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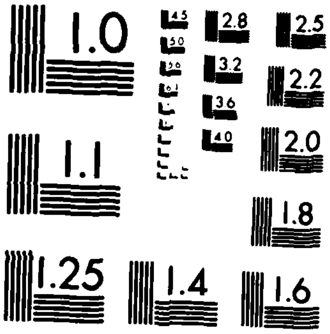

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ESL-TR-82-42

PHOTOGRAPHIC PROCESSING INTERPRETATION FACILITY WASTEWATER CONCEPTUAL TREATMENT DESIGN

EUGENE J. DONOVAN JR.
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HYDROQUAL, INC.
MAHWAH, NJ 07430

MARCH 1983

FINAL REPORT
MAY 1981 - OCTOBER 1982

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The Air Force maintains and operates self-contained, mobile photographic processing and interpretation units in support of air reconnaissance. Should the need arise, these units could be deployed to forward operating areas where there may be no waste treatment facilities available. Hence, an equally deployable treatment system would have to be coupled to the processing unit. To fulfill this need for mobile treatment, a study was undertaken to characterize the wastewater from the Air Force's photographic processing unit (WS430B), investigate treatment alternatives, and develop pilot plant design criteria. (Continued on reverse.)

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20. Abstract (Continued.)

A literature search revealed that of the 11,000 photo processing installations in the U.S., only 20 are direct dischargers of treated waste effluent. Their treatment methods were evaluated and the following were chosen for bench scale testing: chemical precipitation and settling, chemical oxidation, air stripping, carbon adsorption, biological oxidations, and reverse osmosis.

The effluent parameters of primary concern for the study were chemical oxygen demand (COD), total dissolved solids (TDS), heavy metals, and ammonia. Because of this complexity in the WS430B wastewater, and the need for mobility, the "standard techniques employed by the permanently positioned civilian installations were not acceptable. Reverse osmosis (RO), the recommended technique, was chosen because of its ease of operation/maintenance and the ability of the system to process the full spectrum of waste.

The basic plant would consist of three RO units; two working in series on the washwater and one working on the resulting brine. Because the fix and developer solution wastes are already concentrated, they would not be processed. Instead, they would be combined with the brine drawn from the third RO unit and this combined waste would be transported for treatment. Results of the screening tests, waste characterization, and design data are included in the report.

A

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

A. SUMMARY AND CONCLUSIONS

HydroQual has conducted the three major phases of this study, wastewater characterization, wastewater treatment, and conceptual design to meet the project objective of the development of a conceptual design for the treatment of wastewater from the U.S. Air Force WS 430-B Mobile Photographic Processing and Interpretation Facility.

The wastewater characterization study involved field sampling at the Shaw AFB and Birmingham ANG facilities. Wastewater flows were measured and compared with the photo equipment design flows and typical practices based on other studies. This information was analyzed, and projected flows and characteristics for the wastewater were developed, based on Air Force projected average and maximum film production rates of 3,840 feet per day and 26,400 feet per day, respectively.

Total waste flow ranges from 550 to 2225 gallons per day. It was determined that the spent fix and developer solutions comprise only 5 percent of the total volume, but contain about 94 percent of the total contaminant load, and that the washwater contains 6 percent of the contaminant load and comprises 95 percent of the facility wastewater flow.

The pollutant parameters of concern in the total waste, with respect to the effluent levels set for the scope of this project, were determined to be chemical oxygen demand (COD), ammonia, total dissolved solids, and, to a lesser degree, the heavy metals, silver, cadmium and chromium.

Reports and published literature on photoprocessing wastewater treatment were reviewed to evaluate the current state of the art for treatment technologies, and their performance. Of 11,000 photoprocessing installations in the United States, less than 20 are direct dischargers, with the others generally discharging to municipal systems for biological treatment. Limited data on treatment technologies used for various types of photographic wastes were available. In addition to biological treatment and conventional silver recovery by iron exchange or electrolytic regeneration, reverse osmosis (R.O.), ion exchange, and chemical treatment were found to be utilized by a small number of facilities. The applicability of various treatment technologies to the wastewater was reviewed and evaluated. Chemical precipitation and settling, chemical oxidation, air stripping, carbon adsorption, biological oxidation, and reverse osmosis were selected for bench scale testing and evaluation on samples of the WS 430-B wastewater.

The laboratory bench scale testing program was conducted at HydroQual's laboratory, except for the R.O. tests, which were conducted at a manufacturer's facility. Tests were conducted on the total discharge and the washwater to determine effectiveness of removal of the pollutants of concern to the three concentration levels specified. These levels are listed in Table 4.

Chemical precipitation of the total waste with caustic produced a slow settling precipitate, while use of lime resulted in voluminous quantites of sludge. The heavy metals were generally reduced below Level 3 criteria; Levels 1 and 2 were not met except for chromium, which was in very low concentration in the raw waste. Iron from the silver-iron exchange unit in the effluent was precipitated, although 15-25 mg/l remained in solution. Chemical precipitation of the washwater with caustic and polymers, before and after ammonia stripping, produced settleable floc. The results on removal of silver were somewhat anomalous; while significant reduction of silver concentration was achieved, Level 3 concentration goals were not met in the test conducted. Tests on the total washwater also indicated Level 3 concentrations could not be met. Chromium and cadmium concentrations in the washwater were below Level 3 requirements and were not of concern. Chemical precipitation did not significantly reduce COD.

