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COMBINED FINAL REPORT
(Pollution Studies)

Study of Treatment Methods of Used
Processing Solutions* -- Treatment
of Combined Processing Effluent* --
Pilot Testing Study**

12 May 1970

Prepared by:

V. M. Bryant, Jr.
V. M. Bryant, Jr.

Approved by:

R. A. Koch
R. A. Koch

date: 3 Sept. 1970

Contract EK-1904

- * Started under Task 34, Contract EG-400
** Task 3, Item 1(b) of this contract.

- 1 -

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FOREWORD

This report is a comprehensive summary of environmental pollution studies undertaken at a specific photographic processing laboratory. The problem of water pollution associated with the disposal of photographic processing wastes has been considered from both the ecological and the security points of view.

Because this report refers to a specific facility, it contains data and descriptive information which could identify the facility and its output volume. Thus, care must be exercised to avoid compromising security. Release outside the facility is being made at customer request because of the usefulness of the information to other installations.

Also, the measured rates, volumes, sizes, and costs stated within this report are specific in nature and apply to conditions which prevailed at the time of the study.

- 2 -

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(b)(3)

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	7
SUBJECT	9
TASKS (from Study Plan)	9
1. Section IV Task	9
2. Section V Task	9
DISCUSSION	9
3. Description of the Pollution Problem	9
a. Pollution Magnitudes	9
b. Properties of Processing Effluents	12
c. Photographic Wastewater Effluents	13
d. Acceptable Wastewater Treatment and Requirements	18
4. Applicability of Selected Treatment Methods	19
a. General	19
b. Acidification/Aeration of Fixers	20
c. Biochemical Oxidation	21
d. Chemical Precipitation	25
e. Chlorination	29
f. Evaporation	42
g. Pyrodecomposition	44
h. Ozonation	45
i. Reverse Osmosis, Dialysis/Electrodialysis, and Ion Exchange	46
5. Separate versus Combined Treatment	48
6. Acceptable Treatment Methods	48
a. Biochemical Oxidation	48
b. Evaporation/Concentration	51
c. Pyrodecomposition	51
d. Ozonation	51
e. Reverse Osmosis	51
PILOT TESTING STUDY	52
7. Introduction	52
8. Evaporation/Concentration	52
a. General	52
b. Preliminary Investigation	52
c. Pilot Tests	54

~~TOP SECRET~~Handle via **BYEMAN**
Control System Only(b)(1)
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BIF-008-B-00624-I-70-

(b)(1)
(b)(3)

TABLE OF CONTENTS (Cont'd.)

	<u>Page</u>
9. Pyrodecomposition	60
a. Prenco Division of Pickands Mather & Co.	60
b. John Zinc Co.	64
c. Other Incinerators	64
10. Solids Waste Disposal	64
11. Alkaline Chlorination	65
a. Test Objective	65
b. Pilot Equipment	65
c. Experimental	67
d. Results	67
FINAL TREATMENT	71
12. Final Treatment Facilities	71
a. General	71
b. Machine Plumbing Changes	71
c. Effluent Collection Tanks	71
d. The Treatment Unit	72
e. Silver-Recovery System	72
13. Acceptable Treatment Methods	72
a. Biochemical Oxidation	72
b. Concentration by Evaporation and Reverse Osmosis	73
c. Incineration	77
14. Treatment of Toxic Effluents	79
a. Ferri/Ferro Cyanide Bleach	79
b. Cleaning Solutions	79
c. Fungicide Solutions	79
15. Final-Treatment Proposal for BH (Black-and-White)	79
16. Final-Treatment for LP (Color)	80

~~TOP SECRET~~Handle via BYEMAN
Control System Only(b)(1)
(b)(3)

~~TOP SECRET~~

BIF-008-B-00624-I-70-

(b)(1)
(b)(3)

TABLE OF CONTENTS (Cont'd.)

	<u>Page</u>
CONCLUSIONS	81
17. Biochemical-Oxidation	81
18. Incineration	81
19. Concentration by Evaporation and Reverse Osmosis	82
20. Alkaline Chlorination for Color Bleach Wastes	83
RECOMMENDATIONS FOR BH (Black-and-White)	84
21. Final Treatment	84
22. Facility Requirements	84
23. Limitations, Restrictions and Future Efforts	84
24. Future Hardware Efforts	84
25. Future Study Efforts	85
REFERENCES	86
APPENDIX A - FINAL REPORT on Acceptable Pollution Standards	A-1
APPENDIX B - FINAL REPORT on Study of Pollution Contribution from Processing Activities	B-1
APPENDIX C - Tabulated Results of Alkaline Chlorination Pilot Studies	C-1

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~~TOP SECRET~~BIF-008-B-00624-I-70- (b)(1)
(b)(3)

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Schematic Diagram of Alkaline Chlorination Test Equipment	66
2	Alkaline Chlorination of Bleach	70
3	Final Treatment Facility (Plumbing Modifications)	74
4	Biochemical-Oxidation Treatment Facility	75
5	Fluid-Waste Incineration Facility	77

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	Summary of Department Pollution Magnitude	11
2	Properties of Black-and-White Processing Solutions	14
3	Processing Solution Usage and Pollution Magnitude from a Typical Five-Day Black-and-White Processing Mission with Fixer Rejuvenation and Reuse	14
4	Properties of the Department Effluent	16
5	Make-Up, Composition, and Properties of Synthetic Processing Effluents	33
5A	Hypochlorination of Type A Processing Effluent	34
6	Alkaline Chlorination of Processing Solutions	35
7	Chlorine Sources and Chlorination Costs	40
8	Costs of Pollution Abatement Proposals	49
9	Pfaunder's Wiped Film Evaporation Pilot Test	55
10	Bowen Pilot Test	58
11	General Description of Fluid Waste	61
12	Incineration Pilot-Test Results	63

- 6 -

~~TOP SECRET~~Handle via BYEMAN
Control System Only(b)(1)
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SUMMARY

Recommended Treatment

A comparative study of several treatment methods shows that biochemical oxidation is the cheapest, acceptable abatement method for photographic effluents. All of the effluents from black-and-white as well as color processing, excluding used ferri/ferro cyanide bleaches, may be satisfactorily treated, jointly.

For most efficient operation, the biological culture in the activated-sludge or trickling-filter system should be acclimated to a stabilized, photographic waste. BOD reductions of 80 to 95% were obtained at influent loadings of 30 to 50 lbs of O_2 per day per 20,000 gallons of tank volume.

Alternate Treatment Methods

Fluid-waste incineration (pyrodecomposition) is also an acceptable abatement for used processing solutions. This treatment method requires the separation of the concentrated waste (developer, de-silvered fixer, arrest, etc.) at the processor from the wash or rinse process water. Since the concentration of pollutants in the rinse water is low, process water usually may be sewered, discarded without further treatment, or purified by reverse osmosis and re-used for photographic purposes, providing that water conservation is justified economically.

Natural gas or fuel oil must be used as auxiliary fuel to fire the fluid incinerator up to 1400-2000°F. At these temperatures, the solid product of oxidation and decomposition is a small amount of a water-soluble white ash, which may be removed from the stack effluent by a wet-scrubber and sewered. The gaseous products of combustion are nearly odorless and colorless.

For installations where water conservation as well as pollution abatement is a primary objective, evaporation or concentration of the concentrated processing effluent is recommended. However, adequate means must be available for disposal of the residue.

Distillate-to-solid splits of 90% condensate are achievable with thin-film evaporator units operating continuously on used photographic

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solutions. The distillate fraction can be sewered without further treatment or purified by reverse osmosis and re-used.

The residue from the evaporator may be a semi-solid or a slurry. Disposal may be by incineration in a large, industrial facility, or by land-fill in an approved disposal site.

Acceptable treatment methods for effluents containing ferri/ferro cyanide from color bleach processing include alkaline chlorination, pyrodecomposition, and biochemical-oxidation (in a large treatment facility). The discharge of toxic complex cyanides should be restricted to an absolute minimum by the adoption of a bleach regeneration and reuse system.

Final Treatment at BH (Black-and-White Facility)

Adoption of bio-oxidation waste treatment for the facility at BH is prohibited currently by the large space/volume requirement; namely, an activated-sludge unit sized to handle the effluent from this installation would require a treatment tank in excess of 100,000 gallons. The alternate treatment method, pyrodecomposition, cannot be recommended for reasons of operational security: i.e., existing air environmental codes require prior approval by local agencies of all new incinerator units and authorize on-site inspection, sampling, and testing of stack effluents.

Because of the above factors, trucking of the used processing solutions (excluding rinse water) to a near-by industrial bio-chemical treatment facility is recommended as the cheapest, most acceptable abatement method for BH. Rinse water is to be sewered without treatment.

With this abatement method, the in-house treatment facility will consist of:

1. Separate waste lines (for used developers, stops, dyé-removal baths, etc.) from each processor to the collection site and separate lines (for used-hypo) from each processor to the electrolytic silver recovery area.
2. A double-tank collection unit with transfer or pumping equipment.
3. Sufficient tank-truck equipment so that trips can be made routinely to disguise the cyclic nature of production operations.

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SUBJECT: Study of Treatment Methods of Used Processing Solution;
Treatment of Combined Processing Effluent; and Pilot
Testing Study

TASKS:

1. Section IV Task:*a. Conventional (Thin Developers):

(1) Study treatment of developers with calcium to remove sulfite; this study to cover:

- (a) Calcium addition reaction and mixing requirements.
- (b) Filtering requirements for removal of precipitate.
- (c) Solid waste disposal of filtered precipitate.

(2) Conduct a laboratory-level study for removal of organic materials from developers.

b. Viscous Developer. Conduct studies to determine:

- (1) Quantity (current and future) of viscous developer used.
- (2) Pollutant effects of viscous developers. Appearance,

BOD₅ and foaming must be considered.

- (3) Possible treatment methods.

2. Section V Task:*

a. Study for immediate needs the following:

- (1) pH control
- (2) Removal of insoluble compounds
- (3) Removal of any colored material

b. Carry out long-range data gathering necessary to produce high quality effluent and possibly provide reusable water. Distillation and reverse osmosis to be considered as possible methods of treatment.

DISCUSSION

3. Description of the Pollution Problem:

a. Pollution Magnitudes. Two previous reports** have described and discussed the nature of the pollution problem at the BH (Bridgehead) black-and-white facility. For purposes of selecting and sizing suitable

* To thoroughly investigate the pollution problem at BH and to determine a feasible solution to this problem, it was necessary to extend the scope of pollution studies beyond that specified in these two tasks.

** See References 1 and 2. These two reports are included in their entirety as Appendices A and B.

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treatment methods, the salient features of the waste problem are summarized in Table 1 which is based on these reports containing usage data for 1968. The following information about chemical usage, oxygen demand, water usage and rates, and used processing solution volumes was derived from Table 1.

(1) Chemical Usage. Total chemical usage at BH for black-and-white processing during 1968 was 671,500 lbs. From chemical usage estimates for the MPMP Color Processor*, an additional 20,000 lbs per year will be used. Thus, the total chemicals to be discharged via sewers in the near future will amount to about 691,500 lbs (about 350 tons) per year.

(2) Oxygen Demand:

(a) The oxygen demand of the chemicals discharged was determined from chemical usage data and chemical-oxygen-demand (COD) factors published for the pure chemicals^{1,2}. The COD will amount to some 207,000 lbs per year of O₂ (for black-and-white processing), plus an additional 10,000 lbs per year oxygen load due to effluent from the MPMP Color Processor. Thus, total COD load is 217,000 lbs per year.

(b) Biochemical oxygen demand (BOD) for chemicals found in photographic effluents is about two thirds (2/3) of the COD load for these same materials. For black-and-white processing, the annual BOD load is 136,800 lbs/year and, for the MPMP Color Processor, the estimate is an additional 3,200 lbs; thus total load is 140,000 lbs per year.

(3) Water Usage and Rates. The total effluent volume of water consumed for all purposes within the department was estimated from water usage data to be approximately 14.7 million gallons per year. Department usage rates vary significantly for non-mission and mission rates, for nightly rates and daily rates, etc. On the average, some 40 to 60,000 gallons of water are used each day at rates varying from 1600 to 4600 gallons per hour.

* A multi-purpose experimental test processor.

^{1,2} See References.

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(b)(1)
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Summary of Department Pollution Magnitude

	<u>Black-and-White Processing at BH</u>	<u>Estimated from MPMP Color Processor Alone</u>	<u>Dept. Total</u>
<u>Chemical Usage</u>			
Total Annual Usage (lbs)	671,500	20,000	691,500
<u>Oxygen Demands</u>			
Total BOD (lbs/yr)	136,800	3,200	140,000
Total COD (lbs/yr)	206,900	10,000	217,000
<u>Water Usage and Rates*</u>			
Annual Usage (gal)	14,700,000	50,000	14,750,000
Daily Average (gal)	40,000	1,000	41,000
Dept. Usage Rates (gal/hr)	<u>Mission</u>	<u>Non-Mission</u>	
Daily (24 hr avg)	3,120	2,730	
Daily (8 hr avg)	3,800	4,630	
Nightly Average	2,250	1,600	
<u>Processing Effluent Volumes</u>			
Processing Solutions:			
Annual Total (gal)	449,200	20,000	470,000
Annual Average (gal/hr)	100	25	125
Maximum Rate Estimated (gal/day)	3,000	1,000	4,000

* Includes all water used in the department.

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(b)(3)(4) Used Processing Solution Volumes:

(a) If all of the used processing solutions (excluding rinse water) are collected, the annual volume is 470,000 gallons. Most of this volume (about 450,000 gallons) originates from black-and-white processing.

(b) The hourly rate of processing solution usage is 100 gal/hr for black-and-white, and an additional 25 gal/hr for color. The daily volumes therefore will average about 3000 gallons for both black-and-white and color. A total of 4000 gal/day is maximum output for the department.

b. Properties of Processing Effluents:(1) Properties:

(a) The major polluting effects from the discharge of photographic processing solutions are: high total-dissolved-solids content, and high chemical and biochemical oxygen demand (COD and BOD₅). In addition, effluents containing used photographic wastes require special treatment to meet waste-water disposal requirements established for:

1. pH
2. Alkalinity and/or acidity
3. Dissolved solids
4. Phosphates
5. Iron
6. Cyanides (and complex cyanides)
7. Phenols (and phenolic by-products)
8. Other miscellaneous organics

(b) Photographic solutions for black-and-white processing vary greatly in their pollution characteristics and in the relative volumes consumed. Both factors must be considered in selection of a suitable abatement method.

(c) Properties of black-and-white processing solutions are summarized in Table 2. As can be seen from this table, fixer solutions are exceptionally high in solute content, i.e., 30% by wt; while developers, stop baths, and dye removal baths contain only approximately 10% solutes. Developers

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and dye-removal baths are high in alkalinity; on the other hand, fixers and stop baths are high in acidity. All processing solutions, except the dye-removal and Photo Flo baths, are high in oxygen demand (COD and BOD₅). Furthermore, rinse water from black-and-white processing contains about 0.1 g/l dissolved solids, some halides (~ 100 ppm), and has a low oxygen demand (COD ~ 75 ppm, BOD ~ 45 ppm). The pH generally ranges from 6-8 and the water is clear and colorless.

(2) Usage Rates:

(a) Used developers comprise the largest volume of effluent discharged from this installation. If rinse waters are excluded, developers make up 70 to 85%* of the volumes of processing solutions mixed and sewered.

(b) When usage rates as well as the pollution load are considered, it is found that about 51% of the total dissolved solids originate from developer solutions, 44% from fixers, and only 5% from stop and dye-removal baths. Similarly, over 90% of the oxygen demand (both COD and BOD) of processing effluents stems from the developers and fixers. Thus, segregation and treatment of the used developer and fixer solutions will lower most pollution parameters by 90% or more. If the relatively small quantities of stop and dye-removal baths are also treated, excluding only the rinse water, about 99% of the pollution from photographic processing could be removed. (See Tables 2 and 3.)

c. Photographic Wastewater Effluents:

(1) For abatement purposes, two types of waste water will be considered for treatment: the concentrated processing effluent, including all of the used processing solutions, but excluding all process water; or the diluted processing effluent, which combines the used processing solutions with all of the water used by the department. Both types of effluents will be considered in the selection of suitable abatement methods.

* Percentage depends upon whether or not hypo is rejuvenated and reused.

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Table 2

Properties of Black-and-White Processing Solutions

	<u>Solid Content</u> (g/l)	<u>pH</u> (at 70F)	<u>Oxygen Demand</u>	
			<u>Chemical</u> (g O ₂ per l)	<u>Biochemical</u> (g O ₂ per l)
Developers	40 to 120 (87 avg)	10.0 or greater	22 to 42 (35 avg)	22
Fixers	300	4.3 to 5.0	93	58
Stop Baths	82	2.7	39	30
Dye Removal Baths	110	10.0 or greater	0 to 6	0 to 6
Rinse Water Effluent	0.1 to 0.2	6 to 8	75 ppm	35 ppm

Table 3Processing Solution Usage and Pollution Magnitude from
a Typical Five-Day Black-and-White Processing Mission with Fixer
Rejuvenation and Reuse

	<u>Developers</u>	<u>Fixers</u>	<u>Stop Baths</u>	<u>Dye Removal Baths, Etc.</u>	<u>Rinse Water</u>
Volume (gallons)	27,700	6,850	2,100	400	375,000
% of Total Effluent*	84.2	6.7	7.8	1.3	-
Solutes (%)	51	44	4	1	0
Oxygen Demand					
1. Chemical (%)	56	38	5	1	0
2. Biochemical (%)	55	37	6	2	0

* Exclusive of rinse water.

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(a) The Concentrated Effluent. Dilution of the used, concentrated processing solutions would have a harmful affect upon some abatement methods. Therefore, segregation of the developer, fix, stop and dye-removal baths, and exclusion of rinse or other processing water, must be considered. The properties of this concentrated effluent are shown in Table 4, Column 1. Treatment methods proposed for the concentrated effluent must be able to handle a viscous solution, ranging in viscosity (Brookfield) from about 1 to 800 cps (i.e., water-like to thin syrup). The average annual volume will be about 470,000 gallons, or about 125 gal/hr. The maximum daily output should not exceed 4000 gallons per 24 hours for a 5-day period.

(b) The Diluted Processing Effluent. The spent solutions are presently being sewered as used, along with all process water (spray cut-off water, deep-tank rinse water, etc.). This processing effluent is then combined with all other waste water from the department. The properties of this effluent are shown in Column 2 of Table 4. Space requirements must be determined for a treatment plant which has capacity to handle an average of 60,000 gal/day of the diluted effluent.

(2) The pairs of values for the two types of processing effluents in Table 4 differ by a factor of about 30. This difference is due to the dilution factor; i.e., the ratio of processing solution usage to department water usage rate. The dilution ratio can vary from about 13 to 55; therefore, the property values for the department effluent (in Column 2, Table 4) may also vary from about 1/2 to twice these average values.

(3) Other Processing Effluents:

(a) Other process water is used in deep-tank or spray cut-off rinses. To determine whether this process water should be treated before sewerage, a sample of spray cut-off water from a Dundee Processor was analyzed. The operating conditions of this test were as follows:

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Table 4

Properties of the Department Effluent

<u>Property</u>	<u>Column 1</u> Concentrated Processing Effluent*	<u>Column 2</u> Diluted Processing Effluent**
Viscosity (Brookfield) at 70F (cps)		
Range	1 to 800	1 to 5
Average	200	3
pH at 70F		
Range	4 to 10	4 to 10
Average	7.5	7.5
Total dissolved solutes		
(lbs/gal)	1.5	0.05
(ppm)	170,000	5,500
Average COD (ppm)	52,000	1,750
Average BOD ₅ (ppm)	33,500	1,120
Halides (as KBr) (ppm)	180+	6
Nitrogen (as NH ₄ +) (anticipated)	1,500	50
Phosphates (as PO ₄)	900	30
Borates (as BO ₂) (ppm)	2,000	70
Sulfates (as SO ₄)	4,000	140
Miscellaneous organics (ppm)	12,000	400

* Includes used developers, stop baths, fixers, dye-removal baths, Photo Flo, etc.; excludes all process water.

** Includes all used processing solutions, process water, and all water for other use in this department.

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1. Equipment: Dundee Processor equipped with squeegee wiper blades before a water cut-off spray
2. Product: #3404 film (5-inch wide) at 20 ft/min
3. Developer Replenisher: XK-3, 0.020-inch thick coating
4. Developer Viscosity: 7000 cps at 70F (Brookfield)
5. Water Consumption:
 - a. From sump to spray cut-off: 5 gal/min
 - b. From sump to overflow: 3 gal/min
8 gal/min TOTAL (sewered)

(b) Analysis of the spray cut-off sample from the sump gave the following data:

1. Color: Clear, colorless
2. pH at 70F: 7.72
3. Halides: 0.05 g/l as KBr
0.06 g/l as NaCl
4. COD: 75 ppm

(c) An estimate of the concentration of developer and developer constituents in the processing effluent was made from the above data. Each gallon of effluent was estimated to contain about 9 ml of developer; i.e., a dilution ratio of about 440 to 1.0. At this dilution, the concentration of photographic "flags"* from a typical developer solution is as follows:

1. Sodium sulfite: Less than 0.10 g/l
2. Phenidon: Less than 0.01 g/l
3. HQ: Less than 0.01 g/l
4. Thickening agent: Less than 0.03 g/l
5. Bromides (e.g., KBr): Less than 0.05 g/l

* Constituents or characteristics indicative of processing.

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(d) These concentrations of photographic "flags" in the processing effluent are not detectable by the usual analytical methods applied to wastewater³. Thus, process wastewater from deep-tank or spray cut-off rinses can be sewered without jeopardizing the operational security of this department.

d. Acceptable Wastewater Treatment and Requirements:

(1) City Sewer Code Limitations:

(a) To continue the discharge of effluents into sewer, the City Sewer Code restrictions⁴ must be met. Since the department effluent changes drastically in volume and properties, slugging restrictions of the City Sewer Code apply to the effluent. Thus a suitable pollution abatement method must eliminate "slugging" as defined by the City Sewer Code.

(b) The City Commissioner of Public Works might also rule that certain properties of the effluent are "unusual" or might "have an adverse effect" upon the sewer system or treatment process. Effluents with a high BOD, COD, solids content, or high organic level might be the cause for further investigation.

(c) It should be noted that at present there is no actual, defined violation of the City Sewer Use Code at this facility, with the possible exception of pH. Thus, the effluent of this department is essentially acceptable under existing sewer code limitations. With a suitable collection and storage system equipped with automatic pH adjustment equipment, the department effluent could be sewered if it was not required also to maintain operation security.

^{3,4} See References.

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(b)(3)(2) Acceptable Security Standards:

(a) To maintain operational security, pollution control must effectively accomplish the following objectives:

1. Maintain a strictly acceptable waste effluent which will reduce or eliminate the need for a detailed examination of the effluent by an outside agency.

2. Restrict or eliminate photographic flags; i.e., constituents or characteristics indicative of processing.

3. Disproportionatize acceptable constituents of our effluent so that the true magnitude of processing operations cannot be ascertained from the materials and quantities discharged.

4. Disguise the cyclic characteristics of the industrial effluent.

(b) Specific implications for an acceptable pollution control system are given by Table 13 in Appendix A. By adopting these standards for acceptable pollution control, the effluent of this department will have properties similar to those of city sewage; thus, its properties would not be "unusual" nor harmful to the City Sewer System or treatment plant.

(3) Other Limitations. The physical size requirements of any proposed treatment method also must be considered in the feasibility study. Locating a suitable treatment center at this facility could involve serious restrictions in physical dimensions; e.g., in weight, height, area, volume, etc. Also, since costs for pollution control will be shared with the customer, equipment costs and operational costs including labor required, must be considered in selecting an applicable abatement system.

4. Applicability of Selected Treatment Methods:

a. General. A literature search was made of established abatement methods that might be applicable to some of the used processing solutions. Both chemical and physical methods were studied. The applicability of each treatment was determined from published evaluations of the method when

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treating industrial wastes which have properties similar to those of used-processing effluents. The following sections describe several methods which have been proposed for specific types of photographic effluents.

b. Acidification/Aeration of Fixers:

(1) Description. The addition of an acid to a thiosulfate solution decomposes the thiosulfate to sulfur and sulfur dioxide. Sulfites, as well as thiosulfates, are subject to decomposition with strong acids. This method of separately treating fixer solutions has been studied by other investigators who arrived at the following conclusions:

(a) Acidification, alone, is not sufficient to completely decompose all the thiosulfate and sulfite ions.

(b) Acidification with either hydrochloric or sulfuric acid, followed by aeration, will decompose about 90% of the sulfite and thiosulfate in a typical fixer bath.

(c) The method substitutes a degree of air pollution for water pollution because sulfur dioxide is liberated.

(d) Chemical costs (for sulfuric acid) are estimated at \$0.017/lb for destruction of sodium sulfite and \$0.022/lb for sodium hypo; or, about \$0.04 per gallon of fixer, not including capital, air, and operational costs.

(2) Costs:

(a) The cost of sulfuric acid to adequately treat 62,500 liters (1700 gallons) of dye-removal bath would be \$250 per year.

(b) The cost of commercial-grade sulfuric acid to treat and partially remove BOD/COD caused by sulfites and thiosulfates in the combined effluent (excluding rinse water) would be \$8,000 to \$10,000 per year.

(c) Capital items required for the acidification/aeration treatment would cost about \$10,000 as shown below:

<u>1.</u>	Two 3000-gallon collection tanks with mixer	\$ 6,000
<u>2.</u>	pH control	1,000
<u>3.</u>	Acid storage and dispenser	<u>3,000</u>
	Total	\$10,000

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(b)(1)
(b)(3)(3) Conclusions:

(a) Acidification/aeration best applies in the treatment of the sulfite dye-removal bath.

(b) This method will only partially treat fixer, developer, or a combined processing effluent. A reduction of 45 to 50% in BOD/COD will be gained at the expense of air pollution (sulfur dioxide). A follow-up treatment, such as alkaline chlorination, will then be required to further reduce oxygen demand to an acceptable level.

c. Biochemical Oxidation:(1) General:

(a) The secondary treatment of photographic effluents by biological degradation has been evaluated for both color and black-and-white process wastes. Using re-cycled sludges containing micro-organisms acclimated to photographic wastes, the following results have been observed:⁵

1. BOD values are reduced by about 90% and COD by 65%.

2. Photographic effluents are usually toxic to the micro-organisms, unless first acclimated.

3. Ammonium ion is not affected or reduced by this treatment.¹⁰

4. Some organics, especially aromatic compounds, are not degraded by this treatment; notably, phenol derivatives⁷.

5. Photographic waste treated by this method will give an effluent suitable for discharge into a City Sewer without further treatment.

(b) In biological oxidation systems, the design determines the efficiency and size requirements. If enough land is available, lagoons or oxidation ponds can be used to treat wastes at BOD loadings ranging from 50-100 lbs per acre of surface per day. Lagoons are able to absorb 400-500% overloads for short times without adverse affects.

^{5,7} See References.

* A second anaerobic treatment tank is required if ammonia/ammonium ion content is to be lowered.

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(c) When land is not available, other approaches are used to improve the efficiency of biological oxidation systems. Trickling filter beds achieve 1 to 5 lbs/day per cubic yard of stone; efficiency of this method ranges from 35 to 85%. Plastic filter media are also available at about double the surface area/volume ratio. A two-stage trickling filter system is generally 80 to 95% efficient in reducing BOD⁶.

(d) Other methods of reducing the volume/space requirements are to recirculate a portion of the sludge containing the micro-organisms and to increase the oxygen content by aeration of the waste. Thus, in typical activated-sludge units, BOD loads of 15 to 150 lbs per 1000 cu ft of tank volume are handled in retention times of 4 to 24 hours. If oxygen is used instead of air, the tank volume may generally be reduced 30-50%; however, operating costs will actually double.

