogen peroxide at two tanneries. In one tannery, approximately 200 ppm of hydrogen peroxide were applied to reduce sulfides to less than one mg/l. The initial sulfide concentrations ranged from 26 to 449 ppm during the day of the test. The chemical cost was $1.55 per thousand gallons ($0.41/1000L) treated (1978 price level). At a second tannery the sulfide concentration of 60 ppm was reduced to zero by treatment with sulfuric acid and 100 ppm of hydrogen peroxide. Chemical costs (including acid) were approximately $0.36 per thousand gallons ($0.10/1000L).

The primary advantages of treating with hydrogen peroxide are the simplicity of the process and the small capital requirements for chemical feed equipment and reaction vessels. The primary disadvantage is that the chemicals are expensive. Hydrogen peroxide requirements for sulfide oxidation are stoichiometric, hence chemical costs will increase approximately in proportion to the sulfide concentration and the volume of waste being treated. Because of the proportional relationship between hydrogen peroxide requirements and sulfide content, and the high cost of the chemicals, oxidation with peroxide is best suited as a "polishing" step for eliminating small amounts of sulfide.

Sulfide Precipitation. Precipitation of sulfide with iron salts is another effective means of reducing sulfide concentration. The solubility product of ferrous sulfide is approximately 6×10^{-18}, which suggests that small residual concentrations of sulfide can be obtained by adding ferrous ions. Watkins[43] stated that a mixture of ferrous and ferric salts yields better results than ferrous salts alone, and that a slight excess of reagents should reduce the dissolved sulfide concentration to less than 0.5 mg/l.

Sulfide precipitation with iron salts has received little attention in recent literature, but was recommended by two different researchers[45] several years ago, before catalytic

TABLE VII-10

SULFIDE OXIDATION DESIGN AND OPERATION CRITERIA

Plant Number	% of Plant Flow Treated	Catalyst Type	Mn^{++} Dose (mg/l)	Batch Oxidation Time (Hours)	Aeration Equipment Type	Aeration Equipment Horsepower Per 1000 ft^3	Aeration Equipment ($kW/1000m^3$)
14	100(1)	$MnSO_4$	31	3-10	S(2,3)	1.5	(40)
31	40	$MnSO_4$	9.1	4	S	-	(-)
103	40	$MnSO_4$	55(162)(4)	7	S	4.2	(110)
185	15	$MnSO_4$	91	8	M(5)	1.8	(47)
248	25	$MnSO_4$	302	8	M	1.3	(34)
383	40	$MnSO_4$	51	8	S	3.8,5.2(6)	(100,137)
413	-	-	-	-	S	3.5-4.0	(92 -105)
438	100	$MnCl_2$	0.3	24	S	1.5	(40)
502	100	$MnSO_4$	79	960	S	0.14	(4)
507	-	-	None	-	S	-	(-)
37185	40	$MnSO_4$	-	2-3	S	1.5	(40)

1. Only 50% of the hides processed are unhaired.

2. "S" denotes subsurface aeration equipment.

3. Sulfide oxidation is performed in process equipment.

4. 55 mg/l was calculated from data in plant profile; however, data in Reference No. 41 indicated a dose of 162 mg/l.

5. "M" denotes mechanical surface aeration equipment.

6. The lower value is with only one tank; the higher value is with both tanks.

TABLE VII-11

TOXIC POLLUTANTS DETECTED IN SULFIDE OXIDATION EFFLUENTS
SUBCATEGORY ONE

Parameter	Number of Plants	Number of Observations	Number of Samples	Concentration (ug/l)		
				Maximum	Minimum	Median
Lead	1	3	6	520	180	390.0
Cadmium	1	2	6	20.0	10.0	15.0
Chromium	1	1	6	1,500	1,500.0	1,500.0
Copper	2	4	6	1,000	76.0	730.0
Nickel	1	3	6	1,080	750.0	1,040.0
Zinc	2	5	6	15,000	200.0	7,740.0
Mercury	1	1	6	0.2	0.2	0.2
Acenaphthene	1	1	6	3.00	3.00	3.0
Benzene	1	1	6	1,860	1,860	1,800.0
Chlorobenzene	1	1	6	32.0	32.0	32.0
1,2-Dichlorobenzene	2	6	6	110	13.0	56.0
1,3-Dichlorobenzene	1	1	6	11.0	11.0	11.0
2,4-Dichlorophenol	1	1	6	14.0	14.0	14.0
2,4-Dimethylphenol	1	3	6	76.0	7.00	57.0
Ethylbenzene	1	1	6	3.00	3.00	3.0
Naphthalene	2	6	6	23.0	5.00	15.0
4-Nitrophenol	1	1	6	6,100	6,100	6,100.0
Pentachlorophenol	2	4	6	198	60.0	98.5
Phenol	2	5	6	260	69.0	125.0
Bis(2-ethylhexyl)phthalate	2	3	6	140	5.00	45.0
Diethyl Phthalate	1	1	6	1,200	1,200	1,200.0
Acenaphthylene	1	1	6	1.00	1.00	1.0
Fluorene	1	2	6	2.00	2.00	2.0
Toluene	1	1	6	38.0	38.00	38.0
Anthracene/Phenathrene	1	2	6	3.00	2.00	2.5

oxidation with manganous sulfate had been developed. Tannery No. 235 uses spent pickling liquor from a steel mill, with a ferrous ion content of 10 percent, to precipitate sulfide. The process has also been used at European tanneries[46]. One disadvantage of precipitation with iron salts is that an intense black color is generated in the effluent[47] This would probably not be a problem today because subsequent treatment processes could remove this color.

Tannery No. 7, using sulfide precipitation combined with aeration and chlorination, has consistently achieved effluent sulfide concentrations of 0.1 mg/l.

Sulfide oxidation was reportedly practiced at 15 tanneries at the time of the 1979 industry survey. However, review of process characteristics revealed that few of these systems had been designed or were operated with the intent to reduce sulfides to a non-detectable level. In addition, limited effluent data was available.

In the absence of a consistent and extensive data base, alternate approaches were sought to determine an achievable long term effluent sulfide concentration. The first method represents a theoretical approach and assumes that the sulfide oxidation system will be operated to reduce sulfides below the detection limit for the beamhouse waste stream and combines with the estimated carryover of sulfide into the tanyard. The second method involves evaluating the limited sulfide oxidation effluent concentrations reported.

A search of available literature identified three references relative to the sulfide distribution by unit process in tanning operations[7] [13] [33]. Each of these reported (by unit process) sulfide discharges as a percentage of the total present. From these references, it was discerned that between 86 and 99 percent of the sulfides discharged are contained in the beamhouse waste stream. The sulfide oxidation process is applied only to this segregated stream. The average of the three values is 95 percent, which results in 5 percent of the sulfide loading being discharged without passing through the sulfide oxidation process. This sulfide loading is carried from the beamhouse to the tanyard in the hides and is washed out during subsequent tanning processes. The 5 percent carryover represents about 8 mg/l in the combined wastestream or about 13 mg/l in the tanyard stream alone.

Several methods are available to measure sulfide concentrations in wastewater. A review of the currently approved method (Iodometric titration), the Society of Leather Chemists (SLC)

Ferrocyanide titration (SLM 4/2) and a modified Monier-Williams method indicates that in a tannery wastewater, the SLM 4/2 method provides more consistent results and is relatively free from interferences. Assuming sample sizes are chosen properly, this method can detect as little as 0.16 mg/l sulfide (S=). More realistically, however, sample sizes of 50 or 100 ml would be utilized. For a 50 ml sample, the limit of detection would be 3.2 mg/l.

Since the recommended operational mode for the sulfide oxidation process is batch treatment, the system may be operated until analysis indicates "zero" sulfide, actually about 3 mg/l for a 50 ml sample. Considerable research has already been completed which achieved "zero" sulfide with less than one-half the catalyst dosage currently recommended. Review of the analytical techniques utilized during the research study indicates that the "zero" result reported would more appropriately be "less than 6.4 mg/l" sulfide since only 25 ml samples were used.

Recombining this stream (with sulfides reduced to 3 mg/l) with with the tanyard stream would result in a combined wastestream sulfide concentration of 9 mg/l. This level would remain achievable despite varying raw wastewater sulfide concentrations by proper process control of the oxidation system.

Field data was collected during the EPA toxic pollutant verification sampling program (1979) as well as from tannery records. Only three tanneries (Tannery Nos. 55,383, and 37185) utilized systems sufficiently similar to that proposed to allow evaluation.

Tannery No. 55 adds slightly more than the recommended catalyst dosage but operates their oxidation unit on a flow-through basis. The average sulfide concentration of their combined wastestream is 9.8 mg/l (based on 12 observations). Operation on a batch basis would provide improved process control and allow achieving a level of 9 mg/l.

Tannery No. 383 passes their entire waste stream through the sulfide oxidation process and reported an average effluent sulfide concentration of 4.1 mg/l (based on 11 observations).

Tannery No. 37185 provides only two hours of aeration to their beamhouse stream. An independent sampling report indicated an average effluent sulfide concentration of 10.6 mg/l. Additional aeration would reduce this value.

The remaining tanneries which reported use of the sulfide oxidation process either did not provide data or operated their systems in significantly different manners from that recommended.

Both methods of estimating an achievable sulfide concentration indicate that a level of 9 mg/l (long term basis, before applying variability factor of 2.7; maximum day pretreatment standard is 24 mg/l) is reasonable and currently demonstrated with the recommended technology.

Although there might be incidental removals of other pollutants in this process, removals have not been adequately documented and therefore the Agency has assumed in developing pretreatment standards (both PSES and PSNS, see Section XII) that only sulfide is removed.

3. Flue Gas Carbonation for Protein Precipitation

The objective of flue gas carbonation is to lower the pH of segregated unhairing wastewaters so that some of the dissolved and colloidal proteins and excess lime in the beamhouse waste stream will coagulate and settle. The beamhouse wastes are widely recognized as contributing most of the BOD_5 and COD in the raw waste from a side leather tannery. Removing the protein at this stage can have several benefits. For direct dischargers, the BOD_5 loading and therefore the aeration system requirements of the biological treatment will be reduced. Flue gas carbonation will also generate a sludge rich in lime and protein which may be used as a soil conditioner or a source of protein for animal feed. The Agency believes that removing much of the colloidal proteins will enhance the performance of subsequent treatment processes, particularly coagulation and sedimentation.

The chemical basis of the protein precipitation process is related to the electrical charge carried by protein colloids at different pH levels. At the high pH typical of beamhouse wastes, the proteins have a net positive charge. As the pH is reduced toward the isoelectric point of the proteins, the proteins flocculate and settle. Carbon dioxide in a tannery's boiler stack gas is used in the process as an inexpensive source of acid to neutralize caustic alkalinity and reduce pH.

Stack gases from efficiently operated fossil fuel boilers generally contain between 8 and 14 percent carbon dioxide. When stack gas is sparged through beamhouse wastes, the carbon dioxide dissolves in the wastewater and forms carbonic acid. This acid reacts with hydrated lime to form calcium carbonate and calcium bicarbonate. Instead of flue gas, mineral acids may be added directly to the wastewater. As the pH is reduced, the calcium carbonate forms a rapidly settling precipitate which promotes clarification. Optimum protein removal occurs when the pH is reduced to approximately 4.2. The protein removal efficiency will be lower if the pH is only reduced to 7.0. The amount of protein that can be removed with the pH of the beamhouse wastes reduced to 7.0 can be estimated from work done by Van Meer[39]. He reported the results of one experiment in which oxidized beamhouse liquors were neutralized to a pH of 7.0 with a mineral acid; COD reductions were 70 to 80 percent and nitrogen reductions 76 to 80 percent. This resulted in a reduction of COD in the tannery's total effluent of approximately 48 to 55 percent.

Sayers and Langlais[13] conducted some small-scale protein removal experiments on the effluent from the hydrogen sulfide gas stripping tower described previously in the section on sulfide liquor reuse. The combined raw waste stream from a through-the-blue tannery was settled, acidified to a pH of approximately five, then injected into the stripping tower. Effluent from the stripping tower settled for four hours. This treatment reduced the concentrations of BOD_5, COD, suspended solids, and chromium significantly (see Table VII-12). No data were given concerning the removal of protein or nitrogen.

TABLE VII-12

POLLUTANT REMOVALS BY PROTEIN PRECIPITATION

Parameter	Concentration Before Batch Settling mg/l	Final Concentration mg/l	Percent Removal from Final Settling
BOD_5	5,917	3,185	46
COD	12,660	3,260	74
SS	6,560	1,420	78
Cr_2O_3	512	19	96
Oil & Grease	1,032	19	98

Source: Reference No. 13

The staff of the Eastern Regional Research Center (ERRC) has investigated the potential value of proteins recovered from unhairing liquors as a chicken feed supplement[12]. Dewatered protein from treated cattlehide unhairing liquor was found to have a protein content similar to commercial hair meal, and a low percentage (25 percent) of available lysine. Both have a poor essential amino acid balance. The recovered hair-pulp protein was supplemented with amino acids and fed to chickens in small-scale tests. Increasing the amount of protein in the feed led to a decrease in the body weight of the chickens. Work is continuing in this investigation. The grease and lime from the beamhouse wastes may also be used in chicken feed formulations. Flue gas carbonation has been used at four U.S. tanneries: Tannery Nos. 24, 58, 60, and 397. At these tanneries, protein removal is apparently not a priority, as evidenced by the lack of data or discussion in the literature concerning protein removal. Flue gas carbonation has been employed for other reasons: to reduce caustic alkalinity[48], to scrub flue gases from coal boilers[49], to enhance sulfide oxidation or removal[50 51], and to precipitate and remove tannins from vegetable tanning wastes[49]. The use of flue gas sparging to remove sulfides from beamhouse wastes is questionable, although the process could work effectively. The primary means of removing sulfides is probably stripping of hydrogen sulfide gas. Though this would remove sulfide from the wastewater, offensive odors would probably be created.

Field data collected by EPA at Tannery No. 24 indicates that flue gas carbonation is effective in reducing suspended solids, BOD_5, and total alkalinity. Table VII-13 shows the performance of flue gas carbonation, chemical coagulation, and sedimentation during an EPA field-sampling visit to Tannery No. 24.

The flue gas carbonation system at Tannery No. 397 was installed primarily as an air pollution control device on the tannery's coal-fired boiler. The capability of the system to reduce the pH of the tannery's wastewater is of secondary importance.

Some of the data discussed below by parameter were extracted from the literature. The remaining data resulted from sampling efforts and studies conducted under EPA contracts. When differences occurred between the two groups of data, more weight was given to the field data in determining the removals for selected parameters. Removals of specific pollutants by flue gas carbonation are dicussed below.

Total Kjeldahl Nitrogen (TKN)

Only two sources of data were identified which specify TKN removals achieved by protein precipitation. Van Meer[39] obtained 76 percent reduction by treating the hide soaking and unhairing waste streams with acid to a pH of 7.0. At

Tannery No. 397, flue gas carbonation of the entire beamhouse waste stream followed by settling realized a reduction of 57 percent. A conservative TKN removal of 50 percent will be used for flue gas carbonation.

Biochemical Oxygen Demand (BOD_5)

The BOD_5 reductions produced by pH depression of the beamhouse wastewater using sulfuric acid or flue gas addition ranged from 52 to 79 percent. The data for Tannery No. 24 pertains to flue gas carbonation plus coagulation-sedimentation thus, it was not considered in this analysis. Full scale operations at Tannery No. 444[13] and Tannery No. 297 produced BOD_5 reductions of 52 and 54 percent, respectively. Therefore, the BOD_5 reduction which will be applied for the flue gas carbonation process is 50 percent.

Chemical Oxygen Demand (COD)

COD removals ranging from 63 to 71 percent have been observed from tanneries using pH adjustment of beamhouse wastewaters. Based on these observations, a COD reduction of 65 percent will be used for the flue gas carbonation of the beamhouse waste stream.

Total Suspended Solids (TSS)

Data presented in the literature indicated a TSS removal rate of 95 to 96 percent. Performance data for full scale tannery treatment systems for TSS indicate a range of 86 to 96 percent. The lower removal value was reported by a plant that adds flue gas only until the pH is 9.0. The design of the BAT model treatment facility is based on introducing flue gas to depress the pH to 7.0 which effects better protein precipitation. At the lower pH (7 versus 9), greater removals of TKN and TSS should be realized. Therefore, for those tanneries introducing flue gas into the beamhouse waste stream, a 90 percent gas reduction of TSS is achievable.

TABLE VII-13

PERFORMANCE OF FLUE GAS CARBONATION, CHEMICAL COAGULATION, AND SEDIMENTATION AT TANNERY NO. 24

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

4. Ammonia Reduction

The Agency has considered several alternatives for removing ammonia from tannery wastewaters prior to end-of-pipe treatment. These alternatives are physical processes that are generally most effective and least costly when applied to concentrated wastes, such as the deliming waste stream.

Evaporation and Crystalization. When applied to deliming wastes, this process would involve evaporating sufficient water from the waste to reach the saturation concentration of ammonium sulfate. Ammonium sulfate would then be precipitated and removed. One disadvantage of this process is that most of the water in the deliming wastes would have to be evaporated to reach the saturation concentration of ammonium sulfate. If the deliming waste stream initially contained one percent ammonium sulfate, 98 percent of the water would have to be evaporated to reach the saturation concentration of approximately 50 percent. The evaporated water will contain approximately 0.2 percent ammonium sulfate if evaporation takes place at 95°C. Thus, the percent of 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.

Since evaporation is a very energy intensive process, the current high cost of energy will probably limit the application of this process for removing ammonia from tannery wastes.

Ammonia 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 calcium ammonium sulfate causes difficulties in the production of the fertilizer ammonium phosphate. The excess lime contained in beamhouse wastes 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. Therefore, precipitating excess lime by flue gas carbonation may be necessary before attempting to remove the ammonia with phosphoric acid.

Ammonium Precipitation With Ethanol. Ammonium sulfate is insoluble in a solution of ethanol and water when the ethanol content is greater than 90 percent (by weight). Ammonium sulfate could probably be removed from deliming wastes by adding nine parts of ethanol to each part of deliming waste. The high cost of ethanol, however, would make this process prohibitively expensive.

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 also be suitable for concentrating aqueous ammonium sulfate. Free ammonia would probably pass through such a membrane. Pressure requirements are a major limitation on concentration of the ammonium sulfate solution. Concentration to even five percent would require the use of pressures in the realm of several hundred pounds per square inch. Fouling of the membrane could also be a serious problem. Cost and process limitations preclude this technology from further consideration.

D. END-OF-PIPE TREATMENT

1. Primary Treatment Processes

Flow Equalization. Flow Equalization is not intended to provide any treatment or remove pollutants but is important because it improves the consistency of other treatment processes' performance. By reducing flow and pollutant surges, equalization also permits smaller and less costly downstream waste treatment equipment to be utilized.

The objectives of equalization are to dampen wastewater flow surges, dilute slugs of concentrated wastes, partially neutralize high and low pH waste fractions, and provide a relatively constant rate of flow to downstream treatment processes. One example of the last objective is the use of equalization to provide a reserve of biodegradable organic matter to "feed" a biological treatment system during short periods, such as weekends, when a tannery is closed.

Twenty of the 76 tanneries that responded to the 1979 questionnaire have equalization tanks; five of these are direct dischargers. For the 10 tanneries that reported detention times of their equalization basins, actual detention times ranged from one to 75 hours, with a median of seven hours.

Plain Sedimentation. The principal function of primary clarification is to remove suspended solids from wastewater. Since suspended solids in tannery wastes are also a source of BOD_5, COD, and TKN, primary clarification will significantly reduce these pollutants. The Agency also views sedimentation as an important treatment step for removing certain toxic pollutants, particularly chromium.

Sedimentation is one of the most widely-used and studied wastewater treatment processes employed by the tanning industry. Sedimentation has been used to treat individual process wastes, such as spent unhairing liquors, or segregated beamhouse wastes, as well as combined tannery wastes. The 1979 questionnaire indicated that 41 out of 77 tanneries responding had primary sedimentation facilities. Twelve of the 21 direct dischargers used primary clarification. The following discussion will concentrate on applications of primary sedimentation treating combined tannery wastes.

Harnley et al.[52] reported the efficiency of plain sedimentation of combined wastes from a chromium tannery. The tannery's waste treatment system had two settling tanks which operated at an overflow rate of approximately 140 gpd/ft^2 (5.7 m^3/m^2 d). The suspended solids removal efficiency was approximately 85 percent and the BOD_5 removal efficiency was approximately 58 percent. The pH of the combined waste was relatively high, ranging from 9.0 to 12.3 with a typical pH of about 11.0.

After conducting an experiment involving plain sedimentation of wastes from a side leather tannery, Sutherland[53] reported a suspended solids removal efficiency of 69 percent. The detention time was approximately two hours.

Eldridge[54] conducted settling experiments with the liquid wastes from a sheepskin tannery. In his continuous flow studies, plain sedimentation produced removal efficiencies of 43 percent for suspended solids and 48 percent for BOD_5. In another continuous flow test, lime was added as a coagulant aid; the pollutant removal efficiencies were only marginally better, 46 percent for suspended solids and 55 percent for BOD_5. The clarifier overflow rates were not stated. The plain sedimentation and lime-addition tests were repeated using a fill-and-draw operation. Lime addition during the fill-and-draw tests produced the best results of any method. The removal efficiencies were 80 percent for suspended solids and 62 percent for BOD_5.

Thorstensen[41] reported data on chromium removal by plain sedimentation of combined wastes from a side leather tannery. Following sulfide oxidation of the unhairing wastes, the combined tannery flow was treated, without equalization, in a sedimentation tank. The overflow rate at average flow was approximately 410 gpd/ft^2 (16.7 m^3/m^2 d). Pollutant removal efficiencies of these treatment processes are shown in Table VII-14. The removals of BOD_5, suspended solids, and oil and grease could have been affected partly by sulfide oxidation, but the removal of chromium was from sedimentation alone. Thorstensen also suggested that the performance of sedimentation could be improved if equalization were added, or if waste discharges were scheduled to eliminate hydraulic peaks, which apparently occurred at the time the data in Table VII-14 were collected.

The results of plain sedimentation of the screened wastewater from another side leather tannery[33] are shown in Table VII-15. The waste treatment facilities at this tannery included two 35-foot (10.7 m) diameter primary clarifiers operating at overflow rates of approximately 410 gpd/ft^2 (16.7 m^3/m^2 d).

Sayers and Langlais[13] reported the performance of plain sedimentation of the combined wastewater from a modern, through-the-blue tannery (Table VII-16). The overflow rate was approximately 125 gpd/ft^2 (5.1 m^3/m^2 d). The data reported is based on one day, 24-hour composite samples taken in 1973 and 1976. Several small changes occured during the time between these two sampling dates: production increased, unit water use decreased (total use remained the same), a screen was installed to remove hair, and lime use in the beamhouse was reduced. The improved removal of TKN and COD in 1976 was attributed to improved hair removal. The removal of BOD_5 and suspended solids by primary sedimentation seem to be in accord with expectations and other data from the literature. Chromium removal was relatively poor, despite a nearly optimal pH for forming insoluble chromium hydroxide. The percentage removals of chromium are essentially equal to the results listed in Table VII-14. However, the absolute concentrations are higher in Table VII-15 than in Table VII-14.

<u>Coagulation - Sedimentation</u>. An apparently very successful physical-chemical treatment process for tannery wastes was

described in 1929 by Fales[55]. The treatment system employed gravity sedimentation, pH reduction with sulfuric acid, coagulation with alum, second stage sedimentation, and, as a final step, slow sand filtration. After filtration, the raw waste "oxygen consumption" was reduced from approximately 700 ppm to 66 ppm, and "fats" were reduced from approximately 678 ppm to 19 ppm. Data given for the effluent from the second stage sedimentation tanks (before filtration) indicated that the suspended solids in the raw waste were reduced from 1550 ppm to 68 ppm, a reduction of almost 96 percent. The alum dose was reported to be approximately 120 parts per million; clarifier overflow rates were not given.

For several years, Tannery No. 47 has operated a coagulation-sedimentation system as part of its waste treatment system. BOD_5 and suspended solids removals of 57 and 96 percent were achieved by the primary treatment system during an EPA industrial waste survey conducted in 1971[56]. Because Tannery No. 47 uses alum tanning for most of its production, the alum present in the wastewater likely aids coagulation. The pH of the clarifier influent is maintained near 7.0, and an anionic polymer is added to wastewater as it enters the clarifier.

Three wastewater treatment facilities utilizing coagulation-sedimentation process served as the basis for projecting long term achievable chromium concentration with primary coagulation-sedimentation. The operational characteristics, the unit processes, and performance of each of the facilities is described herein. Table VII-17 summarizes the chromium removal performance of the coagulation- sedimentation processes at each of the three wastewater treatment facilities.

Tannery No. 47 - Tannery No. 47 adds polymer to the influent of the primary clarifer. The pH of the influent is maintained at 7.0 or above. The chromium removal of this system is excellent. During a three consecutive day sampling episode, the coagulation-sedimentation achieved 94 percent removal.

Berwick, ME POTW - The Berwick POTW receives in excess of 90 percent of its flow from a subcategory 4 tannery. The pretreatment steps performed at the tannery are screening, equalization, and pH adjustment.

At the POTW the combined tannery and domestic waste is treated by the following steps:

1. pH adjustment to approximately 8.5
2. polymer addition

TABLE VII-14

REMOVAL OF POLLUTANTS WITH SULFIDE OXIDATION OF UNHAIRING WASTES AND SEDIMENTATION OF COMBINED WASTES FROM A SIDE LEATHER TANNERY

	Influent			Effluent			
Parameter	lbs/day	(kg/d)	mg/l	lbs/day	(kg/d)	mg/l	% Removal
BOD_5	2,780	(1261)	1,110	1,560	(703)	623	43.9
SS	4,910	(2227)	1,962	1,584	(719)	633	67.8
Oil & Grease	46	(21)	18	13.2	(6)	5.3	71.4
$S^{=}$	183	(83)	73	0	(0)	0	100
Cr	70	(32)	28	14.2	(6)	5.7	80

Source: Reference No. 41

TABLE VII-15

REMOVAL OF POLLUTANTS BY PRIMARY SEDIMENTATION AT A HAIR-BURN CHROME TANNERY

		Mean Concentration (mg/l)		
Parameter	Number of 24-Hour Composites Taken	Raw Effluent	Primary Effluent	% Removal
BOD_5	28	1,501	907	40
COD	30	4,284	2,319	46
TVS	30	2,570	1,455	43
TSS	30	2,579	1,091	58
Oil & Grease	18	601	207	66
Cr	21	46.8	28.9	38
Phosphorus	20	7.43	3.51	53

Source: Reference No. 33.

TABLE VII-16

SEDIMENTATION PERFORMANCE AT A THROUGH-THE-BLUE TANNERY

Parameter	Influent Composite (mg/l) 1973	Influent Composite (mg/l) 1976	Effluent Composite (mg/l) 1973	Effluent Composite (mg/l) 1976	% Removal 1973	% Removal 1976
pH	9.7*	8.8*	9.8*	8.7*	-	-
BOD_5	9,133	7,586	5,123	4,590	43.9	39.5
COD	19,867	20,286	13,167	8,485	33.7	58.2
Settleable Solids	10,600	7,676	300	3,250	97.2	57.7
Total Solids	48,900	36,282	25,400	27,644	48.0	23.8
Suspended Solids	9,067	7,675	2,767	3,256	69.5	57.6
Sulfide	250	915	264	930	-	-
Alkalinity	2,896	3,946	2,660	3,840	8.1	2.7
Oil & Grease	570	1,140	21	985**	96.3	13.6**
Cr_2O_3	295	242	190	150	35.6	38.
NH_3-N	520	540	517	532	-	-
TKN	1,101	1,395	954	850	13.4	39.
Total Phosphorus	40	-	20	15	50.0	-

*Standard pH units.

**Grease skimmer was not operating during this sampling period.

Source: Reference No. 13.

3. coagulation and sedimentation in two (parallel) reactor-clarifiers. Clarification area for the two, 35 foot diameter clarifiers is 1,800 ft^2 total (9 foot diameter at center influent baffle).

As shown on Table VII-17, the Berwick POTW achieved total chromium effluent concentrations of 6.5 mg/l.

Tannery No. 60 - As shown on Table VII-18, Tannery No. 60 performs treatment of four segregated wastestreams. The average effluent (mathematically calculated) equals approximately 10 mg/l.

The projected long term achievable chromium concentration is 8 mg/l. The Berwick POTW consistently achieved concentrations lower than 8 mg/l during 1979 the period of record described in Table VII-17. Approximately 90 percent of the flow at this wastewater treatment plant is from a subcategory 4 tannery. The performance of the Berwick POTW has weighted heavily in determining the achievable concentration of 8 mg/l because the model process for coagulation-sedimentation is used at this facility. Samples taken on three consecutive days at Tannery No. 47, when production included 25 percent chromium tanned and 75 percent alum tanned cattlehides, also indicate that long term concentrations of less than 8 mg/l are readily achievable with reasonable influent characteristics.

Table VII-17 shows that the projected long term achievable concentration of 8 mg/l was exceeded at Tannery No. 60. At Tannery No. 60 the chromium concentrations of two of the three chromium- bearing waste streams are approximately 8 mg/l. The chromium concentration of the third stream, which includes wastewater from bating and the third chromium rinse, is much higher. Improvements to the coagulation-sedimentation process used to treat this waste stream could decrease its chromium concentration significantly. Decreasing the chromium concentration of the bating and third chromium rinse waste stream from 68.8 mg/l to 19 mg/l would be sufficient to decrease the weighted average plant concentration to less than 5 mg/l.

The projected concentration of 8 mg/l is currently being achieved or surpassed by several plants in the industry, including Tannery No. 13, and can be achieved by several other tanneries through minor changes within the tannery and the treatment system. It should also be noted that further reduction in chromium concentration will be realized in those subcategories where beamhouse waste streams are comingled after coagulation-sedimentation of chromium-bearing waste streams.

TABLE VII-17

SUMMARY OF CHROMIUM REMOVAL BY COAGULATION-SEDIMENTATION

Tannery No. or Treatment Plant Name	Subcategory	Coagulant(s)	Coagulation-Sedimentation Influent		Coagulation-Sedimentation Effluent	
			Mean CrT Conc.	No. of Observ.	Mean CrT Conc.	No. of Observ.
47	2,3[a]	polymer	61[b]	3[b]	3.5[b]	3[b]
Berwick POTW (ME)	4[c]	lime, polymer	34	111	6.5	97
60	1	--[d]	--	--	10[e]	--[d]

[a] In 1979, 75% of production was in subcategory 3 and 25% was in subcategory 2.
[b] Data was collected in December 1979.
[c] Over 90% of the POTW flow is from a subcategory 4 tannery.
[d] See description in Table VII-18.
[e] Estimated value, see description in text.

TABLE VII-18

TREATMENT OF SEGREGATED WASTE STREAMS AT TANNERY NO. 60

Waste Stream Description/ Data Description	Wastewater from split tanning, coloring, fat-liquoring, fleshing	Wastewater from split chrome tanning, first two chrome rinses, and grain tanning	Wastewater from third chrome rinse and bating	Beamhouse wastewater
Sedimentation Process Description	a	b	c	d
Measured CrT Effluent Conc. (mg/l)				
Day 1	7.25	8.50	48.5	0[e]
Day 2	3.50	--	89.0	0[e]
Day 3	10.0	--	--	0[e]
Mean CrT Effluent Conc. (mg/l)	6.92	8.50	68.8	0
Flow (gal/week)[f]	587,000	14,000	140,000	610,000
((m^3/week))	(2,220)	(53)	(530)	(2,310)

[a] Continuous flow, without chemical addition

[b] Batch, with addition of magnesium oxide and polymer, followed by chromium recovery

[c] Batch, with addition of lime and polymer.

[d] Batch settling, after sulfide oxidation and flue gas carbonation.

[e] CrT concentration assumed to be zero

[f] Flow estimated from batch discharge volumes and measured final effluent flow rate.

Perhaps the most efficient coagulation-sedimentation process for removal of chromium was reported by Bishop[8]. A pretreatment system consisting of screening, equalization, pH adjustment, coagulation, flocculation, and suspended solids removal in a lamella/tube settler was employed at a retan-wet finish tannery. After adjusting the pH to approximately 8.5, 25 mg/l of ferric chloride and 1 mg/l of an anionic polyelectrolyte were added to enhance settling. The system is able to reduce chromium in the effluent by approximately 98 percent, producing an effluent with a chromium content of approximately 1 mg/l. Suspended solids removal was 92 percent, BOD_5 removal was 75 percent, and COD removal was 75 percent.

A summary of the performance of the coagulation-sedimentation systems from the literature and data collected by EPA during wastewater sampling is presented in Table VII-19.

Summary The capabilities of this technology in treating leather tanning wastewaters are discussed below:

Total Kjeldahl Nitrogen (TKN)

Three tanneries reported TKN data for the primary coagulation-sedimentation process. Removals ranged from 16 to 72 percent. Since this treatment technology is not designed to remove TKN, the incidental TKN removal should be based on the lowest reported reduction, 15 percent.

Biochemical Oxygen Demand (BOD)

The BOD_5 removal rates obtained using the coagulation-sedimentation process ranged from 34 to 63 percent. The 34 percent removal rate was observed at a retan-wet finish tannery. A 35 percent BOD_5 removal rate will be used to calculate effluent concentrations for the coagulation-sedimentation process for tanneries that either do not operate a beamhouse or those which employ the flue gas carbonation process for the beamhouse waste stream prior to the coagulation-sedimentation step. The BOD_5 removal rate for beamhouse tanneries that do not employ flue gas carbonation will be 50 percent, based on the 63 percent removal measured at Tannery No. 47 and 48 percent removal reported for Tannery No. 388.

TABLE VII-19

PERFORMANCE OF COAGULATION-SEDIMENTATION

Plant Number or Tannery Description	BOD_5 Clarifier Effluent Conc. (mg/l)	BOD_5 Percent Removal	COD Clarifier Effluent Conc. (mg/l)	COD Percent Removal	TSS Clarifier Effluent Conc. (mg/l)	TSS Percent Removal	TKN Clarifier Effluent Conc. (mg/l)	TKN Percent Removal	Oil & Grease Clarifier Effluent Conc. (mg/l)	Oil & Grease Percent Removal	Chromium Clarifier Effluent Conc. (mg/l)	Chromium Percent Removal	Reference Number
47	450	63	1,442	64	293	93	31	72	52	89	3.5	94	
50	448	34	1,480	56	199	82	50	40	74	67	6.5	81	
388	1,272	48	2,684	79	384	98	93	15					
Retan-wet finish tannery	120	75	300	75	50	92					1	98	8
Vegetable tannery	270	84			100	95							SC
Sheepskin tannery, pilot-scale treatment	476	55			469	46							54
Tannery and wool degreasing plant	231	67			67	96							55

SC signifies data collected under the auspices of EPA by Stanley Consultants.

Chemical Oxygen Demand (COD)

The COD removals ranged from 56 to 79 percent. Therefore, a COD removal rate of 60 percent will be used for the primary coagulation-sedimentation of leather tanning wastewaters.

Total Suspended Solids (TSS)

A range of 82 to 98 percent removal of TSS has been experienced at the three tanneries which employ the coagulation-sedimentation process, and supplied wastewater data. Therefore, a 75 percent TSS removal rate will be applied to the coagulation- sedimentation process, when not preceded by the flue gas carbonation treatment step.

Wastewater data reported by Tannery No. 24 pertain to the effluent produced by a combination of flue gas carbonation and coagulation-sedimentation treatment. The TSS removal rate effected by the combined processes is 97 percent. Because the flue gas carbonation system alone removes a significant portion (90 percent) of the TSS in the waste stream, it is anticipated that the removal efficiency of coagulation-sedimentation will decrease slightly.

The available information and wastewater data indicate that a removal efficiency of 50 percent is achieved by coagulation-sedimentation when preceded by flue gas carbonation. The combination of the two unit processes, therefore is projected to remove approximately 95 percent of the influent TSS.

Oil and Grease

Removals of oil and grease by coagulation-sedimentation technology range from 67 percent to 89 percent with the mean removal equal to 81 percent. A removal rate of 80 percent has been projected for oil and grease removal.

Table VII-20 and VII-21 display those toxic pollutants that were detected in the effluents from coagulation-sedimentation and chromium precipitation.

2. Biological Treatment Processes

The Agency views the primary functions of biological treatment of tannery wastewaters as the removal of colloidal and dissolved biodegradable organic matter. Biological treatment processes are also effective in removing both suspended solids that pass

TABLE VII-20

TOXIC POLLUTANTS DETECTED IN PRIMARY EFFLUENTS
SUBCATEGORY ONE

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Lead	6	14	14	3,200	60.0	290.0
Chromium	6	14	14	120,000	3,500	19,070.0
Copper	6	13	14	140	6.00	100.0
Nickel	5	10	14	190	10.0	56.0
Zinc	6	13	14	2,600	38.0	255.0
Mercury	4	8	14	2.80	0.4	0.45
Benzene	1	3	14	6.00	4.00	6.0
Chlorobenzene	1	3	14	2,800	3.00	1,800.0
1,1,2,2-Tetrachloroethane	2	4	14	450	1.00	33.0
2,4,6-Trichlorophenol	3	6	14	10,500	15.0	57.0
Chloroform	4	8	14	52.0	3.00	8.0
1,2-Dichlorobenzene	5	13	14	350	14.0	75.0
1,3-Dichlorobenzene	2	4	14	46.0	7.00	16.0
1,4-Dichlorobenzene	4	8	14	99.0	2.00	6.5
1,2-Trans-dichloroethylene	1	1	14	15.0	15.0	15.0
2,4-Dichlorophenol	2	2	14	82.0	21.0	51.5
2,4-Dimethylphenol	1	3	14	53.0	18.0	38.0
1,2-Diphenylhydrazine	1	1	14	18.0	18.0	18.0
Ethylbenzene	5	9	14	972	5.00	54.0
Fluoranthene	1	1	14	12.0	12.0	12.0
Methylene Chloride	4	6	14	602	17.0	85.5
Naphthalene	5	12	14	98.0	5.00	19.5
Nitrobenzene	2	2	14	29.0	10.0	19.5
4-Nitrophenol	1	4	14	2,358	1,416	1,809.0
N-Nitrosodiphenylamine	1	1	14	36.0	36.0	36.0
Pentachlorophenol	3	6	14	11,000	3.00	215.0
Phenol	5	10	14	2,750	480	1,594.5
Bis(2-ethylhexyl)phthalate	4	9	14	195	2.00	9.0
Butyl Benzyl Phthalate	1	1	14	1.60	1.60	1.6
Di-N-Butyl Phthalate	3	4	14	44.0	1.00	25.0
Diethyl Phthalate	2	3	14	12.0	8.00	12.0
Fluorene	1	1	14	6.00	6.00	6.0
Pyrene	1	1	14	6.50	6.50	6.5
Tetrachloroethylene	2	2	14	28.0	1.00	14.5
Toluene	4	8	14	518	15.0	66.0
Trichloroethylene	3	5	14	250	12.0	46.0
Anthracene/Phenathrene	1	1	14	1.00	1.00	1.0

TABLE VII-21

TOXIC POLLUTANTS DETECTED IN CHROMIUM PRECIPITATION EFFLUENTS
SUBCATEGORY ONE

Parameter	Number of Tanneries	Number of Observations	Number of Samples	Concentration (ug/l) Maximum	Minimum	Median
Cadmium	1	1	1	30.0	30.0	30.0
Chromium	1	1	1	8,500	8,500	8,500.0
Copper	1	1	1	113	113	113.0
2,4-Dimethylphenol	1	1	1	5.00	5.00	5.0
Naphthalene	1	1	1	1.00	1.00	1.0
Phenol	1	1	1	1.00	1.00	1.0
Bis(2-ethylhexyl)phthalate	1	1	1	1.00	1.00	1.0

through primary treatment and some toxic pollutants, although these functions are incidental to the function stated above.

Twenty-one tanneries are known to have operated some type of biological wastewater treatment. Seventeen of these are currently operating direct dischargers (three have closed), and one indirect discharger. In its evaluation of biological treatment, the Agency has analyzed data from these 21 plants including, data from three tanneries that have ceased operations, and data from three captive POTWs (greater than 90 percent of the waste loads are from tanneries at these POTWs). To date, the biological treatment systems used to treat tannery wastes in the United States have been designed and operated primarily to remove BOD_5. A tabulation of the number of direct discharging tanneries (excluding POTWs) using different types of biological treatment is shown in Table VII-22.

TABLE VII-22

BIOLOGICAL TREATMENT PROCESSES USED
BY OPERATING TANNERIES WITH DIRECT DISCHARGE

Type of Treatment	No. of Plants Using Each Process
Aerated lagoons	8
Activated sludge	4
Unaerated lagoons	2
Rotating biological contactors	2
Trickling filter/lagoons	1

Trickling Filters. Trickling filters are being used at a specialty tannery and a vegetable tannery in the United States. In both cases, the trickling filters are used as "roughing" filters, the first stage of a two-stage biological treatment process. The trickling filter installation at the specialty tannery is unique in several respects. The tanning processes employed, the resulting waste loads, and the mode of trickling filter operation are not considered representative or typical of the rest of the industry. Therefore, the pollutant removal data reported for this treatment plant have not been included in this report.

The other trickling filter system, located at Tannery No. 24 (now closed), is a high-rate, plastic-media "biotower." Before passing through the biotower, the combined tannery wastewater is screened, equalized, coagulated with ferric sulfate and a polymer, and clarified. The secondary treatment system consists of the biotower followed by an aerated lagoon. A clarifier is located after the biotower to remove sloughed biological solids[58].

Results of the entire treatment system's performance at Tannery No. 24 is shown in Table VII-23. The data for BOD_5, COD, and TSS are based on samples collected for over 200 days, between 1976 and 1980. The data for oil and grease, chromium, and sulfide were based on 17 to 108 daily samples collected between November 1978 and December 1979. No data were available for intermediate sampling points for 1976 through 1979 so the performance of the trickling filter for this period could not be determined. However, Kinman[58] reported data from February, March, and April 1972 that indicate the biotower and secondary clarifier removed approximately 46 percent of the BOD load and 22 percent of the COD load. The two-stage biological process - the biotower and aerated lagoon - removed 83 percent of the BOD and 42 percent of the COD.

<u>Lagoons</u>. Lagoons are the predominant biological treatment process used in the United States to treat tannery wastewater, as indicated in Table VII-22. Biological treatment lagoons can be classified as aerated or unaerated. Aerated lagoons rely on mechanical or diffused aeration equipment to supply oxygen for biological activity, oxidation of sulfides, and mixing. Aerated lagoons can be completely aerobic or aerobic-anaerobic. Aerobic-anaerobic systems consist of zones with less mixing where sludge generally accumulates and is slowly digested under anaerobic conditions. The usual detention time for aerated lagoons is three to ten days. Final clarifiers are also required to remove microbial suspended solids. The sludge collected in the final clarifier is not recycled continually, but a few aerated lagoon systems have provisions (not often utilized) for recycling some of the solids during winter to improve the otherwise poor performance noted at low temperatures.

TABLE VII-23

LONG TERM MEAN EFFLUENT POLLUTANT CONCENTRATIONS AT TANNERY NO. 24

Parameter	Untreated Effluent Concentration (mg/l)	Final Effluent Concentrations (mg/l)
BOD_5	1,020	72
COD	11,000	1,170
TSS	2,340	91
Oil and Grease	No Data	3
TKN	No Data	74
Total Chromium	No Data	0.05
Sulfide	No Data	0.1

Unaerated lagoons are generally either facultative, in which oxygen is supplied by algae and diffusion of atmospheric oxygen, or anaerobic. Unaerated lagoons are generally not used to treat tannery wastes, partly because severe odors would result from the release of sulfides and reduced sulfates.

Summaries of the performance of biological lagoon treatment processes are presented in Tables VII-24 and VII-25. Table VII-24 presents the long term mean performances and Table VII-25 presents a comparison of summer (June through August) and winter (December through February) performance. As shown by these tables, the general performance of lagoon systems in the industry is very erratic. These systems, at times, provide little or no treatment but at other times provide marginal treatment. Many of the systems are poorly maintained and operated. The unaerated lagoons in particular have been allowed to fill up with sludge. There are a few systems that are moderately well operated and maintained. However, these systems are also subject to periods of poor performance. Aerated lagoon systems with effluent characteristics for BOD_5 and TSS of over 1,000 mg/l are not uncommon. Winter performance, in general is poorer than summer. Although the most common form of treatment in the industry (essentially because little operation and maintenance is required), lagoon systems have demonstrated that they are <u>incapable</u> of providing a <u>consistant</u> <u>and</u> <u>quality</u> <u>effluent</u>. The advantages of a lagoon system are:

- Where land is readily available, it is an inexpensive system to construct and to operate and maintain.
- In typical designs, there is no sludge disposal over the design life of the facility.
- It does not require a highly skilled operator.

<u>Activated</u> <u>Sludge</u>. The activated sludge process is an aerobic biological process. The basic components consist of an aerated biological reactor, a clarifier for separation of biomass and a piping arrangement to return separated biomass to the biological reactor. Aeration provides the oxygen for aerobic biodegration and the mixing to maintain the biological solids in suspension. The aeration requirements for activated sludge are similar to those of the aerated lagoon.

The activated sludge process is flexible and adaptable to many wastewater treatment situations. Factors that are considered in design include: 1) loading criteria, 2) reactor type, 3) sludge production, 4) oxygen requirements and transfer efficiency, 5) nutrient requirements, 6) temperature, 7) solid-liquid

TABLE VII-24

PERFORMANCE SUMMARY
BIOLOGICAL LAGOON TREATMENT SYSTEMS

Tannery No.	Subcategory	Type of Lagoon	BOD_5 Mean (mg/1)	BOD_5 Range (mg/1)	TSS Mean (mg/1)	TSS Range (mg/1)	O&G Mean (mg/1)	O&G Range (mg/1)	CrT Mean (mg/1)	CrT Range (mg/1)
43	2	Unaerated	40	1-295	68	1-586	9	0.1-127	0.61	0.044-2.05
525	1	Unaerated	ND	ND	ND	ND	ND	ND	ND	ND
60	1	Aerated	344	25-1360	319	64-1224	54	16-116	1.01	0.28-1.80
184	1	Aerated	54	5-225	129	5-660	19	1-166	2.00	0.110-13.1
185	8	Aerated	1993	474-4440	1077	620-1350	536	294-720	ND	ND
248	1	Aerated	917	852-984	557	512-660	91	52-130	ND	ND
388	3	Aerated	207	135-255	80	50-105	ND	ND	ND	ND
389	4	Aerated	ND	ND	ND	ND	ND	ND	ND	ND
397	3	Aerated	1111	358-1740	148	40-1096	38	32-48	0.58	0.15-0.90
409	1	Aerated	97	5-421	62	10-330	6.7	1-61	1.90	0.050-8.00
410	2/3	Aerated	97	15-250	490	31-2988	ND	ND	ND	ND
502	6	Aerated	827	760-870	1387	1280-1582	219	132-277	ND	ND

ND indicates no data available

TABLE VII-25

WINTER/SUMMER PERFORMANCE BIOLOGICAL LAGOON SYSTEMS

Plant No. and Season	BOD_5 (mg/l)	COD (mg/l)	TSS (mg/l)	Oil & Grease (mg/l)	NH_3-N (mg/l)	TKN (mg/l)	Total Chromium (mg/l)	Sulfide (mg/l)
43								
Summer	25	335	64	10	14	19	0.5	0.1
Winter	64	260	51	8	14	18	0.5	2
60								
Summer	62	-	117	27	-	-	1	-
Winter	92	4,017	178	33	20	52	2	6.3
184								
Summer	51	285	80	8	127	140	1.7	-
Winter	73	365	217	27	197	204	3.3	-
409								
Summer	22	171	36	5	37	50	0.5	6.6
Winter	157	596	77	14	31	62	4	1.4

separation, and 8) desired effluent characteristics. Depending on these factors, the conventional activated sludge process or a commonly used modification of the conventional process is selected.

The processes that could be used to treat tannery wastewaters include: 1) conventional, 2) complete-mix, 3) tapered-aeration, 4) step-aeration, 5) modified-aeration, 6) contact-stabilization, 7) extended aeration, 8) oxidation ditch and 9) pure oxygen. Of these processes, the best suited for the treatment of tannery wastes is extended aeration. The benefits of using extended aeration activated sludge are: 1) it is a proven technology for treating tannery wastes both on a pilot scale and full scale basis, 2) it has the capability of treating high strength wastes (BOD_5) and providing high quality effluent 3) it provides consistant removal on a year-round basis 4) it is capable of withstanding shock loadings, 5) in relation to many of the above listed processes, it is easier to operate and maintain and, 6) it is cheaper both to construct and to operate and maintain than several other processes. Overall activated sludge and, in particular, extended aeration provides high pollutant removals at a low cost.

There are three activated sludge systems that were properly designed to treat tannery wastes. Two of these systems are POTWs (Hartland, Maine and Berwick, Maine) that are treating predominantly tannery wastes. That is, at least 85 percent of the hydraulic and organic wasteloads is from tanneries. The third system is operated by Tannery No. 47. The long term effluent data for these three systems are shown on Table VII-26.

The three activated sludge systems are treating wastes from tanneries in subcategories 1 (Hartland, ME), 4 (Berwick, ME), and 3 (Tannery No. 47). Table VII-26 summarizes the removals of the pollutants of concern at each of the facilities.

The advantages of activated sludge compared to other biological treatment processes are:

- Its pollutant removal capability equals or exceeds those of other biological treatment processes on a consistent basis.
- Activated sludge systems can be operated efficiently during cold weather. As noted previously, aerated lagoons in particular generally exhibit reduced efficiency during cold weather.

TABLE VII-26

PERFORMANCE SUMMARY
BIOLOGICAL ACTIVATED SLUDGE SYSTEMS

Tannery or Treatment Plant		BOD_5 (mg/l)	COD (mg/l)	TSS (mg/l)	O&G (mg/l)	NH_3-N (mg/l)	TKN (mg/l)	Total Chromium (mg/l)	Sulfide (mg/l)	Phenol (mg/l)
47	Mean	47 (176)	547 (11)	77 (217)	22 (11)	157 (11)	178 (11)	0.27 (5)	4 (11)	0.10 (7)
	Low	3	100	9	2	40	53.8	0.15	0.1	0.04
	High	300	1052	400	44	260	300	0.50	20.0	0.14
Hartland, ME POTW	Mean	22 (179)	150 (5)	35 (262)	10 (23)	37 (27)	13 (3)	0.55 (22)	4 (4)	0.20 (3)
	Low	2.3	20	3	0.01	1.4	10	0.12	0.1	0.105
	High	128	390	408	74	112	15	10.50	8.0	0.330
Berwick, ME POTW	Mean	35 (101)	429 (23)	36 (262)	24 (6)	27 (85)	35 (7)	0.85 (94)	0.27 (3)	0.17 (3)
	Low	4	100	5	1	0.5	2	0.005	0.2	0.013
	High	94	910	340	37	112	84	4.5	0.4	0.440

( ) number of daily data points

- Some activated sludge processes can withstand shock loads.

- Some modified activated sludge systems, if designed and operated properly, can remove ammonia-nitrogen and carbonaceous BOD.

Of the many modifications of the activated sludge process, the extended aeration appears to be the most suitable for the treatment of tannery wastes. Extended aeration is capable of performing consistantly during cold weather and while undergoing shock loadings. Extended aeration basically is an easier process to operate than the other modifications of the activated sludge process. The suitability of the activated sludge process, and in particular the extended aeration form, is demonstrated by the three activated sludge facilities.

The Carrousel™ oxidation ditch system is an extended aeration activated sludge process that operates at a F:M (food to microorganism) ratio of approximately 0.05. The Carrousel™ system is designed so that the dissolved oxygen concentration at some locations in the oxidation ditch approaches zero, while most of the ditch is aerobic. This condition, in addition to the low F:M ratio, is to promote simultaneous nitrification and denitrification. A Carrousel™ system has been used since 1973 to treat the wastewater from a chromium leather tannery in Oisterwijk, Netherlands. Data summarizing the first year of operation are shown in Table VII-27.

Rotating Biological Contactors (RBCs). A rotating biological contactor consists of a series of horizontal shafts, each fitted with many closely spaced discs that serve as a medium for bacterial attachment. The shafts are rotated slowly with approximately 40 percent of the disc submerged in the wastewater. In the appropriate temperature environment, the first stages of contactors develop a heterotrophic bacterial population while in the latter stages, a nitrifying population is developed. As a rule, RBCs are covered for protection from extremely cold weather, to prevent algae growth, and to prevent rain from washing the bacterial slime layers off the discs. RBCs are preceded by primary treatment to remove settleable solids, and followed by clarifiers which remove bacterial solids that continually slough off the RBC discs. RBCs have been used for secondary biological treatment, for nitrification following carbonaceous BOD removal, and for polishing effluent from trickling filters.

An RBC system has been installed at a vegetable tannery; another system is under construciton at a second vegetable tannery. No data concerning the performance of RBCs treating tannery wastes have been made available to the Agency. Including municipal and industrial applications, approximately 300 operating RBC treatment systems exist in the United States, and another 300 are in planning or design stages.

RBCs have several advantages over activated sludge systems. These include significantly lower power requirements, less land requirements, and smaller excavation requirements.

TABLE VII-27

PERFORMANCE OF CARROUSEL™ SYSTEM
OISTERWIJK, NETHERLANDS

Pollutant Parameter	Raw Waste (mg/l)	Secondary Effluent (mg/l)	Percent Removal
BOD_5	1100	20	98
COD	3390	249	93
Cr	19.5	0.27	99
Total N	408	270	34
NH_3-N	264	248	5

The disadvantages of RBC technology include the lack of operating experience in this industry, the design difficulties in scaling up from pilot-plant to full-scale operation, the sensitivity to unequalized shock loading, the potential need for supplemental aeration (as noted from experience at one vegetable tannery), the possibility of breakage of the RBC shaft due in part to scale build-up, and the need for substantially larger contactor area at waste temperatures below 55°F. These problems tend to decrease the lower power requirement advantage, and require additional expenditure for upgrading to overcome deficiencies.

Summary. The achievable effluent concentrations for biological treatment are based on the performance data from three activated sludge systems treating tannery wastes. These three facilities are the only tannery wastewater treatment facilities which currently utilize the biological treatment technology in the form of activated sludge. Two of these treatment systems are POTWs where most (greater than 85 percent) of the waste loads are from tanneries. One POTW treats the wastewater from a subcategory 1 Tannery while the other treats the wastewater from a subcategory 4 Tannery. The tannery employing activated sludge biological treatment is in subcategory 3. Other biological systems were not considered to be demonstrating this level of treatment.

A discussion of the effects of biological treatment on each pollutant parameter of interest is presented below. The data base for regulated parameters has been examined both statistically and in terms of operational characteristics in determining the performance capabilities of this technology. As a result, periods of documented treatment process upset as well as statistical outliers have been deleted from the data base for these four parameters. Thus, the long term averages presented represent the technology's operational capabilities when properly operated within the system's design treatment loadings.

Biochemical Oxygen Demand (BOD_5)

For this parameter, the long term means (arithmetic average concentrations) itemized on Table VII-26 range from 22 to 47 mg/l. These long term values represent both the beamhouse and no beamhouse groups. The weighted average of the long term for these three treatment systems is 35 mg/l. Based on the available information, minor modifications to Tannery No. 47's treatment system will improve its effluent characteristics. Therefore, a long term effluent BOD_5 concentration of 40 mg/l has been selected as achievable.