Chemical oxidation tests were conducted with hydrogen peroxide and chlorine. Both fully oxidized the sulfite in the wastes at expected dosages. Sulfite oxidation by peroxide resulted in COD reductions in the total waste and washwater in the range of 15 to 20 percent; this was insufficient to meet Level 3 criteria for the total wastewater, or Level 2 for the washwater. The chlorine dosages required to satisfy the demand of the total waste and washwater far exceeded theoretical requirements for oxidation of the sulfite and ammonia present. Chlorine dosages of 2000 to 2500 mg/l were required to satisfy the demand of the total waste, and 500 to 650 mg/l were required for the washwater demand. Chlorine oxidation produced 100-percent oxidation of sulfite and ammonia, reduced the COD in the total waste by approximately 30 percent, and reduced COD in the washwaters by approximately 55 percent.

Air stripping of the total wastewater and washwater at a pH between 11 and 12.5 was successful in reducing ammonia concentrations; ammonia concentration levels were dependent on the amount of air and number of passes over the stripping tower. Although ammonia concentrations approaching Level 2 were achieved, air stripping to Level 3 concentration was considered the more likely and practical.

Activated carbon was investigated for removal of COD from the wastewater. The COD of the wastewater was found to be poorly adsorbed. Carbon adsorption was not considered effective on the total waste and was not practical for application to the washwater.

Biological treatment using a nitrifying activated sludge was tested on both the total wastewater and the washwater after ammonia removal by air stripping. On the total waste, which had been pretreated to reduce the COD due to inorganic chemicals, the effluent COD from biological treatment (activated sludge) did not meet Level 1 criteria, and ammonia oxidation was not consistent. After pretreatment by peroxide oxidation and ammonia stripping the washwater was effectively treated biologically, and met Level 1 requirements.

Reverse osmosis tests on the washwater indicated that Level 1 requirements could be met by a two-stage system, and that the concentrate could be reduced to a small volume, about 2 percent of the total waste by incorporating a third R.O. module. Reverse osmosis was not considered a practical or cost-effective application for the total waste; since the separation of the concentrated fix and developer solutions from the washwater prior to treatment is feasible and, in effect, yields a lower volume concentrate than would R.O.

A simple evaporation test on the total waste indicated that the condensate from an evaporation system would be contaminated with ammonia and would have a chemical oxygen demand. Full-scale pilot tests, which were beyond the scope of this study, were recommended by manufacturers to evaluate evaporation and condensate quality.

The information available on photoprocessing waste and the bench scale results was evaluated and a conceptual design for treatment facilities for the mobile WS430-B facility was developed. It was concluded that the concentrated fix and developer solutions should be collected separately from the washwater. This, in effect, would be comparable to a residue from typical treatment operation; the combined fix and developer solutions comprise approximately 5 percent of the total wastewater volume and are at a total solids level of approximately 10 percent.

Two feasible systems were finally developed and were compared for onsite treatment of the remaining wastewater (washwaters). Reverse osmosis was selected over a train of unit operations, including pH adjustment, air stripping, chemical precipitation biological treatment, filtration, and chlorination. The R.O. application was considerably simpler in operation and maintenance, and would likely yield a higher quality effluent. Concentrated brine from the R.O. system would be combined with the fix and developer solutions.

Alternatives for disposal of the concentrated solutions were considered. Evaporation, basically the only onsite alternative available for volume concentration of the fix and developer waste solutions was considered. Evaporation could be accomplished onsite by an evaporation pond or a mechanical evaporation system. The condensate produced from an evaporator would require ammonia removal and would then require further treatment. A slurry of about 60 percent solids concentration amounting to about 8-25 gallons per day would require ultimate disposal offsite in an environmentally acceptable manner. Alternatives for disposal of the concentrated solutions were considered, and it was concluded that selection of a system was site dependent. Therefore, no single recommended system could be proposed. Alternatives included transport of the fix and developer offsite to an approved waste disposal site, a large municipal wastewater treatment plant, or an Air Force base for chemical recovery or treatment. Site-specific alternatives for the washwater included land disposal and discharge to a local sanitary treatment facility.

B. RECOMMENDATIONS

1. For each specific mobile laboratory deployment, all acceptable options for wastewater treatment and residue disposal should be evaluated.

2. For onsite treatment, the fix and developer solutions should be collected separate from the washwater.

3. For onsite treatment, a two-stage reverse osmosis system is recommended for treatment of the washwater. The R.O. brine (concentrate) should be further reduced by a third R.O. unit and combined with the fix and developer solutions for final disposal.

4. Washwater treatment by land disposal or discharge to a local treatment system should be considered and compared to onsite treatment (R.O.) for each site.

5. Alternatives available for residual handling should be evaluated for each specific deployment site to determine the appropriate course of action.

6. In most cases, the residue of spent fix and developer solutions should be transported offsite for disposal, treatment, or chemical recovery.

7. Disposal of residue to onsite solar evaporation ponds where it is feasible should be evaluated and compared to the option of transport to offsite facilities.

8. The Air Force should evaluate the feasibility of establishing centralized facilities for the handling of concentrated residues from several mobile facilities to achieve maximum cost effectiveness.

9. A prototype treatment system should be designed, built and operated to obtain information on performance, maintenance, and operability to standardize the treatment system applicable to those WS430-B facilities requiring onsite treatment.