(2) Size of Unit:

(a) Since land or space for a biological treatment facility will be at a premium, only the trickling-filter and activated sludge methods can be considered. Using a plastic trickling-filter media, the tank volume required would be in the range of 50 to 70 cu yds. The most ideal trickling-filter system would be comprised of two tanks connected in series, each about 10-ft high and 10-ft in diameter. The largest reduction in BOD would take place in the first tank; the second tank would not be required, if the wastewater was to be sewered. If the effluent was to be discarded in a stream, river, or lake, the second tank would eventually be required to meet the Water Quality Classification for the body of water.

(b) The effect of "slugging" on the biochemical system can best be minimized by using two storage-tank systems for the effluents. The concentrated processing solutions should be collected and stored in a 5000-gallon mix tank and fed at a constant rate to the system. A regulated amount of the other, more dilute process water would also be metered to the aeration tank.

⁶ See References.

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(b)(1)
(b)(3)(3) Photographic Flags:

(a) Some organics are only partly oxidized or destroyed by a biological system. Hydroquinone, for example, is oxidized to quinone, which resists further biodegradation⁷. Ferri/ferro cyanide wastes, from color bleaches are not adequately removed by biochemical means, although they can be mixed without any damaging effects upon an acclimated biological system. The effluent from biological treatment will therefore contain some organics which could be flags or indicators of photographic processing.

(b) Ammonium ion generally is not removed by conventional activated-sludge (AS) systems⁹. To remove ammonium, a second treatment tank is used to provide an anaerobic treatment. Since the effluent will be sewered, the small concentration of ammonium ion originating from the treated processing effluent will not be discernible or distinguishable from that already present in the sewer from domestic sources.

(c) The unusually high sulfate content previously present in the effluent will be lowered substantially when hypo rejuvenation and re-use is fully operational. A lime post-treatment to remove sulfate ions (from the oxidation of sulfite and thiosulfate) should not be required if the effluent is sewered. For discharge to a stream, however, a lime treatment is recommended, followed by chlorination. The removal of sulfate by lime precipitation would prevent possible disclosure of the magnitude of processing operations by monitoring the sulfate content and volume of wastewater.

^{7,9} See References.

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(d) The proper operation of a biochemical treatment plant would require:

1. Control of temperature; i.e., steam heating coils for proper operation in the winter months.
2. Laboratory support to monitor pH, BOD, COD, sludge build-up, etc.
3. Chlorination of effluent to kill bacteria or remove traces of photographic flags.
4. Annual sludge disposal in which the removal of sludge from the system would require a weekend shut-down. The solids removed could be trucked to a land fill site or incinerated.

(4) Costs:

(a) To reduce the BOD in this effluent by 140,000 lbs O₂ per year (385 lbs/day), an AS system having a capacity of 75,000 to 100,000 gallons would be required. The dimensions of the AS unit would be approximately 24-ft wide, 50-ft long, and 10-ft high; the initial cost would be \$75,000 to \$100,000*.

(b) Annual operating costs would be \$15,000 for utilities, power, heat, etc.; plus, labor (one-half man) estimated at \$10,000. The estimated cost of treating all processing wastes from this department would therefore be about \$25,000 per year or about \$0.015 per liter (\$0.055 per gallon) of used processing solution.

NOTE: All of the processing wastewater would be treated, including rinse water; this estimate is based on the combined volumes of used developer, fixer, arrest and dye-removal bath.

* This estimate is based upon the performance of a pilot unit (12 ft x 10 ft x 25 ft) treating 20,000 gallons of photographic wastes per day. The BOD is reduced from about 200 ppm to 20 ppm which is equivalent to 30 lbs BOD per day.

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(b)(1)
(b)(3)(5) Conclusions:

(a) A single aeration tank AS unit or a trickling-filter tank would adequately pretreat the department wastewater for discharge to the sewer.

(b) Size requirements would probably prohibit adoption of this treatment method.

d. Chemical Precipitation:(1) General:

(a) The chemical treatment of photographic wastes has been considered by several authors. Mohanrao et al⁹ cited the effects of alum, ferric chloride, ferrous sulfate, lime and their combinations on composite photographic wastes. Lime and alum were found to have some abatement effects; i.e., reduction in color, COD, and dissolved solids content.

(b) Eustance¹⁰ described methods and equipment for chemical abatement by precipitation. Facilities for flocculation, sludge removal, and vacuum drying of solids are required.

(c) A study was made of the solubility data of compounds which could be removed from photographic wastes by chemical means; from this study, it was concluded that:

1. The addition of lime followed by flocculation should significantly reduce total dissolved solids. Ions precipitated would include phosphates, carbonates, borates, and ferri/ferro cyanide complexes.

2. Some "toxic" constituents are reduced; i.e., some organics are adsorbed, or absorbed by the precipitate, and ammonium content is reduced.

3. The color of the effluent is appreciably reduced.

4. Chemical treatment with lime and/or alum is not adequate for removing those constituents of photographic wastes which have a high oxygen demand.

^{9,10} See References.

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(b)(1)
(b)(3)(2) Heavy Metal Precipitation:

(a.) The sulfites and thiosulfates of most commercial coagulants or flocculents are too soluble to remove appreciable amounts of these ions. Only the lead and barium salts of these cations are insoluble. However, since both lead and barium are highly toxic, meticulous control would be required to prevent these cations from being used in excess amounts.

(b) To reduce the BOD/COD load caused by sulfite (SO_3^-) and thiosulfate (S_2O_3^-) by chemical precipitation, two methods may be proposed:

1. Precipitation with lead or barium ions, or
2. Oxidation of SO_3^- and S_2O_3^- to sulfate (SO_4^-), followed by precipitation with lime.

(c) Precipitation of sulfites and thiosulfates with lead or barium would remove 45 to 50% of the BOD/COD load. The use of the cheaper chemical (barium chloride) would require 2 lbs of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ for every pound of hypo or sodium sulfite. Two pounds of solids (BaSO_4) would be produced for each pound of hypo or sodium sulfite treated. The barium sulfate could be used for other purposes; e.g., sizing, baryta, etc.

(3) Lime Precipitation:

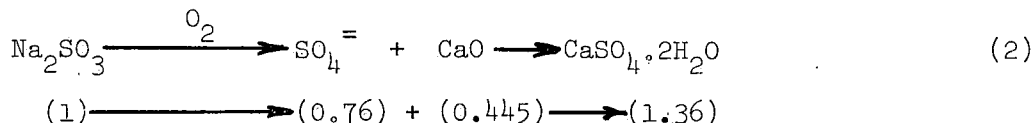
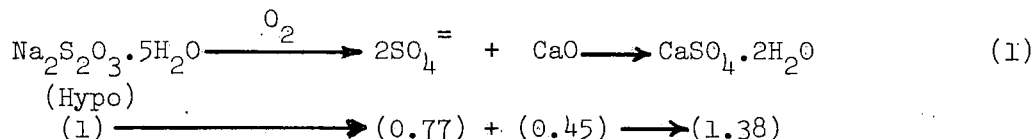
(a) For security reasons, it might be desirable to remove from the oxidized effluent as much of the sulfate and chloride as possible after hypochlorination, ozonation, biochemical treatment, or alkaline chlorination. Precipitation with lime (CaO) removes most of the sulfate as calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

(b) The following equations give the approximate amount of lime required and the weight ratios of solids precipitated per unit weight of hypo or sodium sulfate treated:

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For each pound of hypo ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) or sodium sulfite, about 0.45 lb of lime will be required to adequately precipitate the sulfate ion. Since there will be some moisture in the precipitated solids, there will be about 1.5 lbs of solids per pound of hypo or sulfite treated.

(4) Costs:

(a) The chemical costs for precipitation with barium chloride have been estimated as follows:

1. For treating Na_2SO_3 : \$0.20 per lb
2. For treating $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ("Hypo"): \$0.20 per lb
3. For treating a typical fixer: \$0.08 to 0.10 per gallon

Annual cost for barium chloride to remove 45 to 50% of the BOD/COD load by chemical precipitation would be about \$31,000. (Cost of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ = \$200/ton).

(b) The chemical costs for precipitating sulfates with lime are as follows:

1. Lime: \$20/ton
2. Each pound of sodium sulfite or hypo oxidized to sulfate: \$0.005 per lb

(c) Capital costs would be:

1. Two 3000-gallon tanks \$ 6,000
2. pH controller 1,000
3. Lime storage, mix tank and dispenser 3,000
4. Vacuum or drum filter 5,000
- Total \$15,000

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(d) Cost to operate the system:

1. One man half-time: \$10,000
2. Utilities: 2,000

Total \$12,000 per year

(e) The chemical costs for hypochlorination and chemical precipitation with calcium hypochlorite (HTH) are discussed in paragraph 4.e.(5)(c) on page 36.

(5) Conclusions:

(a) No known single method or combination of chemical treatment methods is adequate for treating processing wastes and maintaining operational security.

(b) Chemical costs for barium or lead salts are high in proportion to the limited reduction in BOD/COD obtained by precipitation with a heavy metal.

(c) With no preliminary oxidation, treating wastewater of this department with lime will give only a 10 to 15% reduction in BOD/COD and a 30 to 40% decrease in total salt content. The effluent from this abatement step will still contain numerous "flags" of photographic processing; thus post-treatment will be necessary.

(d) The oxidation and precipitation could be carried out simultaneously with a bleaching agent such as calcium hypochlorite (HTH). Estimates indicate that 30 to 60% of the BOD/COD could be removed by treatment with HTH.

(e) About 1 lb of bleaching powder (HTH, Maxoclor, or 70% available Cl_2 as calcium hypochlorite) would be required to treat each liter of effluent from a typical processor.

(f) If the sulfite and thiosulfate are first oxidized to the sulfate, then precipitation with lime will be adequate to remove dissolved solids. Oxidation of the effluent may be by chlorination or by biochemical means (activated sludge tank, trickle filter, lagoons, etc). Subsequent treatment with lime would produce an effluent having a solids content of about 2000 ppm and having practically no oxygen demand.

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(g) Treatment of the combined effluent with lime would require 0.45 lb of slaked lime for every pound of hypo or sodium sulfite oxidized by treatment methods. In both instances, 1.5 lbs of solids could be separated for land disposal.

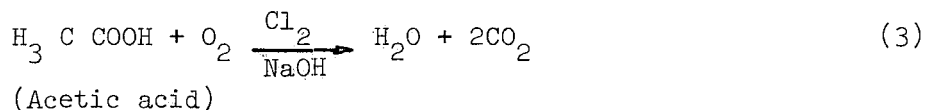
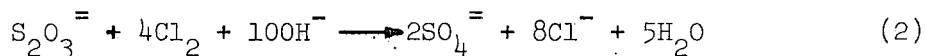
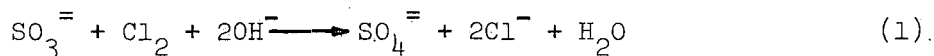
(h) A disposal area for solids would be required. About two pounds of solids would have to be dumped for each pound of solute removed from the processing effluent.

e. Chlorination:

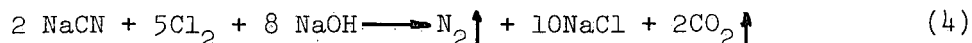
(1) General:

(a) Literature¹¹⁻¹⁴ on chlorination of industrial wastes indicates that alkaline chlorination should be a complete treatment for all used photographic solutions; this method of treatment:

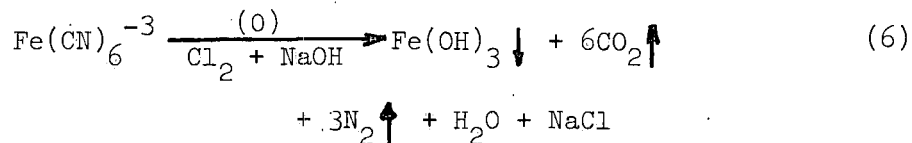
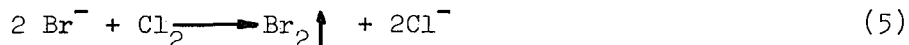
1. Reduces BOD/COD load by oxidation of sulfite, thiosulfate, and organics; examples are:



2. Destroys toxic materials; an example is:



3. Chemically changes/removes processing flags;
two examples are:



¹¹⁻¹⁴ See References.

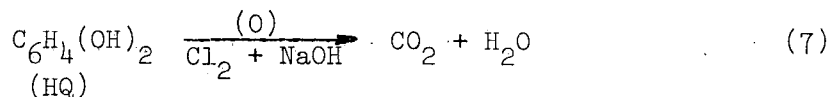
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4. Oxidizes organics; an example is:



(b) There are two methods of applying chlorine. Chlorine gas may be injected into an effluent stream from a liquified chlorine source, or by hypochlorination. Hypochlorination can be achieved by treating the wastewater with a solution of sodium hypochlorite (15% by wt NaOCl) or with a solid chlorine-bleach, such as calcium hypochlorite (HTH) which generally contains about 70% by wt available chlorine.

(c) Modern equipment for applying chlorine gas is relatively simple, inexpensive, and safe. The chlorine source and storage may be distant from the chlorination site. The transfer of the chlorine from the supply to the injection equipment may be made entirely in the gaseous phase via supply lines under a partial vacuum.

(d) Theoretically, for each pound of chemical oxygen demand removed from the effluent, at least 4.43 lbs of gaseous or "available" chlorine are required. However, the oxidation of some processing pollutants requires only small amounts of chlorine and caustic. For example, to oxidize 1 lb of sodium sulfite to sulfate requires 0.53 lb of chlorine plus an equal weight of caustic*. To oxidize 1 lb of sodium thiosulfate, 1.10 lbs of chlorine and 1.6 lbs of caustic are required. The complete oxidation of many compounds necessitates that the chlorination take place in an alkaline solution (pH = 10 to 12). For many organics, the weight ratio of caustic to chlorine is greater than 2 or 3 to one.

(e) Alkaline chlorination will thus introduce at least 9 lbs of dissolved solids (sodium chloride, etc.) for each pound of COD removed. Post-treatment of the chlorinated effluent with lime and/or sulfuric acid could be used to lower the pH and to remove some of the total dissolved solids.

* See equation (1) on previous page

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(b)(3)(2) Hypochlorination of Fixers:

(a) Experimental. In the laboratory, 50cc of used de-silvered (sodium thiosulfate) fixer were treated with 5-gram additions of calcium hypochlorite (HTH - 70% available chlorine). The tan, voluminous, fine precipitate was filtered and the filtrate again treated with a 5-gram portion of HTH. After four such treatments, the solids were white in color and no further chlorination occurred. The filtrate was slightly green in color and highly acidic (pH ~ 1.0). The filtrate was then titrated with a lime slurry until alkaline. Additional white solids were formed and these were allowed to settle. The supernatant liquid was then clear and colorless.

(b) Results:

1. At the end of the fourth treatment with HTH (20 grams), a test for thiosulfate was negative.

2. The COD of the filtrate was found to be 10,000 ppm.

3. After treatment with lime, the total solids content of the filtrate measured about 17 g/l.

(c) Conclusions:

1. The reduction of BOD/COD in a typical (sodium) fixer solution was 85% complete. Treatment with calcium hypochlorite oxidized only the sulfite and thiosulfate.

2. Acetic acid and other organic sources of BOD or COD were not removed by chlorine under these acidic conditions by chlorination.

3. The use of calcium hypochlorite caused precipitation of some of the sulfates (formed by chlorination of sulfite and thiosulfate) as CaSO_4 , reducing the dissolved solids content of the effluent.

4. Considerable heat is liberated in the process.

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(b)(3)(3) Hypochlorination of Bleach:

(a) Experimental. Exactly 10cc of a used bleach solution was diluted to about 50cc with water and then treated with 10 grams of HTH. No reaction was apparent; i.e., no color changes, heating, gasing, etc. A second sample of diluted bleach was made alkaline (pH \approx 10) with NaOH and then similarly treated with 10 grams of HTH. Some lessening in color and heating occurred. After 1 hour, the pH was again adjusted to 10 or greater and an additional 10 grams of HTH was added.

(b) Results and Conclusion. The filtrates from bleach samples treated with HTH consistently gave a positive test for ferricyanide. The destruction of ferri/ferro bleach by hypochlorination is not feasible.

(4) Hypochlorination of Photographic Synthetic Effluents:

(a) Preparation of Two Synthetic Effluents. To study treatment methods for the combination of processing solutions; developers, arrests, dye-removal baths, and fixer processing solutions were combined in the proper proportions to obtain two types of concentrated photographic synthetic effluents. These two concentrated effluents are similar, except that Type A Effluent contained a used, desilvered sodium thiosulfate (F-6) fixer, whereas, an ammonium thiosulfate fixer (KRF-type) was added in Type B Effluent. Selection of the types and the relative volumes of each processing solution was based upon usage data during a typical mission. Table 5 summarizes the make-up, composition, and gives some of the physical and chemical properties of these effluents.

(b) Experimental. One hundred mls of a concentrated synthetic effluent consisting of the proper ratio of fresh developer, used, desilvered fixer, arrest, and dye-removal baths (see Table 5) were diluted to about 1 liter and treated with HTH. Variables in these experiments included the adjustment of pH with caustic solution, repeated additions of HTH, heating, and allowing the treated samples to stand overnight. COD measurements were made on the clear filtrates. Table 5a summarizes the variables and the results.

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(b)(1)
(b)(3)Table 5Make-Up, Composition, and Properties of
Synthetic Processing EffluentsA. Make-Up

<u>Processing Solution</u>	<u>Description</u>	<u>Composition (ml/l)</u>
Developer	#699	412
Developer	#MPG-106	71
Arrest	SB-5	370
Dye-Removal Bath	(Sulfite)	23.5
Dye-Removal Bath	(Caustic)	23.5
Fixer	Type A or Type B*	100
	TOTAL	1000

B. Composition

	<u>Type A</u>		<u>Type B</u>	
	<u>g/l</u>	<u>or % by wt</u>	<u>g/l</u>	<u>or % by wt</u>
Dissolved Inorganic Salts	73.0	6.85	82.0	7.77
Dissolved Organic Salts	12.2	1.15	12.1	1.15
Dissolved Organic Liquids	<u>17.8</u>	<u>1.67</u>	<u>19.3</u>	<u>1.83</u>
TOTAL DISSOLVED SOLUTES:	103.0	9.67	113.4	10.75
	or 0.86 lb/gal		or 0.94 lb/gal	

C. Properties

	<u>Type A</u>	<u>Type B</u>
Specific Gravity (at 70F)	1.062	1.054
pH (at 70F)	6.91	6.87
Viscosity (Brookfield at 70F)	500 cps	700 cps
Freezing Point	26F	26F
Ash (Incinerated)	6.75%	6.75%
Color	Amber	Amber
Oxygen Demand (g O ₂ per liter):		
COD (Theoretical)	48.8	79.2
COD (Observed)	47.0	53.0
BOD (Observed)	36.3	42.0
Chlorine Demand (g Cl ₂ per liter):		
Theoretical	215	350

* Type A Effluent: F-6 (Sodium hypo); Type B Effluent: KRF (Ammonium hypo)

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Table 5A

Hypochlorination of Type A Processing Effluent*

Test No./Sample	Temp (F)	pH (at 70F)	Sodium Hydroxide Added (grams)	Chlorine Source and Amount	COD (ppm)	Notes
11. Type A - 100 mls	80-90	6-8	0.0	0g HTH**	4,400	Before dilution COD is approximately 44,000 ppm
a. Type A - 100 mls	80-90	7.90	0	25g HTH	3,096	
b. Type A - 100 mls	80-90	8.22	0	50g HTH	2,836	
12. Type A - 100 mls	80-90	6-8	0	0g HTH	4,400	
a. Type A - 100 mls	80-90	12-13	10	25g HTH	2,568	
b. Type A - 100 mls	80-90	12-13	20	75g HTH	2,530	
13. Type A - 100 mls	150-160	6-8	0	0g HTH	4,400	
a. Type A - 100 mls	150-160	6-8	0	50g HTH	2,700	
b. Type A - 100 mls	150-160	12.0	10	50g HTH	2,700	
c. Type A - 100 mls	150-160	11.8	20	50g HTH	2,400	
d. Type A - 100 mls	150-160	12.3	30	50g HTH	2,400	
e. Type A - 100 mls	150-160	12.1	20	75g HTH	2,350	
f. Type A - 100 mls	150-160	11.8	20	100g HTH	2,368	
14. Type A - 100 mls	120-160	6-8	0	0g HTH	4,400	
a. Type A - 100 mls	120-160	12-13	10	25g HTH	2,648	Let stand for 5 hours
b. Type A - 100 mls	120-160	12.45	20	50g HTH	1,890	
15. Type A - 100 mls	80-90	6-8	0	0cc Bleach***	4,400	
a. Type A - 100 mls	80-90	13.4	35	150cc Bleach	2,896	Let stand for 30 minutes
b. Type A - 100 mls	150-160	13.5	35	150cc Bleach	2,900	Let stand for 30 minutes

* Before hypochlorination, the sample (100 mls) was diluted to 1000 mls.

** Commercial grade of calcium hypochlorite (70% available Cl_2)

*** Commercial solution of sodium hypochlorite (15% by wt NaOCl)

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(b)(3)(c) Results:

1. The simple bleaching of a combined photographic effluent with calcium hypochlorite at room ambient temperature and without caustic additions reduced COD by about 64%. The addition of caustic to adjust the pH between 12 and 13 increased the chlorination slightly, but half (58%) of the COD still remained (2530 ppm).

2. When the hypochlorination was carried out at 150 to 160F, the chlorination was more complete (53%), leaving an effluent with a COD of 2350 ppm. After standing for 5 hours at 120 to 160F, about 60% of the COD was removed, leaving an effluent having a COD of about 1890 ppm.

3. Hypochlorination with a 15% solution of sodium hypochlorite did not achieve more than a 35% reduction in COD, leaving an effluent with an oxygen demand of about 2900 ppm.

(5) Alkaline Chlorination of Processing Solutions:

(a) Experimental. A small chlorinator was assembled from a 250-ml glass measuring cylinder and a sintered-glass bubbler tube. A 1-lb lecture-bottle cylinder of chlorine was used as the gas source. A known volume of the used processing solution was diluted (as required) and added to the measuring cylinder. The pH was raised to 10 - 12 by adding caustic solution (50% by wt NaOH). Chlorine gas was introduced at a constant rate (0.5 l/min = 1.0 g/min) for periods up to an hour. The temperature was monitored to determine rate of oxidation. The pH was checked periodically and caustic added to maintain a high degree of alkalinity (pH ~ 10 to 13). Table 6 lists some of the test details for processing solutions discussed below.

1. Fixer:

a. A typical sodium thiosulfate fixer, having a theoretical COD of 105 grams of O₂ per liter of fixer, has a (theoretical) chlorine demand of 465 grams of available chlorine (Chlorine Demand = 4.43 x Oxygen Demand, theoretically). Thus, to completely reduce the COD

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Table 6

Alkaline Chlorination of Processing Solutions

Test No.	Solution: Sample	Time (min)	Caustic Solution (mls) (NaOH(g))		Temperature (°C)	Chlorine Rate Weight (l/min) (g)		COD* (ppm)
9.	Color Bleach: 100 mls (Regenerated ferricyanide)	0	100	76	22	0.5	0	[157,500]
a.		30	+50	114	44	0.5	30	4,800
b.		60	+50	152	55	0.5	60	4,600
c.		75			60	0.5	75	6,800
10.	Viscous Developer: 100 mls	0	100	76	23	0.5	0	[25,000]
a.		15			65	0.5	15	<3,500
b.		20	+50	114	100	0.5	20	<3,500
c.		30			67	0.5	30	<3,500
11.	Arrest Bath: 100 mls	0	100	76	23	0.5	0	[19,000]
a.		15			45	0.5	15	8,600
b.		30	+50	114	65	0.5	30	5,400
c.		45			~60	0.5	45	3,500
12.	Developer: 100 mls	0	100	76	25	0.5	0	[16,000]
a.		15			55	0.5	15	9,000
b.		30	+25	95	60	0.5	30	<3,500
c.		45			65	0.5	45	3,200
5.	Sodium Fixer: 100 mls	0	50	38	22	0.5	0	[70,000]
a.		5			56	0.5	5	--
b.		10	+50	76	50	0.5	10	--
c.		30	+50	114	30 (cooled)	0.5	30	4,500
d.		45	+50	152	28	0.5	45	5,000

* COD values in brackets [] are theoretical values of the diluted sample;
all others are observed values on the chlorinated samples.

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of a 100-ml sample of fixer, about 46.5 grams of chlorine are required. In addition, about 50 grams of sodium hydroxide would be theoretically needed to maintain the alkalinity level during complete chlorination.

b. In the laboratory experiment (Test No. 5; see Table 6), the temperature began to drop significantly after chlorination had proceeded for 20 minutes, indicating that the rate of oxidation was decreasing. After 30 minutes of chlorination (30 grams of Cl_2), the effluent had the lowest COD; i.e., 4500 ppm*.

c. Taking into account the dilution factor, about 90% of the COD was removed in less than 30 minutes by 60 grams (or less) of chlorine and 75 grams of NaOH.

2. Viscous Developer:

a. In Tests No. 10 and 12 (see Table 6), 100 mls of a typical viscous developer were chlorinated. After only 15 minutes, the COD of the effluent reached a minimum. Continued chlorination did not reduce the COD below 3200 ppm.

b. The theoretical COD of this developer solution was 50.4 grams of O_2 per liter. The chlorine demand of 100 mls was therefore 22.5 grams of Cl_2 . After 15 minutes of chlorination, the COD therefore was reduced by about 85%.

3. Stop Bath:

a. A 100-ml sample of arrest bath was diluted with an equal volume of caustic solution and the mixture chlorinated for one hour. The COD values were 8600 ppm after 15 minutes (and 15 grams of Cl_2); 5400 ppm after 30 minutes (and 30 grams of Cl_2); and 3500 ppm after 45 minutes (and 60 grams of Cl_2). The theoretical COD is 38.4 grams of O_2 or 170 grams of Cl_2 per liter.

* These COD values were determined by the standard dichromate method. They are not corrected for chloride content; thus, these values may be 1 to 5% high. For this reason, continued chlorination of samples usually gave slightly higher values of COD.

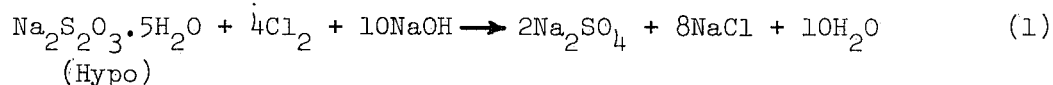
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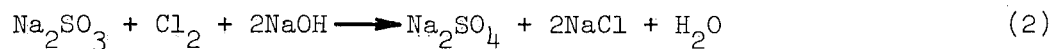
b. After twice the amount of chlorine had been added, the COD was reduced by only 55%; after four times the required chlorine, 28.5% of the COD remained; and after 5.3 times the theoretical chlorine consumption, about 18% of the initial COD still remained.

(b) Summary:

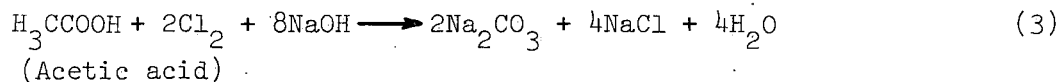
1. The stoichiometric ratios of the following equations best describe the alkaline chlorination of the major constituents of these solutions:



$$(1) + (1.15) + (1.6) = (1.15) + (1.88) + (0.72)$$



$$(1) + (0.563) + (0.635) = (1.14) + (0.93) + (0.156)$$



$$(1) + (2.37) + (5.35) = (3.55) + (3.90) + (1.2)$$

2. For example, for every pound of hypo chlorinated, 1.15 lbs of chlorine and 1.6 lbs of sodium hydroxide are required and about 1.15 lbs of sodium sulfate and 1.88 lbs of salt (NaCl) are produced.

(c) Costs:

1. The chemical costs for alkaline chlorination are dependent upon: the volume and COD of the effluent; the source of the chlorine; and the degree of oxidation desired or required for acceptable treatment.

2. Tables 1 and 3 indicate that the theoretical COD of all chemicals sewered for black-and-white processing at this installation is 217,000 lbs O₂ per year. The average COD of the effluent is about 1750 ppm*. Acceptable pollution control would require sufficient oxidation

* Also, see Table 5

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of the effluent so that the BOD_5 would be about 300 ppm. This would call for an effluent with a COD not greater than 500 ppm; or, the removal of 70 to 75% of the total COD. Annually, about 150,000 lbs of COD should be removed by chlorination.

