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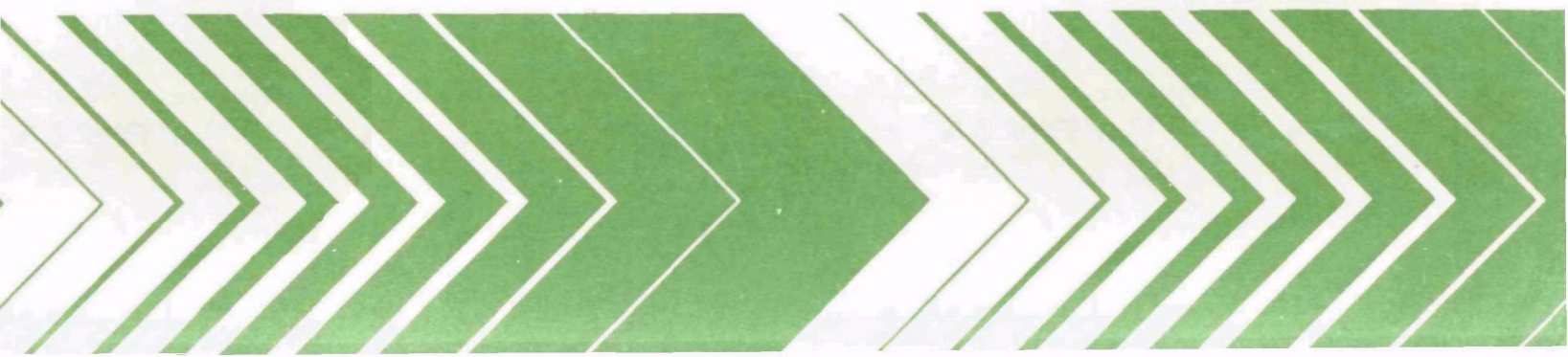
Treatment of Wastewaters From Adhesives and Sealants Manufacture by Ultrafiltration



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TREATMENT OF WASTEWATERS FROM ADHESIVES AND SEALANTS MANUFACTURE BY ULTRAFILTRATION

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

A field demonstration of ultrafiltration for the treatment of wastewaters generated during the manufacture of adhesives and sealants is discussed in this report. The technical merits of various post-treatment unit processes are considered based on pilot-scale tests, bench-scale tests, and literature reviews. A full-scale system design for treatment of this industry's wastewater is conceptualized, and purchased equipment and operating cost projections are made. These costs are compared with those which were included in the preliminary contractor recommendations presented in the draft development document for this industry as Best Practical Control Technology Current Achievable, Best Available Demonstrated Control Technology and Best Available Technology Economically Achievable costs for similar waste streams. It is hoped that the results of this study will increase the knowledge of both the public and industry in this complex area and will promote further activity in the review of waste treatment problems in the adhesives and sealants industry.

The Organic Chemicals and Products Branch of the Industrial Pollution Control Division should be contacted for further information on this subject.

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ABSTRACT

The overall goal of this program was to demonstrate technology for the treatment of effluents from adhesives and sealants manufacture to produce water of a quality suitable for discharge to municipal sewers. A secondary goal was to collect information on the nature and variability of these wastes to better characterize effluents generated in adhesives and sealants manufacture. The principal element of the program was a several-month field demonstration performed at the San Leandro, California, manufacturing facility of the Dewey and Almy Chemical Division of W.R. Grace and Company. Additionally, the program consisted of preliminary studies of UF permeate post-treatment alternatives, documentation of full-scale ultrafiltration system performance at the Dewey and Almy Chicago, Illionis plant, and development of full-scale treatment system designs and economic projections for plants with wastewater flows ranging from 3.8 m^3/day (1,000 gpd) to 75.8 m^3/day (20,000 gpd).

Ultrafiltration was proven to be a viable unit process for separating adhesives and sealants manufacturing wastewaters into a low-volume concentrate stream and a high-volume permeate stream. The UF permeate was characterized by the following average contaminant loadings: 100 mg/ℓ total freon extractibles, <7.4 mg/ℓ nonpolar extractibles, <27 mg/ℓ (typically <5 mg/ℓ) suspended solids, 0.43 mg/ℓ free cyanide, 3.6 mg/ℓ total cyanide, 8,900 mg/ℓ BOD, 36,600 mg/ℓ COD, 44.6 mg/ℓ phenolic compounds, and 1.5 mg/ℓ zinc. A treated effluent of this quality is acceptable for discharge under the San Leandro Municipal Discharge Limitations, with the exception of the phenolic compound and total cyanide loadings. Surcharges would be imposed, however, based on the suspended solids and BOD loadings.

If significant levels of phenolic compounds and cyanide are not present in a particular plant's wastewater discharge, ultrafiltration is judged capable of meeting local municipal discharge standards. This claim has been verified over the past two years by the operation of a full-scale UF system at the Dewey and Almy Chicago Plant. When phenolic compounds and cyanide are present at significant levels, either ozonation or reverse osmosis are considered the preferred post-treatment processes. A UF/ozonation or UF/reverse osmosis treatment system is projected to meet all municipal discharge standards. For either treatment system option, ultrafiltration, or

ultrafiltration followed by a post-treatment process; equalization of the plant wastes before ultrafiltration is recommended. This treatment step dampens flow and composition variations and provides gravity settling and flotation of suspended solids and oils and grease. The latter reduces the loading on the UF system and therefore lowers the membrane area requirement.

The preliminary contractor recommendations as presented in the draft development document for this industry proposed double-effect liquid evaporation as the model technology to meet the proposed standards for two of the six manufacturing subcategories. This treatment technology has not, as yet, been demonstrated. Projected capital investments for double-effect liquid evaporation are conservatively from 4 to 6 times the cost of the equalization/ultrafiltration and post-treatment costs. Projected annual operating costs for the evaporation system are in the range of 3 to 6 times the operating costs for the UF system options.

This report was submitted in fulfillment of Grant No. S804350010 by the Walden Division of Abcor, Inc., and the Dewey and Almy Chemical Division of W.R. Grace and Company under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from March 1, 1976, to July 30, 1977, and work was completed as of November 30, 1977.

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ENGLISH-METRIC CONVERSION TABLE

To Convert from	To	Multiply by
Inch	Meter	2.54×10^{-2}
Feet	Meter	3.05×10^{-1}
Square inch	Square meter	6.45×10^{-4}
Square feet	Square meter	9.29×10^{-2}
Cubic feet	Cubic meter	2.83×10^{-2}
Gallon	Cubic meter	3.79×10^{-3}
Pound	Kilogram	4.54×10^{-1}
Pound per sq. inch	Atmosphere	6.80×10^{-2}
Horsepower	Watt	7.46×10^{2}
Gallon per day	Cubic meter per day	3.79×10^{-3}
Gallon per minute	Cubic meter per day	5.45
Gallon per sq. ft-day	Cubic meter per sq. meter-day	4.10×10^{-2}
Gallon per minute per sq. ft.	Cubic meter per sq. meter-day	5.87×10^{1}

ACKNOWLEDGMENTS

The authors wish to thank Robert Holt, plant manager, and Laughlin Hines, plant engineer at the San Leandro field demonstration site for their support and cooperation throughout the field test program. The efforts of the test system operator, Don Benge, in handling the day-to-day operation of the test system are gratefully acknowledged.

The authors express their appreciation to Ronald Turner, EPA Project Officer on the demonstration grant, for his technical and administrative guidance during the course of this program.

Acknowledgment is also made of the skill and patience of Sharon Collins in preparing this manuscript.

SECTION 1

INTRODUCTION

BACKGROUND

The adhesives and sealants industry consists of 745 companies which operate 1114 manufacturing plants (1). Within this highly competitive industry, manufacturing facilities range from single-man operations to large industrial complexes (2), with the 50 leading adhesives and sealants formulators accounting for less than 33% of industrywide sales (1). Manufacturing facilities for this industry are concentrated mainly within the states of Illinois, New Jersey, California, Massachusetts, and New York.

For the purpose of developing effluent limitation guidelines, only those commodities within Standard Industrial Classifications 2891 and 2899 in the adhesives and sealants category were included. These commodities are listed in Table 1 (2). The diversity of products manufactured by the adhesives and sealants industry is clearly evident. Because of this diversity the industry was subcategorized into six groups in the preliminary contractor recommendations.

A. Water-Based Animal Glues and Gelatins
* B. Water-Based Adhesive Solutions Containing Synthetic and Natural Materials
* C. Solvent Solution Adhesives and Cements Generating Contaminated Wastewaters
D. Solvent Solution Adhesives and Cements generating Noncontact Cooling Water Only
E. Solid and Semi-Solid Hot Melt Thermoplastic Adhesives
F. Dry Blended Adhesive Materials

Detailed descriptions of the manufacturing processes for each subcategory are presented in Reference (2). The major similarity between the six groups is that they are all manufactured in batch processes by compounding raw materials in mix tanks or jacketed kettles.

* San Leandro and Chicago plants are in subcategories B and C.

TABLE 1. STANDARD INDUSTRIAL CLASSIFICATION OF PRODUCTS FROM THE ADHESIVES AND SEALANTS INDUSTRY (2).

SIC 2891

- Adhesives
- Adhesives, plastic
- Calking compounds
- Cement (cellulose nitrate base)
- Cement, linoleum
- Cement, mending
- Cement, rubber
- Epoxy adhesives
- Glue, except dental: animal, vegetable, fish casein, and synthetic resin
- Iron cement, household
- Laminating Compounds
- Mucilage
- Paste, adhesive
- Porcelain cement, household
- Rubber cement
- Sealing compounds for pipe threads and joints
- Sealing compounds, synthetic rubber and plastic
- Wax, sealing

SIC 2899

- Gelatin: edible, technical, photographic, and pharmaceutical

WASTEWATER CHARACTERIZATION

Numerous raw materials are used throughout this industry and therefore complex and varied wastewater streams are developed. The principal raw materials in adhesives and sealants manufactured are listed in Table 2 (2) indicating the wide variety of solvents, latices, surfactants, fillers and preservatives commonly employed. The main source of wastewater from adhesive manufacturing processes is the washing of the process vessels and lines while a small portion of wastewater is generated from area housekeeping and laboratories. The ratio of washwater volume to the other waste volumes is not well-defined.

The wastewater flow from adhesives plants varies markedly between subcategories. Typical averages are 249 m^3/kkg (30,000 gal/1000 lbs) for subcategory A, 0.94 m^3/kkg (113 gal/1000 lbs) for subcategory B, 0.34 m^3/kkg (41 gal/1000 lbs) for subcategory C, and zero discharge for subcategories D, E, and F. Plants in subcategory D discharge noncontact cooling water only. Process vessel cleaning in subcategory E is performed with a hot wax solution which is recycled back into production. For dry blends (group F) neither water nor solvents are compatible with the manufacturing process.

A summary of the raw wastewater loadings, by subcategory, is presented in Table 3 for several major pollutants. The oxygen demand is significant in the wastewater from subcategories A, B, and C. The suspended solids loading in groups A and B is >3,000-4,000 mg/ℓ, while oil and grease levels

TABLE 2. PRINCIPAL RAW MATERIALS USED IN ADHESIVE AND SEALANTS MANUFACTURE (2).

1. Water based solutions containing natural and synthetic materials.

Starches	Polyvinyl acetate - homo-polymers, co-polymers
Dextrins	Acrylic polymers and co-polymers
Sugars	Synthetic and natural elastomeric lattices
Syrups	Polyvinyl chloride
Animal & Fish Glue	Polyvinyl alcohol
Gelatins	Rosin and rosin derivatives
Caseins	Bituminous
Cellulose	Hydrocarbon resins
Marine Colloids	Phenolic resins
Lignin	

2. Solvent solution adhesives and cements (Non-water based solutions).

Synthetic and natural elastomers	Solvents
Synthetic and natural resins	Aliphatic hydrocarbons
Synthetic and natural rosins, and modified rosins	Ketones and mixed ketones
Plasticizers	Aromatic hydrocarbons
Anti-oxidants	Nitrated halogenated hydrocarbons
Peptizing Agents	Alcohols
	Esters
	Ethers
	Amines

3. Solid and Semi-Solid and Thermoplastic Thermosetting Compounds

Synthetic polymers and copolymers	Synthetics and natural waxes
Synthetic and natural rosins and modified rosins	Synthetics and natural oils
	Plasticizers
	Synthetic and natural resins

4. Dry-Blended Adhesive Materials

Silicas	Assorted Cements
Clays	Fillers
Plaster	

5. The following materials can be found, as additives, in the preceeding groups.

Fillers	Solvents and Plasticizers
Clays	Aliphatic hydrocarbons
Calcium carbonates	Ketones and mixed ketones
Calcium sulphates	Aromatic hydrocarbons
Talcs	Nitrated halogenated hydrocarbons
Pigments, dyes, oxides	Alcohols
Asbestos	Esters
Sand	Ethers
Fly Ash, etc.	Amines

TABLE 2 (CONTINUED) PRINCIPAL RAW MATERIALS USED IN ADHESIVE AND SEALANTS MANUFACTURE (2).

Surface Active Agents	Preservatives
Surfactants	Fungicides
Soaps	Mildewicides
Defoamers	Bactericides
Penetrating Agents	
Miscellaneous Components	
Organic Salts	
Inorganic Salts	
Acids	
Bases	
Humectants	
Metals	
Thickeners - Polymeric or cellulosic, etc.	
Anti-oxidants	

TABLE 3. SUMMARY OF THE RAW WASTEWATER LOADING FOR MAJOR POLLUTANTS IN THE ADHESIVES AND SEALANTS INDUSTRY (2)*

Assay		Subcategory A	Subcategory B	Subcategory C
Total Suspended Solids,	kg/kkg	1,140	3.1	0.01
	mg/ℓ	4,560	3,300	29
Total Dissolved Solids,	kg/kkg	800	13.9	0.4
	mg/ℓ	3,200	14,800	1,180
BOD_5,	kg/kkg	942	3.4	4.4
	mg/ℓ	3,770	3,610	12,900
COD,	kg/kkg	2,520	15.5	7.3
	mg/ℓ	10,100	16,500	21,500
TOC,	kg/kkg	669	5.0	1.4
	mg/ℓ	2,680	5,310	4,100
Oil and Grease,	kg/kkg	254	1.28	0.0003
	mg/ℓ	1,020	1,360	0.9
Average Wastewater Flowrate,	m^3/kkg	249	0.94	0.34

*No process water discharged in Subcategories D, E and F.

in these two groups are >1,000 mg/ℓ. Phenolic compounds may be present in significant quantities in wastewaters generated from phenol formaldehyde resins in subcategories B or C (2). Also, these wastewaters contain highly stable chemical emulsions.

Both the flow and composition of wastewaters from adhesives plants are highly variable, over both short term (minutes to hours) and long term (days to months) due to the batch nature of the manufacturing processes.

EFFLUENT LIMITATION GUIDELINES

In February, 1975, the Environmental Protection Agency included the adhesives and sealants industry in a draft report entitled, "Development Document for Effluent Limitations Guidelines and Standards of Performance, Miscellaneous Chemicals Industry" (2)*. Best Practical Control Technology Currently Available (BPCTCA) Standards and Best Available Technology Economically Achievable (BATEA) Standards were developed for existing plants. Best Available Demonstrated Control Technology (BADCT) Standards of Performance were drafted for new sources. The preliminary contractor recommendations are summarized in Table 4 for subsequent comparison with the results of the field demonstration.

Local Municipal Treatment Authorities often have effluent limitation guidelines which are more inclusive, and at times more difficult to satisfy, than the Federal Standards. The discharge limits for two cities; Chicago, Illinois and San Leandro, California and the ranges of sewer discharge standards for approximately 20 municipalities (3) are given in Table 5. Limitations on wastewater BOD and total suspended solids content are generally written such that once a specified level is exceeded, surcharges are imposed. In San Leandro surcharges are assessed on the entire BOD and suspended solids loading of the wastewater, and the wastewater volume per the following schedule (4):

Volume:	\$0.721 per m^3
BOD:	\$1.229 x BOD (mg/ℓ)/1000 per m^3
Suspended Solids:	\$1.244 x SS (mg/ℓ)/1000 per m^3

These rates became effective 1 July 1977 and, in total, represent a 230% increase over previous surcharges.

CURRENT TREATMENT METHODS

The majority of adhesive plants discharge their wastewaters directly to municipal treatment facilities and, therefore, end-of-pipe treatment and control technology are not practiced extensively within this industry (2). In a survey of the adhesives industry conducted during the Effluent Limitation Guidelines development program, "no adhesive plants which conduct

*The miscellaneous chemicals industry classification also includes: pharmaceuticals, gum and wood chemicals, pesticides and agricultural chemicals, explosives, carbon black, photographic processing and hospitals.

TABLE 4. SUMMARY OF EPA PRELIMINARY CONTRACTOR RECOMMENDED EFFLUENT LIMITATION GUIDELINES FOR THE ADHESIVES AND SEALANTS INDUSTRY

Subcategory†	Wastewater Flow, m^3/kkg	Waste Parameter	Raw Wastewater		BPCTCA		BADCT		BATEA	
			Kg/kkg	mg/ℓ	Kg/kkg	mg/ℓ	Kg/kkg	mg/ℓ	Kg/kkg	mg/ℓ
A. Water based animal glues and gelatins	249	BOD	942	3,770	65.9	265	65	260	25	100
		COD	2,520	10,100	176	710	170	680	66.9	267
		TSS	1,140	4,560	--	50	--	20	--	20
B. Water-based ashesive solutions containing synthetic and natural materials	0.94	BOD	3.4	3,610	0.24	255	0.24	255	0.24	255
		COD	15.5	16,500	1.09	1,300	1.09	1,160	1.09	1,160
		TSS	3.1	3,300	--	20	--	20	--	20
C. Solvent solution adhesives and cements generating contaminated wastewaters	0.34	BOD	4.4	12,900	0.31	910	0.31	910	0.31	910
		COD	7.3	21,500	0.51	1,530	0.51	1,500	0.51	1,500
		TSS	0.01	29	--	20	--	20	--	20

†No process water discharge in subcategories D, E, and F.

TABLE 5. MUNICIPAL DISCHARGE LIMITATIONS

Parameter	Chicago, Illinois (3)	San Leandro, California	Ranges for ∿20 Cities (3)
Arsenic, mg/ℓ	-	0.1	<0.05-5
Cadmium, mg/ℓ	2.0	0.2	<0.02-5
Chromium (total), mg/ℓ	25.0	0.5	-
Cyanide (free), mg/ℓ	2.0	-	-
Cyanide (total), mg/ℓ	10.0	1.0	0-10
Lead, mg/ℓ	0.5	1.0	<0.1-5
Mercury, mg/ℓ	0.0005	0.01	<0.0005-1.5
Phenolic Compounds, mg/ℓ	0.1	1.0	<0.02-10
Zinc, mg/ℓ	15.0	3.0	<2-15
Oil and Grease, mg/ℓ	<100*	300/100†	<50-120††
pH, units	4.5-10.0	>6.0	4.5-10.5

* Hexane extractibles

† 300 mg/ℓ oil and grease of animal or vegetable origin, 100 mg/ℓ oil and grease of mineral or petroleum origin.

†† Listed as grease, no details of analysis provided.

complete treatment of their wastewater discharges were found. The only type of treatment observed was physical treatment for suspended solids removal" (2).

Pollution abatement measures which are typically exercised by adhesives and sealants manufacturers include:

1. Controlled rinsing of process vessels and lines with rinse water recycling as opposed to use of a simple filling and draining technique;
2. Scrape down of tank residue where controlled rinsing is not practical;
3. Blowing out process lines and pumping systems where rinse water would not be reusable;
4. Cleaning of accidental spills before they enter the plant effluent; and,
5. Use of a holding tank or pond for flow equalization and suspended solids removal.

Recently, a full-scale ultrafiltration (UF) system was installed at the Chicago Plant of the Dewey and Almy Chemical Division of W.R. Grace, Inc. This plant has an average wastewater discharge of 76 m^3/day (20,000 gal/day). Since the UF system was installed this plant has not been cited by the Metropolitan Sanitary District (MSD) of greater Chicago for any discharge violations.

In contrast, an extensive examination of the application of coagulation and flocculation, followed by dissolved air flotation showed only limited success on Dewey and Almy's Chicago plant waste stream. A tabulation of the best effluent hexane extractible levels attained with this conventional treatment process is given in Table 6, while a summary of a full year's operation of the Chicago Plant's ultrafiltration system is presented in Section 8.

BPCTCA, BADCT AND BATEA TREATMENT METHODS

The preliminary contractor report recommended biological treatment (activated sludge) for subcategory A to provide BPCTCA technology level. For this subcategory dual-media depth filtration (DMDF) of the secondary treated effluent is suggested to meet BADCT requirements and a two-stage activated sludge system with DMDF of the effluent is recommended for BATEA treatment.

The recommended technology to provide an effluent consistent with all three technology levels for both subcategories B and C was double effect liquid evaporation. Two days of detention time in a well-mixed equalization basin were planned prior to evaporation.

TABLE 6. HEXANE EXTRACTIBLE LEVELS FOLLOWING CONVENTIONAL TREATMENT OF DEWEY AND ALMY CHICAGO PLANT WASTE STREAMS

Stream Number	Common Constituents*	Volume m^3, wk	Untreated pH	Untreated Hexane Extractibles, mg/ℓ	Treated Hexane Extractible, mg/ℓ†
1.	Saponified oils, acids and resins	37.9	11.0	8,270	330
2.	Calcium lignin sulfonate, phenol	2.3	10.7	1,330	330
3.	Paraffin wax, PVC resin, oils	3.8	12.0	2,090	172
4.	Resins, SBR latex, mineral oil	76-95	8.9	14,000	243
5.	Latices,wax, resin, oils, surfactants	26.5	9.8	10,600	77
6.	Latex, rubbers, oils, surfactants	17.0	9.2	3,880	108
7.	Dioctyl sebacate and phthalate, zinc resinate	3.9	12.3	11,600	623
8.	Resin, wax, oils, acids	5.7	12.0	2,910	147

*Partial listing.

†Best results with conventional treatment consisting of coagulation and dissolved air flotation.
Note: Chicago Municipal Discharge Limitation for Hexane Extractibles is 100 mg/ℓ.

It is the authors' belief that no full-scale biological treatment or double effect liquid evaporation systems are currently in use in the adhesive and sealants industry.

TREATMENT APPROACH SELECTED FOR EVALUATION

The principal unit operation selected for evaluation was the membrane separation process of ultrafiltration. This unit process had demonstrated the ability to successfully treat one adhesive and sealants plant wastewater discharge and its application to other subcategory B and C waste streams deserved investigation.

Ultrafiltration is particularly effective in removing suspended solids, oil and grease and complexed heavy metals. Advantages of ultrafiltration over conventional treatment processes and evaporation are:

1. Ultrafiltration requires no heat addition (cooling may be required);
2. Ultrafiltration is economical at both small and large sizes, because of its modular nature;
3. Ultrafiltration systems are very simple to operate since they involve, primarily, the pumping of liquids;
4. Energy requirements for ultrafiltration are low since operation proceeds through the pumping of liquids;
5. Ultrafiltration performs best with chemically-stabilized emulsions (as are found in adhesives manufacturing wastewaters);
6. Ultrafiltration is generally insensitive to shock loading. During processing of streams containing latex, latex instability may cause membrane fouling;
7. The ultrafiltrate will be essentially free of suspended solids and will have a low oil and grease content;
8. Heavy metals should be efficiently removed by ultrafiltration. This is because the metals will be insolubilized by reaction with negatively charged colloids and will not pass through the ultrafiltration membranes; and,
9. The concentrate volume will be significantly less than that produced in a coagulation-solids separation process.

Because of these characteristics of ultrafiltration this process has the potential to be a viable alternative to double effect evaporation recommended for subcategory B and C wastes with BPCTCA and BATEA standards.

In conjunction with the ultrafiltration process three methods of post-treatment were studied: reverse osmosis (RO), activated carbon adsorption (ACA) and chemical oxidation. These processes are all capable of removing dissolved organic species from wastewater, thus lowering the ultrafiltrate's biological and chemical oxygen demands. Also, with proper post-treatment water reuse within an adhesives plant is considered feasible.

FIELD DEMONSTRATION SITE

The site of the field demonstration tests was the manufacturing facility of the Dewey and Almy Chemical Division of W.R. Grace & Company located at San Leandro, California. At this plant a variety of adhesives, sealants and construction products additives are produced. Although over twenty "custom tailored" products are manufactured at the San Leandro Plant, the product line can be summarized into five basic categories. These categories are:

Product Identification	Use
Water Base	Sealant for jars, cans, caps, etc.
Cover and Drum	Sealant for drums, large containers
Solvent Base	Sealant (fast drying) for cans and caps
"Z"	Internally used latex product; added to solvent base sealants
Construction Products Additives (CPD)	Various uses include: reducing water content in concrete; reducing setting time of concrete; improving pumpability of concrete, etc.

All products are manufactured in batchwise operations.

Wastewater is generated from the manufacturing of all products with the exception of solvent base sealants. For these products, the cleaning operations are "closed-loop". Table 7 details the principal raw materials used in the manufacture of the other four product types. The most prevalent raw material is styrene-butadiene latex.

Several other waste stream sources are present at the San Leandro Plant. These include: periodic washdown of the crystal flux apparatus (contains zinc ammonium chloride), CPD tank truck rinsing, cooling water overflow and boiler blowdown.

All plant wastewater flows into a sump [estimated capacity 1.9-3.8 m^3 (500-1000 gal)] prior to discharge to the sewer. Approximately 19 m^3 (5000 gal) of wastewater are generated per day .

TABLE 7. PRINCIPAL RAW MATERIALS USED IN MANUFACTURE OF SAN LEANDRO PRODUCT LINE

Product	Raw Materials
Water Base Sealant	Styrene-Butadiene (SBR) latex, alcohol, small quantities of xylene and toluene
Cover and Drum Sealant	SB latex, some neoprene latex
"Z"	SB latex with clay fillers and antioxidants, isopropanol, sodium nitrate, pinene resins
Construction Products Additives	Sodium lignum sulfonate, phenols, wetting agents

SECTION 2

CONCLUSIONS

This demonstration of adhesives and sealants manufacturing wastewater treatment by ultrafiltration has been augmented by a review of a number of post-treatment alternatives for the UF permeate. From this work three treatment system options for adhesives and sealants wastes have been conceptualized and full-scale treatment costs have been projected for system capacities of interest to this industry. In general, a high-quality product water is produced by the UF system; however, it may contain (depending on the manufacturing site) residual quantities of phenolic compounds and cyanide which are in excess of local Municipal Discharge Limitations. These contaminants, which are incompatible with subsequent biological treatment in publicly-owned treatment plants can be removed from the UF permeate by either ozonation or reverse osmosis.* The results of the field demonstration were compared to the preliminary contractor recommendations as presented in the draft development document for this industry. The contractor's recommended values for BOD and COD were not achieved by any combination of waste equalization, ultrafiltration and post-treatment evaluated. The large capital investments associated with double-effect liquid evaporation (the treatment model presented in the Draft Development Document) may, however, severely limit the use of such technology.

These general conclusions are supplemented by the following specific findings:

1. Plant Effluent Characteristics

   - The flow of wastewaters from the San Leandro Plant did not follow any set pattern. This is because of the batchwise nature of all manufacturing operations. Equalization of the plant wastewater flow before UF processing is therefore advisable.
   - The plant effluent exhibited wide ranges in contaminant loadings. For example, the effluent total suspended solids ranged from 59 mg/ℓ to 70,800 mg/ℓ and its zinc content varied from 2.4 mg/ℓ to 740 mg/ℓ. Again, wastewater equalization prior to ultrafiltration would be advisable.
   - The suspended solids loading in the total plant effluent averaged 10,600 mg/ℓ during the field demonstration tests. Gravity settling and/or flotation of a portion of these

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* As indicated by laboratory-scale feasibility tests. These post-treatment processes remain to be demonstrated.

suspended solids would reduce the loading on the ultrafiltration system and therefore lower the membrane area requirement. This, in turn, would reduce the UF system capital cost and would lower the UF system operating expense.

2. Ultrafiltration System Performance Characteristics

- During treatment of the total effluent from the San Leandro Plant the UF permeate averaged 100 mg/ℓ total freon extractibles, < 7.4 mg/ℓ non-polar freon extractibles, < 27 mg/ℓ suspended solids, 0.43 mg/ℓ free cyanide, 3.6 mg/ℓ total cyanide, 8,900 mg/ℓ BOD, 36,600 mg/ℓ COD, 44.6 mg/ℓ phenolic compounds and 1.5 mg/ℓ zinc. The average removal efficiencies for total freon extractibles, non-polar freon extractibles and suspended solids were 92.2%, 94.7%, and 99.6%, respectively. The UF system removal efficiency for BOD averaged 24.0% and for COD averaged 38.2%. The mean zinc removal was 90.8%. Accurate removal efficiencies for free and total cyanide could not be calculated due to interference in the assays for these contaminants. A treated effluent of the above quality is acceptable for discharge under the San Leandro Municipal Discharge Limitations with the exception of the phenolic compound and total cyanide loadings. Surcharges would be imposed, however, based on the suspended solids and BOD loadings. An effluent of this quality does not conform to recommended BPCTCA or BATEA standards for BOD and COD, subcategories B and C.

- The suspended solids loading in the UF permeate was typically below 5 mg/ℓ. Periodically, however, secondary precipitation occurred which increased the permeate suspended solids loading (during processing of the total plant effluent) to as high as 160 mg/ℓ. The mechanism by which this secondary precipitation occurs was not identified during this program. In Chicago it was found that this phenomenon occurred with high bacteria counts and low pH.

- The average plant effluent concentrations of cadmium, total chromium, lead and mercury were below the San Leandro Municipal Discharge Limitations before ultrafiltration. The concentration of arsenic in the wastewater was below the detection limit of the assay method employed (0.2 mg/ℓ). Thus discharge of the plant wastewater is not limited by any of these constituents.

- Average flux for the Abcor, Inc. type HFM ultrafiltration membranes during processing of the total plant effluent was 1.38 m^3/m^2-day (33.8 gfd). This flux was averaged throughout six individual tests with a total operating time of 1021 hours and is an economically acceptable design flux.

- Typically, a short duration (1/2-hour) detergent wash cycle was capable of recovering membrane flux to acceptable levels. In two instances, severe latex fouling occurred. The use of mechanical cleaning in one case, and solvent cleaning with mechanical cleaning in the second case were necessary to affect

membrane flux recovery. Membranes which are solvent cleanable and membrane modules which can be mechanically cleaned (if necessary) are therefore required for ultrafiltration of adhesives and sealant manufacturing wastewaters.

- Continuous addition of surfactant to the UF tank was exercised on two occasions during the field demonstration program. No significant gain or loss in UF membrane flux or rejection characteristics were observed. Therefore, surfactant addition (used at the Chicago plant) is not viewed as a required process step. If, however, fairly unstable latices are present in a plant wastewater surfactant addition may be necessary to maintain economic flux levels.
- Treatment of the total plant effluent less the CPD waste stream during one field test and less the "Z" dispersion waste stream in another test was performed in an effort to identify a "bad actor" stream in terms of either membrane flux or rejection. While no significant benefits in UF system performance were gained by segregation of either stream, it was observed that segregation of the CPD stream lowered the remaining plant effluent phenolic compounds loading to an average of 4.8 mg/ℓ. Even with this lessening of the phenolic compound loading, treatment of the total plant effluent was preferred over stream segregation.