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PREFACE

This report was prepared by [illegible] Plaza, Mahwah, NJ, for the Engineering and Services Laboratory at Tyndall AFB, Florida, 32403, under Air Force Contract [illegible]

The work was performed between [illegible] 1981 and [illegible] 1982. The Project Officer was First Lieutenant Jack H. Jetter, [illegible]

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

A. BACKGROUND

The United States Air Force WS430-B Photographic Processing and Interpretation Facility (PPIF) is deployed worldwide by the Tactical Air Command. Operation of these mobile facilities generates wastewater. Normally, throughout the United States, the vast majority of photoprocessing installations discharge wastewater to sanitary sewage systems for dilution and secondary biological treatment. Pretreatment for silver recovery, and destruction of cyanide, are considered by the EPA as the best practical controls presently available for the photoprocessing industry before discharge to a publicly-owned treatment works (POTW) (Reference 1). Various studies have demonstrated the biological treatability of chemicals used in photoprocessing (References 2 and 3).

WS430-B facilities may, however, be located at sites where existing treatment facilities are too small, inadequate, or simply not available, thus presenting a wastewater disposal problem. The objective of this project was to develop a conceptual process design for a system to treat the facility's entire wastewater effluent. Three specified levels of effluent quality were developed by the Air Force as treatment goals.

B. SCOPE OF WORK

The project scope consisted of three major phases of work:

Phase I	Wastewater characterization - Analyses of existing, available data; field sampling and laboratory analyses of samples; development of wastewater quantity and characteristics for average and maximum projected film production.
Phase II	Wastewater Treatment - Literature reviews and selection of potential candidate treatment processes; laboratory bench scale treatability testing of selected treatment processes to develop preliminary performance and design parameters for the removal of pollutants to specified levels.
Phase III	Conceptual Design - Evaluation of alternative treatment systems to achieve selected effluent levels; and development of recommended schemes for a prototype installation and full-scale evaluation.

The results of Phase I were presented in a report submitted to AFESC/RDVW November 12, 1981 entitled "US Air Force WS430-B Photographic Processing and Interpretation Facility Wastewater Characterization," and are summarized in this report along with the analyses of additional samples collected for treatability studies. This report presents the results of the treatability studies and development of the conceptual design of treatment facilities.

C. WS430-B FACILITIES DESCRIPTION

The WS430B Facility is comprised of Eastman Kodak Versamat® Photoprocessors and related support operations. The USAF is presently converting its photoprocessing operations from the standard 11CN to the high-speed 1140 Versamat®. The enhanced WS430 B facilities will consist of four high-speed 1140s, an upgrading from the present six 11CN systems. The primary differences between the 11CN and 1140 are presented on the following page:

Operational Parameter	11CN	1140
Film Speed	20 ft/min	40 ft/min
Silver Recovery	Two ion exchange canisters (iron replacement)	electrolytic
Fix Replenish	0.240 l/min	0.120 l/min (with 75% recycle)
Developer Replenish	0.267 l/min	0.530 l/min
Washwater Replenish	2.082 l/min	4.164 l/min
Operating Temperature	85°F	105°F

The chemistry in both units is identical; the differences relate primarily to the 1140's ability to process film or paper at approximately twice the rate of the 11CN. An interim measure may involve modification of the existing 11CN to high-speed processing. The flow rates presented are those used for the development of Eastman Kodak type 2402 film (5-inch width).

Film is fed by a series of rollers through the developer, fix and washwater baths and finally dried. The developer bath reduces the exposed silver halide to elemental silver. The image is then "fixed" on the film by the fix solution which complexes the unexposed silver and brings it into solution in the fix bath. The film is then passed through the wash bath and dried.

Replenishment of the three baths is done on a continuous basis when film is being developed. Contamination of each bath is due to "carryover" by the film or paper from one bath to the next. A carryover rate of 3.0 mls per square foot of film has been reported (Reference 4). The spent fix solution, high in silver concentration, is passed through a silver recovery process in both photoprocessing operations. In the standard 11CN, Kodak Iron Replacement Cartridges are used; iron is exchanged in solution for silver, leading to high iron concentrations in the total discharge. The enhanced 1140 uses an electrolytic silver recovery process, with recirculation of about 75 percent of the fix solution.

A Versamat® will be run in either of two modes; film processing or standby. Washwater replenishment is continuous during both modes and the only discharge during the standby mode. Fix and developer are used only during the processing mode, which occurs irregularly, depending on film availability. The duration of the processing mode depends on the amount of film being processed. Typically this is between 1 and 10 minutes for the 11CN and 0.5 and 5 minutes for the 1140.

D. WASTEWATER CHARACTERISTICS

Flow measurement data and samples of wastewater were collected at Shaw AFB (11CN Versamat®) and Birmingham ANG (1140 Versamat®) under actual operating conditions. The measured volumes and concentrations were related to the amount of film processed and then compared to the system design operation conditions.

The observed developer solution replenish rates agreed well with the design rates of either system. The fix replenish rate was observed to be significantly higher than the design rate for the 11CN; the 1140 fix replenish rate was observed to be variable and was higher than the design rate for the film speed used during the sampling period. This was due to an operator error. The washwater rate on the 11CN units was in agreement with design; however, on the 1140 it was double that which should have been used for the film processing speed in use.

The design flow rates and Versamat® film processing speeds previously shown, were used to develop flow projection for each of the units. Developer and fix flows occur only during film processing, while the washwater flow is continuous throughout the operating day. The following film production schedules and Versamat® utilization rates were used to develop design flows and wastewater characteristics:

System	Average Production		Maximum Production	
	No. Units	% Utilization	No. Units	% Utilization
11CN	2	20	4	30
1140	2	10	4	34

Tables 1 and 2 summarize the results of the field sampling surveys conducted at Shaw AFB and Birmingham ANG as part of Phase I. Table 3 presents data on subsequent samples collected and sent to HydroQual's laboratory for treatability testing.