3. Adequate chlorination of the effluent to guarantee operational security will require a thorough oxidation of the effluent, including destruction of organics. If organics are destroyed, about 200,000 lbs of COD must be removed by alkaline chlorination. The weight ratio of caustic to chlorine required in this case would be high; probably, about two to one.

4. The quantity cost for chlorine varies from about \$0.04 to 0.23 per lb, depending upon source and container size (see Table 7). Sodium hydroxide is commercially available at \$0.07 per lb as a 50% (by wt) caustic solution.

5. If chlorine is purchased in 1-ton cylinders, the chlorine cost will be \$0.27 per lb of COD removed. The caustic requirement is estimated at 1.5 lbs of sodium hydroxide for each lb of chlorine; cost is \$0.47 per lb of COD. The estimated chemical cost for alkaline chlorination therefore is about \$0.74 per lb of COD removed. The adequate treatment of the department effluent thus will cost about \$150,000 per year for caustic and chlorine.

6. The cost of treating selected effluents would be proportioned to their COD content. Developers and fixers carry about 100 g/l of COD. Therefore, the cost of completely reducing the oxygen demand of these processing effluents is about \$0.15 per liter. For arrest baths, containing about 40 g/l COD, the alkaline chlorination cost is \$0.06 per liter, and for a dye-removal bath (12 g/l COD), about \$0.02 per liter. If the above used processing solutions are combined, the estimated cost would be about \$0.12 per liter.

7. Assuming that some post-treatment is required to re-adjust pH, to remove dissolved solids, and to dispose of solids, the annual cost for chlorination could be as high as \$200,000.

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Chlorine Sources and Chlorination Costs

<u>Chlorine Source</u>	<u>Chlorine Cost</u>		<u>Chlorination Cost*</u> (per lb of COD)
	<u>(per lb Cl₂)</u>	<u>(per lb of COD)</u>	
Gas:			
Tank Car	0.04	0.18	0.65
1-Ton Cylinder	0.06	0.27	0.74
150-lb Cylinder	0.13	0.58	1.05
Sodium Hypochlorite (15% solution)	0.20	0.89	1.35
Calcium Hypochlorite (70% available Cl ₂)	0.23	1.02	1.48

* Includes the cost of sodium hydroxide required (ratio of NaOH to chlorine is 1.5 by wt); based on NaOH costing \$0.07 per lb. as a 50% by wt caustic solution.

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8. Treatment of the chlorinated effluent with lime and sulfuric acid to lower pH and to remove some dissolved solids would cost an additional \$25,000.

9. Labor, estimated at one man full time, would cost an additional \$25,000.

10. Facilities required for a chlorination system are as follows:

<u>a.</u> Two chlorinators, including controls, safety switches, alarms, etc.	\$12,000
<u>b.</u> Chlorine storage, hoist, etc.	3,000
<u>c.</u> Two storage tanks, 3000 gal. size	5,000
<u>d.</u> Lime treatment and solids removal equipment	<u>5,000</u>
TOTAL	\$25,000

(d) Conclusions:

1. Hypochlorination will not adequately treat processing wastes of this department.

2. Alkaline chlorination will satisfactorily reduce the COD/BOD and destroy the processing flags of photographic wastes.

3. The chlorinated effluent should be post-treated to adjust acidity and to remove sulfates.

4. Capital costs for chlorination are relatively inexpensive; about \$25,000.

5. Chemical cost for chlorine and caustic to adequately treat department waste would be about \$200,000 per year; about \$0.45 per gallon of (concentrated) processing solution.

6. These chemical costs probably are too high to consider this method of treatment.

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(b)(3)f. Evaporation:(1) General:

(a). The evaporation or concentration of fluid wastes is commonly used as an abatement step in the treatment of numerous wastes¹⁶⁻¹⁸. In photographic processing, the developers, fixers, and stop baths account for most of the pollution while pollution from the dye-removal bath and rinse water is small. By changing the plumbing of the machine, all of the processing effluents could be combined and separated from the rinse water. Thus, only 3 to 5% of the total department effluent need be treated by evaporation; i.e., about 470,000 gallons per year (see Table 2).

(b) Several types of equipment are commercially available for the concentration of aqueous solutions: single and multi-effect evaporation will provide concentration of wastes batch-wise; thin-film evaporators operate continuously to concentrate a fluid; and spray-dryers provide another means of removing solids from an effluent. Labor requirements for batch evaporators are generally higher than for continuous, thin-film evaporators. Initial costs for continuous equipment are, however, higher.

(c) A disposal area for solids and trucking facilities to handle about 350 tons per year (7 tons per week) would be required.

(2) Experimental. A known volume of the processing solution was placed in a measuring beaker and allowed to evaporate gently at its boiling point on a hotplate. As the sample volume was reduced, it was periodically cooled to room ambient temperature and seeded to initiate crystal formation.

(3) Results:(a) Sodium Fixer:

1. Two liters of a (fresh) sodium fixer were placed in a stainless steel dish and heated to the boiling point (216F) on a hotplate. After a 60% reduction in volume, the contents were allowed to cool to room ambient temperature (80F). No solid phase formed.

¹⁶⁻¹⁸
See References.

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2. Evaporation was continued giving an 80% reduction in volume; then upon cooling, a white solid cake of dry crystals formed, which weighed 590 to 600 grams.

3. Sulphur dioxide was not detected (by odor).

(b) Combined Processing Solution:

1. One liter of a concentrated combined processing solution (see paragraph 4.e.(4)(a) on page 31) was reduced in volume to 200 cc and allowed to cool. Some solids formed, but a liquid phase also remained.

2. After reduction to only 100 cc, the residue consisted primarily of light tan, granular solids; some liquid still remained.

3. Upon reducing the sample to 65 cc, no liquid remained. The moist, light tan residue consisted of granular material as well as strands of fibrous solids.

4. Sulfur dioxide was not detected during the evaporation.

(4) Costs:

(a) Energy costs for evaporation would be about \$0.04 to \$0.05 per gallon. If all of the processing effluents (excluding rinse water) were treated, the cost for steam or gas heat would be \$20,000 to \$25,000 per year.

(b) In addition to the heat costs, additional expense for packaging, trucking, and disposal of the solids is estimated at \$25,000 per year.

(c) Capital costs for large volume equipment (installed) will be about \$1.00 per gallon per day. However, thin-film evaporators or small evaporative units are much more expensive: e.g., continuous concentrating system for 300 to 5000 gallons per day would cost about \$50,000 to \$75,000 (estimated).

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(5) Conclusion. Assuming a disposal site for solids is available, the concentration of this department's processing effluent by evaporation or spray drying should be considered.

g. Pyrodecomposition:

(1) General.

(a) The Zempro Process (the high temperature wet oxidation of fluid wastes) is a patented system for the smokeless incineration¹⁹⁻²¹ of biological wastes. The method has commonly been used for the disposal of the sludges from primary and secondary sewage treatment. The heat produced in large units is generally adequate for generating the electricity required for operation of the sewage plant. The ash produced is almost completely inorganic, innocuous, and biologically sterile.

(b) Recently, fluid waste burners have been designed to vaporize and oxidize both aqueous and non-aqueous chemical wastes. If the heat of combustion of the solvent plus solute is above 75,000 BTU/gallon, generally no supporting fuel is required. With aqueous wastes having little or no calorific heat value, vaporization, thermal decomposition, and oxidation are achieved by either an oil or gas-fired burner.

(c) Several manufacturers claim efficient and economical application of wet incineration to aqueous wastes. Several commercial units are equipped with scrubber equipment to remove gas or particulate air contaminants. The stack gases are generally colorless and odorless due to the high combustion temperatures (1000 to 2200F) and long dwell times.

(2) Experimental. Two synthetic processing wastes were prepared from the proper proportions of developer, fixer, arrest, and dye-removal solutions. (See Table 5). Samples of these effluents were sent to an outside laboratory for combustion tests.

(3) Results.

(a) The waste was found to have a very meager heat value; i.e., 150 BTU/lb.

¹⁹⁻²¹ See References.

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(b) After ignition, the residue measured 6.75% by wt of a highly-basic, water-soluble ash.

(4) Costs.

(a) Since there is very little fuel value to the solutes, the energy costs will be about the same as for evaporation; 7,500 BTU per lb, or \$0.04 to 0.05 per gallon.

(b) Costs for gas and labor will be \$55,000 per year.

(c) Equipment sized to handle 125 gph will cost about \$100,000.

(5) Conclusions.

(a) Pyrodecomposition of the more concentrated processing effluents (i.e., developers and fixers) should be considered.

(b) Arrest and dye-removal baths could also be treated by pyrodecomposition; but, there are more economical, adequate methods.

h. Ozonation:

(1) Description.

(a) An alternate chemical method of lowering the BOD/COD, destroying toxic materials, and removing processing flags is by ozonation. As in chlorination, sulfites and thiosulfates are oxidized to sulfates, and other organics are oxidized to carbon dioxide and water. Ozonation, however, does not add to the dissolved solids total as does chlorination.

(b) Ozonation has been used in tertiary treatment plants on effluents containing organics²². The destruction of cyanides and ferri/ferro cyanides is reported to be more efficient by ozonation than by chlorination.

(c) Theoretically, 1.5 lbs of ozone are required for each pound of COD or BOD removed.

(2) Costs.

(a) The electrical power costs for the production of ozone by an electrical generator is reported to be \$0.15 per lb of O₃.

²² See References.

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The energy cost of reducing the COD by ozonation is therefore about \$0.22 per lb of oxygen demand, or about one-third that of chlorination. Annually, the power costs for producing the ozone required would cost \$45,000; or, about \$0.10 per gallon of effluent treated.

(b) To produce the 300,000 lbs/yr of ozone required by the treatment center for this department, capital costs would be about \$500,000.

(3) Conclusions:

(a) Reduction of the COD/BOD and destruction of organics by ozonation would be cheaper than by alkaline chlorination.

(b) Ozonation would not add dissolved solids to the effluent.

(c) The major disadvantage to ozonation is the initial cost of the ozone producing equipment.

i. Reverse Osmosis, Dialysis/Electrodialysis, and Ion Exchange

(1) General:

(a) Applications for these physical methods are generally limited to the purification of "brackish" waters or feed solutions having a low solids content; i.e., 0.1 to 5%. Their main value is in water conservation and not as final-treatment methods for pollution control.

(b) Of these four physical methods, reverse osmosis (RO) has been most thoroughly investigated and tested for water conservation with photographic processing solutions²³.

(c) RO units employing cellulose acetate membranes have been used to treat washwaters from the Versamat and other processors. Some specific findings from these studies are as follows:

1. The pH of the product water changes very little with treatment.

2. The average retention ratios of most ions found in processing effluents are high:

a. Thiosulfates (e.g., $\text{Na}_2\text{S}_2\text{O}_3$) - 97 to 1

b. Sulfites (e.g., Na_2SO_3) - 63 to 1

c. Acetate (e.g., acetic acid) - 98/99 to 1

d. Ferri/ferro cyanides [e.g., $\text{Na}_4\text{Fe}(\text{CN})_6$] - 98 to 1

²³ See References.

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- e. Bromides (e.g., NaBr) - 100 to 1
- f. Dichromates (e.g., $K_2Cr_2O_7$) - 94 to 1
- g. Hydroquinone - 88 to 1

3. Some compounds, however, have a very low retention ratio:

- a. Benzyl alcohol - 8 to 1
- b. Formalin - 4 to 1
- c. Elon - 2 to 1

4. At an operating pressure of about 600 psi, RO units tested with the Versamat (Model 11A) Processor satisfactorily purified wash water for re-use; these units cut consumption of water by 25% without affecting the residual hypo level in the film processed.

5. For very dilute feeds, as with some rinse waters, 98% recovery of the water has been achieved. For more concentrated feeds, the purified product may contain 10% of the initial impurity levels and recover 90% of the water.

6. Flux rates obtainable will vary with feed type plus concentration, output rate and purity, pressure, and membranes; but a range is 0.05 to 0.30 gal/day/sq ft of membrane.

7. Commercially available units are offered by several companies; the units vary in size from small laboratory experimental models (2 gpm) to large industrial units (1 mgd).

(2) Costs:

(a) Operating costs (for utilities) are about \$0.60 per 1000 gallons of reclaimed product.

(b) Capital costs for typical large units are about \$1.00 per gallon per day. Thus, a unit to treat wash-water effluents of this department would cost about \$35,000.

(c) Small laboratory or experimental units can be purchased for about \$2000 and will deliver 2 or 5 gallons per minute.

(3) Conclusions:

(a) Reverse osmosis could be used to treat wash water; this method will reduce wash-water consumption by 75%.

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(b) Dye-removal and arrest baths could be treated by reverse osmosis. Reverse osmosis would give a more concentrated (10X) effluent for disposal by other pollution methods and would give a purified product that could be reused for wash water.

(c) The concentrated effluent from a RO unit would require treatment by other pollution methods, such as incineration, evaporation, chlorination, etc.

5. Separate versus Combined Treatment:

a. As indicated by Paragraph 3.c.(3)(d) on page 17, the wash water effluents require no treatment and may be sewered directly. All other processing effluents will require some treatment, either to reduce pollution or to maintain operational security.

b. The separate treatment of arrest and dye-removal baths by reverse osmosis (RO) is the cheapest method studied. The concentrated stream could then be treated by evaporation or pyrodecomposition and the purified product water reused. (If water conservation were a prime objective, the RO equipment should be sized to treat the wash water, jointly.)

c. Developers and fixer baths are adequately treated by biochemical oxidation, alkaline chlorination, evaporation/concentration, pyrodecomposition, or ozonation. These effluents could be treated separately or in combination by these abatement methods. A study of the costs (see Table 8), however, indicates that there are no savings in operating costs by considering separate treatment of developer or fixer by these methods. Developers and fixers should be combined.

d. If RO equipment is used for concentrating the dye-removal and arrest baths or wash water, these concentrates also should be combined with the used developer and fixer solutions.

6. Acceptable Treatment Methods:

a. Biochemical Oxidation:

(1) A biological treatment tank sized to handle about 500 lbs of BOD in 40 to 60,000 gallons/day would be the cheapest treatment studied. An activated-sludge system would require an estimated tank volume of 12,000 cu ft. The effluent then could be sewered without further treatment.

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Table 8

Estimated Costs of Pollution Abatement Proposals

	Concentrated Processing Effluent*	Developers	Fixers	Arrest Baths	Dye Removal Baths	Wash Water
<u>Capacity Required</u>						
Annual volume (liters)	1,745,000	1,212,000	283,000	187,000	62,500	14,000,000
Daily average (liters/day)	5,800	4,000	950	625	210	60,000
<u>Treatment Methods</u>						
<u>Acidification/aeration:</u>	Partial	Partial	Partial	Note 4	Complete	Note 3
Initial Cost (Equip. + Install.)					10K	
Operating Cost (Labor, Chemicals, Power, etc.) per 1000 liters	\$ 5.00	\$ 2.00	\$ 13.00		\$ 4.00	
<u>Biochemical oxidation</u> (Note 2)						
Initial cost (equip. + Install.)	75K					
Operating Cost (Labor, Chemicals, Power, etc.) per 1000 liters.	\$15.00					Note 1
Annual Operating Cost**	25K					
<u>Alkaline Chlorination</u> (Note 2)						
(b)(1) Initial cost (equip. + install.)	15K					(b)(1)
(b)(3) Operating Cost (Labor, Chemicals, Power, etc.) per 1000 liters	\$ 120	\$150	\$160	\$ 60	\$ 20	(b)(3) Note 1
Annual Operating Cost	200K	159,000	40,000	10,000	1,000	

* This effluent contains all of the used processing solutions (i.e., developer, fixer, arrest bath, and dye-removal bath); wash (rinse) water is excluded from this effluent.

** Determined by multiplying Annual Volume (liters) by Operating Cost per 1000 liters.

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Table 8 (cont'd)

Estimated Costs of Pollution Abatement Proposals

<u>Treatment Methods (continued)</u>	<u>Concentrated Processing Effluent</u>	<u>Developers</u>	<u>Fixers</u>	<u>Arrest Baths</u>	<u>Dye Removal Baths</u>	<u>Wash Water</u>
<u>Evaporation/concentration</u>						
Initial cost (equip. + install.)	75K					Note 3
Operating cost (labor, Chemicals, Power, etc.) per 1000 liters	\$32.00	\$32.00	\$35.00	\$20.00	\$20.00	
Annual Operating Cost	55K					
<u>Pyrodecomposition</u>						
Initial Cost (equip. + Install.)	100K					
Operating Cost (Labor, Chemicals, Power, etc.) per 1000 liters	\$32.00	\$32.00	\$35.00	\$20.00	\$20.00	Note 3
Annual Operating Cost	55K					
<u>Ozonation</u>						
Initial Cost (equip. + install.)	500K					Note 3
Operating Cost (Labor, Chemicals, Power, etc.) per 1000 liters	\$ 40	\$ 50	\$ 50	\$ 20	\$ 10	
Annual Operating Cost	70K					(b)(1) (b)(3)
<u>Reverse Osmosis</u>						
Initial Cost (equip. + Install.)						15K
Operating Cost (Labor, Chemicals, Power, etc.) per 1000 liters	Note 4	Note 4	Note 4	\$0.20	\$0.20	\$0.15
Annual Operating Cost						3K

- NOTES: (1) Included in treatment of concentrated processing solution.
 (2) Applies to all effluents, including wash water.
 (3) No treatment required.
 (4) Method does not apply.

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- 50 -

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(2) The annual operating cost is estimated at \$25,000 per year (or \$15.00 per 1000 liters). The initial cost of the facility, about \$100,000.

b. Evaporation/Concentration:

(1) This second choice of treatment is predicated upon the location of a suitable means of solids disposal, either by land-fill or by incineration. Maintaining operational security would require special procedures in the disposal of the solids.

(2) The energy costs of concentrating photographic processing solutions are comparable to those for biochemical treatment. Solids disposal will double the operating expense estimated at \$55,000 per year.

c. Pyrodecomposition:

(1) The incineration of the concentrated fluid waste has the advantage of destroying all of the processing chemicals. The remaining solids (mostly sodium sulfate) therefore are innocuous and may be sewered without jeopardizing security. Solids or residue disposal are not a problem, since their removal is by the stack-gas scrubber; this effluent may be sewered.

(2) The equipment and full costs for pyrodecomposition are higher than for evaporation.

d. Ozonation:

(1) Treatment of all processing effluents, including rinse water, with ozone is also an acceptable method.

(2) The electrical costs for ozonation are cheaper than the chemical costs for alkaline chlorination. However, equipment for producing the ozone required for this installation is expensive; about \$500,000.

e. Reverse Osmosis (RO):

(1) RO equipment would adequately treat arrest and dye-removal baths. If evaporation, pyrodecomposition, or trucking of the concentrated developer and fixer are adopted, the arrest and dye-removal effluents should be pretreated by RO. The concentrated product can then be treated along with the developer and fixer.

(2) Initial cost for RO equipment to treat arrest and dye-removal baths would be \$35,000. The annual operating cost for labor, chemicals, power, etc. will be about \$7,500 per year.

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PILOT TESTING STUDY

7. Introduction

a. Treatment studies indicated that either one of two approaches should be made towards acceptable pollution control for the department:

(1) All effluents from the department, including rinse water, should either be treated by alkaline chlorination or by a biological oxidation system; i.e., activated-sludge or trickling filter; or

(2) The used processing solutions should be combined (rinse water excluded), and this concentrated waste treated either by incineration or by evaporation/concentration.

b. To determine performance data on actual processing waste samples, two synthetic waste concentrates were prepared from used processing solutions. Both effluents are representative of wastes anticipated in 1970 and 1971. They are similar in composition, except that Type A effluent contains used, desilvered, sodium fixer solution; whereas the desilvered ammonium (KRF-type) fixer was used in Type B effluent (See Table 5).

8. Evaporation/Concentration

a. General: A dozen or more manufacturers of evaporation equipment were contacted and given general information on the volume and properties of the waste to be concentrated. The problem was described to each equipment manufacturer as follows: Evaporate 2000 to 3000 gallons/day of an aqueous waste containing about 1 lb/gallon of dissolved solids. Depending upon the response received, follow-up included requests for rough sketches and price estimates, pilot-tests, or interviews with technical representatives.

b. Preliminary Investigation. Numerous types of equipment were proposed by the following companies which responded to inquiries from this department:

(1) Acme Process Equipment Co. Acme proposed a rotary concentrator having approximately 1400 ft² of surface area. Their concentrator units measure 110 ft²/module, necessitating some 13 units at a cost of \$150,000. Drives and other equipment were estimated at an

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additional \$25,000 for an estimated equipment cost in excess of \$175,000. No further action was taken after examination of their initial quotation.

(2) Zoremba Company. Representatives of the Zoremba Co., which designs and makes many different types of evaporator/concentration equipment, indicated their unit would require 75-100 ft² of evaporation surface area. The unit would be 4 ft x 4 ft x 4 ft high and, with all accessory equipment, would cost about \$28,000. Delivery would be in 4 to 5 months from final design and placement of order.

(3) Thermal Research and Engineering Corp. A submerged combustion unit to concentrate the effluent was proposed by Thermal Research and Engineering Corp. Estimated size of the evaporator unit would be 3-1/2 ft in diameter x 4 ft high, not including a 1.25 million BTU/hr burner unit (fuel oil or gas-fired) and a blower to supply 1250 cu ft/hr of hot air. The estimated cost quoted was \$10,000. The submerged combustion unit would also require solids removal equipment, such as a rotary vacuum filter. Heat recovery from the unit was not deemed feasible.

(4) Artisan Industries. An Artisan "Rothotherm" evaporator was demonstrated. This unit is best described as a non-mechanical thin-film evaporator. Estimated size to handle 125 gallons/hour was 4 ft x 6 ft x 27 ft high with equipment costs of \$10,000 to \$12,000 without accessory instrumentation.

(5) Stern-Rogers. As a result of their studies on an effluent sample supplied them, Stern-Rogers proposed a Rotary Dehydrator (Drawing #13209/2). The direct-fired concurrent-flow unit would be about 3 ft in diameter x 12 ft long, including the refractory-lined air heater, burner, and connections. Including a fan, damper, dust collector, and all controls, the system was estimated to cost \$24,800.

(6) Swenson. The Swenson Division of Whiting Corp. proposed a standard single-effect long tube vertical evaporator unit. Estimated cost for the evaporator, condenser, mounts, and controls would be \$18,000.

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A rotary vacuum filter system for solids removal would be required at an additional unspecified cost.

(7) Batch Evaporators. Single-effect evaporator units can be purchased or fabricated to evaporate 750 gallons per 8-hour trick. Estimated costs of operation are \$150/day for 1500 gallons/day, based on two-trick operation. This includes clean out, re-filling, and necessary maintenance.

c. Pilot-Tests

(1) Pfaudler (Div. of Sybron) Thin-Film Evaporation

(a) Testing. A feasibility study using a 2-inch Wiped Film Evaporator Unit (WFE) indicated that waste from this department could be concentrated and 80 to 90% of the water removed by single or multiple passes through their pilot unit. Consequently, arrangements were made for shipping 100 gallons of Type A Effluent (See Table 5) to Pfaudler's and for conducting a pilot-test on their 12-inch WFE unit.

(b) Results. Table 9 summarizes the results of these pilot runs. The COD measurements on the distillate fractions were determined by a standard analytical method²⁴. The pilot test indicated that the Pfaudler unit was not capable of more than a 65% distillate-to-residue split. The apparent reason for this low efficiency was due to the clogging of the unit by the formation of a gelatinous residue, which attached itself to the wiper blades. Further examination of the unit revealed that the many entrainment separators, wiper blade flanges, and other component ledges offered numerous points for the solidified residue to become trapped. The best performance in terms of distillate properties was obtained when the unit was operating under a vacuum. At a reduced pressure of 120 mm (abs), the COD of the distillate was well under 1000 ppm, as compared with 2000 to 3000 ppm for operation at atmospheric pressure.

²⁴ See References.

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Table 9

Pfaudler's Wiped Film Evaporator Pilot-Test
(Selected Runs)

Run No.	Jacket Temp (F)	Rotor Speed (rpm)	Pressure (mm of Hg)	Feed Rate (lbs/hr)	Distillate Split (%)	COD of Distillate (ppm)	Notes
1	280	280	760	195	38	2200	
2	280	280	760	137	55	3000	
4	280	280	760	117	73	1300	
5	308	280	760	117	86	600	Clogging
6	318	280	760	123	85	1900	Clogging
10	330	280	760	93	85	3400	Clogging
13	300	100	760	87	78	2200	
14	303	150	760	97	70	3000	
16	215	280	120	145	58	1300	
17	215	280	120	-	-	600	
19	283	280	760	108	65	1900	
26	275	280	760	103	62	2000	

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(c) Conclusions: The Pfaudler thin-film evaporator will not adequately concentrate effluent of this department without major redesign to avoid clogging problems²⁵.

(2) Votator "Turba-Film" Evaporator:

(a) Testing. During two days of testing, thirteen pilot runs were made using a 1 sq-ft thin-film evaporator unit at the Louisville, Ky, plant of the Votator Division, Chemetron Corp. Two types of rotor blades were used: a fixed-clearance (0.030 inch) and a hinged "Hydra-Film" rotor with "Duron" blades, which actually wiped the inner wall. The operating parameters were as follows:

1. Steam pressure - Atm. to 100 psig
2. Wall temperature - 212 to 350F
3. Feed rates - 55 to 70 lb/hr
4. Rotor speed - 300 to 2100 rpm
5. Pressure - Atm. to 25 in. of Hg (vacuum)

(b) Results:

1. During the first runs with the fixed-clearance rotor, there was a build-up of dried solids on the inner wall of the evaporator. The residue fraction was comprised of polymerized hunks of white solids, suspended in considerable amounts of water. The maximum distillate-to-residue split obtained was 66 to 34%. The pH of the distillate was 9 to 10.5.

2. Tests with the "Hydra-Film" rotor were conducted under similar operating conditions. Build-up on the inner wall did not occur and the solids were discharged as a white, creamy fluid. As the solids separation improved, the viscosity of this paste increased, but no granularity was noted. Upon drying the residue (at 103C), the solids content was 71.5% by wt.

3. A distillate-to-residue split of 92 to 8% was achieved on one test and, over a continuous 2-hour run, a 88 to 12% split was achieved. The distillate fractions were clear and had a COD of less than 100 ppm.

(c) Conclusions:

1. Pilot-tests showed that the "Hydra-Film" evaporator was acceptable in separating dissolved solids from effluent of this

²⁵ See References.

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department. The separation gave a viscous, creamy-looking residue with little free liquid and suitable for solids disposal in a reduced volume. The distillate would be suitable for dumping into the sewer and a 10 to 1 reduction in volume could be achieved by this evaporator equipment.

2. This method would require disposing five 55-gallon drums of a highly viscous slurry each day.

(3) Conical Bottom Laboratory Spray Dryer.

(a) Testing. Feasibility tests on the spray-drying of effluent from this department were conducted on Bowen's Conical Bottom Laboratory Spray Dryer. This gas-fired unit was operated over the range of conditions listed below:

1. Feed rate - 230 to 360 mls/min
2. Feed temp - 65 to 125F
3. Gas inlet temp - 400 to 700F
4. Gas outlet temp - 230 to 415F

Two types of atomization were tested: a two-fluid orifice (air plus the feed) and a centrifugal atomizer. By the proper adjustment of the above parameters, a thoroughly dry, powdery residue was obtained from the effluent. The stack gases were nearly colorless, odorless, and as much as 75% of the solids were recovered in the cyclone dust collector. Table 10 summarizes the feed conditions, operating conditions, and material balance of the Bowen pilot test.

(b) Pilot-Test. Eight pilot runs then were made with Types A and B effluent* in a 7-foot diameter spray-dryer. The operating parameters were similar to those of the feasibility test, except that atomization was accomplished by a high-speed centrifugal atomizer. During the runs, the stack gases were checked and sampled for odor and particulates.