3. Post-treatment Process Evaluation

- Pilot-scale tests performed with the Grace Chicago Plant UF permeate demonstrated the technical feasibility of reverse osmosis post-treatment. However, membrane degradation during one of the two experiments conducted limits the generalization of these results. While phenolic compound and cyanide concentrations in an RO product water are predicted to be below municipal discharge limitations, BOD and COD loadings are expected to be ~3X the values recommended by the contractor as the draft BPCTCA, BADCT and BATEA standards.
- Carbon isotherm experiments with the Grace Chicago Plant UF permeate indicated poor adsorption capacity for BOD and COD. Therefore carbon adsorption is not considered a viable post-treatment unit operation.
- Bench-scale ozonation tests on a sample of the San Leandro plant UF permeate indicated the feasibility of this process for phenolic compound and cyanide destruction. BOD and COD content in the ozonated product water were each an order-of-magnitude above the values recommended by the contractor as the draft BPCTCA, BADCT and BATEA standards.
- Limited literature reviews on the processes of chlorination, hydrogen peroxide oxidation and potassium permanganate oxidation for phenolic compound and cyanide destruction were performed. Each of these processes was eliminated from consideration as a viable posttreatment alternative on either a technical or economic basis.

4. Conceptual Treatment System Design

- Three treatment system design options have been conceptualized. These are:

  Option 1. Equalization → Ultrafiltration → Discharge
  Option 2. Equalization → Ultrafiltration → Ozonation → Discharge
  Option 3. Equalization → Ultrafiltration → Reverse Osmosis → Reuse and/or Discharge

  The Option 1 system is capable of producing an effluent meeting the local municipal discharge standards if significant levels of phenolic compounds and cyanide are not present in the plant wastewater discharge. The Option 2 system is capable of producing an effluent meeting local municipal discharge standards when phenolic compounds and cyanide are present in plant wastewater. System Option 3 is capable of concentrating phenolic compounds and cyanide producing an effluent suitable for discharge. It may also produce a product water reusable within the manufacturing plant. None of the three treatment options described is considered capable of reducing the adhesives and sealants manufacturing plant wastewater BOD and COD loadings to the BPCTCA, BADCT and BATEA levels recommended in the draft development document.

5. Estimated Process Costs

- Purchased equipment costs were projected for each treatment system option for each of three manufacturing plant wastewater flow rates: 3.8 m^3/day (1,000 gpd), 18.95 m^3/day (5,000 gpd) and 75.8 m^3/day (20,000 gpd). One shift operation, two shift operation and three shift operation was assumed for the three system capacities, respectively. A matrix of estimated purchased equipment costs (in thousands of dollars) follows:

System Option	Plant Wastewater Flowrate (m^3/day) 3.8	18.95	75.8
1	$23.5	$52.9	$90.1
2	37.5	66.9	104.1
3	38.5	77.9	125.1

These cost estimates exclude installation costs which are highly site specific.

- Annual operating costs for three capacities of each system option have been developed. The annual operating cost projections (in thousands of dollars) are summarized below.

System Option	Plant Wastewater Flowrate (m^3/day) 3.8	18.95	75.8
1	$8.84	$20.8	$52.8
2	11.0	23.7	56.8
3	13.2	29.9	74.3

- Sludge disposal costs vary from 15% to 31% of the total operating expense. If an effective means of sludge dewatering is identified operating costs could be reduced significantly.

6. Comparison of System Options, 1, 2, and 3 Costs with the preliminary contractor report's BPCTCA, BADCT and BATEA Technology Costs

   - The recommended BPCTCA, BADCT and BATEA technology presented in the Draft Effluent Limitations Guidelines Development Document for the Adhesives and Sealants Industry is double effect liquid evaporation for similar types of wastewater to those under consideration in this report. The following costs (in August, 1972 dollars) were developed:

	Plant Wastewater Flow Rate (m^3/day) 22.7	37.9
Capital Costs ($000)	324	412
Annual Operating Costs ($000)	139	189

   While these costs cannot be directly compared with the treatment system Options 1, 2 and 3 costs, it is clear that double effect liquid evaporation would require a capital investment of from 4 to 6 times (using 1972 dollars) the cost of the equalization/ultrafiltration and posttreatment system costs (using 1977 dollars). Annual operating costs would also be significantly increased if the contractor recommended BPCTCA, BADCT, BATEA treatment model is employed.

7. Evaluation of a Full-scale Equalization/Ultrafiltration System Treating Adhesives and Sealants Manufacturing Wastewaters

   - During the early 1970's a dissolved air flotation system was installed at the Chicago, Illinois plant of the Dewey and Almy Chemical Division of W.R. Grace and Company. The system improved the quality of the plant's effluent in terms of oil and grease, however, due to the effluent's variability from hour to hour, there were frequent periods during which the pollutant levels were excessive. Even with modifications and improvements to this treatment system it was projected that the effluent would be out of specification (> 100 mg/ℓ oils and grease) from 5% to 10% of the time. This treatment method was therefore unacceptable.

- Pilot-scale ultrafiltration tests were performed and a full-scale UF system (design capacity 81.9 m^3/day) was installed in 1974 at a total cost of $180,000. This cost includes all accessory equipment, tanks and piping and installation expenses. The UF permeate oil and grease (hexane extractibles) loading has averaged 35 mg/ℓ compared to a Metropolitian Sanitary District (MSD) of Greater Chicago specification of 100 mg/ℓ. The suspended solids concentration has averaged 24 mg/ℓ. Iron and zinc concentrations in the permeate have averaged 0.8 mg/ℓ and 1.25 mg/ℓ, respectively. Similar to the San Leandro results, modest reductions in BOD are achieved by the UF membranes. The UF permeate has maintained a 99% compliance level with MSD specifications. Thus, UF treatment provides an effluent meeting local municipal discharge standards but the effluent will not achieve the values recommended for the draft Federal BOD and COD discharge limitations.
- The total operating costs for the Chicago Plant pollution control system were $3.34/$m^3$ ($12.66/1000 gal) in 1975 and $3.51/$m^3$ (13.23/1000 gal) in 1976. These costs are in-line with System Option 1 cost projections.

SECTION 3

RECOMMENDATIONS

On the basis of the knowledge gained during this program, the following recommendations are offered:

1. Field demonstration programs should be conducted for the post-treatment alternatives of ozonation and reverse osmosis. Such demonstrations would provide sufficient data for optimization of each system's operating parameters and would develop a data base for design calculations, and economic analyses. An accurate profile of product water quality from each process should be obtained and the reuse potential of each product water should be assessed.

2. A comprehensive investigation should be conducted to identify the preferred dewatering technique(s) for sludges generated during the treatment of adhesive and sealants manufacturing wastewaters. The percentage of the total operating costs contributed by the sludge disposal operation for treatment systems comprised of equalization, ultrafiltration and reverse osmosis (Option 3) is 27% for a system processing 3.8 m^3/day (1000 gpd); 29% for a system processing 18.95 m^3/day (5000 gpd); and, 31% for a system processing 75.8 m^3/day (20,000 gpd). These percentages and their related costs are quite significant. Thus substantial savings in operating costs can be realized and overall attractiveness of the treatment system can be enhanced if an acceptable sludge dewatering method is demonstrated.

3. The contractor's draft development document and the recommended treatment model (double effect liquid evaporation) for the adhesive and sealants industry should be reconsidered. None of the treatment schemes investigated during this program were capable of meeting the contractor's recommended BPCTCA, BADCT and BATEA standards for BOD and COD. However, they were capable of meeting local municipal treatment discharge standards and of removing pollutants incompatible with publicly-owned treatment works. The Draft Development Document for this industry has identified BOD and COD as pollution parameters which are compatible with publicly-owned treatment works.*

* However, COD may not be totally compatible with publicly-owned treatment works in all cases.

Considering the relatively small quantities of wastewater being generated by subcategory B and C manufacturing sites, the capital investment required for the proposed treatment model and the energy-intensive operation of double effect liquid evaporators it does not appear economically feasible to meet the contractor's recommended discharge goals. Rather, "pretreatment" of adhesives and sealants wastes by equalization, ultrafiltration and ozonation or reverse osmosis (or other proven treatment schemes) to remove oils and grease, suspended solids and pollutants incompatible with municipal biological treatment systems should be required.

If the preliminary contractor's recommendations are subsequently endorsed by the U.S. EPA, the proposed model treatment of double effect liquid evaporation should be demonstrated at a representative adhesives and sealants manufacturing site.

SECTION 4

PROGRAM OVERVIEW

The overall goal of this program was to demonstrate acceptable technology for the treatment of effluents from adhesives and sealants manufacture to produce water of a quality suitable for discharge to municipal sewers. A secondary goal was to collect information on the nature and variability of these wastes to better characterize effluents generated in adhesives and sealants manufacture. Toward these ends a pilot-scale ultrafiltration system, incorporating feed pretreatment via gravity settling and flotation, was installed at the San Leandro, California plant of the Dewey and Almy Chemical Division of W.R. Grace and Company. The test program conducted at the San Leandro plant consisted of several tasks including:

a. Determination of UF membrane flux and rejection characteristics with the total plant effluent.

b. Evaluation of the effect of segregating various waste streams on UF membrane performance characteristics.

c. Evaluation of the effect of surfactant addition on UF membrane performance characteristics.

d. Determination of the maximum concentration achievable by ultrafiltration.

e. Evaluation of membrane flux recovery with cleaning.

f. Sampling and analysis of the plant effluent, the effluent after settling, the UF concentrate and the ultrafiltrate.

g. Determination of variability in flow of the plant effluent.

Also at the field demonstration site, samples of the plant effluent and the UF concentrate were treated by several dewatering methods. Although in-depth experiments were not performed a measure of effectiveness for the various dewatering techniques was derived.

As a check of prior experimental work a one week evaluation of a dissolved air flotation process was performed at the San Leandro Plant. The process employed was LECTRO-CLEAR ^{TM} treatment developed by Swift Environmental Systems Company. This is an electrolytic process involving an electrocoagulation cell followed by an electroflotation basin. Periodically, the LECTRO-CLEAR ^{TM} effluent was further treated by the UF pilot system.

The test program described above was supplemented by feasibility experiments on the treatment of the product waters from ultrafiltration by reverse osmosis and carbon adsorption. These experiments consisted of two reverse osmosis batch concentrations and two carbon isotherm tests with ultrafiltrate from the Dewey and Almy Chicago Plant. Additional post-treatment work involved a brief literature survey of cyanide and phenolic compound removal by chemical oxidation processes employing chlorine, hydrogen peroxide, potassium permanganate and ozone. A single sample of ultrafiltrate from San Leandro was ozonated by U.S. Ozonair Corp. to provide an order-of-magnitude estimate of the economics for this process.

Effluent quality and membrane flux performance during one year's operation of the Chicago Plant's ultrafiltration system were analyzed to provide input into an evaluation of the technical feasibility of full-scale treatment systems. Data from this plant also provided accurate operating costs, especially with regard to membrane life, operating labor requirements, and concentrate disposal.

Based on the results of the field demonstration experiments, the post-treatment feasibility studies and the Chicago Plant's UF system operating experience a full-scale treatment for the San Leandro Plant was designed. This design included P & I drawings and sizing of all major process components. The economics of full-scale system operation, including estimates of capital and operating costs, were also developed.

SECTION 5
DISCUSSION OF UNIT PROCESSES

The purpose of this section is to set forth certain principles and definitions which will be used in subsequent sections. Many general references are available which describe the relevant unit processes in more detail.

ULTRAFILTRATION

Ultrafiltration and reverse osmosis are similar processes in that both employ a semipermeable membrane as the separating agent and pressure as the driving force to achieve separation. There are important differences, however, which lead to different applications, process conditions and equipment for each of the two processes. The approach in this program is based on ultrafiltration as the principal unit process with reverse osmosis as a possible posttreatment step. The differences between ultrafiltration and reverse osmosis are summarized in Table 8 while each process is discussed separately below.

In an ultrafiltration process a feed solution/suspension is introduced into a membrane unit, where water and certain solutes pass through the membrane under an applied hydrostatic pressure. Solutes whose sizes are greater than the pore size of the membrane and all suspended solids are retained and concentrated. The pore structure of this molecular filter is such that it does not become plugged because suspended solids are rejected at the surface and do not penetrate the membrane.

For solutions which have no rejected species, such as water, the flux through the membrane is given by:

$$J_o = \frac{\Delta P}{R_m + R_f} \qquad (1)$$

where,

J_o = Flux rate (m^3/m^2 - day)

ΔP = Pressure drop across the membrane (pressure driving force) (atm)

R_m = Resistance of clean membrane (m^2-day-atm/m^3)

R_f = Resistance of fouling layer (m^2-day-atm/m^3)

No material from the process stream builds up on the membrane surface and, therefore, for water the flux is pressure dependent and flow independent.

TABLE 8. DIFFERENCES BETWEEN REVERSE OSMOSIS AND ULTRAFILTRATION

Item	Reverse Osmosis	Ultrafiltration
Size of solute retained	Molecular weights generally less than 500	Molecular weights generally over 1000
	High salt retention	Nil salt retention
Osmotic pressures of feed solutions	Important, can range to over 69 bar	Negligible
Operating pressures	Greater than 28 bar, up to 138 bar	0.7 to 6.9 bar
Nature of membrane retention	Diffusive transport barrier; possibly molecular screening	Molecular screening
Chemical nature of membrane	Important in affecting transport properties	Unimportant in affecting transport properties so long as proper pore size and pore size distribution are obtained.
Typical membrane flux levels	0.08 to 0.61 m^3/m^2-day	0.82 to 8.2 m^3/m^2-day

When ultrafiltering solutions having high concentrations of rejected material, the observed flux levels are much lower than the water flux of the clean membrane. A gel layer develops and the following equation applies:

$$J_1 = AQ^X \ln \frac{C_g}{C_b} \qquad (2)$$

where,

J_1 = Flux rate

A = A constant which is a function of feed channel dimensions and fluid properties

C_g = Concentration of rejected species in the gel layer

C_b = Concentration of rejected species in the bulk solution

Q = Circulation rate of fluid through the membrane modules (m^3/min)

X = Empirical constant (generally $1 < X < 2$)

For solutions with high concentrations of rejected materials, the flux is pressure independent [above 0.7 atm (10 psig)] and flow dependent.

The removal efficiency, r, of a UF module for a given species is defined by the relationship:

$$r = \frac{C_f - C_p}{C_f} \quad (100\%) \qquad (3)$$

where C_f and C_p are the feed and permeate concentrations for a module operated with significant water recovery.

COMMERCIALLY AVAILABLE ULTRAFILTRATION MEMBRANES AND MODULES

Industrial ultrafiltration membranes are classified by molecular weight cut-off, and are available from either cellulosic or non-cellulosic materials. The cellulosic membranes can be employed at pH 2.5 to 9, while the ranges for others vary. For example, Abcor, Inc.'s non-cellulosic Type HFD membrane has a pH tolerance range from 3 to 12 and can withstand operating temperatures in excess of 74°C (165°F). This membrane is, however, sensitive to oxidation by free-chlorine. Abcor, Inc.'s Type HFM non-cellulosic membrane can tolerate up to 50 ppm free-chlorine, has a pH range of 0.5 to 12 and can operate at up to 85°C (185°F).

Four module configurations are available commercially to house the ultrafiltration membranes. These are plate-and-frame, tubular, spiral-wound, and hollow-fine-fiber (tubeside feed) geometries. Each module configuration has particular advantages and disadvantages which are summarized in Table 9. Tubular membranes are desirable in that they can process feeds containing high suspended solids with minimal pretreatment, and can be easily cleaned, either chemically or mechanically, if they

TABLE 9. COMPARISON OF COMMERCIALLY AVAILABLE ULTRAFILTRATION MODULE CONFIGURATIONS

Commercially-Available Configurations	Advantages	Disadvantages
Tubular	1. easily cleaned chemically or mechanically if membranes become fouled	1. relatively high volume required per unit membrane area
	2. can process dirty feeds with minimal pretreatment	2. relatively expensive at present
	3. good hydrodynamic control	
	4. individual tubes can be replaced	
Spiral-Wound	1. compact-good membrane surface to volume ratio	1. susceptible to plugging by particulates
	2. less expensive than tubular modules	2. badly fouled membranes difficult to clean
Hollow Fiber (Tubules), Tubeside Feed	1. compact-very good membrane surface to volume ratio	1. very susceptible to plugging by particulates
	2. economical	2. potentially difficult to clean
Plate-and-Frame	1. good membrane surface to volume ratio	1. susceptible to plugging at flow stagnation points
	2. well-developed equipment	2. potentially difficult to clean
		3. presently very expensive

become fouled. Spiral-wound and hollow fiber modules are less expensive then tubular modules in dollars/m^2 of membrane area, generally have lower power requirements, and are more compact. Both spiral-wound and hollow-fiber modules are, however, more susceptible to plugging and may be difficult to clean. Plate-and-frame modules are quite expensive and, in case of failure, the entire membrane module must be replaced.

For treatment of latex containing wastewaters from adhesives and sealants manufacture the tubular geometry is judged to be most suitable in terms of both process reliability and ease of membrane cleaning. A tubular membrane, as shown in Figure 1, consists of a porous tubular support with the membrane either cast in place, or inserted into the support tube. The feed solution is pumped through the tube; the concentrate is removed downstream; and the permeate passes through the membrane/porous support composite.

SYSTEM DESIGNS FOR ULTRAFILTRATION EQUIPMENT

Three common ultrafiltration system designs are shown in Figure 2. In the batch concentration mode of operation (Figure 2a), the feed tank is charged with waste only at the beginning of each concentration cycle. During operation the permeate is continuously withdrawn while the concentrate is recycled to the feed tank. As the run proceeds the volume of waste in the feed tank decreases, and its concentration increases. When the volume of waste is sufficiently low, it is discharged and a fresh batch of waste is charged to the feed tank. The degree of volumetric concentration is given by

$$C_v = \frac{V_o}{V_o - V_p} \tag{4}$$

where V_o and V_p are the initial batch volume and the collected permeate volume, respectively. The degree of volumetric concentration, C_v, is related to the overall water recovery, by the relationship

$$y\ (\%) = \left(1 - \frac{1}{C_v}\right) x\ 100 \tag{5}$$

Corresponding values of the volumetric feed concentration and the system water recovery are shown below.

C_v	Equivalent Water Recovery (%)
1x (V_p=0)	0
2x	50
10x	90
20x	95
50x	98
100x	99

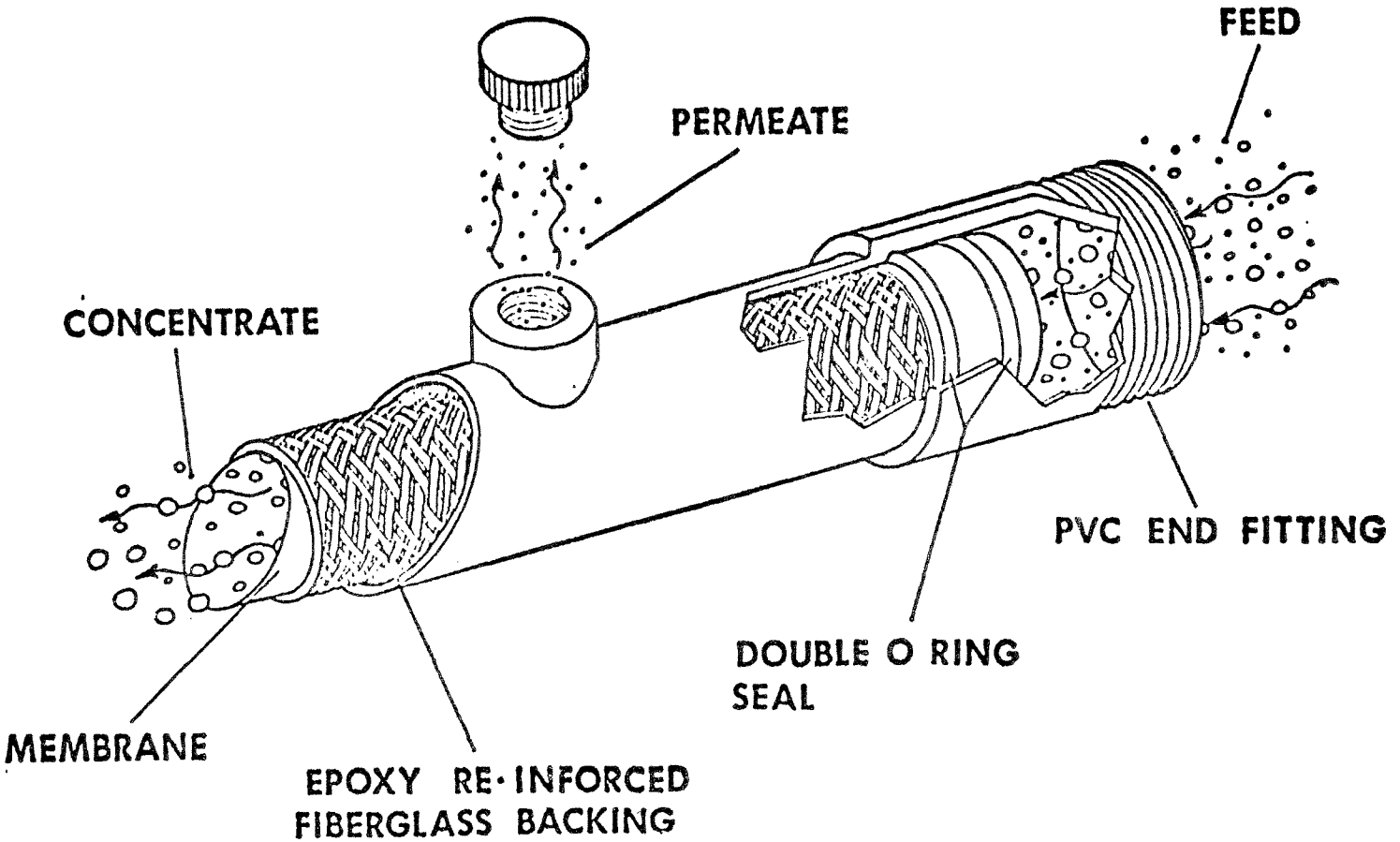
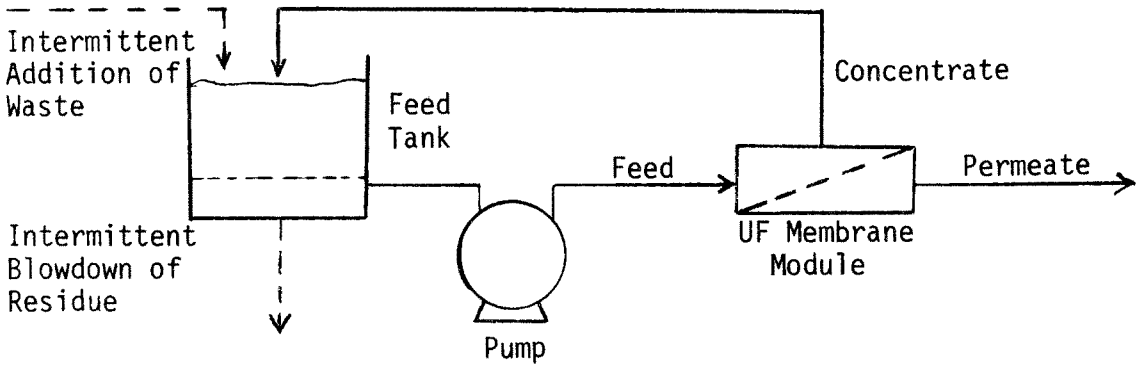
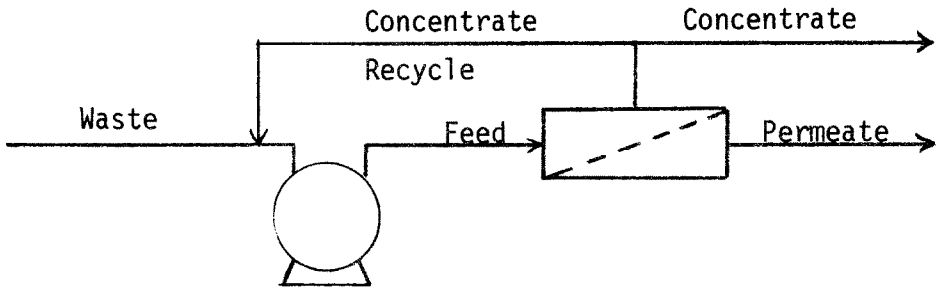


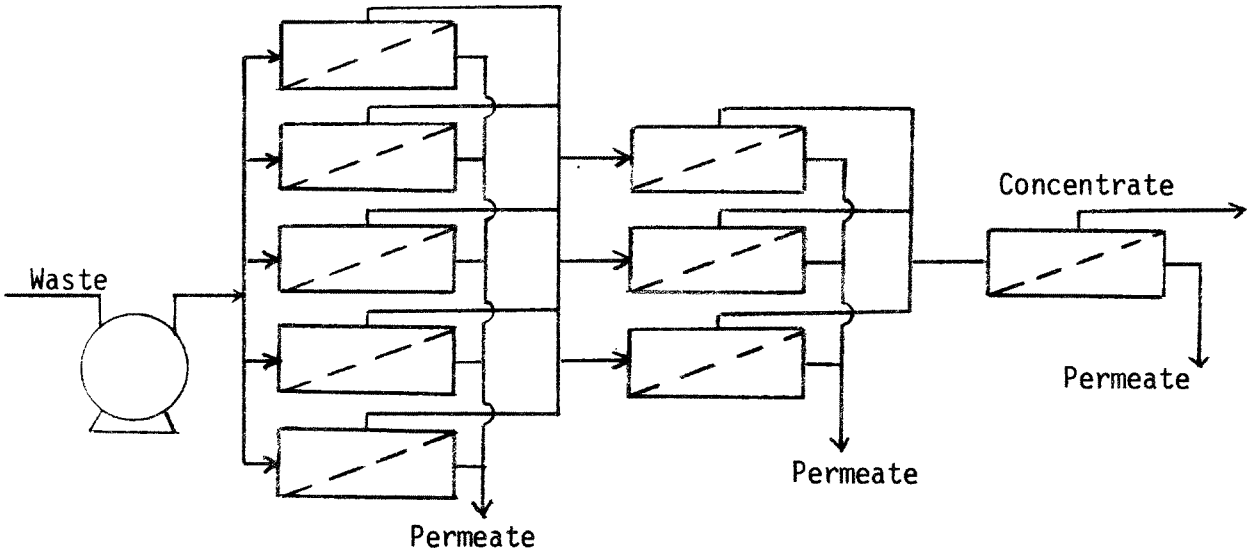
FIGURE 1. CUT-AWAY VIEW OF A TUBULAR ULTRAFILTRATION ASSEMBLY.



(a) Batch Concentration



(b) Continuous Feed and Bleed



(c) Continuous Staged: Once-Through

FIGURE 2. VARIOUS SYSTEM DESIGNS FOR MODULAR MEMBRANE EQUIPMENT.

There are three advantages to the batch concentration mode of operation:

1. Feed circulation rate within the modules can be adjusted to control membrane fouling and/or concentration polarization.
2. High system conversions can be obtained by concentrating to a very low residual volume.
3. The average feed concentration over the batch concentration is minimized (compared to other modes of operation) resulting in a maximum time-averaged module flux and rejection over the concentration cycle.

The disadvantages of this mode relate to its intermittent nature of operation. Since it is not continuous, it requires large holding tank capacity and somewhat more operator time than the other modes.

The continuous feed and bleed mode of operation is shown in Figure 2b. The advantages of this mode are:

1. It is continuous.
2. Feed circulation can be adjusted to control concentration polarization.
3. High system conversions can be obtained.

The disadvantage of this mode is that the system is operated at the concentration level of the concentrate stream. Thus, the average flux and rejection will be low relative to that of the batch concentration mode.

For sufficiently large systems continuous once-through operation, shown in Figure 2c, is preferred. This mode combines the advantages of both the batch and the feed-and-bleed modes of operation. The feed passes through each module in a single-pass which minimizes the average feed concentration and achieves maximum utilization of the modules in terms of flux and rejection. In this mode, operation is continuous and a high overall system conversion can be obtained.

The preferred mode of operation for any given application may be a modified form of one of these three more common modes. The operating mode selection depends upon UF feed flow conditions, membrane flux, water recovery desired, membrane cleaning frequency, etc.

POSTTREATMENT UNIT PROCESSES

Reverse Osmosis

Reverse osmosis, a second membrane separation process, is based on the unique property of semipermeable membranes to selectively pass water while retaining dissolved solutes. If dilute and concentrated solutions are

separated by a semipermeable membrane, water spontaneously passes by direct osmosis from the dilute solution to the concentrated one, in order to establish thermodynamic equilibrium (equal chemical potential on both sides of the membrane). By imposing a hydrostatic pressure on the concentrated solution, exceeding its "osmotic pressure", water can be forced from the concentrated side to the dilute side by reverse osmosis. Separation by reverse osmosis will continue until equilbrium is reestablished, at which point the difference in applied hydrostatic pressure across the membrane will be equal to the difference in osmotic pressure.

Reverse osmosis membranes are characterized by high rejection for dissolved inorganics and poor to high rejection of dissolved organics, depending on the specific characteristics of the organic solutes. For example, the rejection for some low molecular weight uncharged organics is rather poor, and is a complex function of the membrane polymer material and solute diffusivity and solubility in the membrane. Ionic species are highly rejected by interaction with fixed charges on the membrane surface. In general, ionic species and large organics will be substantially rejected by RO membranes; small hydrogen-bonding organics and non-ionized acids and bases will be poorly rejected.

There are a number of reverse osmosis membranes materials presently under development, but only two are in commercial use. The most widely applied is cellulose acetate. It exhibits excellent water permeation rates and high rejection of ionic species. Unfortunately, it is limited to a fairly narrow pH range (2.5-7). The other commercial membrane material is aromatic polyamide. It is available in a spiral-wound configuration from UOP, Inc. or in a hollow-fiber configuration from DuPont, Inc.*. The polyamide membranes have a broader pH range (5-11) but are sensitive to low levels of free-chlorine or other oxidants.

Reverse osmosis systems may be operated in the same manner as discussed for ultrafiltration systems.

Carbon Adsorption

Adsorption by activated carbon is a surface phenomenon in which dissolved organics are removed from wastewater and concentrated at the carbon-liquid interface. The degree of adsorption which occurs is a combination of solute solubility in the wastewater and the strength of the attractive forces between the solute and the carbon. The more hydrophilic the organic, the less likely it is to move toward the carbon-water interface. Thus, highly soluble organics tend to be poorly adsorbed by carbon; whereas less soluble organics are more highly adsorbed.

Activated carbon is a highly porous material which is characterized by a typical surface area yield of 1000 m^2/gram. Since adsorption is a surface

*UOP's PA-300 aromatic polyamide spiral-wound modules were not available commercially until after the posttreatment experiments were completed.

phenomenon, activated carbon has the potential (depending on the nature of the dissolved organics) to be a highly-effective, economical unit process for improving water quality.