Total Suspended Solids (TSS)

Table VII-26 also provides a listing of the long term TSS effluent concentrations achieved by the three activated sludge systems; ranging from 35 to 77 mg/l. The weighted average value for the three facilities is 48 mg/l. Based on the performance at the Berwick and Hartland POTWs, which had long term means of 36 and 35 respectively, the TSS effluent concentration could be projected to be less than 48 mg/l. However, biological solids resulting from treatment of subcategory 3 wastewaters do not settle as well as those from other sources. Therefore, the achievable TSS effluent concentration is projected to be 60 mg/l to allow for the higher values exhibited by Tannery No. 47, and to allow for TSS concentrations projected for other vegetable tanneries when activated sludge biological treatment technology is installed and properly operated.

Oil and Grease

As indicated in Table VII-26, less extensive performance data is available for this pollutant parameter. The weighted average value for the three facilities is 15 mg/l. The data available for the Hartland POTW supports the achievement of effluent oil and grease concentrations of less than 15 mg/l. However, the weighted average is skewed downward due to the large discrepancy in sample sizes. The unweighted average is 19 mg/l. A long term effluent concentration of 20 mg/l is projected for all subcategories.

Total Chromium

Although this pollutant is essentially controlled by the coagulation-sedimentation step, additional removal is realized in the activated sludge system through bioflocculation and sedimentation of insoluble chromium in the secondary clarifier(s). For the three treatment systems listed in Table VII-26, the effluent chromium concentrations range from 0.27 to 0.85 mg/l. The weighted average concentration is 0.77 mg/l. However, the 0.27 mg/l value originates from the Berwick POTW which receives its wastewater from a subcategory 4 tannery, which has lower raw chromium loadings than a complete tannery. The Hartland POTW receives the majority of its wastewater from a subcategory 1 tannery. The long term average effluent concentration of 0.55 mg/l is achieved in part by the excellent (96+ percent) solids removal at this facility which results in a TSS concentration considerably lower than then the 60 mg/l projected for this level of treatment. Therefore, a long term achievable concentration of 1.0 mg/l is projected for this level of treatment.

Although not regulated, other conventional and non-conventional pollutants are removed by this level of treatment. The following discussions indicate anticipated levels of these pollutants following incidental removal by biological treatment.

Sulfide

Sulfate, which is produced during the biological oxidation process, can be converted to sulfide under anaerobic conditions. These conditions can persist in the primary and secondary clarifiers when deviation from established sludge wasting schedules occurs. Some sulfide regeneration may occur despite the exercising of proper control measures. Although residual sulfide in the primary effluent may be oxidized in the aeration system, regeneration of small amounts of sulfide could still occur in the secondary clarifer. In most cases where small sample sizes (25 ml) are used, the limit of detection for sulfide in a tannery wastewater matrix is about 6 mg/l. Thus, as illustrated by Table VII-26, BPT technology should reduce sulfide to its detection limit. (See also discussion of sulfide analysis).

Total Kjeldahl Nitrogen (TKN)

TKN is a measure of ammonia and organic nitrogen in wastewater. Most TKN originates in the beamhouse with the unhairing process, which contributes significant quantities of protein (organic nitrogen). The bating process contributes ammonia, since the general bating practice includes use of ammonium sulfate as a buffer. Thus, the TKN concentration in the raw waste from the beamhouse group (subcategories 1, 2, 3 and 8) is greater than that of no beamhouse wastewaters (subcategories 4, 5, 7 and 9).

The activated sludge biological treatment is not designed to provide for the removal of nitrogen. The effluent concentration is therefore a function of the influent concentration.

Information indicates that TKN concentrations anticipated after upgrading existing systems to function as activated sludge systems (without provision to allow for nitrification) would be about 95 mg/l for subcategories 1,2,3 and 8 and about 35 mg/l for subcategories 4, 5, 7 and 9. No representative effluent data is available for subcategory 6.

Ammonia

Ammonia is measured similarly to TKN and their removals are also inter-related. Therefore, the discussion addressing the performance of biological treatment for TKN removal also applies to ammonia. The data base for biological treatment facitity effluents indicates incidental removals do occur.

Review of Table VII-26 indicates that upgrading to activated sludge may reduce effluent concentrations to 90 mg/l in subcategories 1, 2, 3 and 8, while subcategories 4, 5, 7, and 9 treated effluents will contain about 30 mg/l. Again, no representative data is available for subcategory 6.

Chemical Oxygen Demand (COD)

Table VII-26 indicates substantial differences between the existing facility's effluents.

The average effluent concentration is 430 mg/l, while the median of plant means is 429. An average effluent COD level of 500 mg/l is anticipated following biological treatment.

Phenol

Data concerning effluent phenol concentrations is also very limited. Table VII-26 indicates that an average concentration of at least 0.2 mg/l may be expected following biological treatment.

3. Upgraded Biological Treatment

Upgraded biological treatment incorporates nitrification capabilities and addition of powdered activated carbon (PAC) to aeration basins. These two measures are discussed separately below.

Nitrogen Control. Discharging wastewater with high concentrations of ammonia and organic nitrogen, common in tannery wastewaters, presents additional problems in the receiving water: un-ionized ammonia can be toxic to fish at concentrations of approximately one mg/l, ammonia can exert a significant oxygen demand as bacteria convert the ammonia to nitrate, and nitrogen is a nutrient that can contribute to over-enrichment of a water body. Nitrifying waste treatment processes can mitigate the first two of these problems.

Nitrification, the biological oxidation of ammonia to nitrate, can be viewed as a two-step reaction. In the first step, nitrosomas bacteria oxidize ammonia to nitrite. In the second step, nitrobacter oxidize nitrite to nitrate. Both groups of bacteria are strictly aerobic: they require free dissolved oxygen for metabolism and will not grow under anaerobic conditions. Both groups are also sensitive to treatment system operating conditions, such as solids retention time (SRT), temperature, and pH.

The operating SRT of a nitrification system must exceed the minimum time (the critical SRT) required for nitrifying bacteria to reproduce in the system. If the operating SRT is less than the critical SRT, the nitrifiers will be removed from the nitrification system faster than they can reproduce, and incomplete nitrification will result. Temperature is an important factor in the design and operation of a nitrification system. The optimum temperature range for nitrification is estimated to be 28 to 36°C. Nitrification will occur at temperatures below 4°C, but nitrifying bacteria will grow slowly. Consequently, critical SRTs must be high at low temperatures. The theoretical critical SRT for nitrifications at 20°C is approximately three days. The critical SRT increases to approximately 10 days at 10°C and 18 days at 5°C. Raising the temperature of a waste stream is usually difficult or expensive, so the design of a nitrification system should be based on the lowest wastewater temperature that will occur, if year-round nitrification is required. Some nitrifying activated sludge systems in colder climates have covers over the aeration tank and clarifier to retain heat and promote nitrification in the winter.

As noted above, nitrifying bacteria are strict aerobes and adequate dissolved oxygen must be present for nitrification to occur. Dissolved oxygen concentrations of one to two mg/l are considered adequate. Nitrifying bacteria are not killed by short periods of anaerobic conditions, but their activity is limited in such an environment. When oxygen is restored, nitrification resumes.

Anthonisen *et al.*[60] have shown that nitrification can be inhibited by un-ionized ammonia and free nitrous acid. Inhibition is more likely to occur in wastes with high ammonia and TKN concentrations, such as tannery wastewater. In general, nitrobacter can be inhibited by un-ionized ammonia. Inhibition by ammonia is more likely to occur at higher pH values when the chemical equilibrium between the dissolved ammonia species is shifted toward aqueous ammonia. Nitrosomas, on the other hand, can be inhibited by free nitrous acid, which is more likely at low pH. Two methods of process control can be used to relieve inhibition from un-ionized ammonia or free nitrous acid: reducing the influent concentration of ammonia and adjusting the pH. If inhibitory conditions are to be detected and the appropriate adjustments made to prevent inhibition, the ammonia level and pH in the process influent and effluent and the concentrations of nitrite and nitrate in the effluent must be monitored frequently. Other compounds, including heavy metals, cyanides, certain halogenated compounds, phenols, mercaptans, and thiourea, can also inhibit or be toxic to nitrifiers. Trace amounts of these chemicals may not totally inhibit nitrification, but longer operational SRT values are required to compensate for the slower nitrifier growth.

To assess the performance of nitrifying activated sludge systems treating tannery wastes, the Agency has reviewed the performance data from two plants. This information, obtained from the

Berwick, Maine POTW and the Hartland, Maine POTW is summarized in Tables VII-28 and VII-29.

The data from the Berwick POTW indicate that some nitrification was achieved from September 1979 to May 1980. Nitrification, however, was not complete. The available data also show that the mixed liquor dissolved oxygen concentration was generally low, suggesting that this condition may have limited nitrification.

Data from the Hartland, Maine POTW are limited and conclusions are tentative. For all months except December 1979, the final effluent ammonia concentration is generally based on one sample per month. Very little primary effluent ammonia data were available and determining how much excess ammonia (above the requirements for new biomass growth) was available for nitrification was impossible. The availability of excess ammonia can be reasonably assumed because this POTW receives most of its waste from a subcategory 1 tannery which typically contains excess TKN and ammonia in wastewater discharges. The Hartland POTW can therefore be assumed capable of achieving a high degree of nitrification during the summer and comparatively little nitrification during the winter. This would suggest that the operating SRT at this plant is less than the critical SRT during the winter. The SRT may be increased during the winter months and might achieve consistent nitrification by operating with higher mixed liquor suspended solids concentrations. Moreover, maintenance of higher dissolved oxygen concentrations, and possibly the addition of caustic soda to maintain adequate alkalinity, would further improve operating conditions needed to enhance nitrification. Finally, from available operating data the Agency has observed that when a system successfully nitrifys, very low effluent ammonia concentrations (consistently less than 15 mg/l, often less than 5 mg/l) are produced. However, when conditions necessary to maintain the nitrification process are altered, effluent ammonia concentrations quickly revert to those typical of raw waste (complete pass through without any removal).

Powdered Activated Carbon (PAC). The combined powdered activated carbon-activated sludge process enhances biological treatment by maintaining an inventory of powdered activated carbon (PAC) in the activated sludge. The process is relatively new and data on process performance are fairly limited.

The physical-chemical behavior of powdered activated carbon in activated sludge systems is not known precisely. However, hypotheses have been developed from experimental observations and research concerning adsorption of organic compounds on activated carbon. One mechanism that apparently contributes to the improved performance of the process is that the PAC physically

TABLE VII-28

MONTHLY TREATMENT PERFORMANCE SUMMARY AT BERWICK, MAINE POTW

	BOD_5		COD		TSS		TKN		NH_3-N		Aeration Basin	Final Effluent	
Month	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	D.O. (mg/l)	pH (s.u.)	Temp. °C
1/79	392	28	-	-	198	170	-	-	-	-	0.15	7.58	11.0
2/79	313	19	-	-	139	19	-	-	-	-	0.42	7.53	9.7
3/79	446	40	-	-	179	41	-	-	-	-	0.47	7.39	13.8
4/79	341	36	-	-	291	88	-	-	-	-	0.11	7.30	14.6
5/79	506	21	-	-	294	48	-	-	-	-	0.38	7.67	18.9
6/79	360	49	-	-	197	70	-	-	-	-	0.07	7.65	21.2
7/79	320	51	-	-	247	84	-	-	-	-	0.78	7.43	24.3
8/79	582	64	-	-	267	71	-	-	-	-	0.03	7.37	26.8
9/79	505	69	1,681	568	219	54	-	-	40	16	0	7.56	24.3
10/79	481	38	1,657	430	133	25	-	-	83	23	0	7.30	21.5
11/79	494	28	1,174	338	135	22	-	-	158	27	-	7.54	19.3
12/79	550	16	1,214	296	123	23	-	-	197	38	-	7.51	15.9
1/80	-	-	-	-	-	-	-	-	188	36	-	-	-
2/80	490	<20	947	550	290	43	22	8.5	44	10	-	7	13.8
3/80	-	-	-	-	-	-	-	-	33	9	-	-	-
4/80	-	-	-	-	-	-	-	-	54	20	-	-	-
5/80	-	-	-	-	-	-	-	-	46	6	-	-	-

PE = Primary Effluent
FE = Final Effluent

TABLE VII-29

MONTHLY TREATMENT PERFORMANCE SUMMARY
AT HARTLAND, MAINE POTW

Month	BOD_5		COD		TSS		TKN		NH_3-N		Aeration Basin D.O. (mg/l)	Final Effluent	
	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)	PE (mg/l)	FE (mg/l)		pH (s.u.)	Temp. (°C)
1/78	-	47	-	-	-	47	-	-	-	-	-	7.5	5
2/78	-	25	-	-	-	54	-	-	-	-	-	7.4	6
3/78	-	39	-	-	-	51	-	-	-	95	-	7.3	11
4/78	-	249	-	-	-	389	-	-	-	89	-	7.4	13
5/78	-	84	-	-	-	185	-	-	-	111	-	7.4	19
6/78	-	14	-	-	-	15	-	-	-	106	-	7.4	22
7/78	-	16	-	-	-	34	-	-	-	-	-	6.9	22
8/78	-	12	-	114	-	98	-	-	-	112	-	6.1	23
9/78	-	7	-	-	-	20	-	-	-	-	-	5.7	17
10/78	-	19	-	-	-	33	-	-	-	5.3	-	5.7	15
11/78	-	19	-	-	-	26	-	-	-	46	-	-	-
12/78	-	11	-	-	-	21	-	-	-	-	-	7.0	7
1/79	-	22	-	-	-	20	-	-	-	-	-	7.2	9
2/79	-	19	-	-	-	15	-	-	-	-	-	7.3	8.5
3/79	-	10	-	-	-	11	-	-	-	41	-	7.2	11
4/79	-	16	-	-	-	19	-	-	-	51	-	6.9	12
5/79	-	10	-	-	-	12	-	-	-	2.7	-	6.8	17
6/79	-	12	-	-	-	16	-	-	-	9.5	-	6.4	22
7/79	-	7.6	-	-	-	11	-	-	-	6.7	-	6.6	23
8/79	-	18	-	-	-	15	-	-	-	10	-	6.6	23
9/79	-	15	-	-	-	19	-	-	-	2.0	-	6.6	21
10/79	-	15	-	-	-	21	-	-	-	2.5	-	6.6	21
11/79	-	12	-	-	-	20	-	-	-	13	-	6.7	13
12/79	570	22	1995	173	457	79	27	13	13	14	-	7.0	9
1/80	-	45	-	-	-	66	-	-	-	43	-	7.0	7
2/80	-	57	-	-	-	56	-	-	-	67	-	7.0	8

FE = Final Effluent
PE = Primary Effluent

increases the specific weight of the sludge flocs, promoting faster settling and improved suspended solids capture in the sludge. This reduces effluent suspended solids and oil and grease concentrations. Since suspended solids contribute a portion of the effluent BOD_5 and COD, the effluent concentrations of these parameters are also reduced. Improved sludge settling and suspended solids capture are also thought to promote nitrification by preventing the nitrifying bacteria from being washed from the activated sludge mass.

Adsorption of nondegradable and slowly degradable organic compounds, coupled with biological regeneration of the powdered carbon, is considered the primary mechanism of toxic organic pollutant removal from waste streams. Through adsorption of toxic pollutants on the activated carbon and retention of the toxic pollutants in the sludge mass, the activated sludge bacteria are given a much longer contact time in which to degrade these compounds. Biological degradation of adsorbed compounds is thought to free the activated carbon surface for adsorption of more pollutants and is hypothesized to be the primary mechanism of biological regeneration.

The activated carbon content maintained in the mixed liquor suspended solids (MLSS) is a function of the carbon feed rate and the sludge wasting rate, or sludge age. At this time, the optimum dose of carbon for a particular waste stream cannot be predicted in advance with any degree of certainty. The PAC concentrations in the MLSS varied from 700 to 6400 mg/l during the tests reported in the literature[61 62 63 64 65 66]. Dejohn and Adams[63] have recommended an empirical method for determining the optimum powdered carbon dosage for a particular plant. They suggested adding sufficient carbon to build up and maintain a PAC concentration equal to 25 percent of the original MLVSS, then monitoring the effluent for a two week period. Increasing the PAC concentration to 50 percent of the original MLSS concentration and maintaining this concentration for two more weeks is also recommended. The PAC concentration can be increased in this manner until the desired effluent concentration is achieved. The process is relatively flexible in this regard. However, doubling the carbon inventory would approximately double the cost of this treatment step and may not be necessary.

Only limited full-scale performance data are available for the upgrading of activated sludge systems through PAC addition. Most of the published information addresses the treatment of wastewaters generated by other industries, such as oil refining. Since specific data for the leather tanning industry are limited, the information pertaining to the other industries is used for comparative purposes in considering technology transfer for the control of certain pollutants.

Table VII-30 summarizes the results of several applications of PAC - activated sludge systems treating different industrial wastes, as reported in the literature.

A discussion of the effects of upgraded biological treatment on each pollutant parameter of interest is presented below.

Biochemical Oxygen Demand (BOD_5)

The effluent BOD_5 concentration from biological treatment representing both the beamhouse and no-beamhouse groups is 40 mg/l. Removal of additional BOD_5 will be achieved incidental to the upgrading of the extended aeration activated sludge system to provide nitrification. This removal will also be enhanced by the addition of PAC. Table VII-30 indicates a 24 to 59 percent increase in BOD_5 removal through the addition of PAC alone.

Total Suspended Solids (TSS)

A TSS effluent concentration of 60 mg/l was determined for biological treatment. In upgrading the biological treatment system to provide nitrification, lower clarifier loading rates and increased oxidation will result in a slight additional TSS removal. PAC has been shown to aid the settling of suspended solids in the secondary clarifier. Table VII-30 indicates an 11 to 66 percent increase in TSS removals as a result of PAC addition. In the concentration range of interest, an average 46 percent removal resulted.

Oil and Grease

As indicated in Table VII-30, less extensive performance data is available for this pollutant parameter. It was determined that an effluent concentration of 20 mg/l was achievable through biological treatment. With upgraded treatment and the addition of PAC, the oil and grease removal is enhanced. Average additional removals of 68 percent have been noted in the available PAC data.

Total Chromium

Although discharge levels of this pollutant are primarily controlled by in-plant reuse and the coagulation - sedimentation step, additional removal is realized in the activated sludge system though bioflocculation and

TABLE VII-30

PERFORMANCE OF PAC-ACTIVATED SLUDGE SYSTEMS

	BOD_5		COD		TSS		O&G		NH_3-N		TKN		CrT		S=		Phenol	
Description	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.
Oil refinery																		
PAC @ 100 mg/l	-	-	*52	29	-	-	-	-	0.5	0	-	-	-	-	-	-	0.012	33
PAC @ 200 mg/l	-	-	*26	55	-	-	-	-	00.15	0	-	-	-	-	-	-	0.002	90
Oil Refinery			*44	35	-	-	-	-	3.1	0	-	-	-	-	-	-	0.034	32
Synthetic textile fiber plant	10	-	-	-	51	-	-	-		-	-	-	0.02	-	-	-	0.018	-
Oil refinery and petrochemical plant	-	59	350	70	125	50	8	65	-	-	0.2	78	-	-	-	-	-	-
Poultry processing plant	3	57	-	-	12	66	20	71	4	83	-	-	-	-	-	-	-	-
Carbohydrate and surfactant waste	:250	24	950	44	270	11	-	-	-	-	-	-	-	-	-	-	-	-
Municipal waste with 10% textile dye waste	12	40	110	4	15	40	-	-	-	-	-	-	-	-	-	-	-	-

NOTES:
1. Eff. signifies effluent concentration in mg/l.
2. The "% Rem." represents the incremental improvement of PAC-activated sludge.
3. * signifies soluble COD.
4. Source: Reference No. 64

sedimentation of insoluble chromium in the secondary clarifier(s). With the proper conditions for controlling TSS discharge levels in the secondary system, and PAC addition, there should be a coincident reduction in the effluent chromium concentration. The biological treatment chromium concentration was projected to be 1.0 mg/l. A 11-66 percent reduction in TSS was projected as a result of PAC addition, and therefore chromium levels also should be reduced.

Sulfide

Sulfate, which is produced in the sulfide oxidation step and during the biological oxidation process, can be converted back to sulfide under anaerobic conditions. These conditions can persist in the primary and secondary clarifiers when deviation from established sludge wasting schedules occurs. Some sulfide regeneration may inherently occur despite the exercising of proper control measures. Although residual sulfide in the primary effluent may be oxidized in the aeration system, regeneration could occur in the secondary clarifier. In view of this phenomenon and the limited data for effluent sulfide concentrations discharged by activated sludge systems, no additional reduction of this pollutant is projected and the achievable concentration remains at about 6 mg/l.

Total Kjeldahl Nitrogen (TKN)

The effluent TKN concentrations for biological treatment varied considerably since that technology is not designed to remove nitrogen. With upstream flue gas carbonation, incorporated along with nitrification and PAC addition, the TKN concentration from beamhouse tanneries will approach that from no-beamhouse tanneries. Additionally, a properly designed and operated biological treatment system incorporating nitrification is capable of reducing these varying influent concentrations to the same level. Based on the information contained in Reference Nos. 69 and 70, effluent TKN reduction can be achieved although no performance capabilities have been consistantly demonstrated. Furthermore, properly designed systems have been successfully operated on a year-round basis at lower effluent TKN for other industrial wastewaters. Consistent nitrification has not been achieved in the leather tanning industry.

Ammonia

Ammonia is measured as a part of TKN and therefore the removals of these two are interrelated. Therefore, the discussion addressing the performance of upgraded biological treatment for TKN removal also applies to ammonia. Based on the available data (Reference Nos. 69 and 70), ammonia can be reduced. However, ammonia removal has not been consistently demonstrated for leather tanning wastewaters.

Chemical Oxygen Demand (COD)

With the addition of PAC to the activated sludge system, organics will be adsorbed on the carbon surface and eventually removed from the wastewater. Since a portion of the oxygen demand measured as COD is organic, a reduction in COD will be realized. Information available in the literature for other applications of PAC addition (Table VII-30), indicates a 4 to 70 percent incremental removal of COD is achievable by the addition of PAC.

Phenol

PAC addition should enhance the removal of phenol in the activated sludge system through adsorption and improved biodegradation. Effluent phenol (4AAP) concentrations of 0.2 mg/l or lower are achievable for biological treatment effluents. Table VII-30, which summarizes information presented in the literature, provides the basis for projecting at least 50 percent removal of phenol through upgraded biological treatment.

4. Advanced Treatment Processes

Filtration in deep 1 1/2 ft to 3 ft (0.46 m to 0.9 m) bed granular media filters is a physical-chemical process that involves coagulation of suspended solids and adsorption of these solids onto filter-media particles or onto other adsorbed particles. A gravity flow multimedia filter has a specific design in which different layers of filter media are selected and arranged with the coarsest layer on top and the finest layer on bottom. If the multimedia filter is graded and sized properly, it can run for longer before requiring backwashing than single-media filters because the multimedia filter uses the entire bed to store removed particles. The Agency has considered multimedia filtration as a polishing step to remove suspended solids from biological treatment process effluents. This application of filtration is quite common in the fields of domestic and industrial wastewater treatment.

At this time no tannery employs filtration technology to remove suspended solids from secondary effluent. Technology transfer from other industrial categories and domestic wastewater applications are the basis for determining the performance of multimedia filtration for treating leather tanning wastewaters.

Table VII-31 presents data on the performance of multimedia filtration on several other effluents.

Total Suspended Solids

The data contained in Table VII-31 show six instances in which filter effluent TSS is less than 15 mg/l. The average percent removal of TSS reported in Table VII-31 is 53 percent.

Biochemical Oxygen Demand

The incremental removal of TSS by application of multimedia filtration can also be expected to reduce BOD_5 levels, although to a lesser extent. The data of Table VII-31 indicates incremental BOD_5 removals ranging from 21 to 90 percent.

Chemical Oxygen Demand

Chemical oxygen demand can also be expected to be reduced as a result of multimedia filtration. Table VII-31, shows typical COD reductions of 23 to 25 percent.

Oil and Grease

Table VII-31 indicates that a level of only 10 mg/l has been achieved in the red meat industry.

Total Chromium

The Agency has noted a close relationship between suspended solids levels and total chromium in tannery treated effluents. As shown in Table VII-31 control of effluent TSS by application of multimedia filtration results in consistantly low effluent TSS concentrations. Therefore, additional removal of chromium also would be expected.

Sulfides

Since the sulfides present in the effluent from secondary treatment are soluble, no reduction of this pollutant is projected for this technology.

Ammonia

Because ammonia is highly soluble in the neutral pH range, no reduction in ammonia levels is expected as a result of application of multimedia filtration.

Total Kjeldahl Nitrogen (TKN)

TKN is a measure of both ammonia and organic nitrogen in wastewater. An incremental removal of organic nitrogen might be expected to result from multimedia effluent filtration because of improved removal of residual tannery solids and treatment system biomass. However, no removals have been projected.

Phenol

Because no data are available to indicate an incremental removal of phenol as a result of multimedia filtration, none are projected.

E. SOLIDS HANDLING AND DISPOSAL

When specific measures to control the discharge of pollutants entering receiving waters are implemented, solid and semi-solid materials requiring disposal are produced. The fundamental nature of the recovered solids will vary with the specific technology employed as a pollution control measure. Less significant variations depend on the commodities being processed. Solids recovered as the result of in-plant management practices have greater utilization and eventual marketing potential than the materials resulting from end-of-pipe technology. Generally, the capture of wastes at their source represents the least costly approach for internal waste reduction. The recovery of materials which have been discarded in the past can provide a means of offsetting part or all of the costs associated with waste management. In addition, residual volumes requiring transportation and disposal can be reduced or eliminated.

Portions of the product which are not isolated at their source enter the total waste stream and must then be separated. The biological treatment of leather tanning wastewaters involves converting organic constituents to carbon dioxide with water and to biomass with subsequent phase separation. Activated sludge processes, which have been explored for treating the industry's effluents, produce sludges which are similar in nature to those generated by municipal operations. Therefore, conventional sludge dewatering and disposal practices are applicable to

TABLE VII-31

PERFORMANCE OF MULTIMEDIA FILTRATION ON ACTIVATED SLUDGE PROCESS EFFLUENTS

	BOD_5		COD		TSS		O&G		NH_3-N		TKN		CrT		S=		Phenol	
Description	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.	Eff.	% Rem.
Oil Refinery	3.7	-	-	-	5.9	45	-	-	-	-	-	-	-	-	-	-	-	-
Oil Refinery	23	-	-	-	11	-	-	-	-	-	-	-	-	-	-	-	-	-
Pulp & Paper Mill	8.5	-	-	-	7	30	-	-	-	-	-	-	-	-	-	-	-	-
Yarn Dying Mill	-	-	135	0	76	44	-	-	-	-	-	-	-	-	-	-	0.018	0
Woven Fabric Finishing Mill	19	21	630	23	85	71	-	-	-	-	-	-	-	-	-	-	-	-
Knit Fabric Finishing Mill	3.4	26	55	25	9.5	37	-	-	-	-	-	-	-	-	-	-	-	-
Wool Scouring Facility	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.017	0
Wool Finishing Mill	-	-	-	-	-	-	-	-	-	-	-	-	0.090	50	-	-	-	-
Municipal Wastewater extended aeration plant	2.5	90	-	-	4.6	92	-	-	-	-	-	-	-	-	-	-	-	-
Red Meat Packing Plant	13	-	-	-	13	-	10	-	-	-	-	-	-	-	-	-	-	-

NOTES:
1. Eff. signifies effluent concentration in mg/l.
2. The "% Rem." represents the incremental improvement.

leather tanning and finishing plants operating secondary treatment facilities. An assessment follows of specific handling and disposal alternatives, relating to the specific nature of the solids removed from the waste stream.

1. Solids from In-Plant Manufacturing Processes

Several operations within the beamhouse and tanyard processes result in solids generation. The handling and disposal or utilization of these solids varies from tannery to tannery. Solids include:

- Beamhouse
  - Side and trim - raw hide trimmings
  - Washing - dirt, blood, manure
  - Fleshing - flesh, fat and muscle
  - Unhairing - hair

- Tanyard
  - Splitting and Shaving - splits
    - shavings
  - Finishing - hide trimmings
    - buffing dust

The raw hide trimmings, as well as the flesh, fat, and muscle from the fleshing operation can be rendered or used in making glue, gelatin, animal feed, and fertilizer. Of the tanneries that responded to the 1979 questionnaire, 47 indicated trimmings were sold as by-products; eight plants either rendered flesh at the plant or sold it to an independent renderer. The splits from the splitting operations are normally sold to another tannery and made into suede leather; the splits may also be processed at the tannery from which they originate.

Hair recovered from hair save beamhouse operations can be dried, baled, and made into felt or used as backing for automobile floor mats. Few trimmings result from the finishing operation at most tanneries because of the scraps' minimal value. At several tanneries, these trimmings are collected and sold to leather craft or hobby stores. The shavings and buffing dust are usually used in animal feed.

2. Solids from Wastewater Treatment Plant Operation

Sludge handling and disposal will become a more important and costly aspect of waste treatment as tanneries upgrade their wastewater treatment systems to comply with state and federal waste discharge limitations. To minimize sludge handling and disposal costs, more tanneries will probably install sludge dewatering equipment that will yield the most concentrated end product economically feasible. The following discussion relates to each unit as it applies to wastewater sludge handling. Since these processes are applicable to sludges of general origin and are widely practiced, only brief descriptions are presented here.

Thickening. Thickening processes are designed to concentrate sludges so that smaller and more efficient equipment may be used in subsequent dewatering. This process is usually defined as concentrating sludge to less than ten percent solids. Sludge of this nature can usually be pumped by conventional means and displays the essential characteristics of a liquid. Economic considerations usually dictate the viability of thickening as part of a total sludge management approach. Generally, low initial sludge concentrations (one to two percent) enhance the economics of thickening. The processes available for achieving this sludge concentration include gravity thickening and dissolved air flotation. Coagulants and flocculents can be added to further enhance performance.

Stabilization. The major objective of stabilizing sludge is reducing its putrescible and pathogenic characteristics and therefore minimize impacts to the surrounding environment. The necessity of the process is usually a function of the ultimate disposal method.

Biological techniques (e.g., digestion) generally result in a reduction of sludge volume and weight through decomposition of the organic material and generation of byproducts. Additional benefits include improved sludge dewaterability, and the production of a combustible gas (methane) when the process is anaerobic digestion. Process stability and methane gas production rates may suffer depending upon the concentration of metals (or other potentially inhibiting agent) present in the sludge. In addition, chemical stabilization can be accomplished for certain sludges. The use of chlorine, ozone, and lime is generally associated with domestic sludges for pathogen kill. The dewaterability of the material is also enhanced. Implementing of stabilization techniques is most desirable when sludge is to be deposited on the land.

Conditioning. For most sludges, conditioning is performed to improve dewaterability. Improvements in the dewatering rate, solids capture, and compactibility are generally achievable. A degree of stabilization also is possible if heat treatment or certain chemicals are employed. While conditioning can be an important and economical process, it is only an intermediate step in the total process of sludge handling and disposal. The need and selection of a conditioning method is generally dictated by the subsequent dewatering technology practiced.

Dewatering. Water removal and the corresponding reduction in the weight and volume of sludge requiring disposal is the main objective of any dewatering process. With this thicker, heavier sludge (usually a moist cake with a solids concentration exceeding 20 percent), less energy will be needed to dry or incinerate sludge. The dewatering method is usually governed by the sludge characteristics and the ultimate disposal alternative. Common processes for municipal and industrial applications include vacuum (e.g., rotary) filtration, sludge drying beds, centrifugation, and pressure filtration (belt filter, and plate and frame filter press). Pressure filtration (e.g., plate and frame) has been found to be the most effective dewatering process for tanning industry treatment sludges to obtain high solids (25 percent solids or higher) filter cake. Consideration of minimum percent solids requirements at an ever increasing number of landfills and the economics of sludge transportation costs makes pressure filtration an economically attractive alternative (higher initial investment cost but lower annual O&M and sludge transportation cost).

Drying. Sludge drying, including conventional oxidation processes, incineration, and pyrolysis, goes one step beyond dewatering. Depending on the extent of sludge treatment, the product from the drying stage can either be a dry material high in volatile solids or an inert residue. Additional benefits include sterilization of the sludge and the potential for utilization. Since substantial supplemental fuel is necessary, energy requirements and the associated costs are prime considerations.

Disposal/Utilization. The purpose of the unit processes described previously is to produce a sludge suitable for subsequent utilization or disposal in an environmentally sound manner. Many state-of-the-art disposal techniques, such as land-filling, will encounter additional restrictions in the future due to potential environmental hazards. In view of this aspect, utilizing liquid or dewatered sludge should be given strong consideration. When utilization is technically or economically unfeasible, land application is the next most desirable alternative. The selection of the ultimate disposal or utilization alternative will generally dictate the types and degree of sludge treatment required.

Summary. Tables VII-32, VII-33 and VII-34 summarize the questionnaire responses that concern current sludge handling and disposal practices in the tanning industry. Most of the tanneries with mechanical sludge dewatering equipment use plate and frame filter presses. Although filter presses entail a relatively high energy requirement, they can produce higher sludge solids concentrations than other equipment, as shown by the data in Table VII-34.

TABLE VII-32

SLUDGE DEWATERING TECHNIQUES USED IN THE TANNING INDUSTRY

Type of Equipment	No. of Plants
Plate and frame filter press	10
Vacuum filter	3
Sludge drying bed	2
Belt filter press	1
Centrifuge	1
Sludge concentrator (rotary filter type)	1
Sludge holding tank	1
Total number of plants responding to question	19

TABLE VII-33

SLUDGE CONCENTRATIONS ACHIEVED WITH DIFFERENT TYPES OF DEWATERING EQUIPMENT

Type of Equipment	No. of Plants	Range of Sludge Concentrations Reported (Percent Solids)	Median of Sludge Concentrations Reported (Percent Solids)
Plate and frame filter press	6	27-70	44
Vacuum filter	2	20-30	25
Centrifuge	1	18	18
Belt filter press	1	28	28
Total number of plants responding to question	10		

TABLE VII-34

SLUDGE DISPOSAL METHODS

Method	Number of Plants
Off-site landfill	29
On-site landfill	7
Land application	5
Lagoon	4
Trench	3
Total number of plants responding to question	47

F. DEVELOPMENT OF CONTROL AND TREATMENT OPTIONS

Many demonstrated control and treatment technologies have been discussed and information presented on their capabilities for removal of toxic, nonconventional, and conventional pollutants from leather tanning and finishing industry wastewaters. Alternative control and treatment technology options that represent a range of pollutant removal capabilities and costs were selected from those discussed previously in this Section for detailed analysis. The options that were considered in determining BPT, BCT, BAT, NSPS, PSES and PSNS limitations and standards are presented below.

1. Best Practicable Control Technology Currently Available (BPT)

As stated previously, the Act establishes the requirements for the development of BPT limitations, which are generally based on the average of best existing performance within an industry or subcategory. Where existing performance is uniformly inadequate, BPT may be transferred from a different subcategory or category. Limitations based on transfer technology must be supported by a conclusion that the technology is, indeed, transferable and a reasonable prediction that it will be capable of achieving the prescribed effluent limits. The best practicable (BPT) control technology currently available for the leather tanning and finishing industry has been identified as biological treatment in the form of extended aeration activated sludge. Low solids lagoon technology, which was considered an acceptable alternative biological treatment technology as a basis for the remanded BPT, was not found to provide consistent effluent quality in treating wastewaters from this industry.

One direct discharger and two POTWs, which are treating predominantly tannery wastes (in excess of 90 percent of the wasteload received) utilize extended aeration activated sludge biological treatment. The POTWs; one in Hartland, Maine treats wastewater from a subcategory 1 tannery; the other in Berwick, Maine, treats wastewater from a subcategory 4 tannery. Both POTWs were designed to treat predominantly tannery wastes. The direct discharger tannery employs activated sludge treatment and is in subcategory 3. The performance data from these three facilities has been presented previously in this section. The weighted (according to the number of data points) average concentrations from these plants are as follows: BOD_5-35 mg/l, TSS-48 mg/l, Total Chromium-0.76 mg/l, and Oil and Grease-14.7 mg/l.

The Agency was concerned, for reasons set out below, that without any adjustment, maximum monthly average and maximum day effluent limitations based on these weighted average long term effluent concentrations may be somewhat stringent for some plants to meet. EPA was concerned that all three plants (Tannery No. 47 and the two POTWs) used to develop the limitations should achieve the limitations, at least on a mass basis (lbs/day), approximately within the criteria used to develop them (i.e., max. monthly - 95th percentile; max. day - 99th percentile). The Agency's concern stems from the fact that the weighted average long term effluent concentrations (BOD_5 - 35 mg/l; TSS - 48 mg/l) are below those achieved by Tannery No. 47 (BOD_5 - 48 mg/l; TSS - 77 mg/l). It is important to note that the limitations were not adjusted up to the long term average concentrations being achieved by Tannery No. 47 because engineering evaluation of that plant revealed minor upgrading would be beneficial. Most notably, an additional secondary clarifier would improve capture of TSS (effluent TSS concentration for Tannery No. 47 was more than twice those of the two POTWs) and remove most of the remaining insoluble BOD_5. Another concern EPA had was that a pilot plant activated sludge study performed for one of the vegetable tanning companies revealed that mixed liquor suspended solids settleability was not as good as for other leather tanning wastewaters. While EPA feels strongly that the study results were inconclusive regarding the performance of activated sludge and it disagreed with the final effluent concentrations projected by the study, EPA was concerned that a long term average TSS concentration of 48 mg/l was too stringent. In the Agency's judgment, effluent limitations for TSS based on a long term average of 60 mg/l were more reasonable to accommodate treatment of vegetable tanning wastewaters. Finally, a general concern EPA has is that the degree of operational proficiency required to achieve the weighted average long term effluent concentrations would not allow much flexibility for individual plants in selection among options for upgrading either physical facilities or operation and maintenance procedures, or both. This was important because virtually all direct dischargers require varying degrees of upgrading of both physical facilities and operational practices. Only marginal relaxation in the weighted average concentrations noted above was necessary to afford more upgrading flexibility, especially during the initial period of developing operational skills for newly upgraded physical facilities.

Based on these factors, it was the Agency's best engineering judgment that the weighted average long term effluent concentrations used to develop maximum 30 day average and maximum day effluent concentrations, and in turn mass based (lb/1000 lb) effluent limitations, should be adjusted to the following concentrations:

BOD_5 - 40 mg/l
TSS - 60 mg/l
Oil and Grease - 20 mg/l
Chromium (Total) - 1 mg/l

All three plants use to develop these BPT effluent limitations were found to be in compliance with either the concentrations, or the mass limitations (lbs/day), or both, approximately within the criteria used to establish them (i.e., maximum monthly-95th percentile; maximum day - 99th percentile).

2. Best Available Technology Economically Achievable (BAT)

From the control and treatment technologies discussed previously three technology options were identified as BAT options for the evaluation of pollutant removal capability, calculation of costs, and evaluation of economic achievability. The three options were:

OPTION I - Equal to BPT

OPTION II - OPTION I plus in-plant controls, stream segregation, segregated stream pretreatment, and activated sludge upgraded to provide nitrification and with powdered activated carbon (PAC) addition

OPTION III - OPTION II plus multimedia filtration

OPTION I

Under OPTION I, which establishes BAT technology and limitations equal to BPT, the regulated parameters are BOD_5, TSS, Oil and Grease, and Total Chromium.

OPTION II

OPTION II consists of biological treatment (BAT OPTION I) and several additional unit processes. An integral part of this option is in-plant control to reduce the volume of water used in leather processing, and thereby reduce the volume of wastewater to be treated. Reduced water use achievable by existing sources was discussed and presented in Section V. Therefore, treatment units, such as, clarifiers, pumps, etc., can be designed smaller and subsequently built at a lower cost. As has been noted previously in this document, the beamhouse and tanyard waste streams have different characteristics which require separate treatment. Stream segregation consists of the necessary piping and pumps to separate these streams for additional treatment. Each of the two waste streams undergo screening. The beamhouse stream then undergoes catalytic oxidation of sulfides followed by flue gas carbonation, which neutralizes the high pH and settles out the proteinaceous material. Those tanneries without a beamhouse, subcategories 4, 5, 7 and 9, do not require stream segregation or beamhouse pretreatment. The biological treatment facilities are upgraded to provide nitrification. This is accomplished by the following steps: increasing aeration to accommodate nitrogenous oxygen demand, providing caustic addition to maintain proper pH in the aeration tank, increasing the solids retention time or increasing the aeration tank size, and expanding the sludge dewatering facilities. PAC addition is a part of the cost of this option since it allows for better utilization of oxygen by the bacteria, improves the settling characteristics of the activated sludge, and enhances the opportunity for removal of some adsorbable toxic pollutants.

The pollutants which could be regulated for OPTION II are: BOD_5, TSS, Total Chromium, Oil and Grease, COD, Sulfide, TKN, Ammonia, and Phenol. Sulfide would not be regulated for the tanneries without a beamhouse (subcategories 4, 5, 7, and 9). Specific effluent concentrations resulting from this option are not included because this technology option has not been demonstrated in this industry.

OPTION III

OPTION III consists of the addition of multimedia filtration to OPTION II. The pollutants which could be regulated are the same as for OPTION II. Specific effluent concentrations for this option are not included because this technology option has not been demonstrated.

For each of the BAT options the design criteria are present in Appendix A, Cost of Treatment and Control Systems.

3. Best Conventional Pollutant Control Technology (BCT)

From the control and treatment technologies discussed perviously, three technology options were identified as BCT options for the evaluation of pollutant removal capability, calculation of costs, and evaluation of economic achievability. The three options were the same as the three BAT options, as follows:

OPTION I - Equal to BPT

OPTION II - OPTION I plus in-plant controls, stream segregation, segregated stream pretreatment, and activated sludge upgraded to provide nitrification and with powdered activated carbon (PAC) addition

OPTION III - OPTION II plus multimedia filtration

4. New Source Performance Standards (NSPS)

Section 306 of the Clean Water Act of 1977 requires that new source performance standards (NSPS) be established for industrial dischargers based on the best available demonstrated technology. NSPS establish control of toxic, nonconventional, and conventional pollutants. The same pollutants considered for control under BAT were considered for control under NSPS.

The options considered for NSPS were the same as for BAT. However, the Agency believes that because new facilities will have the ability to select the most efficient processing methods and water conservation measures, further flow reduction can be anticipated. These flow reductions have been demonstrated by at least one tannery in in each of eight subcategories and were presented and discussed previously in Section V. The NSPS technology options are;

OPTION I - Equal to BPT

OPTION II - OPTION I plus in-plant controls, stream segregation, segregated stream pretreatment, and activated sludge upgraded to provide nitrification and with powdered activated carbon (PAC) addition.

OPTION III - OPTION II plus multimedia filtration

The anticipated ranges of effluent reduction were the same as for the BAT options.

5. Pretreatment Standards for Existing and New Sources (PSES and PSNS)

The Clean Water Act requires that pretreatment standards prevent the discharge of pollutants which pass through, interfere with or are otherwise incompatible with the operation of POTWs. The Act also requires pretreatment for pollutants that limit sludge management alternatives at POTWs, including the beneficial use of sludges on agricultural lands.

The Agency has identified one toxic pollutant, total chromium, for regulation in tannery waste streams. One nonconventional pollutant, sulfides, was regulated because of the risk to human life due to the potential for the release of hydrogen sulfide gas in sewers, headworks, preliminary and primary treatment, and sludge management facilities at POTW's. The options the Agency considered for pretreatment standards are:

OPTION I - Stream segregation, sulfide oxidation of the beamhouse waste streams, and neutralization of the combined waste streams

OPTION II - Stream segregation, sulfide oxidation of the beamhouse waste stream, equalization and coagulation-sedimentation of tanyard waste stream, and neutralization of combined wastestreams

OPTION III - Stream segregation, sulfide oxidation and flue gas carbonation of the beamhouse waste stream, and coagulation-sedimentation of the combined waste streams

OPTION I

OPTION I is directed to the control of sulfides. This is applicable to plants in subcategories 1, 2, 3, 6, and 8 which incorporate sulfide unhairing operations and discharge high concentration of sulfides. This includes in-plant controls for water conservation and stream segregation which allows for separate treatment of the beamhouse waste stream. The beamhouse stream undergoes the catalytic oxidation of sulfides to reduce the concentration of sulfides. The waste streams are subsequently recombined before discharge to the POTW. Wastewater neutralization (pH control) technology was included by conservative engineering design to ensure that combined discharges would remain within the required pH ranges for each subcategory. However, it must be noted that existing discharges should be complying with these pH ranges because these pH ranges were promulgated in 1977 and have not been challenged as unachievable. This option establishes only a maximum day limitation for sulfide. The most severe hazard posed by hydrogen sulfide gas occurs during rapid fluctuations in pH caused by slug loading. For this reason, a monthly average limitation does not provide an effective tool for controlling this hazard.

As a result of reviewing the supplemented data base and comments, the Agency is basing the sulfide pretreatment standard on a long term average effluent concentration of 9 mg/l. After application of a variability factor of 2.7, the resulting maximum day sulfide pretreatment standard is 24 mg/l.

OPTION II

In addition to establishing controls for sulfide, OPTION II includes additional pretreatment for the removal of total chromium. This Option consists of in-plant controls, stream segregation and catalytic oxidation of the beamhouse waste stream (if present), and equalization and coagulation-sedimentation with lime of the tanyard stream. For OPTION II, the achievable long term effluent concentration for chromium (total) is 8 mg/l for those subcategories (Nos. 4, 5,7, and 9) which do not have beamhouse operations; the achievable long term effluent concentration for chromium (total) is 5 mg/l for those subcategories (Nos. 1, 2, 3, 6, and 8) which do have beamhouse operations that generate wastewaters which dilute the pretreated tanyard stream prior to discharge to a POTW sewer. The variability factors for maximum day and maximum monthly average are 2.4 and 1.5, respectively. The sulfide limitations are the same as for OPTION I.

OPTION III

OPTION III incorporates controls in addition to those in OPTION II (depending upon subcategory) as follows: segregated stream pretreatment, including flue gas coagulation-sedimentation of beamhouse wastewaters, equalization and coagulation-sedimentation of combined wastewaters in place of the same unit processes applied to segregated tanyard wastewaters. OPTION III also includes control capability for sulfide and chromium.

The regulated pollutants in this option are sulfides, chromium (total), and pH. For sulfides, maximum day pretreatment standard would be applicable to plants in subcategories (Nos. 1, 2, 3, 6, and 8) which incorporate sulfide unhairing operations and discharge high concentrations of sulfides.

For OPTION III, EPA has reviewed the supplemented record and as a result of that review has found that the achievable long term effluent concentration for chromium (total) would be revised to 8 mg/l for all subcategories. The variability factors for maximum day and maximum monthly average are 2.4 and 1.5, respectively. The design criteria for all the pretreatment options are given in Appendix A, Costs of Treatment and Control Systems.

SECTION VIII

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

A. GENERAL

The best practicable control technology currently available (BPT) generally is based on the average of the best existing performance, in terms of treated effluent discharged, by plants of various sizes, ages and unit processes within an industry or subcategory. Where existing performance is uniformly inadequate, BPT may be transferred from a different subcategory or category. Limitations based on transfer of technology must be supported by a conclusion that the technology is, indeed, transferable and a reasonable prediction that it will be capable of achieving the prescribed effluent limits (see Tanners' Council of America v. Train, 540 F.2d 1188 (4th Cir. 1976)). BPT focuses on end-of-pipe treatment technology rather than process changes or internal controls, except where such changes or controls are common industry practice.

BPT considers the total cost of the application of technology in relation to the effluent reduction benefits to be achieved from the technologies. The cost/benefit inquiry for BPT is a limited balancing, which does not require the Agency to quantify benefits in monetary terms (see, e.g., American Iron and Steel Institute v. EPA, 526 F.2d 1027 (3rd cir. 1975)). In balancing costs in relation to effluent reduction benefits, EPA considers the volume and nature of existing discharges, the volume and nature of discharges after application of BPT, the general environmental effects of the pollutants and the costs and economic impacts of the required pollution control level. The Act does not require or permit consideration of water quality problems attributable to particular point sources of industries, or water quality improvements in particular water bodies (see Weyerhaeuser Company v. Costle, 590 F.2d 1101 (D.C. Cir. 1978)).

B. IDENTIFICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPT)

1. Prior Regulations

EPA promulgated BPT for the Leather Tanning and Finishing Point Source Category on April 9,1974 (39 FR 12958; 40 CFR Part 425, Subpart A-F). Several industry members challenged these regulations in the United States Court of Appeals for the Fourth Circuit.

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, supra. 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.

In the remanded regulations, BPT technology was defined as equalization followed by primary treatment and biological treatment, in the form of aerated lagoons or activated sludge. In response to the remand issues, the Agency further investigated 1) aerated lagoon performance, and 2) the use of activated sludge biological treatment in the industry. Considerable data confirmed that aerated lagoons were subject to poor performance during winter months. However, extensive data in the record also showed that, for the pollutants regulated by BPT, winter climate does not affect the performance of properly designed and operated extended aeration activated sludge systems. Therefore, different effluent limitations based upon climate were not warranted.

On July 2, 1979, EPA proposed revised BPT regulations to replace the remanded regulations. In the proposed regulations equalization, coagulation-sedimentation, and biological treatment in the form of extended aeration activated sludge were the technology basis for BPT. Aerated lagoons were no longer considered representative of BPT.

As a result of industry's comments on the proposed regulations, the Agency responded by not only completely reviewing the entire data base and all documentation, but also by conducting a program to acquire supplemented data during the comment period. On June 2, 1982 (47 FR 23958), the Agency made available for public review the technical and economic data and related documentation received after proposal. As a result of the supplemental data base and the refined methodology for evaluating that data, the Agency announced in that notice that it was considering revising its proposed BPT effluent concentrations.

2. Technology Basis for BPT

Current treatment practices in the leather tanning and finishing industry indicate that among the 17 direct dischargers, two plants have primary sedimentation and activated sludge biological treatment. Two others recently have begun operating primary sedimentation and rotating biological contactor (RBCs) systems, but no operational data are available for these systems. The remaining direct dischargers have some form of biological treatment, usually low solids, long hydraulic detention time aerated lagoons, which require upgrading to achieve consistent effluent quality. These inadequate systems include simple lagoons with no aeration, lagoons with some mechanical aeration but no provision for sludge return, and activated sludge systems which are overloaded.

The effluent data collected on aerated lagoons during this study indicate that although lagoons occasionally will perform adequately they are subject to upset and extended periods of poor effluent quality, especially during winter months. The average of the effluent data supplied by the existing eight direct dischargers using lagoon systems was 560 mg/l BOD_5 and 460 mg/l TSS. Concentrations were reported as high as 4440 mg/l BOD_5 and 1500 mg/l TSS. It is apparent that at times little or no treatment is being performed. The Agency, by basing BPT achievable effluent limitations on extended aeration activated sludge, is not stating that this is the only biological system that can achieve the promulgated effluent limitations. Properly designed and operated rotating biological contactors (RBCs) and different modes (such as an oxidation ditch) of activated sludge have shown the potential to achieve these limitations.

The Agency has based BPT on equalization, coagulation-sedimentation, and extended aeration activated sludge. BPT has been demonstrated by plants in subcategories 1, 3, and 4, including two POTWs in Maine; the Hartland POTW receives more than 90 percent of its wastewater from a subcategory 1 tannery, and the Berwick POTW receives more than 90 percent of its wastewater from a subcategory 4 tannery. Tannery No. 47 is a subcategory 3 plant with direct discharge which also has demonstrated this technology. However, this technology has not been applied in all remaining subcategories where wastewater treatment is uniformly inadequate. Most of the existing biological treatment systems in the industry were found to be inadequate, as described previously. EPA has documented these inadequacies on a plant-by-plant basis and evaluated the equipment and costs necessary to achieve high solids extended aeration activated sludge treatment and the BPT effluent concentrations.

As noted in Section IV of this Document the major difference in treatability of raw wastewater pollutant loads among the nine subcategories is the presence or absence of beamhouse (unhairing) operations, included in subcategories 1, 2, 3, 6, and 8. The raw wastewaters from these subcategories are substantially higher in pollutant loads (BOD_5, TSS, TKN, Oil and Grease, etc.), than raw wastewaters from subcategories 4, 5, 7, and 9 which do not include the beamhouse group of subprocesses. Nonetheless, the Hartland, Maine POTW, which treats beamhouse wastewaters (subcategory 1), achieved long term effluent concentrations (see Section VII) which were somewhat lower than the Berwick, Maine POTW, which does not treat beamhouse wastewaters. The latter POTW treats retan wet-finish wastewaters (subcategory 4). The long term effluent concentrations for Tannery No. 47 (subcategory 3) were very close to those utilized for BPT. Effluent concentrations which form the basis of BPT effluent limitations have, therefore, been demonstrated on beamhouse and non-beamhouse raw waste loads.

Therefore, the Agency has determined that, given the similarity in the treatability of wastewaters in all subcategories, this technology will effectively remove pollutants from wastewaters of all subcategories to the same final effluent concentrations. Consequently, the Agency has transferred this technology and the achievable final effluent concentrations, from subcategories 1, 3, and 4 in which this technology has been demonstrated, to the remaining subcategories. To ensure that these effluent limitations were achievable by plants in all subcategories, differences among subcategories in wastewater volumes and pollutant loads were accounted for in different unit process designs and associated costs. Most importantly, adjustments were made in the sizing of primary coagulation-sedimentation tanks, and the aeration capacity and hydraulic detention time required for activated sludge aeration basins. The Agency's design and costing procedures have been tailored further to each individual direct discharger.

3. Engineering Aspects of Best Practicable Technology

Detailed design criteria are presented and discussed in Appendix A of this Document for each of the unit processes. Specific design values also are given for each subcategory. These values were developed using subcategory median raw waste characteristics. The Agency has documented the inadequacies in treatment at each of the existing direct dischargers. The existing facilities also were inventoried. By using existing raw waste data from each tannery (or subcategory median data if no actual data were available), a BPT treatment facility was designed specifically for that tannery. Based on this design and the inventory of existing facilities, a comprehensive list of required modifications was developed. Cost estimates for these modifications were then developed. Credits also were calculated for the existing in-place equipment at each direct discharger as the difference in cost for the complete BPT system and the cost for modifications to upgrade to BPT.

As noted previously, these systems must be properly designed and diligently operated in order to achieve the desired performance. The design must include provisions for: a uniform and constant flow to the coagulation-sedimentation and biological processes by equalization; lime and polymer addition to the primary reactor clarifier; sufficient aeration capacity, hydraulic detention time and solids retention time in the activated sludge aeration basin; a proper nutrient balance (carbon: nitrogen: phosphorus - 100:5:1) for biological growth; and conservative overflow rates for the clarifiers. Some of the important design factors are summarized below:

Flow Equalization	
Hydraulic Detention Time	48 hours at design flow
Coagulation-Sedimentation	
Overflow Rate	400 gpd/ft^2(16.3m^3/m^{2}d)
Lime Feed	800-1600 mg/l(as $Ca(OH)_2$)
Polymer Feed	2-4 mg/l
Activated Sludge	
Oxygen Supplied	2.0 lb/lb (2kg/kg) of BOD_5 removed
Nutrient Addition	Phosphorus, as Phosphoric Acid
Mixed Liquor Liquor Suspended Solids (MLSS)	5,000 mg/l (expected range 3,500-8,000 mg/l)
F/M Ratio (based on MLSS)	0.1 (expected operating range 0.05-0.1)
Final Clarifier	
Overflow rate	200 gpd/ft^2 (8.14 m^3/m^{2}d)

As previously stated, proper operation and maintenance of the facility is a necessary factor to achieve optimum performance. In its O&M cost estimates, the Agency has therefore included: a routine and preventative maintenance program; daily process control activities (sampling and analytical tasks), chemical costs, power costs, and effluent monitoring; and skilled operators to operate these facilities in order to obtain the performance that they are capable of attaining. A great majority of the existing treatment facilities are operated poorly and neglected.