(c) Results

1. For either type of feed (Type A or B), the drying chamber could be operated almost clean when the air inlet temperature was 500 to 600F and the air outlet temperature was 320F. Slightly better atomization was achieved when the feed was heated to

* These effluents are similar in composition except that Type A contains used, desilvered sodium fixer solution, and the Type B contains desilvered ammonium (KFR-type) fixer.

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Table 10

Bowen Pilot Test

RUN NO.	1	2	3	4	5	6	7	8
DATE:	APRIL 7, 1969				APRIL 8, 1969		APRIL 9, 1969	
FEED CONDITIONS:								
Identification	----- Effluent Residue Solution -----							
Feed Make-Up	----- Type 'A' - As Received -----				Type 'B'		Type 'A'	
					As Received		As Received	
Type	----- Solution -----							
Wt. % Solids	----- 8.6 -----				8.5		8.5	
Spec. Gravity	----- 1.05 -----				1.06		1.06	
Temperature F	Room Temperature		120	125	120	120	120 to	66
						Room Temp.		
Feed Rate, lbs/min	10.4	13.3	10.9	10.5	4.4	4.4	7.2	5.2
Total Feed, lbs	478	481	328	335	280	892	4055	2491
OPERATING CONDITIONS:								
Inlet Temp. F	700	1000	700	700	500	500	600	550
Outlet Temp. F	330	425	330	330	320	320	330	330
Type Heat	----- Direct Gas -----							
Atomizer Type	----- Centrifugal -----							
Atomizer Description	----- 7" CSE -----				----- 8" CSE -----			
Atomizing Force, Speed RPM	----- 21,000 -----							
Cold Air Utilization	----- None -----							
Chamber Conditions	Moderate Accum.	Charred Accum. Smoldering on side walls	Moderate Accumulation Mostly in Spray Ring		Slight Accumulation		Moderate Spray Ring	Slight Accum.
MATERIAL BALANCE:								
Cyclone Collector (lbs)	23	18	12	15	20	50	230	184
Chamber Wall, (lbs)	7	6	9	9	1	1	25	6
Total Collected (lbs)	30	24	21	24	21	51	255	190
Total Solids Fed (lbs)	41	41.3	28.2	28.8	24.1	75.8	345	214
% Recovery, Wet Basis	73.2	58.0	74.5	83.3	87.0	67.2	74.0	89.0
ANALYSIS OF CONDENSATES FROM STACK EFFLUENT								
pH					4.2	6.6	6.6	4.7
Color					Dark	Light Yellow	Light Yellow	Dark
COD (ppm)					6000	22,000	22,000 to 24,000	10,000
SO ₃ ⁼ as Na ₂ SO ₃ (g/l)					-	0.0	1.7-1.8	0.0
N as NH ₄ ⁺ (g/l)					-	4.5	-	0.4

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- 58 -

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120°F. At the ideal operating conditions, 80 to 90% of the solids were recovered. Feed rates of about 5 lbs/min or about 35 gallons/hour were feasible for the 7-foot unit.

2. The stack effluent was monitored and sampled during the runs on each type of effluent. Gas samples were collected and analyzed: carbon dioxide and water were the major constituents. Sulfur dioxide and ammonia were estimated to be less than 3 ppm and 50 ppm, respectively. Neither of these constituents could be detected by odor in the stack effluent. The smoke from the stack was nearly colorless; efforts to collect stack particulate matter on a filter were not fruitful.

3. Condensates from the stacks were collected during several of the runs. These samples were analyzed for COD, ammonia, and sulfites as shown in Table 10. The condensates collected during the pilot runs on the Type B effluent (containing the ammonium fixer) showed significantly higher concentrations of both sulfites and ammonia than samples collected during runs on the Type A effluent (containing sodium thiosulfate). This is not too surprising, since ammonium thiosulfate is less thermally stable than sodium thiosulfate.

4. The powdery product from the spray-dryer of the simulated processing effluent (either Type A or B) had a bulk density of 0.20 g/cm^3 (12.5 lbs/ft^3). Thus, after concentration by spray-drying the solids' product occupied one-half the volume of the aqueous waste.

5. The powdery product was compressed to a density of 2.0 g/l (125 lbs/ft^3) giving a 10-fold reduction in volume.

6. To concentrate 125 gal/hr (average) of effluent from the department, a 10-foot diameter spray-drying chamber would be necessary. The preliminary price quoted by Bowen for the system was \$75,000.

(d) Conclusions. Spray-drying could be considered as one method of removing dissolved solids from the department effluent. The water is thoroughly removed, leaving a powdery residue requiring further treatment by incineration or by a disposal area for solids.

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9. Pyrodecomposition. Several manufacturers of waste incinerators were contacted and asked to submit sketches and rough cost estimates for disposal of 75 gal/hr (avg) of an aqueous waste, having the general description given in Table 11. Favorable responses and/or proposals were received from the Prencos Division of Pickands Mather & Co., John Zinc Co., Peabody Engineering Corp., and Hydro Combustion Corp.

a. Prencos Division of Pickands Mather & Co.

(1) Pilot Tests

(a) A study conducted by Prencos indicated that incineration of the waste effluent was feasible. A white, basic, water-soluble ash remained after incineration. The heat value of the feed was found to be low (150 BTU/lb). Prencos recommended further investigation and a pilot test with their Super E³ Pyrodecomposition Unit.

(b) Pilot tests were conducted and stack gases were sampled and analyzed while the unit was operating on both types of simulated processing effluents. At a burning rate of 15 gal/hr, both wastes gave a moderate white plume when incinerated at a combustion chamber temperature of 2200F. There was no odor from the combustion of the waste with this unit.

(c) The incinerator system used in pilot tests consists of a vertical retort with an ignition chamber, blower fans, atomizing feed nozzle, and an auxiliary fuel (natural gas or oil) burner. When the operating temperature is reached (after a 4-hour warm-up), the effluent is pumped through the atomizing nozzle at a pressure of about 70 psi. The blower forced air and fuel mixture enters and mixes with the atomized effluent, pushing it into the ignition chamber (the bottom of the stack). In the ignition chamber, the temperature rises to as high as 2200F where thermal decomposition and further oxidation occurs. As the combustion products approach the top of the stack, an air cone (injection of cooler air) cools the stack gases, and reduces the exhaust temperature to about 1000F.

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(b)(3)Table 11

General Description of Fluid Waste

Solvent:	Water		
Solutes:	Dissolved inorganic solids	7.75%	by wt.
	Dissolved organic solids	1.0	" "
	Dissolved organic liquids	<u>2.0</u>	" "
	TOTAL DISSOLVED SOLUTES	10.75	" "
Density:	1.06		
Viscosity:	From water-like to 800 centipoises (max.)		
pH:	About 7.0		
Temperature:	About 70°F		
Volume:	Maximum rate:	125 gal/hr	
	Average rate:	75 gal/hr	
Other properties:	<ul style="list-style-type: none"> - Non-toxic - Non-corrosive - Heat of Combustion: None - Non-flammable, explosive, etc. - Halides: None 		
Heat of Combustion of Solute:	150 BTU/lb of waste		

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(b)(3)(2) Sampling and Analysis

(a) A local independent testing agency was contracted to monitor some of the operating parameters, collect stack gas samples, and analyze for particulate or chemical pollutants during the pilot runs on the waste. The results are shown in Table 12. The unit was operated on both types of effluent at 20 gal/hr.

(b) The emerging stack gases were found to range in temperature from 1000F to as high as 2100F. Stack gas volumes at these temperatures ranged from 4050 to 3300 cfm.

(c) The carbon dioxide content of the stack emission was 2.8% (by volume) for both feeds. Ammonia content was negligible. The carbon monoxide, oxygen, oxides of nitrogen, and oxides of sulfur were significantly different for each feed type. The highest carbon monoxide content (2.6%) and sulfur dioxide (2.46 ppm) came from the Type A (sodium fixer) feed. The highest concentration of nitrogen oxides (167 ppm as NO₂) in the stack gases was observed with the Type B (ammonium fixer) Feed.

(d) The smoke or plume density was well under 20% or less than Ringelmann Chart #1. The particulate matter collected was completely water soluble and slightly acidic. The mean particle size was 10 microns, with an observed range of from 1 to over 150 microns. Attempts to collect an adequate sample of particulate matter for further evaluation were not successful.

(3) Conclusion. These tests demonstrated that pyrodecomposition or incineration would render suitable treatment for a combined aqueous photographic waste. Further testing would be required to determine whether or not the stack gases contain excess settleable particulate matter and to select suitable equipment that could be used with an adequate stack gas scrubber.

(4) Equipment Size and Cost. A unit sized to handle about 75 gal/hr (average) would require a concrete pad about 10x10 ft and would be approximately 28-ft high. The equipment cost would be about \$40,000, including remote control panels and safety interlocks.

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(b)(3)Table 12Incineration Pilot Test Results²⁶Test Unit: Prencos Super E₃ Pyrodecomposition Unit

Test Conditions: Date: 25-26 September 1969
 Feeds: Type A Effluent
 Type B Effluent
 Feed Temperature: 70 ± 5F
 Feed Rate: 20 gallons per hour
 Fuel: Natural gas

Sampling and Analytical Procedures:

Reference: Holmes Source Testing Manual, Air Pollution Control District,
 Los Angeles Co., California (1963)

Results:

A. Stack gas measurements

Gas volume: 3300 to 4050 cfm
 Gas temperature: 1000 to 2100F
 Moisture content: 8.7 to 11.0% by volume

B. Stack Gas Analysis
(by volume)Type "A" FeedType "B" Feed

Carbon dioxide	2.8%	2.8%
Carbon Monoxide	2.6%	0.6%
Oxygen	12.2%	16.0%
Nitrogen	73.7%	79.6%
Oxides of nitrogen (as NO ₂)	80.6 ppm	167.6
Oxides of sulfur (as SO ₂)	24.6 "	10.9
Ammonia	Less than 0.16 ppm	Less than 0.16

C. Particulate (for both feeds)

Size:

1. range: Less than 1.0 to over 150 microns
2. mean: 10 microns

Amount: Negligible

Density: "Smoke" or plume density less than 20%
 or Ringelmann Chart 1

Water Solubility: Very soluble and slightly acidic
 (pH = 6.4)

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(b)(3)b. John Zinc Co.(1) Equipment

(a) An incinerator system proposed by the John Zinc Co. will thermally decompose and oxidize aqueous effluent of this department and adequately remove pollutants from the stack gases*. The system would consist of four components; namely, burner, a thermal oxidizer, a quencher, and a Venturi-type scrubber. The scrubber would remove and sewer any gaseous and particulate contaminants from the stack gases.

(b) To treat 125 gal/hr of aqueous waste, the burner would consume about 4 million BTU/hour. Either gas or oil can be used to heat the thermal oxidation unit from 1400 to 1600F. The hot gases then are cooled to about 200F in a direct-spray control chamber, before entering the high-energy Venturi scrubber. The system would require a 20- x 40-ft area and a 50-ft stack. Total estimated weight is 50,000 lb.

(2) Cost. The quoted price, including all controls, start-up engineering service, etc., is \$75,000.

c. Other Incinerators:

(1) Units similar to the Preenco design were proposed by Peabody Engineering Corp (Stamford, Conn.) and the Hydro Combustion Corp. (Santa Fe Springs, California).

(2) The Peabody Liquid Waste Combustor properly sized to handle 125 gal/hr, would cost about \$25,000. This system could also be either gas or oil fired, and should include a Venturi-slot gas scrubber.

(3) The units designed by Hydro Combustion Corp are supplied in five standard sizes ranging from 20/hr to 500 gal/hr. The cost of a unit to handle 20 gal/hr is about \$16,500 (for complete package).

10. Solids Waste Disposal

a. Several proposed methods of pollution abatement are predicated

* Eastman Kodak Co. (Longview, Texas) is presently involved with the John Zinc Co. in the development of a suitable waste disposal system for treating/incinerating aqueous acetonitrile waste.

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upon an acceptable means of disposing solid waste; for example:

(1) A thin-film continuous evaporation unit would yield about 4000 lbs/day (maximum) of a thick slurry (75% by wt) of photographic chemicals.

(2) The flash-evaporation (or spray-drying) of the concentrated effluent would yield up to 3000 lbs/day of dry, powdery chemical waste.

(3) Chlorination, followed by a lime treatment to remove dissolved solids, or a chemical precipitation approach, would produce about 2 to 3 tons of calcium sulfate per day.

b. The waste from methods (1) and (2) would be mostly water soluble; the produce from method (3) would be essentially water insoluble.

c. Disposal of a water-soluble waste by land-fill generally presents problems since runoff from the site may be polluted.

d. The disposal of a water insoluble waste, such as one which consists mainly of calcium sulfate, appears to be feasible. A formal request was therefore made to management to investigate the possibility of trucking 2 to 3 tons per day of waste to an industrial disposal site.

11. Alkaline Chlorination

a. Test Objective. These pilot studies were conducted to prove the feasibility of reducing the oxygen demand of a processing effluent by alkaline chlorination and to determine the chemical costs of chlorination.

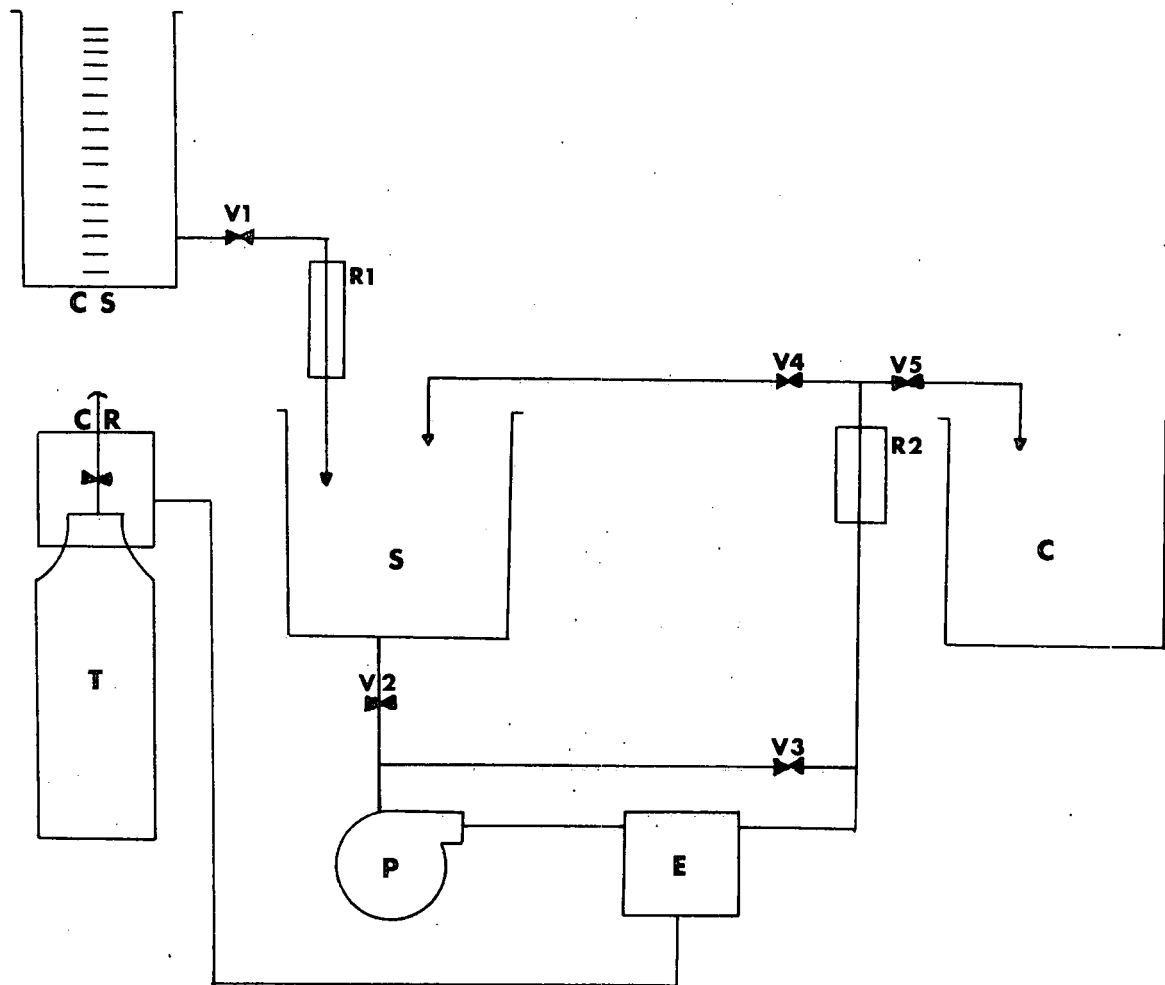
b. Pilot Equipment

(1) The alkaline chlorination pilot unit shown in Figure 1 consisted of a closed loop system with two 10 gallon polyethylene tanks; a circulation pump; connecting lines, rotometers, and valves; and a small chlorine-gas injector unit, capable of delivering 4 lbs/hr of chlorine gas from a 100 lb supply cylinder. The system was assembled under a well ventilated hood.

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(b)(3)Legend:

- S - Supply Tank: 10 gallon polypropylene tank
 C - Collection Tank: 10 gallon polypropylene tank
 CS - Caustic Supply (50% NaOH solution): 5 gallon polypropylene tank
 R₁, R₂ - Rotometers
 V₁ - V₅ - Valves
 P - Pump
 T - Chlorine Supply (100 lb cylinder)
 CR - Chlorine Regulator: Advance Gas Chlorinator
 (Direct cylinder mounted), Model 201 with
 0 - 100 lb/day metering tube
 E - Diffuser: Ejector unit

Figure 1. Schematic Diagram of Alkaline Chlorination Test Equipment

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(2) The chlorinator unit (Advance Model 201) was mounted directly on top of the supply cylinder. When wastewater is circulated through the injector unit (at 10 gal/min), a vacuum is created which opens a spring-loaded diaphragm check valve and chlorine is released from the supply cylinder. The chlorine gas regulator unit is activated by a vacuum created by the gas injector. All supply lines carry only gaseous chlorine at pressures less than 14.7 psia.

c. Experimental

(1) Initially, the supply tank was charged with 2.0 liters of the concentrated processing effluent (See Table 5) and sufficient caustic to raise the pH to 12 or 13. The system (total capacity: 40 liters) was then filled with cold water to establish 1-to-20 dilution of the synthetic processing effluent. The synthetic wastewater thus had pollution characteristics similar in magnitude to the wastewater from the department.

(2) The circulation pump was started, and after thorough mixing, the chlorine was injected into the system. Caustic solution (50% by wt NaOH) was added either intermittently or continuously. The temperature and pH were monitored and samples of the effluent taken periodically.

(3) Eight chlorination runs were made: Runs 1 through 5 were made with Type A Effluent; run 6 with Type B Effluent; and runs 7 and 8 with a ferricyanide bleach. (See Appendix C)

d. Results

(1) Type A and B Effluents

(a) Reduction in Oxygen Demand

1. In runs 3 through 6, the BOD of the processing waste sample was reduced by more than 92%. In each of these runs with Type A or B effluent, the BOD of the wastewater was reduced to less than 40 ppm. This oxygen demand is well below the BOD level of the department's effluent during non-mission non-testing periods.

2. Because of the high chloride content of the treated waste samples, the usual chemical oxygen demand (COD) determinations were not performed.

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(b)(3)(b) Chemical Usage and Costs

1. The amount of caustic required to maintain the pH during the chlorination ranged from 1.1 to 1.2 lbs of NaOH per pound of chlorine. This ratio is close to the anticipated value of 1.1, based on the stoichiometry (see Paragraph 4.e. on page 28). The chemical usage during the chlorination of Type A effluent was the same as that for Type B.

2. To reduce 63.6g of oxygen demand (OD) in 2.0 liters of effluent, 283g (0.625 lbs) of chlorine were required. The chlorine demand for these concentrated effluents was therefore found to be about 4.5 times the oxygen demand; i.e., about 625 lbs of chlorine per 1000 liters of effluent. The sodium hydroxide requirement (to treat 1000 liters of effluent) would be 750 lbs of NaOH (or 120 gallons of a 50% by wt caustic solution).

3. Based upon the preceding chemical requirements, a chlorine cost of \$8.00/100 lbs (in 1-ton cylinders), and caustic solution at \$6.20 (per 100 lbs of NaOH), the chemical costs for alkaline chlorination will be as follows:

<u>a.</u> Chlorine	\$50.00 per 1000 liters
<u>b.</u> Caustic solution	<u>46.50</u> per 1000 liters
	\$96.50 per 1000 liters
	or \$0.36/gal TOTAL COST

4. Annual chemical costs for treating an estimated 450,000 gallons of combined processing effluent by alkaline chlorination therefore would be \$162,000 (without dissolved solids removal).

(c) Processing Flags. The chlorinated effluent gave negative tests for sulfites, thiosulfates, bromides, and iodides.

(2) Ferri/Ferro Cyanide Bleach.

(a) Experimental. A typical ferri/ferro cyanide color bleach sample containing approximately 250 g/l of potassium ferri cyanide was chlorinated in a similar manner as that prescribed for the black-and-white effluent. (See runs 7 and 8, Appendix C.) The chlorinated samples were analyzed for iron cyanide content $[\text{Fe}(\text{CN})_6]$ and BOD_5 .

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1. Reduction in BOD. The reduction in BOD in color bleach by alkaline chlorination occurs at a much slower rate than with other effluents. The more easily oxidized constituents are first chlorinated, giving an immediate reduction of about 80% in BOD. Further reduction in BOD occurs slowly and at a rate controlled by the breakdown of the ferri-cyanide to cyanate and cyanide. It is obvious from comparing the concentration of $\text{Fe}(\text{CN})_6$ with the observed BOD value, that the BOD value does not significantly reflect the concentration of ferri-cyanide in the effluent.

2. Oxidation of Ferri-cyanide. The breakdown of ferri-cyanide by alkaline chlorination occurred very slowly in these experiments (see runs 7 and 8, Appendix C). During a 4-hour chlorination period, 85 to 95% of the ferri-cyanide was gradually destroyed. If alkaline chlorination of color bleach is to be economically practical, the chlorine must be injected at a very slow rate or else the breakdown of complex iron cyanides to the simple cyanide (or cyanate) must be speeded up (perhaps via a suitable catalyst).

(b) Chemical Usage and Costs

1. Twelve lbs of chlorine and 14 lbs of sodium hydroxide are required to reduce the BOD and the iron cyanide content of 2 liters of bleach from 250 g/l to 0.5 - 0.8 g/l. Furthermore, 13.5 lbs * of chlorine and 16 lbs * of caustic would be required to thoroughly destroy 500 g of ferri-cyanide ion. The ratio of caustic-to-chlorine required is 1.2 to 1.0.

2. If chlorine costs are \$8.00 per 100 lbs and if caustic solution is \$6.20 per 100 lbs as NaOH, the chemical costs of destroying the toxic cyanide in color bleach would be about \$1.06 per liter.

* Extrapolated values from curves in Figure 2.

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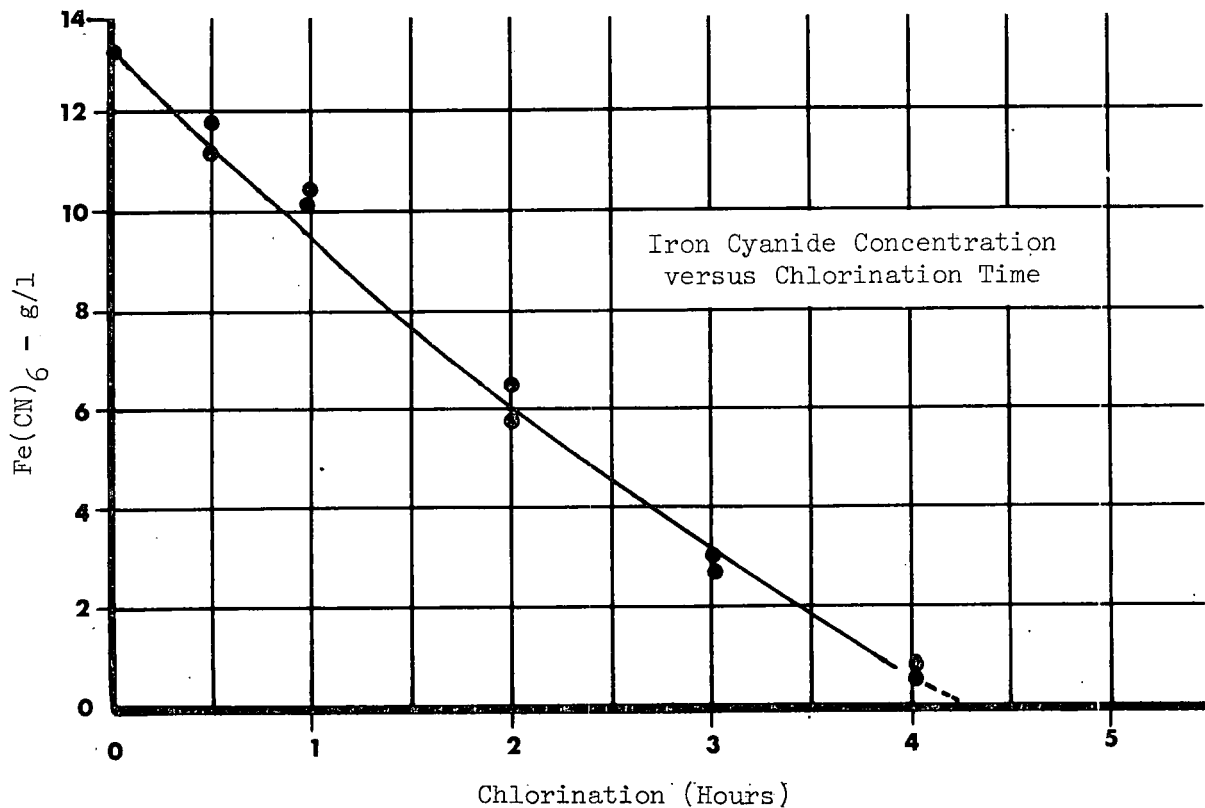
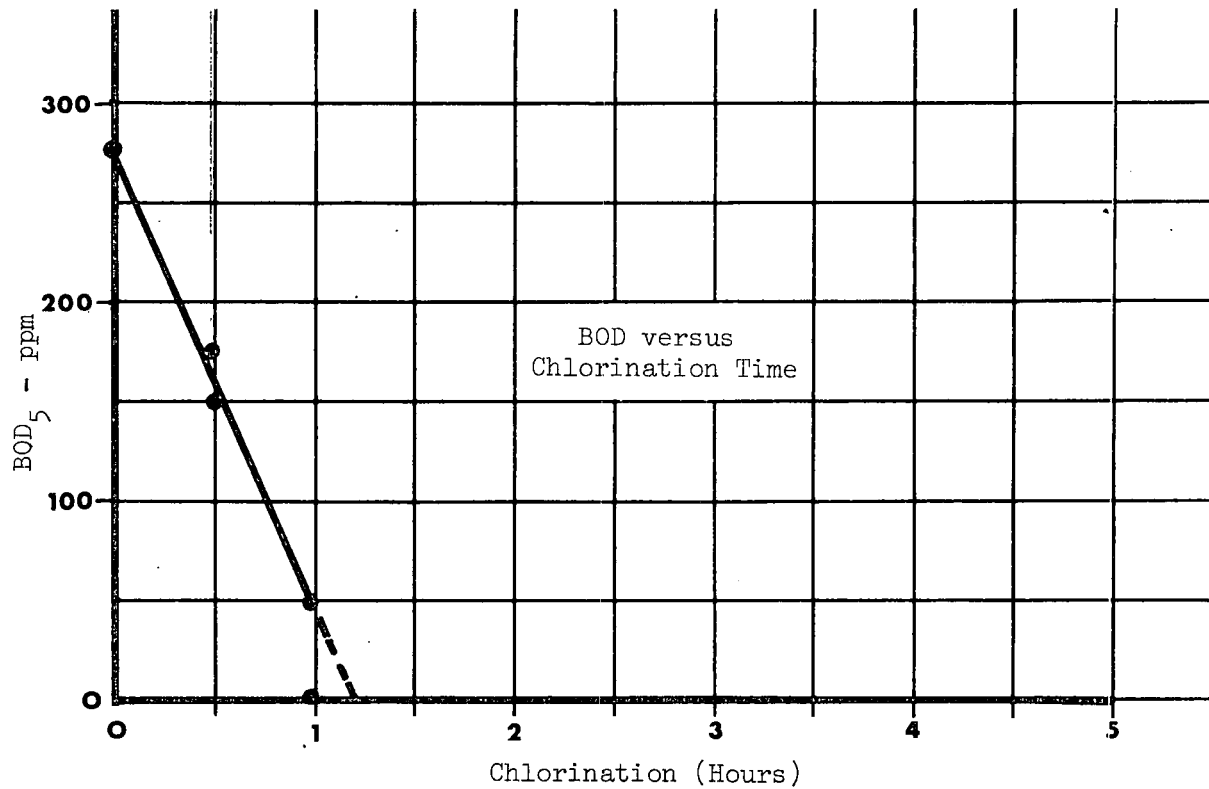
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Figure 2.. Alkaline Chlorination of Bleach

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FINAL TREATMENT

12. Final Treatment Facilities

a. General. Suitable pollution control facilities for the treatment of photographic wastes should include the following items:

(1) A method for separating the concentrated processing solutions from rinse water; i.e., separate lines for used hypo, for rinse water, for developer, etc.