The amount of organic adsorbed at equilibrium is usually expressed by an "adsorption isotherm". The isotherm is a plot of the weight of organic adsorbed per unit weight of carbon (X/M) versus the organic concentration in the waste (C) when equilibrium is established at a constant temperature. A number of mathematical expressions have been proposed (5) to describe the shape of the isotherm. The most generally applicable expression is the Freundlich adsorption equation:

$$\frac{X}{M} = kC^{1/n} \tag{6}$$

where,

X = amount of organic adsorbed
M = weight of carbon
k = constant
n = constant
C = concentration of unadsorbed organic in surrounding solution at equilibrium

Restating this equation in logarithmic form,

$$\log\left(\frac{X}{M}\right) = \log k + \left(\frac{1}{n}\right) \log C \tag{7}$$

A plot of X/M vs. C on logarithmic paper will yield a straight line with slope 1/n if the Freundlich isotherm is followed.

Little progress has been made for liquid systems in predicting the isotherm from the properties of the carbon and organic. Therefore, isotherms must be determined experimentally for each waste-carbon combination. The Freundlich expression given by Equations (6) and (7) is useful for correlating the experimental data.

Chemical Oxidation

Dissolved organics or toxic species can be removed from wastewater by the application of strong chemical oxidants which breakdown the dissolved species into other less harmful species, water and gases. Those oxidants which are currently used to treat industrial wastes include ozone, chlorine, hydrogen peroxide and potassium permangante. The selection of the preferred chemical oxidant depends on several factors including: the type and nature of the organics, the concentration of the organics, the wastewater pH, the degree of organic destruction required (i.e., partial or total destruction), pretreatment requirements, maintenance requirements, and economics.

Two families of compounds which may be present in wastewater generated from adhesives and sealants production are cyanides and phenolic compounds. Discharge limitations on both of these groups are in effect in most municipalities and residual amounts of these compounds are to be expected in an ultrafiltrate stream. Various chemical reactions take place when cyanide or phenolic compounds are exposed to the different chemical oxidants. Table 10 summarizes these chemical reactions and provides relevant comments on the processes, as appropriate.

DEWATERING TECHNIQUES

There are five major types of dewatering methods used for concentrating liquid wastes. These methods are described briefly below.

Gravity Sedimentation

The effluent may be both thickened and clarified using sedimentation which removes suspended solids from the liquid by gravity settling. Examples of gravity settlers are a simple trench and the over-under sump.

Gravity Filters

The separation of solids in this filtering system is the result of the hydrostatic pressure of the effluent on a static, vibrating or rotating screen. Examples of this are the Sweco vibrating separator and the Bauer hydrasieve.

Pressure Filters

Pressure filters are those which operate under forced positive or negative pressure on a filter medium. Examples are the filter press and rotary vacuum drum filter.

Centrigugal Filters

Through centrifugal force and a difference in density, an effective liquid-solids separation can be accomplished. Examples are the basket centrifuge and Bauer's liquid cyclone.

Solids Drying

The removal of a liquid by evaporation can be used when mechanical methods are not feasible. Because of the high energy usage this method may be prohibitive in dewatering sludge. Examples of this are evaporators and spray dryers.

TABLE 10. CHEMICAL REACTIONS WHICH OCCUR DURING OXIDATION OF CYANIDE AND PHENOLIC COMPOUNDS (6, 7, 8, 9, 10)

Chemical Oxidant	Cyanide Destruction	Comments	Phenolic Compound Destruction	Comments
Chlorine	a) $NaCN+Cl_2 \rightarrow CNCl+NaCl$ b) $CNCl+2NaOH \rightarrow NaCNO+NaCl+H_2O$ c) $2NaCNO+4NaOH+3Cl_2 \rightarrow 6NaCl+2CO_2+N_2+2H_2O$	Product of reactions a + b is cyanate. Cyanate can be further oxidized as shown in reaction c. Ratio of chlorine to cyanide for reduction to cyanate is 2; for complete destruction is 8.5.	j) $C_6H_5OH+Cl_2+NaOH \rightarrow C_6H_4ClOH+NaCl+H_2O$	Partial oxidation achieved through reaction j, however chlorinated phenols are also toxic. Complete oxidation may occur in an excess of chlorine (i.e. 25 parts chlorine to 1 part phenol).
Hydrogen Peroxide	d) $CN^- + H_2O_2 \rightarrow CNO^- + H_2O$ e) $CNO^- + 2H_2O \rightarrow CO_2 + NH_3 + OH^-$	Process requires 3-4 parts H_2O_2 and 2-3 parts formaldehyde per part cyanide in the presence of a copper salt catalyst.	k) $C_6H_5OH+14H_2O_2 \xrightarrow{Fe^{++}} 6CO_2+17H_2O$	Iron salts as catalyst. Initial reaction products are hydroquinone and catechol. These are further oxidized to dibasic acids. Destruction of phenols to dibasic acid state requires 2 parts H_2O_2 per part phenol.
Potassium Permanganate	f) $2KMnO_4+NaCN+2KOH \rightarrow 2K_2MnO_4+NaCNO+H_2O$	Process requires 12 parts $KMnO_4$ and 3 parts caustic per part cyanide. Complete destruction is not possible using permanganate.	l) $3C_6H_5OH+28KMnO_4+5H_2O \rightarrow 18CO_2+28KOH+28MnO_2$	Process requires 6-7 parts $KMnO_4$ per part of phenol.
Ozone	g) $CN^-+O_3 \rightarrow CNO^-+O_2$ h) $CNO^-+OH^-+H_2O \rightarrow CO_3^= +NH_3$ i) $NH_3+4O_3 \rightarrow HNO_3+4O_2+H_2O$	Ozone demand is not well defined. Complete destruction estimated to require 3 to 9 parts ozone per part cyanide.	m) $C_6H_5OH+O_3 \rightarrow$ various products $+ O_2$	For removal of phenol and its aromatic oxidation products the stoichometric ratio of O_3 to phenol is 3 to 1. Competing reactions may make it advisable to use a 6 to 1 ratio.

SECTION 6

TEST SYSTEMS, PROCEDURES, AND ANALYSES

FIELD DEMONSTRATION TESTS

Field Test System and Procedures

A flow schematic of the complete San Leandro Plant Test System is presented in Figure 3. Plant wastewater was collected in an existing sump [approximate capacity 3.8 m^3 (1000 gal)] in which high and low level switches were installed. During normal operation a 109 m^3/day (20 gpm) constant volume pump (Moyno Model IL6 Type SSF) transferred the plant effluent to the first stage of a four stage 10.6 m^3 (2800 gal) settling/flotation tank. The Moyno pump was equipped with a timer/recorder to monitor its on/off cycle. If a surge in the plant effluent occurred, a second pump (Gorman-Rupp Model 12C-2B, also equipped with a timer/recorder combination was activated and discharged the effluent to the sewer (by-passing the settling tanks).

The second and fourth stages of the 10.6 m^3 tank acted as flotation tanks while the first and third sections provided settling area. A transfer pump (Gorman-Rupp Model 81-1/2D3) delivered the effluent from the last stage of this tank to a 3.8 m^3 (1000 gal) holding tank. This tank served to further clarify the plant wastewater. Overflow from this tank was piped to the sewer. A solenoid valve regulated by a high/low level switch in the UF system feed tank controlled the flow from the 3.8 m^3 tank. Surfactant could be fed into the UF feed tank by a metering pump (FMI Model RP2G).

Figure 4 presents a detailed flow schematic of the Ultrafiltration Pilot System. The plant effluent, after settling and flotation, entered the 0.57 m^3 (150 gal) UF feed tank and was passed through an in-line strainer for coarse solids removal and into the suction of the centrifugal circulation pump (Worthington Model D12). This pump pressurized the feed and delivered it to the membrane inlet manifold. Pressures before and after the tubular membranes and the feed temperature were measured. A low pressure switch on the membrane outlet shut down the circulation pump when the concentrate pressure fell below 0.3 atm (4 psig). A heat exchanger was provided on the concentrate line to maintain the processing temperature below 52°C (125°F). The concentrated waste returned to the UF feed tank and was combined with fresh feed.

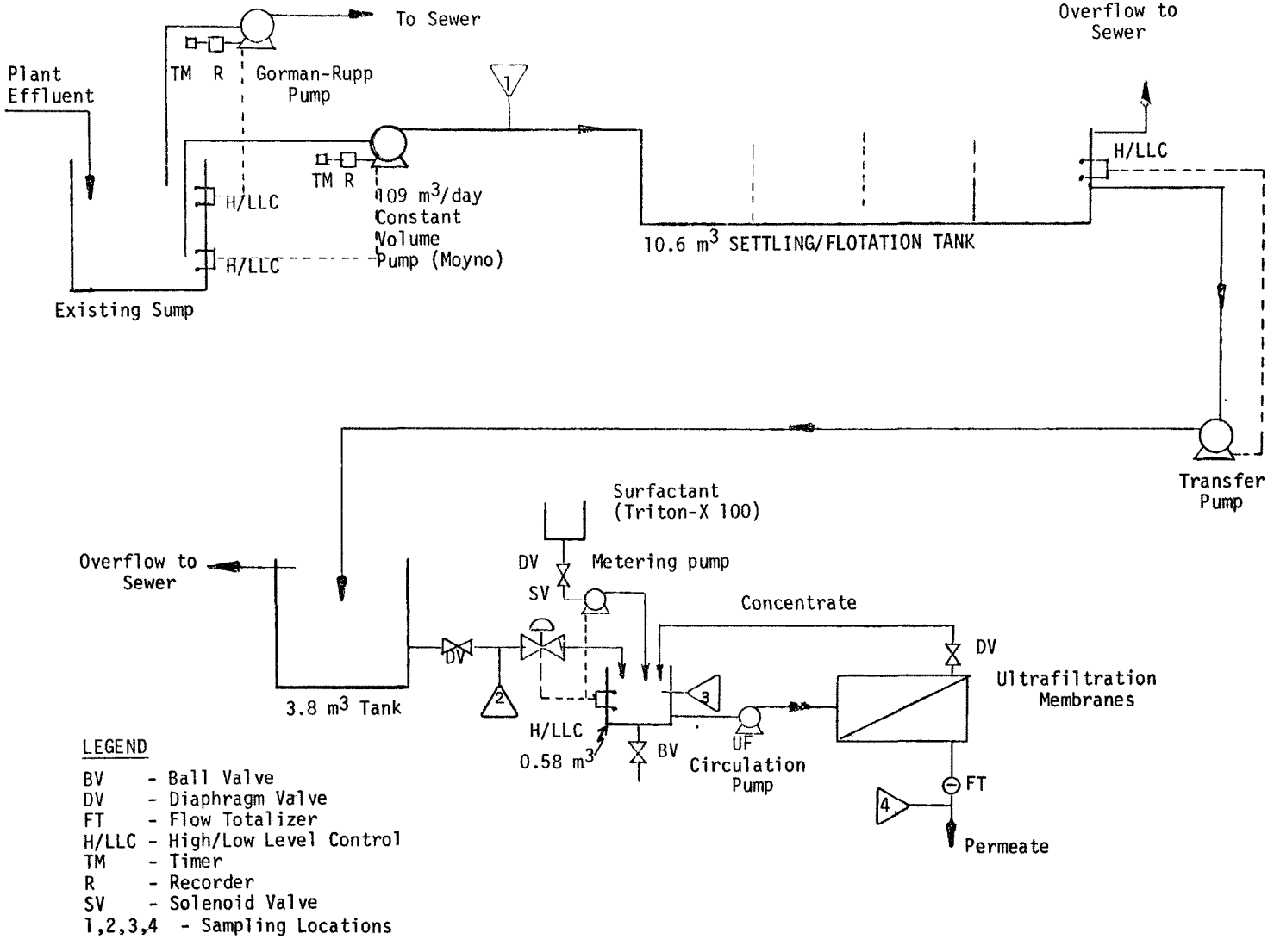


FIGURE 3. FLOW SCHEMATIC OF SAN LEANDRO PLANT FIELD DEMONSTRATION TEST SYSTEM.

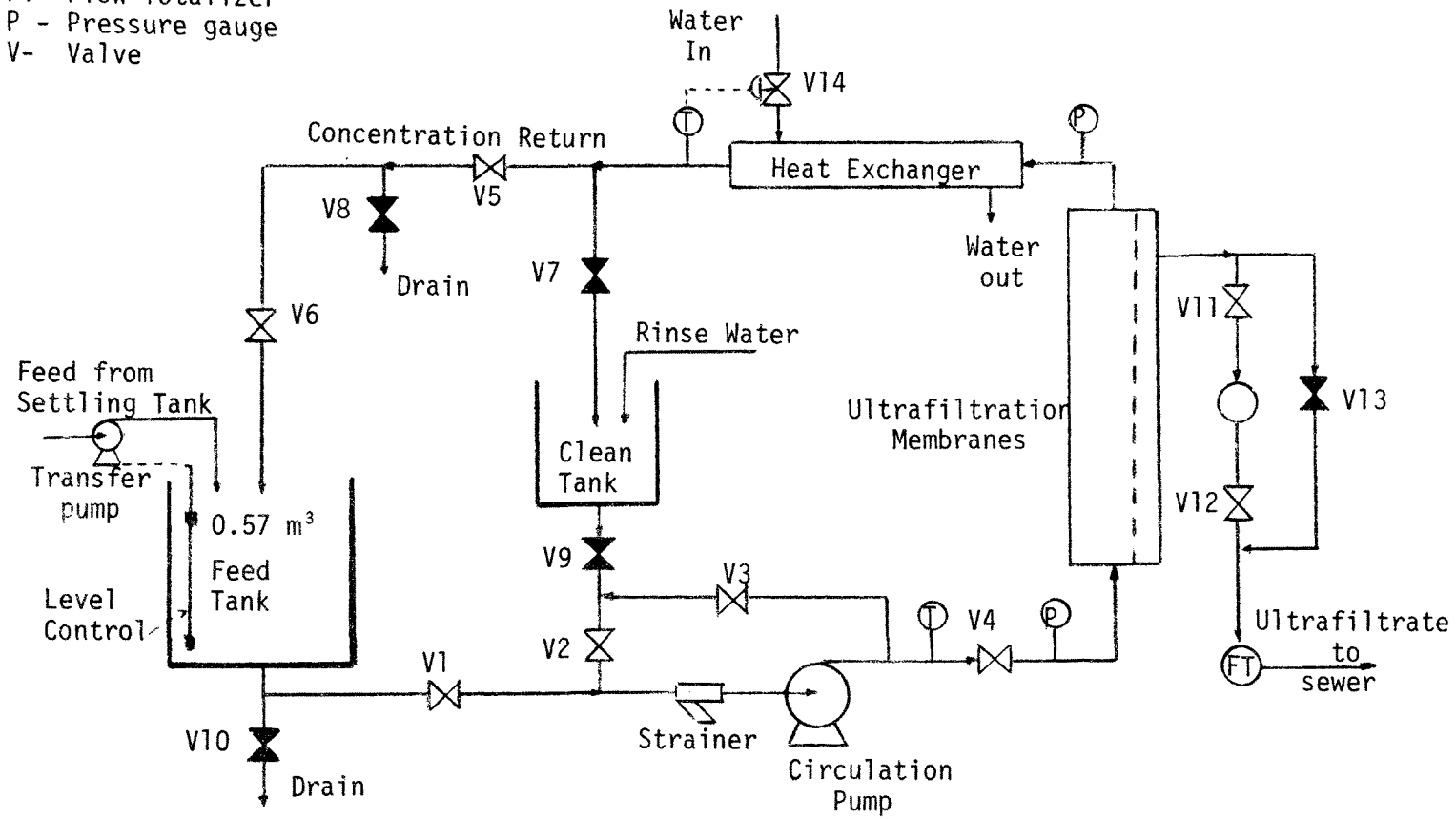


FIGURE 4. ULTRAFILTRATION SYSTEM FLOW SCHEMATIC.

The ultrafiltrate flowrate was measured and the ultrafiltrate was discharged to drain. The ultrafiltrate flow meter was equipped with an alarm to signal low flow (i.e. membrane fouling) and a by-pass loop to allow stop-watch and graduated cylinder flowrate readings should the ultrafiltrate flow be off-scale. A flow totalizer (Kent PSM 190) recorded the cumulative volume of ultrafiltrate produced.

The UF pilot system was operated in a modified batch mode. The concentrate was recycled to the 0.57 m^3 UF feed tank, while the ultrafiltrate was continuously withdrawn.

Each field demonstration test was generally conducted continuously, Monday through Friday, for two consecutive weeks. Following this 10 day concentration cycle the UF feed tank was drained, the membranes were detergent cleaned and the membrane flux recovery was measured.

Two types of ultrafiltration membranes were utilized during this program. Initially, the UF system was equipped only with Abcor, Inc. type HFM (non-cellulosic) tubular membranes. Midway through the program a second Abcor membrane, type HFD (non-cellulosic) was tested in parallel with the HFM membranes. The characteristics of each membrane type are given in Table 11. Both the HFM and HFD membranes were supplied in tubular assemblies, 0.025 m (1 inch) in diameter x 1.52 (5 feet) long. Typically, 21 tubular assemblies (three parallel banks of seven tubes in series) were in place on the ultrafiltration system.

The standard operating conditions for the UF system during the tests at San Leandro were:

Feed circulation rate:	163.5 m^3/day (30 gpm)
Membrane inlet pressure:	2.8-3.4 atm (40-50 psig)
Process temperature:	Typical - 32.2°C (90°F)
	Range - 18.3 to 40.5°C (65 to 105°F)
Feed pH:	natural

Samples were collected of the plant effluent from the sump, the plant effluent after the 3.8 m^3 settling tank, the UF concentrate and the ultrafiltrate. These sampling locations are identified in Figure 3, while the assays performed on these samples are detailed at the end of this section. Daily composite samples were formed by collecting equal volume grab samples throughout an 8-hour day. Weekly samples were composited from the daily samples for determination of certain assays. All samples were refrigerated on-site.

UF System Cleaning Procedures

Detergent Cleaning--

The ultrafiltration membranes were cleaned with a detergent solution between each experiment. Three different detergents were employed at various points in the test program: Ultraclean (Abcor, Inc.), Dishmate

TABLE 11. CHARACTERISTICS OF ULTRAFILTRATION MEMBRANE EMPLOYED DURING FIELD TESTS

Parameter	Membrane Type	
	HFD	HFM
pH range @ 38°C	3-12	0.5 - 12.5
Maximum Temperature (°C) @ pH = 7	85	90
Maximum Operating Pressure (atm)	5.2	5.2
Average Pore Size (Å)	50±25	50±25
Equivalent Molecular Weight Cut-Off	20,000	20,000
Tolerance to Free Chlorine	None	Chemically inert to concentrations to 50 ppm
Resistance to Solvents and Oils	Good	Excellent

(Calgon, Corp.) and trisodium phosphate. Dishmate was used only with HFM membranes since it contains free-available-chlorine. The generalized procedure for detergent washing was as follows:

1. The concentrated waste was drained from the system.
2. Clean water was passed through the system at a low flowrate 109 m^3 (20 gpm) to flush out the residual concentrate.
3. A 1/2% by weight, detergent solution was recirculated through the system for 30 minutes under the following operating conditions:

Recirculation Flowrate:	109-136 m^3/day (20-25 gpm)
Inlet Pressure:	1.4-1.7 atm (20-25 psig)
Temperature:	46-49°C

4. Clean water was passed through the system for 20-30 minutes at low flow and low pressure to flush out the detergent.
5. The water flux of the clean membranes was determined.

Solvent Cleaning--

Twice during the field demonstration tests an irregular, grey rubber (latex) coating deposited on the membrane surface. This latex coating is difficult to remove with detergents, thus cleaning with methyl ethyl ketone (MEK) became necessary. Solvent cleaning was performed both in the field and at Walden's pilot facilities as described below.

1. The tubular assembly was removed from the test unit. Washers were removed and one end of the tube was plugged, at the double o-ring seal (see Figure 1), with a rubber stopper.
2. One liter of MEK was poured into the tube. Care was taken to avoid contact of the MEK with any PVC fittings.
3. After a specified time period (between 5 and 35 minutes), the MEK was drained and the membrane flushed with water.
4. (Field cleaning only). A laboratory test tube brush soaked in MEK was used to remove the softened, swelled rubber coating.
5. Spongeballs (see below) were passed through the tube until the outlet water was clean.
6. The tubular assembly was reinstalled on the test unit and its water flux was measured.
7. (Walden cleaning only.) Steps 1, 2, 3, 5, and 6 were repeated with a Step 3 MEK exposure of 20 minutes.

Mechanical Cleaning--

Mechanical cleaning of the tubular membrane assemblies was periodically performed as an additional step to detergent cleaning and was always used during solvent cleaning procedures. The mechanical cleaning procedures involves the use of "spongeballs", cylindically shaped pieces of polyurethane foam (0.025 m in diameter x 0.050 m long), and proceeds as follows:

1. The inlet of the first tubular membrane and outlet of the last tubular membrane, in series, are disconnected from the rest of the system. Two spongeballs are carefully inserted into the first membrane. Water pressure from a hose is used to force the spongeballs through the membranes.
2. Step 1 is repeated until two spongeballs have passed through the membranes three times.
3. The membrane inlet and outlet are reconnected with the system and the membrane flux recovery is measured.

Measurement of Flux Recovery--

The measurement of the flux of tap water through UF membranes, under standardized conditions, indicates the water transport properties of the membranes and is one means of detecting membrane degradation due to compaction, plugging, biological attack and/or chemical attack. This measurement was routinely made after any membrane cleaning operation.

During flux recovery (i.e. water flux) measurements the system was operated with water at 163.5 m^3/day (30 gpm) recirculation, 3.4 atm (50 psig) inlet pressure, and ambient temperature. The observed ultrafiltrate flux and temperature readings were used to obtain a flux reading corrected to 32.2°C (90°F) by use of the following relationship:

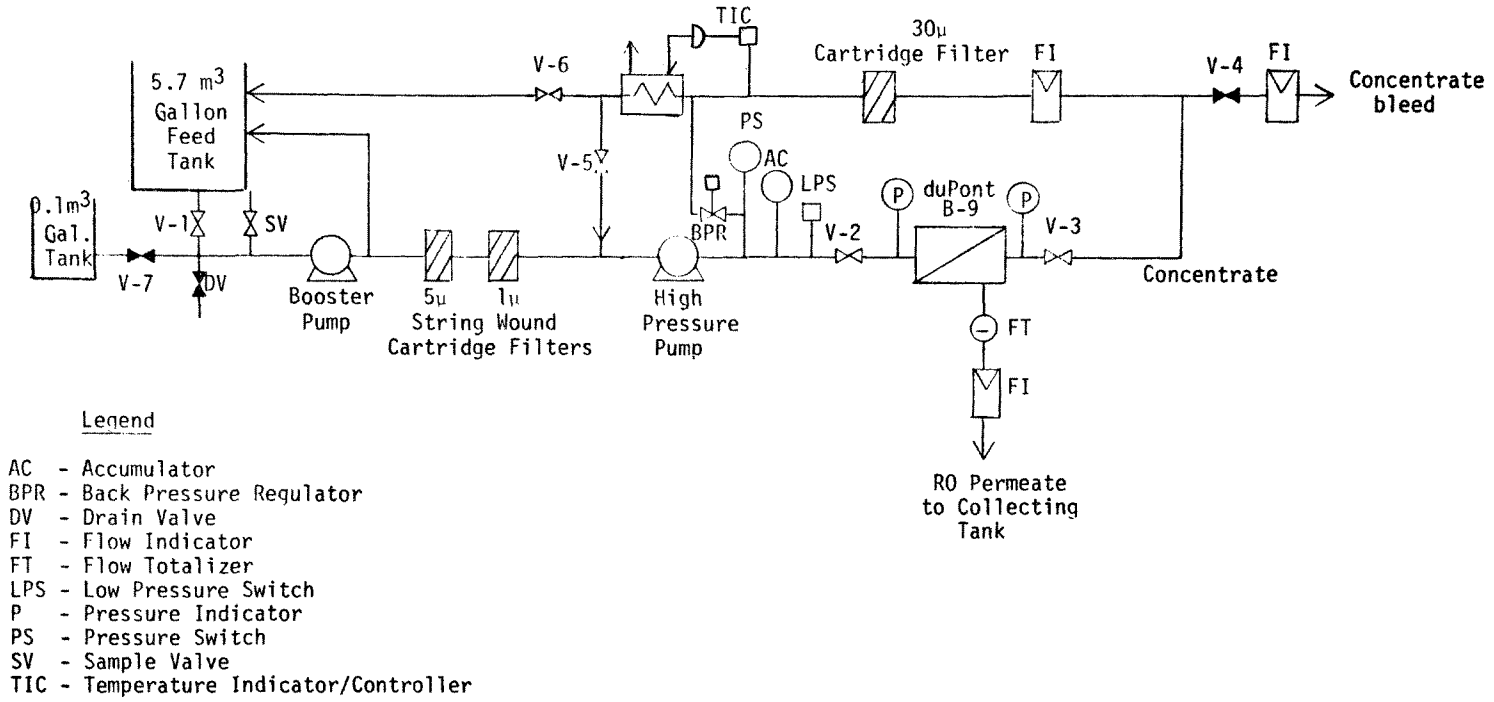
$$(\text{Flux})_{32.2^\circ C} = (\text{Flux})_{T^\circ C} \times \frac{(\text{Viscosity of Water})\ T^\circ C}{(\text{Viscosity of Water})\ 32.2^\circ C} \qquad (8)$$

Reduction of flux data to a standard temperature simplifies data analysis. A standard temperature of 32.2°C was selected since this was the average process temperature during the first field demonstration test.

POSTTREATMENT EXPERIMENTATION

Reverse Osmosis Tests

A simplified flow schematic for the reverse osmosis test system is presented in Figure 5. Ultrafiltrate from the Dewey and Almy's Chicago Plant, was transferred to a 5.68 m^3 (1500 gal) feed tank. A booster pump (Dayton, Model 6F507) was used to pass the feed through two string-wound



Legend

AC - Accumulator
BPR - Back Pressure Regulator
DV - Drain Valve
FI - Flow Indicator
FT - Flow Totalizer
LPS - Low Pressure Switch
P - Pressure Indicator
PS - Pressure Switch
SV - Sample Valve
TIC - Temperature Indicator/Controller

FIGURE 5. SIMPLIFIED FLOW SCHEMATIC FOR REVERSE OSMOSIS TEST SYSTEM.

cartridge filters, in series, to the suction of the high-pressure positive-displacement pump. This pump (Gaulin Model 75E) increased the feed pressure to 27-54 atm (400-800 psig). The feed pressure was controlled by the back pressure regulator (BPR) and the flow rate through the module was controlled by the concentrate throttle valve (V-3). An accumulator (AC) was used to dampen pressure pulsations from the pump. The reverse osmosis module was protected against overpressurization by a high pressure switch (PS), and the pump was protected against running dry by a low pressure switch (LPS). The feed temperature was measured and controlled by an indicating temperature controller (United Electric, Type 1200). The flow rates of the permeate and concentrate were measured, and the feed flow rate was calculated (sum of permeate and concentrate flow rates). The feed pressure and pressure drop across the module were also measured.

The reverse osmosis test system was operated in the batch operating mode (i.e., concentrate returned to the feed tank, permeate continuously withdrawn). The membrane module employed during the RO tests was a B-9 polyamide membrane in a hollow-fine-fiber configuration manufactured by DuPont, Inc., Permasep Products Division (see Figure 6). This module has a pH range of 4-11, a maximum operating pressure of 27 atm (400 psig) and an operating temperature limitation of 35°C.

Typical values of the RO system operating parameters during tests with the adhesives manufacturing plant ultrafiltrate were:

Feed circulation rate:	27.3 m^3/day (5 gpm)
Module inlet pressure:	27 atm (400 psig)
Feed temperature:	27-30°C

Following each reverse osmosis experiment a standard test was performed to determine if any decline in membrane flux or rejection had occurred. After the system was drained and flushed with dechlorinated water, it was operated in the total recycle mode on a standard NaCl solution (5000 ppm). System operation proceeded under the set of conditions given above. At steady state the feed and permeate flows and concentrations were measured and the measured rejection was corrected to a module conversion of 0%.

Carbon Adsorption Isotherms

The carbon adsorption isotherm tests were conducted using the procedure outlined below. Filtrasorb 400 (Calgon Corp.) a general-purpose carbon was used.

1. Filtrasorb 400 granular activated carbon was ground with a mortar and pestle and screened to 45μ (335 mesh) size.
2. Seven samples of dried carbon were weighed out: 2 mg, 5 mg, 10 mg, 20 mg, 50 mg, 100 mg, and 500 mg.
3. Each sample of dried carbon was placed in a separate erlynmeyer flask.
4. 100 (±1) ml ultrafiltrate was added to each flask.

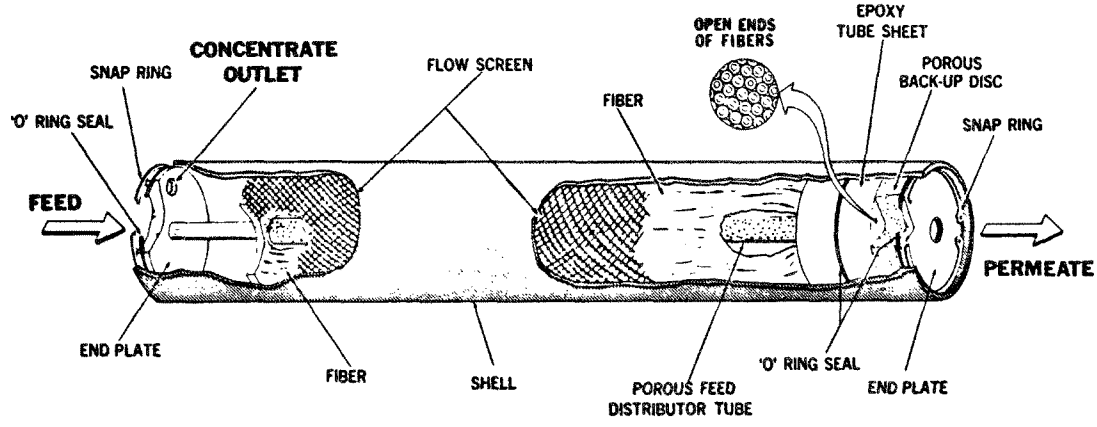


FIGURE 6. CUTAWAY VIEW OF A PERMASEP HOLLOW-FINE-FIBER REVERSE OSMOSIS MODULE.

5. The flasks were stoppered and placed on a Burrel Wrist Action Shaker for 24-48 hours.

6. The flask contents were filtered through a 0.22μ Millipore Filter, and the center portion of filtrate was collected for analysis.

7. The seven carbon treated samples, an original feed sample taken through all procedures except for carbon addition, an original feed sample not taken through the isotherm procedures, and a high purity water sample were analyzed for TOC, BOD, and/or COD.

8. The data were fit to a Freundlich Isotherm Expression by plotting, on log-log paper, X/M, the amount of pollutant adsorbed per unit weight of carbon versus C, the residual pollutant concentration and drawing the best straight line through the points.

SAMPLE ANALYSES

Table 12 lists the sample analyses routinely performed during the field demonstration tests and the methods employed for each analysis. During the first six field tests the samples (both daily and weekly composites of grab samples) were air-freighted to the Walden Analytical Laboratory for analysis. All assays were performed by the Walden Analytical Laboratory except total cyanide and mercury which were performed by Environmental Research and Technology, Concord, Massachusetts. Following the sixth field test, analytical work was performed in California by Engineering Science, Inc. Throughout the field tests pH and total solids measurements were made by the Dewey and Almy San Leandro Plant Analytical Laboratory.