Limited information on the chemicals used in the WS430-B system fix and developer solutions was obtained from Hunt Chemical. Although this does not include certain proprietary chemical agents,

TABLE 1. WASTEWATER CHARACTERIZATION SUMMARY OF SAMPLING PROGRAM AIR FORCE STANDARD 11CN VERSAMAT®(1)

Parameter	Developer	Fix Before Recovery	Fix After Recovery	Washwater	Total Waste
pH (std. units)	-	-	5.0	7.3	7.2
Alkalinity (as $CaCO_3$)	2,950	-	-	64	642
Acidity (as $CaCO_3$)	-	331	-	288	235
Chemical Oxygen Demand (COD)	102,863	114,844	-	1,281	6,170
Ammonia Nitrogen (NH_3-N)	6.55	68,070	-	7	1,900
Kjeldahl Nitrogen (TKN)	1,390	67,200	-	8	1,520
Nitrate Nitrogen (NO_3-N)	11	42	-	-	6.4
Total Solids (TS)	105,199	118,447	-	130	6,040
Total Volatile Solids (TVS)	33,897	64,807	-	51	2,561
Total Organic Carbon (TOC)	23,600	14,595	-	-	1,294
Total Inorganic Carbon (TIC)	3,950	114	-	-	9
Aluminum (Al)	7.4	2,900	-	0.86	92
Barium (Ba)	<0.6	<0.6	-	-	<.1
Cadmium (Cd)	2.4	1.4	1.4	<.01	0.11
Total Chromium (Cr)	1.2	14.5	-	-	0.15
Copper (Cu)	0.42	0.54	-	-	0.08
Iron (Fe)	4.5	5.3	3,333	-	158
Manganese (Mn)	0.36	0.42	-	-	1.4
Mercury (Hg)	0.01	0.011	-	-	0.004
Potassium (k)	10,800	70	-	0.7	286
Silver (Ag)	2.1	2,183	39.3	<.10	0.81
Sodium (Na)	4,200	4,200	-	37	515
Zinc (Zn)	0.16	0.35	-	-	0.15
Biochemical Oxygen Demand (BOD_5)	-	-	-	-	2,567
Sulfate (SO_4)	2,100	3,700	-	1,128	1,544
Boron	1,800	204	-	<.01	44
Sulfite plus Thiosulfate (as SO_3)	26,343	52,013	-	-	2,100

(1) All concentrations as mg/l;
Data represent the average of results from three 8-hour composite samples

TABLE 2. WASTEWATER CHARACTERIZATION SUMMARY OF SAMPLING PROGRAM AIR FORCE ENHANCED 1140(1)

Parameter	Developer	Fix Before Recovery	Fix After Recovery	Washwater	Total
pH (std units)	10.1	4.7	4.7	5.1	9.5
Alkalinity (as $CaCO_3$)	33,400	-	842	14	1,220
Acidity as ($CaCO_3$)	0	-	224	24.5	0
Chemical Oxygen Demand (COD)	72,000	86,400	83,200	188	2,720
Ammonia Nitrogen (NH_3-N)	1,700	-	56,060	109.2	392
Kjeldahl Nitrogen (TKN)	2,400	-	38,400	60	432
Nitrate Nitrogen (NO_3-N)	-	-	-	-	-
Total Solids (TS)	127,689	-	75,501	177	5,131
Total Volatile Solids (TVS)	32,600	-	33,935	73	1,228
Total Organic Carbon (TOC)	16,300	8,844	14,873	33	994
Total Inorganic Carbon (TIC)	2,600	0.5	1.0	0.8	31
Aluminum (Al)	176	-	1,500	2.85	174
Barium (Ba)	-	-	-	<0.10	-
Cadmium (Cd)	0.8	1.0	1.0	<0.01	<0.01
Total Chromium (Cr)	-	-	-	<0.05	-
Copper (Cu)	-	-	-	<0.05	-
Iron (Fe)	-	-	-	-	-
Manganese (Mn)	-	-	-	<0.03	-
Mercury (Hg)	-	-	-	<0.004	-
Potassium (K)	-	-	-	8.3	-
Silver (Ag)	2.2	7.0	17	0.15	2.2
Sodium (Na)	-	-	-	8.2	-
Zinc (Zn)	-	-	-	0.12	-
Biochemical Oxygen Demand (BOD_5)	-	-	-	40	-
Sulfate (SO_4)	6,900	-	29,000	57.5	350
Boron	-	-	-	<0.2	-

(1) All concentrations as mg/l; data represent a single 8-hour shift composite.