4. Regulated Pollutants

The pollutants controlled by this regulation include the same pollutants controlled by the remanded BPT regulation, specifically BOD_5, TSS, Oil and Grease, Total Chromium, and pH. The discharge of these pollutants is controlled by maximum monthly average and maximum daily mass effluent limitations (pounds per 1,000 pounds [kg/kkg] of raw material). The mass effluent limitations are presented in Table VIII-1.

5. Effluent Variability

The variability factors used in developing BPT monthly average and daily maximum effluent limitations were based on a statistical analysis of treated effluent data by pollutant. The data sets subjected to this analysis were for Tannery No. 47, and the Berwick and Hartland, Maine POTWs. All data representing documented periods of plant start-up, upsets, mechanical or power failures, or similar circumstances which result in poor effluent quality (permit violations) were edited from the data base. Normal variability in effluent quality as represented by the resulting data base has been quantified utilizing the following methodology. The data for each plant were fit to a generalized form of the lognormal distribution. Daily maximum variability factors for each plant were determined by taking the ratio of the estimated 99th percentile concentration and the estimated long term mean of the fitted distribution. These values were combined across plants to obtain overall variability factors and effluent concentrations.

Maximum monthly effluent limitations were developed in a manner consistent with the method used to develop maximum day effluent limitations. The same distribution of individual effluent concentrations and estimated long term mean effluent concentrations were used in developing the maximum monthly effluent concentrations. The maximum monthly effluent limitations were based on statistical modeling techniques applied to the edited data base described above to derive maximum monthly effluent limitations assuming eight sample observations per month, because this was expected to be typical in the industry. Monthly variability factors were determined by taking the ratio of the estimated 95th percentile of the distribution of the monthly arithmetic mean concentrations to the estimated long term mean effluent concentration. These factors were combined across plants in the same manner used for the maximum day variability factors.

The expected value of the maximum monthly average, as estimated by statistical modeling techniques, changes with the number of data points (sampling frequency). The expected value of the maximum monthly average based on sampling every day of the month (30 data points per monthly average) is substantially lower than the expected value based on sampling twice per week (eight data points). Appendix B includes graphical representations of the expected monthly average variability factors plotted versus sampling frequency for each of the four regulated parameters. In this regard the Agency recognized that individual plants in the industry may choose to sample more frequently than twice per week, for example to improve process control for biological treatment systems. In other cases, permitting authorities may require on a case-by-case basis more frequent sampling than eight days per 30 day period for water quality or other purposes. However, EPA is requiring achievement of these technology based maximum monthly effluent limitations as derived assuming eight sampling days per 30 day period, or approximately twice per week. Compliance by a given discharger with these (eight day) limitations would be based on the arithmetic average of the actual number of measurements taken during a 30 day period, regardless of their frequency (e.g., three or four samples per week).

Based on the above analysis the following variability factors were established for BPT:

	BOD_5	TSS	Total Chromium	Oil and Grease
Maximum Monthly Average	1.89	1.85	1.59	1.58
Maximum Day	4.21	4.05	4.33	3.54

6. Calculation of BPT Effluent Limitations

a) General

As described previously in Section VII of this Development Document, EPA adopted final effluent concentrations as follows:

BOD_5	40 mg/l
TSS	60 mg/l
Oil and Grease	20 mg/l
Chromium (total)	1 mg/l

The variability factors listed later in this section, together with median flow ratios presented in Section V of this document, have been applied to the above long term average final effluent concentrations to establish monthly average and maximum day mass based effluent limitations for all nine subcategories. The generic formula for calculating monthly average and maximum day mass limitations is as follows:

Effluent Concentration (mg/l) x Subcategory Median Flow Ratio (gal/lb) x

$10^3 \times \frac{8.34}{10^6}$ x Variability Factor = Mass Limitations (lb/1000 lbs)

It must be noted, as described previously in this section, that each of the four regulated pollutants is associated with two unique variability factors, one for the monthly average and one for the maximum day.

BPT mass based effluent limitations were developed using the methodology described above, and are presented in Table VIII-1.

b. Permit Example

The calculation of mass limitations (maximum monthly and day) for a tannery in a single subcategory is a single multiplication of the production (in kkg or 1000 lbs) and mass limitation (kg/kkg or lb/1000 lbs). The calculation of mass limitations for a multi-subcategory tannery is somewhat more complicated and is illustrated below.

The example tannery is classified as a combined subcategory 1 and 9 tannery. The grain leather production is 250,000 lb/day (114 kkg) and the split production is 100,000 lb/day (45 kkg). The following calculations combined these production figures and the mass limitations presented in Table VIII-1.

Tannery Production: Subcategory 1 = 250,000 lb/day (114 kkg/d)
Subcategory 9 = 100,000 lb/day (45 kkg/d)

Maximum Day Discharge Limits

BOD_5

Subcategory 1= (250,000 lb/d) (9.13 lb/1000 lb) = 2383 lb/d
Subcategory 9 = (100,000 lb/d) (4.21 lb/1000 lb) = 421 lb/d

Total = 2804 lb/d
(1,273 kg/d)

TSS

Subcategory 1= (250,000 lb/d) (13.17 lb/1000 lb) = 3293 lb/d
Subcategory 9 = (100,000 lb/d) (6.08 lb/1000 lb) = 608 lb/d

Total = 3901 lb/d
(1,771 kg/d)

O&G

Subcategory 1 = (250,000 lb/d) (3.84 lb/1000 lb) = 960 lb/d

Subcategory 9 = (100,000 lb/d) (1.77 lb/1000 lb) = 177 lb/d

Total = 1137 lb/d
(516 kg/d)

CrT

Subcategory 1 = (250,000 lb/d) (0.23 lb/1000 lb) = 58 lb/d

Subcategory 9 = (100,000 lb/d) (0.11 lb/1000 lb) = 11 lb/d

Total = 69 lb/d
(31 kg/d)

Maximum Monthly Average Discharge Limits

BOD_5

Subcategory 1 = (250,000 lb/d) (4.10 lb/1000 lb) = 1025 lb/d

Subcategory 9 = (100,000 lb/d) (1.89 lb/1000 lb) = 189 lb/d

Total = 1214 lb/d
(551 kg/d)

TSS

Subcategory 1 = (250,000 lb/d) (6.02 lb/1000 lb) = 1505 lb/d

Subcategory 9 = (100,000 lb/d) (2.78 lb/1000 lb) = 278 lb/d

Total = 1783 lb/d
(809 kg/d)

O&G

Subcategory 1 = (250,000 lb/d) (1.71 lb/1000 lb) = 428 lb/d

Subcategory 9 = (100,000 lb/d) (0. 79 lb/1000 lb) = 79 lb/d

Total = 507 lb/d
(230 kg/d)

CrT

Subcategory 1 = (250,000 lb/d) (0.08 lb/1000 lb) = 20 lb/d

Subcategory 9 = (100,000 lb/d) (0.04 lb/1000 lb) = 4 lb/d

Total = 24 lb/d
(11 kg/d)

C. COST AND EFFLUENT REDUCTION BENEFITS

The Agency's analysis indicates implementation of BPT will require investment costs of $10.6 million, and total annualized costs of $5.7 million (first quarter 1982 dollars) in order to upgrade existing treatment facilities for the 17 direct dischargers.

These costs may result in closure of 2 plants causing approximately 155 people to become unemployed. This is approximately 1.3 percent of the plants and 0.8 percent of the total employment in the industry. The cost of production is estimated to increase by 0.6 to 2.3 percent. The total mass of regulated pollutants removed from existing discharges to BPT would be 2.4 million kilograms (5.3 million pounds) per year of conventional pollutants (BOD_5, TSS, and Oil and Grease) and 20 thousand kilograms (44,000 pounds) per year of total chromium (248 thousand kilograms (547,000 pounds) per year from raw waste). EPA has determined that the effluent reduction benefits of this regulation justify its costs.

D. NONWATER QUALITY ENVIRONMENTAL IMPACTS

Eliminating or reducing one form of pollution may cause other environmental problems. Sections 304(b) and 306 of the Act require EPA to consider the nonwater quality environmental impacts (including energy requirements) of certain regulations. In compliance with these provisions, the Agency considered the effect of this regulation on air pollution, solid waste generation, water scarcity, and energy consumption. While it is difficult to balance pollution problems against each other and against energy use, the Agency believes that this regulation will best serve often competing national goals. The Administrator has determined that the impacts identified are justified by the benefits associated with compliance with the limitations.

1. Air Pollution

Implementation of BPT is not expected to have any significant air pollution impacts. However, minimal amounts of volatile organic compounds may be released to the atmosphere by aeration systems in activated sludge treatment facilities at direct dischargers.

2. Solid Waste

Implementation of these BPT regulations will generate sludge from wastewater treatment which must be disposed. A separate Agency action (see the Federal Register for October 30, 1980; 45 FR 72024) has removed both leather tanning process solid wastes and wastewater treatment sludges from the list of hazardous wastes under RCRA, thus facilitating disposal at substantially lower cost than for hazardous wastes. Implementation of BPT will generate 30,000 kkg (metric tons) per year (wet basis, 20 percent solids) of sludge. The Agency has assumed that these sludges will be disposed in available off-site landfills. The cost of off-site landfill disposal of these sludges was assumed to be $20 per wet ton, or $100 per dry ton (20 percent solids). The resulting total annual O & M cost for sludge disposal is $0.7 million for all direct dischargers.

3. Consumptive Water Loss

Treatment and control technologies which require extensive recycling and reuse of water may, in some cases, require cooling mechanisms. Where evaporative cooling mechanisms are used, water loss may result and contribute to water scarcity problems, of concern primarily in arid and semi-arid regions. These regulations do not envision recycling requiring evaporative cooling mechanisms and, therefore, will create no additional consumptive water loss.

4. Energy Consumption

Implementation of BPT will require 17.0 million kwh/yr of electric power. This represents an increase of approximately 3 percent above production power usage.

TABLE VIII-1

BPT EFFLUENT LIMITATIONS

Subcategory 1
Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	9.1	4.1
TSS	13.2	6.0
Oil & Grease	3.8	1.7
Total Chromium	0.23	0.09
pH	Within the range 6.0 to 9.0.	

Subcategory 2
Hair Save/Chrome Tan/Retan-wet Finish

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	8.2	3.7
TSS	11.8	5.4
Oil & Grease	3.4	1.5
Total Chromium	0.21	0.08
pH	Within the range 6.0 to 9.0	

Subcategory 3
Hair Save or Pulp/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	6.9	3.1
TSS	9.9	4.5
Oil & Grease	2.9	1.3
Total Chromium	0.18	0.06
pH	Within the range 6.0 to 9.0	

Subcategory 4
Retan-Wet Finish-Sides

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	6.7	3.0
TSS	9.7	4.4
Oil & Grease	2.8	1.3
Total Chromium	0.17	0.06
pH	Within the range 6.0 to 9.0	

Subcategory 5
No Beamhouse

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	8.2	3.7
TSS	11.8	5.4
Oil & Grease	3.4	1.5
Total Chromium	0.21	0.08
pH	Within the range 6.0 to 9.0	

Subcategory 6
Through-the-Blue

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	3.0	1.3
TSS	4.3	1.9
Oil & Grease	1.2	0.6
Total Chromium	0.08	0.03
pH	Within the range 6.0 to 9.0	

Subcategory 7
Shearling

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	13.2	5.9
TSS	19.1	8.7
Oil & Grease	5.6	2.5
Total Chromium	0.34	0.12
pH	Within the range 6.0 to 9.0	

Subcategory 8
Pigskin

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	7.0	3.2
TSS	10.1	4.6
Oil & Grease	3.0	1.3
Total Chromium	0.18	0.07
pH	Within the range 6.0 to 9.0	

Subcategory 9
Retan-Wet Finish-Splits

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	4.2	1.9
TSS	6.1	2.8
Oil & Grease	1.8	0.79
Total Chromium	0.11	0.04
pH	Within the range 6.0 to 9.0	

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE (BAT) EFFLUENT LIMITATIONS GUIDELINES

A. GENERAL

As a result of the Clean Water Act of 1977, the achievement of BAT has become the principal national means of controlling wastewater discharges of toxic pollutants. The factors considered in establishing this level of effluent control based on the best available technology economically achievable (BAT) are the costs of applying the control technology, the age of process equipment and facilities, the process employed, process changes, the engineering aspects of applying various types of control technologies, and nonwater quality environmental considerations such as energy consumption, solid waste generation, and air pollution (Section 304(b) (2) (B)). In general, the BAT technology level represents, at a minimum, the best economically achievable performance. If the Agency determines that the performance of treatment technology in a given industry is uniformly inadequate, BAT technology may be transferred from a different subcategory or industrial category. BAT may include process changes or internal controls, even when not common industry practice. Best available treatment technology must be implemented no later than July 1, 1984, for the control of toxic and nonconventional pollutants.

The statutory assessment of BAT "considers" costs, but does not require a balancing of costs against effluent reduction benefits (see Weyerhaeuser v. Costle, 590 F. 2d 1101 (D.C. Cir. 1978)). In assessing the proposed BAT, EPA has given substantial weight to the reasonableness of costs. The Agency has considered the volume and the nature of existing 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 using economically achievable technology.

B. PRIOR REGULATIONS

The technology basis of the proposed BAT effluent limitations (see 44 FR 38753-38755; July 2, 1979) was BPT biological treatment, preceded by in-plant control, water conservation, stream segregation, and pretreatment of the segregated beamhouse stream by catalytic sulfide oxidation and flue gas coagulation-sedimentation, and followed by upgraded biological treatment through powdered activated carbon (PAC) addition, and multimedia filtration. The proposed BAT effluent limitations would have controlled one toxic pollutant (total chromium). Five nonconventional pollutants also would have been controlled (chemical oxygen demand (COD), TKN, ammonia, sulfide, and total phenols (as measured by the 4AAP procedure listed in 40 CFR Part 136, Standard Methods)). All of the pollutants controlled by BAT, including the conventional pollutants BOD_5, TSS, Oil and Grease, and pH, were proposed as indicators for the control of toxic organic pollutants discharged from leather tanning and finishing plants.

As a result of comments on the proposed regulations, and comprehensive analysis of supplemental data and documentation gathered after proposal, the Agency indicated in the June 2, 1982 notice of availability (47 FR 23961) that it had reviewed the options previously set forth in the BAT proposal, and was considering redefining those options. Proposed OPTION I had been based on the addition of in-plant controls and segregated stream pretreatment to BPT technology. However, in view of the increase in cost for this control technology and the economic posture of the industry, EPA made BAT OPTION I equal to BPT. In addition, EPA combined the effluent limitations and costs of proposed OPTION II, based on activated sludge upgraded primarily by powdered activated carbon (PAC) addition, with those of proposed OPTION I, primarily based on in-plant control and segregated stream pretreatment. This combination became BAT OPTION II. The addition of multimedia filtration (previously OPTION III), which was the basis for the proposed BAT regulation, remained as OPTION III. The Agency also indicated that it was no longer seriously considering proposed OPTION IV, which was based on the end-of-pipe addition of granular activated carbon columns, because such technology would be too expensive and lacked demonstrated use in this industry.

Section VII of this Document discusses each unit process considered in developing these options, as well as those unit processes included in each option. BAT regulations presented in this document supersede prior BAT regulations.

C. REGULATED POLLUTANTS

One toxic pollutant, total chromium, is regulated in all subcategories.

D. POLLUTANTS NOT REGULATED

Paragraph 8 of the modified Settlement Agreement, approved by the District Court for the District of Columbia on March 9, 1979 (12 ERC 1833), contains provisions authorizing the exclusion from regulation, in certain circumstances, of toxic pollutants and industry categories and subcategories.

On December 18, 1980, EPA submitted an affidavit explaining that the Agency decided not to regulate certain of the 129 toxic pollutants under the authority of Paragraph 8(a) (iii) of the modified Settlement Agreement. Since that time, the Agency acted to remove three organic compounds from the list of toxic pollutants. All three of these pollutants were among those excluded from regulation because "they are not detectable by Section 304(h) analytical methods or other state-of-the-art methods."

The Agency has gathered additional data since these regulations were proposed, as described previously in the Methodology and Data Gathering Efforts sections of this document. Based upon analysis of this additional data, together with the data used in the proposal, the Agency is revising its exclusion of pollutants. Of the remaining 126 toxic pollutants, 71 are excluded from regulation under the authority of Paragraph 8(a) (iii) of the modified Settlement Agreement because "they are not detectable by Section 304(h) analytical methods or other state-of-art methods."

Among direct dischargers, 34 pollutants are excluded from regulation because "they are detected in treated effluents in trace amounts and neither cause nor are likely to cause toxic effects; 7 pollutants are excluded from regulation because "they are detected at only a small number of sources within a subcategory and are uniquely related to those sources;" and 13 pollutants are "present in amounts too small to be effectively reduced by technologies known to the Administrator." These pollutants are excluded under authority of Paragraph 8(a) (iii). The pollutants and the specific reasons for their exclusion are presented in Appendix C. The pollutant (total) chromium is controlled by BPT; because BAT is being promulgated equal to BPT, total chromium is controlled.

E. IDENTIFICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

The technology basis for BAT is identical to BPT, and includes equalization, primary coagulation-sedimentation, and extended aeration activated sludge biological treatment.

F. BAT EFFLUENT LIMITATIONS

BAT effluent limitations for total chromium are the same as those contained in Table VIII-1 of Section VIII (BPT) of this Development Document.

G. RATIONALE FOR THE SELECTION OF BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

BAT OPTION II as amended, would require an incremental investment cost beyond BPT of $17.6 million, with total annualized cost of $7.5 million. This OPTION would remove incrementally 4.2 million pounds per year (1910 kkg/yr) of nonconventional pollutants (COD, TKN, ammonia, sulfide, and total phenol [4AAP]), and 2,000 pounds per year (0.9 kkg/yr) of total chromium beyond BAT OPTION I. Incidentally, this OPTION would remove incrementally 0.84 million pounds per year (380 kkg/yr) of conventional pollutants (BOD_5, TSS, Oil and Grease) beyond BAT OPTION I. The Agency's economic analysis indicated that of the 13 plants analyzed, five may close if this OPTION were selected.

In reviewing all available engineering and economic data and information, the Agency concluded that attainment of BAT limitations based on BAT OPTION II was not economically achievable. In addition, this technology has not been demonstrated in this industry. Based on these findings, the Agency has determined that more stringent regulation of toxic pollutant discharges from the leather tanning industry is not justified at this time and that BAT effluent limitations should be established equal to BPT limitations. Therefore, review of BAT OPTION III was not necessary because it was even more costly and thus not economically achievable, nor has it been demonstrated.

The nonconventional pollutants TKN, ammonia, COD, sulfide, and total phenol (4AAP) were not controlled by BPT technology. However, these pollutants were controlled by BAT OPTIONS II and III. BAT OPTIONS II and III were neither demonstrated nor economically achievable. Therefore, EPA is not incorporating limitations for these nonconventional pollutants in the BAT limitations.

The Agency's review of the direct dischargers indicated that the existing effluent quality generally was very poor; in a small number of cases final effluent concentrations were found to be only marginally lower than raw waste concentrations either periodically or consistently. Environmental analysis of existing discharges indicated that aquatic and human health toxicity values for certain toxic pollutants such as trivalent chromium, were exceeded under low flow conditions. In light of these findings, the Agency has found it to be environmentally necessary and cost-effective to require upgrading of existing treatment facilities in order to improve the general level of effluent quality of most plants, and to improve the consistency of effluent quality of other plants. However, the Agency has not found additional technology options and associated effluent limitations more stringent than BPT to be economically achievable for the category as a whole at this time. Therefore, the Agency has decided BAT should be no more stringent than BPT. However, the Agency also recognizes that in certain instances site-specific water quality considerations may require permit requirements more stringent than BPT effluent limitations based on case-by-case analysis.

State and local regulatory authorities may find it necessary to establish pollutant limitations in addition to and/or more stringent than BPT, where needed to achieve or maintain the receiving water quality. In these instances, Section VII of this Document includes ranges of anticipated performance where appropriate for traditional pollutants of concern by BAT OPTIONS II and III technologies. Specific effluent concentrations have not been included for BAT OPTIONS II and III because these technologies have not been demonstrated in this industry at this time.

The Agency recognizes that the quantity of toxic pollutants discharged from individual plants may, in some cases, be higher than the industry medians and may be significant when viewed as single point source discharges to specific streams. NPDES permit issuing authorities may find it necessary to require individual plants to provide information on toxic pollutant usage, to analyze for specific toxic pollutants, and/or to conduct bioassay testing prior to issuing a NPDES permit. Permit issuing authorities may limit specific pollutants on a case-by-case basis when limitations are necessary to carry out the purposes of the Act, even if the pollutant is not controlled by BAT limitations.

H. NONWATER QUALITY ENVIRONMENTAL IMPACTS

As BAT effluent limitations are equal to BPT effluent limitations, there are no incremental nonwater quality impacts associated with attainment of BAT effluent limitations.

SECTION X

EFFLUENT REDUCTION ATTAINABLE BY BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY

The 1977 amendments added section 301(b) (2) (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), including BOD_5, TSS, fecal coliform and pH, and any additional pollutants defined by the Administrator as "conventional." On July 30, 1979, the Administrator defined oil and grease as a conventional pollutant.

Section 304(b) (4) (B) of the Act requires that the methodology for determining BCT include two major factors: an industry cost-effectiveness test, and a test that compares the cost for private industry to reduce its effluent levels with that incurred by POTWs. The Agency's "cost reasonableness" test was intended to consider these factors. However, that cost test was remanded by the United States court of Appeals for the Fourth Circuit. (American Paper Institute v. EPA, 660 F. 2d 954 (4th cir. 1981)). The Agency proposed on October 29, 1982 (47 FR 49176) a new methodology to replace the remanded methodology.

The proposed regulations had set BCT equal to BAT in all subcategories. BPT is the minimum level of BCT control required by the Act. EPA has not identified any control technology beyond BPT which is economically achievable which would effect significant removal of conventional pollutants. Therefore, the Agency is setting BCT equal to BPT for all subcategories. BCT limitations are those for BOD_5, TSS, Oil and Grease, and pH contained in Section VIII-BPT, Table VIII-1.

In support of this finding, the Agency evaluated the incremental cost of conventional pollutant removal beyond BPT of BAT (BCT) OPTIONS II and III. Estimated pollutant removals were developed for the BCT options for comparison purposes only. Table X-1 presents the results of this analysis. It can be seen that the cost per pound of conventional pollutant removal was far in excess of the cost reasonableness benchmark of $0.27/lb of BOD_5 and TSS removed as set out in the proposed BCT methodology.

TABLE X-1

BCT ANALYSIS

			BPT-BCT (BAT) OPTION I (2)				BCT (BAT) OPTION II (3)				BCT (BAT) OPTION III (4)			
Subcategory	Model Plant Production ($lbs \times 10^3$)	Data Flow (mgd)(1)	Cost Invest. ($\$ \times 10^6$)	Cost Total Annual. ($\$ \times 10^6$)	Pounds of BOD_5 & TSS Removed ($lbs \times 10)^6$/yr	$/lb	Cost Invest. ($\$ \times 10^6$)	Cost Total Annual. ($\$ \times 10^6$)	Pounds of BOD_5 & TSS Removed ($lbs \times 10^6$)/yr	$/lb	Cost Invest. ($\$ \times 10^6$)	Cost Total Annual. ($\$ \times 10^6$)	Pounds of BOD_5 & TSS Removed ($lbs \times 10^6$)/yr	$/lb
1 - Hair Pulp, Chrome Tan, Retan-Wet Finish	89.3	0.60 (0.49)	2.1	0.62	3.1	0.20	1.3	0.49	0.13	3.77	1.5	0.52	0.17	3.00
2 - Hair Save, Chrome Tan, Retan-Wet Finish	41.7	0.24 (0.21)	1.5	0.43	3.3	0.13	0.80	0.29	0.05	5.80	1.0	0.31	0.065	4.77
3 - Hair Save, Non-Chrome Tan, Retan-Wet Finish	59.6	0.29 (0.29)	1.8	0.50	1.9	0.26	1.0	0.40	0.052	7.69	1.2	0.44	0.074	5.95
4 - Retan - Wet Finish, Grain Sides	36.3	0.17 (0.11)	1.1	0.26	0.49	0.53	0.50	0.13	0.043	3.02	0.65	0.15	0.051	2.94
5 - No Beamhouse	9.2	0.053 (0.051)	0.75	0.18	0.18	1.00	0.38	0.093	0.0095	9.79	0.49	0.11	0.013	8.46
6 - Through-the-Blue	55.0	0.12 (0.08)	1.5	0.43	4.6	0.09	0.69	0.27	0.029	9.31	0.82	0.30	0.034	8.82
7 - Shearling	22.6	0.21 (0.19)	1.2	0.31	0.64	0.48	0.60	0.17	0.039	4.36	0.80	0.20	0.054	3.70
8 - Pigskin	28.0	0.14 (0.14)	1.4	0.37	2.1	0.18	0.63	0.20	0.024	8.33	0.80	0.23	0.035	6.57
9 - Retan-Wet Finish, Splits	44.0	0.13 (0.11)	1.0	0.27	0.40	0.68	0.54	0.18	0.028	6.43	0.69	0.20	0.037	5.41

Source: Federal Register for June 2, 1982 (47 FR 23958) and supporting record

(1) - Flow value in parenthesis is reduced flow basis for costing additional technology included in BCT (BAT) OPTIONS II and III
(2) - Cost assumed no treatment in place; pollutant removals taken from raw waste
(3) - Cost and pollutant removals are incremental beyond BPT
(4) - Cost and pollutant removals are total increment beyond BPT, including BCT (BAT) OPTION II
(5) - Costs in 1st Quarter 1982 Dollars (ENRCCI 3730)

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

A. GENERAL

The basis for new source performance standards (NSPS) under section 306 of the Act is the best available demonstrated technology (BADT). At new plants, the opportunity exists to design the best and most efficient production processes and wastewater treatment facilities, so Congress directed EPA to consider the best demonstrated process changes, in-plant controls and end-of-pipe treatment technologies that reduce pollution to the maximum extent feasible.

B. PRIOR REGULATIONS

NSPS for the leather tanning and finishing industry were promulgated on April 9, 1974 (39 FR 12958). The original NSPS established limitations for : conventional pollutants (BOD_5, TSS, Oil and Grease, and pH), and one toxic pollutant (Total Chromium). The technology basis for NSPS was the same as BPT (equalization, primary coagulation-sedimentation, and biological treatment), as were the mass based effluent limitations.

As described previously in Section VIII of this Document, the BPT regulations were remanded for reconsideration by the United States Court of Appeals for the Fourth Circuit. NSPS also were remanded for reconsideration because they were the same as BPT.

The technology basis of NSPS proposed in 1979 was the same as for the proposed BAT limitations. The proposed NSPS limitations (44 FR 38755), were therefore the same as the proposed BAT effluent limitations.

C. REGULATED POLLUTANTS

Pollutants regulated under NSPS include four conventional pollutants, BOD_5, TSS, Oil and Grease and pH; and one toxic pollutant, Total Chromium.

D. IDENTIFICATION OF THE TECHNOLOGY BASIS OF NSPS

THe technology basis for NSPS in all nine subcategories is the same as BPT specifically: equalization, primary coagulation-sedimentation, and extended aeration activated sludge biological treatment.

E. NSPS EFFLUENT LIMITATIONS

NSPS effluent limitations are presented in Table XI-2.

F. RATIONALE FOR THE SELECTION OF NSPS

The June 2, 1982 notice of availability (47 FR 23962) indicated that the Agency was considering adopting BPT technology with reduced flows as the basis for NSPS mass based effluent limitations. The Agency is promulgating NSPS based upon the same end-of-pipe technology and effluent concentration limitations as utilized in the promulgated BPT with reduced flows because this is the most stringent demonstrated technology.

The Agency received comments on the basis for and the achievability of new source water use ratios. The Agency reviewed the data base in response to those comments and adjustments were made in new source water use ratios for four subcategories. These new source ratios (see Table XI-1), identified in eight of nine subcategories, have been demonstrated by at least one plant in each of these eight subcategories, and have been incorporated in the mass based NSPS limitations. See Section V of this Document for further discussion of reduced water use ratios for new sources.

G. METHODOLOGY USED FOR DEVELOPMENT OF NSPS

NSPS were calculated as the product of (a) long term average final effluent concentrations, (b) appropriate variability factors for each pollutant (both of these were utilized in the development of BPT effluent limitations), and (c) reduced water use ratios achievable by new sources summarized in Table XI-1.

TABLE XI-1

NEW SOURCE FLOW RATIOS

Subcategory	New Source Flow Ratio gal/lb (l/kg)	No. of Plants In Data Base Achieving Flow Ratio
1	4.3(35.9)	5
2	4.9(40.9)	1
3	4.2(35.1)	4
4	4.5(37.6)	3
5	3.8(31.7)	3
6	1.4(11.7)	1
7	9.4(78.5)	1
8	4.1(34.2)	1
9	2.5(20.9)	2

H. COST OF APPLICATION AND EFFLUENT REDUCTION BENEFITS

The cost of attainment of NSPS varies by subcategory as discussed in detail in Appendix A. Substantial reductions of BOD_5, TSS, Oil and Grease, and Total Chromium will result upon attainment of NSPS at new direct discharging leather tanning and finishing plants. The cost of NSPS would be less than BAT for an existing source in eight of the nine subcategories because new plants can use more efficient processing methods which require less water use. Because the cost of treatment technology is most dependent upon wastewater volume, new sources would be able to build smaller and less costly treatment systems. Similarly, the mass of pollutants discharged by these new source systems would be less than the mass of pollutants discharged by existing sources. This is true because new sources can achieve the same final effluent concentrations as existing sources. In the shearling subcategory, the new source water use ratio was the same as the median water use ratio. Therefore, the costs of end-of-pipe technology and the mass of pollutants discharged for new sources would be the same as for existing sources. Economic analysis indicates that NSPS regulations are not expected to significantly discourage entry into the industry or result in any differential economic impacts to new plants.

TABLE XI-2
NEW SOURCE PERFORMANCE STANDARDS

Subcategory 1
Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	NSPS Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	6.0	2.7
TSS	8.7	4.0
Oil & Grease	2.5	1.13
Total Chromium	0.16	0.06
pH	Within the range 6.0 to 9.0.	

Subcategory 2
Hair Save/Chrome Tan/Retan-wet Finish

Pollutant or Pollutant Property	NSPS Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	6.9	3.1
TSS	9.9	4.5
Oil & Grease	2.9	1.3
Total Chromium	0.18	0.06
pH	Within the range 6.0 to 9.0.	

Subcategory 3
Hair Save or Pulp/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	NSPS Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	5.9	2.7
TSS	8.5	3.9
Oil & Grease	2.4	1.1
Total Chromium	0.15	0.06
pH	Within the range 6.0 to 9.0	

Subcategory 4
Retan-Wet Finish-Sides

Pollutant or Pollutant Property	NSPS Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	6.3	2.8
TSS	9.1	4.2
Oil & Grease	2.7	1.2
Total Chromium	0.16	0.06
pH	Within the range 6.0 to 9.0	

Subcategory 5
No Beamhouse

Pollutant or Pollutant Property	NSPS	
	Maximum for any one day	Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	5.3	2.4
TSS	7.7	3.5
Oil & Grease	2.2	1.0
Total Chromium	0.14	0.05
pH	Within the range 6.0 to 9.0	

Subcategory 6
Through-the-Blue

Pollutant or Pollutant Property	NSPS	
	Maximum for any one day	Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	2.0	0.88
TSS	2.8	1.3
Oil & Grease	0.8	0.4
Total Chromium	0.05	0.02
pH	Within the range 6.0 to 9.0	

Subcategory 7
Shearling

Pollutant or Pollutant Property	NSPS Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	13.2	5.9
TSS	19.1	8.7
Oil & Grease	5.6	2.5
Total Chromium	0.34	0.12
pH	Within the range 6.0 to 9.0	

Subcategory 8
Pigskin

Pollutant or Pollutant Property	NSPS Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	5.8	2.6
TSS	8.3	3.8
Oil & Grease	2.4	1.1
Total Chromium	0.15	0.05
pH	Within the range 6.0 to 9.0	

Subcategory 9
Retan-Wet Finish-Splits

Pollutant or Pollutant Property	BPT Limitations Maximum for any one day	 Maximum for monthly average
	kg/kkg (or lb/1000 lb) of raw material	
BOD_5	4.2	1.9
TSS	5.1	2.3
Oil & Grease	.5	0.66
Total Chromium	0.09	0.03
pH	Within the range 6.0 to 9.0	

SECTION XII

PRETREATMENT STANDARDS FOR EXISTING AND NEW SOURCES

A. GENERAL

Section 307(b) of the Clean Water Act of 1977 requires EPA to promulgate pretreatment standards for existing sources (PSES) that must be achieved within three years of promulgation, and Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect dischargers, like new direct dischargers, have the opportunity to incorporate the best available demonstrated technologies including process changes, in-plant control measures and end-of-pipe treatment.

Pretreatment standards for existing and new sources are designed to control the discharge of pollutants that pass through, interfere with, or are otherwise incompatible with the operation of a publicly owned treatment works (POTW). The Clean Water Act of 1977 requires pretreatment for pollutants that pass through POTWs in amounts that would violate direct discharger effluent limitations or interfere with the POTW's treatment process or chosen sludge disposal method. EPA has generally determined that there is pass through of pollutants if the percent of pollutants removed by a well-operated POTW achieving secondary treatment is less than the percent removed by the BAT model treatment system. The General Pretreatment Regulations, which served as the framework for the categorical pretreatment regulations, are found at 40 CFR Part 403 (43 FR 27736, June 26, 1978; 46 FR 9404, January 28, 1981).

B. PRIOR REGULATIONS

The Agency promulgated PSNS for the Leather Tanning and Finishing Point Source Category on April 9, 1974 (39 FR 12958). PSNS were equal to the standard set forth in 40 CFR Part 128 (the previous general pretreatment prohibitions which are now included in 40 CFR 403) with the exception that pretreatment standards for incompatible pollutants would be equal to NSPS.

EPA promulgated PSES for the Leather Tanning and Finishing Point Source Category on March 23, 1977 (42 FR 15696). These regulations established general pretreatment prohibitions and specific pH ranges for indirect dischargers.

As a result of the revisions to the Clean Water Act in 1977, the Agency has reassessed PSES and PSNS. On July 2, 1979 EPA proposed PSES and PSNS regulations. The pretreatment standards presented in this document supersede the previously published PSES and PSNS.

C. REGULATED POLLUTANTS

Categorical pretreatment standards are being established for new and existing sources, regulate sulfide and total chromium, and include specific pH ranges for each subcategory.

D. POLLUTANTS NOT REGULATED

Paragraph 8 of the modified Settlement Agreement, approved by the District Court for the District of Columbia on March 9, 1979 (12 ERC 1833), contains provisions authorizing the exclusion from regulation, in certain circumstances, of toxic pollutants and industry categories and subcategories.

On December 18, 1980, EPA submitted an affidavit explaining that the Agency decided not to regulate certain of the 129 toxic pollutants under the authority of Paragraph 8(a) (iii) of the modified Settlement Agreement. Since that time, the Agency acted to remove three organic compounds from the list of toxic pollutants. All three of these pollutants were among those excluded from regulation because "they are not detectable by Section 304(h) analytical methods or other state-of-the-art methods."

The Agency has gathered additional data since these regulations were proposed, as described previously in the Methodology and Data Gathering Efforts section of this Document. Based upon analysis of this additional data, together with the data used in the proposal, the Agency is revising its exclusion of pollutants.

Among indirect dischargers, 54 of the remaining 125 toxic pollutants are excluded from regulation because there is no available pretreatment technology which is economically achievable that will remove these pollutants prior to discharge to POTWs. As noted in Chapter IX describing BAT, 71 toxic pollutants are excluded from regulation under the authority of Paragraph 8(a) (iii) of the modified Settlement Agreement because "they are not detectable by Section 304(h) analytical methods or other state-of-the-art methods." Pretreatment standards for existing sources (PSES) and new sources (PSNS) are included in these regulations to control the remaining toxic pollutant, chromium.

E. IDENTIFICATION OF PRETREATMENT STANDARDS FOR EXISTING AND NEW SOURCES

Under the Clean Water Act and the General Pretreatment Regulations, pretreatment standards for indirect dischargers are required if there is pass through or interference at the POTW. The Agency has determined that pretreatment standards are necessary for the leather tanning industry because trivalent chromium passes through POTWs and because sulfide can interfere with POTWs. Where chromium is removed and does not pass through the POTW, removal credits may be available to reduce the need for pretreatment. POTWs also may certify to EPA that the sulfide pretreatment standards should not apply to specified indirect dischargers if site specific evaluation indicates that sulfide interference is not a problem. In addition, all indirect dischargers are subject to the general pretreatment regulations found at 40 CFR Part 403.

F. PRETREATMENT STANDARDS FOR EXISTING SOURCES (PSES)

1. Manufacturing Processes, Size, Age, and Location of Facilities

The raw materials used and processes employed in different size tanneries within each subcategory are basically similar. Furthermore, the factors of size, age, and location employed do not affect the pretreatment control technology used. Hence, these factors were not directly involved in determining the pretreatment standard. The location of facilities was a factor to be considered regarding the availability of adjacent land and interior plant space for installation of pretreatment technology, as described below.

2. 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/or charges for the proportional share of total O&M costs paid to POTWs. Further discussion of these practices follows in 5. Engineering Aspects of Pretreatment Technology and Relationship to Publicly Owned Treatment Works.

3. Rationale for the Selection of PSES

As noted in the June 2, 1982 notice of availability (47 FR 23962-23963), EPA reviewed the entire basis for the proposed PSES concentration limitations for ammonia, sulfide, and chromium. As part of that review and in response to comments, EPA developed two additional technology options (TECHNOLOGY OPTIONS I and II) which are less costly and require less space for installation than the technology option (TECHNOLOGY OPTION III) which served as the basis for the proposed PSES regulations. All three of these technology options were described in Section VII of this Document.

Ammonia

In-process substitution of Epsom salts for ammonia in the deliming process served as the basis for the proposed pretreatment standard for ammonia. In their comments on the proposed regulations, industry supplied data and information on side-by-side pilot processing tests with and without in-process substitution. Based on that data and information, the Agency agrees with the industry that the substitution of epsom salts for ammonia may adversely affect finished leather quality and increase costs because of its operational difficulty. There are no other available in-plant or end-of-pipe pretreatment technologies which afford substantial removal of ammonia and which are economically achievable. Accordingly, EPA has decided that pretreatment standards for ammonia will not be promulgated.

Sulfide

EPA proposed (44 FR 38756 - 38757) a pretreatment standard for sulfide of "zero discharge" (not detectable by the 304(h) analytical method) based upon catalytic oxidation of segregated unhairing wastewaters. The standard would have been applicable to all subcategories. Sulfides were controlled by PSES because of the potential for interference resulting from release of massive quantities of hydrogen sulfide gas in sewers, headworks, and sludge management facilities at POTWs. Fatalities attributable to release of hydrogen sulfide gas have been documented. In response to the proposal, the industry commented that the standard (0.0 mg/l) was not achievable, and that the standard would not improve treatment efficiency or water quality.

The June 2, 1982 notice of availability (47 FR 23963) indicated that the severity of these problems varies by pH and time (slug loading), and by POTW (comingling of varying quantities of municipal and industrial wastewaters in collection sewers). Review of the supplemented data base regarding the performance of catalytic sulfide oxidation technology revealed that a long term average effluent concentration of 9 mg/l could be achieved in combined discharges. A maximum day variability factor of 2.7 was developed from the data, resulting in a maximum day limitation of 24 mg/l. Only a maximum day limitation would be effective in controlling the most severe hazard posed by hydrogen sulfide which occurs during rapid fluctuations in pH caused by unequalized slug loading. The maximum day concentration reduces the potential for interference problems to the maximum extent feasible by available technology. The maximum day sulfide pretreatment standard (24 mg/l) is applicable to plants in subcategories (nos. 1, 2, 3, 6, and 8) which incorporate sulfide unhairing operations and discharge high concentrations of sulfides. Sulfides are discharged by plants in the remaining subcategories, but at concentrations typical of domestic sewage, thus not imposing any additional interference or operational costs than would be experienced without these wastewaters. Pretreatment Technology OPTIONS I, II, and III all include sulfide control for these five subcategories.

EPA is promulgating a categorical sulfide pretreatment standard (maximum day limitation-24 mg/l) applicable to subcategories with unhairing operations (nos. 1, 2, 3, 6, and 8) based on catalytic sulfide oxidation technology in order to prevent interferences with the operation of POTWs. Hydrogen sulfide at POTWs presents serious fatal hazards to life. Occurrences of hydrogen sulfide related deaths have been noted at POTWs receiving tannery wastewater. However, because the degree of interference will vary, EPA is adopting a procedure which would allow affected POTWs to certify that uncontrolled discharge of sulfide does not interfere with their particular treatment works. The POTW would make this finding based upon an evaluation of a nonexclusive list of criteria set out in the regulations. After making these findings the POTW would be required to allow for public comment by notice in a local newspaper, and by public hearing if requested. The POTW would then forward its findings and results of public comments and certify in writing to the Regional Water Management Division Director that local circumstances do not require a categorical pretreatment standard for sulfide. The Agency will review these certifications for adequacy of consideration by POTWs of all relevant factors and will publish in the Federal Register a notice that lists those indirect dischargers to which the sulfide pretreatment does not apply. The regulations also include a procedure with appropriate deadlines for POTWs to follow for invoking this waiver.

The Agency recognizes that it is virtually impossible to cover all possible combinations of factors which could occur at individual POTWs. Therefore, the Agency has elected to include in the regulations a list of general factors which, at a minimum, must be considered by POTWs when certifying that there is no interference caused by sulfide in their treatment works. These factors are:

1. The presence and characteristics of other industrial wastewaters which can change sulfide concentrations, pH, or both.

   POTWs that serve few if any industrial indirect dischargers, other than tanneries which employ unhairing operations, have little or no wastewater to contribute either to sulfide concentration changes, or to pH changes, especially decreases in pH which tend to liberate hydrogen sulfide gas.

   POTWs that have significant industrial wastewater contributions, especially wastewaters that are not equalized and may include slug loads or consistently low pH wastewater, may experience substantial difficulty in maintaining very high concentrations of sulfide in solution and are likely to have interference.

2. The characteristics of the sewer/interceptor collection system which either minimize or enhance opportunities for release of hydrogen sulfide gas.

   Leather tanneries with unhairing operations connected to POTWs by short pressure mains will experience little or no difficulty in maintaining sulfides in alkaline solution during wastewater transit to the POTW headworks. In this instance, the pressurized sewer system contributes to maintaining dissolved sulfides, thus decreasing the likelihood of interference.

   POTWs with long gravity interceptor sewers, with "dead spots" and other discontinuities in hydraulic profile probably will have difficulty maintaining sulfides in solution, and interference is likely. In this case, reducing the sulfide concentration entering the sewer by sulfide pretreatment will minimize the potential for release of substantial quantities of hydrogen sulfide gas during wastewater transit to the POTW.

3. The characteristics of the receiving POTWs headworks, preliminary and primary treatment systems, and sludge management facilities which either minimize or enhance opportunities for release of hydrogen sulfide gas.

   POTWs with facilities that have very short hydraulic detention times and are enclosed in well ventilated buildings have reduced opportunities for hazards from hydrogen sulfide gas.

POTWs with facilities that are enclosed in very confined and poorly ventilated buildings and have long hydraulic detention times have enhanced opportunities for release of hydrogen sulfide gas and substantial risk to human life.

4. The history of any sulfide related interference problems at affected POTWs is of major importance in determining the need for a pretreatment standard for sulfide.

   Five years is the suggested minimum period of historical review of any interference incidents as they relate to the presence of elevated sulfide concentrations from leather tanneries with unhairing operations, and to the first three factors relating to the POTW noted above.

The Agency considered relying solely on the prohibited discharge standards (Section 403.5) of the General Pretreatment Regulations in place of a categorical pretreatment standard for sulfide. However, the Agency rejected this approach because of the special interference problems presented by the very high concentrations of sulfides in the unhairing wastewaters generated by this industry, the very serious nature of the problem, and the availability of control technology.

The Agency has included in this regulation a sulfide analytical method different from that promulgated under Section 304(h) of the Act. This was necessary because the 304(h) sulfide analytical method was subject to analytical interferences. The method included in this regulation is that utilized by the Society of Leather Trades' Chemists, method SLM 4/2. The sulfide pretreatment standard is based upon this method.

Chromium

The proposed regulation (44 FR 38756-57) included a pretreatment standard (concentration limitation) for chromium (total), 2 mg/l, applicable to all plants and based upon coagulation-sedimentation of combined wastewater streams. The June 2, 1982 notice of availability (47 FR 23963) reasserted the Agency's concern for pass through of chromium (trivalent) based on the performance of well operated POTWs. For the cities studied, chromium removal by well operated POTWs achieving secondary treatment averaged 65 percent. (See the EPA report entitled <u>Determining National Removal Credits for Selected Pollutants for Publicly Owned Treatment Works</u>, EPA 440/2-82-008, September 1982). This is substantially lower than the removals required by BAT level treatment (95-98 percent), and therefore the Agency indicated that it was considering a categorical pretreatment standard for chromium. The Agency indicated that its basis for the standard was pretreatment TECHNOLOGY OPTION II, which included coagulation-sedimentation of segregated and equalized tanyard and retan-wet finish wastewaters. It also was noted that from 5-10 percent of the plants might not have adequate interior space or adjacent land to install this technology.

The Agency has decided to promulgate a categorical pretreatment standard for chromium (total). Categorical pretreatment standards are necessary in this case because the percent of chromium removed by well operated POTWs achieving secondary treatment requirements is less than required by BAT for direct dischargers. This definition of pass through satisfies two competing objectives set by Congress: 1) that standards for indirect dischargers be analogous to standards for direct dischargers, while, at the same time, 2) that the treatment capability and performance of the POTW be recognized and taken into account in regulating the discharge of pollutants from indirect dischargers. The Agency compares percent removal rather than the mass or concentration of pollutants discharged from the POTW because the former would not take into account the mass of pollutants discharged to the POTW from non-industrial sources and the latter would credit the indirect discharger with the dilution of the pollutants in the POTW effluent to lower concentrations due to the addition of large amounts of non-industrial wastewater.

EPA has decided to regulate trivalent chromium in these pretreatment standards because the total quantity of trivalent chromium generated by this industry is nationally significant (5.7 million lbs/yr or 2590 kkg/yr) when compared to other industrial categories, such as the metal finishing industry (8.9 million lbs/yr or 4040 kkg/yr) and the inorganic chemicals industry - chromium pigments subcategory (1.4 million lbs/yr or 635 kkg/yr), where chromium also is regulated. Information in the record indicates that while trivalent chromium is not as toxic as hexavalent chromium from the human health standpoint, trivalent chromium exhibits chronic aquatic toxicity (24 hr toxicity value approximately 50 μg/l), as confirmed by ongoing EPA studies to develop a water quality criteria for trivalent chromium. Therefore, both forms of chromium (trivalent and hexavalent) are environmentally significant and are appropriate to be regulated under the Clean Water Act.

The basis for the chromium pretreatment standard is TECHNOLOGY OPTION II with two different concentration limitations depending upon subcategory. The achievable long term effluent concentration for chromium (total) is 8 mg/l for those subcategories (nos. 4, 5, 7, and 9) which do not have beamhouse operations. The achievable long term effluent concentration for chromium (total) is 5 mg/l for those subcategories (nos. 1, 2, 3, 6, and 8) which do have beamhouse operations. The basis for these concentrations is discussed in Section VII of this Development Document.

EPA's economic analysis projected that the cost of chromium control would result in the potential closure of 4-5 of 6 small plants in subcategory 1, 2 of 3 small plants in subcategory 3, and 4-5 of 9 small plants in subcategory 9. No less costly chromium control technology options or less stringent chromium standards could be identified for these plants. Therefore, these PSES chromium standards do not apply to small plants which process less than 275 hides/day in subcategory 1, less than 350 hides/day in subcategory 3, and less than 3600 splits/day in subcategory 9. However, small plants in subcategories 1 and 3 would still be subject to sulfide pretreatment standards, and small plants in subcategories 1, 3, and 9 would still be required to comply with general pretreatment regulations. Further discussion of the results of this analysis are presented in the economic impact report.

Constraints on the availability of interior plant space and adjacent land were considered by EPA. As noted in Section II of this Document, the Agency obtained information on 64 indirect dischargers regarding availability of interior plant space and adjacent land. The Agency projected, on the basis of this information, that 5-10 percent of all indirect dischargers may not have adequate space to install chromium pretreatment technology included in TECHNOLOGY OPTION II. This tabulation can be found in the technical record. The Agency attempted to develop further separations within subcategories or alternative effluent limitations to take this factor into account. The Agency specifically solicited comment in the June 2, 1982 notice of availability as to whether any plants would have inadequate space to install the recommended chromium control technology. However, EPA did not receive and does not have the detailed information and data needed to define the total population of indirect discharging plants that do not have adequate space to install the model chromium treatment technology. Therefore, the Agency believes that the more appropriate approach is to grant variances from the chromium pretreatment standard based upon a specific demonstration by the indirect discharger, as provided by the General Pretreatment Regulations (Section 403.13), of the fundamentally different factor (FDF) of inadequate interior plant space or adjacent land. Such submissions would have to conform to the requirements of Section 403.13, and include at a minimum:

1) detailed information and data on interior plant layout and adjacent land (diagrams noting all areas with current uses and dimensions); 2) details on the least costly pretreatment system including all unit processes to be used to meet the chromium standard and the area required, as well as pertinent details of any pretreatment facilities already in place; 3) the itemized cost of each of the additional treatment system unit processes which must be added, and the cost of any additional land which must be obtained, or other plant modifications that would be necessary to accommodate the additional facilities; 4) process flow diagram and production rates; and 5) the effluent limitations which could be achieved if the discharger were to spend an amount equal to the Agency's model pretreatment TECHNOLOGY OPTION II (that portion not required to achieve the sulfide pretreatment standard).

In reviewing the information and data submitted by plants in support of their requests for FDF variances, it must be noted that the Agency considers reallocation of that portion of available interior plant space and adjacent land (including parking lots) necessary to install pretreatment technology to be an appropriate requirement. Reallocation of all or a portion of parking lots for treatment facilities has been implemented by a few plants in this industry and by plants in other industrial categories.

Section 403.7 of the General Pretreatment Regulations provides for granting of removal credits at POTWs. In cases where POTW facilities have been specifically designed to treat leather tanning and finishing wastewaters, it is likely that the POTW would be able to grant a credit for chromium removal to the indirect discharger. Where the POTW achieves removals comparable to BAT, credits probably would eliminate the need for pretreatment.

4. Methodology Used to Develop PSES Effluent Limitations

Section VII of this Development Document describes the performance of sulfide and chromium pretreatment technologies. As described in Section VII and above, the performance of catalytic oxidation technology together with the carryover of sulfide in tanyard and retan-wet finish wastewater results in a sulfide concentration of 9 mg/l in total sewer discharge. Application of a variability factor of 2.7 results in a maximum concentration for any one day of 24 mg/l. The achievable long term average concentrations for total chromium are 5 mg/l for subcategories 1,2,3,6 and 8, and 8 mg/l for subcategories 4,5,7 and 9. The variability factor for chromium is 2.4 for the maximum value for any one day. The variability factor for the maximum monthly average assumes 8 sampling days per calender month, and is 1.5. Table XII-1 lists the PSES limitations for the nine subcategories.

TABLE XII-1

PRETREATMENT STANDARDS FOR EXISTING SOURCES

Subcategory 1
Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Sulfide	24	-
Total Chromium	12	8
pH	Within the range 7.0 to 10.0	

The total chromium standards do not apply to plants processing less than 275 hides/day.

Subcategory 2
Hair Save/Chrome Tan/Retan-wet Finish

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Sulfide	24	-
Total Chromium	12	8
pH	Within the range 7.0 to 10.0	

Subcategory 3
Hair Save or Pulp/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Sulfide	24	-
Total Chromium	12	8
pH	Within the range 7.0 to 10.0	

The total chromium standards do not apply to plants processing less than 350 hides/day.

Subcategory 4
Retan-Wet Finish-Sides

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Total Chromium	19	12
pH	Within the range 6.0 to 10.0	

Subcategory 5
No Beamhouse

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Total Chromium	19	12
pH	Within the range 6.0 to 10.0	

Subcategory 6
Through-the-Blue

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Sulfide	24	-
Total Chromium	12	8
pH	Within the range 7.0 to 10.0	

Subcategory 7
Shearling

Pollutant or Pollutant Property	PSES Maximum for any one day	Maximum for monthly average
	milligrams per liter (mg/l)	
Total Chromium	19	12
pH	Within the range 6.0 to 10.0	

Subcategory 8
Pigskin

Pollutant or Pollutant Property	PSES Maximum for any one day	Maximum for monthly average
	milligrams per liter (mg/l)	
Sulfide	24	-
Total Chromium	12	8
pH	Within the range 7.0 to 10.0	

Subcategory 9
Retan-Wet Finish-Splits

Pollutant or Pollutant Property	PSES Maximum for any one day	 Maximum for monthly average
	milligrams per liter (mg/l)	
Total Chromium	19	12
pH	Within the range 6.0 to 10.0	

The total chromium standards do not apply to plants processing less than 3600 splits/day.

5. 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 categorical pretreatment standards which limit chromium, sulfide, and pH ranges for each subcategory.

General Engineering Considerations - Equalization (at least 24 hours) has been an extremely important technology -- 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 systems over weekends, 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.

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 of approximately 0.040 inches to remove easily separated scraps, fibers, and hair) was found to be lacking (see discussion of screening in Section VII) at most plants in the industry. If fine screening is not accomplished, pipes could 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.

The Agency believes that the cost of pretreatment technology can be minimized by first reducing to the maximum extent feasible the volume of wastewater to be treated. For this reason, the Agency has utilized reduced water use ratios (see Section V of the Development Document) achieved by existing sources only in calculating the costs of PSES. This reduction can be achieved by implementing the following suggested 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 flow meters 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 pumps.

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 by-product.

8. Reuse or recover active chemicals from waste streams such as the sulfide-containing stream, pickling solution, and chromium tanning solution.

9. Examine tanning formulas to determine if floats can be reduced. Use of hide processors and other specially designated vessels afford the opportunity for 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 also may be economically attractive through the reduction of municipal water and sewer use charges resulting from lower flows and waste loadings after pretreatment facilities have been installed.

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 economies 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.

Concentration Based Standards - It must be noted that the Agency has promulgated concentration based pretreatment standards for sulfide and chromium. The amount of water used at any plant is not germane to the achievability of these standards. Therefore, indirect dischargers will have added flexibility because water use reduction is not necessary to achieve these standards.