During the posttreatment experiments BOD, COD and TOC assays were conducted by Walden's laboratory.

TABLE 12. ASSAYS AND METHODS EMPLOYED DURING EXPERIMENTAL PROGRAM.

Constituent	Assay Method	Reference
Arsenic	Dithiocarbamate Colorimetric	SM 404A*
BOD	5 Day Incubation, Electrode	SM 507, 422F, 422B
Cadmium	Atomic Adsorption	SM 301A
Chromium (total)	Atomic Adsorption	SM 301A
COD	Dichromate Reflux	SM 508; EPA, p. 21**
Cyanide (free)	Selective Ion Electrode	Orion Manual
Cyanide (total)	Distillation, Titration	SM 413B, 413C
Freon Extractibles (total)	Separtory Funnel Extraction	SM 502A
Freon Extractibles (non-polar)	Extraction, Gravimetric	SM 502A, EMSL***
Lead	Atomic Adsorption	SM 301A
Mercury	Atomic Adsorption	SM 301A VI
pH	Meter Reading	Manufacturer's Manual
Phenolic Compounds	Distillation, AAP Colorimetric	SM 510, 510A, 510C
TOC	Combustion-Methane Detection	EPA, p. 236
Total Solids	Gravimetric	SM 208A
Total Suspended Solids	Glass Fiber Filtration	SM 208D
Zinc	Atomic Adsorption	SM 301A

* SM 404A (etc) refers to procedure number In "Standard Methods for Examination of Water and Wastewater", 14th Edition, APHA, 1975.

** EPA refers to "Manual of Methods for Chemical Analysis of Water and Wastes", U.S. EPA, 1974.

*** EMSL refers to method developed by Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, Ohio (July 1975), Referenced in AQC Newsletter 22.

SECTION 7

EXPERIMENTAL RESULTS AND DISCUSSION

SURVEY OF PLANT EFFLUENT CHARACTERISTICS

The batchwise nature of the manufacturing operation at San Leandro, and throughout the industry, results in intermittant wastewater discharges. Information was collected on the variability in flow and composition of the San Leandro Plant effluent to better characterize effluents generated in the manufacture of water-based adhesive solutions containing synthetic and natural materials (Subcategory B), solvent solution adhesives and cements generated contaminated wastewaters (Subcategory C) and solvent solution adhesives and cements generating non-contract cooling water only (Subcategory D).

Wastewater Flow Patterns

All the wastewater generated at the San Leandro Plant flowed into the 3.8 m^3 sump (see Figure 3). In general, the constant volume Moyno pump had the necessary capacity to transfer all wastewater to the first settling tank. When the Moyno pump's capacity was exceeded a gear pump was activated by a high level control in the sump.

The initiation and duration of each pumps activities were noted by strip chart recorders during the first five field demonstration tests. Throughout 56 days (including weekends) no repetitive wastewater discharge cycles developed. This result, in conjunction into the fact that the batch production processes are used exclusively, accentuates the high variability of effluent flow within this industry and identifies the need for flow equalization in any wastewater treatment system.

Wastewater Composition

A summary of the composition of the San Leandro Plant effluent is shown in Table 13. Low, high and average values are presented for both daily and weekly composite samples and overall mean values are given. For all assays where the detection limit of the analysis was not reached, excepting mercury, there is at least an order-of-magnitude difference between the high and low contaminant levels. For example, the effluent total suspended solids ranges from 59 mg/ℓ to 70,800 mg/ℓ and its zinc content varies from 2.4 mg/ℓ to 740 mg/ℓ. These data clearly point out the high variability of the San Leandro Plant effluent and re-enforce the requirement for a wastewater treatment system which is insensitive to shock loading.

TABLE 13. SUMMARY OF SAN LEANDRO PLANT EFFLUENT COMPOSITION

Assay	Number of Daily Composite Samples	Average Value (mg/ℓ)	Number of Weekly Composite Samples	Average Value (mg/ℓ)	Low Value (mg/ℓ)	High Value (mg/ℓ)	Overall Average Value (mg/ℓ)
Total Freon Extractibles	29	2,000	16	2,620	58	22,000*	2,220
Non-polar Freon Extractibles	23	314	10	256	16.0	2,370	296
Total Solids	10	11,900	6	17,800	1,810	49,100*	14,100
Suspended Solids	31	10,500	17	10,800	59	70,800	10,600
BOD	7	5,650	16	10,100	980	22,000*	8,740
Soluble BOD	6	6,530	2	7,440	3,140	17,200	6,760
COD	6	22,500	7	31,000	5,820	71,700*	27,100
Soluble COD	6	17,800	2	15,600	5,320	30,900	17,300
Arsenic	1	< 0.2	9	< 0.2	< 0.2	< 0.2	< 0.2
Cadmium	1	< 0.2	6	< 0.2	< 0.2	< 0.2	< 0.2
Total Chromium	1	< 0.5	6	< 0.5	< 0.5	< 0.5	< 0.5
Free Cyanide	1	2.6	8	1.83	0.36	2.6	1.92
Total Cyanide	2	2.75	9	1.69	0.40	5.3	1.88
Lead	1	< 1	6	< 1	< 1	< 1	< 1
Mercury	--	--	2	0.003	0.001*	0.005*	0.003
Phenolic Compounds	13	158	16	151	0.5	1,130	154
Zinc	13	81.5	15	114	2.4	740*	98.9

*Indicates low or high value observed in weekly composite sample.

FIELD DEMONSTRATION TESTS

An extensive evaluation of ultrafiltration for adhesives and sealants wastewater treatment was conducted by performing twelve field demonstration tests at the San Leandro Plant. During nine of these experiments the total plant effluent was processed. The remaining three tests were performed with the following wastewaters: total effluent less CPD stream, total effluent less "Z" stream, and, electrocoagulation process effluent. Twice during the tests with the total plant effluent surfactant was continuously added to the UF feed stream to assess changes in UF membrane performance associated with increased latex stability.

The results of these field demonstration tests are discussed, in detail, below.

Ultrafiltration Membrane Flux Performance

The rate of ultrafiltration production per unit membrane area is termed the membrane flux and is expressed in cubic meters per square meter per day (m^3/m^2-day) (gallons per square foot per day (gfd)). The time-averaged flux for a given concentration experiment is determined by dividing the volume of ultrafiltrate produced during the run by the elapsed time and the membrane area. A summary of time-averaged UF membrane flux data is shown in Table 14, for the entire field program. This table provides an overview of UF flux performance and will be referred to in the following discussions.

Flux with Total Plant Effluent--

Figure 7 presents the UF permeate flux vs. time plots for two typical runs with the total plant effluent as the feed stream. The data shown are for runs #2 and 6. In both instances, and generally throughout the test program, a very irregular flux pattern is observed. This non-linearity in the flux vs. time curves is most likely associated with changes in the waste stream composition. During the night no wastewater is generated by the plant and thus the contents of the 3.8 m^3 (1000 gal) holding tank (see Figure 3) feeding the UF feed tank are continuously reduced. As normal plant operations resume in the morning the 3.8 m^3 tank is refilled with an equalized, but not identical, wastewater for processing by the UF system.

During run #2 only type HFM membranes were employed and an average flux of 1.84 m^3/m^2-day (44.9 gfd) was recorded over a 208 hr processing period. In Run #6 both type HFM and HFD membranes were used. The HFM tubular assemblies averaged 2.09 m^3/m^2-day (51.0 gfd) during a 172 hr concentration. The HFD membranes averaged 1.97 m^3/m^2-day (48.0 gfd), however no flux readings were recorded after 66 hours operating time.

Overall, throughout 6 individual tests with a total operating time of 1021 hours, the HFM membranes averaged 1.38 m^3/m^2-day (33.8 gfd) while processing the total plant effluent. The total solids concentration achieved by the end of each of these six runs varied from 2.3% to 12.8%

TABLE 14. SUMMARY OF ULTRAFILTRATION MEMBRANE FLUX DURING SAN LEANDRO FIELD TESTS

Test #	Feed Stream Description	Total Operating Time (hrs)	Membrane Type	Time-Averaged Flux @ 32°C, m^3/m^2-day (gfd)	Final Concentrate Total Solids, %	Comments
1	Total effluent with surfactant addition	198	HFM	1.47 (35.8)	9.7	
2	Total effluent	208	HFM	1.84 (44.9)	4.8	
3	Total effluent	99	HFM	0.94 (23.0)	2.3	Test terminated to conduct dye test.
4	Total effluent	220	HFM	0.84 (20.6)	3.1	Surfactant added at 167 hours operating time
5	Total effluent	152	HFM HFD	1.43 (35.0) 1.60 (39.0)	7.6	
6	Total effluent	172 66	HFM HFD	2.09 (51.0) 1.97 (48.0)	7.6	HFD flux readings not recorded after 66 hours
7	Swift effluent	17.6	HFM HFD	1.99 (48.7) 2.17 (53.0)		
8	Total effluent with surfactant addition	137	HFM	1.92 (46.9)	9.4	
9	Total effluent less CPD stream	141	HFM	1.71 (41.7)	6.9	
10	Total effluent less "Z" stream	162	HFM (orig.) HFM (new)	1.35 (33.0) 1.88 (46.0)	16.4 16.4	
11	Total effluent, maximum concentration test	28	HFM (orig. and new)	0.43 (10.6)	0.73	Test aborted due to latex fouling of UF membranes
12	Total effluent, maximum concentration test	170	HFM (orig.) HFM (new)	1.15 (28.0) 1.39 (34.0)	12.8 12.8	

Average HFM membrane flux during processing of total effluent = 1.38 m^3/m^2-day (33.8 gfd)

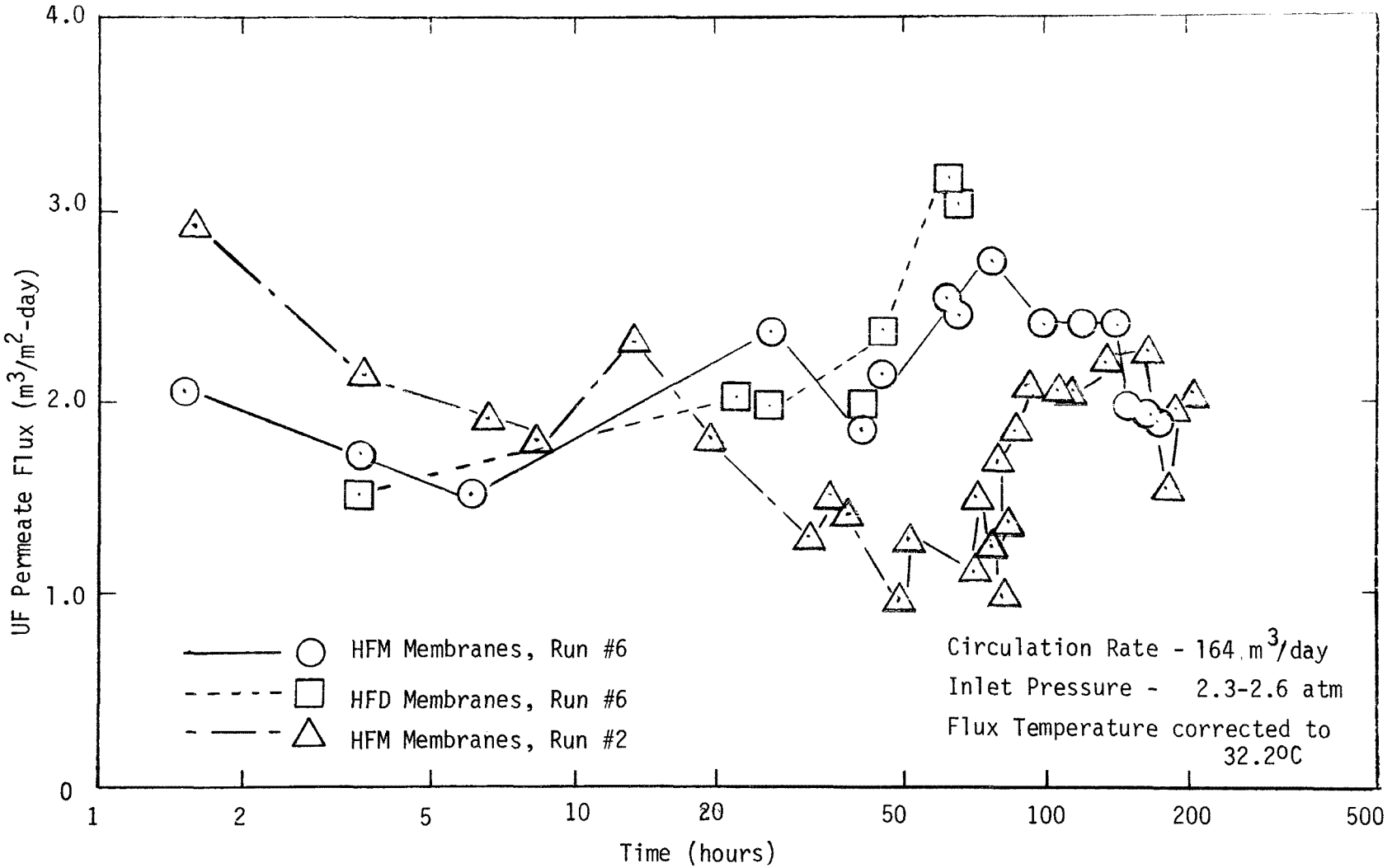


FIGURE 7. UF PERMEATE FLUX VS. TIME FOR SAN LEANDRO PLANT WASTEWATER CONCENTRATION RUNS #2 AND #6.

(see Table 13), however no correlation was observed between average membrane flux levels and final concentrate total solids levels. The reason that no flux vs. final solids concentration relationship developed is that only during the final hours of some runs did the solids concentration increase significantly. This short time at a high concentration becomes relatively insignificant when averaged over a two-week operating period.

Flux with Surfactant Addition--

The addition of surfactant to the plant effluent prior to ultrafiltration was given attention based on experience gained during operation of the UF system at the Grace Chicago Plant. The surfactant acts to stabilize both latex particles and oil emulsions, thereby reducing UF membrane fouling. The addition of surfactant is a major operating expense at Chicago (see page 92, Section 8), therefore, its elimination as a processing steps at San Leandro would be preferrable.

During two experiments (run #1 and 8) surfactant (Rohm and Haas, Triton-X-100) was continuously added to the UF feed tank during processing of the total plant effluent. The flux vs time plot for run #8 is presented in Figure 8. As was the case with the total effluent without surfactant addition, erratic flux behavior is observed. The average flux for run #8 during 137 hours operation was 1.92 m^3/m^2-day (46.9 gfd). For run #1 the flux averaged 1.47 m^3/m^2-day (35.8 gfd) throughout 198 hours processing. These data are not significantly different from data obtained without surfactant addition. Therefore, considering the additional costs associated with surfactant addition, this procedure is not considered desirable for the treatment of the San Leandro Plant effluent.

Flux with Segregation of Specific Streams from Total Plant Effluent--

During two of the field demonstration tests a selected process stream was pumped directly to the sewer while the remaining waste streams entered the plant sump and were processed by the pilot system per standard test procedures. The objective of these tests was to determine if either the CPD waste stream or the "Z" waste stream were "bad actors" in terms of UF membrane flux or contaminant rejection.

The UF permeate flux vs. time plot during the processing of the plant effluent, exclusive of the CPD stream, is given in Figure 9. Again, the flux curve is fairly erratic. The average flux for the entire experiment (141 hours) was 1.71 m^3/m^2-day (41.7 gfd). This is somewhat misleading, however, because of a high initial flux level which was not maintained. For design purposes an average flux of 1.43 m^3/m^2-day (35 gfd) would be appropriate since nearly 50% of the time the flux stabilized at this level. An average flux of 1.43 m^3/m^2-day (35 gfd) is similar to total plant effluent test results and does not indicate any benefit in membrane flux performance from segregating the CPD stream.

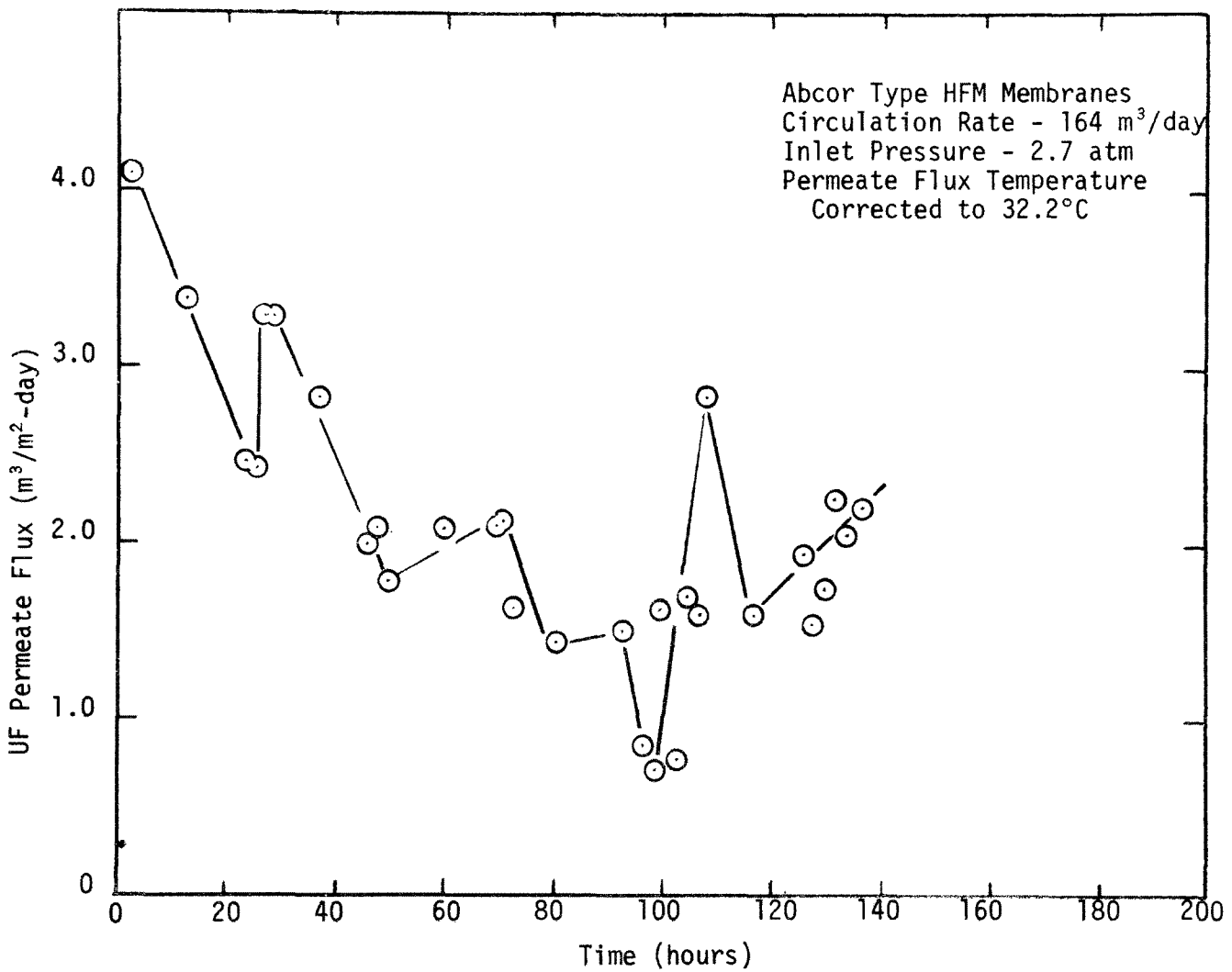


FIGURE 8. UF PERMEATE FLUX VS. TIME FOR SURFACTANT ADDITION TEST AT SAN LEANDRO.

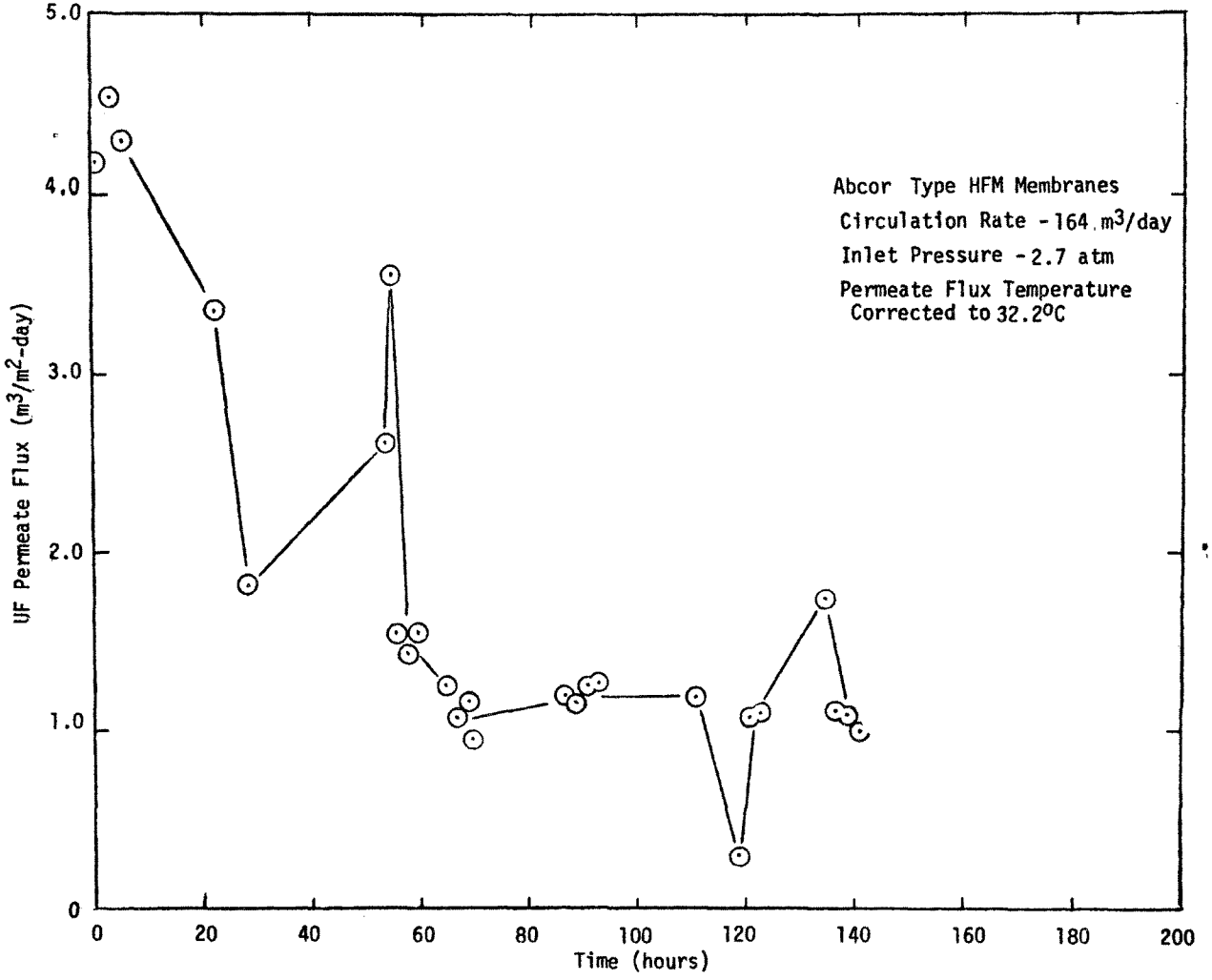


FIGURE 9. UF PERMEATE FLUX VS. TIME FOR TOTAL EFFLUENT LESS CPD STREAM TEST AT SAN LEANDRO.

Prior to the processing of the total plant effluent less the "Z" dispersion wastewater stream seven new tubular membranes were placed on the UF system (see details under UF Flux Recovery discussion, below). As observed in the data plot of Figure 10, the flux for the new membranes exceeded the original membrane flux throughout the test period. This flux differential, slightly more pronounced at the lower concentrations, is to be expected since the surface of the original membranes following 1345 hours of exposure to the San Leandro Plant wastes was not as clean as the surface of the new membranes.

For both the original and the new membranes, permeate flux followed the same pattern. An initial sharp increase in flux was followed by a gradual flux decline. The average flux rates for the entire 162 hour experiment were 1.35 m^3/m^2-day (33 gfd) and 1.88 m^3/m^2-day (46 gfd) for the original and new membranes, respectively. Since the original membranes averaged 1.38 m^3/m^2-day (33.8 gfd) while processing the total plant effluent, no benefit in membrane flux performance is indicated from segregation of the "Z" wastewater stream.

Flux During Maximum Concentration--

Due to latex instability, the first experiment designed to assess the maximum solids concentration achievable by ultrafiltration (run #11) was aborted. A second attempt at defining the solids concentration achievable before uneconomical flux levels are encountered (run #12) was interrupted after 170 hours because of pump failure. Up to this point the concentrate stream had reached a 12.8% total solids level with average flux values of 1.15 m^3/m^2-day (28 gfd) and 1.39 m^3/m^2-day (34 gfd) recorded for the original and new membranes, respectively. Had pump failure not occurred the UF concentration could have been continued with the contents of the UF feed tank processed without fresh feed addition. The maximum concentration achievable by ultrafiltration was, therefore, not assessed.

Ultrafiltration Membrane Flux Recovery and Cleaning

Overview--

Table 15 presents the flux recovery and accumulated operating time for the UF membranes on the San Leandro Plant wastewater. One set of seven HFM membranes remained in use throughout the entire test program (1704 hrs). These membranes are termed "original" HFM. Following run #9, severe membrane fouling problems occurred (see below) and seven "new" HFM membranes were installed. Between runs #5 and 7 type HFD membranes were operated in series with the HFM membranes.

On the basis of the data presented in Table 15, no irreversible membrane fouling occurred during processing of the adhesives and sealants manufacturing wastewater. While final water flux data were not available because of pump failure at the end of the test program, the water flux for

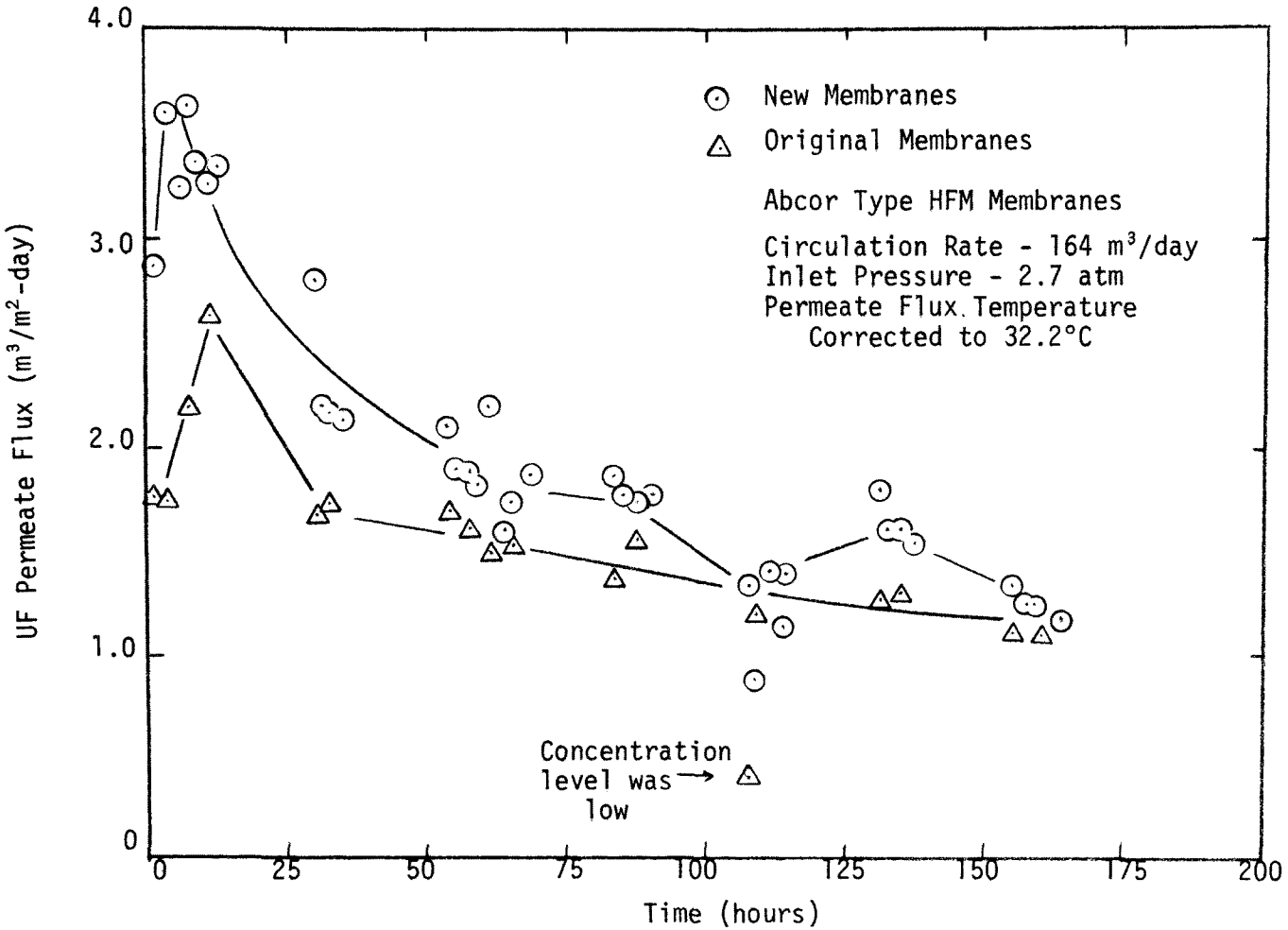


FIGURE 10. UF PERMEATE FLUX VS. TIME FOR TOTAL EFFLUENT LESS "Z" STREAM TEST AT SAN LEANDRO.

TABLE 15. FLUX RECOVERY AND ACCUMULATED OPERATING TIMES FOR UF MEMBRANES OPERATED ON THE SAN LEANDRO PLANT EFFLUENT

Membrane Type	Accumulated Exposure Time, hrs	Water Flux at 32.2°C, m^3/m^2-day (gfd)	Comments
HFM (original)	0	8.2 (200)	
	198	8.5 (208)	
	406	6.5 (158)	
	505	6.5 (159)	
	725	7.1 (173)	
	---	9.7 (237)	After "spongeball"
	877	5.0 (123)	
	1049	6.3 (153)	
	---	8.3 (203)	1.5 months later
	1067	10.3 (250)	
	1204	--- ---	Water flux not recorded
	1345	4.7 (115)	After solvent cleaning
	1507	6.6 (161)	
	1534	6.2 (151)	After aborted run #11. Detergent washed and "spongeballed" several times
	1704	--- ---	Final water flux not recorded due to pump malfunction
HFM (new)	0	6.3 (153)	Installed after run #9
	162	9.0 (220)	
	189	6.2 (151)	After aborted run #11. Detergent washed and "spongeballed" several times
	359	--- ---	Final water flux not recorded due to pump malfunction
HFD	0	--- ---	New membranes, flux not recorded
	152	5.5 (134)	
	324	--- ---	Flux not recorded
	342	--- ---	Membranes removed, flux not recorded

the original HFM membranes was 6.2 m^3/m^2-day (151 gfd) after 1534 hrs accumulated operating time. A water flux of this magnitude is quite acceptable. In most instances, detergent cleaning cycles of only 1/2 hour duration were able to fully recover the membrane water flux.