(2) Facilities for the adequate desilvering of used hypo.

(3) Storage facilities for the concentrated processing waste and holding tanks for all (or part) of the rinse water required by the treatment facility; and

(4) The treatment unit.

b. Machine Plumbing Changes

(1) A separate drain must always be provided for collecting used hypo. After the de-silvering step, hypo may then be combined with other processing wastes or rejuvenated and re-used.

(2) If water conservation is being considered, the arrest, Photo-Flo, dye-removal bath, and rinse water may be combined at the processor and treated jointly by Reverse Osmosis.

(3) If water conservation is not required, all black-and-white processing effluents may be combined at the processor. However, certain abatement methods (e.g., evaporation, incineration) will require a separate waste line for excluding rinse water from this concentration combined effluent.

c. Effluent Collection Tanks

(1) Two collection tanks should be provided for effluent collection and storage. The dual tanks will make it possible to collect in one tank and to feed from the other; i.e., to treat the effluent via a batch system as required. The collection tanks would have to be equipped with a thermo-regulated heat-exchanger system, since the freezing point of the concentrated effluent is about 26F. The holding tanks should be constructed of corrosion-resistant stainless-steel; they should be glass-lined, or their interior made from suitable acid-and-base resistant fiber glass material.

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(2) Collection tanks for some (or all) of the process water may be required for use by the treatment unit. If water re-use is being considered, additional holding tanks will be required for the purified wastewater.

d. The Treatment Unit. Since a biochemical treatment unit to adequately reduce BOD would be prohibitive in size, no unit will be installed at BH. The effluent of this department will be trucked to a nearby biochemical-oxidation facility for treatment (see paragraph 21.d. under RECOMMENDATIONS).

e. Silver-Recovery System

(1) All used-hypo should be treated to reclaim silver before disposal. If the hypo solution is also to be rejuvenated and re-used, an electrolytic de-silvering treatment must be used. The iron replacement method (by treatment with steel-wool) is adequate for salvaging silver, only if the hypo is not to be re-used.

(2) A large processing facility also should have facilities for the electrolytic de-silvering, rejuvenation, and re-use of hypo. In addition, suitable laboratory facilities will be required for monitoring and controlling the pollution abatement activities.

13. Acceptable Treatment Methods

a. Biochemical Oxidation

(1) The most economical method of treating photographic wastewater is by biochemical oxidation. If adequate secondary sewage-treatment facilities are available in the community at favorable sewer tax rates, these treatment-centers should be used. However, dichromate and ferri/ferro cyanide wastes must be excluded. All of the biological systems (e.g. septic tank, trickling filter, or activated sludge units) are adequate as long as oxygen (or air) is supplied by some mechanical means. Domestic sewage and photographic effluents can be combined and treated jointly by biological means.

(2) If municipal facilities are not used, a biological treatment center for the treatment of photographic wastes should include the following items:

(a) The means (plumbing) for separating the concentrated

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processing solutions from the rinse water,

(b) Storage tanks for the concentrated processing waste.

(c) Storage tanks sized to hold all the rinse water, if water conservation is being considered; or tanks sized to hold any water needs of the treatment facility.

(d) The treatment tank sized to handle the (daily) average BOD load of the waste, and

(e) A small hypochlorination unit to sterilize the effluent before discharge to a sewer or natural body of water.

(3) These facilities are shown schematically by Figures 3 and 4. In addition, laboratory facilities will be required for monitoring and controlling the influent and effluent characteristics.

(4) Pilot studies indicate that the effluent from a biochemical-oxidation treatment facility will have a BOD as low as 20 ppm, with operating efficiencies of 90-95%. This effluent is suitable for discharge to a natural body of water, if the effluent is first hypo-chlorinated to render it sterile.

(5) To adequately treat the photographic effluent from this department, the treatment facility would have to be sized to handle a BOD₅ load of approximately 500 lbs/day. This would require locating a 100,000 to 200,000 gallon activated-sludge treatment unit. Since space at this department is limited, it is concluded that a biochemical-oxidation Final Treatment Center would not be recommended as a feasible abatement method*.

b. Concentration by Evaporation and Reverse Osmosis

(1) When water conservation as well as pollution abatement is of prime consideration, concentration by evaporation is the preferred, acceptable treatment method. Estimated energy costs are about \$32.00 per 1000 liters of effluent.

(2) The most economical method for treating the dye-removal bath, arrest, and rinse water is by reverse osmosis. About 90-95% of this wastewater can be reclaimed at a power cost of \$0.60 per 1000 gallons.

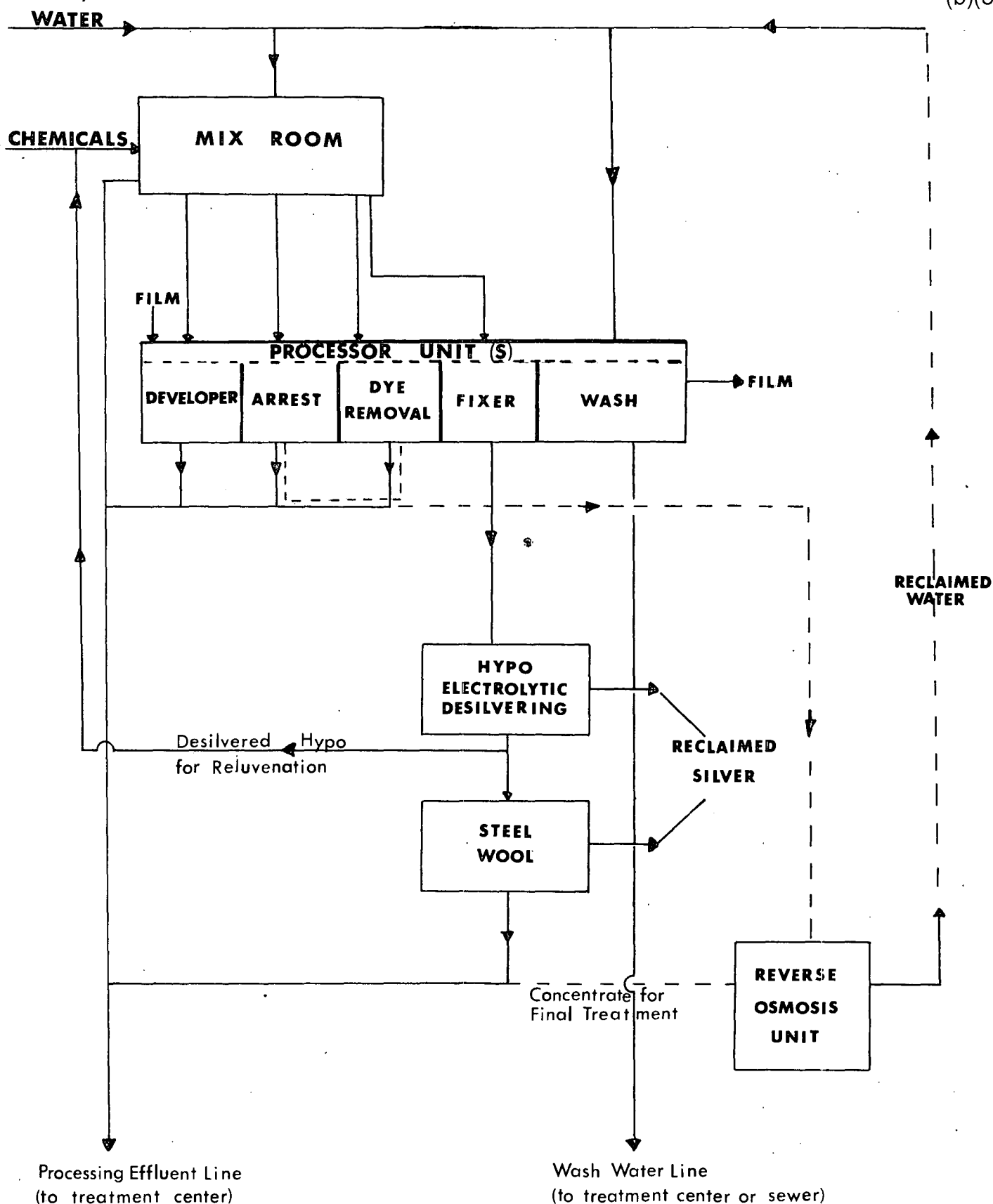
(3) The concentrated effluent from the RO unit should be combined with the spent developer, and the used desilvered fixer, then treated in the evaporator/condenser system. A thin-film evaporator unit

* See paragraph 17.h. under CONCLUSIONS.

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(b)(1)
(b)(3)Figure 3. Final-Treatment Facility
(Plumbing Modifications)

- 74 -

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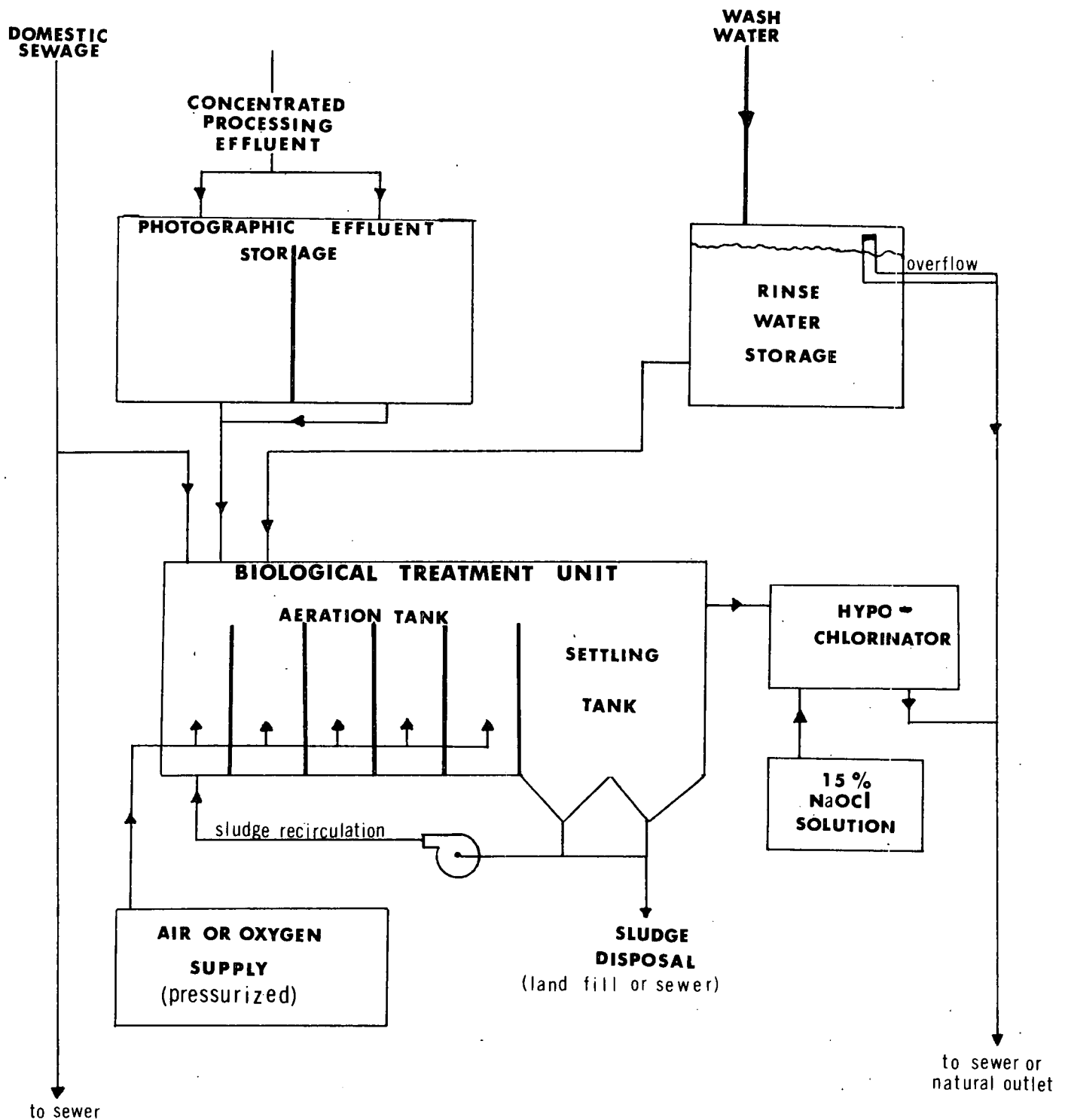
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Figure 4. Biochemical-Oxidation Treatment Facility

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(available in many sizes) offers minimum space requirements and produces a semi-solid product which is easiest to handle and package for disposal.

(4) Final disposal of the residue from concentrating photographic effluents can be by land-fill or incineration. The land-fill site should be above the ground-water table and disposal should be in moisture-proof, water-tight containers. If the solids are incinerated, the incinerator should be equipped with a stack-gas scrubber for removal of sulfur dioxide.

(5) Treatment by concentration/evaporation is recommended only in those cases where water conservation is of prime importance.

c. Incineration

(1) Incineration of the concentrated processing solutions in a fluid-waste burner is an acceptable method of pollution control when water conservation is not required. Power consumption for incineration is higher than for evaporation, but the savings in labor for solids handling are expected to make the cost for treatment by incineration equal to that for evaporation (approximately \$32.00 per 1000 liters).

(2) Incineration at temperatures of 1400 to 2200F produce a stack effluent consisting mostly of nitrogen, oxygen water vapor, carbon dioxide, and carbon monoxide. There are also small amounts of oxides of nitrogen, sulfur dioxide, and particulate matter. The concentration of carbon monoxide can be decreased by increasing the air intake rate.

(3) Particulate matter and sulfur dioxide can be removed from the stack gases by conventional wet-scrubber equipment, if required by local air environmental codes. The effluent from the scrubber will consist mainly of sodium sulfate and may be sewered without violating most sewer codes.

(4) A fluid-waste incineration system (see Figure 5) for this facility should include:

(a) The separate collection lines and storage tanks for the concentrated effluent and the rinse water,

(b) The fluid-waste burner sized to operate continuously at 75 gallons per hour,

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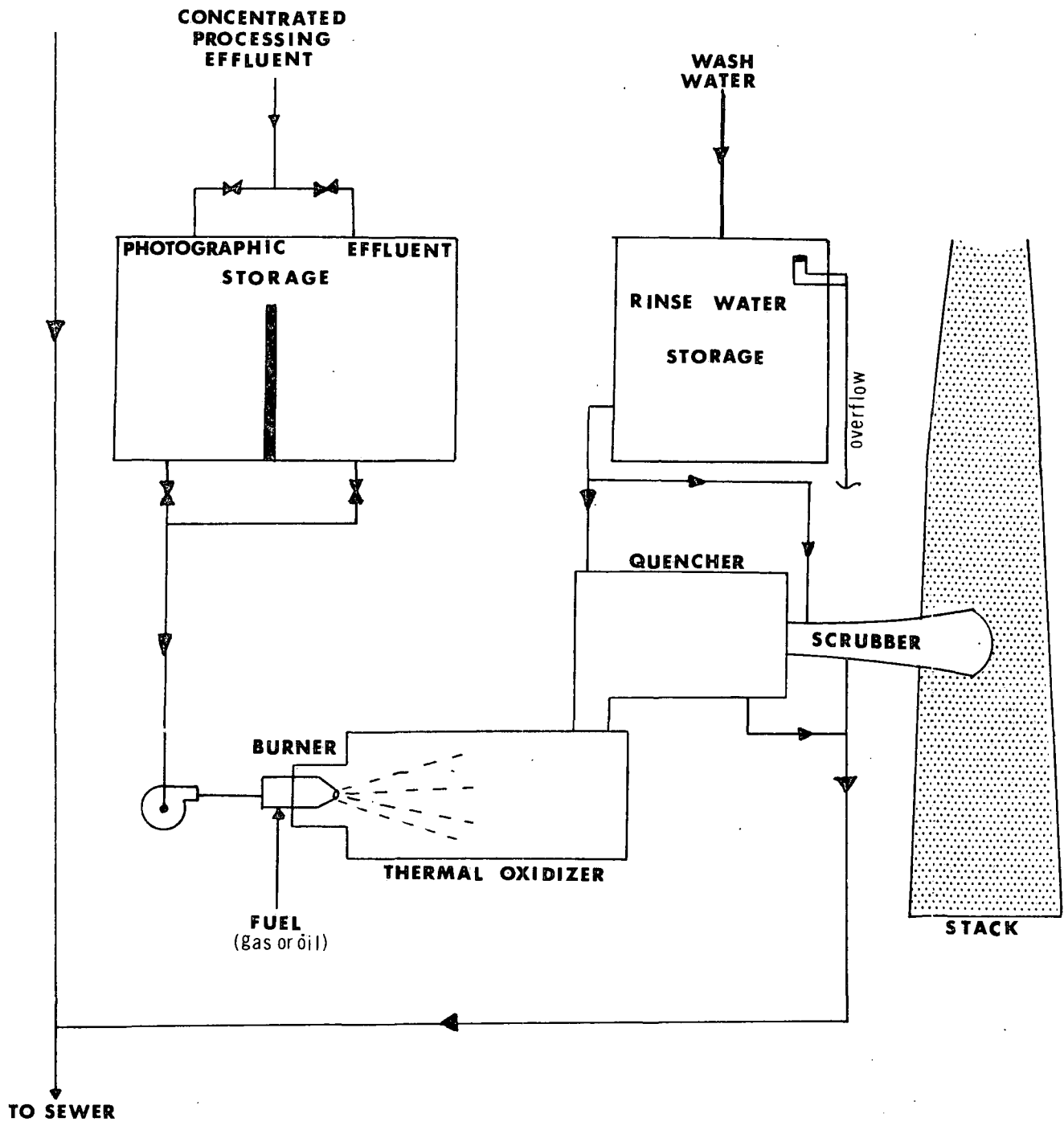
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Figure 5. Fluid-Waste Incineration Facility

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- (c) The stack-gas quencher and scrubber unit, and
- (d) The stack.

(5) Rinse water can be used in the quencher/scrubber unit and then sewered. The temperature of this wastewater should be maintained below 100F. This wastewater will contain an increased amount of dissolved solids, mostly sodium sulfate.

(6) An Incineration System

(a) Based upon Michigan Testing's sampling and analysis while Prencos Super E₃ Pyro-decomposition unit was operating at 25 gal/hr on effluent from this department, the stack emissions will meet all existing applicable air pollution codes with the possible exception of particulate matter. Theoretically, this department should have as much as 75 lbs/hour of ash or residue from an incinerator operating at 100 gal/hr. However, Section 8 of the Monroe Co. Air Pollution Code establishes a limit of 2.5 lbs/hr as rate of feed for this department. Thus, a scrubber may be necessary to remove about 97% of the ash (theoretically) expected from this department's waste. It should be noted that actual measurements of the stack emission for particulates with Prencos's incinerator did not exceed the particulate limitation set by Section 8 of the existing code.

(b) If it is found necessary (after installation) to collect and remove ash and/or fly ash from an incinerator unit via a scrubber unit, two following approaches are possible.

1. A dust collector (centrifugal, electrostatic, or bag house type) would remove an estimated 150 tons/year of solids, consisting mostly of sodium sulfate (Na₂SO₄) and oxides of sodium, potassium, aluminum, boron, etc. This by-product could not be readily associated with photographic processing and, therefore, its disposal could be made in most any solids waste area.

2. A wet scrubber (spray, impingement, or baffle-type) can be used and the scrubbing solution sewered. In this case, the residue from the scrubber would increase the total dissolved solids of this department's sewage to about 3400 ppm (average annually) or about 0.50% by wt under the worst conditions. This minor contribution to "water pollution" would be acceptable under the City Sewer Code.

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14. Treatment of Toxic Effluents. Photographic effluents may be considered to be non-toxic industrial wastes, provided color bleach, dichromate cleaners, and fungicide solutions are excluded. Color bleach, cleaning, and fungicide solutions are discussed below.

a. Ferri/Ferro Cyanide Bleach

(1) The preferred pollution abatement step for ferri/ferro cyanide bleach is regeneration and re-use.

(2) When color bleach must be disposed of, alkaline chlorination will effectively destroy ferri/ferro cyanide and render color bleach waste non-toxic and low in BOD.

(3) The chemical costs for complete treatment of a typical color bleach (containing 250 g/l of potassium iron cyanide) is \$1.00 per liter.

(4) Alternate methods of bleach treatment (such as electrolysis, ozonation, and incineration) should be explored and pilot tested.

b. Cleaning Solutions

(1) Cleaning agents containing dichromates * should be avoided, since most city codes prohibit the discharge of wastewater containing chromium or "heavy metals".

(2) A suitable, non-toxic cleaning agent for the fix and wash equipment is chlorinated trisodium phosphate, used at a concentration of 1 oz/gal.

(3) A suitable non-toxic cleaner for developer equipment is a mixture comprised of 75% (by wt) hypo plus 25% EDTA (mono-sodium ferri salt), used at a concentration of 4 oz/gal.

c. Fungicide Solutions. The use of organic phosphorous compounds as fungicide solutions should be avoided. No anti-fungicide treatment is required if chlorinated cleaning solutions are used.

15. Final-Treatment Proposal for BH (Black-and-White)

a. All of the acceptable treatment methods investigated were considered, but finally rejected for the BH facility. The specific reasons for their rejection are as follows:

(1) Bio-oxidation system. Too much area and volume required for location at this facility.

* An example of a commercially available cleaner containing potassium dichromate, is Kodak Developer Systems Cleaner.

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(2) Concentration by evaporation: This method requires a solids disposal site, and no adequate land-fill is available. Furthermore, the disposal of photographic residue from this department would be a potential security problem.

(3) Incineration: Local air environmental regulations require that applications for the installation of all new incinerators be approved, investigated, and tested by local health authorities. These regulations present potential hazards to maintaining operational security.

b. *The alternative solution to an in-house treatment center was therefore considered; namely, using an outside treatment facility. The costs for trucking to a near-by industrial waste treatment facility were found to compare favorably to the most economical in-house treatment (biochemical-oxidation).*

16. Final-Treatment for LP (Color)

a. Pollution abatement and control steps at LP included:

- (1) Reduction in fixer replenisher rates.
- (2) Electrolytic desilvering, rejuvenation, and re-use of fixer, and
- (3) Regeneration and re-use of color bleach.

b. No final-treatment system was planned for this facility, although the bio-oxidation method would be the preferred abatement.

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CONCLUSIONS

17. Biochemical-Oxidation

- a. The most economical, acceptable treatment method for photographic effluents is biochemical oxidation.
- b. All photographic effluents including rinse water may be treated by this method jointly with the exception of color (ferri/ferro) bleach, which should be excluded.
- c. It will generally be advisable to use municipal treatment facilities whenever they are available.
- d. An activated-sludge treatment tank is the most compact system. The BOD load for photographic effluents is about 1.5 to 2.0 lb of O₂ per day per 1000 gallons of tank volume. The effectiveness of the AS treatment in removing BOD is 90% or better.
- e. By acclimation of the system, using oxygen instead of air and by adding domestic sewage (or other nutrients), the BOD load of an AS system can probably be raised to about 3.0 lb/day/1000 gallons.
- f. The estimated treatment costs for a biochemical oxidation system is \$15.00 per 1000 liters of concentrated photographic effluent.
- g. Equipment costs for the BH facility are estimated at \$75,000. The total annual operating expense (power, labor, and chemicals) would be about \$25,000.
- h. *A biochemical treatment facility for the BH facility sized to adequately reduce the BOD would be prohibitive in size.*

18. Incineration

- a. Incineration of the concentrated, combined processing solutions is an acceptable alternative treatment method. The adoption of this method necessitates equipment changes for the separation and exclusion of rinse water. Air environment codes may require corrective pollution abatement equipment for the stack emissions.
- b. Rinse water from photographic processing generally constitutes 90 to 98% of the volume of the total effluent. It usually requires no treatment and may be sewered without treatment.
- c. The segregation and separate treatment by pyrodecomposition of the concentrated processing solutions (i.e., used developer, fixer, arrest, dye removal baths, etc.) reduces BOD/COD and pollutants by more than 99%.

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d. The cost for incineration of used, processing effluents is \$32.00 per 1000 liters (about double that for AS treatment).

e. Equipment costs for the BH facility are estimated at \$100,000. Annual operating expenses (including labor, power, and fuel) would be about \$55,000.

f. The thermal decomposition and oxidation of the constituents of photographic solutions give water vapor, carbon dioxide, carbon monoxide, some oxides of sulfur and nitrogen, and a water-soluble arrest ash.

g. The use of a wet-scrubber may be required to remove particulate matter; mostly, sodium oxides and sulfate. The effluent from the scrubber has no BOD/COD, is non-toxic, and may be sewered.

h. *The incineration of the effluent from the BH facility was not recommended for security reasons: 'the nature and volume of processing operations might be ascertained if local officials for the environment are authorized to approve, inspect, and test all new incinerator equipment.*

19. Concentration by Evaporation and Reverse Osmosis

a. When maximum water re-use and conservation is a primary objective, the concentrated processing effluents (fixer, developers, etc.) should be separated and further concentrated by evaporation and the dilute processing solutions (arrests, dye-removal baths, wash water) treated by reverse osmosis. Land-fill and incineration are suitable methods for the final disposal of the residue or concentrate.

b. Evaporation of the concentrated processing effluents yields a white solid or slurry and a condensate that can be re-used in photographic processing. Residue-to-distillate splits in excess of one-to-ten have been achieved by both batch and continuous evaporation equipment.

c. No suitable use for the residue has been established. The suggested methods for disposal are incineration or suitable land-fill.

d. Thin-film evaporators are suitable for concentrating photographic effluents to a semi-solid slurry which can be easily handled.

e. The stop, dye-removal bath and other processing effluents having a low solids content may be combined and treated by reverse osmosis (RO). The concentrate from the RO unit may be further concentrated by the evaporator.

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f. Energy costs for evaporation are only \$0.04 per gallon (\$10.00 per 1000 liters), but the costs for labor and solids disposal are expected to raise this value to about \$32.00/1000 liter. Equipment costs for a thin film evaporator unit which will handle 125 gallons per hour will be approximately \$75,000. Annually labor and power would cost \$55,000.

g. Power costs for RO are \$0.60 per 1000 gallons of treated wastewater.

20. Alkaline Chlorination for Color Bleach Wastes:

a. Color bleach wastes, containing toxic ferri/ferro cyanide ions, require the following abatement steps:

(1) Reduction of carry-over volumes used by installation of squeegee rollers.

(2) Regeneration and maximum re-use of all color bleach solutions; and

(3) Adequate treatment of alkaline chlorination.

b. Alkaline chlorination is the best established method of destroying cyanide wastes.

c. The chemical costs are high; about \$1.00 per liter for a typical color bleach, or \$2.00 per pound of potassium ferricyanide treated.

d. This treatment is applicable by batch or continuous methods.