Compliance Date - The Agency has considered the time for compliance for PSES. Few if any leather tanning and finishing plants have installed and are properly operating the treatment technology for PSES. Additionally, many plants in this and other industries will be installing the treatment equipment suggested as model technologies for this regulation at about the same time, and this may result in delays in engineering, ordering, installing, and operating this equipment. For these reasons, the Agency has decided to set the PSES compliance date at three years after promulgation of this regulation.

G. COST AND EFFLUENT REDUCTION BENEFITS

Pretreatment Technology OPTION II includes both sulfide and chromium control, and serves as the basis for PSES. Investment to implement the promulgated pretreatment standards are estimated to be as high as $159 million, with an annualized cost of $45 million if all 141 plants covered by these standards are required to comply. These costs could increase the cost of production by an average of 0.5 to 3.3 percent over the life of the investment. This regulation may result in the closure of up to 1 to 3 plants causing approximately 100 to 305 people to become unemployed. This is approximately 1 to 2 percent of the plants and 0.5 to 1.6 percent of the employees in the industry. These economic effects take into account that small plants in the retan-wet finish, splits subcategory (9), small plants in the hair save or pulp, nonchrome tan, retan-wet finish subcategory (3), and extra-small plants in the hair pulp, chromium tan, retan-wet finish subcategory (1) are not covered in the chromium pretreatment standards. Coverage of these regulations was limited in order to avoid an unacceptably adverse economic impact on those small segments of industry. The 18 small plants in subcategories 1, 3, and 9 that have been exempted from the chromium categorical pretreatment standards would have incurred an additional investment cost of $9.4 million, and total annual costs of $2.4 million. EPA estimates that if these plants were subject to the chromium pretreatment standards, 10 to 12 of the 18 small plants may have closed rather than install treatment technology. Accordingly, the chromium pretreatment standards do not apply to these small plants. No less costly technology to control chromium could be identified for these plants. However, all of these plants remain subject to general pretreatment regulations, and the nine small plants in subcategies 1 and 3 may still be required to comply with the sulfide pretreatment standards. The cost of PSES will remove a total mass of up to 5.2 million pounds per year (2360 kkg/yr) of trivalent chromium, and a total mass of up to 5.3 million pounds per year (2410 kkg/yr) of sulfide.

H. NONWATER QUALITY ENVIRONMENTAL IMPACTS

Implementation of PSES is not expected to have any significant air pollution impacts. In fact, sulfide control will reduce substantially odor problems at POTWs. Existing sources will generate sludges from wastewater pretreatment facilities which must be disposed. Implementation of TECHNOLOGY OPTION II will generate 116,000 kkg (metric tons) per year (wet basis, 20 percent solids) of sludge. The Agency has assumed that these sludges will disposed in available off-site landfills. The cost of off-site landfill disposal was assumed to be $20 per wet ton, or $100 per dry ton (20 percent solids). Compliance with these regulations will not require evaporative cooling and, therefore, will create no additional consumptive water loss. Implementation of TECHNOLOGY OPTION II will require 53 million kwh/yr of electric power. This represents an increase of approximately 1 percent above power usage for production to achieve PSES.

I. 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.

J. RATIONALE FOR THE SELECTION OF PSNS

The Agency proposed pretreatment standards for new sources (PSNS) which were based on the same technology required for PSES, plus physical-chemical treatment. In the June 2, 1982 notice of availability (47 FR 23963), EPA indicated that it was considering establishing PSNS based on the same pretreatment technology option chosen for existing sources (PSES). The Agency has decided to adopt TECHNOLOGY OPTION II and the same concentration based pretreatment standards for sulfide and chromium (total) as promulgated for PSES. As noted in the discussion of PSES, reduced water use is not necessary to achieve these concentration based standards.

It must be noted that because new sources can select among the most efficient processing methods and the most advantageous sites at which to locate, variances based upon fundamentally different factors (FDF) (Section 403.13) are not available. However, if a POTW certifies that the discharge of a new facility (operating in any of subcategories 1, 2, 3, 6, or 8) would not interfere with its treatment works, the sulfide pretreatment standards would not apply as noted for PSES. EPA does not consider the sulfide waiver to be an FDF variance because the waiver relates to conditions at the POTW, not the new source.

SECTION XIII

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SECTION XIV

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SECTION XV

APPENDICES

APPENDIX A

COSTS OF TREATMENT AND CONTROL SYSTEMS

A. PURPOSE OF COST DATA

In Section VII, different treatment options were developed and discussed for BAT, PSES, NSPS, and PSNS. Also BPT technology was identified. The treatment options that were developed for each of the aforementioned regulations (or standards) represented a higher degree of pollution abatement. The costs increase with each increase in pollutant removal. The cost data presented in this appendix are intended to illustrate the economic impact that each level of treatment will have on the industry. These data were used to determine the maximum level economically achievable of treatment or pollution abatement for the Leather Tanning and Finishing Industry.

B. GENERAL APPROACH

Treatment options described earlier were formulated according to subcategory (e.g., beamhouse or no beamhouse), the type of discharge (indirect or direct), and the degree of treatment or effluent limitation desired. These treatment options have certain unit processes in common. Moreover, most of the treatment options are the result of unit processes being added in building-block fashion to achieve higher pollutant removals.

In developing costs for the various treatment options, all the unit processes included in the various treatment options were identified. Design criteria were established for each unit process. Flow was determined to be the primary factor for estimating the cost for most of the unit processes. The organic loading (BOD_5) was the most significant design parameter for the biological treatment system (extended aeration activated sludge), while the solids concentration (TSS) was the most significant design parameter for sludge dewatering and disposal. Therefore, once the flow and raw waste characteristics of a tannery were determined, the unit process(es) could be designed. Since the characteristics of each subcategory are different, no two designs are the same. Once the design of the unit process is established, the costs can be calculated from the cost curve for that unit process.

The procedure for formulating the unit process cost curves was to select several tannery wastewater loadings that would be representative of the industry. Based on available data, wastewater flows of 35,000 gal/day, 105,000 gal/day, 420,000 gal/day and 1,400,000 gal/day were selected for model tanneries. Conceptual drawings, layouts, process piping, diagrams, and equipment requirements were developed for each of these four facilities. These schematics were used to determine cost estimates for sitework, concrete, building construction, electrical, process piping, and process equipment for each of the unit processes.

Manufacturers supplied cost estimates for different pieces of equipment, and construction component costs were calculated by applying unit costs to quantity estimates. Expenditures for engineering and an amount for contingencies were included in the total capital cost for each unit process. Utilizing the four cost estimates for each of the unit processes, cost curves were plotted for the full range of tannery wastewater flows.

Similarly, operation and maintenance cost curves were developed for each of the unit processes at the selected wastewater flows. The annual operation and maintenance costs included operation (labor), electrical, chemical, and maintenance costs.

C. COST REFERENCES AND RATIONALE

Capital Costs

Estimates of the capital expenditures required for the construction and installation of applicable treatment systems were developed using the unit process approach. The following unit processes have been assessed:

- stream segregation;
- sulfide oxidation (with and without neutralization facilities);
- flue gas carbonation;
- flow equalization (one and two-days detention time);
- coagulation - sedimentation;
- activated sludge (alone and with nitrification as well as powdered activated carbon addition);
- multimedia filtration;
- sludge dewatering;
- effluent monitoring;
- neutralization facilities; and
- tanyard wastewater screening.

For each of the model plants, conceptual drawings were developed for each of the above unit processes. These drawings included building layout, outside equipment locations, and process piping. Purchased equipment and custom built structures were sized according to the design criteria presented in Section E of this appendix. From the conceptual drawings, quantity estimates were developed for each of the unit processes at the model plant flow rates. Construction cost estimates were categorized as follows:

- sitework;
- concrete;
- building construction (including heating and ventilating);
- electrical;
- process piping; and
- process equipment.

Unit costs were based on the 1980 Means Unit Cost and Cost Data Guides; 1980 Richardson Rapid Construction; Cost Estimating Guide; and recent contractors' bid prices. All cost curves are indexed with the Engineering News Record Construction Cost Index (ENRCCI) of 3142 for the first quarter of 1980. However, all cost summary tables presented in this appendix have been updated to first quarter of 1982 (ENRCCI = 3730).

Cost estimates for each of the unit processes were developed independently (i.e., separate tanks, buildings, and equipment were used for each unit process). In some cases, installing equipment from two or more different unit processes in a central building, or using common walls between tanks of different unit processes, would have resulted in a lower capital cost. However, to perform a cost analysis in which unit processes can be either added on or subtracted in a building-block fashion, each unit process cost was estimated as being complete and separate from the others.

Building construction costs were included to house equipment such as pumps, motors, blowers, chemical feed systems, controls, etc. Building costs were not included to house items like flow equalization tanks, clarifiers, or aeration tanks because 1) these units are being operated in northern climates without freezing, and, 2) these units are being operated in residential urban areas without odor related problems.

The following basic assumptions were made concerning on-site construction conditions:

- dewatering for construction was not required;
- rock excavation was not required;
- piling was not required for excavation;
- general soil conditions consisted of coarse textured soils; and
- existing piping to existing facilities was of adequate size and structurally sound.

The cost of land was not included in the capital cost. Since the cost estimating procedure assumed that an engineer would evaluate and design the treatment systems, an engineering fee equal to 10 percent of the construction cost was included. In addition, a contingency factor, also equal to 10 percent of the construction cost, was included in the total cost to account for the uncertainties inherent in capital cost estimating. It is assumed that construction of the facilities would be done by a contractor and not tannery labor. In most cases, if tannery labor was used there would be a reduction in costs.

Using the above procedure, a total capital cost was developed for each of the unit processes with respect to the four model plant sizes. The four capital costs for each unit process provided the basis for the development of the capital cost curve. In all cases, except sludge dewatering and the activated sludge system curves, the average daily tannery flow is defined as the daily average wastewater flow from the tannery for a five-day work week. Sludge dewatering is based on the weight of the dry solids processed each day. Sludge dewatering is discussed in Section E. The activated sludge curves are explained in further detail in Section E of this appendix.

Operation and Maintenance Costs

Operation and maintenance costs were developed for each technology based on the average daily wastewater flow from the tannery. These costs were calculated using the same four model plants which were used for the capital costs. Three operation and maintenance cost curves were computed for each of the unit processes. Each curve represents a different level of utilization of tannery facilities and a corresponding level of wastewater flow. The utilization levels selected were 50, 75, and 100 percent.

Included in the annual operation and maintenance costs were the following components:

- operation (labor) costs;
- energy costs;
- chemical costs; and
- maintenance costs.

Operation costs were calculated by estimating the number of manhours required: 1) to inspect equipment; 2) to perform activities associated with chemical feed systems; 3) for process monitoring; and 4) to perform additional activities not associated with equipment maintenance. Manpower for operation was assumed to cost $80 per day for a chief operator (or supervisor) and $64 per day for a laborer. These costs included fringe benefits. Total manpower requirements for a complete upgraded biological process with multimedia filtration treatment plant (direct discharger) were estimated for each of the four model plants. The total manhours per day were subsequently broken down and assigned to each of the unit processes. The amount of time assigned to each process depended on: 1) the complexity of the process; 2) the presence of chemical feed systems, if any; 3) the time required for process monitoring or operation; and 4) general determination of the amount of actual time an operator or laborer would have to spend at the process unit.

Operation was based on a five-day work week. In using a five-day week, it was taken into consideration that a small amount of time might be required for short inspections of the unit processes during the weekend. The majority of the tanneries would operate the treatment facility with one eight-hour shift per day. The larger plants would require a twelve-hour working day, primarily for sludge dewatering. Energy costs included electrical requirements for all equipment, such as pumps, blowers, mixers, and motors. Electricity was assumed to cost $0.05/kwh. Chemical costs were based on the average use of chemicals required for treatment.

The chemicals required for the various processes and the associated costs used to determine annual chemical costs are shown below.

Lime		
Hydrated Lime ($Ca(OH)_2$)	$ 0.05/lb	($0.11/kg)
Pebble Quicklime (CaO)	$ 0.03/lb	($0.07/kg)
Anionic Polymer	$ 2.00/lb	($4.41/kg)
Powdered Activated Carbon (PAC)		
- less than 100 lb/day	$ 0.53/lb	($1.17/kg)
- more than 100 lb/day	$ 0.43/lb	($0.95/kg)
Caustic ($NaOH$)	$ 0.085/lb	($0.19/kg)
Phosphoric Acid (H_3PO_4)	$ 2.00/lb	($4.41/kg)
Ferric Chloride ($FeCl_3$)	$ 0.075/lb	($0.17/kg)
Manganese Sulfate ($MnSO_4$)	$ 0.42/lb	($0.93/kg)

Annual maintenance costs included expenditures for routine maintenance, replacement of worn parts, lubricants, and equipment replacement. These costs were estimated to be approximately one to three percent of the total equipment costs for each of the unit processes.

D. COSTS CONSIDERATIONS FOR RCRA REQUIREMENTS

The cost of disposal of solids from the treatment facility has been estimated at $17.00 per ton of sludge (1980 dollars). Tannery solids and sludge are not listed as a hazardous waste under RCRA.

E. DEFINITIONS OF LEVELS OF TREATMENT AND CONTROL COST DEVELOPMENT

Based on the treatment technology development presented previously, treatment costs have been developed for stream segregation, sulfide oxidation, flue gas carbonation, flow equalization, coagulation-sedimentation, activated sludge biological treatment, multimedia filtration, as well as solids handling and disposal. Except for solids handling and disposal, cost estimates for the implementation of these unit processes were established for wastewater flows and pollutant concentrations. By determining the wasteloads and flow from a specific subcategory (these data are provided in Section V of this document) or tannery, the cost of the unit process is calculated from the cost curves. For each unit process, design criteria have been established to formulate the basis for the development of capital costs.

Preliminary Treatment - Stream Segregation

Because beamhouse wastewater differs substantially from tanyard wastewater, these streams were separated to provide specific treatment. The capital costs for implementing stream segregation were based on the design criteria listed in Table A-1. The capital costs are shown in Figure A-1, the operation and maintenance costs in Figure A-2. The components of a typical system are shown schematically on Figure A-3.

Estimates for stream segregation include the following items:

- Additional piping within beamhouse for wastewater collection;
- A wet well, pumps, and force main for transporting beamhouse wastewater to the screen;
- Static tangential screen;
- A building to house the screen; and
- Expenditures for water and electricity.

In a typical tannery with a beamhouse and tanyard, the wastewater flow from the beamhouse is approximately 40 percent of the total flow. In most cases, however, this flow occurs over a short period of time. For model plants A and B, it was assumed that the beamhouse flow would occur in a four-hour period, and for plants C and D, in an eight-hour period. Each of the two pumps in the beamhouse pumping station is individually capable of pumping the entire flow, allowing for 100 percent standby capacity. Below-ground wet wells with submersible pumps were selected because they require minimal space and are less expensive.

The amount of interior piping required for the beamhouse and the length of the force main from the beamhouse to the building housing the screen will vary from tannery to tannery. The lengths assumed for the model plants are shown on Table A-1. Solids screened from wastestreams in plants A and B would be removed manually and loaded into a portable receptacle. For plants C and D, the solids would be transported by conveyor belts to an outside receptacle.

The estimated operation and maintenance costs include expenditures for solids removal, power for the pumps, and maintenance for the pumps and screen. It was assumed that this system would operate only when the tannery operates, about 260 days per year.

Preliminary Treatment - Sulfide Oxidation

This process is useful only in treating wastewater from the beamhouse. Sulfide can be oxidized in an aerated tank to which a catalyst, usually manganese sulfate ($MnSO_4$) has been added. Two tanks (each about 60 percent of expected flow) have been recommended for plants C and D so that treatment can be staggered between tanks. The capital costs for implementing sulfide oxidation are based on the design criteria listed in Table A-2. The capital costs are shown on Figure A-4, the operation and maintenance costs on Figure A-5. The components of a typical system are shown schematically on Figure A-6.

Estimates for sulfide oxidation include the following items:

- A concrete aeration tank(s) and building where effluent pumps will be situated and manganese sulfate stored;
- Floating mechanical aerator(s) and effluent pumps;
- Water and electricity; and
- Neutralization facilities (if required).

The estimated pollutant removals are discussed in Section VII.

Batch treatment was selected because discharges from the beamhouse are intermittent. In larger tanneries, the discharge of wastewater from the beamhouse usually lasts longer than in smaller tanneries. The detention time in the aeration tank and the rate at which manganese sulfate is to be fed into the system were determined after data from tanneries currently operating sulfide oxidation systems were reviewed. Literature sources were also consulted.

The amount of sulfuric acid (H_2SO_4) required to lower the pH of the wastes in the sulfide oxidation tank to nine was based on results from sulfuric acid titration of actual beamhouse wastes. It has been assumed that sulfuric acid will be pumped to the tank, instead of fed manually, because of the hazards involved with handling sulfuric acid.

The operation and maintenance costs for sulfide oxidation include allowances for chemical costs, electrical costs, labor for manganese sulfate addition, and maintenance for aerator(s) and pumps. It was assumed that sulfide oxidation would be performed only when the tannery is operating, about 260 days per year.

Preliminary Treatment - Flue Gas Carbonation

This process is useful only in treating wastewater from the beamhouse and is accomplished by sparging the emissions from a fossil fuel boiler through the beamhouse wastewater. Carbon dioxide (CO_2) contained in the stack gas (flue gas) lowers the pH in the beamhouse wastewater by neutralizing the residual caustic alkalinity from the hair removal process. This allows the proteins to flocculate and settle. The estimated costs for implementing flue gas carbonation are based on the design criteria listed in Table A-3. The capital costs are shown on Figure A-7, the operation and maintenance costs on Figure A-8. The components of a typical system are shown schematically on Figure A-9.

Estimates for flue gas carbonation include the following items:

- A concrete tank(s) and building to house the effluent and sludge pumps;
- Effluent and sludge pumps;
- Flue gas blower, piping from stack to carbonation tank, and perforated piping and supports within tank; and
- Water and electricity.

The estimated pollutant removals are discussed in Section VII.

Batch treatment was selected because discharges from the beamhouse are intermittent. Based on a literature search, approximately 20,000 pounds (9,072 kg) of carbon dioxide (CO_2) would be required to neutralize the residual caustic alkalinity remaining after beaming operations and to reduce to seven the pH of one million gallons (3.7854×10^3 m^3) of beamhouse wastes. For plants A and B, one carbonation tank was used. For the larger plants, C and D, two tanks were recommended so that treatment could be staggered. CPVC pipe was used for the flue gas distribution because of its ability to withstand the high temperature of the gas. The blower was lined with Type 316 stainless steel because of the sulfur content and corrosiveness of the flue gas. The volume of sludge produced by flue gas carbonation depends upon the characteristics of a particular wastestream. The use of flue gas carbonation also has an influence on the quantities of sludge generated from the coagulation-sedimentation and activated sludge processes. The volume of sludge from the flue gas carbonation process can be calculated by using Table A-14.

The operation and maintenance costs for flue gas carbonation include labor for washing the tank and removing sludge; expenditures for electricity; process monitoring (pH analysis); and maintenance of the blower and pumps. It was assumed the flue gas carbonation system would operate only when the tannery operates, about 260 days per year.

Primary Treatment - Flow Equalization

In flow equalization, the wastewaters from the tanyard and/or beamhouse are pumped into the equalization tank. The tanyard wastestream is pumped through a static, tangential screen prior to discharge into the equalization tank. Wastewater in the equalization tank, which provides either a one or two-day detention time, is mixed and aerated by subsurface static aerators. A one-day detention time was deemed sufficient for pretreatment facilities and those treatment facilities operating five days per week but not using biological treatment. A two-day detention time was recommended for facilities where biological treatment is used. The capital costs for implementing flow equalization are based on the design criteria listed in Table A-4. The capital costs are shown on Figure A-10 for both one and two-day detention times. Operation and maintenance costs for systems having a one-day detention time are shown on Figure A-11; Figure A-12 shows operation and maintenance costs for systems having a two-day detention time. The components of a typical system are shown schematically on Figure A-13.

Estimates for flow equalization include the following items:

- Additional piping within tanyard for wastewater collection;
- A wet well, along with pumps and force main, to transport wastewater from tanyard to screen;
- A building to house the screen and blowers (with overhead hoist system); and
- A concrete tank including air header, distribution piping, and static tube aerators.

Subsurface aeration and below-ground concrete tanks were selected to keep the temperature of the wastewater above freezing during cold weather in northern climates. Surface aeration in southern climates will perform satisfactorily and is acceptable. The amount of interior piping required for the tanyard, and the distance from the tanyard to the screen, will vary from tannery to tannery. The lengths assumed for the model plants are shown on Table A-4. Below-ground wet wells with submersible pumps were selected because they require minimal space and are less expensive. Solids screened from wastestreams at plants A and B are to be removed manually and loaded into a portable receptacle. At plants C and D, screened solids are to be transported by conveyor belts to an outside receptacle. In calculating the operation and maintenance costs, the flow equalization system was assumed to be operating 365 days per year and the tanyard pumps and screen 260 days per year. The costs include expenditures for electricity and for maintenance of the blowers, pumps, and screen.

Primary Treatment - Coagulation-Sedimentation

The unit processes following flow equalization are chemical coagulation and sedimentation. Wastewater is pumped at a constant rate from the equalization tank to a flash-mix tank where lime is added. As the water leaves this tank on its way to the clarifier, anionic polymer is added in the pipeline. Settling is accomplished in a solids-contact clarifier. Scum and sludge are pumped from the clarifier to the solids handling facility. The capital costs for implementing coagulation-sedimentation are based on the design criteria listed in Table A-5. The capital costs are shown on Figure A-14, the operation and maintenance costs on Figure A-15. The components of a typical system are shown schematically on Figure A-16.

Estimates for coagulation-sedimentation include the following items:

- Solids-contact clarifier;
- Influent, scum, and sludge pumps;
- Lime feed system and lime storage;

- Polymer feed system and polymer storage;
- Air compressor for valve operation; and
- A building to house the items above.

The estimated pollutant removals are discussed in Section VII.

The solids-contact clarifier was selected because settled sludge can be recycled with the influent wastewater, taking advantage of any unreacted lime remaining in the sludge. The rate at which lime and polymer are to be added was determined after reviewing data from tanneries where these types of treatment systems are used. Both the lime and polymer feed systems can function over a weekend without an operator. The lime feed system utilizes pinch valves to control the amount of lime added to the wastewater.

Operation and maintenance costs include expenditures for electricity and chemicals (based on average feed rates); operation costs for the lime, polymer, and clarifier systems; and maintenance costs for the pumps, clarifier mechanism, and chemical feed systems. In calculating these costs, the coagulation-sedimentation system was assumed to be operating 365 days per year.

Biological Treatment - Activated Sludge (extended aeration)

Biological treatment of the tannery wastewater is accomplished in an extended-aeration type activated sludge system. Phosphorous, a nutrient necessary for the biological process, is typically absent from tanneries' wastewater and must be fed into the system.

The capital costs for implementing activated sludge are based on the design criteria listed in Table A-6. Capital costs for aeration basin, aeration system, and secondary clarifier are shown on Figures A-17, A-19, and A-21, respectively. The operation and maintenance base costs for the activated sludge system which includes the secondary clarifier, blowers (maintenance only), and phosphoric acid feed system, are shown on Figure A-18. The power costs for the aeration system are shown on Figure A-20. The components of a typical activated sludge system are shown schematically on Figure A-22. In calculating these costs, the activated sludge system was assumed to be operating 365 days per year.

Estimates for the activated sludge process include the following items:

1. An aeration basin with:

   - a below-ground, rectangular concrete tank with vertical sides;
   - a phosphoric acid feed system; and
   - sludge pumps.

2. An aeration system with:

   - a building for blowers, pumps, and related equipment; and
   - blowers/motors, an air header, in-basin piping, and static tube aerators.

3. A secondary clarifier with:

   - a below-ground concrete tank; and
   - a secondary clarifier mechanism and accessories.

The detention time within the aeration basin was calculated with the intent of maintaining a food to microorganism ratio (F/M) of 0.1 and a mixed liquor volatile suspended solids (MLVSS) concentration of 3500 mg/l. Aeration requirements were based on either the amount of air needed for mixing [25 cfm/1000 ft^3 (0.025 m^3/m^3 min)] or the oxygen requirement for the organic loading, whichever was higher. The oxygen requirement for the organic loading is the amount of oxygen required for BOD removal; 2 lb O_2/lb of BOD removed (2 kg O_2/kg of BOD removed) .

The estimated pollutant removals are discussed in Section VII.

The phosphoric acid feed system was designed to provide phosphorus equal to one percent of the concentration of the influent BOD.

The volume of the aeration tank and the amount of aeration required depend on the wastewater's characteristics, which vary from one subcategory to another. These requirements can be calculated from Table A-14.

Upgraded Biological Treatment - Activated Sludge (Extended Aeration) With Nitrification And Powdered Activated Carbon (PAC) Addition

A more advanced biological treatment method is an extended aeration type activated sludge process which provides nitrification and has the capability of PAC addition. A phosphoric acid feed system is required to provide phosphorus, a nutrient necessary for the biological treatment process. Tannery wastes are typically deficient in phosphorus. Because the nitrification process decreases the pH, a caustic feed system is included to maintain the proper pH for the biological process. The biological treatment process is followed by a secondary clarifier which removes solids. Powdered activated carbon is added to enhance the performance of biological treatment.

The capital costs for implementing activated sludge with PAC addition are based on the design criteria listed in Table A-7. Capital costs for aeration basins, aeration system, secondary clarifier and caustic (NaOH) feed system are shown on Figures A-17, A-19, A-21, and A-23, respectively. The base operation and maintenance costs for the activated sludge system with nitrification and PAC addition, which includes the secondary clarifier, blowers (maintenance only), phosphoric acid feed system, and PAC addition (labor only), are shown on Figure A-25. The power costs for the aeration system are shown on Figure A-20 and the operation and maintenance costs for the NaOH feed system are shown on Figure A-24. Chemical costs for PAC addition were calculated based on maintaining a PAC concentration of 1,000 mg/l in the aeration basin. The components of a typical activated sludge system are shown schematically on Figure A-22. While calculating the operation and maintenance costs, the activated sludge system was assumed to be operating 365 days per year.

Estimates for activated sludge systems include the following items:

1. An aeration basin with:
   - a below-ground, rectangular concrete tank;
   - a phosphoric acid feed system; and
   - sludge pumps.
2. An aeration system with:
   - blowers/motors, air header, in-basin piping, and static tube aerators; and
   - a building to house blowers, pumps, and related equipment.
3. An NaOH feed system with:
   - metering pumps;
   - NaOH storage (heated and insulated); and
   - piping (heat traced and insulated).

4. A secondary clarifier with:

- a below ground concrete tank; and
- a secondary clarifier mechanism and accessories.

The detention time within the aeration basin was calculated with the intent of maintaining a food to microorganism ratio (F/M) of 0.1 and a mixed liquor volatile suspended solids (MLVSS) concentration of 3500 mg/l. Aeration requirements were based on either the amount of air needed for mixing 25 cfm/1000 ft^3 (0.025 m3/m3 min.) or the oxygen requirement for the organic loading, whichever was higher. The oxygen requirements for the organic loading are the sum of the BOD requirement 2 lb O_2/lb of BOD removed (2 kg O_2/kg of BOD removed) and the nitrification requirement 4.6 lb O_2/lb of N nitrified (4.6 kg O_2/kg of N nitrified).

The size of the caustic (NaOH) feed system was determined by calculating the amount of calcium carbonate ($CaCO_3$) that will be consumed during biological treatment and then determining the amount of NaOH that will be required to replace it. Approximately 40 mg of NaOH is needed to replace 50 mg of $CaCO_3$. The amount of $CaCO_3$ that has to be replaced is the sum of the following factors:

- $CaCO_3$ consumed during the conversion of organic nitrogen to nitrate (NO_3). Approximately 3.51 mg $CaCO_3$ is consumed for each milligram of organic nitrogen converted to nitrate. Some organic nitrogen will be synthesized into bacteria during the removal of BOD. This amounted to approximately 2.5 percent of the BOD removed.

- $CaCO_3$ consumed during the conversion of ammonia (NH_3) to nitrate (NO_3). Approximately 7.14 mg $CaCO_3$ is consumed for each milligram of ammonia converted to nitrate (NO_3).

- $CaCO_3$ consumed during the removal of BOD. Approximately 0.5 mg $CaCO_3$ is consumed for each milligram of BOD removed.

- $CaCO_3$ available in the wastewater. This is assumed to be 50 mg/l and is a negative quantity in the calculation.

The estimated pollutant removals are discussed in Section VII.

The phosphoric acid feed system was designed to provide phosphorus equal to one percent of the concentration of the influent BOD.

The volume of the aeration tank, the amount of aeration required, and the amount of NaOH required depends on the wastewater loadings by subcategory. These requirements can be calculated from Table A-14.

Advanced Treatment - Multimedia Filtration

Multimedia filtration follows activated sludge. Filtration entails passing the wastewater through a filter bed composed of anthracite coal, silica sand, and garnet sand to remove the suspended solids. When a limiting head loss occurs, the filter must be backwashed to remove the material that has accumulated in it. By reversing the flow through the filter (backwashing), the filter bed is expanded and the accumulated solids are washed out and returned to the headworks of the plant.

The capital costs for implementing multimedia filtration are based on the design criteria listed in Table A-8. The capital costs are shown on Figure A-26, the operation and maintenance costs on Figure A-27. The components of a typical system are shown schematically on Figure A-28.

Cost estimates for multimedia filtration systems include the following items:

- Filter building;
- Filter media, underdrain system, tanks, and valves;
- Influent and backwash pumps; and
- Air compressor.

The estimated pollutant removals for multimedia filtration are discussed in Section VII. It was assumed while calculating the operation and maintenance costs, which include expenditures for electricity, maintenance of pumps and filters, and operation, that the system would be operating 365 days per year.

Sludge Dewatering Facilities

Sludge dewatering is required to reduce the moisture content of the sludge to an acceptable level for ultimate disposal. There are two feasible technology options for sludge dewatering: sludge drying beds and plate filter presses. Both technologies have been shown to adequately treat sludge from tanneries and both are currently being used in the industry. The design of either type of sludge dewatering facility and therefore the costs are dependent on the volume (or weight) of sludge to be treated each day. The weight of sludge (lbs of dry solids/day) for each subcategory or tannery is based on the waste loads (BOD_5, TSS, flow) being treated and the degree of treatment being performed. The weight of solids for each subcategory and each treatment option is given on Table A-14. The use of this table is demonstrated later in this Section. The advantages and disadvantages, as well as costs, are given in the following discussion.

Filter Presses

Sludge is dewatered in a filter press by forcing the liquid portion of the sludge through a fine filtering media under high pressure. A filter press consists of a series of rectangular plates supported on a frame. A filter cloth is fitted over each plate. A hydraulic ram is used to move the plates together and hold them so that sufficient high pressure may be maintained internally while dewatering. During the filtering cycle the conditioned sludge is pumped into the press and the liquid portion or filtrate is forced through the filter cloth to discharge ports. The plates are then separated and the dewatered sludge drops onto a conveyor. The sludge cake is conveyed to a truck and removed to the ultimate disposal site.

The capital costs for sludge dewatering filter presses were based on the design criteria listed in Table A-9. The capital costs are shown on Figure A-29, and the operation and maintenance costs on Figure A-30. The components of a typical system are shown schematically on Figure A-31.

The filter press system has been designed to dewater seven days of sludge during a five-day period. Mixing has been included in sludge storage facilities to prevent the sludge from settling or turning septic. The volume of sludge to be treated depends on the specific subcategory wastewater characteristics and the unit processes included in the treatment system. The volume of sludge can be calculated for the various subcategories and treatment schemes from Table A-14 in Section E. The operation and maintenance costs and capital costs are calculated by determining the weight of the dry solids to be processed each day. It has been assumed, while calculating the operation and maintenance costs, that the sludge dewatering system will be operating 260 days per year. These estimates do not include any allowance for hauling and ultimate disposal of the sludge. Sludge disposal costs (at $17.00/ton (1980 costs)) are added in separately.

Sludge Drying Beds

Sludge drying bed technology involves reducing the water content in sludge by spreading it on the surface of a sand bed and allowing drainage and evaporation to the atmosphere to dry the sludge. This process is used for the drying of sludge prior to removal for ultimate disposal.

As a waste treatment procedure, sludge drying beds are employed to reduce the water content of a variety of sludges to the point where they are amenable to mechanical collection and removal. These beds usually consist of six to 18 inches (15.24 to 45.72 cm) of sand over a 12-inch (30.48 cm) deep gravel drain system made up of 1/8 to 1/4 inch (3.175 to 6.35 mm) graded gravel overlying drain tiles.

Drying beds are usually divided into sectional areas approximately 25 feet (7.62 meters) wide by 100 to 200 feet (30.48 to 60.96 meters) long. The partitions may be earth embankments, but more often are made of planks and supporting grooved posts.

To apply liquid sludge to the sand bed, a closed conduit or a pressure pipeline with valved outlets at each sand bed section is often employed. Another method of application is by means of an open channel with appropriately placed side openings which are controlled by slide gates. With either type of delivery system, a concrete splash slab should be provided to receive the falling sludge and prevent erosion of the sand surface.

When sludge must be dewatered continuously throughout the year regardless of the weather, sludge beds may be covered with a fiberglass reinforced plastic roof. Covered drying beds permit a greater volume of sludge drying per year in most climates because of the protection afforded from rain or snow and because of more efficient control of temperature. Depending on the climate, a combination of open and enclosed beds will provide maximum utilization of the sludge drying bed facilities.

The capital costs for sludge dewatering-sludge drying beds were based on information supplied by the leather tanning and finishing industry. Typical design criteria are shown on Table A-10. The capital costs are shown on Figure A-32, the operation and maintenance costs on Figure A-33. The components of a typical system are shown schematically on Figure A-34.

Unit Processes for Pretreatment Options

The treatment options that were considered for pretreatment involved several other unit processes that have not been discussed. These processes are discussed in detail in this section.

Sulfide Oxidation With Neutralization Facilities

This unit process is specific for PSES Option 2 and PSNS Option 2, and for those tanneries with beamhouses (subcategories 1,2,3,6, and 8). As described previously, catalytic oxidation of sulfides is a batch treatment operation and therefore once treatment is completed a fairly substantial volume of wastewater will be discharged over a short period of time. This flow will be combined with the tanyard flow prior to discharge to the municipal system. The pH of the effluent from the oxidation process will be high (11-12) while the pH of the tanyard stream will be approximately 8.5. The pretreatment standards for pH in these subcategories is 7 to 10. Although it is anticipated that the comingling of these two wastestreams will have a neutralizing effect, the possibility exists that the pH could exceed 10. This unit process includes an acid feed system to slightly lower the pH, if necessary. This is a conservative design and approach since it is likely the pH will exceed the standard infrequently. This unit process is used to neutralize (adjust the pH of) the effluent from sulfide oxidation. The design criteria and description of the facilities for sulfide oxidation are included in the section on sulfide oxidation. A sulfuric acid storage and feed system to lower the pH to an acceptable level (approximately nine) for discharge to a municipal system is added to this unit process. The design feed rate of the sulfuric acid is based on a titration curve provided by a tannery which performs sulfide oxidation of its beamhouse wastes.

The sulfuric acid is added directly to the basin where it is mixed with the wastewater until the proper pH is obtained. The capital costs for implementing sulfide oxidation with neutralization are based on the design criteria listed in Table A-11 (see Table A-2 for summary on sulfide oxidation process). The capital costs are shown on Figure A-35, the operation and maintenance costs on Figure A-36. The components of a typical system are shown schematically on Figure A-37.

In addition to those items included in the estimate for sulfide oxidation, the estimates for sulfide oxidation with neutralization include:

- o Chemical metering pumps, piping, and electrical;
- o On-site storage facilities for sulfuric acid (if required).

In calculating the operation and maintenance costs, a sulfide oxidation with neutralization facility was assumed to be operating 260 days per year.

Tanyard Wastewater Screening

In the development of the other treatment options this unit process is included in the flow equalization process. However, there is no flow equalization for PSES Option 1 or PSNS Option 1. Tanyard wastewater screening which includes the items listed below, is necessary prior to discharge or further treatment for these options.

This unit process includes installation of piping for collecting wastewater from the tanyard, a force main, screens, and construction of a pumping station with submersible pumps. The capital costs for implementing this unit process are based on the design criteria listed in Table A-12. The capital costs are shown on Figure A-38, the operation and maintenance costs on Figure A-39. The components of a typical system are shown schematically on Figure A-40.

Estimates for this unit process include the following items:

- Additional piping within the tanyard for wastewater collection (see above);
- A wet well, pumps, and force main from tanyard to screen; and
- Building for screen.

The operation and maintenance costs include expenditures for electricity, maintaining pumps, and labor for cleaning the screen. These costs were calculated assuming that the system would be operating 260 days per year.

Neutralization Facilities - As described previously in PSES Option 1 and PSNS Option 1 the beamhouse and tanyard streams are combined after treatment and discharged to the municipal system. These two streams (the beamhouse stream - high pH; the tanyard stream - low pH) will usually neutralize each other upon combining. However to ensure that the pH range is met consistantly the conservative engineering approach is to include neutralization capabilities for these options. The no beamhouse subcategories will more than likely require the pH to be raised to meet the standards.

This process is useful in neutralizing combined tanyard/beamhouse wastes or tanyard wastes only. In either case, the wastestream enters a mixing tank and is mixed with either caustic soda or an acid to obtain a proper pH (seven to ten) for discharge to a municipal system. The capital costs for implementing neutralization are based on the design criteria listed in Table A-13. The capital costs are shown on Figure A-41, the operation and maintenance costs on Figures A-42 and A-43. The components of a typical system are shown schematically on Figure A-44.

The amount of caustic (NaOH) required to raise the pH of the tanyard wastes to six was based on the results from NaOH addition to sample tanyard wastes. In the case where tanyard and beamhouse wastestreams are combined in the mixing tank, no data are available on the types or amount of chemicals required for pH adjustment. The mixing of the two waste streams does have a neutralizing effect, but the results are highly variable. To determine annual chemical costs, the amount of each chemical required was assumed to equal the fraction of the total flow (that the wastestream represented) multiplied by the amount of chemical that would be required to neutralize only that waste stream. For example, approximately 0.46 gallons of sulfuric acid are required to lower the pH of 1000 gallons of beamhouse wastes to nine. If combined beamhouse and tanyard wastes are being neutralized, the amount of sulfuric acid required per 1,000 gallons of beamhouse waste would be 0.18 (40 percent of 0.46) gallons. In actuality, less sulfuric acid might be required. However, the more conservative approach was used for determining costs.

Operation and maintenance costs include expenditures for electricity and chemicals. These costs were calculated assuming that the system would be operating 260 days per year.

Estimates for neutralization include the following items:

- A building to house mixing tank and chemical feed equipment;
- Expenditures for water and electricity; and
- Chemical feed equipment.

Effluent Monitoring

To assure a quality effluent, a tannery will be required to monitor the effluent from the treatment facility prior to discharge. Most tanneries lack the laboratory facilities and qualified personnel to perform this task. In lieu of constructing laboratory facilities and hiring (or training) personnel to perform the sampling and analysis, the most cost-effective procedure for effluent monitoring would be for an outside contractor to conduct the sampling and perform the analysis. An independent laboratory will be able to certify the sampling results and assure the integrity of the results.

A permanent structure providing easy access to the effluent pipe is necessary. This will be a below-ground concrete structure that will house sampling, flow monitoring, and any required pH monitoring equipment. The capital cost of the effluent monitoring station is estimated at $19,000 (1980 costs).

It is projected that a tannery, whether an indirect or direct discharger will take eight samples per month. The parameters sampled for and analyzed are those that are regulated by the promulgated standards or effluent limitations. For BPT, BAT, BCT, and NSPS the parameters are BOD_5, TSS, Total Chromium, and Oil and Grease. The pH of the discharge is continually monitored as is flow. For PSES Option I, samples are taken for sulfide in subcategories 1, 2, 3, 6 and 8. Flow and pH are continually monitored. For PSES Option II, sulfide is also monitored for the subcategories noted above. Chrome is sampled for and analyzed in all subcategories. Flow and pH are continually monitored.

For the purposes of assigning an expenditure for sampling and analysis, it is assumed that non-tannery labor will perform both the sampling and analysis. The annual costs associated in PSES/PSNS Option I is $2,000 and for PSES/PSNS Option II is $11,000. The annual cost for BPT, BCT, BAT, and NSPS is $17,600.

F. SUMMARY

Figures A-45 and A-46 present a range of costs (capital and operation and maintenance) for BPT treatment facilities. These curves assume that there is no existing equipment or facilities. The costs are based on the wastewater flow from the tannery and not productions.

Costs for the 17 existing direct dischargers to meet BPT are presented on Table A-15. BAT Options and Costs are given on Tables A-16 and A-17. New Source Options and Cost are presented in Tables A-18, A-19, A-23, and A-24. PSES options and costs are presented on Tables A-20, A-21, and A-22. A BPT cost example utilizing Table A-14 (design summary) and the cost curves is given in Table A-25.

TABLE A-1

DESIGN CRITERIA FOR PRELIMINARY TREATMENT - STREAM SEGREGATION

1. Beamhouse Screens	
Type of Screen	Static, tangential
Number of Screens	1
Opening Size	0.04 in. (1.02 mm)
2. Beamhouse Pumps	
Type of Pump	Submersible, centrifugal
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
3. Piping	
Beamhouse Piping	
Plant A	20 ft.-4 in. dia. (6.1 m-102 mm dia.)
Plant B	60 ft.-6 in. dia. (18.3 m-152 mm dia.)
Plant C	240 ft.-8 in. dia. (73.2 m-203 mm dia.)
Plant D	640 ft.-12 in. dia. (195.1 m-305 mm dia.)
Force Main (Beamhouse to Screen)	
Plant A	200 ft.-4 in. dia. (61 m-102 mm dia.)
Plant B	200 ft.-4 in. dia. (61 m-102 mm dia.)
Plant C	500 ft.-6 in. dia. (152 m-152 mm dia.)
Plant D	500 ft.-8 in. dia. (152 m-203 mm dia.)

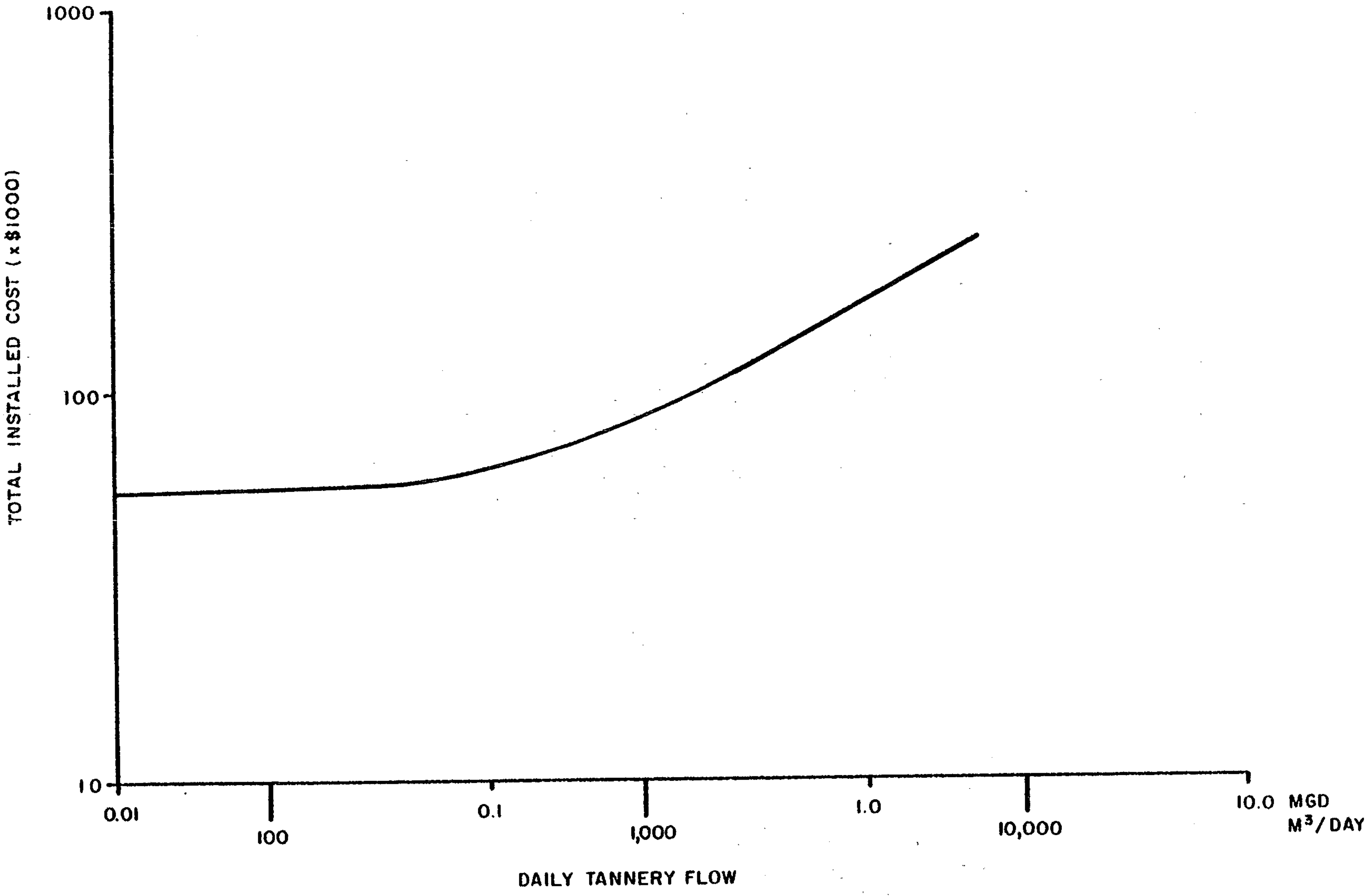

FIGURE A-1 CAPITAL COST CURVE FOR STREAM SEGREGATION

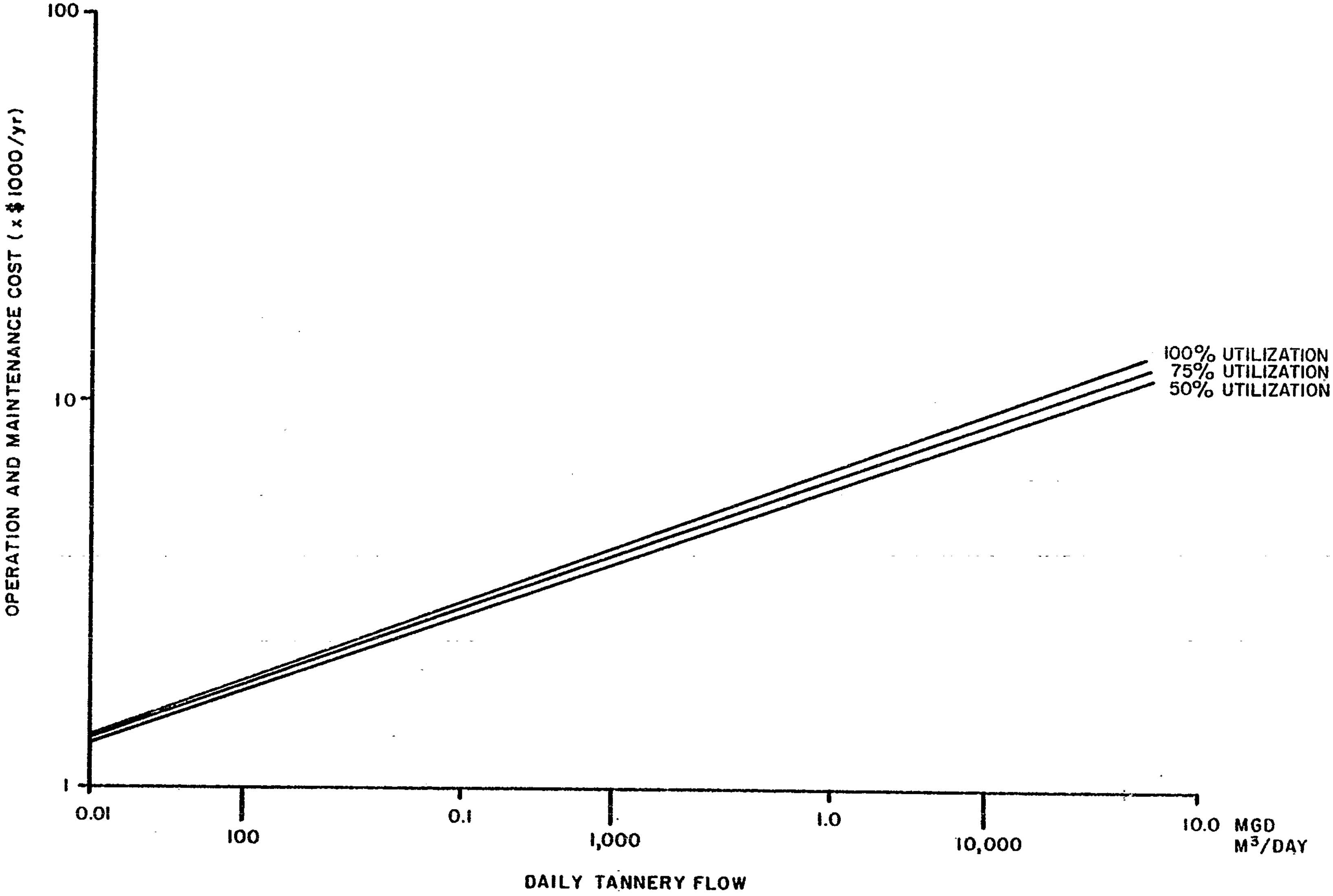

FIGURE A-2 OPERATION AND MAINTENANCE COST CURVES FOR STREAM SEGREGATION

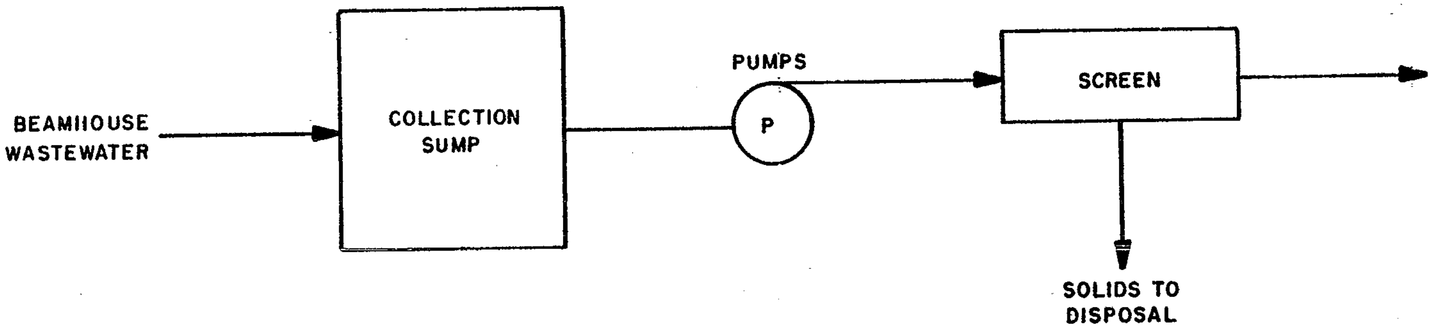

FIGURE A-3 SCHEMATIC LAYOUT FOR STREAM SEGREGATION

TABLE A-2

DESIGN CRITERIA FOR PRELIMINARY TREATMENT - SULFIDE OXIDATION

1. Method of Operation	Batch
2. Aeration	
Type	Mechanical
Mixing Intensity	1.5 hp/1000 ft^3 (39.5 kW/1000 m^3)
Number of Aerators	
Plant A	1
Plant B	1
Plant C	2
Plant D	4
3. Aeration Tanks	
Side Water Depth	10 ft (3.0 m)
Number of Tanks	
Plant A	1
Plant B	1
Plant C	2
Plant D	2
Total Volume of Tank(s)	125% of daily beamhouse flow
Detention Time	8 hrs
4. Catalyst	
Type	Manganese sulfate ($MnSO_4$)
Method of Feed	Manual
Feed Rate	0.4 lb Mn/lb $S^=$ (0.4 kg Mn/kg $S^=$)
5. Effluent Pumps	
Type of Pumps	Solids handling, centrifugal, dry pit
Number of Pumps	2 (1 standby)
Spare Capacity	100%
6. Neutralization Facilities (If Required)	
Chemical	H_2SO_4 (66° Baume)
Dosage	0.43 gallons/1000 gallons (0.43 m^3/1000 m^3)
Feed System	Metering pump (manual adjustment)
Storage	
Plant A	drum
Plant B	drum
Plant C	drum
Plant D	Storage tank (1 tank truck and 10 days storage)