Flux Recovery Following Latex Destabilization--

On two separate occasions during the test program severe UF membrane fouling occurred. The first instance was between runs #9 and 10*, while the second occurrance was during run #11. In the first case, the UF permeate flux decreased to 0.62 m^3/m^2-day (15 gfd) during normal operation. The system was operated for an additional week with no improvement in flux observed. A series of detergent wash cycles employing respectively, "Ultra-Clean", "Dishmate" and trisodium phosphate were followed by hot water (60°C) rinsing and spongeball cleaning. The average water flux increased to only 1.9 m^3/m^2-day (48 gfd). Inspection of the UF membranes showed an irregular grey rubber coating had deposited on the membrane surface. The nature of the coating and a review of the plant production schedule indicated that the effluent stream from an extremely heat sensitive neoprene rubber based product had entered the plant sump prior to the fouling problem. Unstable latex in this stream had previously coagulated within the plant sump, however up until this instance a latex skin had not developed on the membrane surface.

Once the fouling was identified as latex, standard solvent cleaning procedures for latex removal were employed (see page41). Flux recovery data following MEK cleaning are given in Table 16. A standard 20 minute solvent exposure time was used at San Leandro with resultant water flux measurements ranging from 2.9 to 5.6 m^3/m^2-day (72-136 gfd). These values correspond to flux increases of 26%-231%. Initial water flux measurements on tubular assemblies returned to Abcor were substantially above the 1.6-2.5 m^3/m^2-day (40-60 gfd) readings observed in San Leandro. Variations in MEK soaking times of from 5 to 35 minutes for these tubes produced little variation in resultant water flux and only modest improvement over initial values. An additional 20 minute exposure to MEK followed by spongeball cleaning gave flux levels of 7.6-11.5 m^3/m^2-day (185-280 gfd). It thus appears advantageous to expose the membranes to MEK twice. The first exposure removes the thinner latex deposits and begins to attack the more heavily coated areas. The second exposure swells the residual latex skin. An initial exposure of 5-10 minutes appears adequate. No optimization of the second exposure time was attempted.

The second occurrance of a latex skin formation on the membrane surface took place during run #11, causing the permeate flux to fall below 0.21 m^3/m^2-day (5 gfd). It is believed that a few gallons of concentrated hydrochloric acid were spilled into the effluent stream, lowering the wastewater pH and thus destabilizing the latex. Detergent cleaning was not successful in removing the latex skin, however spongeball cleaning was able to recover the membrane water flux (for both the new and original membranes) to 6.2 m^3/m^2-day (151 gfd). Solvent cleaning was not required.

*No run number was assigned to this aborted test.

TABLE 16. UF MEMBRANE FLUX RECOVERY DATA SUBSEQUENT TO LATEX FOULING*

Tubular Assembly Number	Initial Flux (m^3/m^2-day)	Time Soaked in MEK (min)	Resultant Flux (m^3/m^2-day)	Additional Time in MEK (min)	Resultant Flux (m^3/m^2-day)	Overall Δ%
1	1.93	20	4.80	-	-	148
2	1.68	20	5.58	-	-	231
3	1.76	20	4.80	-	-	172
4	2.34	20	2.95	-	-	26
5	1.97	20	4.71	-	-	139
6	2.09	20	3.20	-	-	53
7	1.93	20	5.58	-	-	189
Mean Value for Tubes 1-7	1.97	20	4.51	-	-	137
8	3.12	5	4.26	20	7.63	144
9	3.97	10	4.96	20	8.90	124
10	3.12	15	3.97	20	7.91	153
11	2.55	20	4.26	20	7.18	181
12	4.67	25	3.97	20	7.91	69
13	4.39	30	5.66	20	9.35	112
14	7.18	35	5.66	20	11.5	60
Mean Value for Tubes 8-14	4.14	-	4.67	-	8.61	120

* NOTES: 1) Tubes 1 to 7 were cleaned at San Leandro.
2) Tubes 8 to 14 were cleaned at Walden.
3) Tubes 1 to 7 were cleaned with a test tube brush soaked in MEK before spongeball cleaning

Summary--

Throughout most of the field demonstration program routine detergent cleaning was satisfactory to recovery membrane water flux to acceptable levels. It is evident, however, that periodically severe membrane fouling due to latex destabilization can occur during processing of adhesives and sealants manufacturing wastewaters. No fail-safe solution to the problem of latex destabilization is available.

Prior to design of a full-scale system for a particular site it should be determined by plant personnel (if possible) whether a latex fouling problem may be a reoccurring circumstance or only the result of an accidental spill. If latex stabilization is envisioned to occur several times a year one or more of the following options should be considered if full-scale UF treatment is to be employed:

1. Divert the effluent from a particular product's wash cycle and treat it separately.
2. Stabilize the latex in the wastewater with surfactant prior to UF treatment.
3. Stabilize the latex in the wastewater by maintaining the effluent pH above 8.
4. Provide a solvent soak tank so that fouled membranes can be removed from the UF system, soaked in MEK, returned to the system and then spongeballed in place.
5. Construct the UF system with carbon steel membrane shells and piping, and explosion proof pumps and controls to allow solvent cleaning in situ.

Product Water Quality

Introduction--

A summary of the plant effluent composition throughout the field demonstration program was given in Table 13. Samples were also collected of the feed after settling, the ultrafiltration concentrate and the ultrafiltration permeate. The analytical data sets for these sampling stations are summarized, respectively, in Tables 17, 18, and 19. Because of the unique nature of the electrocoagulation test (Run #7) analytical data from this experiment were not included in Tables 17-19. The analytical data from individual tests are given in Appendix A.

Some analytical chemistry problems developed during the course of this program. In particular, difficulties were encountered in the assays for total cyanide, phenolic compounds and total freon extractibles. In many instances, the free cyanide levels in the wastewater samples were reported to be in excess of the total cyanide levels. Also, the level of total cyanides were often higher after treatment than in the raw waste. To

TABLE 17. SUMMARY OF ANALYTICAL DATA FOR ULTRAFILTRATION FEED AFTER SETTLING AT SAN LEANDRO PLANT THROUGH TEST #12

Assays	Number of Daily Samples	Average Value mg/l	Number of Weekly Composite Samples	Average Value mg/l	Low Value mg/l	High Value mg/l	Overall Average Value mg/l
Total Freon Extractible *	12	544	7	486	50	1230	522
Non-Polar Freon Extractible	6	117	2	133	11	248	121
Total Solids	10	7580	6	8120	4320	14300	7780
Suspended Solids	16	2200	15	2320	242	4820	2260
BOD	6	7730	7	5750	1880	13000	6670
Soluble BOD	6	6870	2	7710	2220	13200	7080
COD	6	20400	7	29600	13100	77300	25300
Soluble COD	6	16200	2	16500	11000	26800	16300
Arsenic	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-
Total Chromium	-	-	-	-	-	-	-
Free Cyanide	-	-	-	-	-	-	-
Total Cyanide *	2	4	1	5.5	3	5.5	4.5
Lead	-	-	-	-	-	-	-
Mercury	-	-	-	-	-	-	-
Phenolic Compounds *	12	81	7	89.3	1	295	84.0
Zinc	12	38.7	7	66	1.1	200	48.7

* Interference in assay suspected. See page 61.

TABLE 18. SUMMARY OF ANALYTICAL DATA FOR ULTRAFILTRATION CONCENTRATE AT SAN LEANDRO PLANT THROUGH TEST #12

Assays	Number of Daily Samples	Average Value mg/l	Number of Weekly Composites Samples	Average Value mg/l	Low Value mg/l	High Value mg/l	Overall Average Value mg/l
Total Freon Extractible*	29	5130	16	4720	100	22700	4980
Non-Polar Freon Extractible	23	1280	10	1310	28	7600	1291
Total Solids	10	68600	6	55300	4440	160000	63600
Suspended Solids	31	34000	17	27500	680	140000	31700
BOD	7	11500	16	13600	3600	32000	13000
Soluble BOD	6	10000	2	11700	3680	17200	10400
COD	6	130000	7	143000	17100	340000	137000
Soluble COD	6	93700	2	111000	14800	183000	98100
Arsenic	1	<0.2	9	<0.22	<0.2	<0.35	<0.21
Cadmium	1	<0.2	6	<0.2	<0.2	<0.2	<0.2
Total Chromium	1	<0.5	6	<0.5	<0.5	<0.5	<0.5
Free Cyanide	1	2.6	8	4.1	0.53	11	3.94
Total Cyanide*	2	4.0	9	3.58	0.1	11	3.66
Lead	1	<1	6	<1.23	<1	<2.4	<1.2
Mercury	-	-	6	.0045	0.002	0.007	.0045
Phenolic Compounds*	13	54.7	16	66	0.25	600	60.3
Zinc	13	924	15	427	24	2800	658

* Interference in assay suspected. See page 61.

TABLE 19. SUMMARY OF HFM PERMEATE QUALITY

Assay	Number of Daily Composite Samples	Average Value (mg/ℓ)	Number of Weekly Composite Samples	Average Value (mg/ℓ)	Low Value (mg/ℓ)	High Value (mg/ℓ)	Overall Average Value (mg/ℓ)
Total Freon Extractibles†	33	130	19	218	9	953	162
Non-Polar Freon Extractibles	23	9	10	7	2	43	8.4
Total Solids	14	4,340	10	5,020	1,460	9,700	4,620
Suspended Solids	35	51.4	21	58	5	192	53.9
BOD	7	5,390	20	7,660	590	19,000*	7,070
Soluble BOD	6	6,640	2	7,715	3,990	10,400	6,910
COD	6	16,500	7	27,000	6,570	53,200	22,200
Soluble COD	6	15,900	2	16,700	10,500	22,800	16,100
Arsenic	1	< 0.2	9	< 0.2	< 0.2	< 0.2	< 0.2
Cadmium	1	< 0.2	6	< 0.2	< 0.2	< 0.2	< 0.2
Total Chromium	1	< 0.5	6	< 0.5	< 0.5	< 0.5	< 0.5
Free Cyanide	1	0.26	8	0.41	0.26	0.65*	0.39
Total Cyanide†	2	4.26	9	5.18	0.5	12*	5.01
Lead	1	< 1	6	< 1	1	< 1	< 1
Mercury	--	--	6	0.0017	0.001*	0.003*	0.0017
Phenolic Compounds †	17	60.9	20	52	0.5	388	56.1
Zinc	17	73.7	19	9.0	0.34	1,100	39.5

* Indicates low or high value observed in weekly composite sample.
† Interference in assay suspected. See page 61.

investigate these inconsistencies, selected waste samples were "spiked" with known amounts of cyanide and analyzed. For feed and concentrate samples it was found that when 500 ml of sample were spiked with cyanide only 50% of the added cyanide was picked up by the assay. When a 50 ml sample was used, cyanide recovery was 80%. It is known that grease, upon sample acidification, becomes a fatty acid and distills over along with the cyanide. By employing a smaller sample volume, less interferring species distill over and a more accurate cyanide reading is obtained. Permeate samples spiked after the distillation step showed nearly complete cyanide recovery, however a yellow organic compound was present in the distillate. No further investigation of the total cyanide assay was performed.

Interferences from surfactants present in the waste were suspected in the colorimetric assay for phenolic compounds. To test for interferences permeate samples were spiked with Triton-X-100. The results of the phenols assays are shown below:

HFD Permeate Sample	Phenolic Compounds (mg/ℓ)
As Received	203
With 211 ppm Surfactant Added	220
With 787 ppm Surfactant Added	214

No interference from surfactants is indicated from these data. Thus, inconsistencies observed in the phenolic compound assays are unexplained.

Two problems arose in the assays for total freon extractibles. First, all of the total freon extractible assays on Runs #1, 2 and 3 samples and some of the assays on Runs #4 and 5 samples were performed with a container of freon which was later found to be contaminated. Therefore, average values for this assay, and many individual data points represent the highest possible freon extractibles content rather than precise values.

The second difficulty with the total freon extractibles analysis was that surfactant in the permeate was partially extracted by the freon. This resulted in observed oil and grease levels higher than actually present in the product water. This phenomenon was verified by analyzing two samples of D.I. water, one spiked with Triton-X-100 and one control sample for total freon extractibles. The results were as follows:

Sample No.	Concentration of Triton-X-100 in Sample (mg/ℓ)	Total Freon Extractibles (mg/ℓ)
1	0	< 5
2	1,190	296

Recovery of Triton-X-100 by the freon was ~25% indicating a positive interference exists.

Effect of Settling on Plant Effluent Composition--

The scheme of employing a settling/flotation tank ahead of the ultrafiltration system was adapted from the Grace Chicago Plant's treatment system. By reducing the suspended solids loading on the UF system, higher flux levels are achieved and less membrane area is required for a full-scale treatment system. In addition, to suspended solids reduction, reduced loadings were observed for several other contaminants. These data are summarized in Table 20.

TABLE 20. EFFECT OF SETTLING PRETREATMENT ON SAN LEANDRO PLANT EFFLUENT

Assay	Overall Average Value (mg/ℓ) Plant Effluent	Effluent after Settling	Removal Efficiency, %
Total Freon Extractibles*	2,220	522	76.5
Non-Polar Freon Extractibles	296	121	59.1
Total Solids	14,100	7,780	44.8
Suspended Solids	10,600	2,260	78.7
BOD	8,740	6,670	23.7
Soluble BOD	6,760	7,080	----
COD	27,100	25,300	6.6
Soluble COD	17,300	16,300	5.8
Total Cyanide*	1.88	4.5	----
Phenolic Compounds*	154	84	45.5
Zinc	98.9	48.7	50.8

* Interference in assay suspected. See page 61.

The most significant reductions (75% - 80%) occurred in the effluent suspended solids and total freon extractible loadings. However, the average loadings of these contaminants; 2,260 mg/ℓ and 522 mg/ℓ, respectively, are still significant and exceed discharge standards. In fact, in the final settling tank overflow, none of the contaminants assayed met the San Leandro Municipal Sewer Discharge Standards.

Ultrafiltration Membrane Removal Efficiency--

The ultrafiltration membrane removal efficiency data discussed below was obtained with type HFM membranes unless otherwise stated. The membrane removal efficiency data includes the effect of the settling/flotation tanks

since it is based on the plant effluent as the feed stream. The analytical data summary for the HFM permeate during all field demonstration tests was given in Table 19.

Total Plant Effluent--Average UF membrane removal efficiencies during tests with the total plant effluent (runs #2, 3, 4, 5, 6 and 12) are summarized in Table 21.

TABLE 21. AVERAGE UF MEMBRANE REMOVAL EFFICIENCY DATA DURING PROCESSING OF THE TOTAL PLANT EFFLUENT

Assay	Average Concentration in Plant Effluent After Settling (mg/ℓ)	Average Concentration in UF Permeate (mg/ℓ)	Typical Range of Removal Efficiency (%)	Average Removal Efficiency## (%)
Total Freon Extractibles*	3,250	100.0	65- 99.7	92.2
Non-Polar Freon Extractibles	415	< 7.4**	90 -> 99.9	94.7
Total Suspended Solids	13,400	< 27.0**	98.7 -> 99.9	99.6
BOD_5	11,300	8,890	5- 50	24.0
COD	56,100	36,600	25- 50	38.2
Free Cyanide	< 2.6†	0.43	32- > 85	< 77.5
Phenolic Compounds #	244	44.6	0- 70	44.0
Zinc	104	1.5††	60- 99	90.8

* Interference in analysis suspected. Maximum possible oil and grease reported. See page 61.
** Most readings were <5 mg/ℓ.
† Samples diluted 1:10 to minimize interference; detection limit increased to 2.6 mg/ℓ.
†† Excludes the 1 reading out of 11 which was >5.4 mg/ℓ.
# Interference in analysis suspected. See page 61.
Includes effect of settling. Absolute UF removal efficiency may be lower.

The UF system exhibited excellent removal for total freon extractibles. The average oil and grease level in the permeate was 100 mg/ℓ; the average removal efficiency was 92.2%. In actuality, improvements in these figures are to be expected since the difficulties previously mentioned with this assay often gave false positive readings. The non-polar freon extractibles assay is performed by passing the extract from the total freon extractible

assay through a silica gel column. The silica gel adsorbs surfactants and animal and vegetable fats.* Thus, this assay in effect represents the oils and grease of mineral and petroleum origins. The removal efficiency for non-polar freon extractibles averaged 94.7% with a mean UF permeate concentration of <7.4 mg/ℓ.

The suspended solids level in the permeate averaged <27.0 mg/ℓ. While most readings were below the detection limit of the assay (5 mg/ℓ) three readings of ~100 mg/ℓ were recorded and one reading of 160 mg/ℓ was noted. It is believed that secondary precipitation resulting from permeate instability occurred. The mechanism by which the secondary precipitation took place was not investigated during this program. It was determined, however, that the higher readings of suspended solids were a result of this chemical reaction and not a function of membrane degradation or failure. As stated, in most instances, the UF system reduced the suspended solids loading in the plant effluent to <5 mg/ℓ .

BOD and COD reductions in the total plant effluent averaged 24% and 38%, respectively. These data indicate that a significant portion of the organic pollutant loading in this wastewater is present as soluble matter.

An exact measure of the reduction in free cyanide by the treatment process was not obtainable because the feed samples had to be diluted 1:10 to minimize interferences. This dilution increased the assay detection to 2.6 mg/ℓ which was above the actual feed free cyanide level. Interferences with the total cyanide assays were discussed previously.

Phenolic compound removal was moderate, ranging from 0% to 70% and averaging 44%. The average phenolic compound concentration in the UF permeate was 44.6 mg/ℓ representing a range of values from 0.62 to 220 mg/ℓ.

The detection limit of the analysis was reached for the feed, concentrate and permeate samples for cadmium, total chromium and lead. The same is true for all arsenic assays except one feed and one concentrate sample. Therefore, no removal efficiency data could be calculated for these assays.

The degree of mercury of removal was essentially nil, however this is of little practical significance since the level of mercury in the plant effluent averaged only 0.0028 mg/ℓ. Zinc removal of 91% was averaged throughout the tests with the total plant effluent. The overall average permeate loading was 1.5 mg/ℓ when a single, extreme reading (47 mg/ℓ) was eliminated from the data analysis. It is believed that this high reading was the result of poor "housekeeping" measures in the crystal flux area, where zinc ammonium chloride is present, and that it was therefore not a representative data point.

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*Based on unpublished information from EPA, Cincinnati; animal and vegetable fats are adsorbed up to the capacity of the silica gel-about 500 mg oil and grease/15 grams silica gel. Also, it is expected that < 7% of non-polar oil and grease might be adsorbed.

Effect of Surfactant Addition On UF Permeate Quality--The pertinent analytical data from the two surfactant addition tests are summarized in Table 22. Removal efficiency data are not presented because several inconsistencies in the data make these numbers suspect. For instance, the total freon extractibles loading in the feed during runs #1 and 8 was only 15% of the average loading in the feed during the other runs with the total plant effluent. Also, in many instances (see Table A8, Appendix A) contaminant loadings in the treated wastewater were higher than in the feed.

TABLE 22. AVERAGE UF PERMEATE QUALITY DURING PROCESSING OF THE TOTAL PLANT EFFLUENT WITH SURFACTANT ADDITION

Assay	Average Concentration in Plant Effluent (mg/ℓ)	Average Concentration in UF Permeate (mg/ℓ)
Total Freon Extractibles *	478	184
Non-Polar Freon Extractibles	117	< 7.8
Total Suspended Solids	4,230	61.3
BOD_5	8,700	8,570
COD	23,000	16,900
Phenolic Compounds *	148	102
Zinc	116	9.3**

* Interference in assay suspected. See page 61.
** Excludes one reading of 1,100 mg/ℓ.

The permeate total freon extractibles were higher than observed for the runs without surfactant addition (184 mg/ℓ vs. 100 mg/ℓ). As mentioned previously these higher readings reflect the extraction of surfactant in the permeate by the freon. The added surfactant neither prevented, nor reduced, secondary precipitation in the UF permeate. In fact, the suspended solids loading in the permeate during the surfactant addition tests was greater than twice the loading when no latex stabilization was attempted.

Surfactant addition did not result in improved permeate quality in terms of phenolic compounds or zinc. BOD and COD levels were lower in both feed and permeate streams during the surfactant addition tests, again indicating no improvement in treated effluent quality.

In summary, surfactant addition lessens, rather than improves, permeate quality.

Effect of CPD Stream Segregation on Permeate Quality--Analytical data are presented in Table 23 for the field demonstration experiment performed with the exclusion of the CPD stream. UF membrane removal efficiencies for most assays were similar to the data obtained with the total plant effluent. In terms of actual permeate quality, the oil and grease, suspended solids and zinc loadings were lower in the total plant effluent than in the effluent less the CPD stream.

TABLE 23. AVERAGE UF PERMEATE QUALITY DURING PROCESSING OF THE TOTAL PLANT EFFLUENT LESS THE CPD STREAM

Assay	Average Concentration in Plant Effluent (mg/ℓ)	Average Concentration in UF Permeate (mg/ℓ)	Average Removal Efficiency (%)
Total Freon Extractibles	2,490	178	†
Non-Polar Freon Extractibles	288	22.8	61.2
Total Suspended Solids	16,200	18.4	98.6
BOD_5	5,330	4,640	15.6
COD	20,800	11,630	40.6
Phenolic Compounds *	5.7	2.6	42.0
Zinc	117	3.1	96.2

†Data are highly inconsistent, see Table A9.
*Interference in assay suspected. See page 61.

The only significant improvement in water quality from segregation of the CPD stream resulted from a 2 order-of-magnitude decrease in the feed phenolic compound loading. This decrease alone is not deemed sufficient to warrant segregation of the CPD stream during full-scale treatment operations.

Effect of "Z" Stream Segregation on Permeate Quality--Analytical data for the "Z" stream segregation test are shown below (Table 24).

TABLE 24. AVERAGE UF PERMEATE QUALITY DURING PROCESSING OF THE TOTAL PLANT EFFLUENT LESS THE "Z" STREAM

Assay	Average Concentration in Plant Effluent (mg/ℓ)	Average Concentration in UF Permeate (mg/ℓ)	Average Removal Efficiency (%)
Total Freon Extractibles	1,020	192	79.4
Total Suspended Solids	6,940	155	95.2
BOD_5	1,620	2,000	--
COD	19,800	10,000	39.3
Phenolic Compounds *	82.9	78.5	33.5
Zinc	51.5	16.2	68.3

* Interference in assay suspected. See page 61.

Assays performed on samples collected from the plant sump show considerable variation from the average total plant effluent values (see Table 21). Major deviations from the total effluent analytical data are observed in the lower loadings for suspended solids, BOD and total freon extractibles. The average UF removal efficiencies are lower with the "Z" stream segregated for all assays except COD. Permeate quality is significantly worsened by segregating the "Z" stream in terms of oil and grease, suspended solids, phenolic compounds and zinc. Permeate quality is improved in terms of BOD and COD, resulting from reduced organics loadings in the feed stream. Overall, the permeate quality is judged to degrade when the "Z" stream is segregated.

Comparison of Effluent Quality with Local and Preliminary Federal Discharge Standards--

Table 25 summarizes type HFM membrane permeate quality during processing of the total plant effluent, San Leandro and MSD of Chicago Municipal Discharge Standards and the recommended BPCTCA, BADCT and BATEA standards. For oil and grease, free cyanide and zinc both the San Leandro and MSD discharge limitations are met. The plant effluent, without treatment already met the standards or reached the assay detection limit for arsenic, cadmium, total chromium, lead and pH. The plant effluent also met the San Leandro discharge limit for mercury. The metropolitan Chicago mercury limit of 0.05 mg/ℓ was not reached even after UF treatment.

The total cyanide content of the UF permeate (~5 mg/ℓ) was acceptable for discharge in the Chicago area but not San Leandro. The phenolic compounds level in the permeate exceeded San Leandro limits while no discharge limitation was published for Chicago.

For total solids, suspended solids, BOD and COD no municipal discharge limitations are set, however, surcharges are imposed on the basis of BOD and suspended solids loadings. The UF permeate suspended solids level is quite low, however, the ~9,000 mg/ℓ BOD level could incur a several thousand dollar sewer surcharge.

The EPA Draft Development Document is written in terms of BOD, COD and suspended solids loadings. While the UF permeate is essentially equal to the draft BPCTCA, BADCT and BATEA discharge limits for suspended solids, it is greatly in excess of the preliminary contractor recommendations for BOD and COD.

Summarizing, ultrafiltration of the San Leandro Plant effluent cannot produce a product water meeting all local and preliminary Federal discharge standards. Some form of post-treatment will be required to make this adhesives and sealants wastewater compatible with the discharge regulations.

TABLE 25. COMPARISON OF HFM PERMEATE QUALITY WITH LOCAL AND FEDERAL DISCHARGE STANDARDS DURING TREATMENT OF THE TOTAL PLANT EFFLUENT

Parameter	Average Concentration in UF Permeate	San Leandro Municipal Discharge Limits	Metropolitan Chicago Sewer Discharge Standards	Range for Subcategories A, B and C		
				BPCTCA	BADCT	BATEA
Total Freon Extractibles (mg/ℓ)††	100	300**	<100	--	--	--
Non-Polar Freon Extractibles (mg/ℓ)	<7.4*	100**	--	--	--	--
Total Solids (mg/ℓ)	3,700	--	--	--	--	--
Total Suspended Solids (mg/ℓ)	<27*	--	--	20-50	20	20
BOD (mg/ℓ)	8,890	--	--	255-910	255-910	100-910
COD (mg/ℓ)	36,600	--	--	710-1,530	680-1,500	267-1,500
Arsenic (mg/ℓ)	0.2†	0.1	--	--	--	--
Cadmium (mg/ℓ)	0.2†	0.2	2.0	--	--	--
Total Chromium (mg/ℓ)	0.5†	0.5	25.0	--	--	--
Free Cyanide (mg/ℓ)	0.43	--	2.0	--	--	--
Total Cyanide (mg/ℓ)††	4.95	1.0	10.0	--	--	--
Lead (mg/ℓ)	1.0†	1.0	0.5	--	--	--
Mercury (mg/ℓ)	0.0017	0.01	0.0005	--	--	--
Phenolic Compounds (mg/ℓ)††	44.6	1.0	--	--	--	--
Zinc (mg/ℓ)	1.5	3.0	15.0	--	--	--
pH (units)	7-9	> 6.0	4.5-10.0	--	--	--

*Most readings were < 5 mg/ℓ.

†Detection limit of assay.

**300 mg/ℓ oil and grease of animal or vegetable origin, 100 mg/ℓ oil and grease of mineral or petroleum origin.

††Interferences suspected in some assays. See page 61.

POST TREATMENT TESTS

Reverse Osmosis

Reverse osmosis experimentation was conducted in Walden's Pilot Laboratory on two different ultrafiltrate samples obtained from the Grace Chicago Plant. A DuPont B-9 (polyamide) hollow-fine-fiber permeator was used throughout both tests.

RO Module Productivity--

The B-9 permeate flow rate as a function of volumetric feed concentration is plotted in Figure 11 for both pilot plant runs. The productivity of the B-9 module decreases with increasing volumetric concentration in both cases. This trend is typical of reverse osmosis operation since dissolved solids build-up within the feed solution raises the feed osmotic pressure and reduces the overall driving force across the membrane.

The average module productivity (m^3 processed ÷ processing time) in the first test was 10.4 m^3/day (1.91 gpm) during concentration to 13.7X (92.7% conversion). Processing beyond this point was precluded due to the dead volume holdup of the test system. For the RO experiment with the second ultrafiltrate sample the initial module productivity of 8.2 m^3/day (1.5 gpm) was 25% lower than the 1X productivity achieved during the first test. The reduced permeate flow rate throughout the run is partially attributed to the higher conductivity of the ultrafiltrate; 3000 µmhos/cm vs. 980 µmhos/cm for the first sample.

Another factor influencing the lower module productivity was the presence of suspended matter in the second ultrafiltrate sample. Since ultrafiltrate is typically free of all suspended solids, the particulate matter in the sample was believed to be a biological (bacteria) related floc, which may have developed during a delay in sample shipment. The suspended matter was allowed to settle overnight and the RO feed solution was passed (as always) through 5µ and 1µ string-wound cartridge filters, in series, before processing. The average module productivity during this test was 4.85 m^3/day (0.89 gpm) during concentration to 7.9X (87% conversion).

The ultrafiltrate sample used in the second experiment was aged longer than the first sample and is thus believed to have degraded. Therefore, the flux vs. volumetric feed concentration data developed in the first experiment are considered more valid for design purposes.

RO Module Removal Efficiency--

Assays performed on the initial feed, final mixed composite permeate and final concentrate are detailed in Table 26 for both RO tests. Significant differences in the RO feed contaminant levels are observed for the two tests. (It is also of note that the contaminant concentrations in the San Leandro ultrafiltrate (see Table 19) were much higher than those observed in either of the Chicago ultrafiltrate samples.)