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(b)(3)RECOMMENDATIONS FOR BH (Black-and-White)21. Final Treatment

- a. Separate the rinse water and Photo-Flo bath from all other processing effluents; sewer without treatment.
- b. Collect, desilver, rejuvenate, and re-use fixer solutions.
- c. Combine used developers, stops, dye-removal baths, and any used fixers; collect and store in storage facility (described in paragraph 12.c.)
- d. Truck and treat in nearby biochemical-oxidation facility.

22. Facility Requirements:

- a. Provide a waste line for collecting used developers, arrests, and dye-removal baths from each processor.

NOTE: Photo-Flo and all other process water may be sewered using existing waste lines.

- b. Install two 5,000 gallon tanks for effluent storage. If units are installed out-of-doors, each should be equipped with thermally regulated heating elements (set for 26F minimum).
- c. Provide chemical dump lines from the collection tank facility to the mix room, to the chemical laboratory, and to each processing area.

23. Limitations, Restrictions and Future Efforts:

- a. Establish a normal routine for trucking the effluent from the collection facility to the treatment facility to eliminate clues to the cyclic nature of operations.
- b. Restrict the use of chromic acid cleaners (e.g. Kodak Developer System Cleaner).
- c. Use bio-degradeable substitute cleaners whenever possible.
- d. Periodically collect samples of effluent and analyse for photographic flags, BOD, COD, and other waste water characteristics.

24. Future Hardware Efforts:

- a. Investigate commercially available biochemical-oxidation treatment units. Conduct pilot-tests using black-and-white and color processing effluents.

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- b. Investigate small fluid waste incinerator units.
 - (1) Conduct pilot tests on processing wastes.
 - (2) Sample and analyze stack emissions for possible air pollutants; and, if necessary
 - (3) Investigate and test stack-scrubbing equipment.
- c. Test a thin-film evaporator and condenser system jointly with a Reverse Osmosis unit for water conservation.

25. Future Study Efforts:

- a. Ozonation:
 - (1) Purchase a small (electric) ozone generator and test the effectiveness of ozonation as a means of reducing the BOD/COD of photographic effluents.
 - (2) Explore aeration of photographic effluents using oxygen-ozone mixtures.
- b. Bleach Treatment:
 - (1) Conduct laboratory studies on the following approaches to cyanide bleach treatment:
 - (a) Electrolysis
 - (b) Ozonation
 - (c) Alkaline chlorination, using catalysts.
 - (2) Conduct pilot tests on the pyrodecomposition (incineration) of bleach wastes.
 - (3) Pilot test alkaline chlorination of bleach, using catalysts.
- c. Computerized Pollution Program:
 - (1) Compile a card-file listing of the salt composition and polluting properties of processing solutions.
 - (2) Establish a computer program for determining the pollution magnitude of effluents from the various processing equipment using the established processing chemistry and machine specifications.

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- 86 -

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APPENDIX A

This appendix contains a reproduction of FINAL REPORT on
"Acceptable Pollution Standards," Contract EG-400, Task 34,
Section I, 16 June 1969. This report was published
28 July 1969.

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Section I, Task 34

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	4
SUBJECT	5
TASK (from Study Plan)	5
INTRODUCTION	5
1. - 3.	5
DISCUSSION	6
4. Pollution Magnitude	6
a. Annual Chemical Usage	6
b. Water Effluents	9
c. Processing Solution Usage	10
d. Sewer Samples	13
5. Established Pollution Standards	18
a. City Sewer Code	18
b. Rules, Classifications, and Standards for the State	20
c. Federal Attitude and Standards	20
d. Summary	21
6. Acceptable Security Control	21
a. Control Measures	21
b. Acceptable Department Waste Characteristics	21
c. Toxic Standards	22
d. Non-toxic Standards	22
e. Ammonium Compounds	24
f. Photographic Flags	25
g. Disproportioning Constituents	25
h. Cyclic Variations	26
CONCLUSIONS	28
7. - 13.	28
RECOMMENDATIONS	30
14. - 16.	30
REFERENCES	31
APPENDIX A ¹ - Industrial Waste Characteristics	32

A-2

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Section I, Task 34

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Sampling Diagram of Plumbing Areas -- Color	15
2	Sampling Diagram of Plumbing Areas -- B&W	16

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	Chemical Usage and Pollution at BH (B&W)	7
2	Chemical Usage and Pollution at LP (Color)	8
3	Chemicals Causing Pollution at BH	9
4	Chemicals Causing Pollution at LP	9
5	1968 Processing Solution Use at BH	11
6	1968 Processing Solution Use at LP	12
7	Comparison of Pollution at BH vs. LP	10
8	1968 Summary of BH and LP Pollution Magnitudes	14
9	Industrial Waste Characteristics and Quantities	23
10	Non-Toxic Limitations for Wastes Accepted by City	22
11	Suggested Effluent Limitations	22
12	Ammonium Ion Concentrations at Various pH Levels	24
13	Acceptable Department Waste Characteristics	27

A-3

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Section I, Task 34

SUMMARY

Safe levels of toxic and non-toxic pollutants are recommended for this processing facility. When adhered to, the recommended standards satisfy the requirements of both pollution abatement and security against disclosing the nature of our operations.

Only the local city Sewer Use Code is directly applicable as a guide for pollution standards. Even here, the local code does not cover the majority of constituents characteristic to photographic processing facility effluents. Because the code is subject to change or more strict enforcement at any time, and also because of the contractor's concern for security and the general nature of the pollution problem, standards are recommended to cover a considerably wider scope of pollutants than given in the code at present. In total, the standards encompass all conceivable sources of pollution or of effluent clues to the nature of operations.

The results indicate that either a single treatment or a series of treatments is feasible to effect compliance with the recommended standards. Further, the comprehensiveness of the standards will dictate the suitable choices of treatment without requiring separate consideration of the two aspects of the problem: pollution abatement and security.

A-4

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Section I, Task 34

SUBJECT: Acceptable Pollution Standards

TASK

A. Study and define safe security standards as applicable to this project for discarded chemicals via minimum identifiable levels of processing chemicals in this contractor's effluent.

B. Study and define a safe pollutant level or a scale of levels to which each pollutant can be referred. This study would produce two major categories:

(1) Toxic standards, and (2) non-toxic standards. The standards that will be adapted will conform with those for the building complex, that in turn will be guided by local, state, and federal requirements.

INTRODUCTION

1. All photographic processing effluents from the contractor's facilities at both LP and BH are discharged into the city sanitary sewers. The security of these processing operations is therefore in jeopardy, should the sewer effluent be sampled and analyzed by the city during a mission period. An unusually high BOD, a toxic constituent, high pH, or other sewer code violation might easily lead to the discovery of the exact chemical effluent, since pollution literature already describes characteristics of the various wastes discharged from other processing laboratories^{1,2}. By use of a 24-hour composite sample (or a series of samples), the periodic or cycle nature of operations could also be determined; and, with water-usage data (or flow measurements), it would further be possible to estimate magnitude and frequency of processing operations.

2. Because it is generally known that operations at the contractor's facilities are related to the manufacture and checkout of photographic equipment, it should not be unreasonable to assume that normal testing of photographic equipment might include some limited use of processing solutions. Consequently, a "secure" department effluent could contain photographic effluents, provided the concentrations of certain key processing chemicals are lowered (or significantly disproportionalized).

^{1, 2} See References.

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Section I, Task 34

Presently, the contractor's effluents at both LP and BH fail to meet such security requirement for continued discharge into city sewers.

3. Also, the discharge of all industrial effluents into the public sewage system is now subject to regulation by the city Sewer Use Code³. Maximum allowable standards and concentrations have been established for both toxic and non-toxic industrial wastes which can be accepted by the City Sewage System. The eventual enforcement of this code will prohibit continued discharge of some types of photographic effluents now being released into city sewers.

DISCUSSION

4. Pollution Magnitudea. Annual Chemical Usage

(1) An earlier report⁴ listed in tabular form the major processing chemicals and their usage during 1968 at the contractor's BH facility (Table 1). More recently, a survey has been made of chemical usage at LP for color processing (Table 2). Using literature values for chemical oxygen demand factors, f^* , for each chemical, the amount of dissolved oxygen required by the waste constituents was calculated as one estimate of pollution magnitude.

(2) At BH, some 671,500 lbs. of chemicals were used and sewered during 1968 in black-and-white processing. These chemicals had a total chemical oxygen demand (COD) of approximately 207,000 lbs.; or, if oxidized by biochemical means, a total BOD (biochemical oxygen demand) of 137,000 lbs. The annual average oxygen demand factor, f , was found to be 0.20 for biochemical oxidation and 0.31 for chemical (dichromate) oxidation.

(3) For color processing at LP about 140,000 lbs. of chemicals were used, or about one-fifth the amount at BH. The average COD factor is significantly higher (0.51) for color processing chemicals than for black-and-white, because of the greater predominance of organic chemicals used. The total COD amounted to over 71,000 lbs. and a BOD total of nearly 22,000 lbs.

^{3,4} See References

* Oxygen demand factor, f : Ratio of the mass of oxygen required per unit mass of the chemical.

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Table 1

Chemical Usage and Pollution at BH (B&W)

	Chemical Usage (lbs.)		(f)	COD Load (lbs. of O ₂)		(f)	BOD Load (lbs. of O ₂)	
	1966	1968		1966	1968		1966	1968
Sodium thiosulfate (Hypo)	480,000	216,000	0.32	154,000	69,000	0.20	96,000	43,200
Sodium sulfite	270,000	202,000	0.12	32,400	24,200	0.12	32,500	24,200
Sodium meta-borate	145,000	13,200	0			0	0	0
Soda ash	69,000	100,000	0			0	0	0
Acetic acid	68,000	36,000	1.06	72,000	38,100	0.77	52,400	27,700
Sodium sulfate	51,000	34,000	0			0	0	0
Potassium alum	32,000	6,000	0			0	0	0
Potassium bromide	8,120	7,540	0			0	0	0
Ammonium thiosulfate	-	4,500	1.62	-	7,300	0.36	-	1,620
Sodium iso-ascorbate	13,000	6,400	0.81	10,500	5,200	0.29	3,770	1,850
Sodium hydroxide	3,000	13,400	0			0	0	0
Elon	16,000	7,200	1.86	29,800	13,400	0.90	14,400	6,500
Hydroquinone	13,000	5,200	1.89	24,400	9,800	1.1	14,300	5,720
Hexaethylcellulose	(2,000)	3,000	1.33	(2,660)	4,000	(1.33)	(2,660)	(4,000)
Phenidone	3,570	5,520	2.67	9,500	14,700	0.165	590	910
Diethylaminoethanol	10,000	7,400	(2.57)	(28,700)	(21,200)	(2.87)	(28,700)	(21,200)
Sodium bisulfate	-	2,500	0			0	0	0
Sulfuric acid	-	720	0			0	0	0
Sodium carbonate	-	500	0			0	0	0
TOTALS: (lbs)	1,183,690	671,480	.31	363,960	206,900	.20	225,320	136,900
(tons)	592	336		182	103		113	68

Note: Values in parentheses () are estimates.

Dashes mean data not available.

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Section I, Task 34

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Section I, Task 34

Table 2

1968 Chemical Usage and Pollution at LP (Color)

<u>Inorganics</u>	Usage (lbs.)	COD Load			BOD Load		
		(f)	(lbs.)	%	(f)	(lbs.)	%
Ammonium thiosulfate	13,500	1.62	22,000	30.8	0.36	4,850	22.2
Sodium sulfite	15,300	0.12	1,830	2.5	0.12	1,830	8.4
Sodium sulfate	20,000	0	-		0	-	
Trisodium phosphate	8,500	0	-		0	-	
Sodium carbonate	8,500	0	-		0	-	
Sodium biosulfite	2,000	0.16	320	.4	0.16	320	1.5
Sodium bromide	7,100	0	-		0	-	
Sodium thiosulfate	2,600	0.32	835	1.2	0.20	520	2.4
Sodium ferrocyanide	2,650	0.16	425	0.6	0.003	8	0.0
Potassium ferricyanide	4,750	0.26	1,240	1.7	0.003	15	0.1
Potassium persulfate	1,060	0	-		0	-	
Sodium thiocyanate	415	0.78	325	0.5	0.03	12	0.0
Potassium iodide	13	0	-		0	-	
Misc. - "Calgon", "Borax", H ₂ SO ₄ , NaOH, etc.	6,226	0	-		0	-	
Inorganic Totals:	92,614	(0.29)	26,875	37.7	(0.08)	7,555	34.6
<u>Organics</u>							
CD-3	26,000	0.90	23,400	32.7	0.1	2,600	11.9
Acetic acid	7,450	1.06	7,900	11.0	0.77	5,700	26.2
NA-1	3,800	0.47	1,800	2.5	0.04	160	0.7
Hydroquinone	1,830	1.89	3,450	4.8	1.1	2,000	9.2
Formalin	2,900	0.57	1,660	2.3	0.38	1,100	5.0
Sodium acetate	2,150	0.67	1,440	2.0	0.49	1,050	4.7
Benzyl alcohol	870	2.5	2,170	3.0	1.8	1,560	7.2
Ethylene diamine	780	1.20	940	1.3	0.03	10	0.0
Phenidone	108	2.67	290	.4	0.165	18	0.0
Citrazinic acid	530	0.67	350	.5	0	-	
Carbowax	190	1.80	345	.5	0.03	10	0.0
SA-1	56	1.45	80	.1	0.03	2	0.0
DMIF (HA-1)	390	1.90	740	1.0	0.075	30	0.1
Misc. organics	63	(2.0)	(125)	.2	(1.0)	(60)	0.3
Organic Totals:	47,107	(0.95)	44,690	62.3	(0.30)	14,300	64.4
TOTALS:	139,721	0.51	71,565	100.0	0.156	21,855	100.0

NOTE: Values in parentheses () are estimates.

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Section I, Task 34

(4) For black-and-white processing at BH 73% to 85% of the pollution load sewerer came from four chemicals:

Table 3

Chemicals Causing Pollution at BH - 1968	Percent of Total Oxygen Demand	
<u>Chemical</u>	<u>Biochemical</u>	<u>Chemical</u>
Sodium thiosulfate (hypo)	32	33
Sodium sulfite	18	12
Acetic acid	20	18
Diethylaminoethanol	<u>15</u>	<u>10</u>
Totals:	85%	73%

In color processing at LP, the 1968 annual survey of chemicals used showed that the magnitude of pollution at that facility is caused by several compounds, mostly organics:

Table 4

Chemicals Causing Pollution at LP - 1968	Percent of Total Oxygen Demand	
<u>Chemical</u>	<u>Biochemical</u>	<u>Chemical</u>
Acetic Acid	26.2	11.0
Ammonium Thiosulfate	22.2	30.8
CD-3 Kodak Developer	11.9	32.7
Sodium Sulfite	8.4	2.5
Hydroquinone	9.3	4.8
Formalin	5.0	2.3
Sodium Acetate	4.7	2.0
Benzyl Alcohol	<u>7.2</u>	<u>3.0</u>
Totals:	94.9%	89.1%

Thiosulfates, sulfites, and acetates are the common, major pollutants in both Black-and-white and color processing.

b. Water Effluents

(1) Water usage rates for BH and LP were determined annually, daily, and for both mission and non-mission periods⁵.

⁵ See References.

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Section I, Task 34

Calculations were then made on the characteristics of the waste effluent. At BH, the water usage rate is 14.7 million gallons annually (or approximately 40,000 gallons per day). At these volumes effluent from the BH facility will contain about 0.5% by weight solutes (or dissolved chemicals). The oxygen demand averages are a BOD of 1000 ppm, or a COD of 1600 ppm.

(2) At LP the water usage rate is considerably higher, giving a department effluent of about 25.5 million gallons/year (70,000 gallons/day). The average solute content is therefore considerably lower (about 0.06% by weight) and the average BOD and COD values are about the same as domestic sanitary sewage (95 and 310 ppm, respectively).

c. Processing Solution Usage

(1) A third approach to estimating pollution from photographic processing is by considering the volumes, chemical content, and oxygen demand of the processing solutions. Tables 5 and 6 show the annual usage, solute composition, total solute content, and BOD/COD values for most of the processing solutions which were prepared at each facility during 1968. It will be noted that the magnitude of pollution as determined by processing solution usage is somewhat less than the values obtained by calculation from chemical-usage data. Part of this difference arises from the use of some chemicals for testing or other support activities, such as cleaning. Table 7 illustrates on a yearly basis, the magnitude of pollution as calculated from the two approaches, i.e., from chemicals used and from processing solutions prepared.

Table 7

Comparison of Pollution at BH vs. LP

	<u>AT BH</u>		<u>At LP</u>	
	<u>From Total Chemical Usage</u>	<u>From Processing Mix Room Solutions</u>	<u>From Total Chemical Usage</u>	<u>From Processing Mix Room Solutions</u>
Solutes (lbs/yr)	671,500	456,000	139,700	110,000
BOD (lbs O ₂ /yr)	136,900	87,000	21,855	19,400
COD (lbs O ₂ /yr)	206,900	122,500	71,565	54,000

A-10

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Table 5

1968 Processing Solution Usage at BH

Processing Solution	Approx. Solute Composition (g/l)	Annual Usage (liters)	Total Solute Content		Observed COD Load			Observed BOD Load		
			(lbs)	(%)#	g DO per liter	Total (Kg DO)	Total (%)#	g DO per liter	Total (Kg DO)	Total (%)#
Developers	87	1,217,000	232,000	51	21.7	26,500	47.8	13.8	16,800	42.5
Fixers	300	283,000	187,000	41	76.3	21,800	39.2	60.3	17,400	44.1
Arrest Bath	82	187,000	33,700	7.3	38.5	7,200	12.9	28.2	5,250	13.2
Dye removal and Stop baths	110	14,000	3,300	0.7	6	84	0.1	6	84	.2
Totals:		1,701,000 liters	456,000 lbs			55,584 Kg			39,534 Kg	
		449,200 gal				122,500 lbs			87,000 lbs	

- Percent of Total
DO - Oxygen Demand

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Section I, Task 34

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Table 6

1968 Processing Solution Usage at LP

Processing Solution	Approx. Solute Composition (g/l)	Annual Usage (liters)	Total Solute Content		Observed COD Load			Observed BOD Load		
			(Kg)	(%)#	g DO per liter	Total (Kg DO)	Total (%)#	g DO per liter	Total (Kg DO)	Total (%)#
Prehardener	213	49,400	10,500	21.4	41.6	2,050	8.1	20.5	1,010	11.6
Neutralizer	45	61,000	2,750	5.6	23.9	1,460	5.8	9.2	560	6.3
1st Developer	85	138,000	11,750	24.0	18.2	2,760	10.8	11.9	1,630	18.5
1st & 2nd Stops	35	87,200	3,030	6.2	33.5	2,920	11.5	24.5	2,130	24.4
Color Developers	81	105,200	8,500	17.3	24.2	2,540	10.2	7.9	830	9.4
Bleach	221	20,700	4,550	9.3	55.1	1,220	4.8	0.6	13	0.0
Fixers	186	41,900	7,800	16.0	293.2	12,300	48.8	62.4	2,620	29.8
Stabilizers	4	20,800	93	0.2	0.2	5	0.0	0.1	3	0.0
Starters	-	2,166	-	-	-	-	-	-	-	-
Totals:		526,966	48,973			25,255		8,796		
		liters	Kg			Kg		Kg		
		139,225	110,000			55,500		19,400		
		gal	lbs			lbs		lbs		

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- Percent of Total

DO - Oxygen Demand

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Section I, Task 34

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Section I, Task 34

Thus, a significant percentage of each facility's pollution comes from the use of chemicals in the laboratory, from pre-packaged processing chemicals, and miscellaneous tests which involve chemicals that do not pass through the chemical mix rooms.

(2) In black-and-white processing during 1968, over half (51%) of the total chemicals used and 71% of all processing solutions prepared were developers (Table 5). They also accounted for nearly half of the COD and BOD loads sewerred (47.8 and 42.5% respectively). Fixers constituted only 16.7% of the total volume of the combined processing effluent; however, they were responsible for most of the remaining COD and BOD; i.e., 39.2% and 44.1%, respectively. The arrest and dye-removal baths for black-and-white processing accounted for about 1% of the effluent volume, 8% of the total salts sewerred, and about 13% of the total BOD and COD loads.

(3) Effluents from color processing are considerably different (Table 6). Fixers in color processing are the highest contributors of COD and BOD (48.8 and 29.8%), but they constitute only 8% of the combined processing solution volume. Stop baths also exhibit high oxygen demand. In contrast to black-and-white processing, each of the several color solutions contributes its proportionate share of the total pollution. Table 8 summarizes the magnitude of pollution from each facility.

d. Sewer Samples

(1) Twenty-one samples of sewer effluents were collected and analyzed during selected times of mission and non-mission operation. Seven samples were taken from the LP facility and fourteen from BH. At LP the effluent was sampled through a clean-out valve in the basement floor, east of Column #17 (Figure 1). At BH samples were collected from two different locations: Manhole #1 into which only the contractor's waste flows, and from Manhole #2, which receives effluent from other departments in the contractor's organization as well as the waste from Manhole #1 (See Figure 2).

(2) Preliminary analyses were made in house for pH, alkalinity, temperature, color, clarity, etc. Other analytical work was done elsewhere in the contractor's parent company according to ASTM's "Standard Procedures for the Examination of Water and Wastewater"⁶.

⁶See References.

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Section I, Task 34

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Table 8

1968 Summary of BH and LP Pollution Magnitudes

<u>Chemical Usage:</u>	Black-and-White Processing (at BH)	Color Processing (at LP)
Total Annual Usage (lbs)	671,500	139,700
Total BOD (lbs/yr)	136,900	21,855
Total COD (lbs/yr)	206,900	71,565
Average BOD Factor, f (#)	0.20	0.16
Average COD Factor, f (#)	0.31	0.51
<u>Department Effluent:</u>		
Total volume (water usage) (gal/yr)	14,700,000	25,500,000
Average volume (Water Usage) (gal/day)	40,000	70,000
Average solute content (% by wt.)	0.51	0.061
Average BOD (ppm)	1,000	95
Average COD (ppm)	1,600	310
<u>Combined Processing Effluent (##)</u>		
Total annual volume (gal)	449,200	139,225
Average volume (gal/day ###)	1,800	560
Average solute content (lbs/gal)	1.0	0.8
Average BOD (ppm)	21,500	15,500
Average COD (ppm)	30,200	44,500

(#) Pounds of oxygen required per pound of chemical

(##) Exclusive of rinse and wash water

(###) Two-hundred fifty (250) days/year

A-14

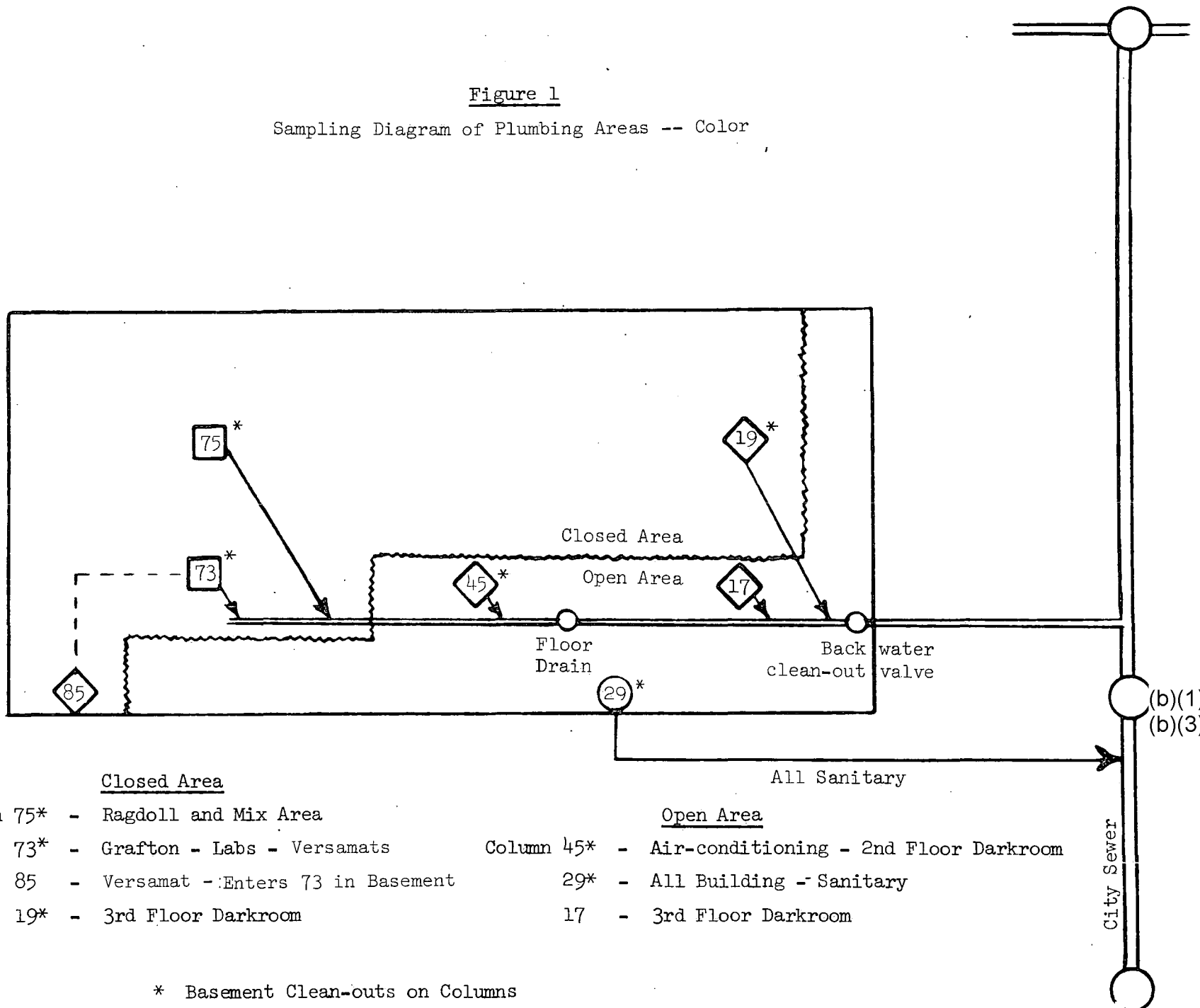
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Figure 1

Sampling Diagram of Plumbing Areas -- Color



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Closed Area

- Column 75* - Ragdoll and Mix Area
 73* - Grafton - Labs - Versamats
 85 - Versamat - Enters 73 in Basement
 19* - 3rd Floor Darkroom

Open Area

- Column 45* - Air-conditioning - 2nd Floor Darkroom
 29* - All Building - Sanitary
 17 - 3rd Floor Darkroom

* Basement Clean-outs on Columns

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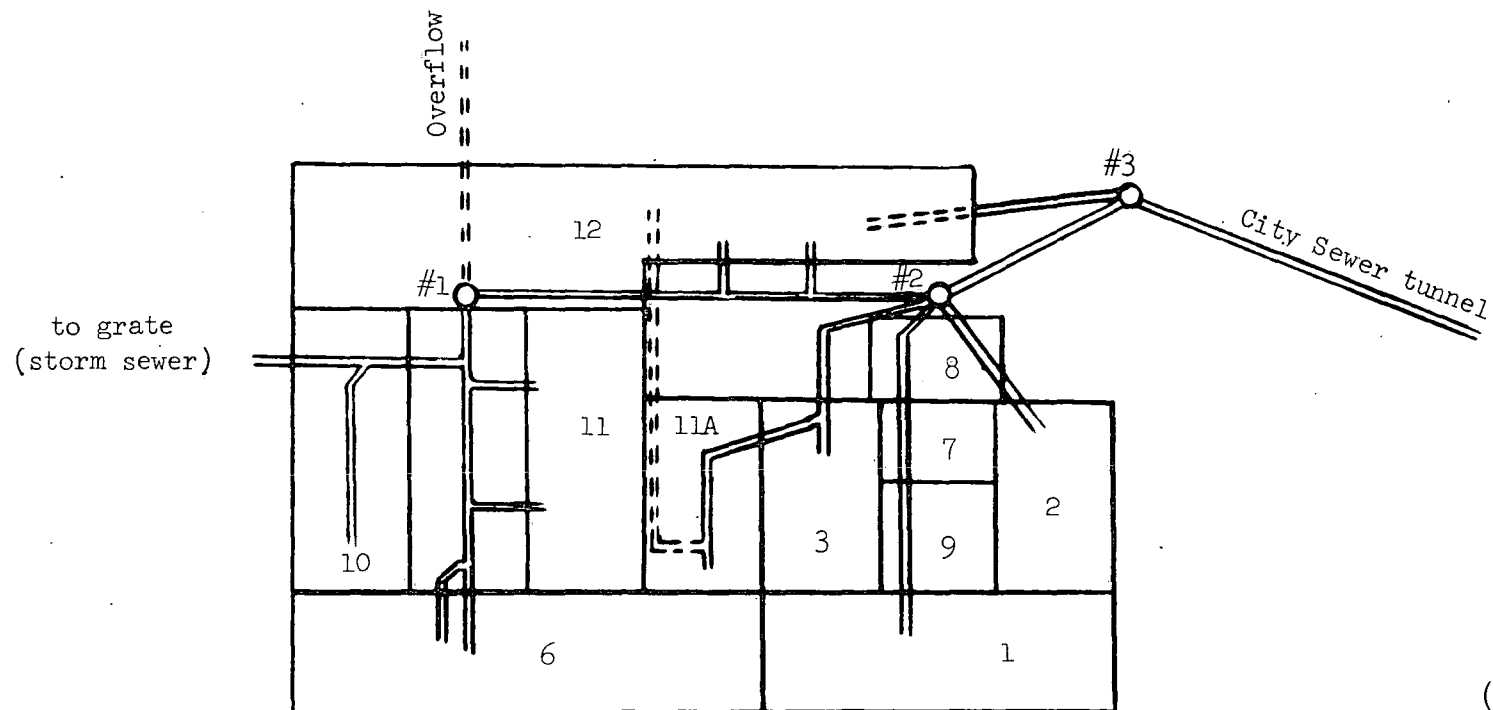
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Section I, Task 34

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Figure 2

Sampling Diagram of Plumbing Areas -- Black-and-White

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(b)(3)Manhole #1

All Area 10 processing (Production and Q.C.)
 All Area 11 Sanitary Drains
 All Area 6 Sanitary Drains
 All Area 6 Processing (1 Versamat and 3 Darkrooms)

Manhole #2

All From Manhole #2
 All Area 1, 2, 3, 7, 8, 9, 11A
 All Area 12 (Mostly Sanitary)

Manhole #3

All from Manholes #1 and 2
 Outside Line from Area 12

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Section I, Task 34

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Section I, Task 34

Complete analytical data are given in the tables of Appendix A.