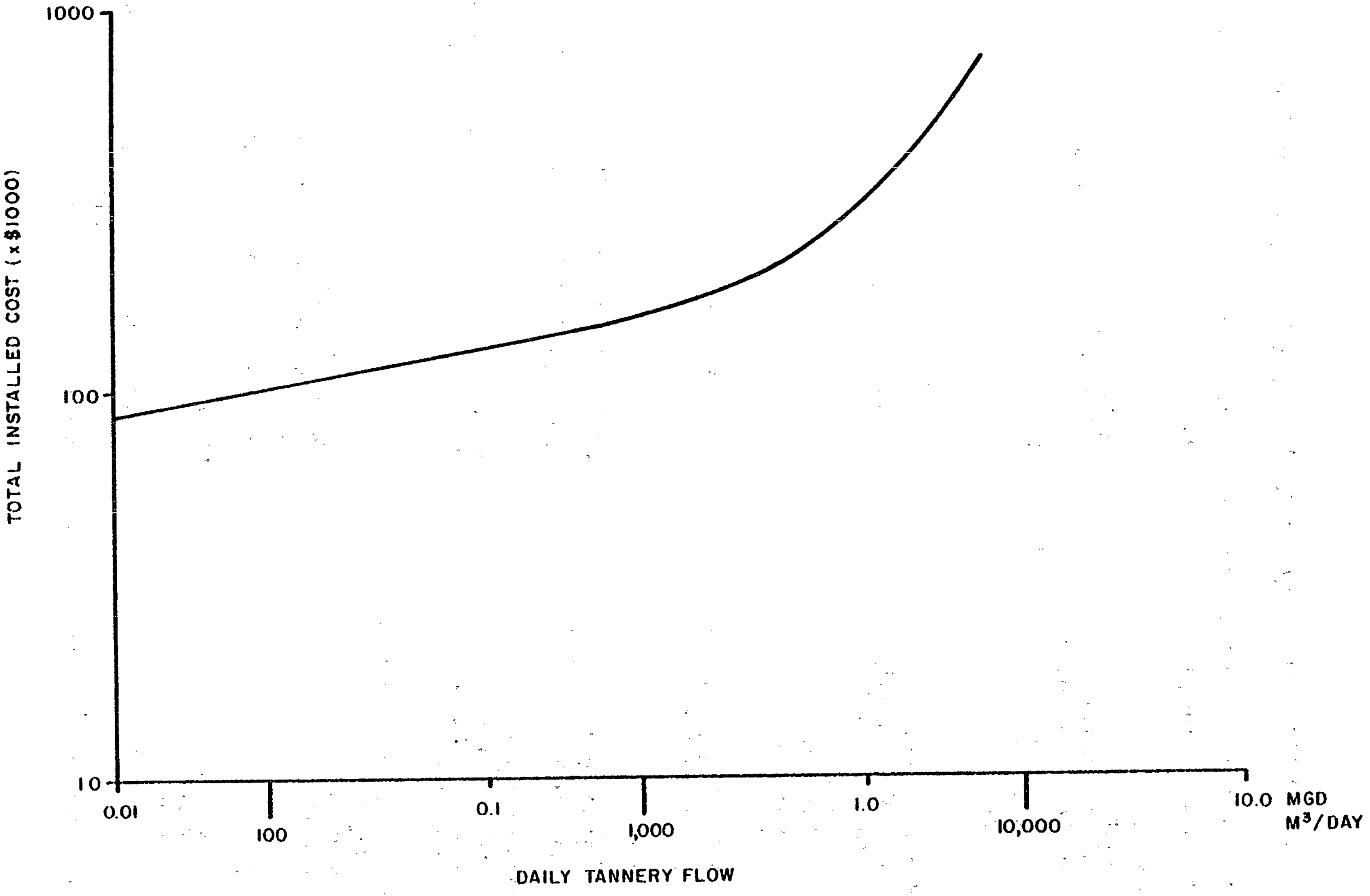

FIGURE A-4 CAPITAL COST CURVE FOR SULFIDE OXIDATION

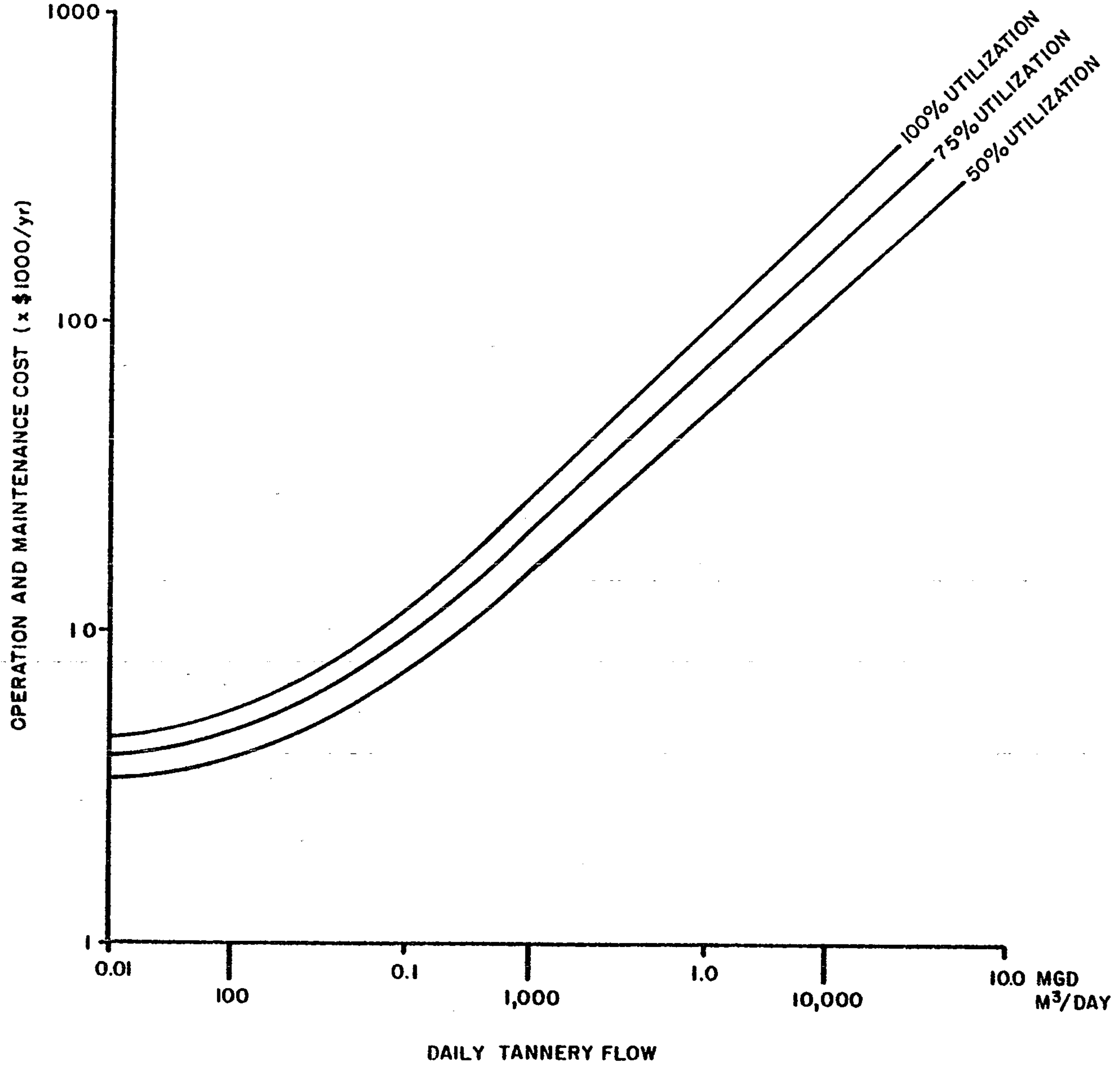

FIGURE A-5 OPERATION AND MAINTENANCE COST CURVES FOR SULFIDE OXIDATION

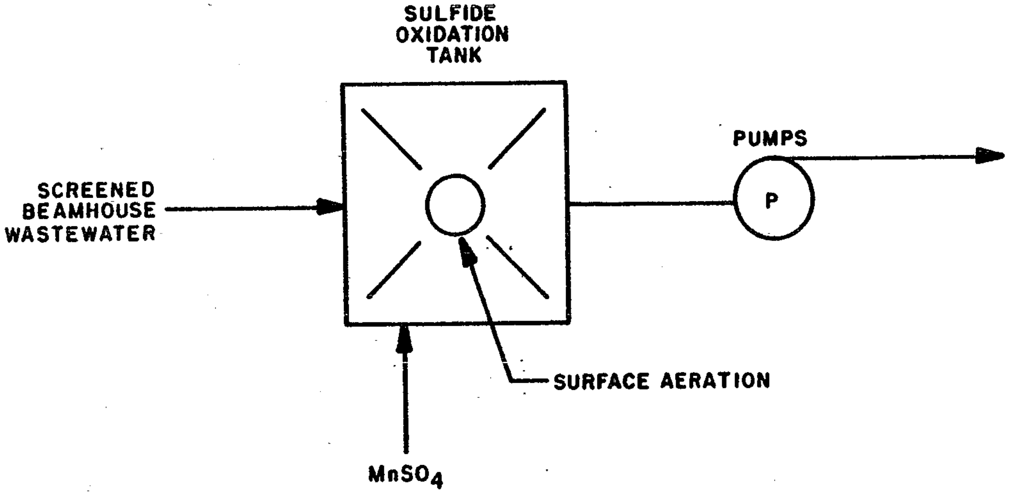

FIGURE A-6 SCHEMATIC LAYOUT FOR SULFIDE OXIDATION

TABLE A-3

DESIGN CRITERIA FOR PRELIMINARY TREATMENT - FLUE GAS CARBONATION

1.	Method of Operation	Batch
2.	Carbon Dioxide Content in Flue Gas	10%
3.	CO_2 Transfer Efficiency	80%
4.	Carbonation Time	8 hrs
5.	Settling Time	2 hrs
6.	Side Water Depth	10 ft (3 m)
7.	Effluent Pumps	
	Type of Pumps	Solids handling, centrifugal, dry pit
	Number of Pumps	2 (1 standby)
	Spare Capacity	100%
8.	Sludge Pumps	
	Type of Pumps	Solids handling, centrifugal, dry pit
	Number of Pumps	2 (1 standby)
	Spare Capacity	100%
9.	Distance from Stack to Tank	
	Plants A & B	200 ft (61 m)
	Plants C & D	500 ft (152 m)

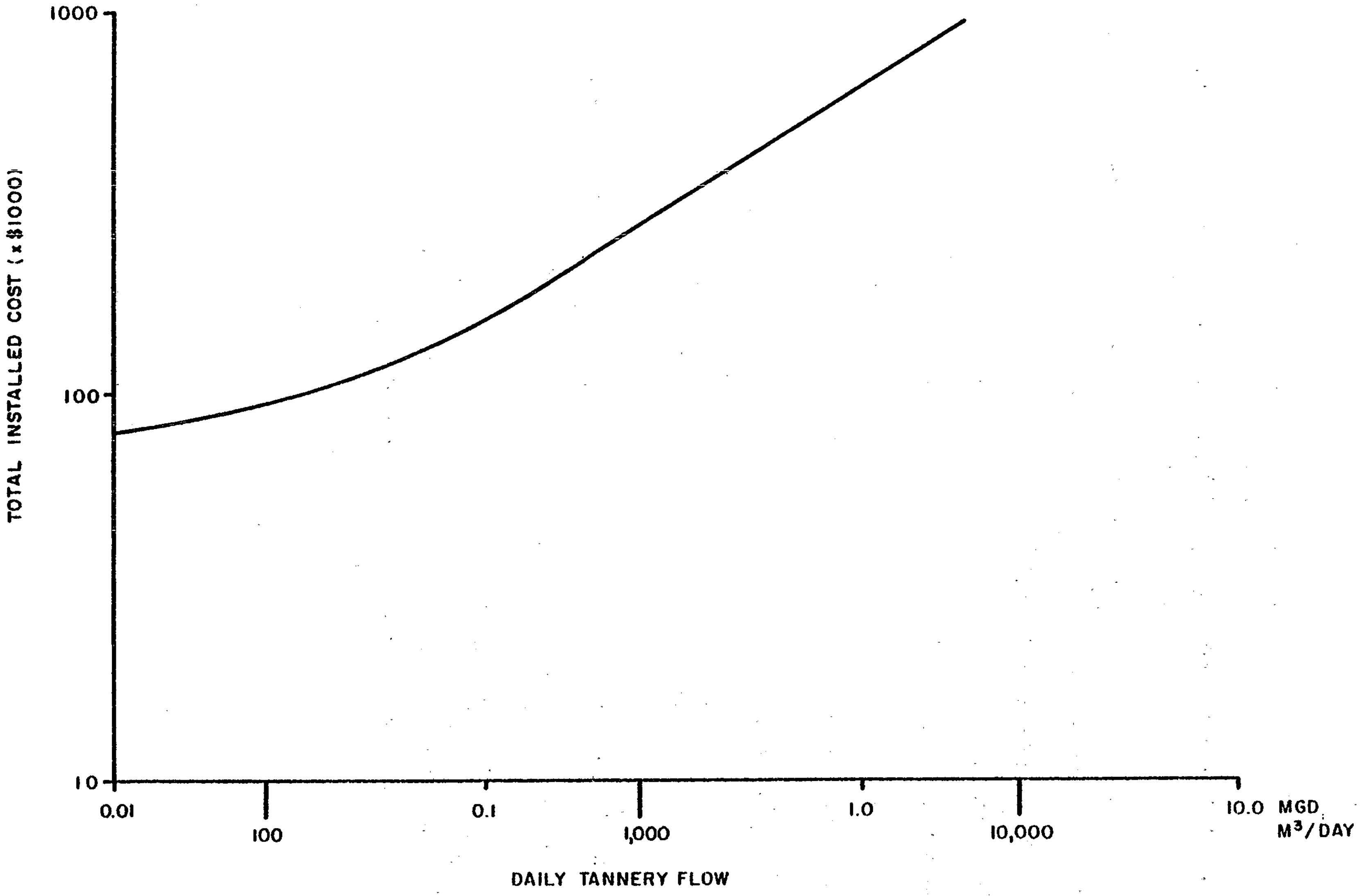

FIGURE A-7 CAPITAL COST CURVE FOR FLUE GAS CARBONATION

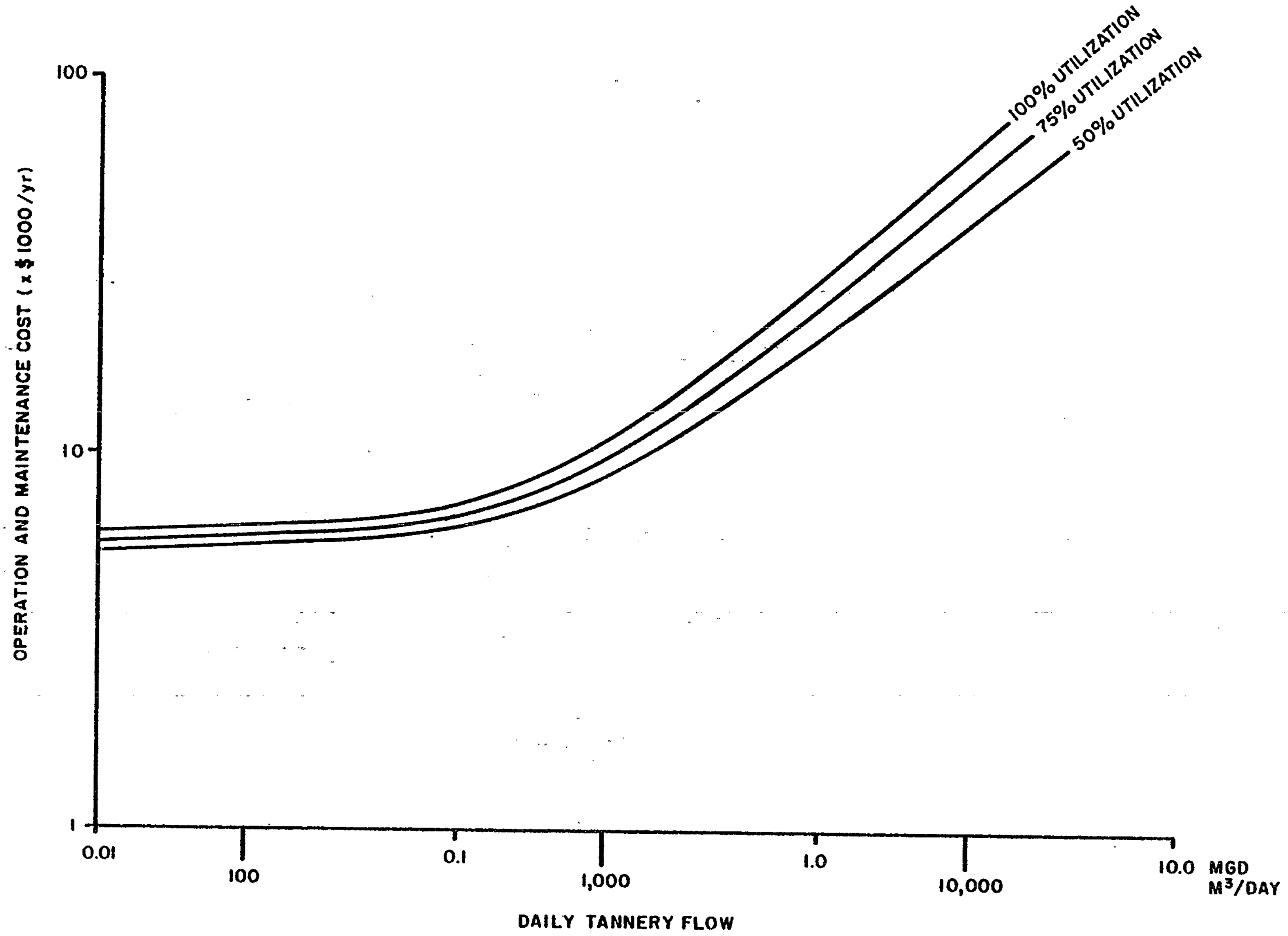

FIGURE A-8 OPERATION AND MAINTENANCE COST CURVES FOR FLUE GAS CARBONATION

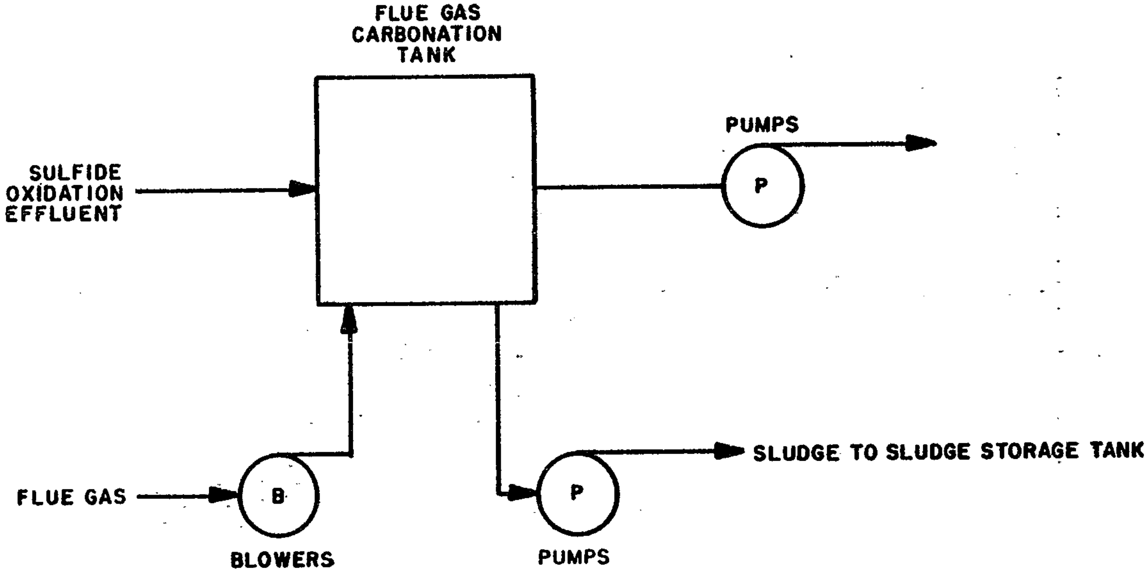

FIGURE A-9 SCHEMATIC LAYOUT FOR FLUE GAS CARBONATION

TABLE A-4

DESIGN CRITERIA FOR PRIMARY TREATMENT - FLOW EQUALIZATION

1. Tanyard Screens	
Type of Screen	Static, tangential
Number of Screens	1
Opening Size	0.04 in. (1.02 mm)
2. Tanyard Pumps	
Type	Submersible, centrifugal
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
3. Piping	
Tanyard Piping	
Plant A	10 ft.-4 in. dia. (3.0 m-102 mm dia.)
Plant B	30 ft.-6 in. dia. (9.1 m-152 mm dia.)
Plant C	120 ft.-8 in. dia. (36.6 m-203 mm dia.)
Plant D	320 ft.-12 in. dia. (97.5 m-305 mm dia.)
Force Main (Tanyard to Screen)	
Plant A	200 ft.-4 in. dia. (61 m-102 mm dia.)
Plant B	200 ft.-4 in. dia. (61 m-102 mm dia.)
Plant C	500 ft.-6 in. dia. (152 m-152 mm dia.)
Plant D	500 ft.-8 in. dia. (152 m-203 mm dia.)
4. Equalization Tank	
Side Water Depth	18 ft (5.5 m)
Detention Time	2 days (or 1 day)
Type	Below ground, concrete
5. Aeration	
Type	Subsurface, static tube aerators
Air Required	25 cfm/1000 ft^3 ($25m^3$/min/1000 m^3)
Type of Blowers	Positive Displacement
Number of Blowers	2 (1 standby)
Spare Blower Capacity	100%

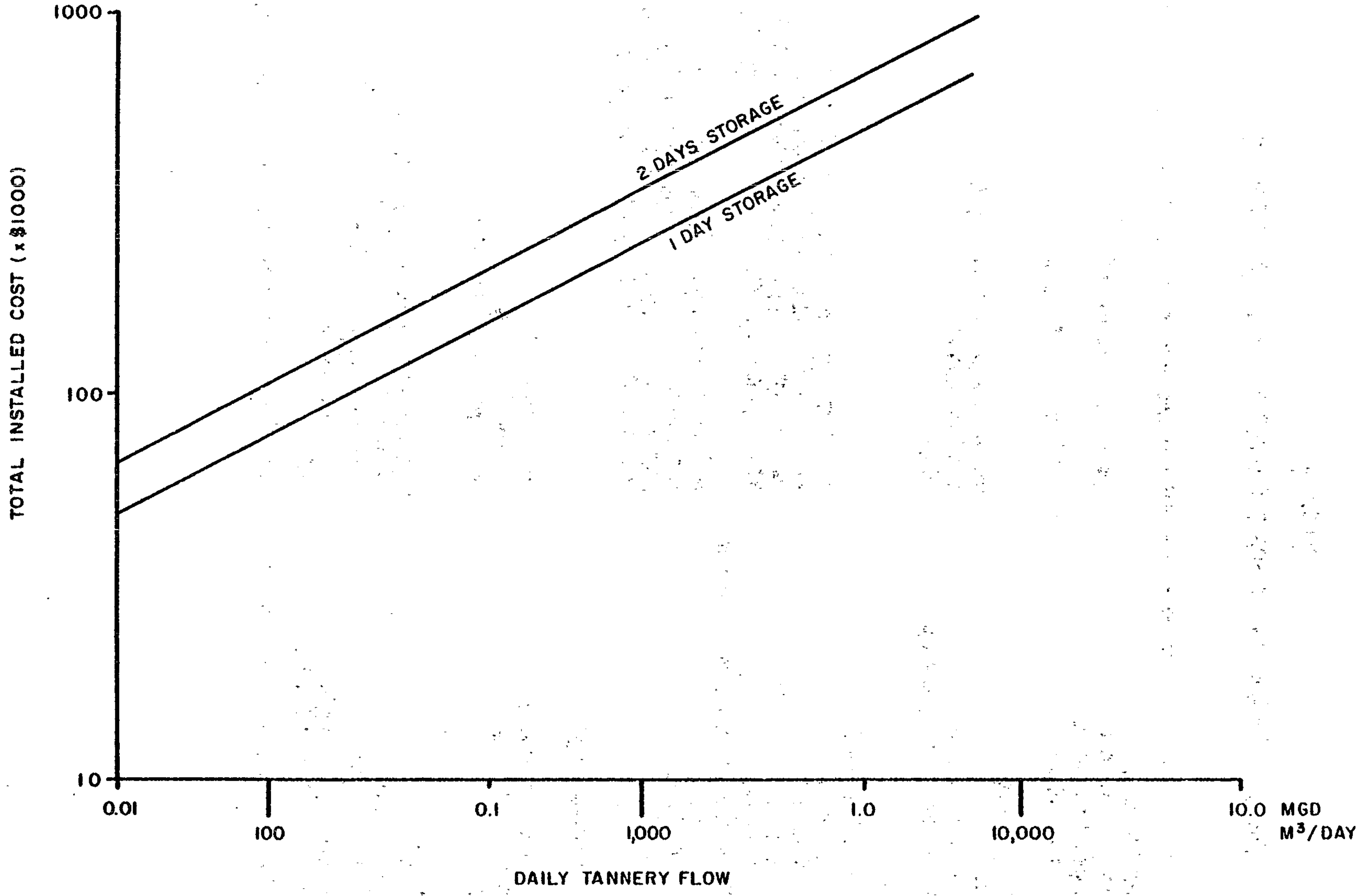

FIGURE A-10 CAPITAL COST CURVE FOR FLOW EQUALIZATION

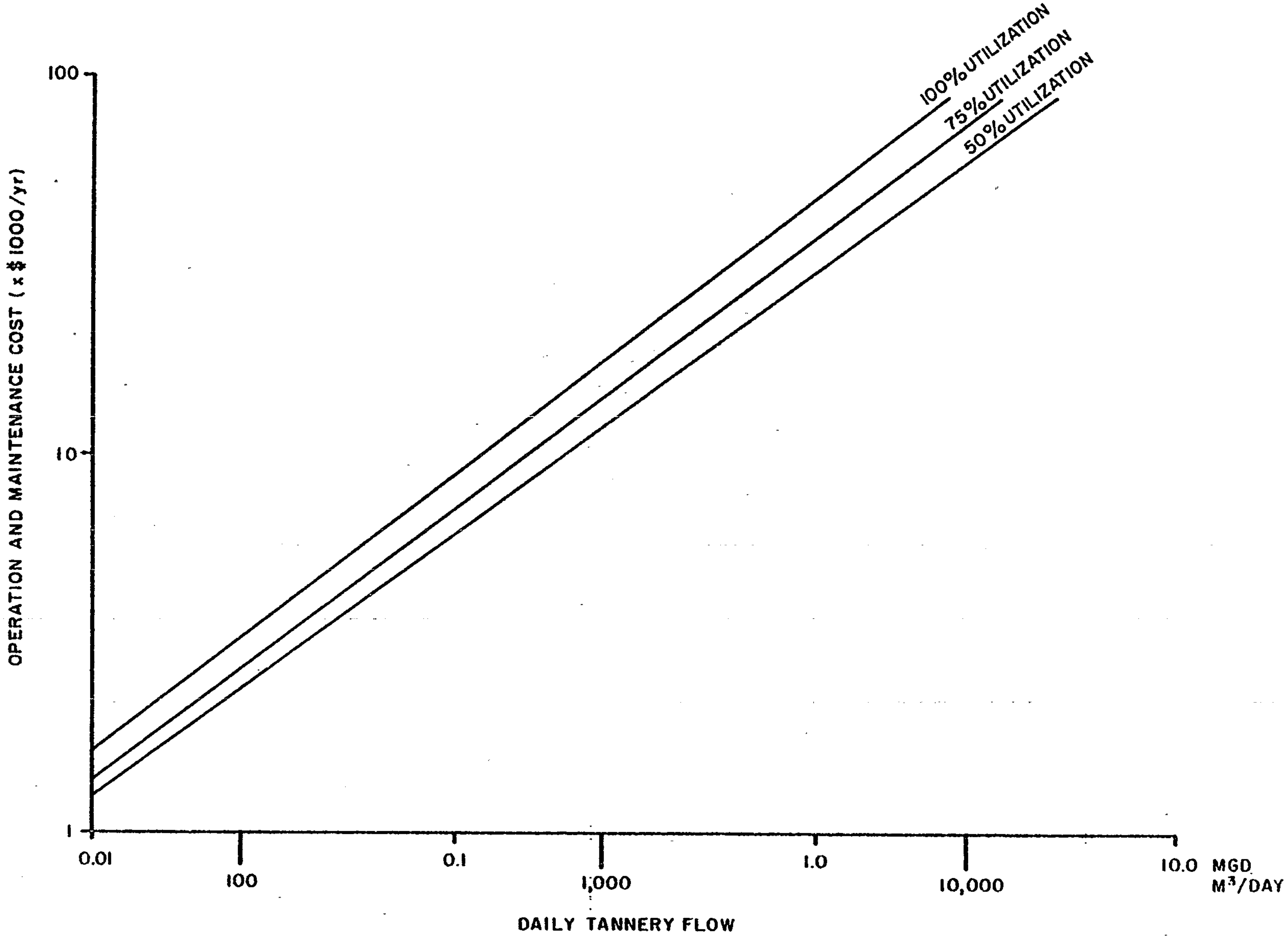

FIGURE A-11 OPERATION AND MAINTENANCE COST CURVES FOR FLOW EQUALIZATION (1 DAY STORAGE)

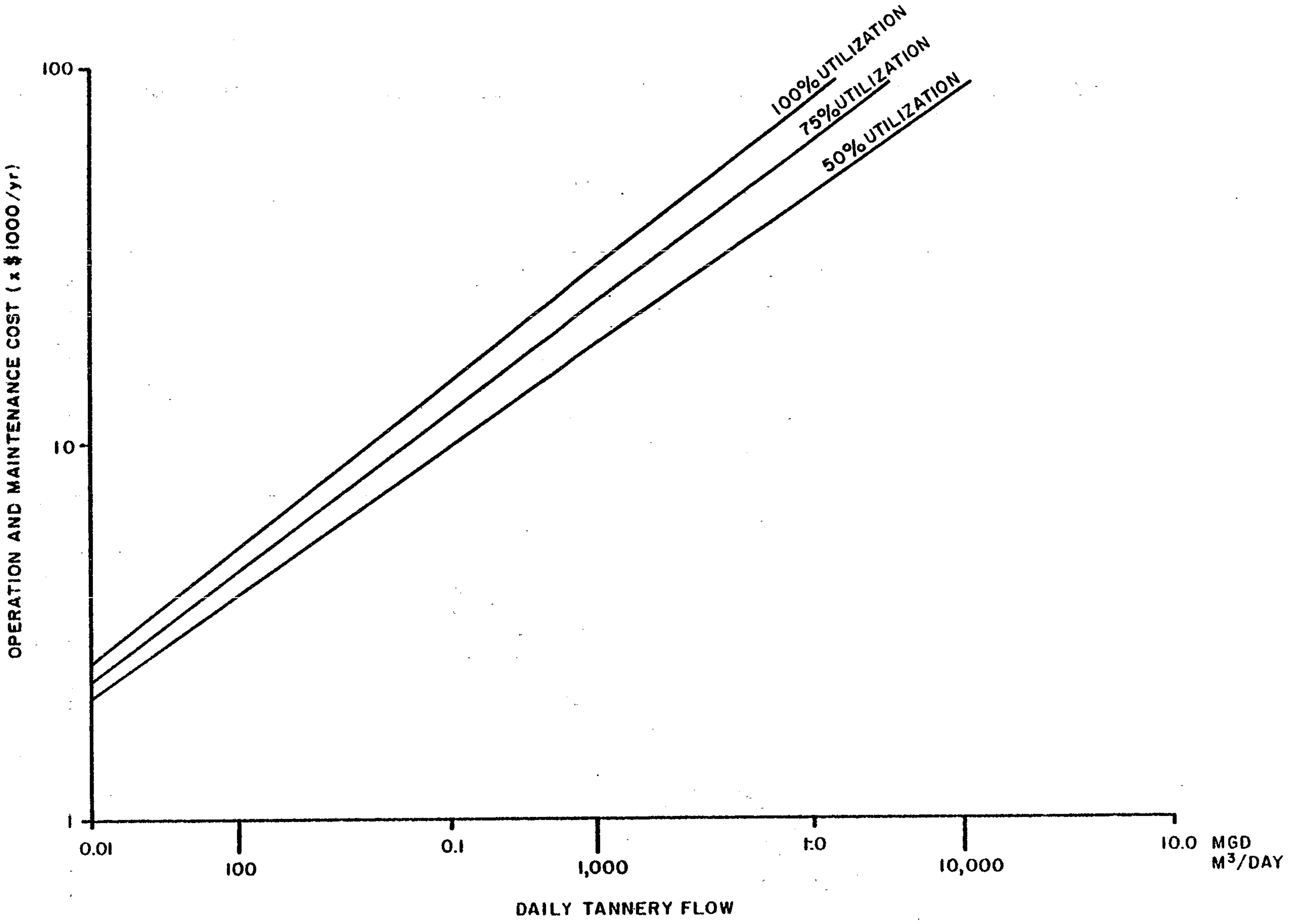

FIGURE A-12 OPERATION AND MAINTENANCE COST CURVES FOR FLOW EQUALIZATION (2 DAY STORAGE)

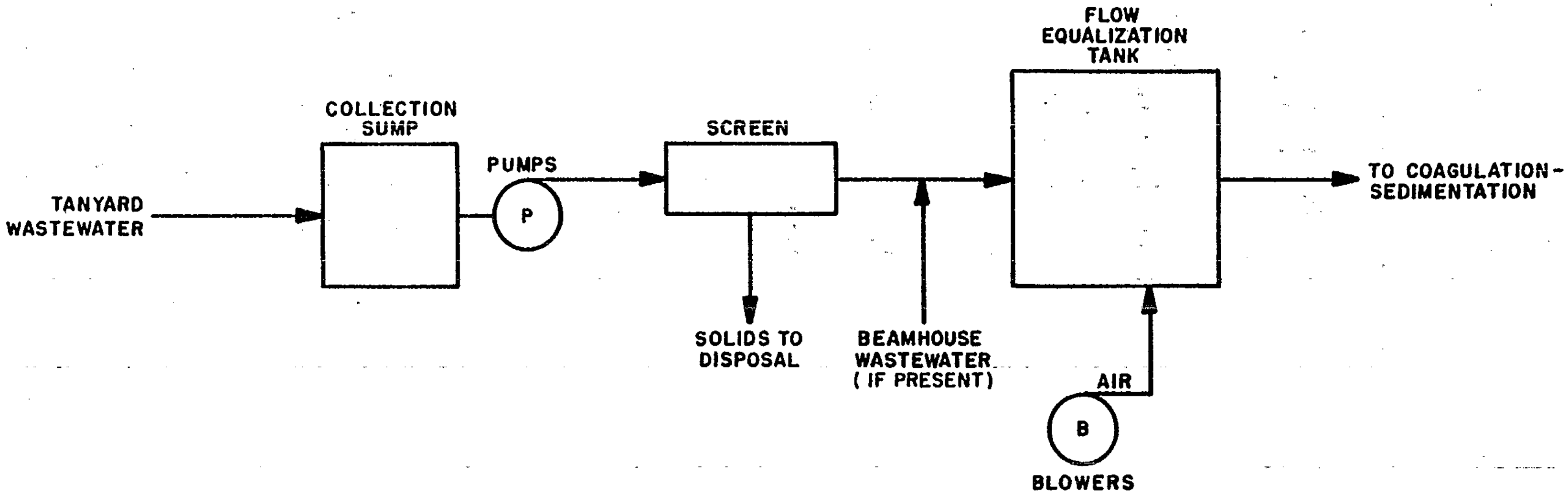

FIGURE A-13 SCHEMATIC LAYOUT FOR FLOW EQUALIZATION

TABLE A-5

DESIGN CRITERIA FOR PRIMARY TREATMENT - COAGULATION-SEDIMENTATION

1. Influent Pumps	
Type of Pumps	Solids handling, centrifugal, dry pit
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
2. Lime Feed System	
Average Feed Rate	800 mg/l [as $Ca(OH)_2$]
Design Feed Rate	1600 mg/l [as $Ca(OH)_2$]
Type of Lime	
Plants A & B	Hydrated Lime [$Ca(OH)_2$]
Plants C & D	Pebble Quicklime (CaO)
Lime Makeup	
Plants A & B	Manual
Plants C & D	Slaker
Lime Storage	
Plants A & B	Bags
Plants C & D	Bulk storage silo (10 days storage plus 1 truck shipment)
pH Monitoring	
Plants A & B	Manual
Plants C & D	Automatic
Flash Mix Tank	
Detention Time	4 minutes
3. Polymer Feed System	
Average Feed Rate	2 mg/l
Design Feed Rate	4 mg/l
Type	Anionic
Polymer Makeup	
Plants A & B	Manual
Plants C & D	Automatic
4. Clarifier	
Type	Solids contact, circular
Tank	Below ground, concrete
Overflow Rate	400 gpd/ft^2 (16.3 m^3/m^{2}d)
Inlet	Center Feed
Scum Removal	
Type of Pumps	Plunger
Number of Pumps	1
5. Sludge Pumps	
Type of Pumps	Solids handling, centrifugal, dry pit
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%

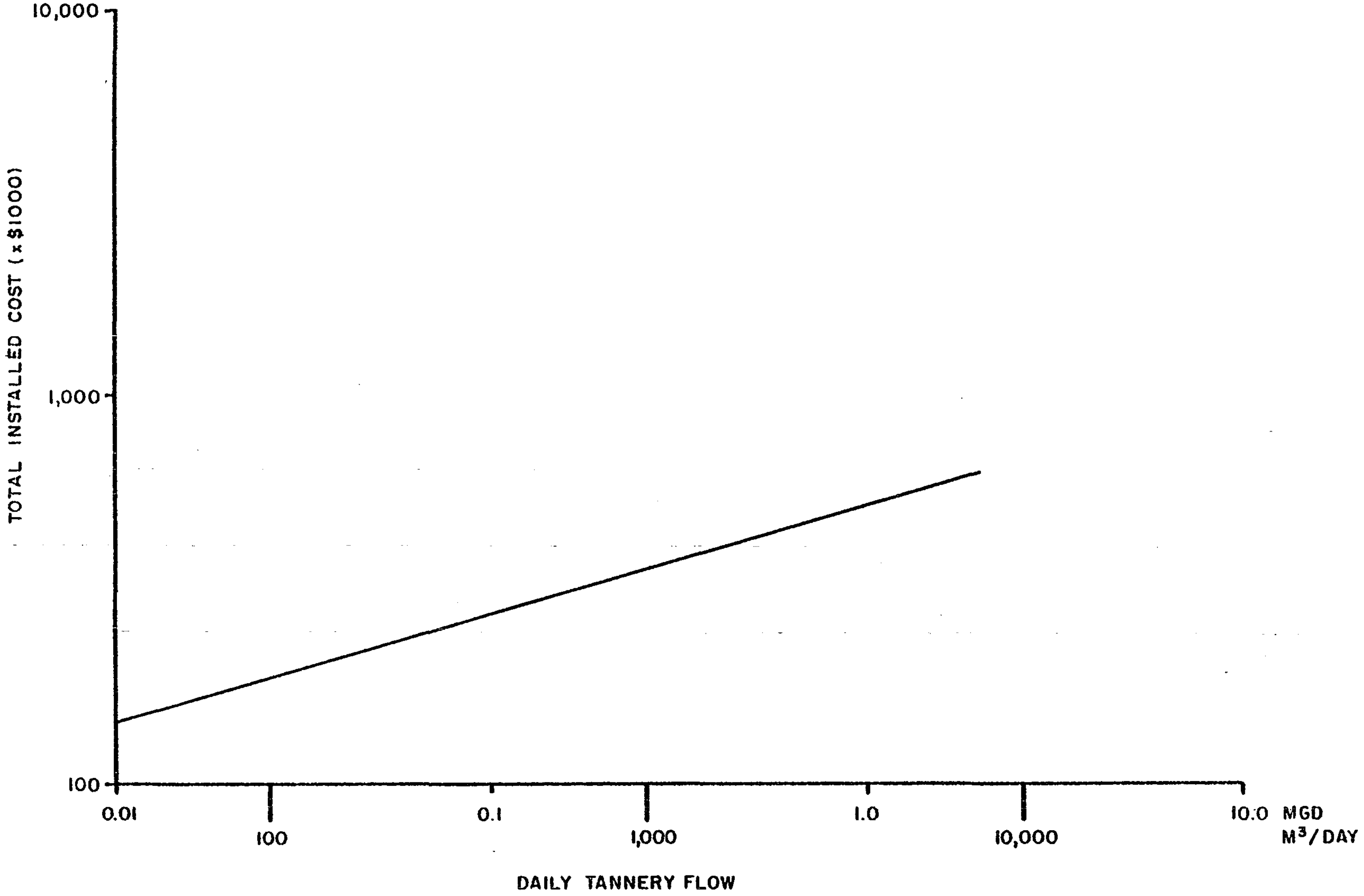

FIGURE A-14 CAPITAL COST CURVE FOR COAGULATION-SEDIMENTATION

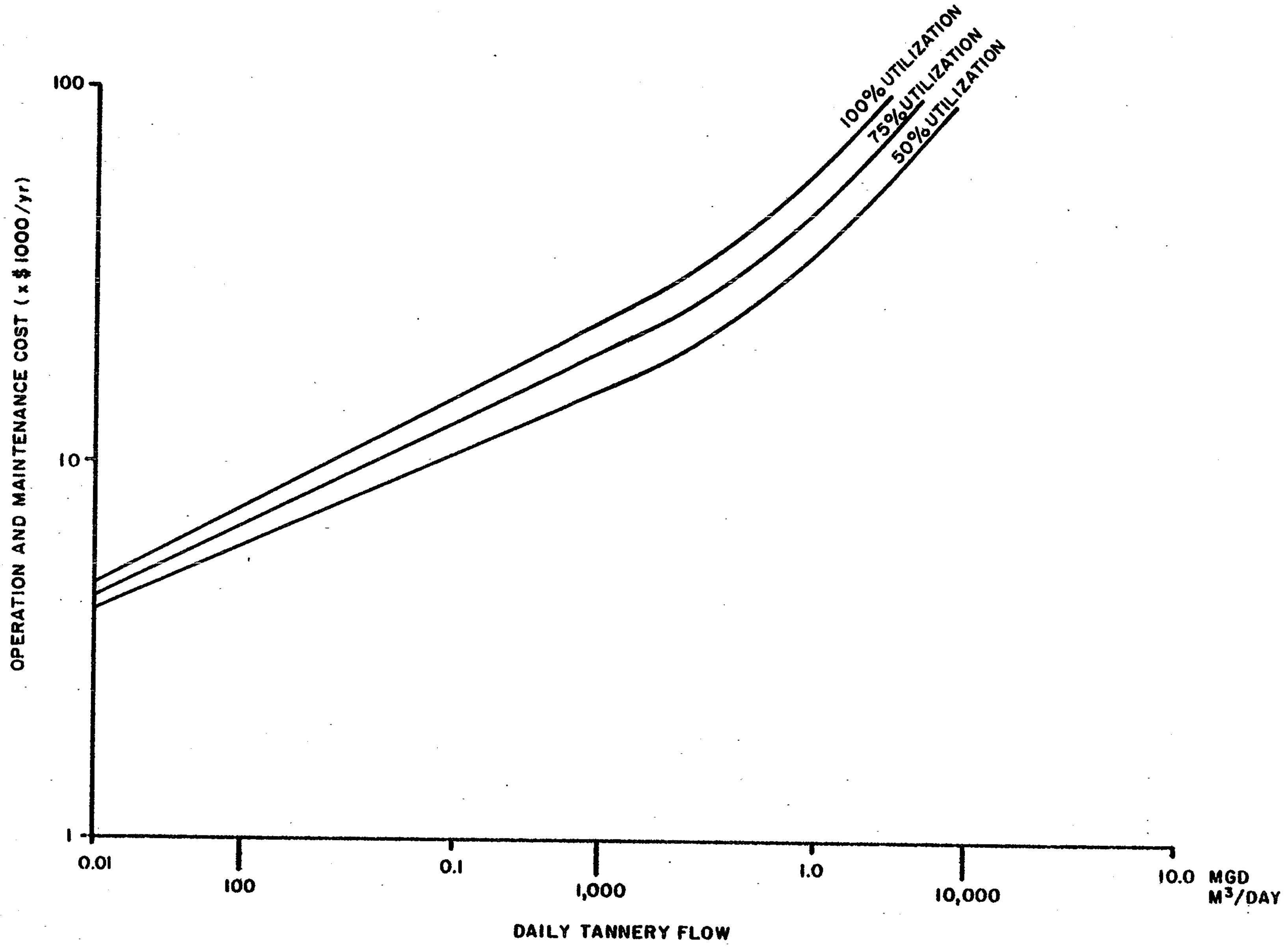

FIGURE A-15 OPERATION AND MAINTENANCE COST CURVES FOR COAGULATION-SEDIMENTATION

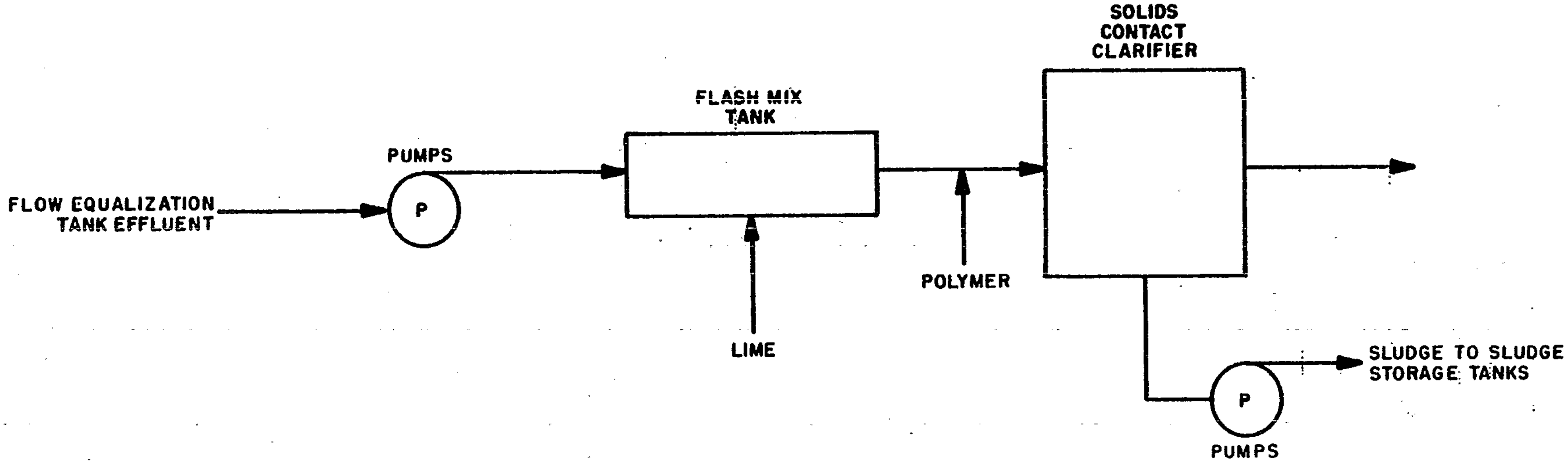

FIGURE A-16 SCHEMATIC LAYOUT FOR COAGULATION-SEDIMENTATION

TABLE A-6

DESIGN CRITERIA FOR BIOLOGICAL TREATMENT - ACTIVATED SLUDGE (EXTENDED AERATION)

1. Aeration Basin	
Type	Rectangular, below ground, concrete
Side Water Depth	
Plant A	15 ft (4.6 m)
Plants B, C, D	18 ft (5.5 m)
Detention Time	See text
2. Aeration System	
Type	Subsurface, static tube
Air Flow Per Unit	20 cfm (0.6 m^3/min)
Oxygen Transfer Efficiency	
Plant A @ 15'	6.3%
Plants B, C, D @ 18'	8%
Oxygen Transferred Per Unit	
Plant A	25.4 lb O_2/day (11.5 kg O_2/day)
Plants B, C, D	32.3 lb O_2/day (14.6 kg O_2/day)
3. Secondary Clarifier	
Type	Circular, below ground, concrete
Overflow Rate	200 gal./ft^2d (8.14m^3/m^2d)
Sludge Pumps	
Type of Pumps	Solids handling, centrifugal, dry pit
Number of Pumps	3
Flow Capacity (0-100% average daily flow)	
1 Pump	25% average flow (constant speed)
1 Pump	75% average flow (constant speed)
1 Pump	75% average flow (variable speed)
4. Phosphoric Acid	
Type	75% H_3PO_4
Feed	
Plants A & B	Manual
Plants C & D	Metering Pumps
Feed Rate	See text