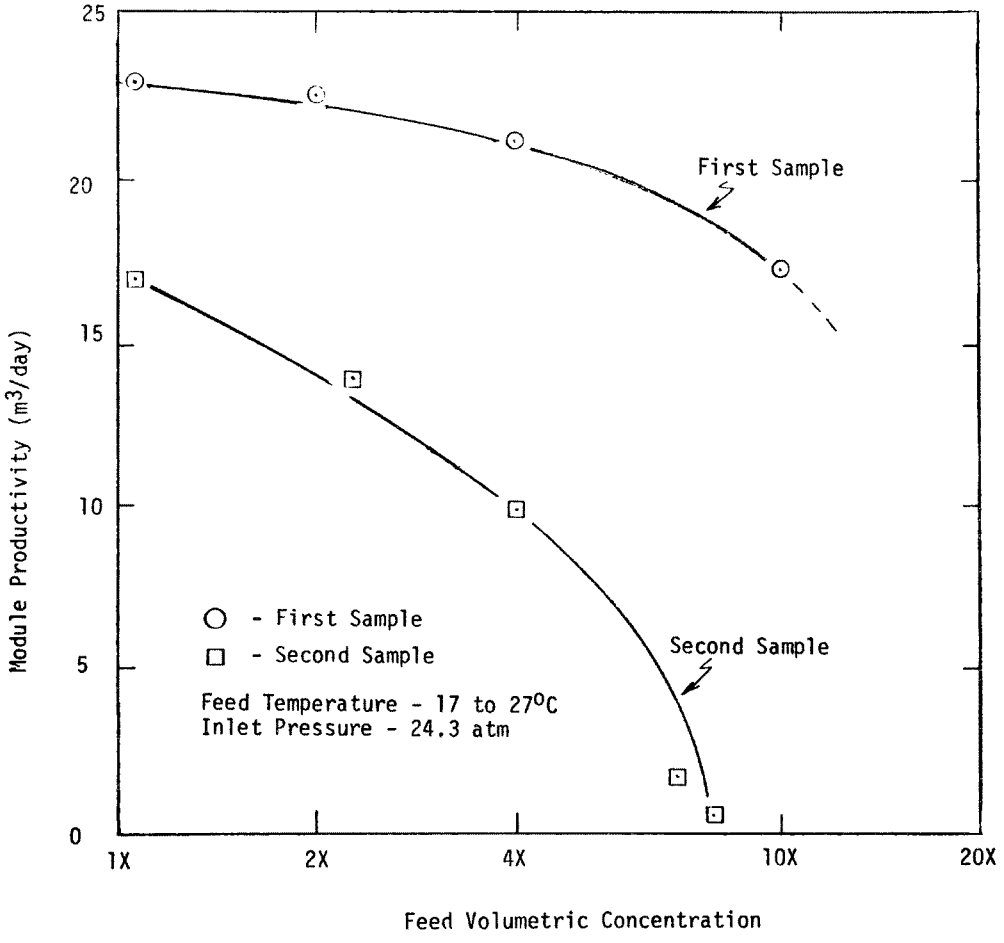

FIGURE 11. PRODUCTIVITY VS. FEED VOLUMETRIC CONCENTRATION FOR DUPONT B-9 PROCESSING OF DEWEY AND ALMY CHICAGO PLANT ULTRAFILTRATE

TABLE 26. ANALYTICAL DATA AND RO MODULE REMOVAL EFFICIENCIES DURING PROCESSING OF THE GRACE CHICAGO PLANT ULTRAFILTRATE

Test Number	Assay	Initial Feed (mg/ℓ)	Final Concentrate (mg/ℓ)	Final Composite Permeate (mg/ℓ)	Removal Efficiency (%)
1	Total Solids	1,270	22,500	48	96.2
	COD	1,890	27,000	282	90.3
	BOD	450	3,800	58	87.1
2	Total Solids	6,840	82,800	261	96.2
	COD	12,200	110,500	1,190	90.2
	BOD	2,100	18,800	800	61.9

The DuPont B-9 permeator removal efficiencies for total solids and COD were essentially identical in both tests and were 96% and 90%, respectively. For BOD, which is a much less precise analysis, the removal efficiency declined from 87% in the first test to 62% in the second. Assuming the same RO removal efficiencies for total solids and COD and a 75% removal efficiency for BOD, RO treatment of the San Leandro UF permeate (to a 10X concentration factor) would result in a product water with approximately 150 mg/ℓ total solids, 3,700 mg/ℓ COD and 2,200 mg/ℓ BOD. Since all of the total solids would be dissolved, the RO product water would satisfy the contractor's recommended values for BPTCA, BADCT and BATEA for suspended solids. It would not, however, achieve the values recommended for either BOD or COD.

The RO product water from the pilot plant tests was not assayed for total cyanide or phenolic compounds. Reverse osmosis is capable of concentrating either cyanide or phenols in the UF permeate when processing takes place under basic (pH > 8) conditions. It is assumed that a properly designed RO system could consistently produce a product water meeting the San Leandro Municipal Discharge Limitations of 1.0 mg/ℓ total cyanide and 1.0 mg/ℓ phenolic compounds.

RO Module Standard Salt Rejection Tests--

The B-9 salt rejection data for both batch pumpdowns are presented in Table 27. A decline in module salt rejection to only 50% was noted after the second processing period. The B-9 permeator was cleaned per DuPont's recommendation with a solution of citric acid and then treated with PTA, a proprietory DuPont product. A slight increase in NaCl rejection, to 61.9%, resulted from the cleaning/treatment operation. The decline in module performance is believed to be related to the suspended matter in the feed stream, however the exact mechanism of the module failure is not known.

Carbon Adsorption

The equilibrium adsorption isotherms for Filtrasorb 400 granular activated carbon (Calgon Corp.) at 20°C for the second sample of Grace Chicago plant ultrafiltrate are shown in Figures 12 and 13 for BOD and COD removal, respectively. In each figure the logarithm of the contaminant loading (mg adsorbed per gram of carbon) is plotted against the logarithm of the equilibrium contaminant concentration. The points fall reasonably close to a straight line in both cases, indicating agreement with the Freundlich isotherm expression.

The adsorption isotherm for BOD removal shown in Figure 12 indicates an equilibrium loading of 2g BOD/g carbon at the initial ultrafiltrate BOD level of 1,325 mg/ℓ. The adsorption capacity of the carbon decreases rapidly from this point. At a BOD concentration of 1,000 mg/ℓ the carbon loading reduces to 0.1 g BOD/g carbon.

An even greater decline in adsorptive capacity is observed in the isotherm for COD removal shown in Figure 13. The initial COD concentration of the untreated ultrafiltrate, C_o, was 12,460 mg/ℓ and the equilibrium

TABLE 27. STANDARD SALT REJECTION TEST DATA FOR DUPONT B-9 HOLLOW-FIBER MODULE DURING PROCESSING OF DEWEY AND ALMY CHICAGO PLANT ULTRAFILTRATE

Cumulative Operating Time (hrs)	Feed Concentration NaCl (ppm)	Temperature (°C)	Permeate Flowrate (m^3/day)	Feed Flowrate (m^3/day)	Conversion (%)	Rejection (%)	Intrinsic Rejection	Remarks
0	1800	25	13.9	28.0	49.7	96.1	.972	
3.6	5750	27	11.1	29.0	38.1	95.5	.964	After test #1
7.6	5900	28	13.9	28.3	49.0	50.0	----	After test #2
---	5250	22	11.4	30.5	37.5	61.9	----	After citric acid cleaning and PTA treatment

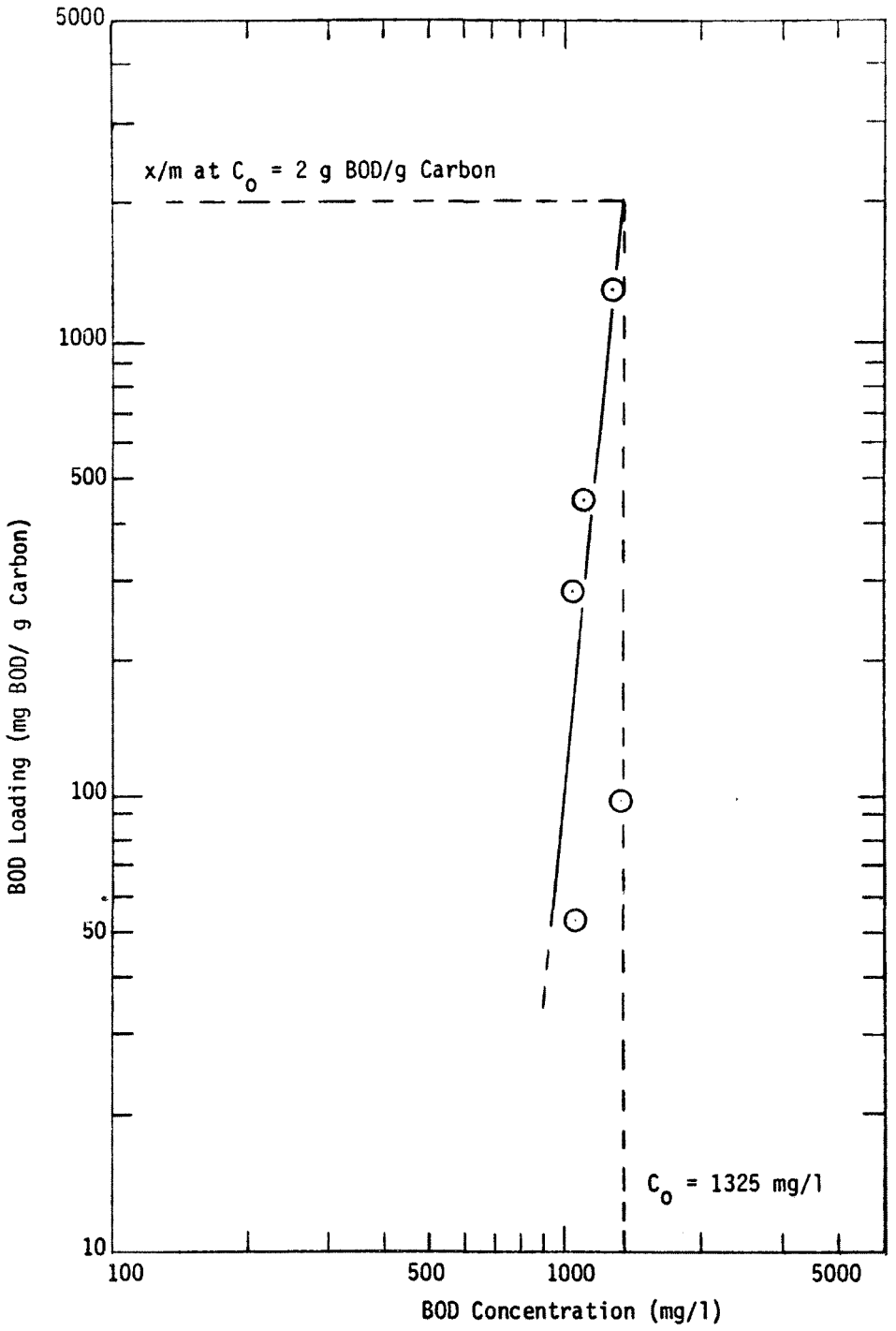

FIGURE 12. EQUILIBRIUM ADSORPTION ISOTHERM AT 20°C FOR BOD REMOVAL FROM DEWEY AND ALMY CHICAGO PLANT ULTRAFILTRATE (SECOND SAMPLE).

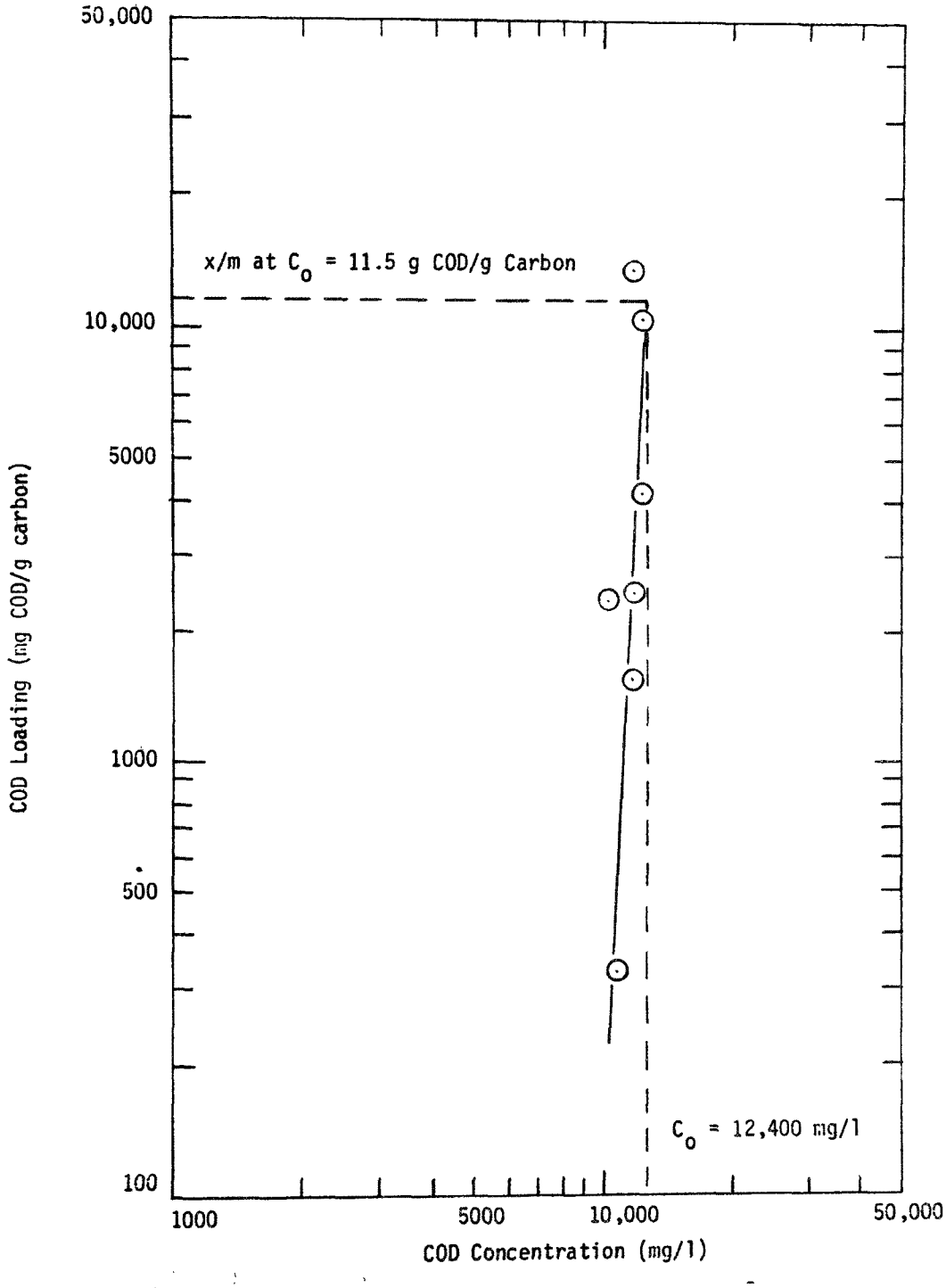

FIGURE 13. EQUILIBRIUM ADSORPTION ISOTHERM AT 20°C FOR COD REMOVAL FROM DEWEY AND ALMY CHICAGO PLANT ULTRAFILTRATE (SECOND SAMPLE).

loading at this concentration as determined from the isotherm, was 11.5g COD/g carbon. A 20% reduction in the ultrafiltrate COD concentration to 10,000 mg/ℓ would result in nearly a 100-fold loss in adsorptive capacity to 0.12 mg COD/g carbon.

The steep slope of the isotherms of Figures 12 and 13 indicates that the Chicago plant ultrafiltrate is composed of a small amount of strongly adsorbed material and a larger amount of weakly adsorbed material. From isotherms of this nature, we can predict rapid breakthrough of BOD and COD to occur during processing of this ultrafiltrate through carbon columns.

Similar results were obtained for a TOC isotherm performed with the first Chicago ultrafiltrate sample.

Ozonation

A 20 liter (5 gal) sample of the San Leandro ultrafiltrate was ozonated by U.S. Ozonair Corporation (South San Francisco, California). The analytical data from ozonation tests with a single catalyst and with 3 catalysts plus electro-coagulation are given in Table 28. For total solids, suspended solids and total cyanide the loading in the wastewater increases following ozonation. The increases observed in the solids assays are believed to be a result of conversion of volatile solids into non-volatile solids resulting from catalysis and electro-coagulation (12). The increase in total cyanide is likely the effect of positive interferences in the assay.

BOD and COD reduction for the two tests averaged approximately 9% and 80%, respectively. While the COD reduction was significant the ozonated product water COD content (12,000 to 16,000 mg/ℓ) was still an order-of-magnitude above the value recommended in the draft development document. Clearly, the BOD level was above the recommended value.

The UF permeate total freon extractibles and zinc content were below the San Leandro Municipal discharge standards before ozonation and therefore the 96% removal efficiencies observed for these contaminants are not of primary importance. On the other hand, the reduction of phenolic compounds from 47 mg/ℓ, to <0.15 mg/ℓ, representing a >99% reduction, is highly significant. Thus, with ozonation post-treatment an effluent meeting all San Leandro Municipal Discharge Limitations has been demonstrated in a laboratory test to be readily achievable.

Alternative Oxidation Processes

Three alternative oxidation processes; chlorination, hydrogen peroxide oxidation and potassium permanganate oxidation were considered for post-treatment of the UF permeate to effect further cyanide and phenolic compound reductions. Chlorination was ruled out as viable alternative since chlorinated phenols are toxic and may import a disagreeable odor to the water. Hydrogen peroxide treatment was judged unsatisfactory because it is most attractive economically when the range of cyanide in the

TABLE 28. ANALYTICAL DATA FOR OZONATION OF SAN LEANDRO PLANT ULTRAFILTRATE

Assay	UF Permeate	Ozonation with 1 Catalyst		Ozonation with 3 Catalysts plus Electrocoagulation	
		Level	Removal Efficiency, %	Level	Removal Efficiency, %
Total Solids (mg/ℓ)	7,200	14,500	—	33,100	—
Total Suspended Solids (mg/ℓ)	64	140	—	290	—
Total Freon Extractibles (mg/ℓ)	130	4.0	96.9	4.0	96.9
BOD (mg/ℓ)	5,780	5,190	10.2	5,340	7.6
COD (mg/ℓ)	76,700	12,100	84.2	16,700	78.2
Total Cyanide (mg/ℓ)	0.56	1.5	—	1.1	—
Phenotic Compounds(mg/ℓ)	47	0.13	99.7	0.10	99.8
Zinc (mg/ℓ)	2.2	0.09	95.9	0.08	96.4
pH (units)	8.4	9.4	—	9.8	—

wastewater 100 to 1000 mg/ℓ (as sodium cyanide). For San Leandro the range is 1 to 10 mg/ℓ. The dosage of potassium permanganate required to oxidize the phenolic compounds in the San Leandro ultrafiltrate was excessive, therefore $KMnO_4$ oxidation was also deemed economically prohibitive.

Post-Treatment Summary

Six post-treatment processes were studied in varying degrees. None of the processes were deemed capable of lowering ultrafiltrate BOD and COD loadings to Federal discharge standards. All six processes are able, however, to produce an effluent meeting local municipal discharge regulations. Carbon adsorption, hydrogen peroxide oxidation and potassium permanganate oxidation were judged to be uneconomical for polishing of the San Leandro UF permeate and are therefore eliminated from further consideration. Chlorination was eliminated from consideration on technical grounds since it produces chlorinated phenols.

Only reverse osmosis and ozonation are thought to be both technically and economically viable. The economics of each will be discussed in a subsequent section.

DEWATERING TESTS

Introduction

Promulagation of future "zero discharge" regulations may prevent disposal of the concentrate from adhesives and sealants wastewater treatment facilities in sanitary landfills. Unless the sludge contains a minimum of 35% solids there may be leaching of soluble contaminants into ground waters. Also the cost of sludge disposal is a significant treatment expense. Therefore, several methods of dewatering the settling tank bottoms were investigated at San Leandro.

Gravity Sedimentation

In an effort to improve the performance of the gravity sedimentation currently employed at San Leandro, the Lamella Gravity Settler manufactured by Parkson Corporation was investigated. The basic principle of utilizing a series of inclined settling plates in close proximity to each other increases the settling area ten times that of a conventional unit. Another advantage of this system is a simplified sludge removal technique and use of a low amplitude vibrator pack to further thicken the settled solids.

A 20 liter (5 gal) sample taken from the underground sump at San Leandro was tested at the Parkson Laboratory. The sample had a suspended solids loading of 3,000 mg/ℓ and was therefore, representative of the raw effluent from the plant. The results of this test were not encouraging since only a 4% underflow concentration was achieved. Even with the addition of flocculating aids the settling properties were not significantly improved.

Gravity Filters

As "pre-concentration" steps a Bauer Hydrasieve and a SWECO Centrifugal Wastewater Concentrator/Vibro-Energy Separator Combination were tested at San Leandro. Blinding of the screens on both the Hydrasieve and the Vibro-Energy Separator preclude their use with adhesives and sealants wastewaters.

Pressure Filters

A sample taken from the sump in San Leandro could not be filtered using an open mud discharge filter press without any filter aids. The filterability was improved slightly through the addition of a coagulant at low pH. A good break was achieved but the gelatinous nature of the created floc greatly inhibited filtration.

These tests were conducted by personnel of Industrial Filter and Pump Mfg., Chicago, Illinois who estimated that the amounts of filter aid, fly-ash, and/or other coarse material necessary to dewater this sludge may be economically prohibitive.

Centrifugal Filters

A liquid cyclone was evaluated in San Leandro for sludge thickening but was ineffective due to the small differences in the specific gravities of the suspended solids.

ELECTROCOAGULATION TEST

An electrocoagulation process (Swift Environmental Systems Co.) was tested both as an alternative to, and a pretreatment for ultrafiltration. Essentially all of the wastewater generated by the San Leandro Plant in one week was processed by the electrocoagulation system. A portion of the electrocoagulation system effluent was then processed by the UF system. Details of the electrocoagulation test are presented in Reference 13, UF operating performance is discussed below.

The UF membrane flux vs. time curves while processing the pretreated feed are given in Figure 14. Average flux levels were 2.3 m^3/m^2-day (55 gfd) for the HFD membrane and 2.1 m^3/m^2-day (50 gfd) for the HFM membranes. For both membrane types, the flux varied considerably during the 18 hour test period. These variations in flux levels are attributed to the intermittent nature of the UF system operation (six hours per day for three days), the variability of the plant effluent and changes in the electrocoagulation process chemical dosages. However, neither these flux variations nor the relatively high flux levels can be associated solely with the electrocoagulation process. For example, during run #6 (see Figure 7) flux for both the HFD and HFM membranes ranged from 1.4 to > 2.7 m^3/m^2-day (35 to >65 gfd) with averages of >2.1 m^3/m^2-day (50 gfd). The duration of run #6 was 172 hours.

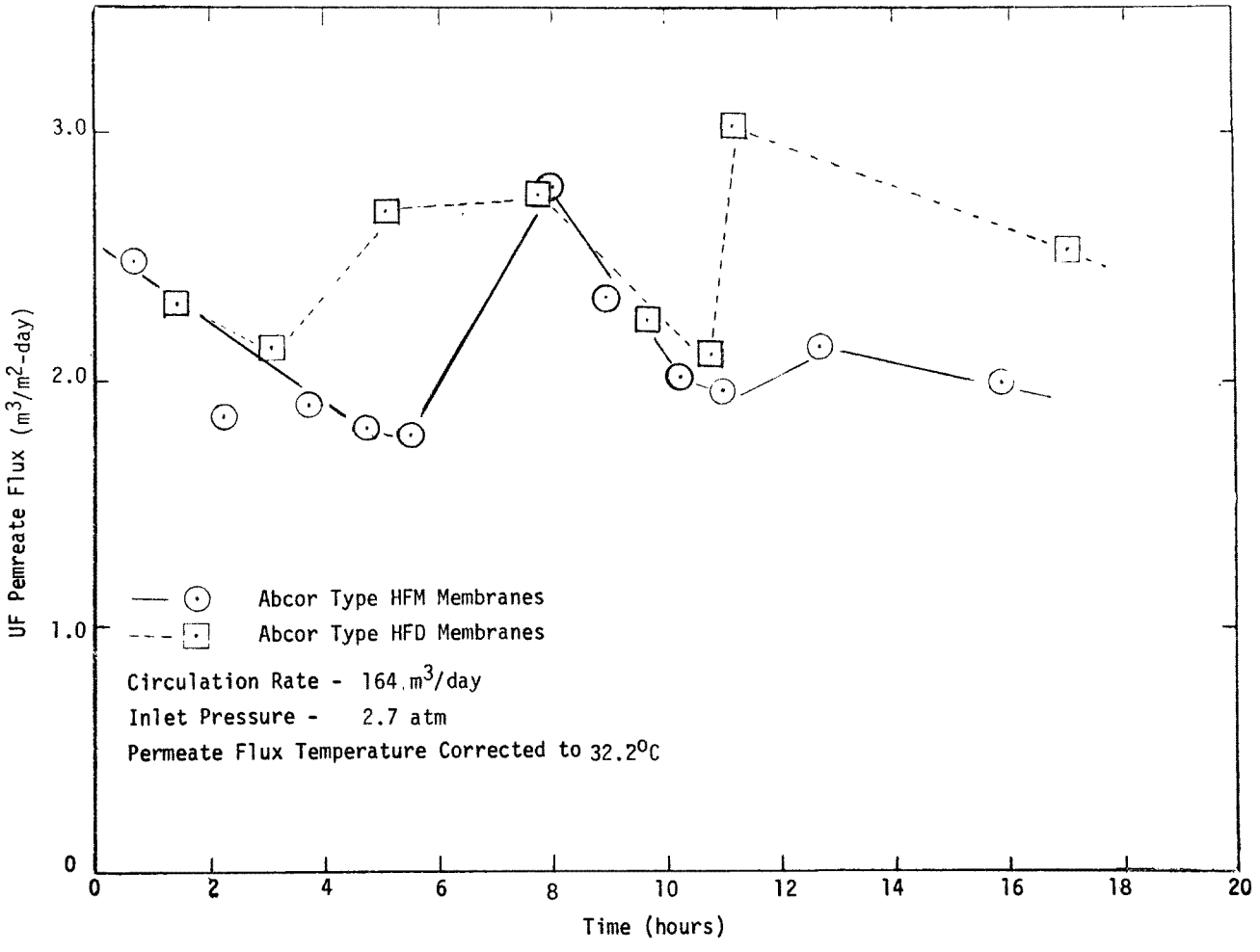

FIGURE 14. UF PERMEATE FLUX VS. TIME FOR ELECTROCOAGULATION PROCESS TEST AT SAN LEANDRO.

The analytical data obtained during UF processing of the electrocoagulation system effluent are presented in Appendix A. Average permeate loadings and removal efficiencies for the UF process (type HFM membranes only) are listed below (Table 29).

TABLE 29. AVERAGE UF SYSTEM REMOVAL EFFICIENCIES FOLLOWING ELECTROCOAGULATION PRETREATMENT

Assay	Average UF Permeate Concentration (mg/ℓ)	Average Removal Efficiency (%)
Total Freon Extractibles	20.5	5.1
Total Suspended Solids	34.0	62.4
BOD_5	6,480	32.2
COD	15,700	2.6
Total Cyanide	4.6	---
Phenolic Compounds	61.7	27.9
Zinc	0.59	85.0

Essentially, no reduction in total freon extractibles or COD is evident. The suspended solids levels in the UF permeate ranged from 32 to 54 mg/ℓ which is above the average value observed during ultrafiltration of the total plant effluent without pretreatment. The destabilizing mechanism of the electrocoagulation process is most likely responsible for this increased secondary precipitation in the permeate stream.

The increase in the removal efficiency for phenolic compounds was ~30%. However, the San Leandro Municipal Discharge Limit for phenols was still exceeded. BOD reduction was also ~30%. As had been observed in all other instances, the BOD level in the treated effluent was still significantly above the proposed federal guidelines.

Zinc levels in the UF permeate were below the discharge level and ranged from 0.32 to 1.0 mg/ℓ. Interferences in the total cyanide assays are indicated from the analytical data.

Based on the above discussion and the data in Reference 13, the following conclusions are drawn relative to electrocoagulation treatment of the San Leandro Plant effluent.

-- Electrocoagulation is not recommended as a pretreatment to UF since improvements in final effluent quality are modest. Also, no significant increase in UF flux is observed.

-- The plant wastewater flow is only 19 m^3/day (5000 gpd). The electrocoagulation process is better suited for total wastewater flows of >38 m^3/day (10,000 gpd).

-- The high variability of the San Leandro effluent makes electrocoagulation treatment difficult. Continuous operator attendance would be predicted.

-- While electrocoagulation treatment (or pretreatment) is not recommended at San Leandro, it may be suitable, in terms of both effluent quality and cost-effectiveness, at larger plants.

SECTION 8

SUMMARY OF ULTRAFILTRATION SYSTEM OPERATION AT THE DEWEY AND ALMY CHICAGO, ILLINOIS, PLANT

INTRODUCTION

The Chicago, Illinois plant of the Dewey and Almy Chemical Division of W.R. Grace & Co. manufactures the division's line of container sealing compounds and produces Darex and Rock Processing Chemicals for the Construction Products Division. Although the Chicago plant produces a similar line of products as the San Leandro, California plant, there are wide variations in product mix and hence differences exists in the type and quantity of pollutants generated between the two plants. This dissimilarity was sufficient to warrant separate piloting of waste treatment schemes at both locations.

In 1971, a Dissolved Air Flotation (DAF) system was installed to reduce the oils and grease loading in the Chicago plant effluent. The system improved the quality of the plant's effluent in terms of oil and grease content, however, due to the effluent's variability from hour to hour, there were frequent periods during which the pollutant levels were excessive. A chemical treatment pilot system was installed in conjunction with the DAF unit in 1973 after an initial feasibility study by Dearborne Environmental Engineers (a division of W.R. Grace) and successful bench-scale tests. Experience with the pilot system, discussions with chemical treatment system users, and computer simulations indicated that this treatment method still had some disadvantages. In particular, the system was unable to handle certain chemical compositions, thus the effluent would be out of specification (i.e., greater than 100 ppm oils and grease) 5% to 10% of the time. To obtain a higher degree of compliance over that attainable with chemical treatment an alternative method, ultrafiltration, was proposed, piloted, and finally accepted.

OVERVIEW OF UF SYSTEM OPERATION

A full-scale ultrafiltration system was installed in the Chicago plant under Metropolitan Sanitary District (MSD) of greater Chicago Permit Number 74-602 in 1974 at a capital cost of $180,000. This cost includes the UF system and all associated controls; platforming around the system; tanks with capacities of 0.95 m^3 (250 gal), 9.5 m^3 (2,500 gal), 18.9 m^3 (5,000 gal), 26.5 m^3 (7,000 gal) and 75.8 m^3 (20,000 gal); transfer pumps; piping with

electrical tracer lines; a building to house the secondary sump; and, all installation expenses. The UF system is an Abcor, Inc. Model UF 384 FEG incorporating 78.5 m^2 (845 sq. ft.) of Type HFD* membrane in a tubular configuration. The time-weighted average permeate flow (during 1976) has been 71.1 m^3/day (18,750 gpd) while concentrating the retained pollutants to an average of 10% total solids.

A summary of UF system separation performance for a number of contaminants is presented in Table 30. The removal efficiency data in Table 30 are calculated on a UF concentrate, rather than plant effluent basis. Therefore, the more meaningful data are the average contaminant loadings in the permeate. The oil and grease (hexane extractibles) loading has averaged 35 mg/ℓ compared to an MSD specification of 100 mg/ℓ; the suspended solids concentration has averaged 24 mg/ℓ. Iron and zinc concentrations in the permeate have averaged 0.8 mg/ℓ and 1.25 mg/ℓ, respectively. Similar to the San Leandro results, modest reductions in BOD are achieved by the UF membranes and average BOD and COD loadings are in excess of the contractor's recommendations for BPCTCA, BADCT, and BATEA guidelines.

It has been observed in Chicago that permeate quality does not degrade as the process waste material builds in concentration. As expected, however, permeate flow decreases with increasing solids concentration. A regression analysis was performed on data collected during the first two months of system operation to model the relationship between permeate throughput and percent total solids. The following relationship was derived:

$$J_S = 1.324 \log (38.52/C_b) \qquad (9)$$

where,

J_S = permeate flux, m^3/m^2-day
C_b = bulk solids concentration, % total solids.

This model, together with plant operating conditions, aids the UF system operator in predicting when the system should be shut down, the concentrate scavenged, and the membranes cleaned.

The concentrated wastes are disposed of by contract hauling and the waste sludge is chemically treated by the scavenger prior to its ultimate discharge. EPA regulations maintain, however, that liabilities reside with the plant producing the sludge for all damages incurred by any party as a result of adverse environmental effects, directly or indirectly related to the disposed wastes.

OPERATING DATA AND COSTS FOR 1976

For the year 1976 the UF system processed 15,463 m^3 (4,080,000 gal) of wastewater averaging 71.1 m^3/day (18,750 gpd). The UF system throughput and the permeate oils and grease loading are summarized in Table 31 by month

*Note: Type HFM membranes were not commercially available in 1974.