(3) Sampling was scheduled to be representative of "average", "best", and "worst" conditions of pollution. The average condition was defined as during the regular weekly work-day for non-mission testing, and between the hours of 9 - 11 a.m., when the whole facility is under conditions of normal operation. The worst condition, or greatest degree of pollution, occurs when a mission is in house, the processing of duplicates is underway, and when water usage from all other operations is at a minimum, i.e., nights, mornings, or weekends. The best, or least, condition of water pollution was selected as being early in the morning during a non-mission period.

(4) At LP during a simulated mission condition, BOD, COD, solids (total and volatile), phosphates, and alkalinity were observed to increase dramatically. However, no specifically defined limitation of the existing sewer code is violated, other than the "slugging" or "not amenable to treatment" clauses. Each of the above mentioned properties of the LP effluent is certainly "unusual", and each therefore provides a potential basis for further analysis and investigation of the effluent by agencies outside the city.

(5) The heavy metals do not vary much from maximum to minimum conditions; nor is there the expected increase in phenols from developer use. Cyanides are low in concentration, since color bleaches are no longer being sewered, except on rare occasions. (This is because rejuvenation is in operation at LP.) There are no toxic properties indicated by the observed characteristics of these samples.

(6) The outstanding non-toxic properties of the LP effluent at its worst condition are high BOD, COD, and phosphates. A hundred-fold increase in phosphate concentration and in COD is clearly indicative of mission operations or photographic testing at LP. It is also very likely that the true BOD is much higher than the 820 ppm reported: BOD measurements on effluents containing sanitary wastes are generally low, unless they are made almost immediately after sampling.

(7) Samples taken from the two locations at BH show similar properties to the processing effluents at LP: High pH, high BOD, high COD, high solids (total and volatile), high phosphates, and high alkalinity.

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BIF-008-B-00624-I-70-

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Section I, Task 34

In addition, the effluent at BH contains significant amounts of phenols, from developer by-products.

(8) The effluent from Manhole #1 is solely from this facility, and drains into Manhole #2. Analysis indicates that some dilution of our effluent occurs in Manhole #2. During week days or nights this dilution factor is about 1:2 or 1:3. However, when contributing areas outside the facility are "down", such as on a Sunday night, our effluent passes through Manhole #1 and #2 with little or no dilution.

5. Established Pollution Standards

a. City Sewer Code

(1) The City Sewer Use Code³ has set specific limitations on only a few of the common pollutants or deleterious properties of industrial waste. Moreover, to date this code has not been strictly policed or enforced; it has therefore been possible to utilize the City's sewers and treatment center for photographic processing effluents. A strict interpretation of the code, however, might prohibit the continued sewerage of effluent by present disposal practices.

(2) Under the terms of the City Sewer Use Code, the discharge of any water, sewage, or industrial waste "which in concentration of any given constituent or in volume of flow, exceeds for any period of duration longer than five (5) minutes more than five (5) times the average twenty-four (24) hour concentration or flows during normal operation," is termed a "slug". Slugs are prohibited if, "in the opinion of the Commissioner of Public Works," they are "likely to harm" or "have an adverse effect" upon the sewer system or treatment process.

(3) Since photographic effluents change drastically in volume and in properties (more than a factor of five from the average values*) the term "slugging" is applicable to our effluent. At BH, samples taken from Manhole #2 indicate:

- (a) COD values of 150 ppm (average) and 17,200 ppm (maximum).
- (b) Total solids, from 380 ppm (average) and 4,000 ppm (maximum).
- (c) Total suspended solids, 10 ppm (average) and 100 ppm (maximum).

³See References.

* Appendix A' Tables.

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Section I, Task 34

Iron, alkalinity, and phosphates also vary considerably (more than five times the average concentration), but these properties are not presently detrimental to sewage treatment at current volumes and concentrations.

(4) At LP, "slugging" conditions exist, again attributable to COD, BOD total and volatile solids, phosphate concentration, and alkalinity. Each of these effluent characteristics (except alkalinity), are serious changes in properties and should receive corrective abatement measures. If security were not also involved, storage facilities for the LP installation would probably be adequate to prevent "slugging" and provide an "acceptable" effluent.

(5) The pH of the effluent is a likely sewer use code violation at both installations, as the alkalinity is above 10.0 when developer use is at a maximum*.

(6) Another possible sewer code violation could involve sewerage "toxic" materials or wastes not "amenable" to waste treatment. Under this category heavy metals such as chromium, zinc, copper, lead, tin, and nickel are often restricted, as well as toxic materials, such as cyanides. Our effluent contains chromium ion from potassium dichromate - sulfamic acid cleaning solution (Kodak System Cleaner) and organic phosphorous compounds, i.e., the bactericide solution, Dowicide G. An established limit has been set for cyanides (2 mg/l as CN). However, most sewer codes⁷ have specific limitations on some or all of the toxic heavy metals.

(7) It should be noted, however, that at present there are no actual, defined violations of the City Sewer Use Code at either facility, with the possible exception of pH. Adjustment in pH, if found to be necessary to comply with the code, can easily be made by storage and treatment with an inexpensive acid, such as sulfuric acid. Storage tanks would also reduce any potential problems due to slugging.

* The alkaline effluent is generally diluted with a more acidic waste. However, during mission periods over weekends, when other contributing areas outside the facility are "down", the combined effluent to the sewer exceeds the pH limit of 10.0.

⁷ See References.

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Section I, Task 34

(8) As more is learned by the city about the effect of specific industrial wastes on the performance of its treatment center, no doubt additional restrictions will be added and enforced. Current research literature indicates that some photographic effluents are not amenable to city primary and secondary treatment plants⁸.

b. Rules, Classification, and Standards for the State

(1) It is the declared "public policy of the state to maintain reasonable standards of purity of the waters of the state consistent with public health, and enjoyment thereof," including the "propagation and protection of fish and wild life"⁹

(2) In accordance with the above policy, and under the authority of the state public health law, rules and regulations on the discharge of any waste effluent have been adopted by the State's Water Pollution Control Board. The established rules and standards are based upon the principle that an effluent being discharged into any natural body of water must not so pollute the receiving body that its classified best usage will be impaired.

(3) Water resources within the state are therefore classified according to their "best usage," and quality standards have been established for twelve water classes⁹. Untreated photographic wastes, such as from our facilities, could be disposed only in receiving bodies having the lowest ratings, i.e, rated as Class E or F (for sewage, industrial wastes, or transportation only).

c. Federal Attitude and Standards

(1) Five Federal laws containing provisions related to water pollution have been enacted by the Congress. Two of these are primarily concerned with preventing damage to shipping. The Public Health Service Act of 1912 gave specific authority for the PHS (Public Health Service) to conduct investigations and research on the pollution of streams and lakes by sewage and other causes. The Water Pollution Control Act of 1948 (P.L. 845, 80th Congress) authorized expanded activities and responsibility of the federal government; added the principles of state-federal cooperative program development, limited Federal enforcement, but gave financial aid.

^{8,9} See References.

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Section I, Task 34

In 1961 the water-pollution-control program became administered directly by the Secretary of the Department of Health, Education, and Welfare and a previous restriction limiting federal enforcement to interstate waters was amended to include interstate or navigable waters.

(2) The federal position in regard to quality is clearly one of concern, but Congress recognizes that primary responsibility in the field of water pollution rests with the states. The federal role is to provide technical services and financial aid to states, agencies, and municipalities. NO national standards or regulations have been developed for control of wastes into surface waters¹⁰.

d. Summary. The pollution control standards which most directly apply to the discharge of photographic effluents by this contractor are those established by the city in its Sewer Use Code. Standards accepted to meet the security requirement (See next Section) will more than adequately comply with the established city sewer usage code.

6. Acceptable Security Control

a. Control Measures. The maintenance of operational security and prevention of a breach of security via waste discharge necessitates several pollution-control steps for our department: (1) Strict maintenance of an acceptable waste effluent, which will reduce or eliminate the need for a detailed analysis of our effluent by an outside agency. (2) Keeping photographic flags at a minimum: constituents or characteristics indicative of processing, (3) Disproportionatizing so that the true magnitude of such operations will not be revealed, (4) Disguising the cycle characteristics of our industrial waste.

b. Acceptable Department Waste Characteristics

(1) Continued use of the sewer means that the city will eventually collect and analyze samples of waste water containing effluents from this facility. It is therefore of prime importance that our discharge be an "acceptable" industrial waste in every way to the city.

¹⁰ See Reference.

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Section I, Task 34

(2) Industrial waste-water characteristics that are of present interest to the city are listed in Table 9. Both toxic and non-toxic limitations are specified.

c. Toxic Standards. The specific toxic limitations imposed by the city code that are relevant to our effluent are for cyanide and heavy metals. Only 2 mg/l (or ppm) of both simple and complex cyanides (as CN) are allowed. Also limited are the heavy metals, such as chromium, zinc, copper, lead, tin, and nickel. Their content should not exceed 10 ppm in solution or more than 30 ppm in total. These toxic standards mean that color bleaches and acid-dichromate solutions must be eliminated from our effluents.

d. Non-Toxic Standards

(1) Non-toxic characteristics acceptable as waste for the city sewer include the following specific limitations:

Table 10

Non-toxic Limitations for Wastes Accepted by City

Flammables: None

Temperature of effluent: Not over 150°F.

pH (at 70°F.) Between 5.5 and 10.0

Oils and grease Not over 100 ppm

(2) In addition, under the restrictions, "no unusual" or "excessive" conditions, our effluent should not violate the following suggested limitations:

Table 11

Suggested Effluent Limitations

BOD:	Not over 300 ppm	
COD:	Not over 750 ppm	
Color:	Pale colors only	
Solids (Total):	Not over 1000 ppm	
Solids (Suspended):	Not over 400 ppm	
Total Nitrogen:	Not over 50 ppm	} See also paragraph e., below
Ammonia Nitrogen (NH ₃):	Not over 25 ppm	

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Table 9

Industrial Waste Characteristics and Quantities

	At BH, Manhole #1			At BH, Manhole #2			At LP		
	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum
Volume (gal/day)	40,000	38,400	111,000	-	-	-	70,000	61,000	120,000
Temperature (°F)	70	56	68	71	58	68 - 74	100	106	100
pH (at 70°F)	7.5	8.0	10.4	7.9	8.0	10.1	9.5	8.2	8.7
Color (as noted)	Pale Yellow	Colorless	Yellow	Cloudy	Colorless	Yellow	Pale Yellow	Colorless	Pale green
BOD (ppm)	280	68	130##	96	19	320##	19	10	820##
COD (ppm)	410	105	16,200	150	45	17,200	265	19	33,000
Solids - Total (ppm)	1000	360	4,340	380	230	3,860	460	170	6,790
- Volatile (ppm)	480	90	1,530	150	80	770	170	150	1960
- Total suspended (ppm)	100	10	20	10	10	90	10	10	20
- Volatile suspended (ppm)	80	10	10	10	10	10	10	10	10
Oils and grease (ppm)	420	40	23	90	20	84	35	22	10
Phosphate (PO ₄) (ppm)	21	1.0	23.7	2.9	1.1	17.7	0.9	1.9	187
Flammables	None	None	None	None	None	None	None	None	None
Acids	None	None	None	None	None	None	None	None	None
Alkalinity # (as CaCO ₃) (ppm)	22	12	194	12	10	150	16	8	200
Copper (Cu) (ppm)	0.4	0.5	0.8	0.3	0.2	0.9	0.4	0.5	1.0
Nickel (Ni) (ppm)	0.3	0.3	0.4	0.3	0.3	0.7	0.3	0.8	0.6
Iron (Fe) (ppm)	5.0	0.7	5.0	2.5	0.4	15.0	1.0	3.0	5.0
Lead (Pb) (ppm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Chromium (Cr) (ppm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cyanide (CN) (ppm)	0.88	0.01	0.01	1.24	0.01	0.01	0.03	0.24	0.01
Phenols (as C ₆ H ₅ OH) (ppm)	0.09	0.05	0.11	ND	0.05	1.0	ND	0.05	0.07
Cadmium (Cd) (ppm)	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.1
Zinc (Zn) (ppm)	0.3	0.8	0.3	0.3	0.3	0.3	0.3	0.4	0.3
Tin (Sn) (ppm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

- Dashes mean data not available.

ND means not detected, or less than 0.01 ppm.

Alkalinity to pH = 4.5.

Probably too low (See text).

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Section I, Task 34

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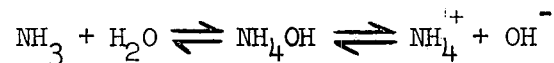
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Section I, Task 34

Adoption of the above restrictions would give our photographic effluent properties similar to the non-toxic characteristics of city sewage.

e. Ammonium Compounds

(1) Most decomposing organic matter, if nitrogenous, will liberate ammonia. Being highly soluble in water (100,000 ppm at 20°C), ammonia gas reacts quickly with water, forming ammonium hydroxide and much heat. The hydroxide readily dissociates, producing ammonium and hydroxyl ions, and raises the pH (alkalinity) of the solution:



In as much as the dissociation constant for NH_4OH is 1.8×10^{-5} at 25 C, the relative concentrations of ammonia, ammonium hydroxide, and ammonium ions are a function of pH:

Table 12

Ammonium Ion Concentrations at Various pH Levels

pH	Ratio of NH_4^+ to NH_4OH
6	1800
7	180
8	18
9	1.8
10	0.18

In neutral or acid solutions nearly all of the "ammonia nitrogen" will be found as ammonium ions - less than 0.5% will be as NH_4OH or available as NH_3 . In alkaline media (high pH) the equilibrium will be shifted to the left, producing NH_4OH , which will undergo decomposition to produce ammonia.

(2) At a pH of 7.4 solutions of ammonium salts will liberate ammonia if boiled. At higher alkalinities, they may have a distinct odor of ammonia, even at room ambient temperatures.

(3) Sewage normally will carry from 15 to 35 ppm or more of total nitrogen¹¹. About 1/3 to 1/2 of this amount will eventually decompose to form ammonia and/or ammonium salts.

¹¹See References.

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Section I, Task 34

(4) The Sewer Use Code obviously does not apply a limitation for ammonium compounds. Nor is it easily possible to discern whether ammonium ions in an effluent originated from the usual biochemical sources or from effluents initially containing ammonium salts. However, a total nitrogen content of over 50 ppm would probably be unusual, and therefore subject to scrutiny.

(5) For adequate security, effluent should not have a total nitrogen content of over 50 ppm, nor contain ammonia or ammonium salts in excess of about 25 ppm (measured as NH_3).

f. Photographic Flags

(1) Two of the items listed earlier in Table 9, cyanides and phenols, are specific flags for photographic processing. A high cyanide content (greater than 2.0 mg/l as CN) is an obvious sewer code violation that might easily lead to the further analyses and identification of ferri/ferro cyanide complex ions present in color bleaches.

(2) A high phenol content could similarly lead to the isolation of any of several developing agents that have the fundamental aromatic benzene structure (C_6H_5-): Phenidone, CD-3, CD-2, Elon, Hydroquinone, etc. Both spent as well as unused developers formulated from these developing agents could show a high phenol value when analyzed by the ASTM analytical procedure for Water and Wastewater¹². These organics -- and perhaps others, too -- are mainly responsible for the gross difference between observed values for COD and BOD with effluent samples.

(3) Sulfites, thiosulfates, and halides (iodides, bromides) may also be considered as photographic flags. They are found in numerous other industrial wastes, but usually in smaller concentrations than other common ions. They do not need to be completely eliminated from our effluent, but their concentration should be significantly reduced from that found in the photographic processing solution.

g. Disproportioning Constituents

(1) In order for processing chemicals to be sewered without jeopardizing security, they must be changed chemically, or in concentration, or by both means. For example, a photographic effluent containing thiosulfate and/or sulfite ions may be oxidized (by chlorination) to sulfate. The sulfate

¹² See References.

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Section I, Task 34

ions would then be precipitated from solution with lime and removed by settling as calcium sulfate.

(2) The resulting effluent will still be saturated with calcium sulfate (2000 ppm as CaSO_4), but this concentration is much less than the solute content of the original untreated effluent and it does not reflect the initial concentration of either thiosulfate or sulfite ion.

(3) Similar approaches may be used for other constituents.

h. Cyclic Variations

(1) A cyclic variation in the concentration or volume of our effluent could be used to ascertain information on the nature of in-house operations. Variations in the concentration of photographic flags such as bromides, iodides, sulfites, thiosulfites, cyanides, or phenols, would be most revealing. The concentrations would not even need to be so high as to indicate an appreciable degree of pollution. Storage tanks of adequate size to hold the effluent collected during a typical mission, would eliminate an indirect security break through this potential means.

(2) Table 13 summarizes the restrictions imposed by the city sewer code along with the "average" and "maximum" waste characteristics found by analysis of samples of our effluents at both installations. Also, the table shows recommended limits for each applicable characteristic. By maintaining these limits, the effluent should be "acceptable", for the city sewer, and, therefore, more secure.

A-26

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Section I, Task 34

Table 13

Acceptable Department Waste Characteristics

	Established	Observed Waste Characteristics				Prescribed or
	City Code	at BH*		at LP		Recommended
	Restriction	Average	Maximum	Average	Maximum	Limit
Volume (gal/day)	(1)	40,000	111,000	110,000	120,000	N/A
Temperature (°F)	150	71	74	83	106	150
pH (at 70°F)	5.5 - 10.0	7.9	10.1	9.0	9.5	5.5 - 10.0
Color	(1)	Lt. Yellow	Yellow	Lt. Yellow	Pale Green	Pale colors only
BOD (5-Day Test)	(1)	100	320	20	820	300
COD	(1)	150	17,200	265	33,000	750
Solids (Total)	(1)	380	3,860	450	6,790	2,000 (3)
Solids (Volatile)	(1)	150	770	170	1960	250
Solids (Total suspended)	(1)	10	90	10	20	400 (3)
Solids (Volatile suspended)	(1)	10	10	10	10	50
Oils and greases	100	80	90	35	35	100
Phosphate (PO ₄)	NLE	2.9	17.7	1.9	187	15
Flammables	None	None	None	None	None	None
Acidity (as CaCO ₃)	(1)	None	None	None	None	Minimal
Alkalinity (as CaCO ₃)	NLE	12	150	14	200	75
Copper (Cu)	0.3	0.9	0.5	1.0	1.0	(5)
Nickel (Ni)	(5)	0.3	0.7	0.3	0.6	(5)
Iron (Fe)	NLE	2.5	15.0	1.0	5.0	75
Lead (Pb)	(5)	1.0	1.0	1.0	1.0	(5)
Chromium (Cr)	(5)	1.0	1.0	1.0	1.0	(5)
Cyanide (CN)	2.0	0.01	1.24	0.03	0.24	2.0
Cadmium (Cd)	(5)	0.1	0.1	0.1	0.2	(5)
Zinc (Zn)	(5)	0.3	0.3	0.3	0.4	(5)
Tin (Sn)	(5)	1.0	1.0	1.0	1.0	(5)
Phenols (as C ₆ H ₅ OH)	(2)	0.5	1.0	0.01	0.07	(2)
Total Nitrogen ⁵ (N)	NLE	Not Measured	Not Measured	Not Measured	Not Measured	50
Ammonia (NH ₃)	NLE	Not Measured	Not Measured	Not Measured	Not Measured	25
Misc. solids or viscous materials	(1)	None	None	None	None	None
Radioisotopes	(4)	None	None	None	None	None
Silver (as Ag)	NLE	None	None	None	None	(5)

NOTES:

- (1) No specific limit given; but no "unusual" condition allowed.
- (2) No specific limit set by provisions of the city Sewer Use Code; however, may be considered toxic and therefore, not "amenable" to treatment and restricted.
- (3) Suggested limits set by other Sewerage Codes (Ref. 7, 11).
- (4) Any radioactive waste must meet applicable State or Federal regulations.
- (5) Total of chromium, zinc, cadmium, copper, lead, tin, nickel, silver -- not to exceed 10 ppm in solution and 30 ppm in total (Ref. 7).
- (6) All values given in ppm, unless stated otherwise.
- (7) * Based on analysis of samples from manhole #2.
- (8) NLE - No limit established by City Sewer Code.
- (9) None - Means none allowed.

A-27

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Section I, Task 34

CONCLUSIONS

7. Safe levels of the more significant characteristics requiring control for pollution abatement and security are:

a. Non-toxic Characteristics

- (1) COD of 750 ppm
- (2) BOD of 300 ppm
- (3) Phosphate of 15 ppm
- (4) Total solid content of 2000 ppm

b. Toxic Characteristics*

(1) Chromium ion (mainly from cleaning solutions) - complete removal or prohibition of discharge in the effluent.

(2) Cyanide (or ferrous and ferric salts) - complete removal or prohibition of discharge in the effluent.

8. In addition to the above, cyclic clues to the nature of our operations should be removed by minimizing or reducing "slugging", or periodic discharge of high and low concentration chemical effluent. Among the clues of chief concern are the concentrations of phenols, halides, acetates, thiosulfates and sulfites.

9. Adherence to the needs specified by paragraphs 7 and 8 above will specify the choices of treatment to satisfy both pollution abatement and security. Also, it appears that a single treatment or series of treatments is feasible to achieve these objectives.

10. Of local, state and federal regulations, only the local city Sewer Use Code is strictly applicable as a guide for establishing pollution standards. At present, this guide is broadly worded, not strictly enforced, and otherwise unsuitable to define our total needs for pollution control.

11. While the major concern is the abatement of pollution from mission processing operations, the total problem must embrace photographic support activities, such as laboratory testing and other use of chemicals not used directly for mission processing. These additional sources make up 25 to 30%

* A contractor's study was completed under Phase I, Section II of this task¹⁴ to find a common bleach and a method to regenerate and reuse color bleaches. As a consequence of this study, we have discontinued zinc precipitation of cyanides in spent bleaches and sewerage of the toxic solids. Also, we have taken steps to eliminate or minimize the acid dichromate cleaning solution previously used to clean equipment at the end of each mission.

¹⁴ See References.

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BIF-008-B-00624-I-70-

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Section I, Task 34

of the pollution contribution from this facility.

12. To maintain a more accurate concept of the type and magnitude of pollutants, all processing, testing and other chemicals should be recorded.

13. We need an automatic sampling device to further improve sampling accuracy and better assure that samples are representative of critical periods in the operation cycle. Such devices are commercially available, and once installed would have the additional advantage of more economical sampling activity.

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Section I, Task 34

RECOMMENDATIONS

14. Adopt and maintain standards of the type summarized in paragraphs 7 and 8, and as given more completely in Table 13 of the text, to adequately achieve pollution abatement and security.

15. Record all chemicals, chemical mixes and other preparations used by the contractor to facilitate adequate monitoring.

16. Purchase a commercially available twenty-four hour sampling device for use in future effluent sampling and analysis.

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Section I, Task 34

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Section I, Task 34

APPENDIX A'

Industrial Waste Characteristics

Tables A'-1 and A'-2 list separately the characteristics of the effluents from each of the contractor's two facilities, BH and LP.

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Table A-1

Industrial Waste Characteristics of Samples from BH

Sample No.	1	2	3	4	6	7A	11A	1A	4A	7	8A	12A	2A	5A
	Manhole #2				Manhole #1					Manhole #2				
Sampling - Source	Pipe	Bottom	Pipe	Bottom			Trough				Bottom			
- Date	Jan. 29	Jan. 29	Jan. 29	Jan. 29	Feb. 4	Mar. 17	May 11	Feb. 26	Mar. 5	Feb. 4	Mar. 17	May 11	Feb. 26	Mar. 5
- Time	4:30 a.m.	4:30 a.m.	11:00 a.m.		4:20 a.m.	4:30 a.m.	8:00 p.m.	9:20 a.m.	4:30 a.m.	4:20 a.m.	4:30 a.m.	8:00 p.m.	9:25 a.m.	4:30 a.m.
Temperature (°F)	61	73	71	71	68	68	75	70	56	70	68	74	71	58
pH (e 70°F)	7.54	7.95	7.62	8.16	10.32	9.31	10.35	7.49	7.98	10.03	9.51	10.06	7.91	7.95
Alkalinity														
#(to pH = 8.3)	--	--	--	--	54	--	55	--	--	16	--	45	--	--
Alkalinity														
(to pH = 4.5)	12	12	32	25	168	250	194	22	12	54	94	150	12	10
Acidity #														
(to pH = 8.3)	0.28	0.08	0.20	0.04	--	--	None	--	--	--	--	None	--	--
Color	Colorless	Pale	Colorless	Pale	Yellow	Dark	Yellow	Pale	Colorless	Yellow	Yellow	Yellow	Slightly	Colorless
Clarity	Clear	Clear	Clear	Clear	Clear	Cloudy	Clear	Yellow	Clear	Clear	Cloudy	Clear	Cloudy	Clear
BOD	--	--	--	--	--	830	130	280	68	--	320	80	96	19
COD	--	--	--	--	--	2,820	16,200	410	105	--	985	17,200	150	45
Solids - Total	--	--	--	--	--	10,770	4,340	1,000	360	--	3,860	3,670	380	230
- Volatile	--	--	--	--	--	1,420	1,530	480	90	--	650	770	150	80
- Total Suspended	--	--	--	--	--	230	20	100	10	--	90	20	10	10
Volatile Suspended	--	--	--	--	--	60	10	80	10	--	10	10	10	10
Oils and Grease	--	--	--	--	--	80	23	420	40	--	80	4	90	20
Phosphate (PO ₄)	--	--	--	--	--	29.0	23.7	20.7	1.0	--	11.0	17.7	2.9	1.1
Flash Point	--	--	--	--	--	None	None	None	None	--	None	None	None	None
Copper (Cu)	0.4	0.3	0.5	0.6	0.4	0.5	0.8	0.4	0.5	0.5	0.6	0.9	0.3	0.2
Nickel (Ni)	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.3	0.3	0.7	0.3	0.3
Iron (Fe)	6.0	1.5	1.5	2.5	5.0	40.0	5.0	5.0	0.7	0.6	15.0	3.0	2.5	0.4
Lead (Pb)	1.0	1.0	1.0	4.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Chromium (Cr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cyanide (CN)	--	--	--	--	--	0.01	0.01	0.08	0.01	--	0.01	0.01	1.24	0.01
Phenols (C ₆ H ₅ OH)	--	--	--	--	--	0.68	0.11	0.09	0.05	--	1.00	0.09	None	0.05
Cadmium (Cd)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1
Zinc (Zn)	0.4	0.4	0.3	1.0	0.3	0.3	0.3	0.3	0.8	0.3	0.3	0.3	0.3	0.3
Tin (Sn)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Notes:

Best Condition → Average Condition → Worst Conditions →

(Non-Mission, No testing) (Non-Mission, Testing) (Mission, 1 Dalton) (Mission, 2 Daltons) (Mission, 2 Daltons) (Non-Mission, Testing) (Non-Mission, Testing) (Mission, 1 Dalton) (Mission, 2 Daltons) (Mission, 2 Daltons) (Non-Mission, Testing) (Non-Mission, No Testing)

Other Notes:

All values are in ppm (parts per million) unless stated otherwise.
 Alkalinity and values expressed in ppm CaCO₃.
 Dashes mean data not available.
 N. D. stands for not detected; or less than 0.01 ppm.