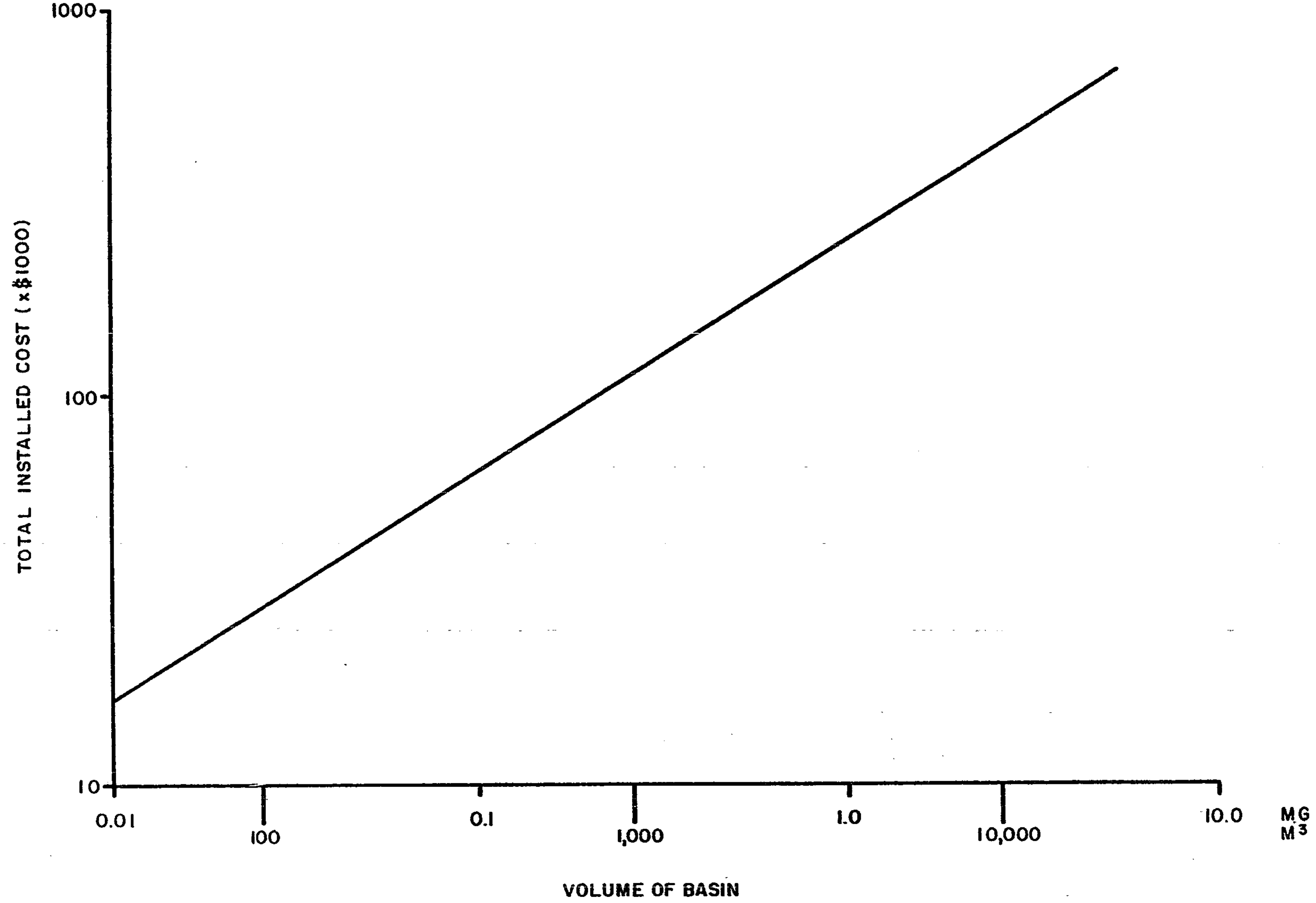

FIGURE A-17 CAPITAL COST CURVE FOR AERATION BASIN

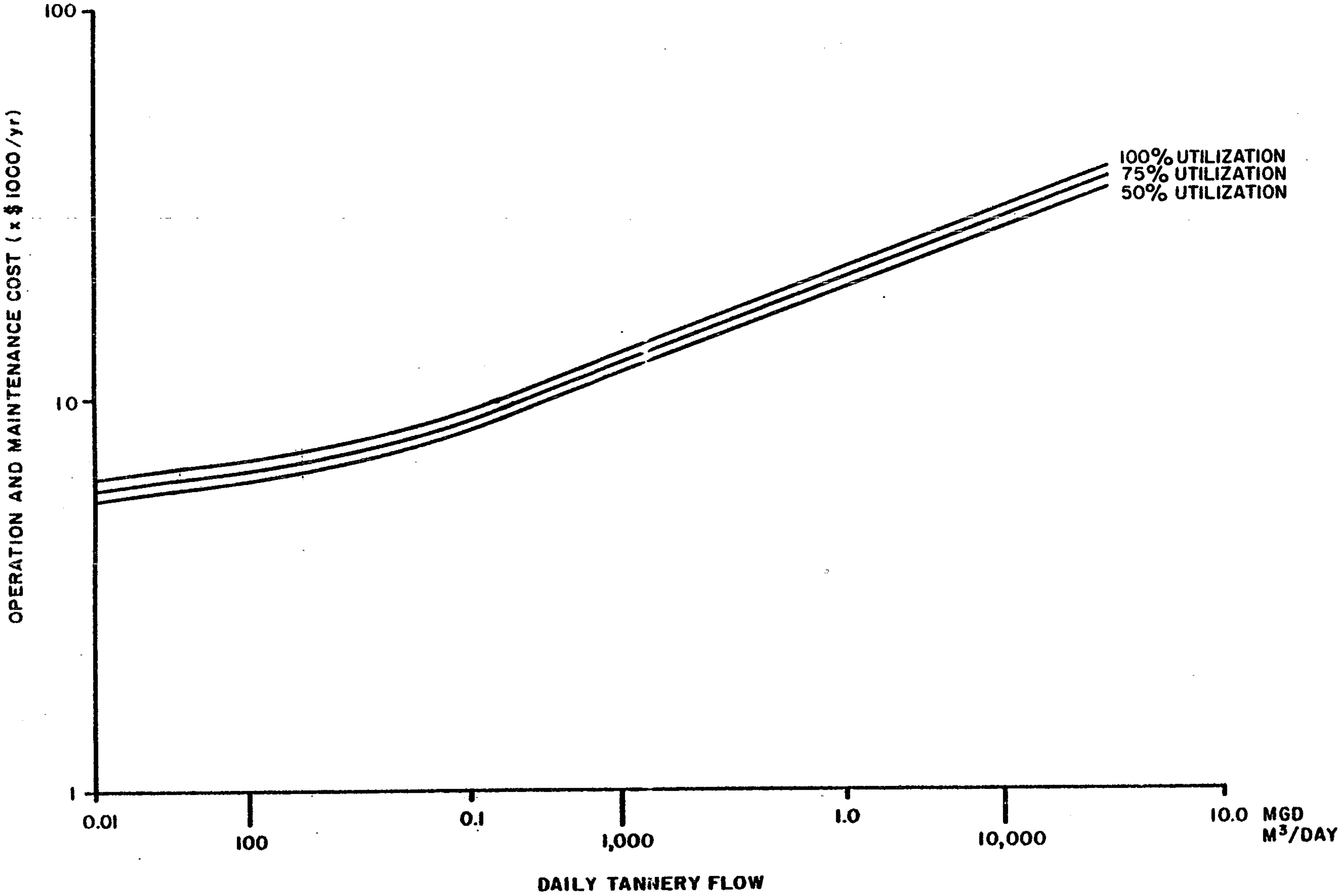

FIGURE A-18 OPERATION AND MAINTENANCE BASE COST CURVES FOR ACTIVATED SLUDGE WITHOUT NITRIFICATION

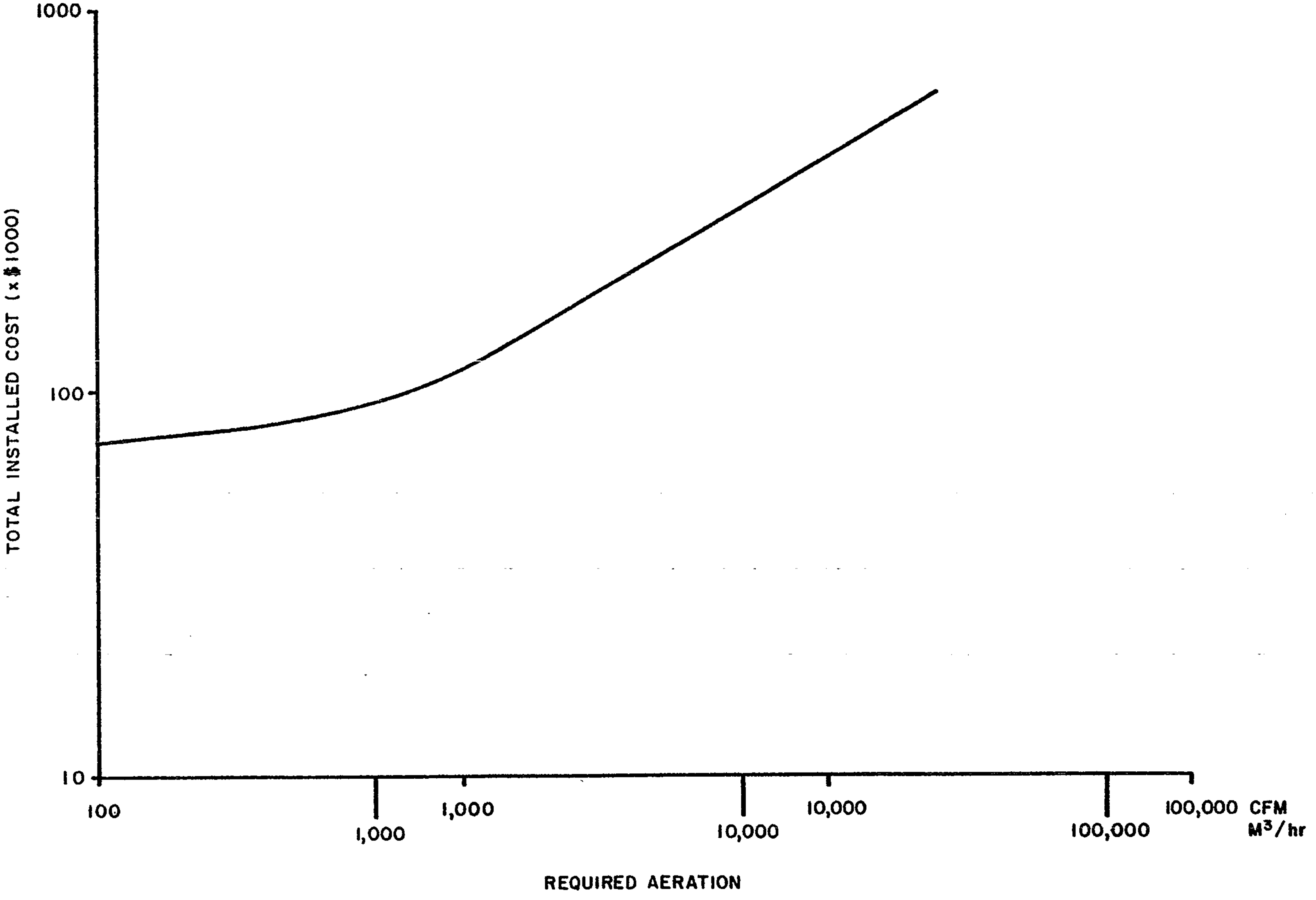

FIGURE A-19 CAPITAL COST CURVE FOR ACTIVATED SLUDGE AERATION SYSTEM

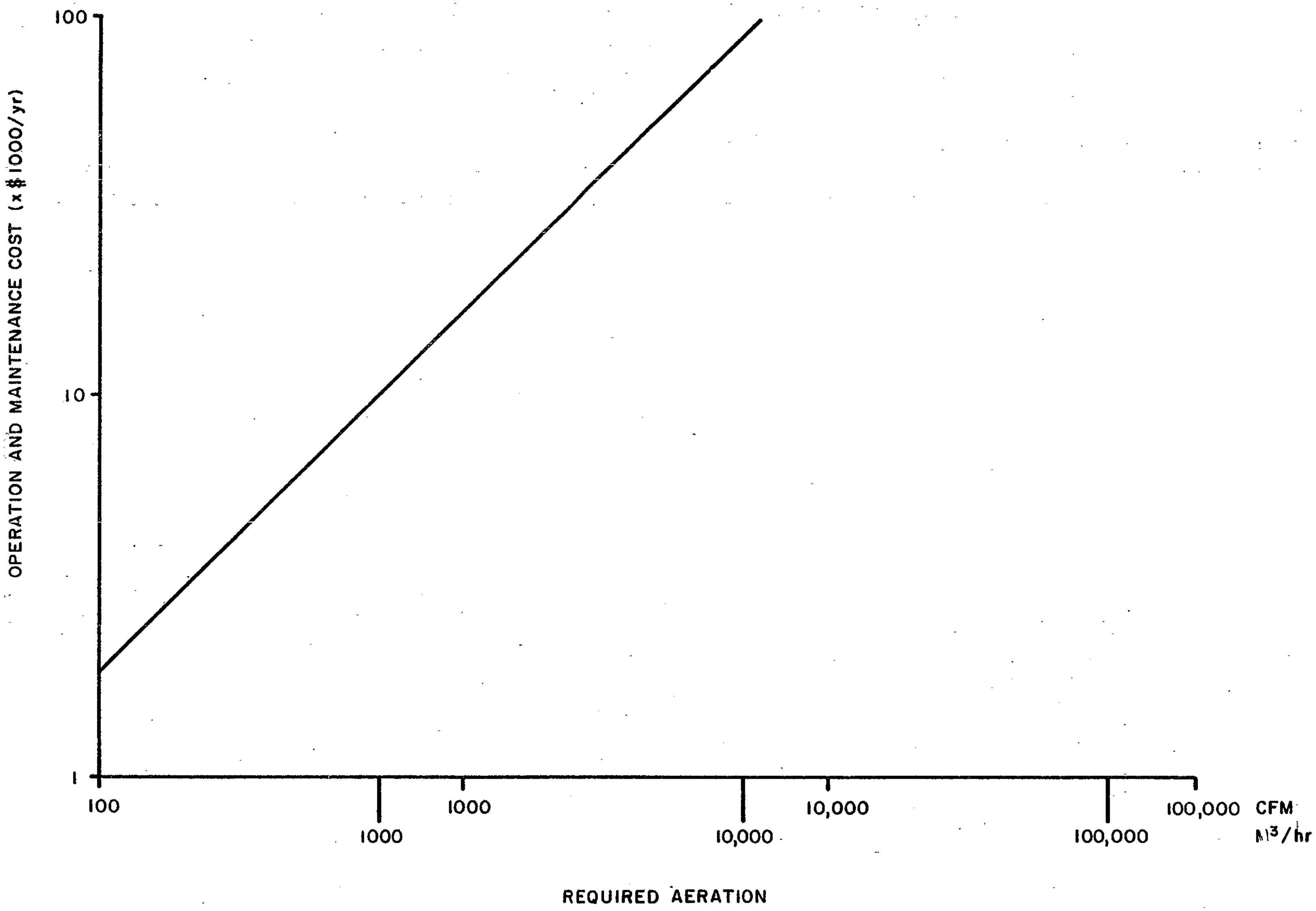

FIGURE A-20 POWER COST CURVE FOR AERATION SYSTEM

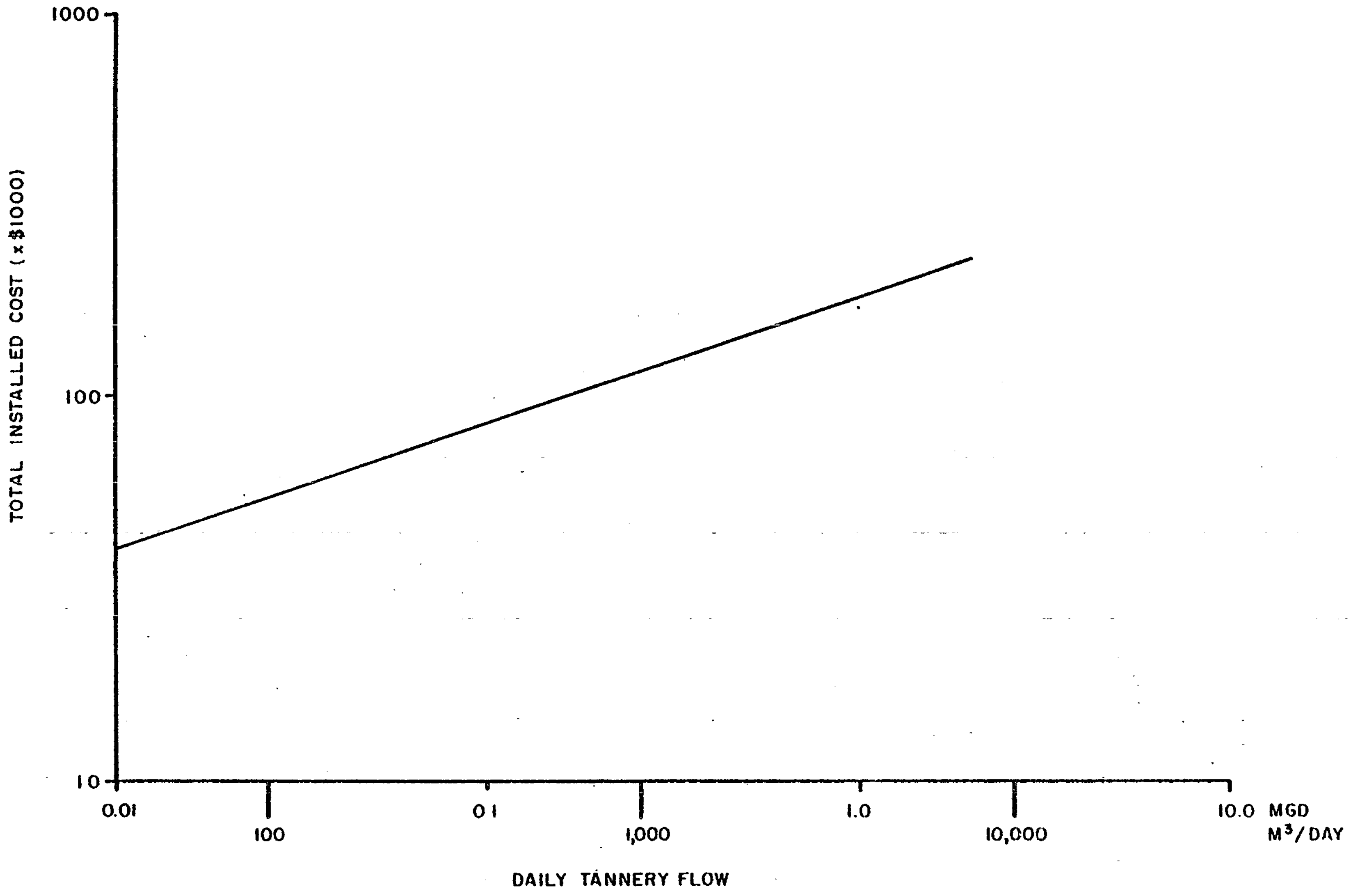

FIGURE A-21 CAPITAL COST CURVE FOR SECONDARY CLARIFIER

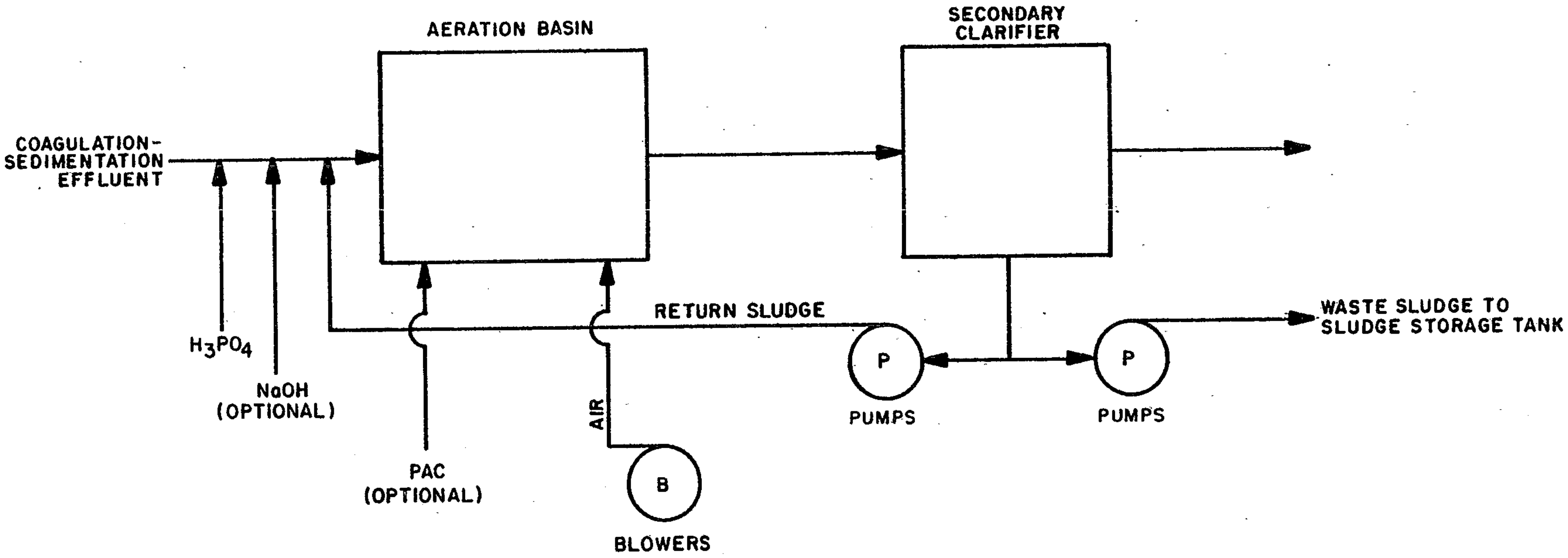

FIGURE A-22 SCHEMATIC LAYOUT FOR ACTIVATED SLUDGE (EXTENDED AERATION)

TABLE A-7

DESIGN CRITERIA FOR UPGRADED BIOLOGICAL TREATMENT - ACTIVATED SLUDGE (EXTENDED AERATION) WITH NITRIFICATION AND PAC ADDITION

1. Aeration Basin	
Type	Rectangular, below-ground, concrete
Side Water Depth	
Plant A	15 ft (4.6 m)
Plants B, C, D	18 ft (5.5 m)
Detention Time	See text
2. Aeration System	
Type	Subsurface, static tube
Air Flow Per Unit	20 cfm (0.6 m^3/min)
Oxygen Transfer Efficiency	
Plant A @ 15'	6.3%
Plants B, C, D @ 18'	8%
Oxygen Transferred Per Unit	
Plant A	25.4 lb O_2/day (11.5 kg O_2/day)
Plants B, C, D	32.3 lb O_2/day (14.6 kg O_2/day)
3. Secondary Clarifier	
Type	Circular, below ground, concrete
Overflow Rate	200 gal./ft^2d (8.14 m^3/m^2d)
Sludge Pumps	
Type of Pumps	Solids handling, centrifugal, dry pit
Number of Pumps	3
Flow Capacity (0-100% average daily flow)	
1 Pump	25% average flow (constant speed)
1 Pump	75% average flow (constant speed)
1 Pump	75% average flow (variable speed)
4. NaOH Feed System	
Type	50% NaOH solution
Feed	Metering pumps
Feed Rate	See text
Storage	
Plant A	Drum
Plants B, C, D	Outside, heated storage tank
5. Phosphoric Acid	
Type	75% H_3PO_4
Feed	
Plants A & B	Manual
Plants C & D	Metering pumps
Feed Rate	See text

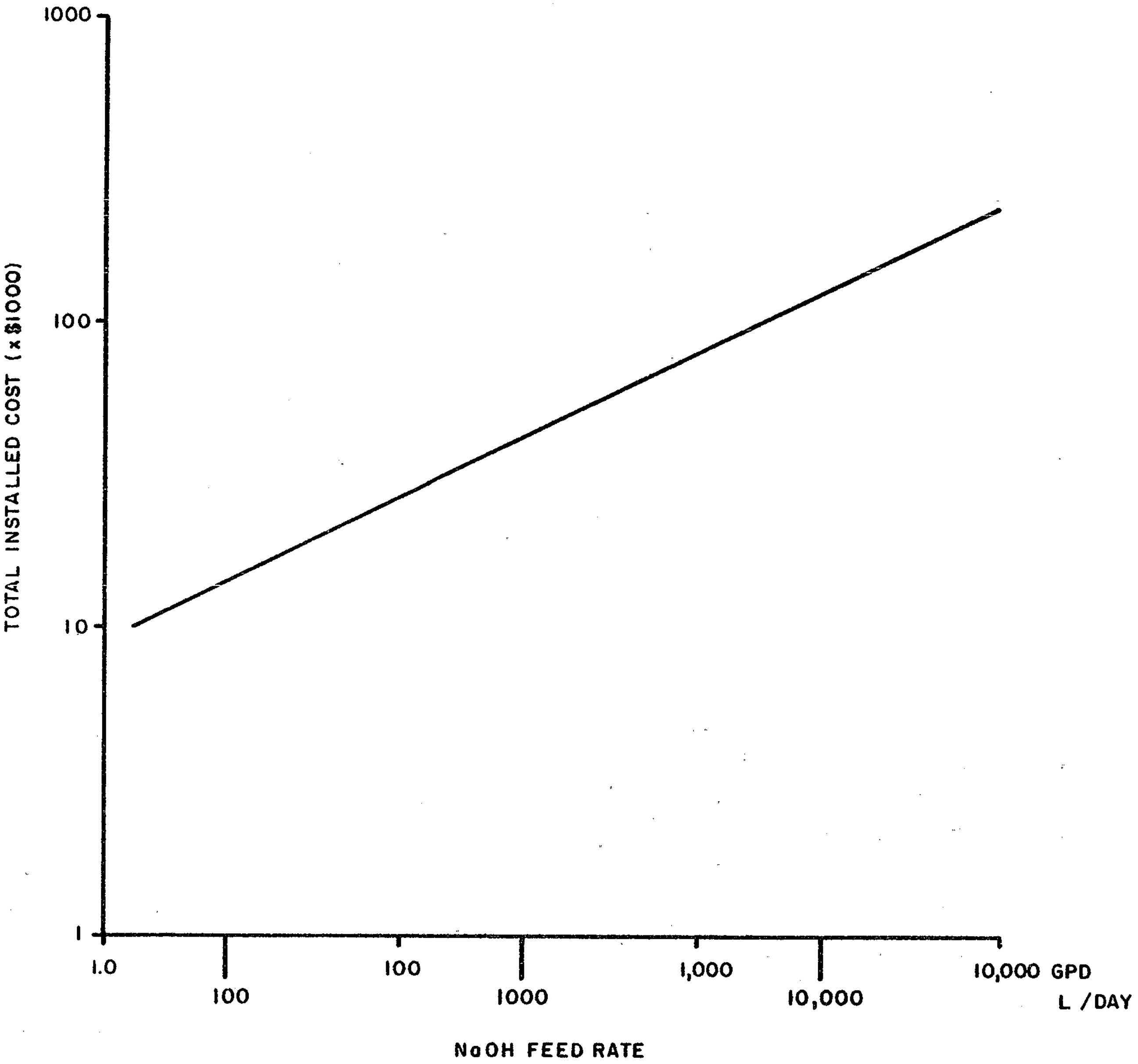

FIGURE A-23 CAPITAL COST CURVE FOR CAUSTIC (NaOH) FEED SYSTEM

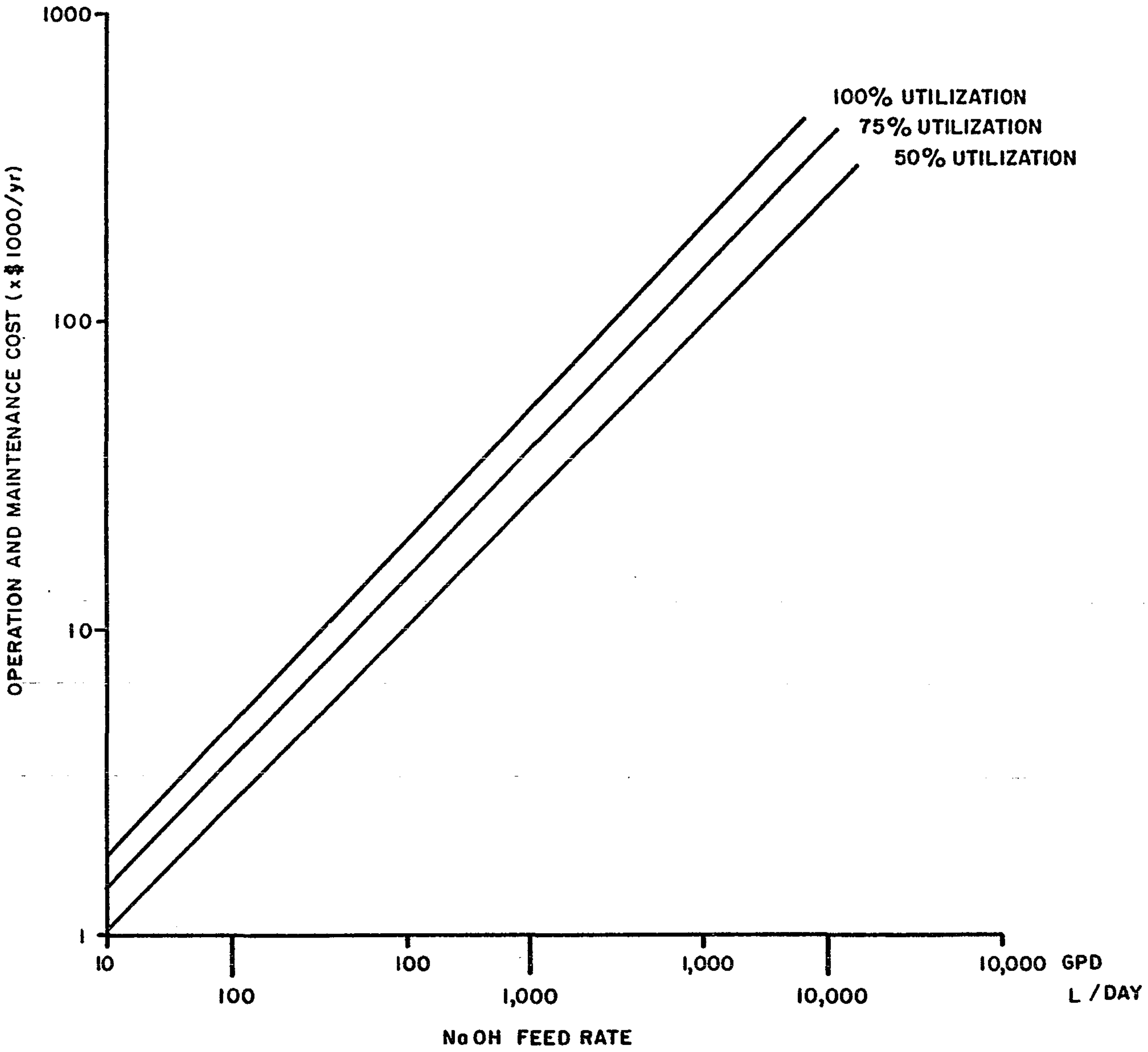

FIGURE A-24 OPERATION AND MAINTENANCE COST CURVES FOR CAUSTIC (NaOH) FEED SYSTEM

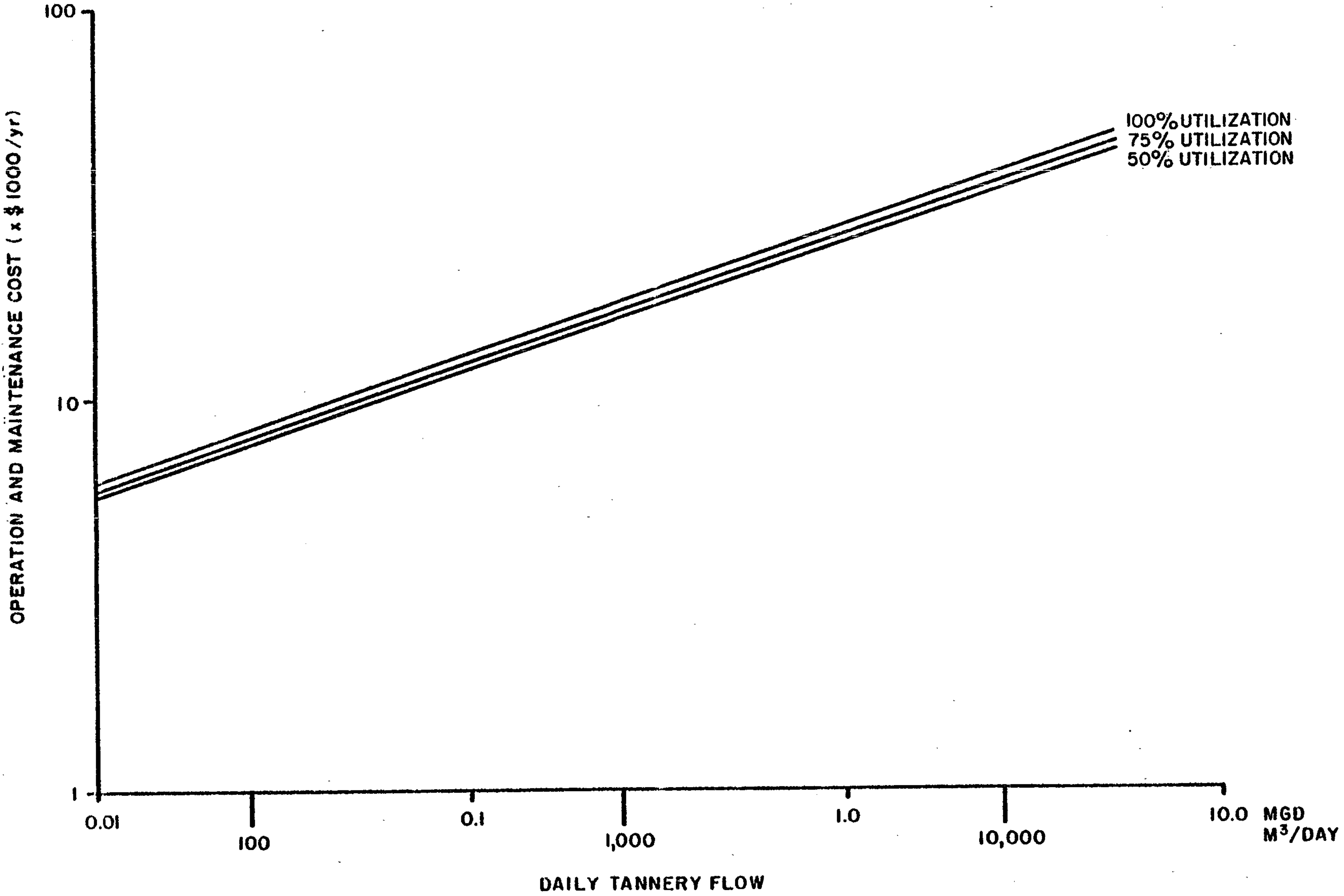

FIGURE A-25 OPERATION AND MAINTENANCE BASE COST CURVES FOR ACTIVATED SLUDGE WITH NITRIFICATION AND PAC ADDITION

TABLE A-8

DESIGN CRITERIA FOR ADVANCED TREATMENT - MULTIMEDIA FILTRATION

1. Influent Pumps	
Type of Pumps	Centrifugal, dry pit
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
2. Filter	
Type of Media	Anthracite coal, silica sand, garnet sand
Number of Filters	
Plants A, B, C	2
Plant D	3
Spare Filter Capacity	
Plants A, B, C	100%
Plant D	50%
Hydraulic Loading Rate	4 gal./ft^2 min. (163 l/m^2 min.)
3. Backwash	
Type of Pumps	Centrifugal, dry pit
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
Backwash Rate	15 gal./ft^2 min. (611 l/m^2 min.)
Backwash Duration	15 min.
Air Surface Scour	5 ft^3/ft^2 min. (1.5 m^3/m^2 min.)

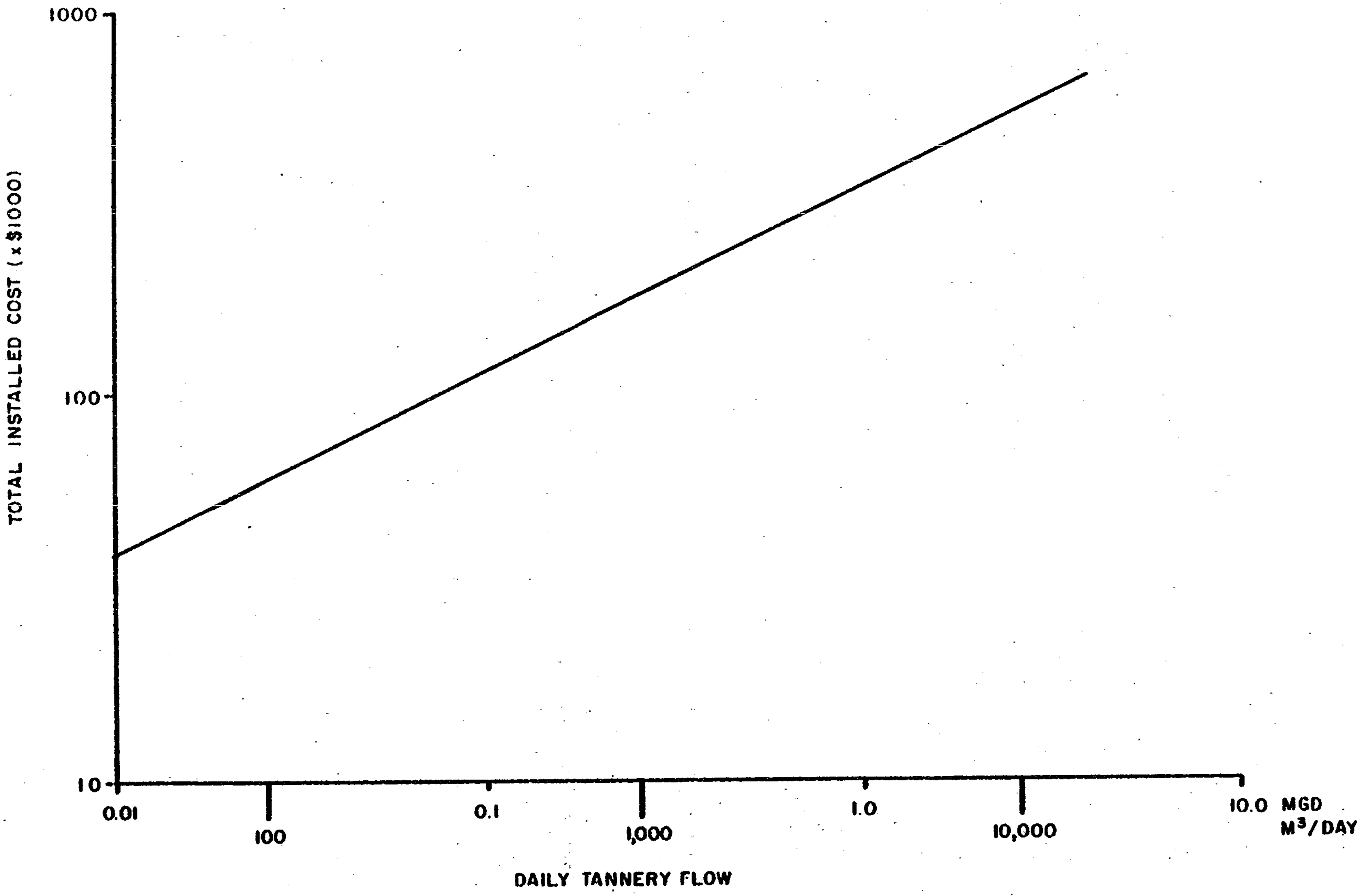

FIGURE A-26 CAPITAL COST CURVE FOR MULTIMEDIA FILTRATION

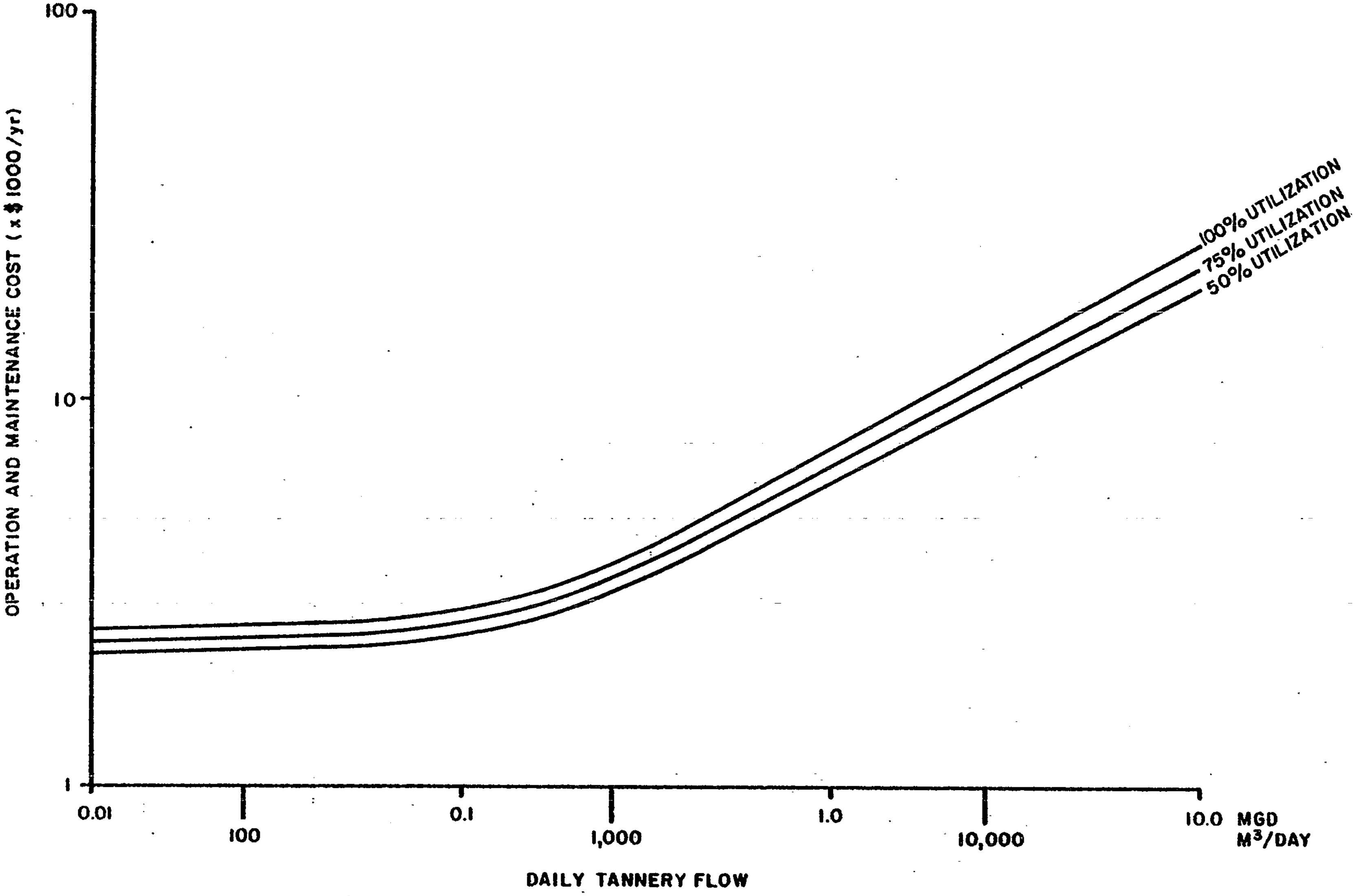

FIGURE A-27 OPERATION AND MAINTENANCE COST CURVES FOR MULTIMEDIA FILTRATION

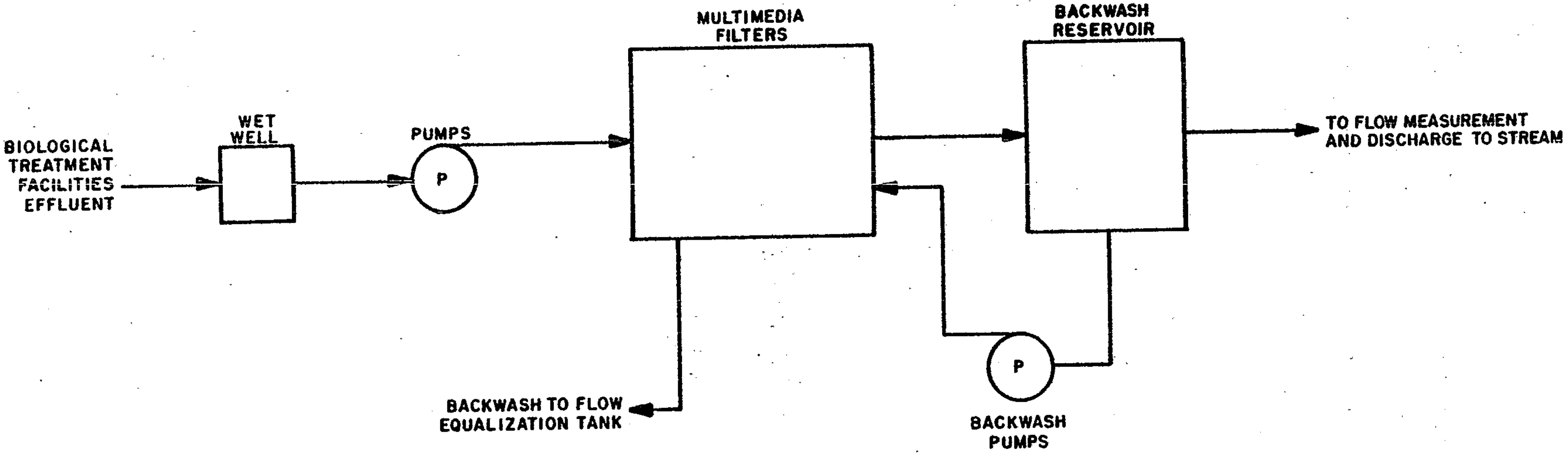

FIGURE A-28 SCHEMATIC LAYOUT FOR MULTIMEDIA FILTRATION

TABLE A-9

DESIGN CRITERIA FOR SLUDGE DEWATERING - FILTER PRESS

1. Filter Press	
Type	Plate and Frame
Operating Pressure	100 psig
Press Cycle	4 hrs
Number of Presses	
Plants A, B, C	1
Plants D	3
Number of Cycles per Press Per Day	
Plants A & B	1
Plants C & D	2
Filter Cake Solids	20% (min)
Cake Thickness	1.25 in. (31.8 mm)
Plate Dimensions	
Plant A	4 ft x 4 ft (1.2 m x 1.2 m)
Plants B, C, D	4.9 ft x 6.6 ft (1.5 m x 2.0 m)
Sludge Production (dry weight)	
Plant A	900 lb/day (408 kg/day)
Plant B	2,700 lb/day (1,225 kg/day)
Plant C	10,900 lb/day (4,944 kg/day)
Plant D	36,000 lb/day (16,330 kg/day)
Feed Pumps	
Type of Pumps	Air operated, diaphragm
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
2. Sludge Conditioning	
Conditioner	Ferric chloride ($FeCl_3$)
Feed Rate	7% (by weight/dry solids)
Storage	
Plants A & B	Drum
Plants C & D	Bulk storage tank
Mix Tank (Detention Time)	1 min.
3. Sludge Storage	
Number of Tanks	1
Storage Capacity	1 day
Mixing	Fixed platform mixer

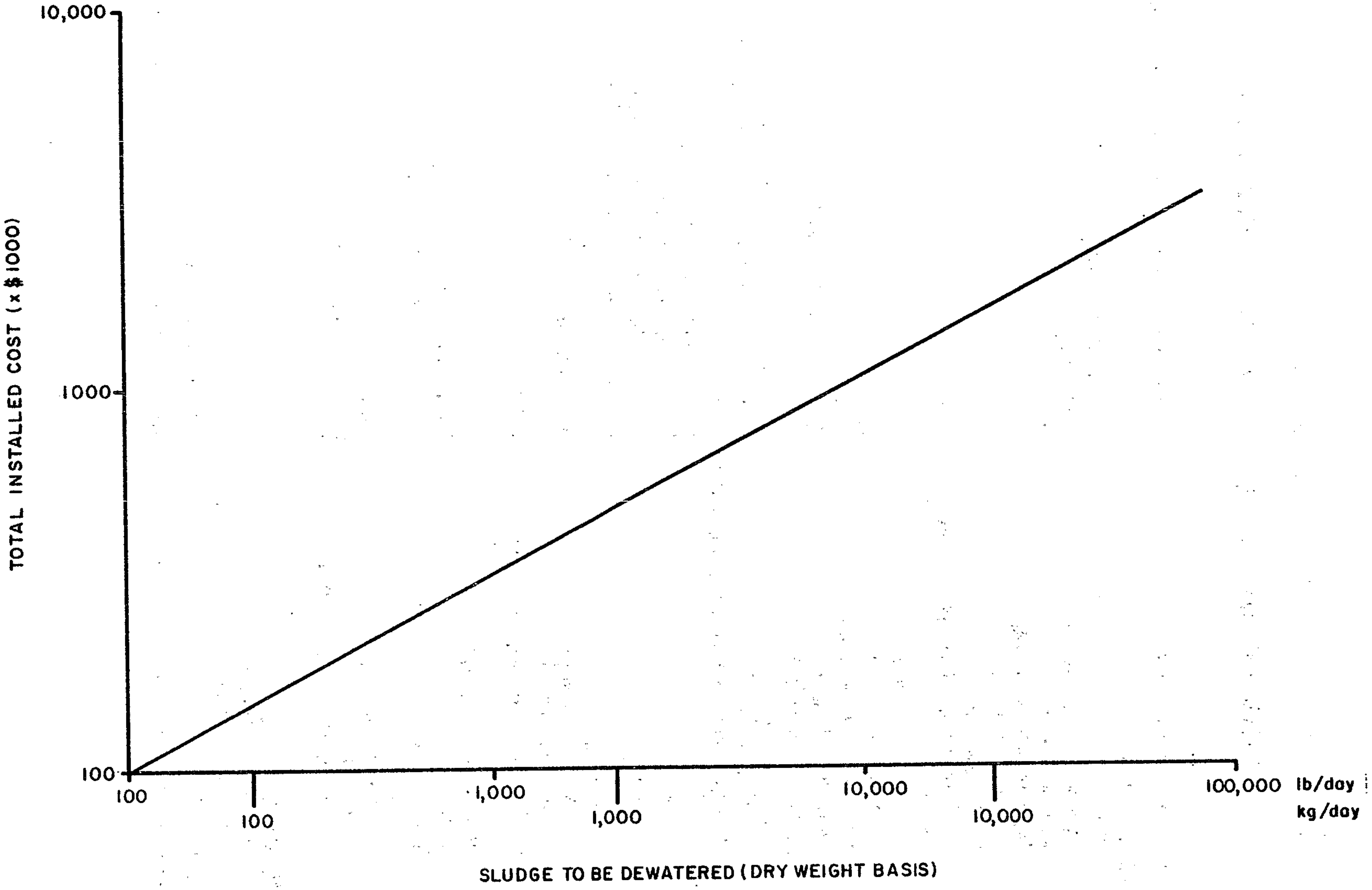

FIGURE A-29 CAPITAL COST CURVE FOR SLUDGE DEWATERING (FILTER PRESS)

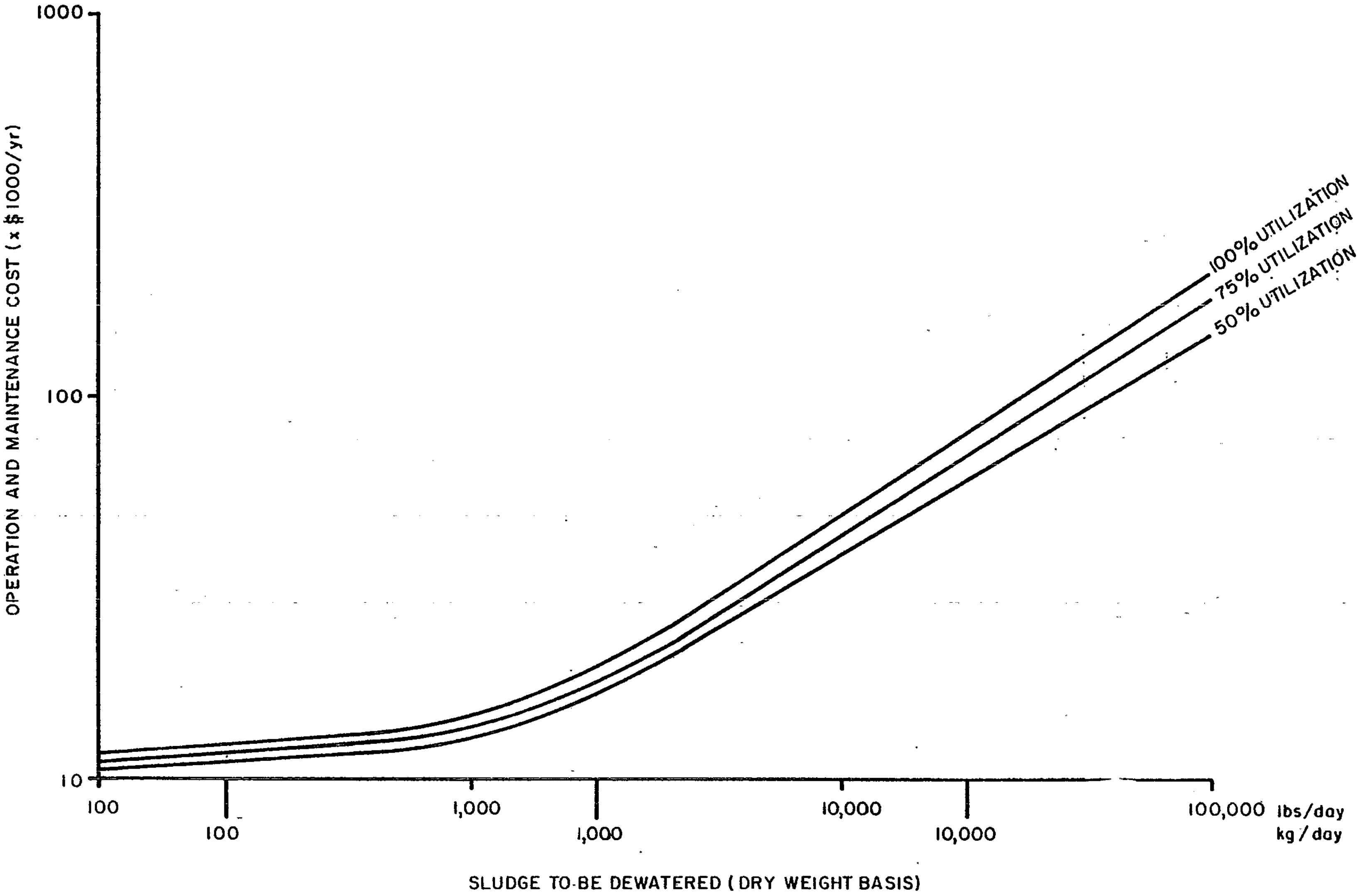

FIGURE A-30 OPERATION AND MAINTENANCE COST CURVES FOR SLUDGE DEWATERING (FILTER PRESS)

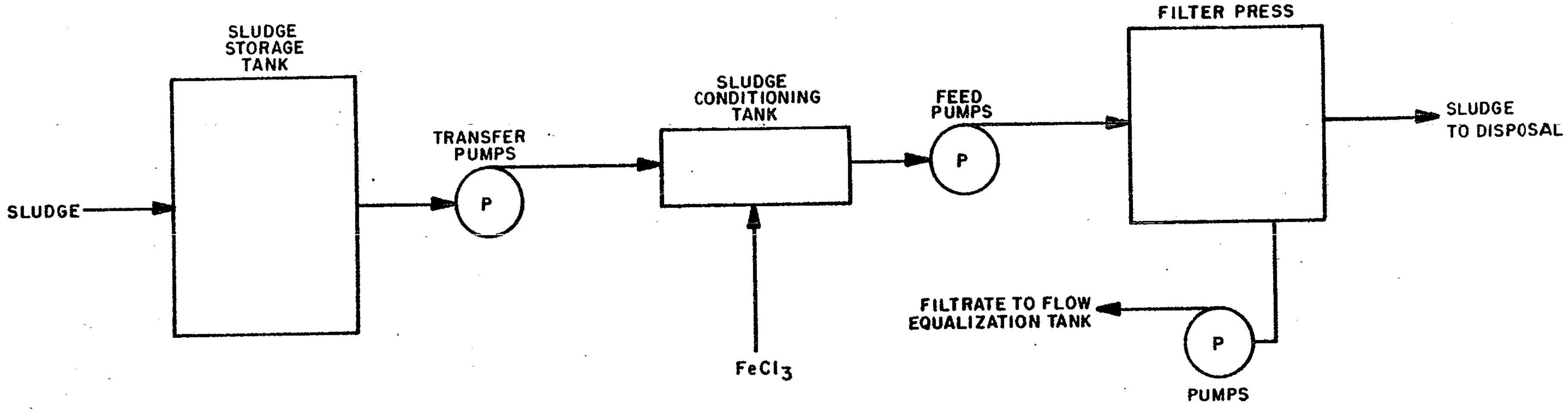

FIGURE A-31 SCHEMATIC LAYOUT FOR SLUDGE DEWATERING (FILTER PRESS)

TABLE A-10

DESIGN CRITERIA FOR SLUDGE DEWATERING
SLUDGE DRYING BEDS

1. Design Loading Rate	20 lbs dry solids/ft^2/yr (97.6 kg dry solids/m^2/yr)
2. Sludge Production (dry weight)	
Plant A	900 lb/day (408 kg/day)
Plant B	2,700 lb/day (1,225 kg/day)
Plant C	10,900 lb/day (4,944 kg/day)
Plant D	36,000 lb/day (16,330 kg/day)
3. Drying Bed Material and Depth	
Fine Sand	6 in. (150 mm)
Coarse Sand	3 in. (75 mm)
Fine Gravel	3 in. (75 mm)
Medium Gravel	3 in (75 mm)
Coarse Gravel	3 to 6 in. (75 to 150 mm)

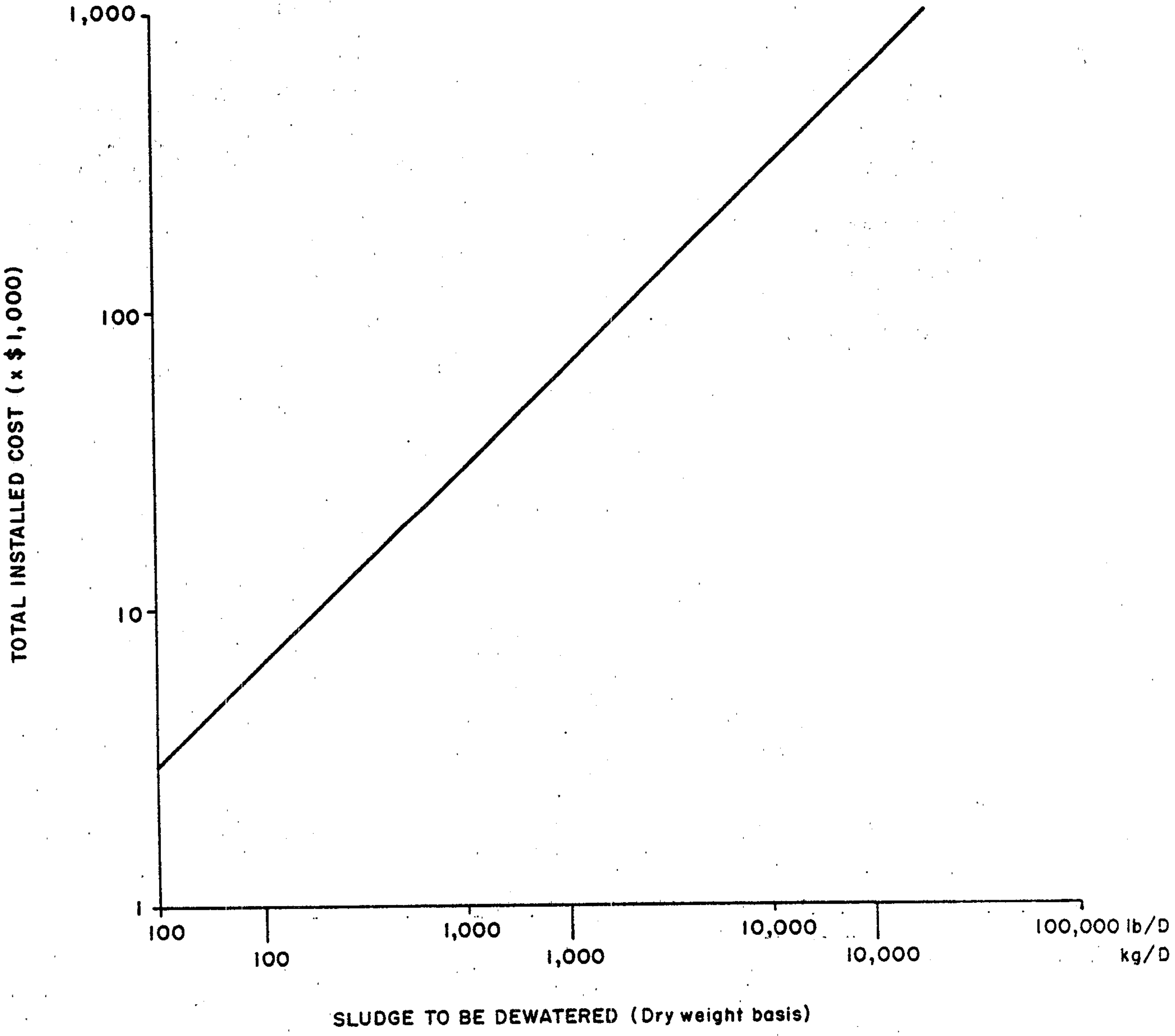

FIGURE A-32 CAPITAL COST CURVE FOR SLUDGE DEWATERING (SLUDGE DRYING BEDS)

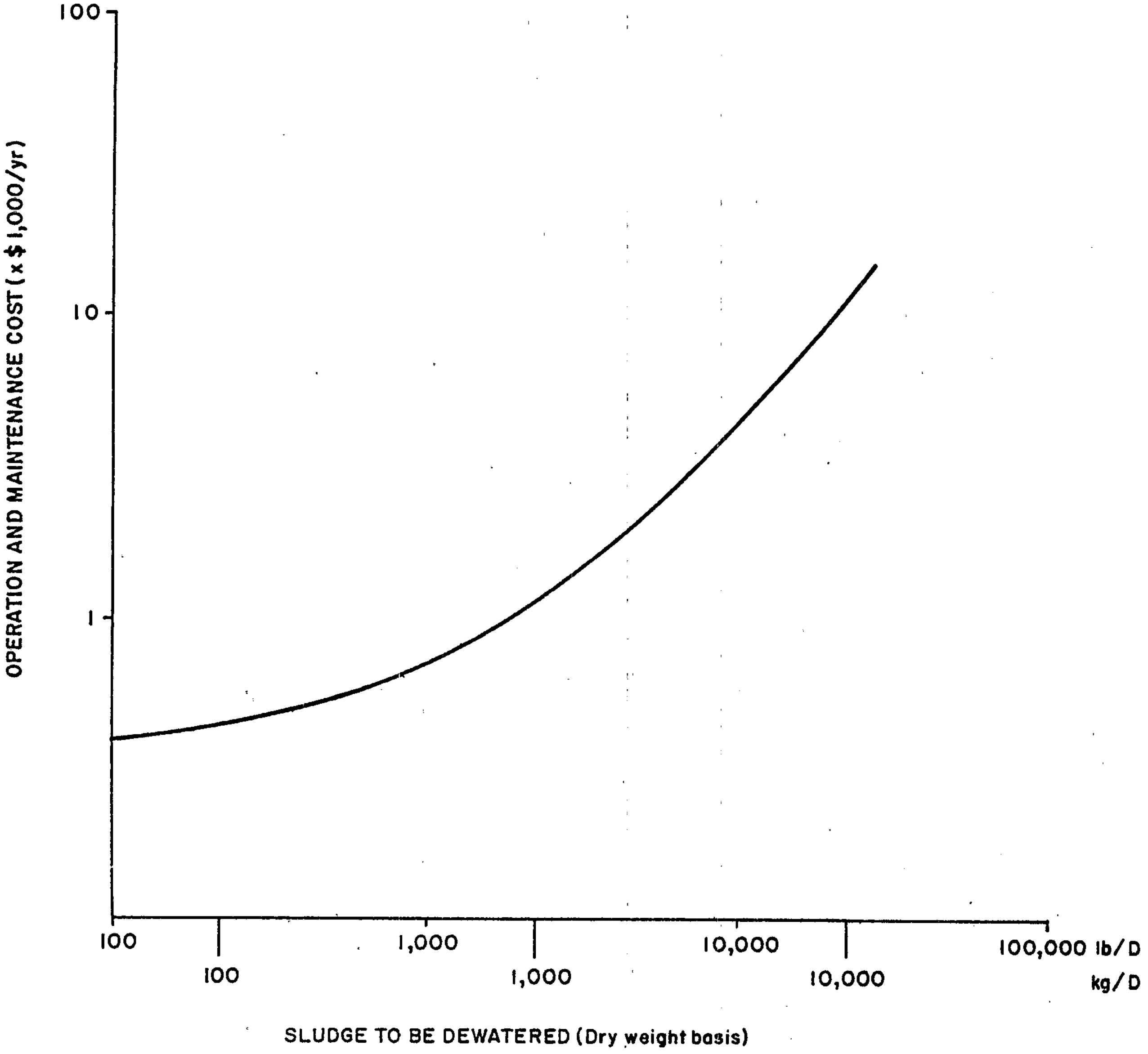

FIGURE A-33 OPERATION AND MAINTENANCE COST CURVE FOR SLUDGE DEWATERING (SLUDGE DRYING BEDS)