TABLE 30. AVERAGE UF PERMEATE QUALITY DURING PROCESSING OF CHICAGO PLANT EFFLUENT.

Assay	Average Concentration in UF Concentrate (mg/ℓ)	Average Concentration in UF Permeate (mg/ℓ)	Average Removal Efficiency*	MSD Specification (mg/ℓ)
Total Hexane Extractibles	3,580	35	99.1	100
Biodegradable Hexane Extractibles	3,290	31	99.1	
Non-Biodegradable Hexane Extractibles	242	4	98.3	
Total Suspended Solids	1,640	24	98.5	
BOD	1,290	1,200	7.0	
COD	21,200	6,080	71.3	
Iron	7.5	0.8	40.0	50
Zinc	104.0	1.25	98.8	15

*Removal efficiency calculated on concentrate, rather than feed, basis.

TABLE 31. AVERAGE CHICAGO PLANT UF SYSTEM OPERATING DATA DURING 1976.

Month	Total Permeate Flow (m^3)	% of Design Capacity	Hexane Extractibles (mg/ℓ)
January	1,189	75.6	55
February	1,920	121.9	38
March	1,619	99.3	43
April	1,603	116.6	39
May	2,269	116.0	45
June	1,137	75.5	106 *
July	1,694	105.9	77
August	594	55.5	N.A.**
September	1,114	76.1	58
October	1,230	59.1	32
November	459	53.9	31
December	633	67.0	34
Average	1,288	86.8	51

* Major product spill incurring 2 days out of compliance. Remainder of month averaged 30 mg/ℓ.

** Not available.

and broken down to weekly averages in Appendix B. The system throughput averaged 86.8% of the design capacity in 1976. In 1975 this figure was 110.9%. The problems which led to lower flux levels stemmed from accidental product and/or raw material spillage resulting in either a fouling of the membrane or a lowering of feed pH. On one occasion approximately 90.7 kg (200 lbs) of a latex were inadvertently spilled. This resulted in a non-removable coating of the membrane necessitating total membrane replacement.*

Due to the design and layout of the Chicago plant and pollution control system, rain water and material spillage from one railroad track gets carried into the system's collection network. This results, on a rainy day, in low pH; the level of acidity being proportional to the severity of the rain storm. Low pH (<7) has been found to decrease the permeation rate by as much as 28%. If a further decrease in pH occurs (to <5.5) fouling results and the system must be shutdown and cleaned.

The operating costs incurred during 1976 are presented in Table 32. For comparison, both the 1975 and 1976 operating costs are given. The total costs were $\$3.34/m^3$ ($12.66/1000 gal) in 1975 and $\$3.51/m^3$ ($13.23/1000 gal) in 1976. The increase of $\$0.15/m^3$ ($0.57/1000 gal) in 1976 over 1975 is attributable to a 5% increase in total operating time and increased power costs. The 18% lower throughput in 1976, resulted for the cost saving measure of increasing the UF concentrate solids loading before scavenging. By operating at a higher system conversion a $\$0.14/m^3$ ($0.53/1000 gal) reduction in operating costs was realized. The most significant operating expense at the Chicago plant is surfactant addition. This process step accounts for 26.5% of the total waste treatment operating costs but, as observed in the San Leandro field demonstration test, it will not be required at all manufacturing sites. The labor costs of $0.45 to $\$0.50/m^3$ ($1.7 to 1.9/1000 gal) are associated almost entirely with sludge handling activities and do not represent operator requirements for the UF system per se.

In conclusion, the Chicago Plant's water pollution control system, utilizing ultrafiltration as the means of treatment has:

1. Reduced the concentration of oils and grease and other major pollutants to well within MSD specifications.
2. Maintained a 99% compliance level with MSD specifications.
3. Required minimal operator attention.

Furthermore, unlike chemical treatment, ultrafiltration is capable of accepting tertiary treatment equipment in the form of ozonation or reverse osmosis. In light of the national goal to eliminate all industrial discharges by 1985, this adaptability is a decided advantage.

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*Again, it must be noted that Type HFM membranes which can be solvent cleaned were not commercially available at the time of the Chicago UF system installation.

TABLE 32. ANNUAL OPERATING COSTS FOR CHICAGO PLANT WASTE TREATMENT SYSTEM

Item	1976 FY Costs $	1976 FY Costs $/m^3	1975 FY Costs $	1975 FY Costs $/m^3
Payroll	7,163	0.46	9,579	0.51
Sewer Tax	1,346	0.09	1,484	0.08
Surfactant	14,306	0.93	16,677	0.89
Sludge Removal	5,195	0.34	6,100	0.32
UF Concentrate Removal	2,849	0.18	6,087	0.32
Analytical Laboratory Charges	1,684	0.11	2,409	0.13
Power	9,760	0.63	6,822	0.36
Abcor, Inc. Services	2,366	0.15	1,498	0.08
Membrane Replacement	8,693	0.56	8,965	0.48
Miscellaneous	999	0.06	3,208	0.17
Total	$54,361	$3.51/m^3	$62,829	$3.34/m^3
Total m^3 Permeated	15,463		18,810	
Design Capacity, m^3, @ 81.75 m^3/day	17,813		16,964	
Total Operating Hours	5,223		4,973	
% Time on Stream	59.6		56.8	
% of Design Capacity	86.8		110.9	

SECTION 9

FULL-SCALE SYSTEM DESIGN AND ECONOMICS

FULL-SCALE SYSTEM DESIGN

Based on the experimental results of the field demonstration program, the preliminary posttreatment process experimentation and the operation of the ultrafiltration system at the Grace Chicago Plant a full-scale treatment system has been conceptualized. A P&I drawing of the proposed treatment system for adhesives and sealants manufacturing wastes is presented in Figure 15. The various plant waste streams flow into the plant sump where partial equalization takes place. A transfer pump, signaled by a level controller in the sump, passes the plant effluent to the first of a series of settling, flotation, settling tanks. These tanks have a combined capacity of 1-1/2 days of waste equalization.

The overflow from the final settling tank is pumped to the ultrafiltration system feed tank. A pH monitor/controller is signaled by a probe in the UF feed tank and caustic is added as needed to maintain the waste pH above 8.0. The stability of the latices and oil emulsions is believed to improve when basic conditions are maintained. The pH adjustment step is, therefore, a precautionary step against latex destabilization and subsequent UF membrane fouling. This precaution may not be necessary at all manufacturing sites.

The pH adjusted feed is then circulated through the ultrafiltration membranes. Because of the nature of the waste stream and the possibility of severe latex fouling, tubular modules are preferred. The tubular modules can treat very dirty wastewaters and can be mechanically cleaned if necessary. Of the two Abcor, Inc. membrane types tested, the HFM membrane is preferred over the HFD membrane because of its greater resistance to environmental attack (i.e., its ability to be solvent cleaned, if necessary).

The UF system is operated in a semi-batch concentration mode. That is, fresh feed is continuously added to the UF feed tank until the desired system conversion (95%-98%) is nearly attained. At this point the contents of the UF feed tank are batch processed to the maximum conversion achievable. The concentrate is then drained from the UF system and hauled away by scavenger to land fill. The UF permeate is continuously withdrawn throughout the entire processing period.

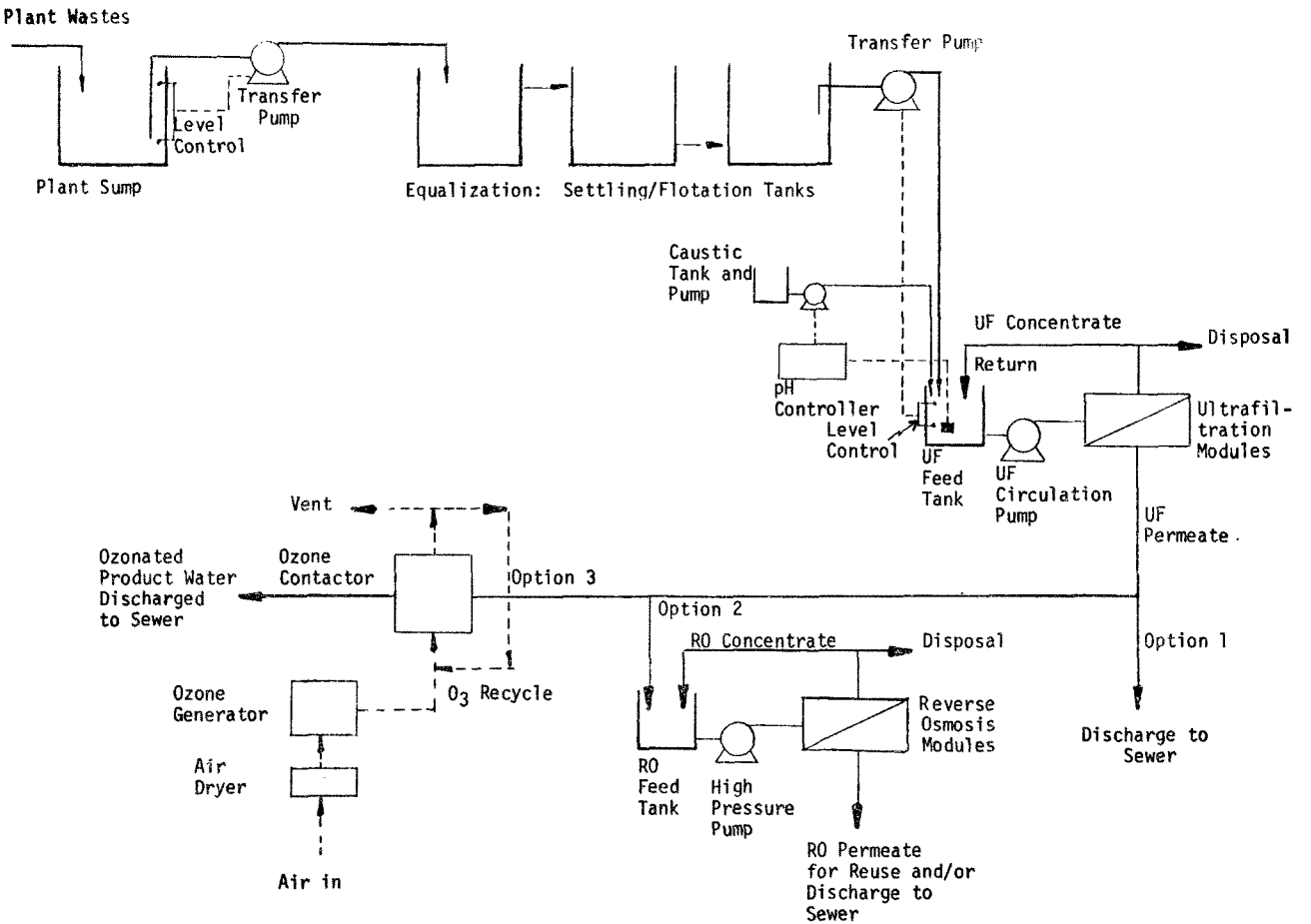

FIGURE 15. PROPOSED TREATMENT SYSTEMS FOR ADHESIVES AND SEALANTS MANUFACTURING WASTES.

The ultrafiltration system is constructed of carbon steel. The membrane shells (see Figure 1) are made of PVC plastic. The UF membranes can easily be removed from their shells and soaked in a solvent bath, if necessary.* A semi-automatic detergent cleaning package including clean tank, valving arrangements and timer-controlled alarms for signalling the system operator is included with the UF system.

The preferred ultrafiltration system operating conditions are a feed circulation rate of 163.5 m^3/day (30 gpm), an inlet pressure of 3.4 atm (50 psig) and a temperature of 32 to 43°C. Operation above 43°C may increase latex destabilization and promote membrane fouling. Operation below 32°C will lower membrane flux and cause an increase in the membrane area requirement.

Three options are considered for posttreatment of the UF permeate. The first option is to discharge the UF permeate directly to the sewer and allow Municipal Authorities to treat it biologically. It has been determined by the preparers of the draft "Development Document for Effluent Limitations Guidelines and Standards of Performance, Miscellaneous Chemicals Industry, Adhesives and Sealants Industries" (2) that BOD and COD are pollutants compatible with publicly-owned treatment plants. If the levels of non-compatible pollutants (e.g. phenolic compounds and cyanide) are below local standards it is anticipated that ultrafiltration will produce an effluent acceptable to Municipal Treatment.

The second posttreatment option involves the use of ozonation for oxidation of phenolic compounds and cyanide to acceptable discharge levels and for partial reduction in the BOD and COD loading of the ultrafiltrate. Dried, compressed air is passed through a corona discharge to generate the ozone on-site. The UF permeate is contacted with the ozone in a reaction vessel sized for the proper residence time. This residence time and the dosages of ozone required were not investigated during this program. It is expected that the high dissolved solids content of the ozonated product water will preclude its reuse within the plant and therefore, the ozone contactor effluent is discharged to the sewer.

The third posttreatment option is processing of the UF permeate by reverse osmosis. A polyamide membrane (PA-300, UOP, Inc.) in a spiral-wound configuration is potentially preferred. This membrane is selected

*A highly sophisticated system capable of solvent cleaning in situ, semi-automatic spongeball cleaning and designed with an explosion proof electrical system is available. The need for such a sophisticated system is questionable and, in most cases, will not justify the 40%-60% capital cost increase over a standard system.

because of the high pH of the UF permeate. The spiral-wound geometry is chosen over the hollow-fiber module design because the secondary precipitation of suspended solids, which was observed periodically in the UF permeate, may readily foul a hollow-fiber module.

The reverse osmosis membrane separation system is operated much the same as the UF system and is therefore not described. A system conversion of 90% to 95% is anticipated and it is projected that the RO product water will be reuseable within the plant for cooling water makeup. However, reuse has not been demonstrated during this program. Alternatively, the RO product water can be discharged directly to the sewer.

FULL-SCALE SYSTEM ECONOMIC PROJECTIONS

Economic projections are presented for the three options discussed above, namely:

Option 1: Equalization → Ultrafiltration → Discharge
Option 2: Equalization → Ultrafiltration → Ozonation → Discharge
Option 3: Equalization → Ultrafiltration → Reverse Osmosis → Reuse and/or Discharge

Cases are presented for adhesives and sealants manufacturing facilities discharging 3.8 m^3/day (1,000 gpd), 18.95 m^3/day (5,000 gpd) and 75.8 m^3/day (20,000 gpd) of wastewater. It is believed that a range of treatment systems of this magnitude will encompass the majority of manufacturing sites.

For the smallest plant (discharging 3.8 m^3/day) it was assumed that all manufacturing activities would occur during a single 8-hour shift. While the treatment system could operate 24 hours/day, it was designed on a single shift basis and therefore has an actual capacity of 11.4 m^3/day (3,000 gpd). The system to be used with plants discharging 18.95 m^3/day is designed for complete waste processing in two shifts (16 hours). This system therefore has the capability of treating 28.4 m^3/day (7,500 gpd). Thus, if either plants discharging 3.8 m^3/day (1000 gpd) or plants discharging 18.95 m^3/day (5000 gpd) expand their manufacturing operations, the originally purchased UF system will be able to handle the increased wastewater flow. The largest system (treating 75.8 m^3/day) is designed for 3 shift (24 hours) operation.

The design bases used for calculating the purchased equipment and annual operating costs are given in Table 33.

Purchased Equipment Cost Projections

Estimated purchased equipment costs for each unit process (equalization, ultrafiltration, ozonation and reverse osmosis) are presented in Table 34. Excluded from these cost projections are installation costs which will be highly site specific. If all utilities (power, water, and sewer connections,

TABLE 33. DESIGN BASES FOR PROJECTIONS OF UNIT PROCESS PURCHASED EQUIPMENT AND OPERATING COSTS.

Item	Total Plant Discharge (m^3/day) 3.8	18.95	75.8
EQUALIZATION			
1. Holding time, days	1.5	1.5	1.5
ULTRAFILTRATION			
1. Design flux, m^3/m^2-day	1.23	1.23	1.23
2. No. of shifts operated	1	2	3
3. Membrane area required, m^2	9.28	23.2	61.9
4. Expected membrane life, years	3	3	2
5. Membrane replacement costs, $/$m^2$	367	367	367
6. Pump efficiency, %	70	70	70
7. Membrane type	Abcor, Inc., Type HFM (non-cellulosic)		
8. Membrane configuration	Tubular, 0.025m dia. x 3.05m long		
9. Membrane area per module, m^2	0.2		
10. Module operating pressure, atm	3.4		
OZONATION			
1. Maximum power requirement projected by manufacturer, kw/day	5	5	5
REVERSE OSMOSIS			
1. Assumed flux, m^3/m^2-day	0.95	0.95	0.95
2. No.of shifts operated	1	2	3
3. Membrane area required, m^2	12	29.9	79.8
4. Expected membrane life, years	3	3	2
5. Membrane replacement costs, $/$m^2$	80.8	80.8	80.8
6. Pump efficiency, %	70	70	70
7. Membrane type	UOP, Inc., PA-300		
8. Module configuration	Spiral-wound,0.1m dia. x 0.97m long		
9. Membrane area per module, m^2	5.57		
GENERAL			
1. Operating labor, hours/day	1	2	4
2. Supervisory labor, hours/day	0.5	1	2
3. Power, $/kwh	0.04	0.04	0.04
4. Sludge and UF concentrate disposal costs, $/$m^3$ inlet to system (based on actual Chicago Plant operating costs)	0.19 to 0.34		
5. RO concentrate disposal costs, $/$m^3$ inlet to system	0.65		

TABLE 34. ESTIMATED PURCHASED EQUIPMENT COSTS FOR SELECTED UNIT PROCESSES OF VARIOUS CAPACITIES (THOUSANDS OF DOLLARS)

Item	Actual Capacity (m^3/day) 11.4	28.4	75.8
EQUALIZATION			
1. Settling/flotation tanks with 1-1/2 days retention	0.7	4.6	6.3
2. Transfer pumps, before and after item 1	1.0	1.5	2.0
	1.7	6.1	8.3
ULTRAFILTRATION			
1. Ultrafiltration system	20.0	45.0	80.0
2. pH control loop	1.8	1.8	1.8
	21.8	46.8	81.8
OZONATION			
1. Smallest capacity system of U.S. Ozonair Corp, including ozone generator, air dryer, air compressor, pump, contactor and automatic controls.	14.0	14.0	14.0
REVERSE OSMOSIS			
1. Reverse osmosis system (estimated from Reference (11))	15.0	25.0	35.0

etc.) are in place, and no new facility need be constructed, installation costs might be as low as 25% of the purchased equipment cost. On the other hand if significant site preparation is required, installation costs might be as high as 75% to 100% of the purchased equipment costs.

For ease of discussion the costs for the three system options are summarized in Table 35. For the smallest size system, designed to treat 3.8 m^3/day (1000 gpd) during 1 shift operation, purchased equipment costs range from $23,500 to $38,500 depending on the degree of treatment selected. Since the wastewater flow from these plants is so small, equalization and UF processing is the most practical treatment scheme. This would provide excellent "pretreatment" prior to discharge to a municipal sewer. The purchased equipment cost per m^3 of waste treated, based on Option 1 costs, is $6,184 ($23.50/gpd).

The purchased equipment costs for the 18.95 m^3/day (5000 gpd) systems range from $52,900 to $77,900. The costs per m^3 of waste treated are $2,792 ($10.58/gpd), $3,530 ($13.38/gpd) and $4,110 ($15.58/gpd) for Options 1, 2 and 3, respectively.

A range of purchased equipment costs from $90,100 to $125,100 is estimated for treatment systems handling 75.8 m^3/day (20,000 gpd) of wastewater. These costs translate to costs of $1,189/$m^3$/day ($4.5/gpd) for an Option 1 system, $1,373/$m^3$/day ($5.2/gpd) for an Option 2 system and $1,650/$m^3$/day ($6.26/gpd) for an Option 3 system.

Operating Cost Projections

Table 36 contains the annual operating cost projections for the three system capacities of each unit process. These costs were calculated using the design bases presented in Table 33 and are summarized in Table 37 by treatment system option. In both Tables 36 and 37 the costs given for disposal of the settling/flotation tank sludges and the UF concentrate are based on the actual Chicago Plant operating data for 1976. The costs for the RO concentrate disposal assume 95% conversion and a hauling cost of $0.013/liter ($0.05/gal). Thus, the RO concentrate disposal costs are $0.65/$m^3$ of inlet wastewater to the system.

Reviewing Table 36, it can be observed that the two most significant contributors to the operating costs are sludge disposal and labor. The sludge disposal costs may be significantly reduced if an effective means of sludge dewatering is identified. The labor costs, as observed from the Grace Chicago UF system experience, are mainly associated with sludge handling and not with the UF system. This labor can, therefore, be unskilled and for non-union plants the annual operating costs will lower significantly.

TABLE 35. ESTIMATED PURCHASED EQUIPMENT COSTS FOR THE THREE TREATMENT SYSTEM OPTIONS (THOUSANDS OF DOLLARS)*

	Option	Actual Sys. Cap. (m^3/day) 11.4	28.4	75.8
1.	Equalization → Ultrafiltration → Discharge	23.5	52.9	90.1
2.	Equalization → Ultrafiltration → Ozonation → Discharge	37.5	66.9	104.1
3.	Equalization → Ultrafiltration → Reverse Osmosis → Reuse and/or Discharge	38.5	77.9	125.1

* Does not include installation costs which are highly site specific.

TABLE 36. ESTIMATED ANNUAL OPERATING COSTS FOR UNIT PROCESSES OF VARIOUS CAPACITIES (THOUSANDS OF DOLLARS)*

Item	Actual Capacity (m^3/day) 11.4	28.4	75.8
EQUALIZATION			
1. Sludge Disposal	1.01	2.51	6.70
2. Capital amortization @ 10% for 10 yrs	0.17	0.61	0.83
ULTRAFILTRATION			
1. Membrane Replacement	1.14	2.83	11.3
2. Power	0.28	1.28	5.2
3. Chemicals, cleaning and pH adjustment	0.4	1.4	4.6
4. Concentrate Disposal	0.6	1.4	3.7
5. Capital amortization @ 10% for 10 yrs	2.18	4.68	8.18
OZONATION			
1. Power	0.42	0.83	1.25
2. Capital amortization @ 10% for 10 yrs	1.4	1.4	1.4
REVERSE OSMOSIS			
1. Membrane Replacement	0.45	0.90	3.4
2. Power	0.10	0.20	0.30
3. Concentrate Disposal	1.94	4.82	12.90
4. Capital amortization @ 10% for 10 yrs	1.5	2.5	3.5
GENERAL			
1. Operating Labor @ $7.5/hr plus 75% fringe and OH	3.4	6.8	13.6
2. Supervisory Labor @ $15/hr plus 75% fringe and OH	3.4	6.8	13.6

* Annual operating costs assume 260 days/year of operation

TABLE 37. ESTIMATED ANNUAL OPERATING COSTS FOR THE THREE TREATMENT SYSTEM OPTIONS (THOUSANDS OF DOLLARS)*

Option	Actual System Capacity (m^3/day) 11.4	28.4	75.8
1. Equalization → Ultrafiltration → Discharge	8.84	20.8	52.8
2. Equalization → Ultrafiltration → Ozonation → Discharge	11.0	23.7	56.8
3. Equalization → Ultrafiltration → Reverse Osmosis → Reverse and/or Discharge	13.2	29.9	74.3

* 90% of the treatment system operating and supervising labor is credited to the equalization/UF system.

The costs of operating a treatment system for a plant discharging 3.8 m^3/day (1000 gpd) are estimated to be \$8.91/m^3 (\$33.8/1000 gal) for Option 1; \$11.1/m^3 (\$42.0/1000 gal) for Option 2; and \$13.4/m^3 (\$50.8/1000 gal) for Option 3. For systems treating 5 times this amount of wastewater (18.95 m^3/day) the operating costs are \$4.22/m^3 (\$16.0/1000 gal) for Option 1; \$4.81/m^3 (\$18.2/1000 gal) for Option 2; and\$6.07/m^3 (\$23.0/1000 gal) for Option 3. The highest capacity system, treating 75.8 m^3/day (20,000 gpd) of wastewater has associated with it operating costs of \$2.68/m^3 (\$10.1/1000 gal) for Option 1; \$2.88/m^3 (\$10.9/1000 gal) for Option 2; and \$3.78/m^3 (\$14.3/1000 gal) for Option 3.

In none of the above cost projections for Option 3 (equalization, ultrafiltration, reverse osmosis, reuse and/or discharge) are any credits given for water reuse. The RO product water is believed to be reusable within the plant for cooling water makeup and area washdowns and may have other uses as well. However, until reuse is demonstrated application of credits may be premature. Also, the amount of credit to be applied would be highly site specific and would depend upon water use charges, sewer surcharges and the degree of water reuse achievable.

Comparison of Options 1, 2, and 3 Costs with the Preliminary BPCTCA, BADCT and BATEA Technology Costs

The Draft Development Document which presents the recommended Effluent Guidelines for the Adhesives and Sealants Industries (2) gives capital and operating costs for double-effect liquid evaporation of Subcategory B (water-based adhesive solutions containing synthetic and natural materials) and Subcategory C (solvent solution adhesives and cements generating contaminated wastewaters). These costs are given only for plants of a single size in each subcategory and are given in August, 1972 dollars. The same level of treatment is required to meet all three sets of standards: BPCTCA, BADCT and BATEA. Table 38 summarized the Development Document's cost projections. The Development Document also indicates that for a Subcategory B plant discharging 37.9 m^3 of waste per day (10,000 gpd), 56,700 kg (125,000 lbs) of sludge (dry-weight basis) will be generated from double-effect liquid evaporation and that for a Subcategory C plant discharging 22.7 m^3/day (6,000 gpd) of waste, 567 kg (1,250 lbs) of sludge will be generated. It is not clear, however, whether sludge disposal costs are included in the annual operating cost estimates.

Table 39 presents a comparison of Option 1, 2 and 3 system costs with the costs for double-effect liquid evaporation. The latter's costs were left in 1972 dollars. Using the costs derived during this program for a plant discharging 18.95 m^3/day (5,000 gpd) of waste and the Development Document's costs for a plant discharging 22.7 m^3/day (6,000 gpd) of waste as the closest point of comparison and leaving the Development Documents Costs in 1972 dollars the following observations are made:

TABLE 38. SUMMARY OF DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES PROJECTED COSTS FOR TREATMENT OF SUBCATEGORY B AND C ADHESIVES AND SEALANTS WASTEWATERS (2)*

Subcategory	Plant Wastewater Flow (m^3/day)	Proposed Treatment	Capital Costs, $	Annual Operating Costs Breakdown, $	
B. Water-based adhesives solutions containing sythetic and natural materials	37.9	double-effect liquid evaporation	412,000	Operating & Maintenance Energy & Power Capital Recovery plus return @ 10%, for 10 yrs Total	65,000 57,000 67,000 189,000
C. Solvent solution adhesives and cements generating contaminated wastewaters	22.7	double-effect liquid evaporation	324,000	Operating & Maintenance Energy & Power Capital recovery plus return @ 10%, for 10 yrs Total	56,000 30,000 53,000 139,000

* Costs are presented in August, 1972 dollars.

TABLE 39. COMPARISON OF OPTION 1, 2 AND 3 SYSTEM COSTS WITH DOUBLE-EFFECT LIQUID EVAPORATION COSTS

Treatment System Description	Daily Wastewater Discharge, m^3	Estimated Capital Costs, $	Estimated Annual Operating Costs, $	Estimated Operating Costs, $/m^3$ processed
Option 1. Equalization → Ultrafiltration → Discharge	3.8	23,500	8,800	8.91
	18.95	52,900	20,800	4.22
	75.8	90,100	52,800	2.68
Option 2. Equalization → Ultrafiltration → Ozonation → Discharge	3.8	37,500	11,000	11.1
	18.95	66,900	23,700	4.81
	75.8	104,100	56,800	2.88
Option 3. Equalization → Ultrafiltration → Reverse Osmosis → Reuse and/or Discharge	3.8	38,500	13,200	13.4
	18.95	77,900	29,900	6.07
	75.8	125,100	74,300	3.78
Development Document Proposed Treatment Equalization → Double-Effect Liquid Evaporation → Reuse and/or Discharge	22.7	324,000*	139,000*	23.6*
	37.9	412,999*	189,000*	19.1*

*Costs presented are in August, 1972 dollars

1. The capital cost for double-effect liquid evaporation is 6 times the Option 1 system cost, 4.8 times the Option 2 system cost and 4 times the Option 3 system cost.

2. The operating costs for double-effect liquid evaporation were estimated at $\$23.6/m^3$ ($\$89.4/1000$ gal) in 1972. Energy and power costs, which have clearly risen since 1972, make up 30% of this operating cost. The estimated operating costs for the Option 1, 2 and 3 systems are $\$4.22/m^3$ ($\$16.0/1000$ gal), $\$4.81/m^3$ ($\$18.2/1000$ gal) and $\$6.07/m^3$ ($\$23.0/1000$ gal), respectively.

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TABLE A1. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, TEST #1

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Suspended Solids	ASSAY (mg/ℓ) BOD_5	Arsenic	Cadmium	Total Chromium	Free Cyanide	Total Cyanide[1]	Lead	Mercury	Phenols	Zinc
Sump	8/16	1,050	408	7.5	3580	---	---	---	---	---	---	---	---	---	---
	8/20	468	96	8.4	3380	---	---	---	---	---	---	---	---	---	---
	8/16-8/20	575	110	7.7	9850	13,500	<0.2	<0.2	<0.5	0.36	1.7	<1	0.004	68	100
	8/23	364	116	7.1	924	---	---	---	---	---	---	---	---	---	---
	8/26	952	196	8.3	9350	---	---	---	---	---	---	---	---	---	---
	8/23-8/26	568	95	7.8	4650	14,000	<0.2	<0.2	<0.5	0.44	0.4	<1	0.001	60	740
After Settling	8/16-8/20	---	---	7.7	2320	---	---	---	---	---	---	---	---	---	---
	8/23-8/27	---	---	8.7	2820	---	---	---	---	---	---	---	---	---	---
UF Concentrate	8/16	755	110	8.4	1210	---	---	---	---	---	---	---	---	---	---
	8/20	11,000	800	6.3	6720	---	---	---	---	---	---	---	---	---	---
	8/16-8/20	4,580	268	6.5	7700	12,500	<0.2	<0.2	<0.5	0.53	11	<1	0.003	66	86
	8/23	6,650	408	7.5	7300	---	---	---	---	---	---	---	---	---	---
	8/26	18,800	2540	8.5	56,200	---	---	---	---	---	---	---	---	---	---
	8/23-8/27	9,320	1030	8.0	27,800	32,000	<0.2	<0.2	<0.5	2.44	<0.1	<1	0.007	38	920
UF Permeate	8/16	167	<5	8.9	80		---	---	---	---	---	---	---	---	---
	8/20	174	<5	6.6	100	---	---	---	---	---	---	---	---	---	---
	8/16-8/20	181	<5	7.2	110	13,500	<0.2	<0.2	<0.5	<0.26	9	<1	<0.001	24	15
	8/23	147	6	7.7	33	---	---	---	---	---	---	---	---	---	---
	8/26	205	9	8.9	13	---	---	---	---	---	---	---	---	---	---
	8/23-8/27	164	6	8.1	<5	12,000	<0.2	<0.2	<0.5	0.27	12	<1	0.002	6	60
San Leandro Municipal Discharge Limits			300/100[2]	>6.0	---	---	0.1	0.2	0.5	---	1.0	1.0	0.01	1.0[3]	3.0

[1] Interference in analysis suspected

[2] 300 mg/ℓ Oil and Grease of animal or vegetable origin, 100 mg/ℓ Oil and Grease of mineral or petroleum origin.