TABLE 3. ADDITIONAL 11CN AND 1140 WASTE SAMPLES

	11CN			1140						11CN Washwater		1140 Washwater	
				DAY 1			DAY 11						
	Fix B	Fix A	Dev.	Fix B	Fix A	Dev	Fix B	Fix A	Dev	106-1	106-3	Day 1	Day 11
Ft. Film		-	-	-	-	-	-	-	-	203	463	1000	1000
COD	82,800	97,600	90,400	91,872	81,409	87,120	90,288	97,282	98,208	145	145	158	523
TOC	5,555	26,000	4,800	-	-	-	-	-	-		-	-	
NH_3N	32,500	26,000	0.18	14,386	13,215	1.79	10,874	21,754	38.0	17.8			106.9
TKN	-	127,200	8,000	-	-	-	-	-	-		-		
TS	-	80,810	141,386	-	-	-	-	-	-	-	-		
TDS	135,857	107,600	77000	-	-	-	-		-				
TVS	-	23,278	98,204	-	-	-	-	-	-				
SO_3	56,600	41,525	28,125	45,700	47,600	25,000	45,400	47,600	26,000	65	74	14	176
Ag	2,040	4.4	-	1,480	566	2.03	1,900	517	2.15	0.388	0.407	[illegible]	[illegible]
Fe	2.49	5,800	-	-		-				<.05	.07	<.05	<.07
Cd	2.03		-	-	-	-	-			<.02	<.02	<.02	<.02
Cr	0.27		-	-	0.50	-	0.50	0.58	0.24	<.06	<.06	<.06	<.06
Zn	0.45	0.45	-	-	-	-	-		-	.05	.11	.04	.04
Hg		-	-	-	-	-	-	-	-	<.0004	<.0004	<.0004	<.0004
Cu		-	-	-	-	-	-			<.01	<.01	0.16	[illegible]
B		-	2,000	-	-	-	-						
K			21,700	-	-	-	-						
Al	2,300	1,840	-	-	-	-							

Fix B = Before Silver Recovery
Fix A = After Silver Recovery
Data in mg/l
Dev - Developer Solution

the following provides an indication of the major constituents of the developer and fix solutions used by the Air Force:

Developer:

60 gm/l	Na_2SO_3
2-3 gm/l	Sequesterants (EDTA)
12-16 gm/l	Boric Acid
6-9 gm/l	Hydroquinone
2 gm/l	Secondary developers

Fix: (two types are used)

AeroFix®		Flash-O-Graph®
250 gm/l	$(NH_4)_2S_2O_3$	-
18 gm/l	Na_2SO_3	-
15 gm/l	Acetic Acid	20 gm/l
40 gm/l	$Al_2(SO_4)_3 \cdot 14H_2O$	80 gm/l
5 gm/l	H_2SO_4	-

Manufacturer's information indicates the developer has a BOD of 18,000 mg/l. The BODs of the fix solutions were estimated to be 48,000 and 172,000 mg/l for the Aero® and Flash-O-Graph® fixes, respectively.

Total wastewater discharge characterizations were calculated for the design flows, over 8-hour shifts, for both the average and maximum film production projections. These results, shown as Tables 4 and 5, were taken from the wastewater characterization report. The 1140 maximum production values were recalculated for 26,400 feet of film based on subsequent information received from the Air Force. The three treatment levels specified by the Air Force are also shown and compared with the total wastewater characteristics.

TABLE 4. PROJECTED EFFLUENT CHARACTERIZATION FOR 11CN DISCHARGE (8-HOUR SHIFT)

	Average Production (2-11CN Versamats, at 20% Production)		Maximum Production (4-11CN Versamats, at 30% Production)		Effluent Criteria (mg/l) Level 1	2	3
Film Speed	20 ft/min		20 ft/min				
Feet of Film	3,840 ft		11,520 ft				
Q_T	554. gal		1,144.4 gal				
Q_F	12.2 gal		46.[illegible] gal				
Q_D	13.5 gal		40.6 gal				
Q_{WW}	528 gal		1,056 gal				
	(mg/l)	(gms)	(mg/l)	(gms)			
pH					6-9		
Alkalinity	-	-	-	-	-	-	-
Acidity	-	-	-	-	-	-	-
COD	5,038	10,560	7,404	31,763	50	100	500
NH_3-N	750	1571	1100	4728	1.0	2.0	10.0
TKN	1,514	3,173	2,226	9,550	-	-	-
NO_3-N	1.2	2.5	1.76	7.55	-	-	-
TS	5,174	10,846	7,606	32,630	1,520	3,040	15,200
TVS	2,188	4,586	3,216	13,797	-	-	-
TOC	897	1,880	1,319	5,659	-	-	-
TIC	98.8	207	145	622	-	-	-
Al	64.1	134	94.2	404	-	-	-
Ba	<0.027	<0.057	<0.04	<0.17	2.0	4.0	20.0
Cd	0.09	0.19	0.13	0.56	0.01	0.02	0.1
Cr (Total)	0.35	0.73	0.51	2.19	0.1	0.2	1.0
Cu	0.022	0.046	0.032	0.137	0.3	0.6	3.0
Fe	73.5	154	108	463	-	-	-
Mn	0.018	0.038	0.026	0.112	-	-	-
Hg	0.009	0.019	0.01	0.04	0.01	0.02	0.1
K	279	585	410	1,758	-	-	-
Ag	1.2	2.5	1.76	7.55	0.05	0.10	0.5
Na	195	409	287	1,231	-	-	-
Zn	0.01	0.02	0.015	0.06	1.0	2.0	10.0
BOD_5	-	-	-	-	20	40	200
SO_4	133	279	196	841	-	-	-
B	48.4	101	71	304	-	-	-
S_2O_3	1,788	3,748	2,628	11,274	-	-	-

TABLE 5. PROJECTED EFFLUENT CHARACTERIZATION FOR 1140 DISCHARGE (8-HOUR SHIFT)