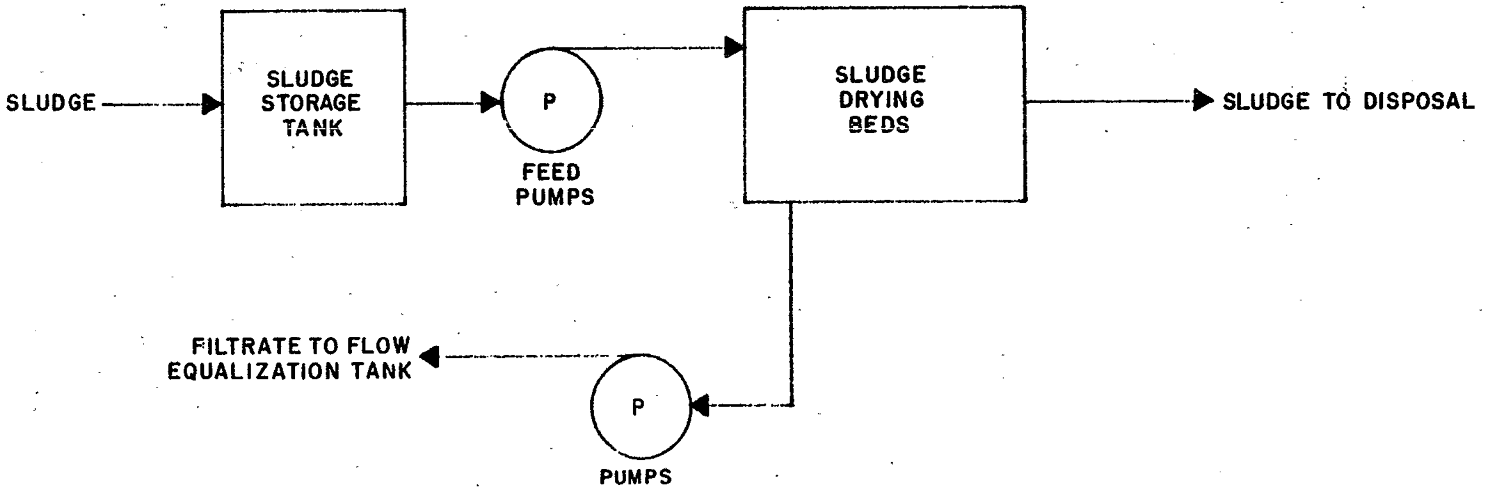

FIGURE A-34 SCHEMATIC LAYOUT FOR SLUDGE DEWATERING (SLUDGE DRYING BEDS)

TABLE A-11

DESIGN CRITERIA FOR SULFIDE OXIDATION WITH NEUTRALIZATION FACILITIES

Sulfuric Acid Feed System	
Chemical	H_2SO_4 (66° Baume)
Dosage	0.43 gallons/1000 gallons (0.43 m^3/1000 m^3)
Feed System	Metering pump (manual adjustment)
Storage	
Plant A	drum
Plant B	drum
Plant C	drum
Plant D	Storage tank (1 tank truck and 10 days storage)

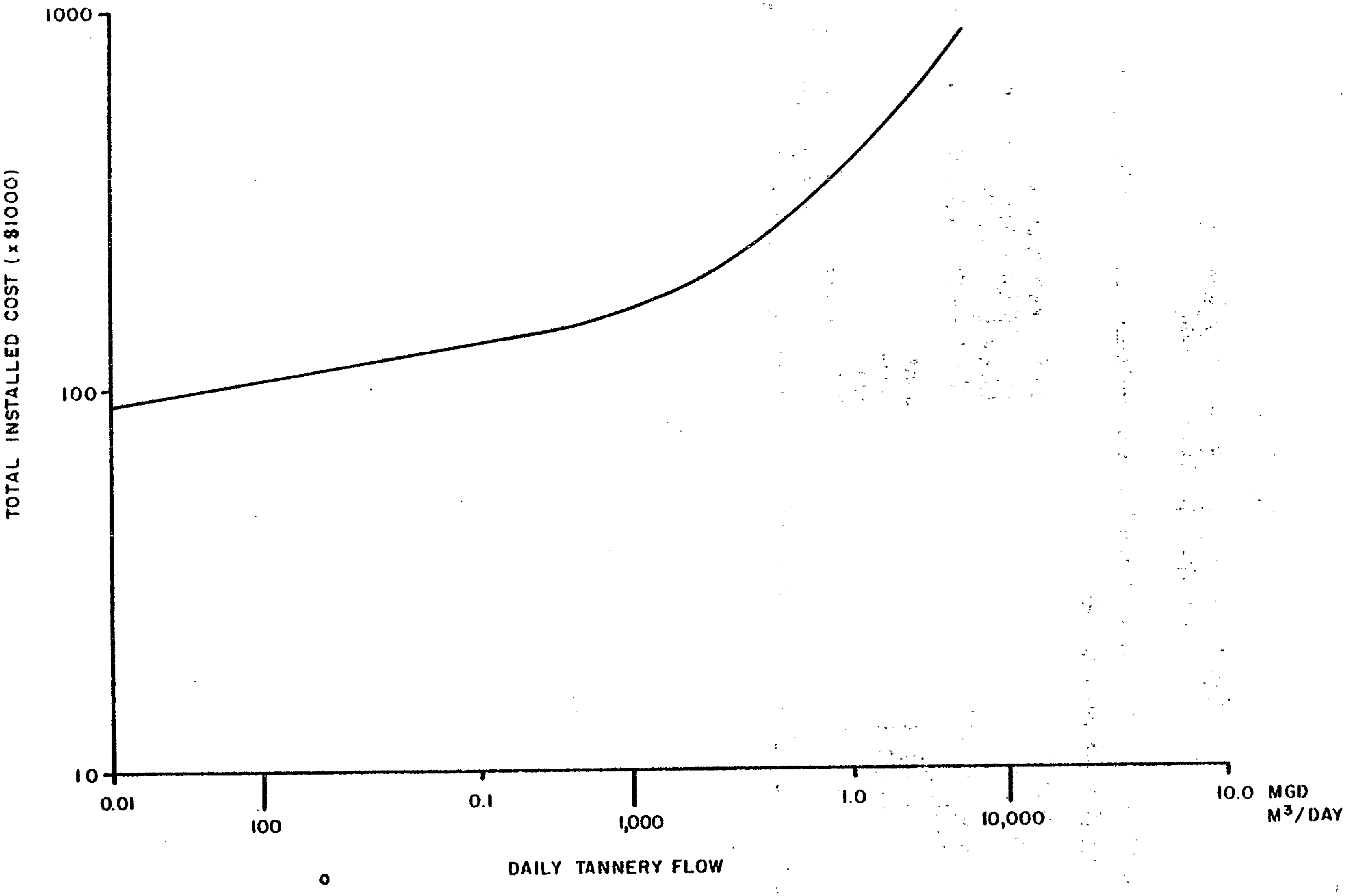

FIGURE A-35 CAPITAL COST CURVE FOR SULFIDE OXIDATION WITH NEUTRALIZATION FACILITIES

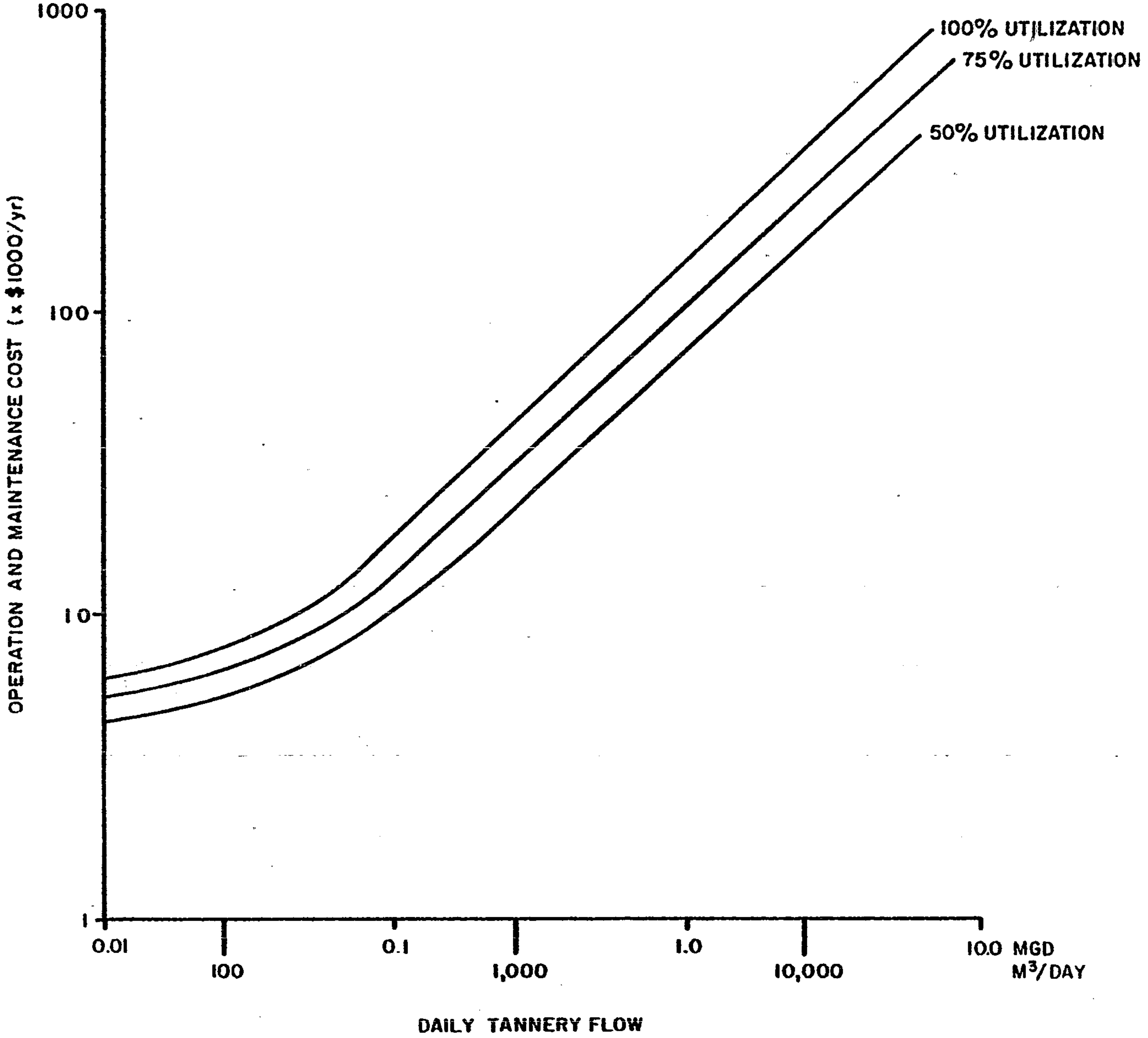

FIGURE A-36 OPERATION AND MAINTENANCE COST CURVES FOR SULFIDE OXIDATION WITH NEUTRALIZATION FACILITIES

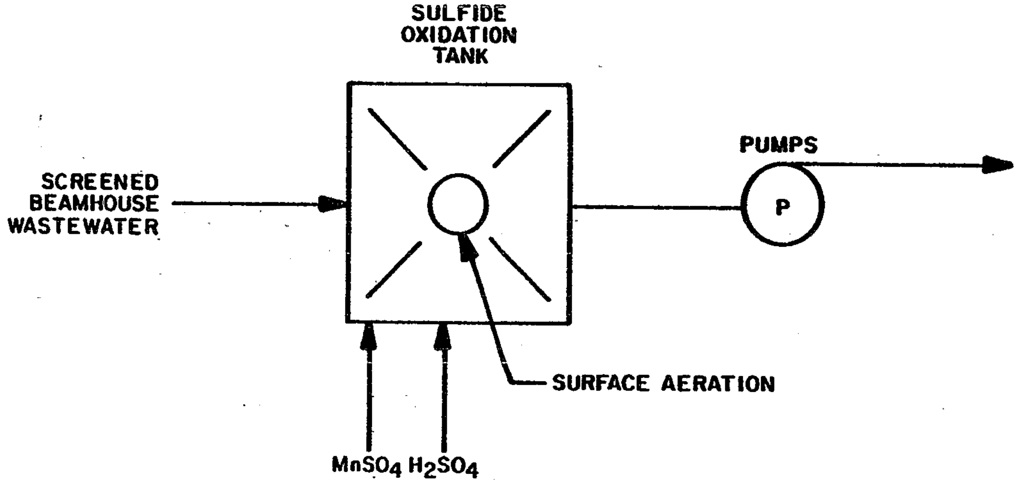

FIGURE A-37 SCHEMATIC LAYOUT FOR SULFIDE OXIDATION WITH NEUTRALIZATION FACILITIES

TABLE A-12

DESIGN CRITERIA FOR TANYARD WASTEWATER SCREENING

1. Tanyard Screens	
Type of Screen	Static, tangential
Number of Screens	1
Opening Size	0.04 in. (1.02 mm)
2. Tanyard Pumps	
Type	Submersible, centrifugal
Number of Pumps	2 (1 standby)
Spare Pumping Capacity	100%
3. Piping	
Tanyard Piping	
Plant A	10 ft.-4 in. dia. (3.0 m-102mm dia.)
Plant B	30 ft.-6 in. dia. (9.1 m-152 mm dia.)
Plant C	120 ft.-8 in. dia. (36.6 m-203 mm dia.)
Plant D	320 ft.-12 in. dia. (97.5 m-305 mm dia.)
Force Main (Tanyard to Screen)	
Plant A	200 ft.-4 in. dia. (61 m-102 mm dia.)
Plant B	200 ft.-4 in. dia. (61 m-102 mm dia.)
Plant C	500 ft.-6 in. dia. (152 m-152 mm dia.)
Plant D	500 ft.-8 in. dia. (152 m-203 mm dia.)

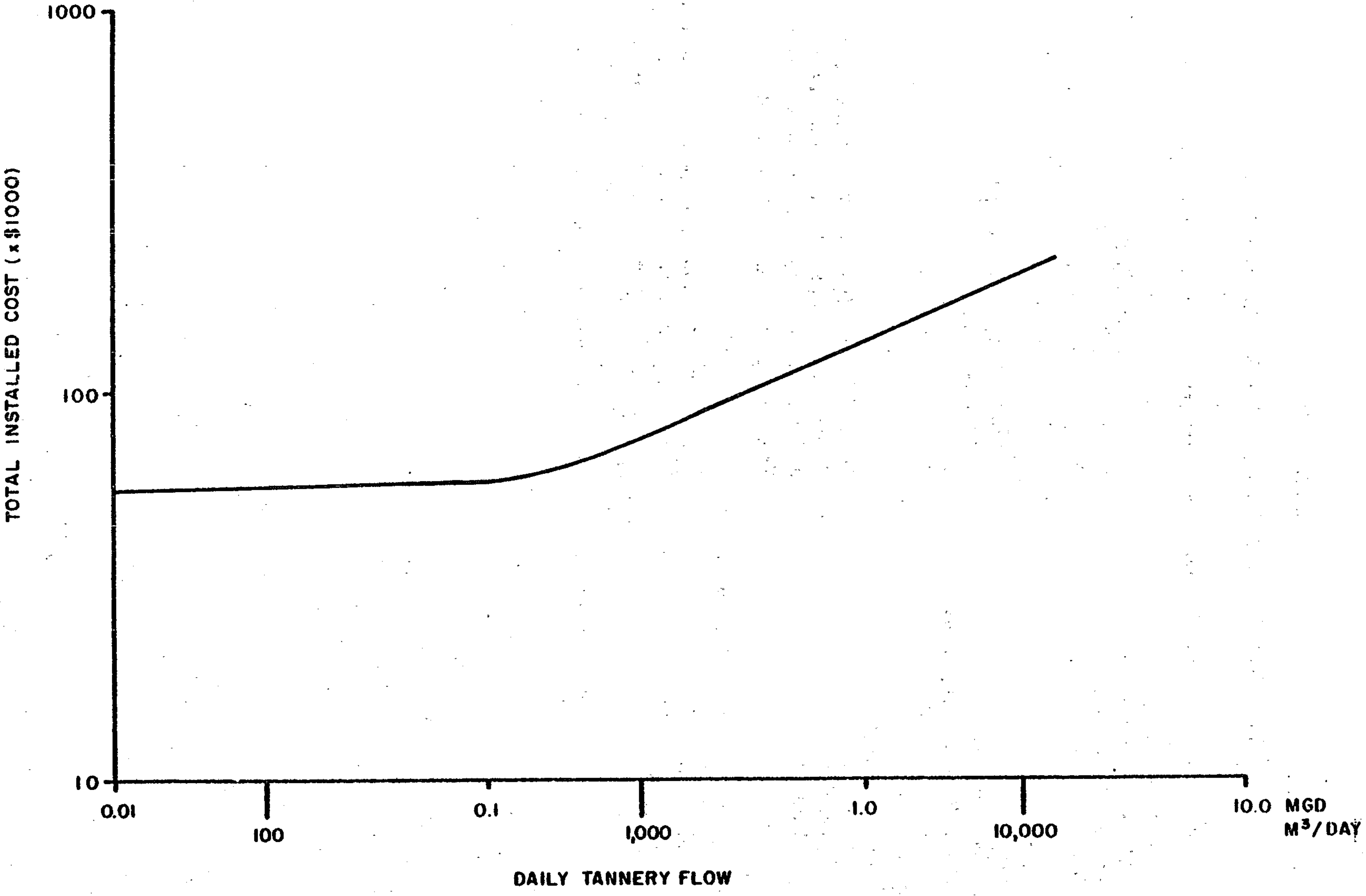

FIGURE A-38 CAPITAL COST CURVE FOR TANYARD WASTEWATER SCREENING

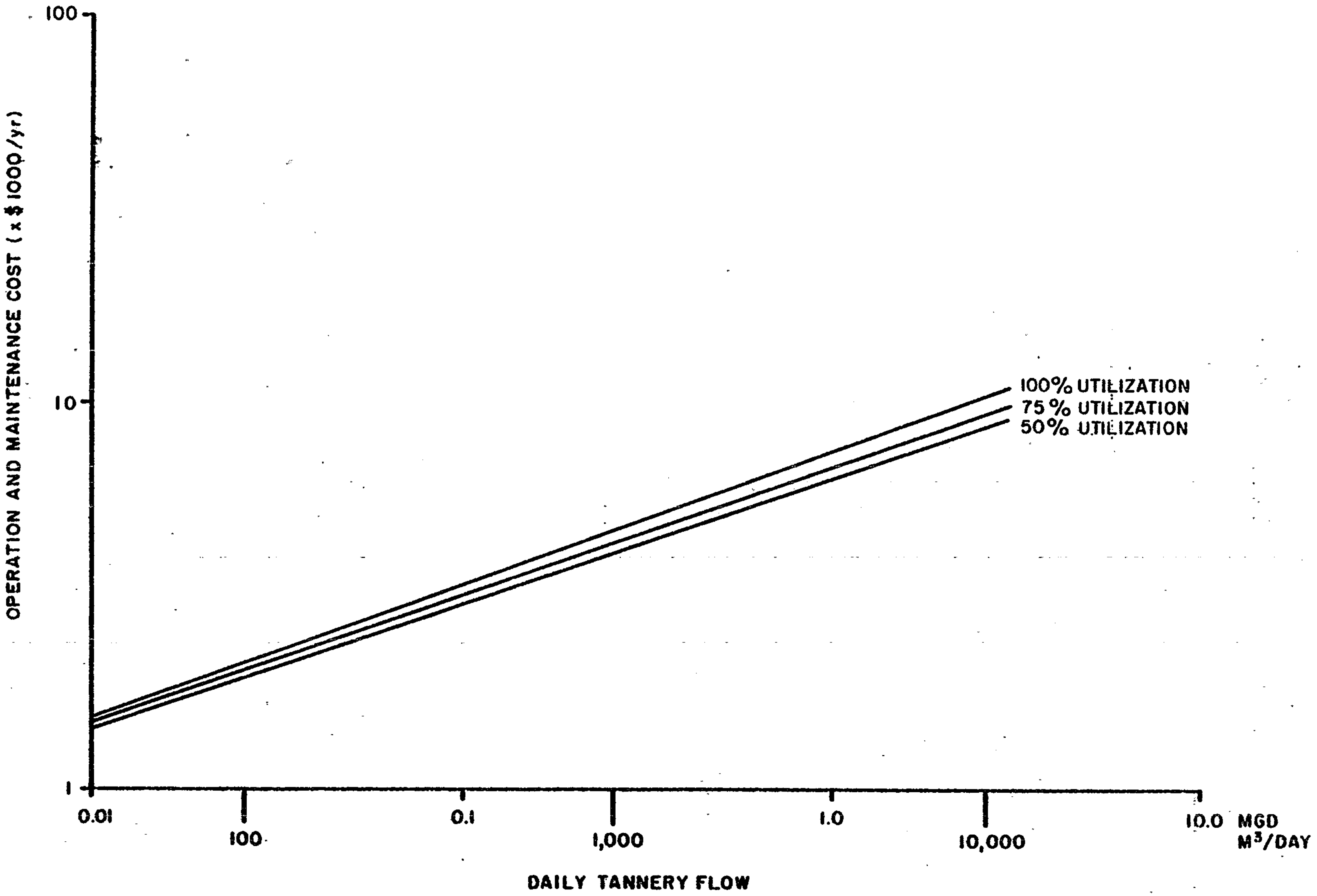

FIGURE A-39 OPERATION AND MAINTENANCE COST CURVES FOR TANYARD WASTEWATER SCREENING

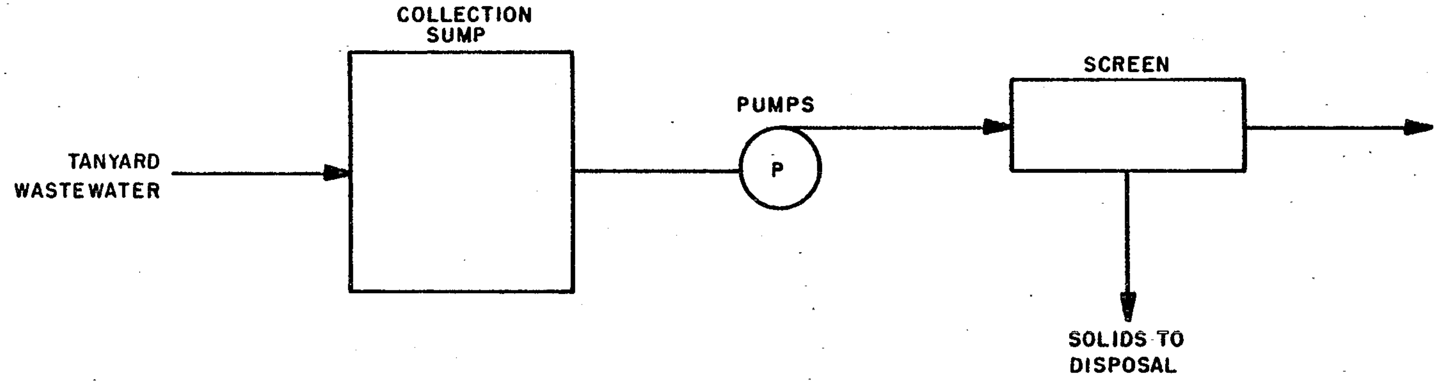

FIGURE A-40 SCHEMATIC LAYOUT FOR TANYARD WASTEWATER SCREENING

TABLE A-13

DESIGN CRITERIA FOR NEUTRALIZATION FACILITIES

1. Caustic Feed System	
Chemical	NaOH (50% solution)
Feed System	Metering pumps (1 spare) Plants A & B - manual adjustment Plants C & D - pH meter controlled
Feed Rate	1.6 gallons/1000 gallons (1.6 m^3/1000 m^3)
Storage	
Plant A	drum
Plant B	drum
Plant C	drum
Plant D	Bulk storage tank (10 days storage plus 1 tank truck)
2. Acid Feed System	
Chemical	H_2SO_4 (66° Baume)
Feed System	Metering pumps (1 spare) Plants A & B manual adjustment Plants C & D pH meter controlled
Feed Rate	0.43 gallons/1000 gallons) (0.43 m^3/1000 m^3)
Storage	
Plant A	drum
Plant B	drum
Plant C	drum
Plant D	Bulk storage tank (10 days storage plus 1 tank truck load)
3. Mixing Tank	
Detention Time	5 minutes
Mixer	Platform

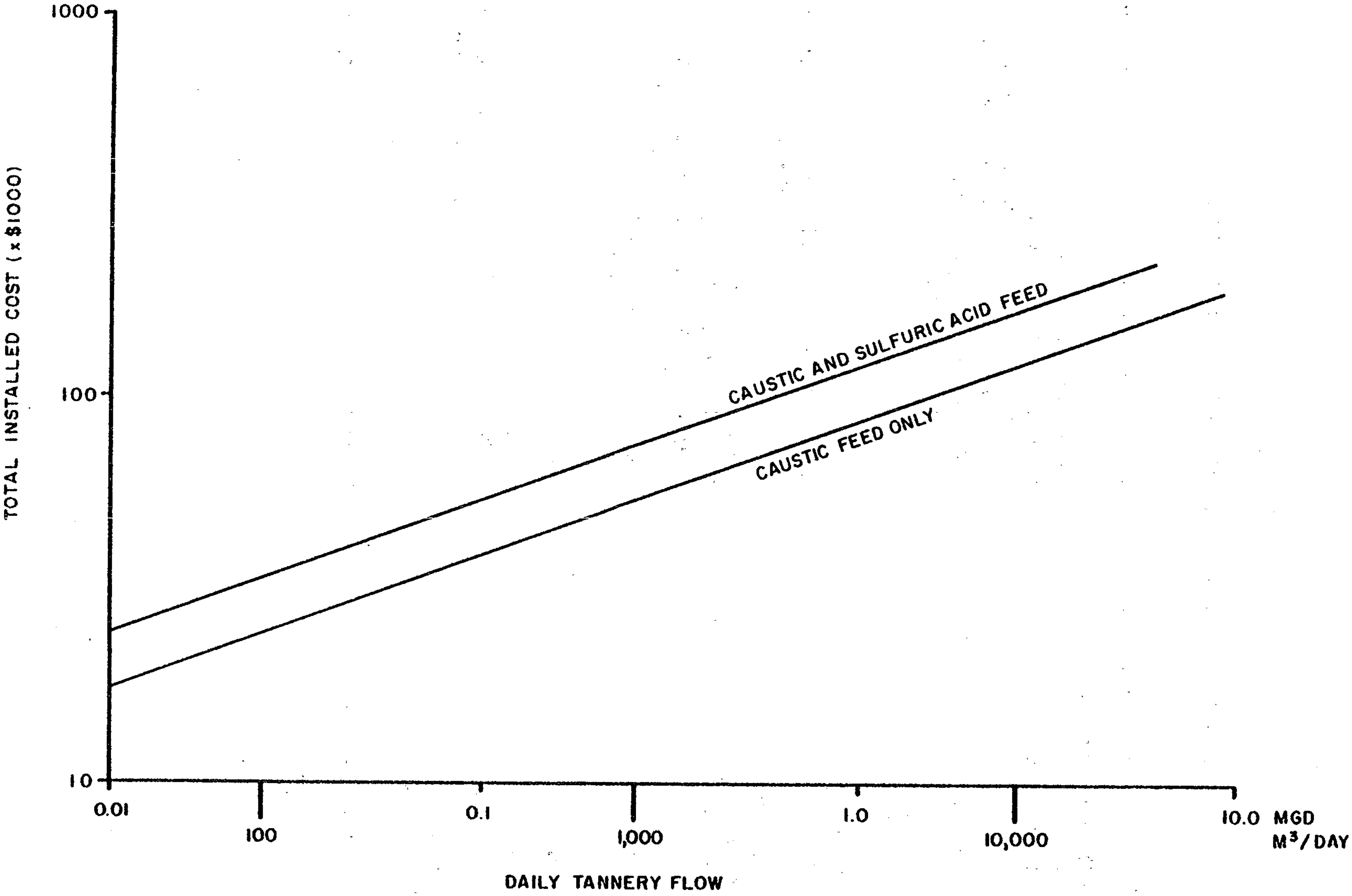

FIGURE A-41 CAPITAL COST CURVE FOR NEUTRALIZATION FACILITIES

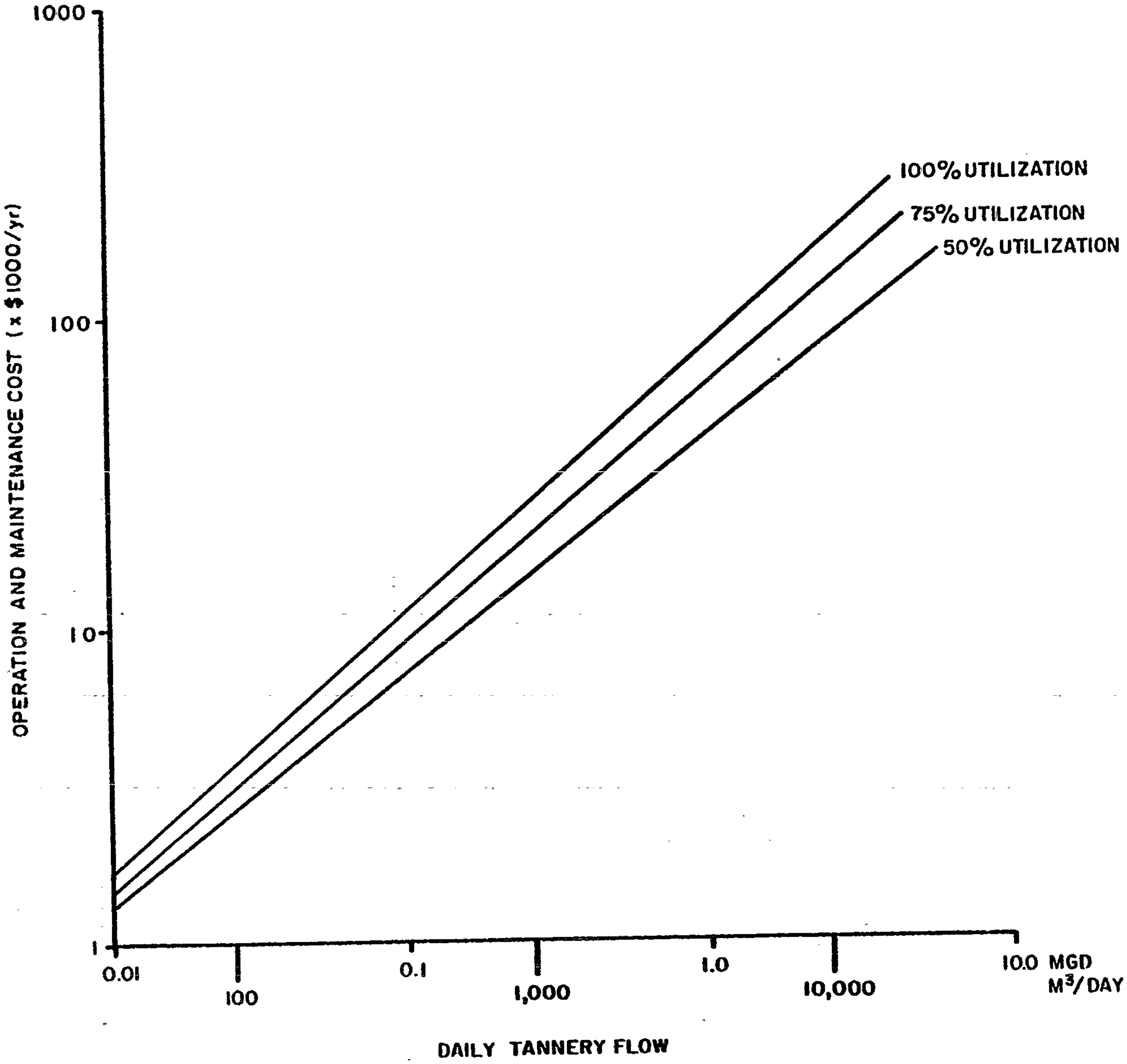

FIGURE A-42 OPERATION AND MAINTENANCE COST CURVES FOR NEUTRALIZATION FACILITIES (CAUSTIC AND SULFURIC ACID FEED)

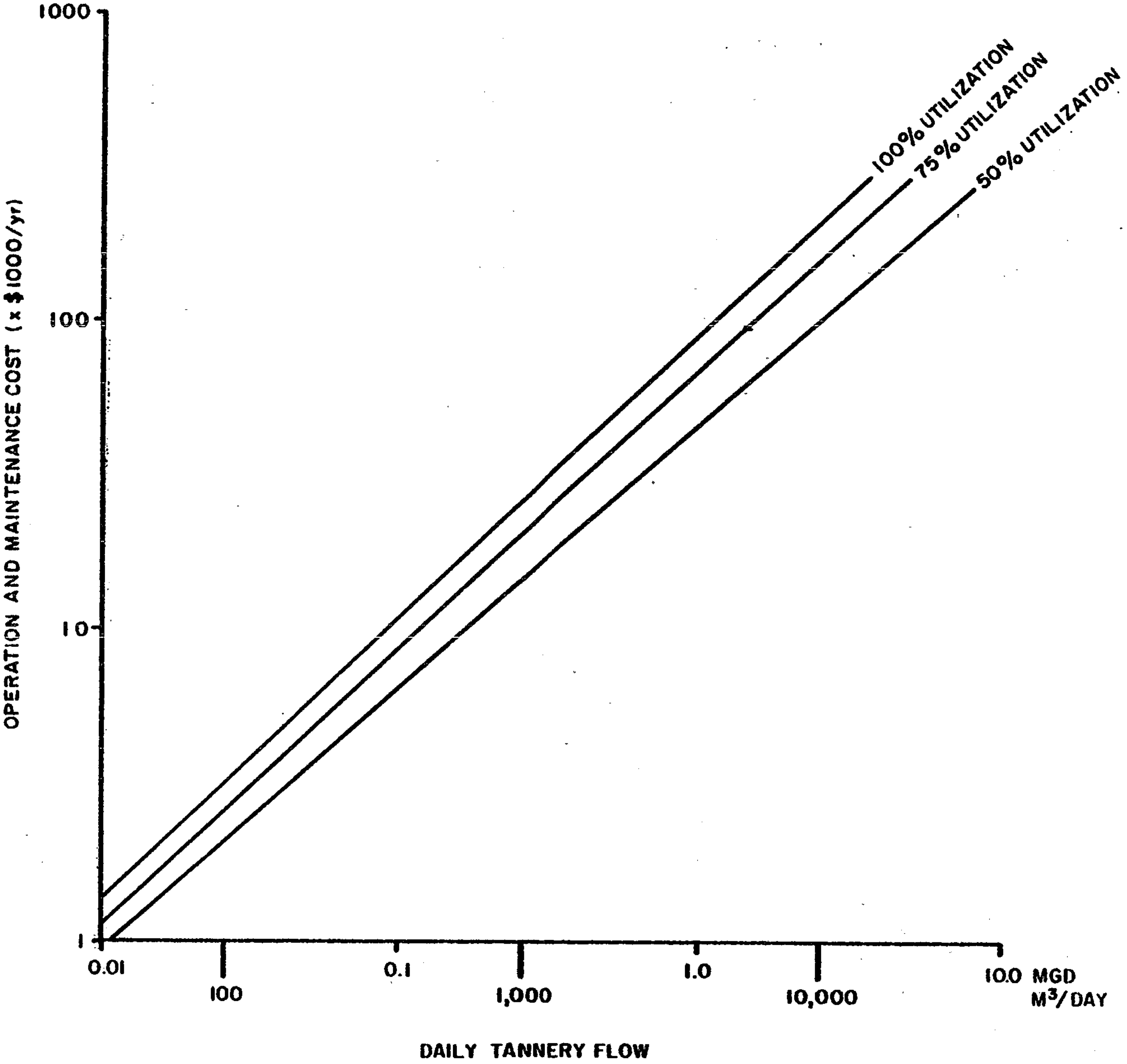

FIGURE A-43 OPERATION AND MAINTENANCE COST CURVES FOR NEUTRALIZATION FACILITIES (CAUSTIC FEED ONLY)

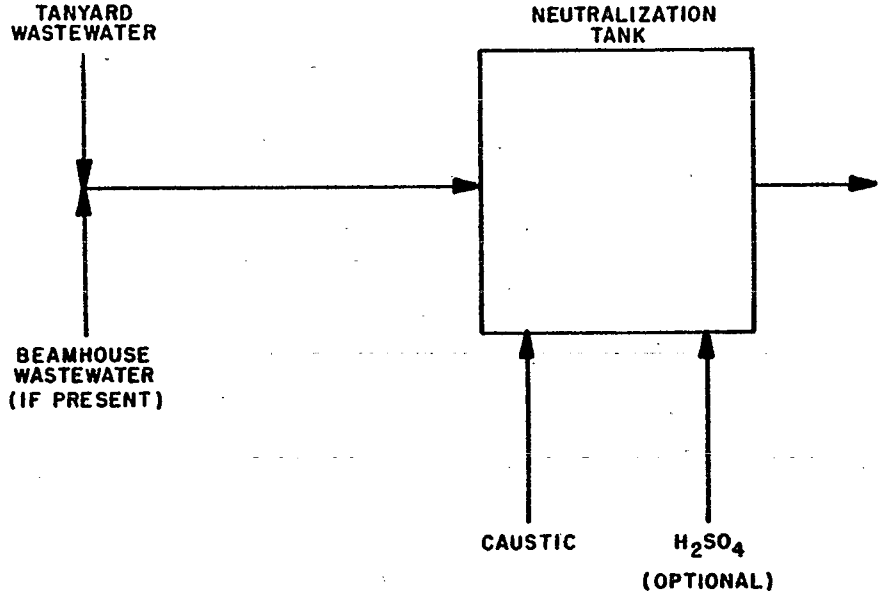

FIGURE A-44 SCHEMATIC LAYOUT FOR NEUTRALIZATION FACILITIES

TABLE A-14

SUBCATEGORY DESIGN SUMMARY FOR COST ESTIMATES

		Activated Sludge System					Sludge Dewatering System			
Subcategory	Treatment Technology	Aeration Basin Volume (MG/mgd)(1)	Aeration Capacity (scfm/mgd)(2)	PAC Addition (lb/MG)(3)	Caustic Addition (gal/MG)(4)	Phosphorous Addition (lb/MG)(3)	Calcium Carbonate Sludge (lb dry solids/ MG)(3)	TSS Removal Sludge (lb dry solids/ MG)(3)	Waste Activated Sludge (lb dry solids/ MG)(3)	Total Sludge (lb dry solids/ MG)(3)
1	BPT/BAT (I)	1.2	4,000	0	0	50	0	9,900	2,100	12,000
	BAT (II)	1.3	6,400	380	720	50	14,000	13,000	2,700	29,700
	BAT (III)	1.3	6,400	380	720	50	14,000	13,000	2,800	29,800
2	BPT/BAT (I)	1.3	4,500	0	0	50	0	30,000	4,300	34,300
	BAT (II)	1.4	7,500	690	890	50	16,000	38,000	4,800	58,800
	BAT (III)	1.4	7,500	690	890	50	16,000	38,000	4,900	58,900
3	BPT/BAT (I)	2.4	7,900	0	0	90	0	22,000	4,700	26,700
	BAT (II)	2.1	12,000	660	1,300	80	16,000	23,000	4,600	43,600
	BAT (III)	2.1	12,000	660	1,300	80	16,000	23,000	4,700	43,700
4	BPT/BAT (I)	0.6	1,900	0	0	20	0	7,100	1,100	8,200
	BAT (II)	0.9	4,000	340	430	30	0	11,000	2,400	13,400
	BAT (III)	0.9	4,000	340	430	30	0	11,000	2,500	13,500
5	BPT/BAT (I)	2.4	8,000	0	0	90	0	4,500	3,000	7,500
	BAT (II)	2.2	8,300	480	390	90	0	4,600	3,400	8,000
	BAT (III)	2.2	8,300	480	390	90	0	4,600	3,500	8,100
6	BPT/BAT (I)	6.3	22,000	0	0	250	0	54,000	13,000	67,000
	BAT (II)	7.3	36,000	2,000	4,000	290	57,000	96,000	14,000	167,000
	BAT (III)	7.3	36,000	2,000	4,000	290	57,000	96,000	14,100	167,100
7	BPT/BAT (I)	1.0	3,200	0	0	40	0	5,900	1,500	7,400
	BAT (II)	1.1	4,000	280	230	40	0	6,400	2,000	8,400
	BAT (III)	1.1	4,000	280	230	40	0	6,400	2,100	8,500
8	BPT/BAT (I)	3.6	12,000	0	0	140	0	32,000	7,200	39,200
	BAT (II)	3.2	12,000	1,000	560	120	16,000	35,000	7,000	58,000
	BAT (III)	3.2	12,000	1,000	560	120	16,000	35,000	7,100	58,100
9	BPT/BAT (I)	1.2	4,000	0	0	50	0	7,700	1,900	9,600
	BAT (II)	1.4	10,000	520	1,500	60	0	9,200	2,900	12,100
	BAT (III)	1.4	10,000	520	1,500	60	0	9,200	3,000	12,200

(1) or $m^3/m^3/d$

(2) scfm/mgd x 4.49×10^{-4} = $m^3 air/hr/m^3/d$

(3) lb/MG (or lb dry solids/MG) x 1.2×10^{-4} = $kg/m^3/d$

(4) gal/MG x 10^{-3} = $L/m^3/d$

All flows represent daily flow from tannery.

There is a reduction in tannery flow as the result of in-plant controls for BAT treatment levels (II and III).

TABLE A-15

COST SUMMARY FOR BPT TREATMENT TECHNOLOGY CAPITAL AND ANNUAL OPERATION AND MAINTENANCE (O&M) COSTS

Tannery Number	Flow[1] (mgd(m^3/day))	Total Capital Cost[2] To Upgrade Facilities To BPT ($)	Credit Allowed for Existing Treatment Facilities[2] ($)	Annual O&M Cost[1] ($)
43	0.095 (360)	944,000	0	138,100
47	0.030 (114)	150,000	378,400	57,700
54	0.065 (246)	93,000	592,600	73,000
60	0.846 (3,200)	2,016,000	971,000	692,000
184	1.020 (3,860)	1,327,000	1,118,600	570,800
185	0.064 (242)	290,000	495,000	108,800
248	0.145 (549)	547,000	670,000	189,300
253	0.370 (1,400)	344,000	1,446,000	221,600
320	0.332 (1,260)	1,161,000	1,319,700	521,900
385	0.230 (871)	12,000	1,843,300	303,300
388	0.048 (182)	543,000	483,100	198,200
389	0.050 (189)	0	665,200	65,800
400	0.0047 (18)	0	273,700	34,100
409	0.420 (1,590)	1,541,000	165,400	274,300
415	0.410 (1,550)	24,000	2,132,500	423,200
502	0.143 (541)	300,000	1,304,200	332,000
525	0.188 (712)	1,303,000	0	174,300
Total	4.46 (16,900)	10,595,000	13,858,700	4,378,400

All costs correspond to ENRCCI of 3730 (First Quarter 1982).

[1] Based on tannery operating at 100% capacity.

[2] Adjusted to reflect local conditions.

TABLE A-16

BAT OPTION DEVELOPMENT

Unit Processes	OPTION I		OPTION II		OPTION III	
	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9
In Plant Controls			X	X	X	X
Stream Segregation			X		X	
Sulfide Oxidation			X		X	
Flue Gas Carbonation			X		X	
Flow Equalization (2-Day Storage Capacity)	X	X	X	X	X	X
Coagulation-Sedimentation	X	X	X	X	X	X
Biological Treatment (Extended-Aeration)						
Aeration System	X	X	X	X	X	X
Aeration Tank	X	X	X	X	X	X
Base O&M	X	X	X	X	X	X
Phosphorus Addition	X	X	X	X	X	X
PAC Addition			X	X	X	X
Caustic Addition (NaOH)			X	X	X	X
Secondary Clarifier	X	X	X	X	X	X
Multimedia Filtration					X	X
Sludge Dewatering	X	X	X	X	X	X
Sludge Disposal	X	X	X	X	X	X
Effluent Monitoring	X	X	X	X	X	X

TABLE A-17

COST SUMMARY FOR BAT TREATMENT TECHNOLOGY OPTIONS CAPITAL AND ANNUAL OPERATION AND MAINTENANCE (O&M) COSTS

		EXISTING TO BPT/BAT I		BAT I TO BAT II		BAT II TO BAT III	
Tannery Number	Flow (mgd(m^3/day))	Incremental Capital Cost ($)	Incremental Annual O&M Cost ($)	Incremental Capital Cost ($)	Incremental Annual O&M Cost ($)	Incremental Capital Cost ($)	Incremental Annual O&M Cost ($)
43	0.095 (360)	944,000	138,100	1,213,000	137,600	138,000	3,500
47	0.030 (114)	150,000	57,700	390,000	56,100	82,000	3,200
54	0.065 (246)	93,000	73,000	20,000	22,100	114,000	3,300
60	0.846(3,200)	2,016,000	692,000	446,000	734,700	382,000	8,400
184	1.020(3,860)	1,327,000	570,800	1,759,000	753,900	395,000	8,800
185	0.064 (242)	290,000	108,800	268,000	105,500	118,000	3,300
248	0.145 (549)	547,000	189,300	1,433,000	232,800	173,000	3,900
253	0.370(1,400)	344,000	221,600	26,000	95,900	252,000	5,400
320	0.332(1,260)	1,161,000	521,900	2,668,000	505,900	275,000	5,800
385	0.230 (871)	12,000	303,300	1,610,000	458,100	214,000	4,500
388	0.048 (182)	543,000	198,200	376,000	138,400	102,000	3,300
389	0.050 (189)	0	65,800	198,000	28,600	105,000	3,300
400	0.0047 (18)	0	34,100	0	17,800	0	3,100
409	0.420(1,590)	1,541,000	274,300	2,056,000	315,300	262,000	5,500
415	0.410(1,550)	24,000	423,200	1,878,000	546,100	284,000	6,000
502	0.143 (541)	300,000	332,000	1,577,000	371,500	151,000	3,600
525	0.188 (712)	1,303,000	174,300	1,634,000	218,500	196,000	4,300
Total	4.46 (16,900)	10,595,000	4,378,400	17,552,000	4,738,800	3,243,000	79,200

All costs correspond to ENRCCI of 3730 (First Quarter 1982).

TABLE A-18

NSPS OPTION DEVELOPMENT

Unit Processes	OPTION I		OPTION II		OPTION III	
	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9
In Plant Controls	X	X	X	X	X	X
Stream Segregation			X		X	
Sulfide Oxidation			X		X	
Flue Gas Carbonation			X		X	
Flow Equalization (2-Day Storage Capacity)	X	X	X	X	X	X
Coagulation-Sedimentation	X	X	X	X	X	X
Biological Treatment (Extended-Aeration)						
Aeration System	X	X	X	X	X	X
Aeration Tank	X	X	X	X	X	X
Base O&M	X	X	X	X	X	X
Phosphorus Addition	X	X	X	X	X	X
PAC Addition			X	X	X	X
Caustic Addition (NaOH)			X	X	X	X
Secondary Clarifier	X	X	X	X	X	X
Multimedia Filtration					X	X
Sludge Dewatering	X	X	X	X	X	X
Sludge Disposal	X	X	X	X	X	X
Effluent Monitoring	X	X	X	X	X	X

TABLE A-19

COST SUMMARY FOR NSPS TREATMENT TECHNOLOGY OPTIONS
CAPITAL AND ANNUAL OPERATION AND MAINTENANCE (O&M) COSTS

				OPTION I		OPTION II		OPTION III	
Subcategory Description	Model Plant Size	Production (Units/Day)[1]	Flow (mgd(m^3/day))	Total Capital Cost ($)	Annual O&M Cost ($)	Total Capital Cost ($)	Annual O&M Cost ($)	Total Capital Cost ($)	Annual O&M Cost ($)
1. Hair Pulp/Chrome Tan/Retan-Wet Finish	Medium	1,000	0.232 (878)	2,148,000	238,400	3,158,000	440,700	3,373,000	444,300
	Large	2,000	0.464(1,760)	2,976,000	398,500	4,429,000	773,700	4,727,000	780,000
	Extra Large	5,000	1.254(4,750)	4,812,000	915,000	7,328,000	1,841,700	7,802,000	1,852,400
2. Hair Save/Chrome Tan/Retan-Wet Finish	Large	2,000	0.490(1,850)	3,572,000	577,700	4,922,000	969,900	5,230,000	976,400
3. Hair Save-Pulp/ Non-chrome Tan/ Retan-Wet Finish	Medium	750	0.189 (715)	2,242,000	253,700	3,150,000	461,300	3,346,000	465,600
	Large	2,200	0.554(2,100)	3,752,000	614,700	5,336,000	1,181,600	5,663,000	1,188,600
4. Retan-Wet Finish (Grain Sides)	Large	6,600	0.609(2310)	2,650,000	310,000	2,731,000	388,300	3,068,000	395,700
5. No Beamhouse	Medium	2,700	0.021 (79)	720,000	57,200	751,000	65,800	820,000	69,000
	Large	8,600	0.065 (246)	1,141,000	93,700	1,207,000	119,900	1,327,000	123,200
6. Through-The-Blue	Small	600	0.048 (182)	1,762,000	189,700	2,391,000	313,800	2,439,000	317,100
	Large	4,200	0.338(1,280)	4,596,000	1,007,000	6,031,000	1,715,500	6,288,000	1,721,000
7. Shearling	Large	2,500	0.282(1,070)	1,792,000	177,700	1,840,000	204,800	2,078,000	209,800
8. Pigskin	Small	3,625	0.282(1,070)	3,130,000	474,100	4,131,000	715,500	4,369,000	720,500
9. Retan-Wet Finish (Splits)	Large	7,400	0.185 (700)	1,695,000	152,500	1,847,000	258,600	2,041,000	262,900

All costs correspond to ENRCCI of 3730 (First Quarter 1982).

[1] Production given in number of hides or sides, or splits depending on subcategory.

TABLE A-20

PSES OPTION DEVELOPMENT

Unit Processes	OPTION I		OPTION II		OPTION III	
	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9
In Plant Controls	X	X	X	X	X	X
Stream Segregation	X		X		X	
Sulfide Oxidation	X				X	
Sulfide Oxidation with Neutralization			X			
Flue Gas Carbonation					X	
Flow Equalization (1-Day Storage - Tanyard Stream Only)			X	X		X
Flow Equalization (1-Day Storage - Combined Streams)					X	
Tanyard Wastewater Screening	X	X				
Coagulation-Sedimentation (Combined Streams)					X	
Coagulation-Sedimentation (Tanyard Stream)			X	X		X
Neutralization Facilities	X	X				
Sludge Dewatering			X	X	X	X
Sludge Disposal			X	X	X	X
Effluent Monitoring	X	X	X	X	X	X

TABLE A-21

COST SUMMARY FOR PSES TREATMENT TECHNOLOGY OPTIONS-INDIVIDUAL PLANTS CAPITAL AND ANNUAL OPERATION AND MAINTENANCE (O&M) COSTS

Subcategory Description	Model Plant Size	Production (Units/Day)[1]	Flow (mgd(m^3/day))	OPTION I		OPTION II		OPTION III	
				Total Capital Cost ($)	Annual O&M Cost ($)	Total Capital Cost ($)	Annual O&M Cost ($)	Total Capital Cost ($)	Annual O&M Cost ($)
1. Hair Pulp/Chrome Tan/Retan-Wet Finish	Extra Small	175	0.051 (193)	358,000	24,200	358,000	24,200	1,265,000	88,600
	Small	500	0.146 (553)	433,000	41,800	1,073,000	90,300	1,930,000	152,700
	Medium	1,000	0.292(1,110)	534,000	74,400	1,391,000	145,100	2,622,000	269,600
	Large	2,000	0.583(2,210)	697,000	120,300	1,871,000	227,700	3,625,000	446,500
	Extra Large	5,400	1.575(5,960)	1,238,000	281,900	3,105,000	521,500	6,062,000	1,099,700
2. Hair Save/Chrome Tan/Retan-Wet Finish	Small	500	0.125 (473)	417,000	37,400	1,197,000	94,600	2,077,000	183,200
	Large	2,000	0.500(1,890)	651,000	105,700	2,118,000	256,000	3,904,000	564,000
3. Hair Save-Pulp/ Non-chrome Tan/ Retan-Wet Finish	Small	150	0.043 (163)	352,000	22,500	352,000	22,500	1,280,000	91,400
	Medium	750	0.216 (818)	484,000	60,000	1,357,000	130,800	2,487,000	258,200
	Large	2,200	0.634(2,400)	725,000	135,700	2,158,000	285,800	4,135,000	613,000
4. Retan-Wet Finish (Grain Sides)	Small	1,350	0.127 (481)	170,000	30,000	958,000	69,200	958,000	69,200
	Large	6,600	0.622(2,350)	298,000	116,600	1,864,000	187,600	1,864,000	187,600
5. No Beamhouse	Small	900	0.007 (26)	114,000	6,200	314,000	32,900	314,000	32,900
	Medium	2,700	0.022 (83)	126,000	10,000	470,000	40,300	470,000	40,300
	Large	8,600	0.069 (261)	146,000	21,100	735,000	56,700	735,000	56,700
6. Through-The-Blue	Small	600	0.048 (182)	356,000	24,200	852,000	65,200	1,849,000	191,000
	Large	4,200	0.338(1,280)	558,000	81,800	1,830,000	195,800	4,410,000	889,900
7. Shearling	Small	900	0.102 (386)	161,000	27,500	841,000	65,500	841,000	65,500
	Large	2,500	0.282(1,070)	226,000	60,100	1,279,000	104,800	1,279,000	104,800
8. Pigskin	Medium	3,625	0.344(1,300)	563,000	87,200	1,759,000	203,800	3,233,000	435,300
9. Retan-Wet Finish (Splits)	Small	2,700	0.068 (257)	145,000	19,200	145,000	19,200	780,000	56,400
	Large	7,400	0.185 (700)	194,000	44,400	1,185,000	94,500	1,185,000	94,500

All costs correspond to ENRCCI of 3730 (First Quarter 1982).