[3] 1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

TABLE A2. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, TEST #2

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Suspended Solids	BOD_5	Arsenic	Cadmium	Total Chromium	Free Cyanide	Total Cyanide[1]	Lead	Mercury	Phenols	Zinc
		ASSAYS(mg/ℓ)													
Sump	8/30	720	204	8.8	3060	---	---	---	---	---	---	---	---	---	---
	9/3	572	100	8.7	2580	---	---	---	---	---	---	---	---	---	---
	8/30-9/3	608	192	8.8	2900	14,000	<0.2	<0.2	<0.5	0.81	0.9	<1	.002	26	96
	9/6-9/10	3070	---	9.4	14,400	22,000	---	---	---	---	---	---	---	---	---
	9/14	136	36	7.8	387	---	---	---	---	---	---	---	---	---	---
	9/15	672	204	7.2	2580	---	---	---	---	---	---	---	---	---	---
	9/14-9/17	1150	248	7.3	4430	21,000	0.22	<0.2	<0.5	<2.6[4]	5.3	<1	.006	6.9	26
After Settling	8/30-9/3	---	---	8.6	1140	---	---	---	---	---	---	---	---	---	---
	9/6-9/10	584	---	8.7	1750	10,000	---	---	---	---	---	---	---	---	---
	9/14-9/17	---	---	7.6	697	---	---	---	---	---	---	---	---	---	---
UF Concentrate	8/30	220	28	8.9	680	---	---	---	---	---	---	---	---	---	---
	9/3	2140	964	9.0	24,100	---	---	---	---	---	---	---	---	---	---
	8/30-9/3	1680	664	9.0	14,700	14,000	<0.2	<0.2	<0.5	2.6	9	<1	.003	15	340
	9/6-9/10	4310	---	9.1	32,800	20,000	---	---	---	---	---	---	---	---	---
	9/14	4180	3990	9.1	23,200	---	---	---	---	---	---	---	---	---	---
	9/15	3600	1840	7.6	25,200	---	---	---	---	---	---	---	---	---	---
	9/14-9/17	6140	4750	8.3	31,600	30,000	0.35	<0.2	<0.5	3.9	1.5	<1	.006	11.3	810
UF Permeate	8/30	34	<5	7.2	<5	---	---	---	---	---	---	---	---	---	---
	9/3	71	<5	9.8	6	---	---	---	---	---	---	---	---	---	---
	8/30-9/3	55	<5	7.8	11	10,000	<0.2	<0.2	<0.5	0.55	9	<1	.003	2.0	1.9
	9/6-9/10	61	---	8.7	14	10,500	---	---	---	---	---	---	---	---	---
	9/14	60	14	8.2	<5	---	---	---	---	---	---	---	---	---	---
	9/15	28	<5	7.1	10	---	---	---	---	---	---	---	---	---	---
	9/14-9/17	47	<5	7.9	<5	19,000	<0.2	<0.2	<0.5	0.26	2.3	<1	<.001	6.1	5.4
San Leandro Municipal Discharge Limits		300/100[2]		>6.0	---	---	0.1	0.2	0.5	---	1.0	1.0	0.01	1.0[3]	3.0

[1] Interference in analysis suspected.

[2] 300 mg/ℓ Oil and Grease of animal or vegetable origin, 100 mg/ℓ Oil and Grease of mineral or petroleum origin.

[3] 1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

[4] Sample diluted 1:10 to minimize interference; detection limit increases.

TABLE A3. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, TEST #3

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Suspended Solids	ASSAYS (mg/ℓ) BOD_5	Arsenic	Cadmium	Total Chromium	Free Cyanide	Total Cyanide	Lead	Mercury	Phenols	Zinc
Sump	9/20	2430[5]	124	8.8	1680	---	---	---	---	---	---	---	---	---	---
	9/23	3060[5]	312	9.0	2950	---	---	---	---	---	---	---	---	---	---
	9/20-9/24	2800[5]	136	9.1	5750	10,000	<0.2	<0.2	<0.5	<2.6[4]	1.6	<1	.005	275	31
After Settling	9/20	---	---	9.6	1390	---	---	---	---	---	---	---	---	---	---
UF Concentrate	9/20	2470[5]	284	8.8	1570	---	---	---	---	---	---	---	---	---	---
	9/23	2140[5]	68	9.3	11,000	---	---	---	---	---	---	---	---	---	---
	9/20-9/24	2300[5]	172	9.3	7,580	12,000	<0.2	<0.2	<0.5	<2.6[4]	0.8	<1	.006	132	72
UF Permeate	9/20	234[5]	10	8.6	<5	---	---	---	---	---	---	---	---	---	---
	9/23	260[5]	<5	9.4	26	---	---	---	---	---	---	---	---	---	---
	9/20-9/24	237[5]	<5	8.4	14	9,500	<0.2	<0.2	<0.5	0.36	1.8	<1	.002	52	0.66
San Leandro Municipal Discharge Limits		300/100[2]		>6.0	---	---	0.1	0.2	0.5	---	1.0	1.0	0.01	1.0[3]	3.0

[1] Interference in analysis suspected.

[2] 300/ mg/ℓ Oil and Grease of animal or vegetable origin, 100 mg/ℓ Oil and Grease of mineral or petroleum origin.

[3] 1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

[4] Sample diluted 1:10 to minimize interference; detection limit increases.

[5] Freon contaminated. Value reported is maximum possible oil and grease.

TABLE A4. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, TEST #4

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Suspended Solids	BOD_5	ASSAYS(mg/ℓ) Arsenic	Cadmium	Total Chromium	Free Cyanide	Total Cyanide	Lead	Mercury	Phenols	Zinc
Sump	9/29	1,120[5]	456	11.0	34,000	---	---	---	---	---	---	---	---	---	---
	10/1	478[5]	100	6.1	14,000	---	---	---	---	---	---	---	---	---	---
	9/29-10/1	494[5]	132	8.3	4,760	9,300	<0.2	<0.2	<0.5	<2.6[4]	0.9	<1	.001	23	35
After Settling	9/30	---	---	8.5	2,300	---	---	---	---	---	---	---	---	---	---
UF Concentrate	9/29	416[5]	184	8.0	17,500	---	---	---	---	---	---	---	---	---	---
	10/1	522[5]	100	9.1	4,280	---	---	---	---	---	---	---	---	---	---
	9/29-10/1	866[5]	520	8.9	4,360	15,600	0.2	<0.2	<0.5	<2.6[4]	4.5	2.4	.002	63	170
UF Permeate	9/29	9[5]	15	8.3	12	---	---	---	---	---	---	---	---	---	---
	10/1	65[5]	11	9.7	91	---	---	---	---	---	---	---	---	---	---
	9/29-10/1	22[5]	10	8.9	18	10,000	<0.2	<0.2	<0.5	0.65	3.8	<1	.001	49	0.61
San Leandro Municipal Discharge Limits		300/100[2]		>6.0	---	---	0.1	0.2	0.5	---	1.0	1.0	0.01	1.0[3]	3.0

[1] Interference in analysis suspected.

[2] 300/mg/ℓ Oil and Grease of animal or vegetable origin, 100 mg/ℓ Oil and Grease of mineral or petroleum origin.

[3] 1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

[4] Sample diluted 1:10 to minimize interference; detection limit increases.

[5] Freon contaminated. Value reported is maximum possible oil and grease.

TABLE A5. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, TEST #5

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Suspended Solids	ASSAYS(mg/ℓ) BOD_5	Arsenic	Cadmium	Total Chromium	Free Cyanide	Total [1] Cyanide	Lead	Mercury	Phenols	Zinc
Sump	10/14	725[5]	203[5]	9.2	1,950	980	<0.2	<0.2	<0.5	<2.6[4]	---	<1	---	1.3	80
	10/15	3020[5]	984[5]	9.5	14,500	---	---	---	---	---	---	---	---	---	---
	10/18	4140[5]	1060[5]	8.6	11,500	---	---	---	---	---	---	---	---	---	---
	10/22	1370[5]	220[5]	9.0	1,860	---	---	---	---	---	---	---	---	---	---
	10/18-10/22	1120	780[5]	9.2	6,220	8600	<0.2	---	---	<2.6[4]	<0.5	---	---	15.8	58
After Settling	10/14	---	---	7.8	800	---	---	---	---	---	---	---	---	---	---
	10/15	---	---	9.3	1,800	---	---	---	---	---	---	---	---	---	---
	10/18-10/22	---	---	9.4	3,780	---	---	---	---	---	---	---	---	---	---
UF Concentrate	10/14	900[5]	238[5]	7.2	7,000	3,600	<0.2	<0.2	<0.5	<2.6[4]	---	<1	---	3.9	900
	10/15	2040[5]	556	8.8	11,700	---	---	---	---	---	---	---	---	---	---
	10/18	2000[5]	484[5]	9.1	11,400	---	---	---	---	---	---	---	---	---	---
	10/22	7230[5]	1760[5]	9.4	82,600	---	---	---	---	---	---	---	---	---	---
	10/18-10/22	6870	3010[5]	9.0	27,900	13,000	<0.2	---	---	9.4	0.6	---	---	16.4	1200
UF Permeate HFD	10/14	254[5]	<5[5]	7.2	<5	450	<0.2	<0.2	<0.5	<0.26	---	<1	---	1.7	36
	10/15	91[5]	<5[5]	9.3	<5	---	---	---	---	---	---	---	---	---	---
	10/18	13	14[5]	9.1	22	---	---	---	---	---	---	---	---	---	---
	10/22	37	16[5]	9.4	9	---	---	---	---	---	---	---	---	---	---
	10/18-10/22	22	13[5]	8.7	16	4200	<0.2	---	---	0.77	0.4	---	---	3.6	3.4
HFM	10/14	256[5]	<5[5]	7.0	<5	590	<0.2	<0.2	<0.5	<0.26	---	<1	---	1.7	47
	10/15	110[5]	6[5]	9.0	<5	---	---	---	---	---	---	---	---	---	---
	10/18	17	15[5]	9.1	<5	---	---	---	---	---	---	---	---	---	---
	10/22	38	13[5]	9.3	8	---	---	---	---	---	---	---	---	---	---
	10/18-10/22	20	17[5]	8.8	14	4000	<0.2	---	---	0.65	0.4	---	---	8.0	4.3
San Leandro Municipal Discharge Limits		300/100[2]		>6.0	---	---	0.1	0.2	0.5	---	1.0	1.0	0.01	1.0[3]	3.0

[1] Interference in analysis suspected.

[2] 300 mg/ℓ Oil and Grease of animal or vegetable origin, 100 mg/ℓ Oil and Grease of mineral or petroleum origin.

[3] 1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

[4] Sample diluted 1:10 to minimize interference; detection limit increases.

[5] Freon contaminated. Value reported is maximum possible oil and grease.

TABLE A6. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, TEST #6

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Suspended Solids	ASSAYS (mg/ℓ) BOD_5	Arsenic	Cadmium	Total Chromium	Free Cyanide	Total Cyanide[1]	Lead	Mercury	Phenols	Zinc
Sump	11/2	321	35	9.3	940	---	---	---	---	---	---	---	---	---	---
	11/1-11/5	1820	735	9.3	9,900	9,900	<0.2	---	---	2.6	<0.5	---	---	624	35
	11/8	4650	2370	9.5	70,800	---	---	---	---	---	---	---	---	---	---
	11/12	21,400	500	9.3	17,700	---	---	---	---	---	---	---	---	---	---
	11/8-11/12	22,000	820	9.2	18,400	10,500	<0.2	---	---	<2.6	0.9	---	---	28	13
After Settling	11/1-11/5	---	---	9.3	4,820	---	---	---	---	---	---	---	---	---	---
	11/8-11/12	---	---	8.8	1,130	---	---	---	---	---	---	---	---	---	---
UF Concentrate	11/2	846	334	8.9	7,540	---	---	---	---	---	---	---	---	---	---
	11/1-11/5	1790	1060	9.1	11,900	6,800	<0.2	---	---	7.2	<0.5	---	---	172	140
	11/8	4600	3170	9.0	18,400	---	---	---	---	---	---	---	---	---	---
	11/12	13,800	3750	9.6	50,100	---	---	---	---	---	---	---	---	---	---
	11/8-11/12	13,900	4170	9.3	33,100	17,200	<0.2	---	---	11	0.75	---	---	123	170
UF Permeate HFD	11/2	90	8	8.8	8	---	---	---	---	---	---	---	---	---	---
	11/1-11/5	67	7	9.0	19	6,400	<0.2	---	---	0.55	0.2	---	---	203	0.51
	11/8	99	20	9.0	6	---	---	---	---	---	---	---	---	---	---
	11/12	62	12	8.6	<5	---	---	---	---	---	---	---	---	---	---
	11/8-11/12	65	<5	8.5	<5	10,600	<0.2	---	---	0.39	3.2[6]	---	---	140	0.69
HFM	11/2	58	<5	8.8	12	---	---	---	---	---	---	---	---	---	---
	11/1-11/5	38[5]	9	9.0	12	6,400	<0.2	---	---	0.52	0.5	---	---	220	1.0
	11/8	107	<5	8.9	<5	---	---	---	---	---	---	---	---	---	---
	11/12	116	<5	8.7	<5	---	---	---	---	---	---	---	---	---	---
	11/8-11/12	65	<5	8.6	<5	11,400	<0.2	---	---	0.39	4.1[6]	---	---	100	1.4
San Leandro Municipal Discharge Limits			300/100[2]	>6.0	---	---	0.1	0.2	0.5	---	1.0	1.0	0.01	1.0[3]	3.0

[1] Interference in analysis suspected.

[2] 300 mg/ℓ Oil and Grease of animal or vegetable origin, 100 mg/ℓ Oil and Grease of mineral or petroleum origin.

[3] 1.0 mg/ℓ phenolic compounds which cannot be recovered by the Agency's wastewater treatment process.

[4] Sample diluted 1:10 to minimize interference; detection limit increases.

[5] Total hexane extractibles on same sample = 44 mg/ℓ.

[6] Assay being repeated.

TABLE A7. ANALYTICAL DATA FROM THE UF CONCENTRATION OF LECTROCLEAR EFFLUENT, TEST #7

Sampling Station	Date	ASSAYS (mg/l) Total Freon Extractibles	pH	Total Suspended Solids	BOD_5	COD	Total Cyanide	Phenolic Compounds	Zinc
Swift	12/14	20.7	--	188	--	--	--	246	3.5
Lectroclear	12/15	17.2	--	59	5,610	12,200	0.8	29.5	9.5
Effluent	12/16	26.0	--	85	12,500	20,200	4.4	9.9	2.8
UF Concentrate	12/14	51.6	--	490	--	--	--	145	7.9
	12/15	50.0	8.8	274	6,020	15,500	13.4	8.0	8.9
	12/16	40.8	8.6	350	9,800	19,900	5.8	11	5.2
UF Permeate	12/14	19.2	--	32	--	--	--	158	1.0
HFM	12/15	15.8	8.6	26	3,210	12,300	0.6	18.0	0.42
	12/16	26.4	7.4	44	9,750	19,100	8.6	9.0	0.34
HFD	12/16	25.4	7.3	54	8,790	19,100	5.0	11	0.32
San Leandro Municipal Discharge Limits		300	>6.0	--	--	--	1.0	1.0	3.0

TABLE A8. ANALTYICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT WITH SURFACTANT ADDITION, TEST #8

Sampling Station	Date	Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Solids	Total Suspended Solids	BOD	Soluble BOD	COD	Soluble COD	Phenolic Compounds	Zinc
Sump	2/14	338	110	8.7	9,350	1,580	7,270	6,030	33,900	30,900	638	18
	2/18	668	68	8.9	13,200	7,040	5,640	3,760	28,600	20,600	6.0	14
	2/14-2/18	144	45	8.9	9,030	4,720	7,560	7,480	23,800	19,300	235	19
	2/22	58	16	8.4	1,980	320	2,460	3,140	6,350	5,520	68	24
	2/25	288	20	7.9	6,520	2,100	12,300	17,200	30,200	26,500	2.8	2.4
	2/22-2/25	162	54	8.7	3,310	3,300	6,860	7,400	14,900	12,000	110	12
Feed After Settling	2/14	410	160	9.2	6,180	3,620	6,110	3,140	21,300	15,000	18	40
	2/18	50	11	8.7	7,330	546	5,280	4,680	13,100	11,000	205	23
	2/14-2/18	438	226	9.2	4,520	932	4,120	2,220	16,800	13,100	80	22
	2/22	111	11	8.3	9,490	1,440	13,000	12,700	31,000	26,800	210	18
	2/25	322	74	8.7	4,890	1,650	12,400	10,900	20,900	18,500	46	23
	2/22-2/25	181	40	8.4	6,130	1,370	12,000	13,200	23,900	20,000	118	22
UF Concentrate	2/14	580	64	9.2	4,440	1,080	4,900	3,680	17,100	14,800	35	27
	2/18	668	230	8.6	91,800	72,000	17,200	13,200	181,000	149,000	375	1,100
	2/14-2/18	1,810	394	9.0	36,500	17,000	11,640	10,160	140,000	84,100	77	250
	2/22	344	31	8.8	137,000	91,000	24,800	17,200	200,000	183,000	600	2,000
	2/25	503	78	9.3	54,000	34,000	16,400	14,000	143,000	91,200	170	620
	2/22-2/25	557	96	8.8	93,900	61,300	22,200	13,300	196,000	138,000	136	24
UF Permeate	2/14	156	9.0	9.2	2,260	27	3,990	3,990	13,300	13,000	60	10
	2/18	214	14	8.6	8,100	80	5,160	4,620	23,800	22,800	49	16
	2/14-2/18	299	11	8.9	3,410	27	5,840	5,130	14,000	13,900	32	8.5
	2/22	196	7.0	8.7	6,700	132	8,860	10,200	21,800	20,600	388	1,100
	2/25	147	10	8.9	3,340	48	9,010	10,400	17,000	16,100	96	3.4
	2/22-2/25	156	7.0	8.7	5,080	80	10,200	10,300	19,500	18,600	160	8.5
San Leandro Municipal Discharge Limits			300/100[1]	>6.0	---	---	---	---	---	---	1.0[2]	3.0

[1] 300 mg/l Oil and Grease of animal or vegetable origin, 100 mg/l Oil and Grease of mineral or petroleum origin.

[2] 1.0 mg/l phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

TABLE A9. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT LESS CPD STREAM, TEST #9

Sampling Station	Date	ASSAYS (mg/ℓ) Total Freon Extractibles	Non-Polar Freon Extractibles	pH	Total Solids	Total Suspended Solids	BOD	Soluble BOD	COD	Soluble COD	Phenolic Compounds	Zinc	Total Cyanide
Sump	3/3	2,320	520	8.4	17,200	11,100	6,100	5,260	29,900	18,000	5	48	-
	3/4	228	56.4	8.7	1,810	666	4,740	3,780	5,820	5,320	12	32	-
	3/7	119	-	6.9	-	594	-	-	-	-	0.50	250	2.5
	3/11	7,160	-	8.3	-	57,400	-	-	-	-	1.0	75	3
	3/7-3/11	2,610	-	7.7	-	11,200	5,070	-	26,800	-	10	180	3
Feed After Settling	3/3	816	201	8.5	5,350	3,170	4,480	4,760	18,900	13,500	22	18	-
	3/4	577	248	8.6	4,420	2,190	5,130	5,040	17,300	12,500	7.5	28	-
	3/7	97	-	8.2	-	242	-	-	-	-	1	2	3
	3/11	667	-	8.3	-	2,510	-	-	-	-	4.3	1.1	5
	3/7-3/11	736	-	8.3	-	2,370	6,740	-	16,400	-	6.5	38	5.5
UF Concentrate	3/3	6,670	2,160	9.0	40,400	24,900	6,150	5,540	95,900	58,500	45	280	-
	3/4	14,900	7,600	9.0	66,100	54,700	7,700	6,310	143,000	66,000	8.3	140	-
	3/7	7,180	-	9.1	-	95,400	-	-	-	-	5.0	450	4.0
	3/11	10,200	-	8.1	-	69,500	-	-	-	-	9.0	750	7.0
	3/7-3/11	8,490	-	8.3	-	49,000	12,500	-	114,000	-	6.0	380	4.0
UF Permeate	3/3	149	2.0	8.6	1,460	12	4,790	5,040	10,600	10,500	5.0	0.6	-
	3/4	132	43.6	8.6	1,820	12	5,290	5,600	12,900	12,400	0.6	1.4	-
	3/7	234	-	9.2	-	28	-	-	-	-	5	0.9	4
	3/11	195	-	8.3	-	24	-	-	-	-	0.8	11.0	4.5
	3/7-3/11	953	-	8.5	-	16	3,840	-	11,400	-	0.5	1.6	4.0
		300/100[1]		>6.0	-	-	-	-	-	-	1.0[2]	3.0	1.0

[1] 300 mg/ℓ oil and grease of animal or vegetable origin, 100 mg/ℓ oil and grease of mineral or petroleum origin.

[2] 1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

TABLE A10. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT LESS "Z" STREAM, TEST #10

Sampling Station	Date	Total Freon Extractibles (mg/ℓ)	pH (units)	Total Solids (mg/ℓ)	Total Suspended Solids (mg/ℓ)	BOD (mg/ℓ)	COD (mg/ℓ)	Phenolic Compounds (mg/ℓ)	Zinc (mg/ℓ)
Sump	4/29	1,280	8.5	3,700	2,370	--	--	6.6	47
	4/26-4/29	626	9.4	8,000	2,390	1,390	13,900	106	65
	5/6	880	9.2	7,890	5,580	--	--	175	39
	5/2 -5/6	1,290	9.1	8,180	5,230	1,850	25,700	44	55
Sump After Settling	4/29	793	9.3	14,300	2,910	--	--	140	110
	4/26-4/29	483	9.7	14,100	2,970	3,750	24,400	103	100
	5/6	1,230	9.2	9,240	4,820	--	--	22	55
	5/2 -5/6	712	9.1	10,100	4,400	1,880	21,100	45	50
UF Concentrate	4/29	5,450	9.3	86,600	62,600	--	--	80	2000
	4/26-4/29	1,490	9.6	44,200	20,700	5,470	86,100	72	650
	5/6	22,700	8.9	160,000	140,000	--	--	32	2800
	5/2 -5/6	16,300	8.9	124,000	94,800	7,760	340,000	98	2100
UF Permeate (New Membranes)	4/29	124	9.4	7,810	154	--	--	112	16
	4/26-4/29	294	9.8	7,000	150	2,230	10,900	56	14
	5/6	74	9.0	2,960	138	--	--	28	9.5
	5/2 -5/6	139	9.0	5,100	136	1,300	6,570	89	16
UF Permeate (Original Membranes)	4/29	106	9.5	9,700	192	--	--	143	23
	4/26-4/29	205	9.7	8,370	132	2,500	13,800	52	18
	5/6	160	9.0	3,240	108	--	--	30	9.6
	5/2 -5/6	298	9.0	5,550	186	1,500	6,990	89	14
San Leandro Municipal Discharge Limits		300/100*	>6.0	--	--	--	--	1.0†	3.0

*300 mg/ℓ oil and grease of animal or vegetable origin, 100 mg/ℓ oil and grease of mineral or petroleum origin.
†1.0 mg/ℓ phenolic compounds which cannot be removed by the agency's wastewater treatment process.

TABLE A11. ANALYTICAL DATA FROM UF CONCENTRATION OF SAN LEANDRO PLANT EFFLUENT, MAXIMUM CONCENTRATION TEST, TEST #12

Sampling Station	Date	Total Freon Extractibles (mg/ℓ)	pH (units)	Total Solids (mg/ℓ)	Total Suspended Solids (mg/ℓ)	BOD (mg/ℓ)	COD (mg/ℓ)	Phenolic Compounds (mg/ℓ)	Zinc (mg/ℓ)
Sump	5/27	1,320	8.2	19,500	9,950	-	-	7.2	130
	6/3	1,530	8.9	38,100	30,400	-	-	1130	300
	5/27-5/30	1,400	9.1	29,200	27,700	5,960	40,500	10	65
	5/31-6/3	2,600	8.7	49,100	47,200	9,350	71,700	775	245
Feed After Settling	5/27	301	8.8	4,320	1,320	-	-	1.4	20
	6/3	1,150	8.5	10,300	4,510	-	-	295	126
	5/27-5/30	328	8.9	4,750	1,030	4,130	26,700	27.5	30
	5/31-6/3	526	8.6	9,110	3,240	7,650	77,300	245	200
UF Concentrate	5/27	587	8.5	16,700	13,200	-	-	0.25	140
	6/3	3,810	8.8	28,900	28,300	-	-	50	800
	5/27-5/30	856	8.9	10,800	6,880	6,840	37,700	2.5	80
	5/31-6/3	1,190	8.9	22,600	17,800	9,540	90,500	27.5	450
UF Permeate (New Membranes)	5/27	63	8.1	2,500	40	-	-	0.75	0.5
	6/3	116	8.4	3,820	102	-	-	60	1.0
	5/27-5/30	73	8.7	3,320	44	5,790	20,200	6.9	0.76
	5/31-6/3	571	8.4	4,560	84	6,170	50,900	45.0	1.3
UF Permeate (Original Membranes)	5/27	65	8.1	3,270	160	-	-	0.62	0.66
	6/3	124	8.3	3,820	106	-	-	55	1.3
	5/27-5/30	69	8.7	3,360	46	5,800	20,000	8.8	1.0
	5/31-6/3	208	8.4	4,450	118	5,750	53,200	32.5	1.0
San Leandro Municipal Discharge Limits		300/100*	>6.0	-	-	-	-	1.0†	3.0

*300 mg/ℓ oil and grease of animal or vegetable origin, 100 mg/ℓ oil and grease of mineral or petroleum origin.

†1.0 mg/ℓ phenolic compounds which cannot be removed by the Agency's wastewater treatment process.

TABLE B1. WEEKLY SUMMARY OF CHICAGO PLANT UF OPERATING DATA DURING 1976.

Week Ending	m^3 Per Week	Operating Hours/Week	Throughput vs. % of Design	Cumulative m^3	% of Design	Oil & Grease ppm
1-07-76	143	95	44.2	143	44.2	33
1-14-76	157	91	50.7	301	47.3	67
1-21-76	298	68	128.6	599	69.1	50
1-28-77	287	107	78.6	886	71.9	88
2-04-76	304	100	89.0	1,190	75.6	40
2-11-76	498	119	122.8	1,690	85.3	59
2-18-76	548	135	119.0	2,240	91.7	40
2-25-76	479	115	122.0	2,720	95.9	30
3-03-76	471	121	114.0	3,190	98.2	21
3-10-76	433	122	104.0	3,620	98.9	38
3-17-76	206	82	73.7	3,820	97.1	42
3-24-76	487	151	94.6	4,310	96.8	29
3-31-76	493	123	117.4	4,800	98.6	63
4-07.76	436	125	102.2	5,240	98.8	37
4-14-76	93	40	68.3	5,330	98.1	41
4-21-76	360	82	128.9	5,690	99.6	45
4-28-76	713	156	134.0	6,400	102.5	32
5-05-76	419	99	124.1	6,830	103.6	42
5-12-76	497	117	124.5	7,320	104.8	59
5-19-76	454	125	106.6	7,780	104.9	65
5-26-77	353	101	102.4	8,130	104.8	54
6-02-76	432	103	123.1	8,560	105.6	6
6-09-76	357	122	85.7	8,920	104.6	11
6-15-76	193	80	70.7	9,110	103.6	41
6-22-76	305	126	70.9	9,420	102.1	63
6-29-76	321	128	73.4	9,740	100.8	292*

TABLE B1. (CONTINUED) WEEKLY SUMMARY OF CHICAGO PLANT UF OPERATING DATA DURING 1976

Week Ending	m^3 Per Week	Operating Hours/Week	Throughput vs. % of Design	Cumulative m^3	% of Design	Oil & Grease ppm
7-06-76	402	107	110.2	10,100	101.1	8
7-13-76	451	120	110.3	10,600	101.5	52
7-20-76	384	120	93.8	11,000	101.2	221*
7-27-76	431	94	134.5	11,400	102.1	48
8-03-76	173	69	73.4	11,600	101.5	58
8-10-76	135	68	58.0	11,700	100.7	N.A.**
8-17-76	127	62	60.0	11,800	99.9	N.A.
8-24-76	237	119	58.5	12,100	98.6	N.A.
8-31-76	96	65	43.1	12,200	97.6	N.A.
9-07-76	193	59	96.0	12,400	97.6	N.A.
9-14-76	387	137	92.9	12,800	97.0	54
9-21-76	313	132	69.6	13,100	96.1	64
9-28-76	220	101	63,9	13,300	95.3	130*
10-05-76	298	137	63.8	13,600	94.3	43
10-12-76	222	117	55.7	13,800	93.3	28
10-19-76	190	118	47.3	14,000	92.1	32
10-26-76	305	127	70.4	14,300	91.5	27
11-02-76	214	111	56.7	14,500	90.6	30
11-09-76	140	103	39.9	14,700	89.5	27
11-16-76	123	105	34.3	14,800	88.4	35
11-23-76	44	41	31.4	14,900	87.9	N.A.
11-30-76	System Down - Replaced one half of ultrafiltration Membranes					
12-07-76	254	113	65.9	15,100	87.4	23
12-14-76	244	127	56.4	15,300	86.6	48
12-21-76	System Down - Membranes Fouled					
12-28-76	System Down - Membranes Fouled					
12-21-76	135	37	106.6	15,500	86.8	30

* Raw material spillage - low molecular rosins
** Not Available

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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EPA-600/2-78-176		

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16. ABSTRACT

Ultrafiltration was proven to be a viable unit process for separating adhesives and sealants manufacturing wastewaters into a low volume concentrate stream and a high volume permeate stream. The UF permeate was characterized by the following average contaminant loadings: 100 mg/ℓ total freon extractibles, <7.4 mg/ℓ non-polar freon extractibles, <27 mg/ℓ (typically <5 mg/ℓ) suspended solids, 0.43 mg/ℓ free cyanide, 3.6 mg/ℓ total cyanide, 8,900 mg/ℓ BOD, 36,600 mg/ℓ COD, 44.6 mg/ℓ phenolic compounds and 1.5 mg/ℓ zinc. A treated effluent of this quality is acceptable for discharge under the San Leandro Municipal Discharge Limitations with the exception of the phenolic compound and total cyanide loadings. Surcharges would be imposed, however, based on the suspended solids and BOD loadings.

If significant levels of phenolic compounds and cyanide are not present in a particular plant's wastewater discharge, ultrafiltration is judged capable of meeting local Municipal Discharge Standards. When phenolic compounds and cyanide are present at significant levels either ozonation or reverse osmosis are considered the preferred post-treatment processes. None of the treatment system options investigated is considered capable of reducing adhesives and sealants manufacturing plant wastewater BOD and COD loadings to the recommended Effluent Limitations Guidelines.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Adhesives Latex Sealers	Effluent Guidelines Wastewater Treatment Carbon Absorption Reverse Osmosis Ultrafiltration	68D

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