	Average Production (2-1140 Versamats® at 10% Production)		Maximum Production (4-1140 Versamats® at 34% Production)		Effluent Criteria (mg/l) Level		
					1	2	3
Film Speed	40 ft/min		40 ft/min				
Feet of Film	3,840 feet		26,400 ft				
Q_T	1,072 gal		2,225 gal				
Q_F	3.0 gal		20.9 gal				
Q_D	13.5 gal		92.4 gal				
Q_{WW}	1,056 gal		2,112 gal				
	(mg/l)	(gms)	(mg/l)	(gms)			
pH	-	-	-	-	-	-	-
Alkalinity	-	-	-	-	6-9		
Acidity	-	-	-	-	-	-	-
COD	1,147	4,650	3,780	31,832	50	100	500
NH_3-N	90	367	300	2512	1.0	2.0	10.0
TKN	139	563	458	3,854	-	-	-
NO_3-N	-	-	-	-	-	-	-
TS	1,822	7,386	6,004	50,562	1,520	3,040	15,200
TVS	507	2,055	1,670	18,068	-	-	-
TOC	247	1,001	814	6,852	-	-	-
TIC	33	134	109	917	-	-	-
Al	6.5	26.4	21.5	181	-	-	-
Ba	-	-	-	-	2.0	4.0	20.0
Cd	0.013	0.052	0.04	0.36	0.01	0.02	0.1
Cr (Total)	-	-	-	-	0.1	0.2	1.0
Cu	0.15	0.6	0.49	4.1	-	-	-
Fe	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-
Hg	-	-	-	-	0.01	0.02	0.1
K	-	-	-	-	-	-	-
Ag	0.82	3.34	2.73	2.3	0.05	0.10	0.5
Na	-	-	-	-	-	-	-
Zn	-	-	-	-	1.0	2.0	10.0
BOD_5	-	-	-	-	20	40	200
SO_4	169	685.1	559	4,709	-	-	-
B	-	-	-	-	-	-	-
S_2O_3	-	-	-	-	-	-	-

The pollutant concentrations are significantly higher in the flow from the 11CN, as may be expected, because of the lower total flow and greater replenish volume of fix per unit of production, than the 1140. At maximum production in each facility, total COD loads are similar in quantity, while other parameters, for purposes of developing and sizing a treatment system design, are in the same general order-of-magnitude range. The higher 11CN concentrations were used with the higher flow values of the 1140 to develop projected waste loads. This conservative approach was felt to be appropriate for preliminary conceptual design and sizing. The ammonia concentration found in the 11CN characterization sample, however, was higher those than found in subsequent samples by a factor of 2. Since the projected ammonia concentrations would be doubled, they were adjusted in this report.

The fix and developer constituents are relatively constant, since the formulation of the fresh solutions in both systems is the same. These are only replenished while film is being processed. The washwater characteristics can be quite variable, however, and depend upon the operating speed of the equipment, the rate of carryover of fix solution on the film, the quantity of film processed, and the actual washwater flow rate. The characterization study obtained highly variable results on the washwater, and it was not possible to relate these results with confidence to the design conditions. The Air Force had previously estimated (Reference 4) that 3 ml of fix solution were carried over on each square foot of film processed. A second set of samples were collected, as summarized in Table 3, to refine this washwater characterization. These results were used to estimate fix carryover. The limited data developed from this analysis are felt to be a reasonable confirmation of the previous estimate of 3 mls/ft^2 of film processed:

Parameter Used to Estimate Carryover
(refer to Table 3)

Sample	COD (mls/ft^2)	NH_3-N (mls/ft^2)	SO_3 (mls/ft^2)	Average (mls/ft^2)
11CN 106-1	3.46	3.38	3.64	3.5
11CN 106-3	4.5	-	5.4	5.0
1140 Day I	0.78	-	0.34	0.6
1140 Day II	2.63	4.46	1.60	2.9
Average				3.0

The average fix characteristics from the 11CN facility were then used to calculate washwater characteristics for a design washwater flow at projected production rates. These results are shown in Table 6. Table 7 identifies those parameters in the total wastewater and in the washwater, determined by the characterization study, which exceed the effluent level goals.

E. DESIGN ASSUMPTIONS

A number of task elements and design values which were incorporated in the original Air Force scope of work were revised, based on the results of the wastewater characterization study. These revisions were reviewed with the Air Force and it was agreed that they would be used in the development of the conceptual design.

An initial objective of the study was to develop an end-of-pipe system to treat the entire effluent. The waste characterization study showed that there are three identifiable, separable waste streams from the production units which are combined to produce the end of pipe effluent. Two of these streams, the fix and developer,

TABLE 6. PROJECTED WASHWATER CHARACTERIZATION

BASIS - *Fix Solution Carryover* Rate of 3 ml/ft^2 of Production
11CN Avg Fix Concentrations

Parameter	11CN				1140			
	Average		Maximum		Average		Maximum	
Ft. of Film	3,840		11,520		3,840		26,400	
WW Q gal.	528		1,056		1,056		2,112	
Drag Out Vol (liters)	4.8		14.4		4.8		33	
	mg/l	gms	mg/l	gms	mg/l	gms	mg/l	gms
COD	276	551	414	1,653	138	551	478	3788
NH_3-N	164	327	245	981	82	327	284	2248
TKN	162	323	242	969	81	323	280	2,221
NO_3-N	0.1	0.2	.15	.6	.05	0.2	0.18	1.4
TS	285	569	427	1,707	142	569	494	3,912
TVS	156	311	233	933	77.8	311	270	2,138
TOC	35	70	53	210	17.5	70	61	481
TIC	.28	.55	.41	1.65	0.14	.55	0.48	3.78
Al	7	13.9	10.4	41.7	3.48	13.9	12.1	95.6
Cd	.0035	.007	.005	.02	.001	.007	0.006	0.048
Cr	.035	.07	.05	.21	.018	.07	0.06	0.48
Ag	5.25	10.5	7.86	31.4	2.6	10.5	9.1	72.2
SO_4	8.9	17.8	13.4	53.4	4.45	17.8	15.5	122.4
S_2O_3/SO_3	125	250	188	750	62.5	250	217	1719