[1] Production given in number of hides or sides, or splits depending on subcategory.

TABLE A-22

COST SUMMARY FOR PSES TREATMENT TECHNOLOGY OPTIONS-INDUSTRY CAPITAL AND ANNUAL OPERATION AND MAINTENANCE (O&M) COSTS (COSTS ARE IN MILLIONS OF DOLLARS)

				OPTION I			OPTION II		OPTION III	
Subcategory Description	Model Plant Size	Production (Units/Day)[1]	Flow (mgd/m^3/day))	Number of Plants	Total Capital Cost ($)	Annual O&M Cost ($)	Total Capital Cost ($)	Annual O&M Cost ($)	Total Capital Cost ($)	Annual O&M Cost ($)
1. Hair Pulp/Chrome Tan/Retan-Wet Finish	Extra Small	175	0.051 (193)	6	2.15	0.15	2.5	0.15	7.59	0.53
	Small	500	0.146 (553)	22	9.53	0.92	23.61	1.99	42.46	3.36
	Medium	1,000	0.292(1,110)	12	6.41	0.89	16.69	1.74	31.46	3.24
	Large	2,000	0.583(2,210)	11	7.67	1.32	20.58	2.50	39.88	4.91
	Extra Large	5,400	1.575(5,960)	5	6.19	1.41	15.53	2.61	30.31	5.50
2. Hair Save/Chrome Tan/Retan-Wet Finish	Small	500	0.125 (473)	3	1.25	0.11	3.59	0.28	6.23	0.55
	Large	2,000	0.500(1,890)	2	1.30	0.21	4.24	0.51	7.81	1.13
3. Hair Save-Pulp/Non-chrome Tan/Retan-Wet Finish	Small	150	0.043 (163)	3	1.06	0.07	1.06	0.07	3.84	0.274
	Medium	750	0.216 (818)	4	1.94	0.24	5.43	0.52	9.95	1.03
	Large	2,200	0.634(2,400)	1	0.73	0.14	2.16	0.29	4.14	0.61
4. Retan-Wet Finish (Grain Sides)	Small	1,350	0.127 (481)	7	1.19	0.21	6.71	0.48	6.71	0.484
	Large	6,600	0.622(2,350)	7	2.09	0.82	13.05	1.31	13.05	1.31
5. No Beamhouse	Small	900	0.007 (26)	7	0.80	0.043	2.20	0.230	2.20	0.230
	Medium	2,700	0.022 (83)	7	0.88	0.070	3.29	0.282	3.29	0.282
	Large	8,600	0.069 (261)	10	1.46	0.211	7.35	0.567	7.35	0.567
6. Through-The-Blue	Small	600	0.048 (182)	7	2.49	0.170	5.96	0.456	12.94	1.34
	Large	4,200	0.338(1,280)	5	2.79	0.41	9.15	0.98	22.05	4.45
7. Shearling	Small	900	0.102 (386)	3	0.48	0.083	2.52	0.197	2.52	0.197
	Large	2,500	0.282(1,070)	3	0.68	0.180	3.84	0.314	3.84	0.314
8. Pigskin	Medium	3,625	0.344(1,300)	1	0.56	0.087	1.76	0.204	3.23	0.435
9. Retan-Wet Finish (Splits)	Small	2,700	0.068 (257)	9	1.31	0.173	1.31	0.173	7.02	0.51
	Large	7,400	0.185 (700)	5	0.97	0.222	5.93	0.473	5.93	0.473
Totals					53.93	8.14	158.46	16.33	273.80	31.73

All costs correspond to ENRCCI of 3730 (First Quarter 1982).

[1] Production given in number of hides, sides, or splits depending on subcategory.

TABLE A-23

PSNS OPTION DEVELOPMENT

Unit Processes	OPTION I		OPTION II		OPTION III	
	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9	Subcategory 1,2,3,6 & 8	Subcategory 4,5,7 & 9
In Plant Controls	X	X	X	X	X	X
Stream Segregation	X		X		X	
Sulfide Oxidation	X				X	
Sulfide Oxidation with Neutralization			X			
Flue Gas Carbonation					X	
Flow Equalization (1-Day Storage - Tanyard Stream)			X	X		X
Flow Equalization (1-Day Storage - Combined Streams)					X	
Tanyard Wastewater Screening	X	X				
Coagulation-Sedimentation (Combined Streams)					X	
Coagulation-Sedimentation (Tanyard Stream)			X	X		X
Neutralization Facilities	X	X				
Sludge Dewatering			X	X	X	X
Sludge Disposal			X	X	X	X
Effluent Monitoring	X	X	X	X	X	X

TABLE A-24

COST SUMMARY FOR PSNS TREATMENT TECHNOLOGY OPTIONS CAPITAL AND ANNUAL OPERATION AND MAINTENANCE (O&M) COSTS

Subcategory Description	Model Plant Size	Production (Units/Day)[1]	Flow (mgd(m^3/day))	OPTION I Total Capital Cost ($)	OPTION I Annual O&M Cost ($)	OPTION II Total Capital Cost ($)	OPTION II Annual O&M Cost ($)	OPTION III Total Capital Cost ($)	OPTION III Annual O&M Cost ($)
1. Hair Pulp/Chrome Tan/Retan-Wet Finish	Medium	1,000	0.232 (878)	492,000	68,000	1,308,000	136,300	2,478,000	272,900
	Large	2,000	0.464(1,760)	627,000	115,500	1,747,000	221,700	3,411,000	474,400
	Extra Large	5,000	1.254(4,750)	1,029,000	257,300	2,825,000	477,600	5,592,000	1,118,000
2. Hair Save/Chrome Tan/Retan-Wet Finish	Large	2,000	0.490(1,850)	643,000	120,000	2,107,000	287,200	3,899,000	641,600
3. Hair Save-Pulp/Non-chrome Tan/Retan-Wet Finish	Medium	750	0.189 (715)	461,000	57,800	1,315,000	130,000	2,418,000	268,700
	Large	2,200	0.554(2,100)	677,000	131,700	2,069,000	284,000	3,995,000	645,400
4. Retan-Wet Finish (Grain Sides)	Large	6,600	0.609(2,310)	279,000	82,100	1,854,000	201,000	1,854,000	201,000
5. No Beamhouse	Medium	2,700	0.021 (79)	121,000	8,600	464,000	41,700	464,000	41,700
	Large	8,600	0.065 (246)	138,000	16,100	730,000	58,800	730,000	58,800
6. Through-The-Blue	Small	600	0.048 (182)	356,000	24,700	847,000	66,700	1,845,000	196,800
	Large	4,200	0.338(1,280)	558,000	89,000	1,766,000	211,800	4,425,000	472,200
7. Shearling	Large	2,500	0.282(1,070)	213,000	44,800	1,278,000	111,400	1,278,000	111,400
8. Pigskin	Medium	3,625	0.282(1,070)	525,000	77,800	1,685,000	193,500	3,098,000	435,600
9. Retan-Wet Finish (Splits)	Large	7,400	0.185 (700)	183,000	32,500	1,184,000	100,300	1,184,000	100,300

All costs correspond to ENRCCI of 3730 (First Quarter 1982).

[1] Production given in number of hides, or sides, or splits depending on subcategory.

TABLE A-25
BPT COST EXAMPLE

Tannery Information

Subcategory: Hair Pulp/Chrome Tan/Retan-Wet Finish (One)
Production: 61,500 lb/d
Flow: 0.400 mgd

Unit Process	Flow (mgd)	x	Design Parameter* (units/mgd)	=	Cost Parameter†	Figure Number	Capital Cost ($)	Annual O&M Cost ($)
Flow Equalization	0.4	x	1.0 mgd	=	0.4 mgd	A-10	450,000	-
	0.4	x	1.0 mgd	=	0.4 mgd	A-12	--	46,000
Coagulation	0.4	x	1.0 mgd	=	0.4 mgd	A-14	410,000	--
Sedimentation	0.4	x	1.0 mgd	=	0.4 mgd	A-15	--	33,000
Biological Treatment								
Aeration Basin	0.4	x	1.2 MG	=	0.48 MG	A-17	170,000	--
Aeration System	0.4	x	4,000 scfm	=	1600 scfm	A-19	148,000	--
	0.4	x	4,000 scfm	=	1600 scfm	A-20	--	27,000
Base O&M	0.4	x	1.0 mgd	=	0.4 mgd	A-18	--	17,000
Phosphorus Addition	0.4	x	50 lb	=	20.0 lb/d	**	--	10,400
Secondary Clarifier	0.4	x	1.0 mgd	=	0.4 mgd (D = 44ft)††	A-21	143,000	--
Sludge Dewatering (Drying Beds)	0.4	x	12,000 lb	=	4,800 lb/d	A-32	145,000	--
	0.4	x	12,000 lb	=	4,800 lb/d	A-33	--	21,000
Sludge Disposal	0.4	x	12,000 lb	=	4,800 lb/d	***	--	53,000
Effluent Monitoring	--				--	--	19,000	17,600

Total Cost (1980)	1,485,000	225,000
Adjustment Factor	1.19	1.19
Total Cost (1982)	1,767,000	268,000

* From Table A-14

** 20.0 lb/d x $2.00/lb x 260 d

*** @ $85.00/Ton (dry solids-1980 costs)

† Number Used on Cost Curves (horizontal axis)

†† Secondary Clarifier Diameter = $(\text{MGD} \times 5/7 \times 1/200 \text{ gal/ft}^2 \times 4/\pi)^{\frac{1}{2}}$ rounded up to the next even number.

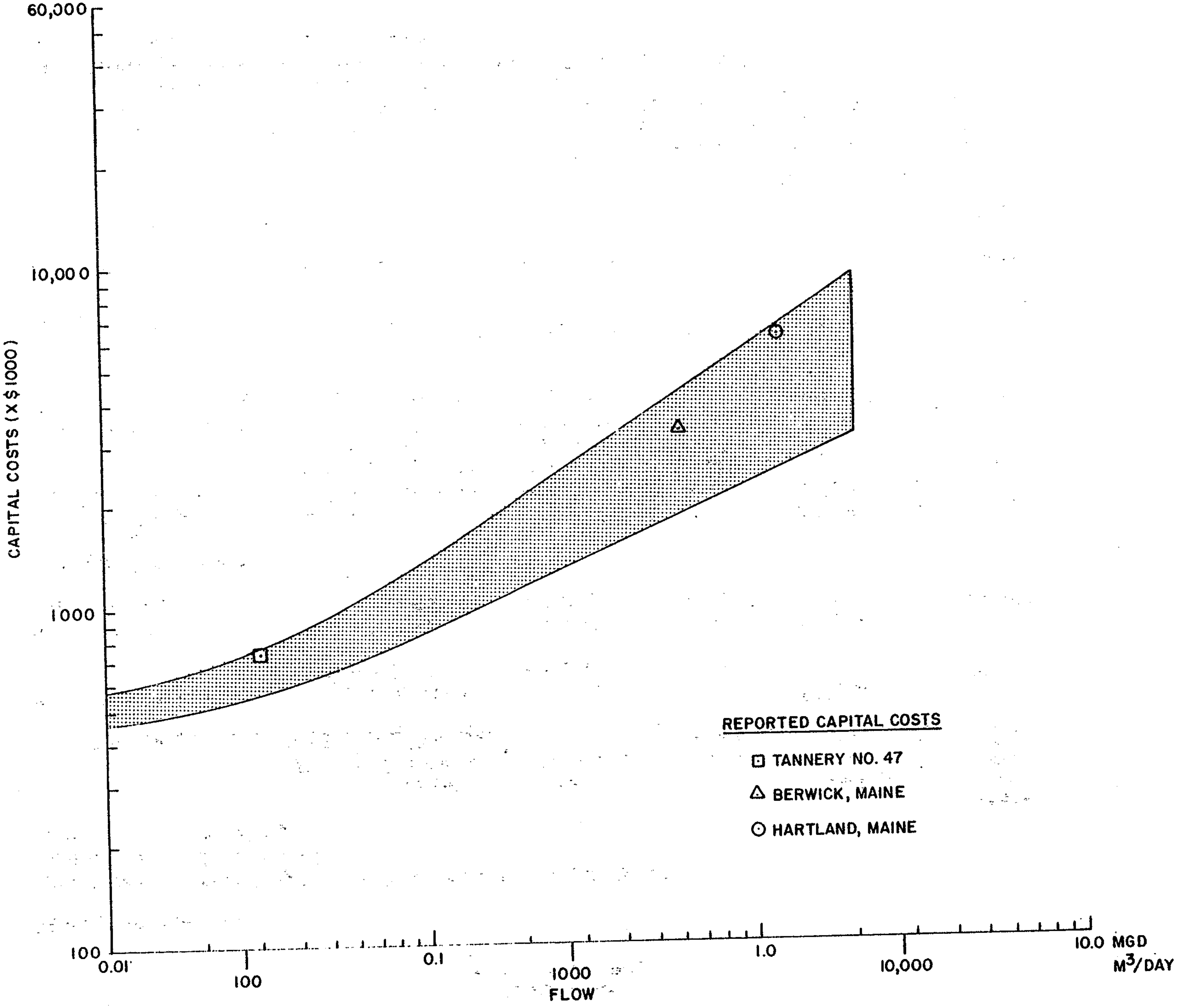

FIGURE A-45 CAPITAL COST CURVE FOR BPT TREATMENT

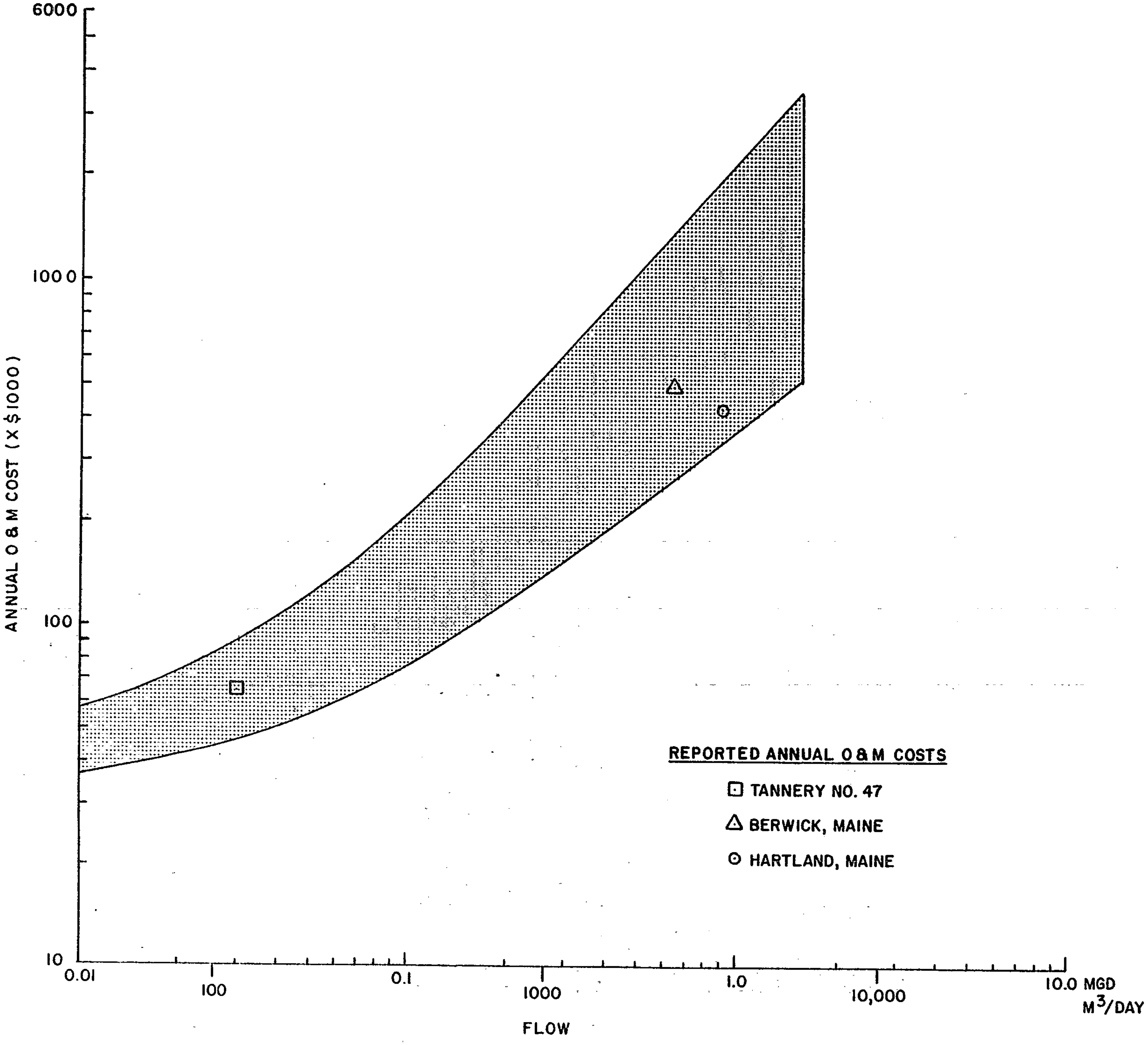

FIGURE A-46 OPERATION & MAINTENANCE COST CURVE FOR BPT TREATMENT

APPENDIX B

BPT EFFLUENT VARIABILITY FACTORS VS. SAMPLING FREQUENCY

"N" Day Variability Curves

The following four graphs depict the change in monthly variability factors for biologically treated effluents (BPT) with change in the sampling frequency, for values of "N" from one to 30 days, for BOD_5, TSS, Oil and Grease, and Total Chromium. The statistical modeling methodology utilized to estimate numerical values for the monthly variability factors is included in the EPA report entitled "Development Document for Existing Source Pretreatment Standards for the Electroplating Point Source Category," EPA-440/1-79/003, U.S. EPA, August, 1979. Discussion of the methodology also is presented in the Technical Record at III G, Treated Effluent Variability Analysis.

These graphs are included for reference purposes only. It must be noted that EPA is requiring compliance with maximum monthly average effluent limitations and pretreatment standards, developed on the assumption of eight sampling days per month, regardless of sampling frequency (see 40 CFR 425.01(i) and 47 FR 52853, November 23, 1982). The actual sampling frequency for purposes of compliance monitoring at any individual plant is to be established by cognizant NPDES authorities for direct dischargers and by cognizant pretreatment authorities for indirect dischargers.

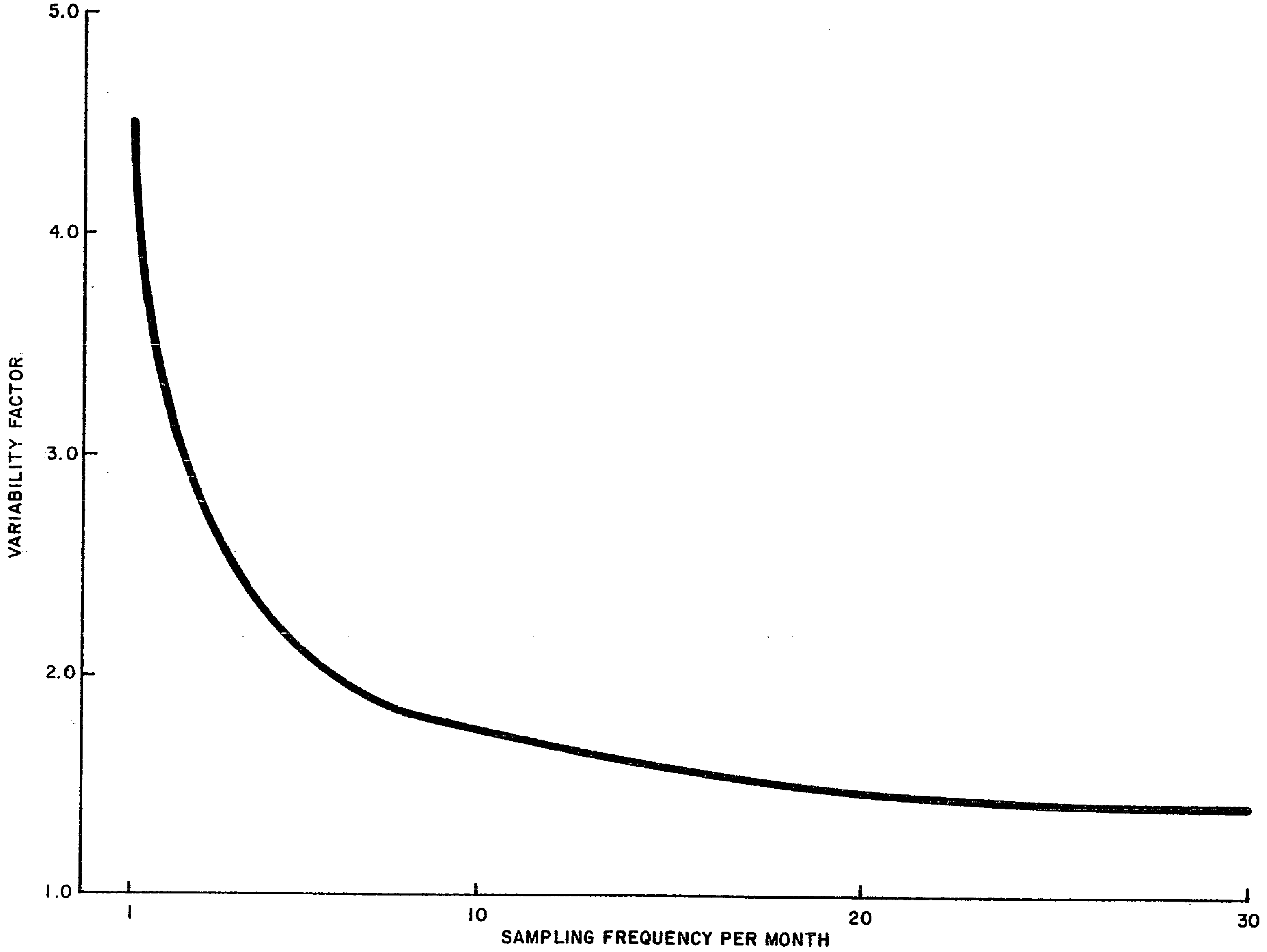

FIGURE B-1 BPT EFFLUENT BOD VARIABILITY FACTOR VS. SAMPLING FREQUENCY

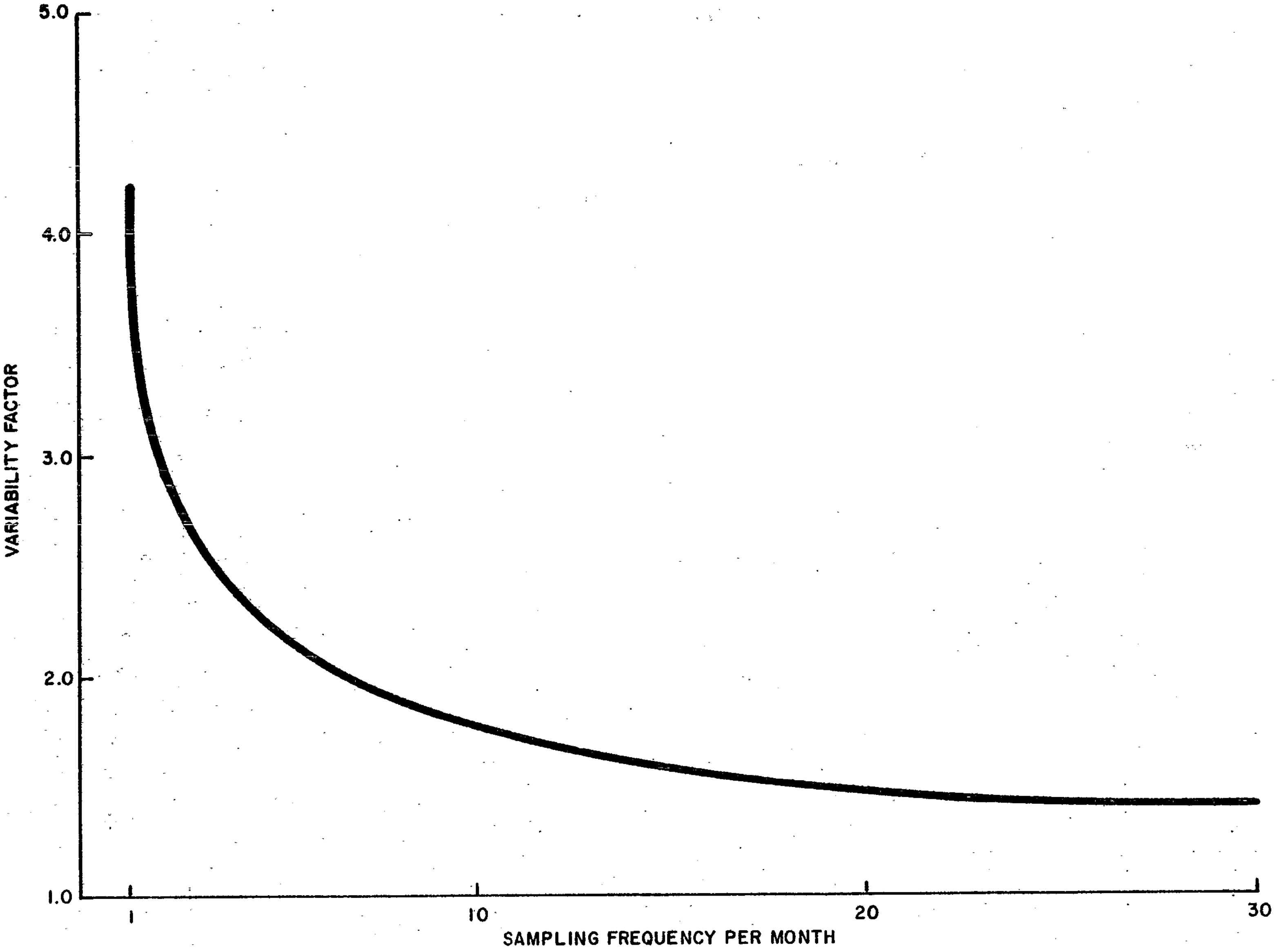

FIGURE B-2 BPT EFFLUENT TSS VARIABILITY FACTOR VS. SAMPLING FREQUENCY

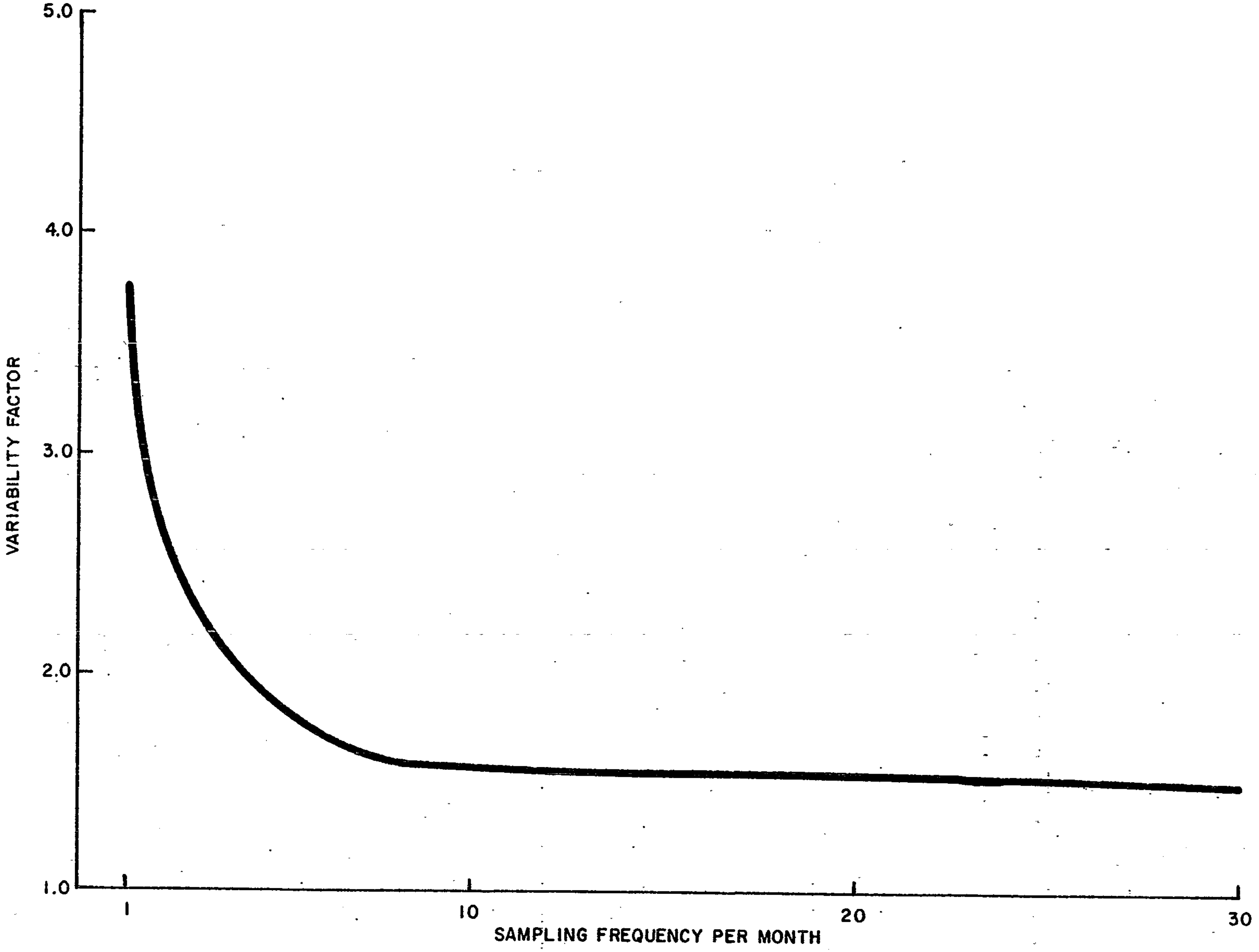

FIGURE B-3 BPT EFFLUENT OIL & GREASE VARIABILITY FACTOR VS. SAMPLING FREQUENCY

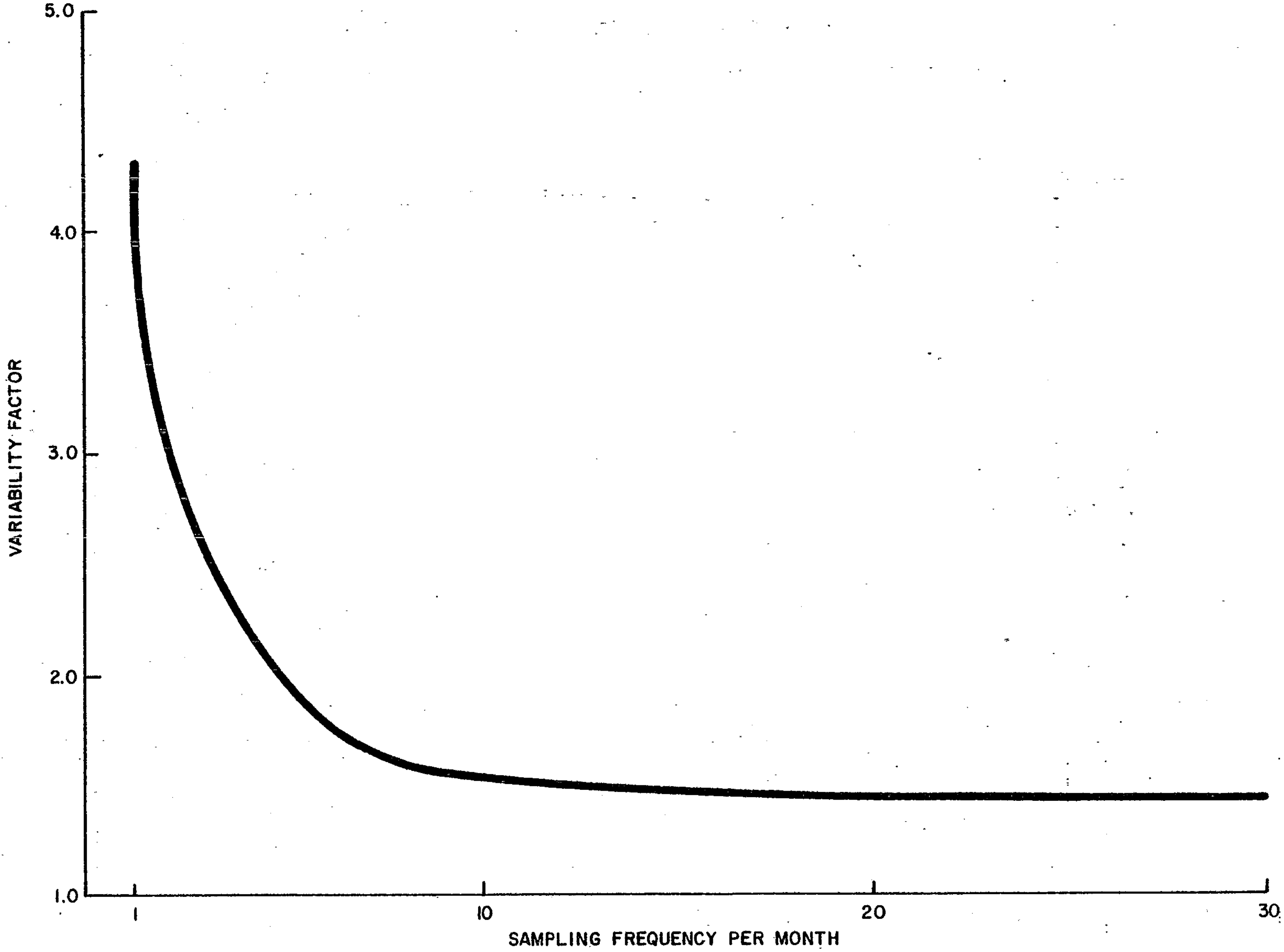

FIGURE B-4 BPT EFFLUENT TOTAL CHROMIUM VARIABILITY FACTOR VS. SAMPLING FREQUENCY

APPENDIX C

TOXIC POLLUTANTS EXCLUDED

(1) Toxic pollutants not detectable with the use of analytical methods approved pursuant to section 304(h) of the Act:

Acenaphthene
Acrolein
Acrylonitrile
1,2,4-Trichlorobenzene
Hexachloroethane
1,1-Dichloroethane
Chloroethane
Bis(2-Chloromethyl) Ether
2-Chloroethyl Vinyl Ether
2-Chloronaphthalene
Parachlorometa Cresol
2-Chlorophenol
1,3-Dichlorobenzene
1,2-Dichloropropane
1,3-Dichloropropylene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluoranthene
4-Chlorophenyl Phenyl Ether
4-Bromophenyl Phenyl Ether
Bis(2-Chloroisopropyl) Ether
Bis(2-Chloroethoxy) Methane
Methyl Chloride
Methyl Bromide
Bromoform
Dibromochloromethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4,6-Dinitro-O-Cresol
N-Nitrosodimethylamine
N-Nitrosodi-N-Propylamine
Butylbenzyl Phthalate
Di-N-Octyl Phthalate
Dimethyl Phthalate
1,2-Benzanthracene
3,4-Benzopyrene
3,4-Benzofluoranthene

11,12-Benzofluoranthene
Acenaphthylene
1,12-Benzoperylene
1,2,5,6-Dibenzanthracene
Indeno (1,2,3-CD) Pyrene
Pyrene
Vinyl Chloride
Aldrin
Dieldrin
Chlordane
4,4'-DDT
4,4'-DDE (P,P'-DDX)
4,4'-DDD (P,P'-TDE)
Alpha-Endosulfan
Beta-Endosulfan
Endosulfan Sulfate
Endrin
Endrin Aldehyde
Heptachlor
Heptachlor Epoxide
Alpha-BHC
Beta-BHC
Gamma-BHC (Lindane)
Delta-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

(2) Toxic pollutants detected at only a small number of sources within a subcategory and uniquely related to the source:

Benzene
Benzidene
1,1,1-Trichloroethane
2,4-Dichlorophenol
2,4-Dimethylphenol
Naphthalene
Toluene

(3) Toxic pollutants detected in treated effluents in trace amounts and neither cause nor are likely to cause toxic effects:

Tetrachloromethane
Chlorobenzene
Hexachlorobenzene
1,2-Dichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
Chloroform
1,4-Dichlorobenzene
3,3-Dichlorobenzidene
1,1-Dichloroethylene
1,2-Trans-Dichloroethylene
1,2-Diphenylhydrazine
Dichlorobromomethane
Isophorone
Nitrobenzene
2-Nitrophenol
N-Nitrosodiphenylamine
Di-N-Butyl Phthalate
Diethyl Phthalate
Chrysene
Anthracene/Phenanthrene
Fluorene
Tetrachloroethylene
Trichloroethylene
Antimony
Arsenic
Asbestos
Beryllium
Cadmium
Mercury
Selenium
Silver
Thallium

(4) Toxic pollutants in treated effluents present in amounts too small to be effectively reduced by technologies known to the Administrator:

Copper
Lead
Nickel
Zinc
Cyanide
1,2-Dichlorobenzene
2,4,6-Trichlorophenol
Ethylbenzene
Methylene Chloride
4-Nitrophenol

Pentachlorophenol
Phenol
Bis(2-Ethylhexyl) Phthalate

(5) Toxic pollutants excluded from regulation because there is no available pretreatment technology which is economically achievable that will remove these pollutants prior to discharge to POTWs:

Benzene
Benzidene
Tetrachloromethane
Chlorobenzene
Hexachlorobenzene
1,2-Dichloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
Chloroform
2,4-Dichlorophenol
2,4-Dimethylphenol
1,4-Dichlorobenzene
3,3-Dichlorobenzidene
1,1-Dichloroethylene
1,2-Trans-Dichloroethylene
1,2-Diphenylhydrazine
Dichlorobromomethane
Isophorone
Nitrobenzene
2-Nitrophenol
N-Nitrosodiphenylamine
Di-N-Butyl Phthalate
Diethyl Phthalate
Naphthalene
Toluene
Chrysene
Anthracene/Phenanthrene
Fluorene
Tetrachloroethylene
Trichloroethylene
Antimony
Arsenic
Asbestos
Beryllium
Cadmium
Copper
Lead
Mercury

Nickel
Selenium
Silver
Thallium
Zinc
Cyanide
1,2-Dichlorobenzene
2,4,6-Trichlorophenol
Ethylbenzene
Methylene Chloride
4-Nitrophenol
Pentachlorophenol
Phenol
Bis(2-Ethylhexyl) Phthalate

APPENDIX D

SULFIDE ANALYTICAL METHOD

The following method is to be used for the determination of sulfide in alkaline wastewaters.

(a) Outline of Method.

The sulfide solution is titrated with standard potassium ferricyanide solution in the presence of a ferrous dimethylglyoxime ammonia complex. The sulfide is oxidized to sulfur. Sulfite interferes and must be precipitated with barium chloride. Thiosulfate is not titrated under the conditions of the determination. (Charlot, Ann. chim. anal., 1945, 27, 153; Booth, J. Soc. Leather Trades' Chemists, 1956, 40, 238).

(b) Reagents.

(1) 0.1N potassium ferricyanide-32.925 g. per liter-this solution must be kept in the dark.

(2) Buffer. 200 g. NH_4Cl
200 ml. ammonia (Sp.g. 0.880)
per liter

(3) Barium Chloride Solution-12.5 g. per liter 10 ml. of this solution will precipitate the equivalent of about 0.3 g. sodium sulfite.

(4) Indicator-10 ml. 0.6% $FeSO_4$
50 ml. 1% dimethylglyoxime in ethanol
0.5 ml. conc. H_2SO_4.

(c) Procedure.

(1) The liquor is filtered rapidly through glass wool or a coarse filter paper to remove suspended matter.

(2) 20 ml. buffer, 1 ml. indicator and excess barium chloride solution up to a maximum of 25 ml. are placed in a 250 ml. stoppered flask.

(3) A suitable sample of the sulfide solution containing, if possible between 0.04 and 0.08 g. sodium sulfide is added. The flask is stoppered and left for one minute to precipitate the sulfite.

(4) The solution is then titrated with the standard ferricyanide solution until the pink color is destroyed. During titration the solution sometimes goes a dirty color but near completion the pink color becomes more definite and disappears momentarily before the final end point is reached. The solution is titrated until there is no reappearance of the pink color after 30 seconds.

1 ml. 0.1N ferricyanide = 0.00390 g. Na_2S.

Note (i) In order to reduce loss of sulfide the determination should be carried out as rapidly as possible and the solution titrated with the minimum of agitation. It is recommended that a rough titration be made and then in further titrations the ferricyanide added rapidly to within 1 ml. of the expected value.

Note (ii) If it is suspected that the concentration of sulfite is high, and approaches that of the sulfide, the waiting time after the addition of barium chloride should be extended to ten minutes, to allow for complete precipitation of the barium sulfite.

SOURCE: Official Methods of Analysis, Society of Leather Trades' Chemists, Fourth Revised Edition, Redbourn, Herts., England, 1965.

APPENDIX E

LAND REQUIREMENTS FOR PRETREATMENT FACILITIES

Appendix A presented and described the procedure for developing the costs of the various treatment technology options. This procedure included separate and distinct unit treatment processes which could be combined to create more advanced treatment technologies in a building block fashion. For this reason, each unit treatment process usually includes its own building (to house controls, pumps, chemicals, etc.), piping to and from other processes, and separate tank construction (i.e., no common wall construction with another tank). For the purposes of developing and comparing costs this procedure was adequate. However, on a practical and realistic basis, the actual treatment facilities would not be built in this manner.

Common and well known engineering practices dictate that the least expensive construction would minimize the number of buildings, utilize common wall contruction of tanks, install equipment (such as pumps) that can be used for several purposes and decrease the amount of building area required. These practices not only can significantly decrease the cost of construction but also decrease the amount of area required for the treatment facilities.

The Agency has incorporated these "real-life" considerations in developing land requirements for pretreatment facilities. By utilizing one building for many functions and common wall tank construction, sizeable reductions in land requirements are possible. The land requirements, as shown on Figures E-1 and E-2 reflect this. The Agency, however, did not decrease the amount of area around equipment. It is important that the operator has adequate area to safely maintain and repair this equipment. Standard engineering practices regarding this were not sacrificed.

The Agency notes that these techniques will more often than not result in lower capital costs; however, the Agency did not reduce the capital costs used in the economic impact analysis. The Agency believes that it will be only under the most severe and uncommon physical constraints that a tannery will have insufficient area for pretreatment facilities.

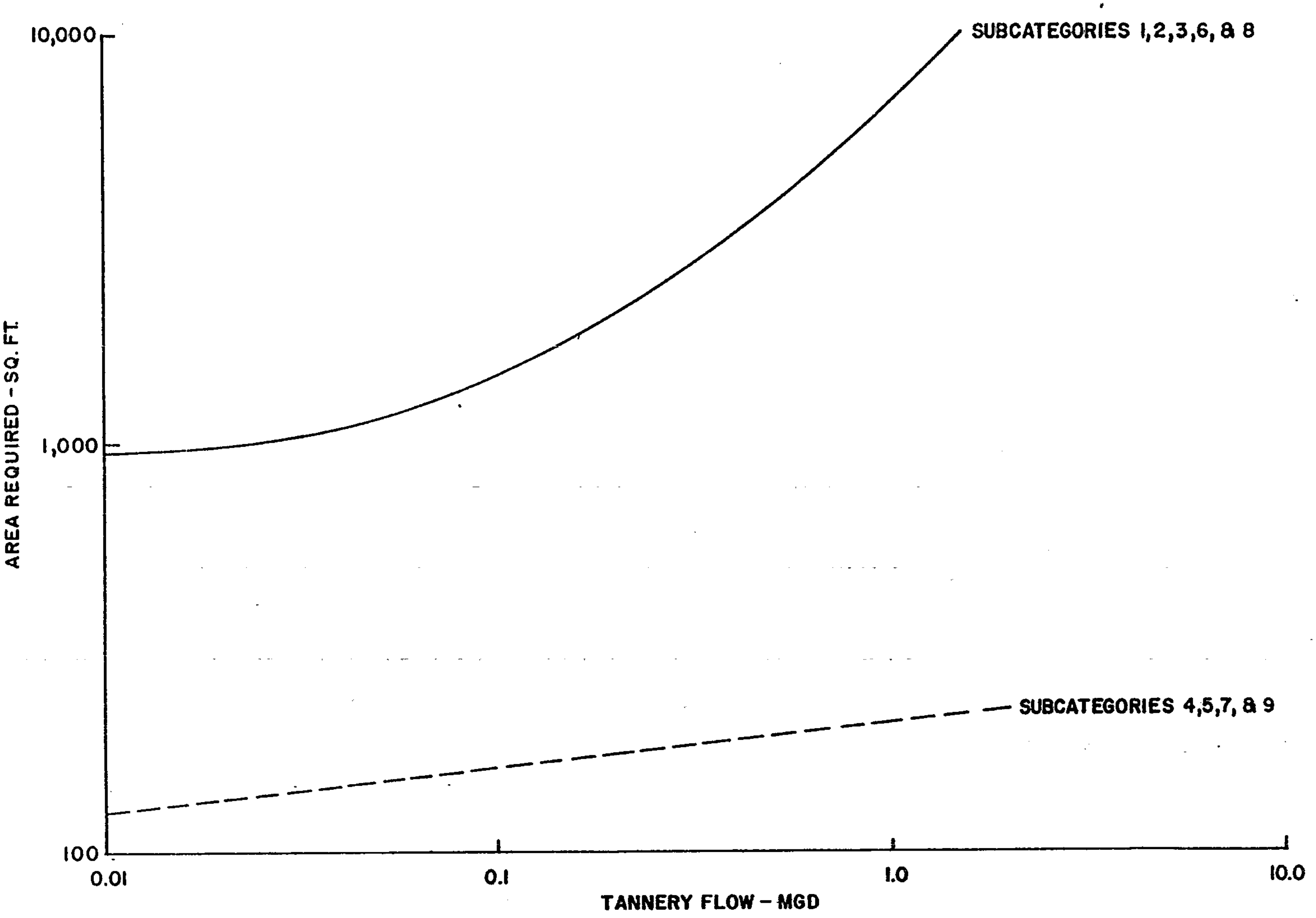

FIGURE E-1 MINIMUM AREA REQUIREMENTS- PSES OPTION I

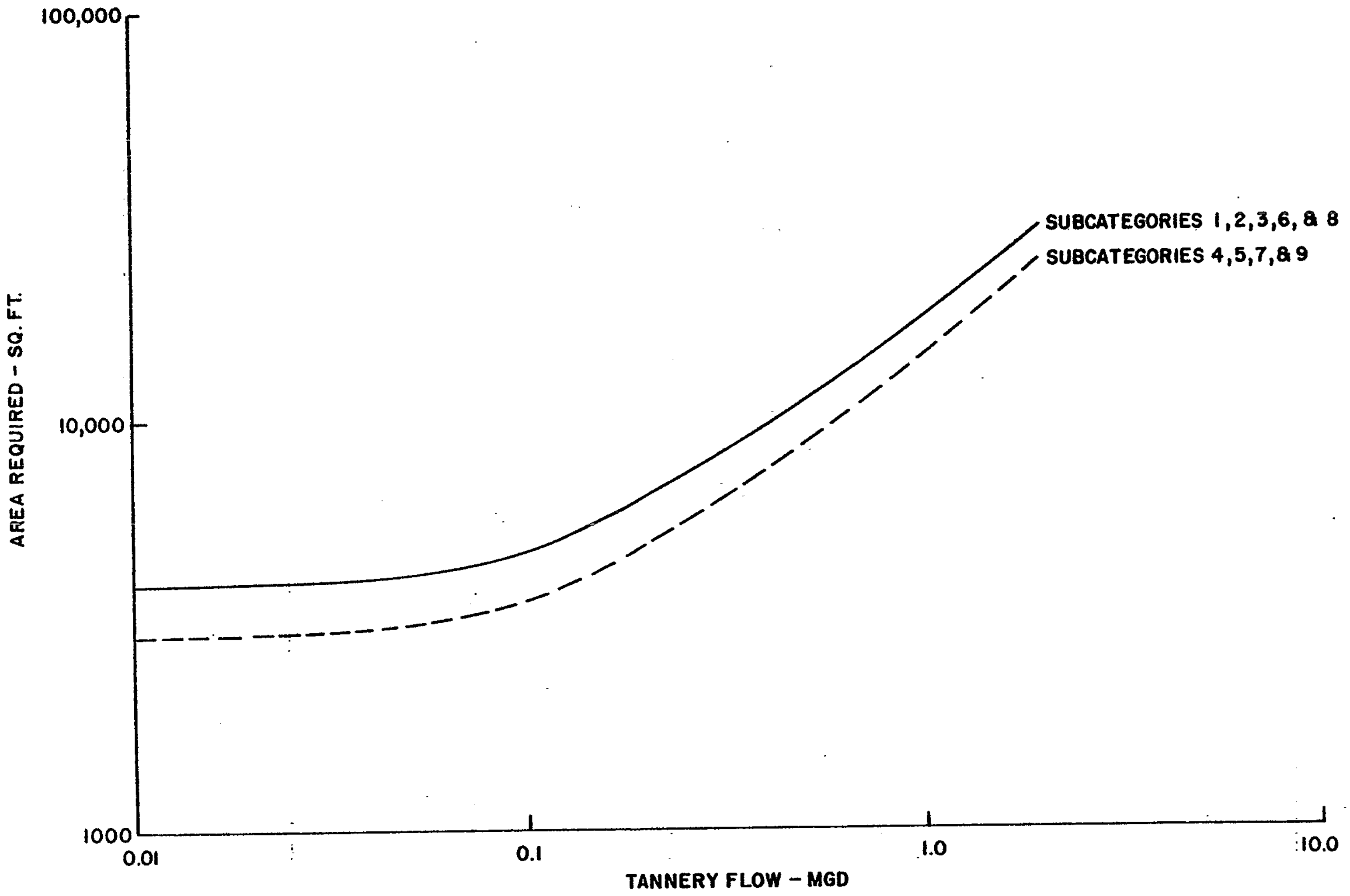

FIGURE E-2 MINIMUM AREA REQUIREMENTS– PSES OPTION II

APPENDIX F

PSES SUGGESTED MASS EFFLUENT LIMITATIONS

Subcategory 1: Hair Pulp/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.54	0.36
Sulfide	1.08	-

The total chromium standards do not apply to plants processing less than 275 hides/day

Subcategory 2: Hair Save/Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.50	0.33
Sulfide	1.00	-

Subcategory 3: Hair Save or Pulp/Non-Chrome Tan/Retan-Wet Finish

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.48	0.32
Sulfide	0.96	-

The total chromium standards do not apply to plants processing less than 350 hides/day

Subcategory 4: Retan-Wet Finish-Sides

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.73	0.46
Sulfide	-	-

Subcategory 5: No Beamhouse

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.63	0.40
Sulfide	-	-

Subcategory 6: Through-the-Blue

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.14	0.09
Sulfide	0.28	-

Subcategory 7: Shearling

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	1.49	0.94
Sulfide	-	-

Subcategory 8: Pigskin

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.50	0.33
Sulfide	1.00	-

Subcategory 9: Retan-Wet Finish-Splits

Pollutant or Pollutant Parameter	Maximum for Any One Day	Maximum for Monthly Average
	kg/kkg (or pounds per 1,000 lb) of raw material	
Total Chromium	0.40	0.25
Sulfide	-	-

The total chromium standards do not apply to plants processing less than 3600 splits/day

APPENDIX G

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 (BOD_5)

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 chromium 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).

Clean Water Act

The Federal Water Pollution Control Act Amendments of 1972 (33 U.S.C. 1251 et seq.), as amended by the Clean Water Act of 1977 (Public Law 95-217).

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 chromium-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.

Direct Discharger

A facility where wastewaters are discharged or may be discharged into waters of the United States.

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 chromium 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.

Multimedia Filter

A filtration device designed to remove suspended solids from wastewater by trapping the solids in a porous medium. The multimedia 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.

Indirect Discharger

A facility where wastewaters are discharged or may be discharged into a publicly owned treatment works.

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 pulping 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 square 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 (grain) 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.

Tannins

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 H

ENGLISH UNITS TO METRIC UNITS CONVERSION TABLE

Multiply English Units		By	To Obtain Metric Units	
(English Unit)	(Abbreviation)	(Conversion)	(Abbreviation)	(Metric Unit)
cubic feet per minute	cfm	0.0283	cu m/min	cubic meters per minute
cubic feet per second	cfs	1.707	cu m/min	cubic meters per minute
cubic feet	cu ft	0.0283	cu m	cubic meters
cubic feet	cu ft	28.32	1	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Farenheit	°F	0.555 (°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	1	liter
gallon per minute	gpm	0.0631	1/sec	liters per second
gallon per lb	gal/lb	8.346	1/kg	liters per kilogram
horsepower	hp	0.7457	kw	kilowatts
inches	in	2.54	cm	centimeters
pounds per square inch absolute	psia	0.06803	atm	atmospheres (absolute)
million gallons per day	MGD	3.785 x 10-3	cu m/day	cubic meters per day
pounds per square inch (gauge)	psi	(0.06805 psi + 1)*	atm	atmospheres

APPENDIX H (cont.)

Multiply English Units		By	To Obtain Metric Units	
(English Unit)	(Abbreviation)	(Conversion)	(Abbreviation)	(Metric Unit)
pounds	lb	0.454	kg	kilograms
ton	ton	0.907	kkg	metric ton
mile	mi	1.609	km	kilometer
square feet	ft2	.0929	m2	square meters

*Actual conversion, not a multiplier.

APPENDIX I

ABBREVIATIONS

Agency - The U.S. Environmental Protection Agency. (EPA)

BAT - The best available technology economically achievable, under section 301(b)(2)(A) of the Act.

BCT - The best conventional pollutant control technology, under section 301(b)(2)(E) of the Act.

BMPs - Best management practices, under section 304(e) of the Act.

BPT - The best practicable control technology currently available, under section 301(b)(1)(A) of the Act.

BOD_5 - Biochemical oxygen demand (five day)

COD - Chemical oxygen demand

CrT - Chromium (total)

m^3/d - Cubic meters per day

DCP - Dichlorophenol

gpd - Gallons per day

gal/lb - Gallons per pound

GC-MS - Gas chromatograph - mass spectrophotometer

g/l - Grams per liter

HCN - Hydrogen cyanide

kg - kilogram

kg/kkg - kilogram(s) per 1000 kilograms

l - liter

m - meter

mm - millimeter

ug - microgram

mg - milligram

MG - Million gallons

MGD - Million gallons per day

NPDES PERMIT - A National Pollutant Discharge Elimination System permit issued under section 402 of the Act.

NRDC - Natural Resources Defense Council

NPV - Net Present Value

NSPS - New source performance standards under section 306 of the Act.

NOD - Nitrogenous oxygen demand

ppb - parts per billion

ppm - parts per million

PCB - Polychlorinated biphenols

KCN - Potassium cyanide

lb - pound

POTW (POTWs) - Publicly owned treatment works.

PSES - Pretreatment standards for existing sources of indirect discharges, under section 307(b) of the Act.

PSNS - Pretreatment standards for new sources of indirect discharges, under section 307(c) of the Act.

O_2 - Oxygen

RCRA - Resource Conservation and Recovery Act of 1976 (Pub. L 94-580), Amendments to Solid Waste Disposal Act.

NaCN - Sodium cyanide

TCA - Tanners' Council of America

The Act - The Clean Water Act of 1977.

TDS - Total dissolved solids

TKN - Total Kjeldahl nitrogen

TSS - Total suspended solids

TVS - Total volatile solids

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