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Section I, Task 34

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Table A-2

Industrial Waste Characteristics of Samples from LP

Sample No.	5	3A	8	6A	9A	2	10A
Sampling Date	Jan. 29	Feb. 26	Feb. 4	Mar. 5	May 11	Feb. 4	May 11
Sampling Time	9:30 a.m.	10:30 a.m.	5:45 a.m.	5:15 a.m.	6:30 a.m.	7:35 a.m.	7:00 p.m.
Temperature (°F)	100	83	99.5	76	106	96	100
pH (at 70°F)	8.51	9.45	8.20	8.11	8.26	8.69	8.67
Alkalinity (to pH = 8.3#)	-	-	-	-	0	3	10
(to pH = 4.5#)	12	16	8	8	8	76	200
Acidity (to pH = 8.3#)	-	-	-	-	None	-	None
Color	Pale Yellow	Pale Yellow	Colorless	Colorless	Colorless	Colorless	Pale Green
Clarity	Clear	Clear	Clear	Clear	Clear	Clear	Clear
BOD	-	19	-	10	2	-	820
COD	-	265	-	10	19	-	33,000
Solids - Total	-	460	-	160	170	-	6,790
- Volatile	-	170	-	50	150	-	1960
- Total suspended	-	10	-	10	10	-	20
- Volatile suspended	-	10	-	10	10	-	10
Oils and grease	-	35	-	20	22	-	10
Phosphate (PO ₄)	-	0.9	-	1.9	1.2	-	187
Flash point	-	None	-	None	None	-	None
Copper (Cu)	0.4	0.4	0.5	0.2	0.5	1.5	1.0
Nickel (Ni)	0.3	0.3	0.3	0.3	0.8	0.3	0.6
Iron (Fe)	1.0	1.0	2.5	0.8	3.0	3.0	5.0
Lead	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Chromium (Cr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cyanide (CN)	-	0.03	-	0.01	0.24	-	0.01
Phenols (C ₆ H ₅ HO)	-	None	-	0.05	N.D.	-	0.07
Cadmium (Cd)	0.1	0.1	0.2	0.1	0.1	0.1	0.1
Zinc (Zn)	0.3	0.3	0.3	0.4	0.4	0.3	0.3
Tin (Sn)	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Notes:

Average
Condition
(Misc. testing)

Best
Condition
(Downtime)

Worst
Condition
(Grafton)

Other Notes:

All samples taken from clean-out valve near Column 17 (Figure 2).
All values are in ppm (parts per million), unless stated otherwise.
#: Alkalinity/acidity as ppm CaCO₃.
Dashes mean data not available.
means less than.
N.D. - Not detected, or less than 0.01 ppm

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Section I, Task 34

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(b)(3)APPENDIX B

This appendix contains a reproduction of FINAL REPORT on
"Study of Pollution Contribution from Processing Activities,"
Contract EK-1904, Task 34, Section VII, 3 March 1969. This
report was published 21 April 1969.

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Section VII, Task 34

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	4
SUBJECT	5
TASK (from Study Plan)	5
DISCUSSION	5
1. Chemical Usage	5
2. BOD/COD Load	5
3. Processing Solution Volumes	6
4. Water Usage and Dilution Ratio	8
5. Systems Cleaner	8
6. Ammonium Salts	11
7. Dowicide G	11
CONCLUSIONS	13
8.	13
RECOMMENDATIONS	14
REFERENCES	15

B-2

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LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	Chemical Usage and Pollution at Bridgehead	7
2	Processing Solution Volumes - 1968	9
3	Water Usage and Dilution Ratios	10

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Section VII, Task 34

SUMMARY

A survey was made of the types and amounts of photographic chemicals used as well as department water-usage rates and volumes for black-and-white mission and testing activity at Bridgehead during 1968. From these data, the pollution problem has been characterized.

Developers constituted 71.0% of the volume of processing effluent at Bridgehead -- exclusive of rinse waters. Fixers and arrest baths accounted for 16.5% and 11.5%, respectively*. Under typical mission conditions, about 2300 gallons of processing solutions are prepared, used, and sewered each 24-hour day. The worst condition observed in 1968 was for a 13-day period when an average of 2500 gallons were used each day.

Department water-usage rates vary from 1600 to 4600 gallons per hour; the peak rate is observed on the "A" shift during testing activities between missions. Water usage rates constitute a reliable indication of mission activities, however, only when observed hour-by-hour. About 14.7 million gallons of water was used by the department in 1968. The dilution factor (ratio of water volume to processing effluent) averaged about 33 and ranged from 13 to 55.

Recommendations are:

- a. Reduce and/or control the discharge of "toxic" chromic acid cleaner solution.
- b. Study arrest replenisher rates or water cut-off (without use of arrest bath) to further reduce pollution.

* The other 1.0% was made up of miscellaneous chemical solutions.

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Section VII, Task 34

SUBJECT: Study of Pollution Contribution From
Processing Activities

TASK

A. Determine Processing Solution Usage For:

1. Non-mission processing.
2. Machine checkout.
3. Pre-mission checkout.

B. Determine Cleaning Solution Usage for Cleaning Processors. Consideration will be given to the concentration and possible effects of the chromium ion contained in waste cleaning solutions.

1. Pre-mission.
2. Post-mission.
3. Other cleaning.

C. Study Pollution Contribution From Versamats and Other Small Processors In House

DISCUSSION

1. Chemical Usage

a. Earlier pollution reports^{1,2} list the processing chemicals used and machine replenisher rates for 1966 at Bridgehead. More recent data for black-and-white processing were obtained in a survey of make-up sheets from the chemical mix room. These data, shown in Table 1, represent actual chemicals used and sewered for testing and production during 1968.

b. Over 335 tons of 19 different chemicals were used at Bridgehead during 1968. This tonnage is a significant reduction from the quantity used two years earlier (1966 usage was nearly 600 tons), when pollution abatement began with a study and subsequent readjustment of replenisher rates. As the annual water usage for 1968 was 14.7 million gallons, the solids content in the department's effluent for that year average 0.46 lb. per gallon (55,000 ppm or 5.5% by weight).

2. BOD/COD Load

a. Currently, the degree of water pollution is generally determined by the quantity of oxygen required to oxidize constituents of the effluent. In a treatment center this oxygen demand (DO) may be satisfied either chemically as in chlorination, or biochemically, as by the bacteria in an activated sludge system. The degree of oxidation is not usually the same.

^{1,2} See References.

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Section VII, Task 34

The Chemical Oxygen Demand (COD) of a pollutant is generally greater than the Biochemical Oxygen Demand (BOD). Because most large treatment centers use an activated-sludge process, the BOD load of an effluent is generally involved. Unfortunately, the analytical procedure for determining BOD usually requires a minimum of five days so that, whenever possible, pollution is evaluated by means of COD tests. Analytical procedure for COD testing requires only one to two hours.

b. In Table 1, the BOD and COD factors (f) are given for each of the chemicals used. Multiplying the annual usage by this factor gives the COD load or amount of pollution. During 1966 and 1968, the oxygen demand for processing was 0.31 lb. of chemical oxygen (or 0.20 lb. of biochemical oxygen) for every pound of chemicals used. The amount of pollution in 1968 was about 35% lower than for 1966.

c. Seventy-three to eighty-five percent of the pollution load in 1968 came from four chemicals:

	<u>% of Total DO</u>	
	<u>BOD</u>	<u>COD</u>
Sodium thiosulfate (hypo)	32	33
Sodium sulfite	18	12
Acetic acid	20	18
Diethylaminolthanol	15	10
Totals	85	73

The balance of the pollution load comes from several other chemicals, most of which are organic solids.

3. Processing Solution Volumes

a. Most of the chemicals sewered in 1968 were dumped as used developers, fixers, arrests, or dye removal baths. Half (about 51%) of the total chemicals used were formulated in developers, about 41% in fixers, and only about 8% in arrest and dye removal baths. Some 1.7 million liters (450,000 gallons) of processing solutions were used for testing or mission work, as shown in Table 2, Part A. About 71% of this total were developers, and only 16.5% were fixers. These figures do not reflect potential reductions in fixer, as hypo rejuvenation and re-use was employed only infrequently.

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Table 1

Chemical Usage and Pollution at Bridgehead

	Chemical Usage (lbs.)		(f)	COD Load (lbs. of O ₂)		(f)	BOD Load (lbs. of O ₂)	
	1966	1968		1966	1968		1966	1968
Sodium thiosulfate (Hypo)	480,000	216,000	0.32	154,000	69,000	0.20	96,000	43,200
Sodium sulfite	270,000	202,000	0.12	32,400	24,200	0.12	32,500	24,200
Sodium meta-borate	145,000	13,200	0			0	0	0
Soda ash	69,000	100,000	0			0	0	0
Acetic acid	68,000	36,000	1.06	72,000	38,100	0.77	52,400	27,700
Sodium sulfate	51,000	34,000	0			0	0	0
Potassium alum	32,000	6,000	0			0	0	0
Potassium bromide	8,120	7,540	0			0	0	0
Ammonium thiosulfate	-	4,500	1.62	-	7,300	0.36	-	1,620
Sodium iso-ascorbate	13,000	6,400	0.81	10,500	5,200	0.29	3,770	1,850
Sodium hydroxide	3,000	13,400	0			0	0	0
Elon	16,000	7,200	1.86	29,800	13,400	0.90	14,400	6,500
Hydroquinone	13,000	5,200	1.89	24,400	9,800	1.1	14,300	5,720
Hexaethylcellulose	(2,000)	3,000	1.33	(2,660)	4,000	(1.33)	(2,660)	(4,000)
Phenidone	3,570	5,520	2.67	9,500	14,700	0.165	590	910
Diethylaminoethanol	10,000	7,400	(2.87)	(28,700)	(21,200)	(2.87)	(28,700)	(21,200)
Sodium bisulfate	-	2,500	0			0	0	0
Sulfuric acid	-	720	0			0	0	0
Sodium carbonate	-	500	0			0	0	0
TOTALS: (lbs)	1,183,590	671,480	.31	353,960	206,900	.20	225,320	136,900
(tons)	592	336		182	103		113	68

Note: Values in parentheses () are estimates.

Dashes mean data not available.

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Section VII, Task 34

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Section VII, Task 34

b. The processing solutions required for a typical black-and-white mission in 1968 are given in Table 2, Part B. Developers account for over 70% and fixers 19% of the combined processing effluents, which average 2300 gallons per day for a 15-day period.

c. In 1969, when the rejuvenation and re-use of hypo is in full operation, developers should constitute 84% of the processing solutions prepared for each mission. Hypo and arrest combined, in about equal quantities, will account for only 15%. The average daily volume of processing solutions (exclusive of rinse water) should drop slightly to about 2000 gallons per day (85 gallons per hour) during mission work.

d. The worst condition observed in 1968 was for a 13-day mission during which some 120,750 liters of processing solutions were prepared, used, and sewered, giving an average of 2500 gallons/day. The worst condition in 1969 should not exceed 3000 gallons of combined processing effluents.

4. Water Usage and Dilution Ratio

a. Water meter readings were taken twice daily throughout 1968. Total department usage was 14.7 million gallons for processing, testing, mix room, etc. An analysis was made of the data to determine how much usage rates varied during the day, night, or over the weekend for both mission and non-mission intervals. Significant differences in usage rates were observed, as noted in Table 3.

b. The maximum rate occurs on non-mission days when there is considerable in-house testing. From 4 PM to 8 AM daily and over weekends, water usage is 1600 gph for non-mission periods and 2250 gph for mission periods, an increase of 650 gph which is clearly discernable. If only daily (24 hour interval) records are taken, the rates would be 2730 and 3120 gph respectively for non-mission and mission days. Thus, water usage rates are valid indicators of mission activities if hourly checks are made on nights, holidays, or weekends. If only daily, weekly, or monthly data are obtained, reliable correlation with mission activities would probably not be possible.

5. Systems Cleaner

a. During 1968, 3000 lbs. of Kodak Developer Systems Cleaner was used within the department. This product is approximately 65% sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) and 35% potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). As potassium dichromate contains 35.35% chromium, some 370 lbs. of chromium was sewered in

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Table 2

Processing Solution Volumes - 1968

Part A: Annual Usage

		Approx. Conc.	Volume			Solid Content		
	Major Constituents	<u>g/l</u>	<u>liters/yr.</u>	<u>gallons/yr.</u>	<u>%</u>	<u>lbs/yr</u>	<u>%</u>	
1. Developers:	Misc. organic & inorg. chemicals	40-120 (87 av)	1,217,000	321,000	71	232,000	51	
2. Fixes:	Na ₂ S ₂ O ₃ ·5H ₂ O	240						
	Na ₂ SO ₃	15	300	283,000	75,000	16.5	187,000	41
	HC ₂ H ₃ O ₂	14						
3. Arrest Bath:	Na ₂ SO ₄	45						
	HC ₂ H ₃ O ₂	36	82	187,000	49,500	11.5	33,700	7.3
4. Dye-removal baths	Na ₂ SO ₄	100						
	NaOH	10	110	14,000	3,700	1	3,300	0.7
Annual Total:			1,701,000	449,200		456,000		

Part B: Mission Conditions

Processing Solutions Used		1968 (Actual)		1969 (Anticipated)	
Developers		100,500 liters	73.4%	100,500 liters	84.2%
Fixer:	Fresh: 22,500				
	Rejuv. 3,500			9,400	
	Total:	26,000	19.2	26,000	6.7
Arrest		8,000	6.3	8,000	7.8
Dye-removal bath		1,500	1.1	1,500	1.3
	Total Used	136,000		136,000	
	Total Mixed	132,500		119,400	
Combined Processing Effluent:					
Total for Mission		34,500 gallons		30,300 gallons	
Daily Average		2,300 gallons/day		2,000 gallons/day	

* Mission: 5 days (Oct. 12-17, 1968)
 Negative footage ("J") -46,000 ft.
 Negative footage ("G") -11,000 ft.

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Section VII, Task 34

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Section VII, Task 34

Table 3
Water Usage and Dilution Ratios

Department Usage:

1968 Total 14,710,000 gallons

Department Usage Rates:*

	<u>Mission</u>	<u>Non-Mission</u>
	(gallons/hour)	
Daily (24-hour) average:	3120	2730
Daily (8-hour):	3800	4630
Nightly average:	2250	1600

Dilution Ratios

	<u>Combined</u> <u>Processing Effluent</u>	<u>Water</u> <u>Usage Rate</u>	<u>Dilution</u> <u>Ratios</u>
Best Conditions: (Mission; "A" Shift)	85 to 125 gph (2000 to 3000 gpd)	4630 gph	37 to 55
Worst Conditions: (Mission; Weekends, Nights)	85 to 125 gph (2000 to 3000 gpd)	1600 gph	13 to 19
Yearly Average Condition:	450,000 gallons	14,700,000 gal.	33

* Based on a 6-month survey in 1968.

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BIF-008-B-00624-I-70-

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1968 in the form of soluble salts. About half the value of this chromium could be realized in a recovery system³.

b. In a typical cleaning operation, 51 lbs. of Kodak Systems Cleaner are used to prepare 400 gallons of cleaning solution. After circulation throughout the equipment, during which time only part of the dicromate is reduced to the trivalent state (Cr^{+++}), the used solution is sewerred over a period of about five minutes. Occasionally, two 400-gallon cleaner solutions may be dumped simultaneously, generally when the water usage rate is at a minimum (at the end of a mission). At these times the chromium salt concentration in the department effluent often approaches 5 g/l.

c. Chromium salts are cited as toxic in numerous water quality standards⁴. Their discharge into any natural outlet would generally be prohibited in concentrations exceeding 0.1 to 5.0 mg/l^{5,6}. They are generally considered to be "toxic" and "not amenable to treatment or reduction" by a city sewage treatment plant. Our usual technique of dumping used systems cleaner solution to the sewer is also prohibited by the city's Sewer Use Code under their definition of "slugging"⁷.

6. Ammonium Salts. Ammonia and ammonium salts presently constitute a small part of the processing effluent. During 1968, about 4500 lbs. of ammonium thiosulfate were sewerred, chiefly as Type A Fixer from Versamats or other small processors (see Table 1). The ammonia (NH_3) or ammonium ion (NH_4^+) in this effluent amounted to only 1100 lbs. annually at an average concentration of about nine parts per million. The contribution to pollution from Versamats and other small processors is therefore quite small, compared to the total pollution load.

7. Dowicide G

a. Another "toxic" constituent of our effluent is the organic phosphorous bactericide solution "Dowicide G," also used at the end of each mission. Some 25 grams of this product are used in a recirculating solution for each Trenton and 6.7 grams per machine for the Dalton system. The solutions are then drained to the sewer in 5-10 minutes.

³⁻⁷ See References.

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b. Organic phosphates vary greatly in toxicity and they affect various aquatic life forms quite differently⁸. The discharge of this bactericide solution might also be subject to regulation, should the city declare it "toxic" or "not amenable" to its treatment plant.

⁸ See References.

B-12

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CONCLUSIONS

8. We have an adequate description of the pollution problem for proceeding to further study under Sections I, IV and V to complete the Task.

9. Treatment capability requirements for all department effluents can be set at an average 42,000 gallons per day with peak load capability at 100,000 gallons per day.

10. Treatment of chemical solutions only (excluding rinse waters) requires capacity for an average of only 2,500 gallons per day -- peak load 5,000 gal/per/day.

11. Storage systems for effluents appear to be the logical choice in a treatment facility for the department. It would best protect the security of our operations by subtending the cyclic "clue" of mission operations.

12. Toxicity is better defined by this study than it is in municipal ordinances or codes. This may become a problem, but we can design a system to eliminate the dangerous chemicals, or reduce their concentrations to an innocuous level.

13. It should be feasible to avoid some treatment problems by eliminating or reducing undesirable chemicals. As cases in point:

a. A substitute formula for the Kodak (dichromate) Systems Cleaner.

b. Reduced use of the arrest bath by either water cut-off or re-use methods.

B-13

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Section VII, Task 3⁴

RECOMMENDATIONS

14. Reduce pollution treatment requirements by minimizing the number and amount of objectionable (especially 'highly toxic') chemicals. Of most immediate concern is the concentration of chromium ion, and a substitute cleaning solution such as chlorinated trisodium phosphate may solve this problem. If an acceptable substitute cannot be found, the used Kodak Systems Cleaner should at least be stored, and re-used, until its cleaning powers are virtually spent.

15. Employ storage systems in general, for all chemical effluent, to avoid cyclic "clues" as to the nature of our operations.

16. Defer decisions as to total treatment of all effluent versus treatment of chemical solutions excluding rinse waters. When the studies under this task are complete, a more valid choice will be possible.

B-14

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Section VII, Task 34

REFERENCES

1. Task 34 STUDY PLAN, "Water Pollution and Operational Security,"
Contract EG-400, 5 June 1967.
2. Task 34 FIRST QUARTER FY-68 REPORT, Contract EG-400,
20 September 1967.
3. Watson, Channon, Greer and Armstrong, Sewage and Industrial Wastes
Vol. 25, No. 8, pp 921-937, August 1953.
4. McKee and Wolf, Water Quality Criteria, State Water Quality Control
Board, Sacramento, California, No. 3A, p 163, 1963.
5. Ibid, pp 417-421.
6. "Rules and Classifications and Standards of Quality and Purity
for Waters of NYS," NY Water Resources Commission, Chapter 490
of Laws of 1961.
7. Sewer Use Code, Code of the City of Rochester, Chapter 97.
8. McKee and Wolf, op. cit., p 381.

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APPENDIX C

TABULATED RESULTS OF ALKALINE CHLORINATION PILOT STUDIES

Tables C-1 through C-8 list the conditions and results of the eight test runs conducted during the alkaline chlorination pilot studies. See paragraph 11 under DISCUSSION (page 65).

C-1

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Table C-1
Run No. 1 Using Type A Effluent as Feed

Chlorination			Temp	pH	Caustic		BOD	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)	(°F)		Reading (l)	Total (lbs)	(ppm)	
0	2.0	0	70	13.6	10	17		
10			110					Foaming; "Foamex" added to retard foaming
20			120	13.5				
30		1	125	13.6				
45			130					
60	4.0	2	127	13.4				Dark floating solids
90			120	13.5				
120		6	135					
150			145					
180		10	152					Shut down overnight
240		14	80-120	13.5	< 10	< 17		

Table C-2
Run No. 2 Using Type A Effluent as Feed

Chlorination			Temp	pH	Caustic		BOD	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)	(°F)		Reading (l)	Total (lbs)	(ppm)	
0	4	0	60	8.35	0	0		Clear, amber color.
5				4.0				
15				3.0				
30		2	70	2.5				Foamex added
				12.7	1.0	1.7		Yellow-green solvent
40				12.2				
45		3	75	10.9				
			80	7.20				
60		4		12.0	2.0	3.4		
90		6	100	7.9	3.0	5.1		

Table C-3
Run No. 3 Using Type A Effluent as Feed

Chlorination			Temp	pH	Caustic		BOD	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)	(°F)		Reading (l)	Total (lbs)	(ppm)	
0	2	0	70	13.1	1.0	1.7	530	Clear, amber soln.
5								Dark, clear
10								Red-brown soln.
15			80	13.0				Yellow, clear
30		1	100	12.6			<40	
45				8.6	2.0	3.4		
60		2	114	12.9				
75			118	12.9				
90		3		8.3	3.0	5.1		
105			125	12.8				
120		4	125	12.6				
135				7.8				
					4.0	6.8		
150			125	12.4			<40	
180		6	130	11.9				

Table C-4
Run No. 4 Using Type A Effluent as Feed

Chlorination			Temp	pH	Caustic		BOD	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)	(°F)		Reading (l)	Total (lbs)	(ppm)	
0	1.0	0	70	13.1	2	3.4	550	Amber, clear
15	"		88	12.8				Red, clear.
30	"		92	12.8				Amber, clear
60	"	1	96	12.8			< 40	
90	"		102	12.8				
120	"	2	108	12.5				
150	"		110	12.3				
165	"			9.6				
					3.0	5.1		
180		3		12.8			<40	
210			114	12.5				
240		4		12.3				
270				8.9				
					4.0	6.8		
300		5	118	12.5			<40	Clear
330			120	12.2				
360		6	120	8.4				Amber, some ppt.
					5.0	8.5		
390				12.4				Turbid
420		7		11.9				
450		7.5		7.7			<40	

Table C-5
Run No. 5 Using Type A Effluent as Feed

Chlorination			Temp	pH	Caustic		BOD	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)	(°F)		Reading (l)	Total (lbs)	(ppm)	
0	3	0	84	13.6	1.0	1.7	530	Clear, amber color
15			94	13.0				
30			100	7.6			<40	
					2.0	3.4		
45			106	12.6				
60		3	110	8.0	3.0	5.1	<40	
75			114	12.6				
90			116	8.6				
105			120	4.8				
					4.0	6.8		
120		6	126	11.4			<40	
135			128	4.5				
					5.0	8.5		
150			144					
					6.0	10.2		
195			144	10.5			<40	
					7.0	11.9		
210			144	12.5				
					8.0	13.6		
330		16.5		12.9			<40	

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Table C-6
Run No. 6 Using Type B Effluent as Feed

Chlorination			Temp (F°)	pH	Caustic		BOD (ppm)	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)			Reading (l)	Total (lbs)		
0	3.0	0	70	12.9	1.0	1.7	600	
15			80	9	2.0	3.4		
30			104	12.8	3.0	5.1	< 40	
45			110	12.9			< 40	
60		3	110	12.5				
75			115	12.3	5.0			
90			120	8.6	6.0	10.3		
105		6	132	11.2				
120			135	12.3	7.0	11.9	< 40	Caustic rate: 23 cc/min.
135				12.4	7.75	13.2		Caustic rate: 24 cc/min.
165		9		12.3				Caustic rate: 27 cc/min.
180				12.3				
195				12.1				
210		12		11.9				
225				12.1				
240			136	12.3			< 40	
255			138	12.3				
270		15	138	12.3				Caustic rate: 27 cc/min.
285			138	12.3				
300			144	12.3				
315			144	12.4	12.5	21.3		
330		18	145	12.4	13	22.2		
345			156	12.4				
360			161	12.5	14	23.8	< 40	
375								
390		21						
405								
420								

Table C-8
Run No. 8 Using Ferri/Ferro Cyanide Bleach as Feed

Chlorination			Temp (F°)	pH	Caustic		BOD (ppm)	Fe(CN) ₆ (g/l)	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)			Reading (l)	Total (lbs)			
0	3	0	58	13+	1.0	1.7	242	13.0	Light blue
15			60	13+					
30			68	13+			175	12.6	
45			80	13+					
60		3	90	13+	2.0	3.4	0#	10.2	Red ppt.
75			100	12.9					
90			110	12.8	3.0	5.1			
105			116	12.3					
120		6	104	12.0	4.5	7.7	0#	6.4	
175			122	11.4	5.5	9.4			
180		9	130	9.1			0#	2.7	
195			12.9		6.5	11.0			
210			136	12.4	7.5	12.7			
			12.2						
240		12	140	11.9	8.25	14	0#	0.5	
[270]		[13.5]	-	-	[16]			[0.0]	Extrapolated values to complete destruction of cyanide

Table C-7
Run No. 7 Using Ferri/Ferro Cyanide Bleach as Feed

Chlorination			Temp (F°)	pH	Caustic		BOD (ppm)	Fe(CN) ₆ (g/l)	Notes
Time (min)	Rate (lbs/hr)	Cl ₂ (lbs)			Reading (l)	Total (lbs)			
0	3.0	0	70	10	1.5	2.6	267	12.4	Caustic rate: 27 cc/mm
15			93						
30			100	13+			145	11.0	Caustic rate: 27 cc/mm
45			110		2.5	4.3			
60		3	118	13+			50	10.0	Caustic rate: 27 cc/mm
75			126	13					
90			130	12.8	4.5	7.5			
105			136	12.7					
120		6	140	12.2			0#	5.7	Caustic rate: 27 cc/mm
135			152	10	5.5	9.3			
135			110	11.9					
150			130	11.0	6.5	11.0			
165									
180		9	135	11.9	7.5	12.8	0#	3.0	Caustic rate: 27 cc/mm
195			136	11.9	8.5	14.5			
210			138	11.9					
225			140	11.9					
240		12	142	11.8	9.5	16.2	0#	0.8	Caustic rate: 27 cc/mm

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