TABLE 7. TOTAL WASTE AND WASHWATER CONSTITUENTS EXCEEDING EFFLUENT GOALS

	Level 1	Level 2	Level 3
Total Waste			
Major			
	COD	COD	COD
	NH_3-N	NH_3-N	NH_3-N
	TDS	TDS	-
Minor			
	Ag	Ag	Ag
	Cd	Cd	-
	Cr	Cr	-
Washwater			
Major			
	COD	COD	-
	NH_3-N	NH_3-N	NH_3-N
	Ag	Ag	Ag

are low volume and highly concentrated (greater than 10 percent dissolved solids). The third stream, the washwater, is a dilute, high volume discharge containing less than 10 percent of the total load in 95 percent of the total volume. The segregation of these streams and their separate treatment, handling, or disposal was determined to be an appropriate design consideration.

The original work scope provided by the Air Force indicated that the PPIF facilities could generate up to 11,000 gpd in developing 7,200 ft^2 of film. Actual flow (and design flow) information for the photoprocessing equipment indicates that the maximum daily waste flow generated from the processing of 11,000 square feet of film in an 8 hour shift (revised design maximum production) is approximately 2,225 gpd. This latter estimate was used for conceptual design purposes.

A concern was also indicated for waste ferricyanide bleach, dichromate bleach, color developer, and bleach fix solutions, all of which are associated with color development. Since only black and white film is to be processed in the WS430 B facilities, such pollutants are not addressed as an element of this study. Because silver recovery is practiced and operates efficiently, recovery of the low residual silver from the wastewater is not addressed in these studies.

The overall waste loads and flow projections proposed for design (shown in Tables 5, 6 and 7), incorporated the above revisions and the following:

1. Photoprocessing Equipment <u>design</u> flows;
2. Waste loads determined from the 11CN;
3. The assumption that washwater would be run continuously during the 8-hour shift, even during periods when no film was being processed; and,
4. The production schedule determined for average and maximum daily film processing over an 8-hour shift.

This basis was reviewed and confirmed with AFESC/RDVW.

Task II of the work scope stated that treatment schemes to be considered should be operable, portable, and maintainable by unskilled personnel in a remote site. Since all treatment schemes will require some degree of skill, it has been assumed that sufficient training would be available. However, the required skills for a given treatment system would have to be evaluated and a final judgment would be required by the Air Force with respect to its applicability.

SECTION II

PHOTOPROCESSING WASTEWATER TREATMENT

A. TREATMENT STUDIES

A number of studies have been conducted on the treatment of photoprocessing wastewaters and the specific chemicals used in photoprocessing. Thus, it is appropriate to summarily review several of the more recent and pertinent studies providing a framework from which to select and study specific treatment technologies for the WS430B wastewaters application.

The USEPA Guidance Document (Reference 1) for the Control of Water Pollution in the Photographic Processing Industry was published in April 1982. This report described the characteristics of photoprocessing operations, provided waste characteristics, and discussed control and treatment technologies. Information on actual current practices of the photoprocessing industry is evaluated to determine effluent guideline requirements. Toxic pollutants of concern were silver, cyanide and chromium. Conventional pollutants include pH, BOD, and COD; nonconventional pollutants include boron, dissolved solids, halides, iron, ammonia, nitrogen, phenols, sulfate and TOC. Over 99 percent of the 11,000 photoprocessing installations in the United States discharge raw or partially pretreated wastewater to municipal treatment systems. Fewer than 20 are direct dischargers, as determined by an NPDES permit search.

In-process controls to recover and reuse chemical solutions, minimize water usage and loss of chemicals to the washwater was reviewed. The typical silver recovery system consists of an electrolytic primary unit and a secondary tailings metallic replacement unit on the fix solution. Silver in the washwater, typically 1 to 50 mg/l, is minimized by control of carryover to the wash tanks. Although silver can be removed from the washwater by precipitation, ion exchange or reverse osmosis, the practice for recovery is not considered economically viable.

End-of-pipe treatment technologies are also reviewed. In many cases, wastewaters are segregated between the concentrated chemical replenish streams and the dilute washwater streams; treatment is then applied to one or both. Technologies encountered in the industry included precipitation for silver, chromium and cadmium; settling; ozonation to oxidize various oxidizable components; filtration; aeration to reduce oxygen demand; pH adjustment; equalization; chlorination; reverse osmosis; evaporation; and chemical reduction of the hexavalent chromium. The report did not include biological treatment as an end-of-pipe technology; however, as previously mentioned, essentially all of the industry wastewater receives final treatment in municipal treatment systems which employ biological treatment.

In a paper presented at the Photoprocessing and Environment Seminar of the National Associaton of Photographic Manufacturers (NAPM), Barnhart (Reference 2) reported on the impact of photoprocessing wastes on municipal treatment systems and concluded, from experimental studies, that up to 50 percent photo wastes did not affect treatment efficiency or physical operating parameters, such as settling and chlorination. He did find that the waste may contribute significantly to nitrogen and phosphorus levels and chlorine demand. Silver in the photo wastes was found to be precipitated as silver sulfide and accumulated in the biological sludge with no discernible adverse affects, [illegible] (Reference 3) presented a paper on the biodegradability of selected photoprocessing chemicals, describing a study conducted for NAPM. The paper listed components found to be degradable, inhibitory or having no effect. Five color developers, potassium dichromate and sodium selenite were found to be inhibiting under test conditions. Compounds often used in large quantities in photoprocessing such as hydroquinone, sodium thiocyanate, ammonium thiosulfate, and sodium thiosulfate pentahydrate, were found to be biodegradable.

Dagon (Reference 5) reported on small-scale activated sludge testing on typical photoprocessing effluents, and concluded that the effluents could be treated biologically and that wastewater could be safely sent to municipal systems for subsequent treatment. He estimated that up to 20 percent of the daily waste volume could be discharged if considerations were given to waste concentration and other factors with respect to the plant's loading capabilities. His studies indicated that the ammonia in photoprocessing could be nitrified to nitrate in the biological systems. He also conducted ozone tests for treatment of photoprocessing chemicals, and concluded that the acetate ion, which constitutes much of the BOD and COD of the typical waste was untreatable by ozone, while many other chemicals such as thiosulfate and hydroquinone were treatable. Activated carbon treatment studies on various chemicals indicated that activated carbon adsorption was marginal for the treatment of acetic acid or overall photographic effluent. Activated carbon was [illegible] effective for several chemicals including sodium thiosulfate pentahydrate. However, carbon was effective on certain chemicals used in various developer mixes. Use of carbon was discussed for load reduction or for polishing a biologically treated effluent.

A 1972 questionnaire study (Reference 6) of chemical wastes generated by the Air Force photographic operations characterized waste volumes, types, methods of silver recovery, and effluent discharge. Eighty-three of the 96 Air Force Bases were found to discharge wastes to a sanitary sewer, others discharged to storm drains or did not indicate a disposal method. Studies (Reference 7) conducted by the USAF Environmental Health Lab on Norton AFB concentrated photographic processing wastes concluded that the waste could be effectively treated biologically, and that the wastes should be disposed of by discharging to the City of San Bernardino's 370 mgd secondary biological treatment plant.

A study (Reference 8) conducted for Wright-Patterson AFB on a photographic liquid waste disposal system by FMC, developed a conceptual design and cost estimate for a treatment system to handle approximately 40,000 gallons per day of waste from processing both black and white and color film. The system involved separate collection of the washwater and the fix and developer solutions. The washwater was to be recovered by reverse osmosis and reused. Fix recovery by electrolytic removal of silver was included; however, a similar recovery system for an ammonium type hypo was not considered practical at the time. The concentrated solutions (8-12 percent) were stored and concentrated further to 30 to 40 percent solids by a spray film type vapor compression evaporator. The vapor phase would carry some organics; therefore, treatment of the condensate was recommended prior to reuse. The concentrate from the evaporator, at 35 percent solids, would be further concentrated to 80 percent in scrapped surface, jacketed kettles, extruded into bricks, dried, and asphalt coated for disposal in a landfill. The estimated cost for the system in 1971 dollars was $1.4 million.

The study also considered evaporation, ion exchange, [illegible] osmosis and electrodialysis for washwater recovery. [illegible] osmosis was selected on the basis of costs and simplicity.

A subsequent study (Reference 9) by FMC on the [illegible] solid wastes generated from treatment of photographic processing wastewaters evaluated 10 alternatives. It concluded at [illegible] that landfill or a salt sink (contractor-hauled) disposal [illegible] require minimum cost and inconvenience. Recovery of [illegible] chemicals from evaporated photo wastes (Reference 10) was [illegible] in 1976 and process schemes were developed. It was [illegible] that recovery of sodium thiosulfate and sodium sulfite [illegible] efficiencies of 35 to 90 percent and 10 to [illegible] respectively, were possible and cost effective. Further [illegible] including a pilot investigation, was recommended to [illegible] workable system and to better determine the system costs. [illegible] second study by Horizons Inc. (Reference 11) on incorporating photographic processing wastes into a useful product or to [illegible] them harmless for a Class 3 landfill was conducted. The [illegible] identified two products, a ceramic foam which could be used [illegible] insulating fire brick, and a ceramic castable which could be [illegible] for insulation. The 1000° F cured clay containing foam [illegible]. preferred for disposal in a landfill if it was not excessively [illegible] alkaline. Photo wastes are incorporated into the green ceramic [illegible] approximately 10 to 20 percent, by weight.

A study (Reference 12) conducted for the U.S. Army [illegible] and evaluated available technology relative to the treatment [illegible] the ES-38 Mobile Photoprocessing Laboraty wastewaters. Wastewaters were characterized based on available data. [illegible] processes considered included reverse osmosis, electrodialysis, carbon adsorption, ion exchange, metals precipitation, chemical oxidation, electrolytic oxidation and evaporation. The [illegible] recommended that further evaluation be conducted on actual wastes; the recommended processes were metal precipitation, chemical oxidation, electrolytic oxidation and evaporation. Hydrogen peroxide was suggested as the most practical chemical oxidant. Electolytic oxidation was considered very costly. Evaporation was felt to be an extreme solution for onsite waste handling because of the high costs.

One large commercial photoprocessing facility developed and designed a waste treatment facility for a flow of about 18,000 gallons per day, to result in zero discharge (Reference 13). The system design incorporated separation of washwater and concentrated solutions, and anticipated recovery of 90 percent of the washwater by reverse osmosis. Evaporation of the concentrated solutions and reverse osmosis concentrate, silver recovery from the concentrate, and recovery of the evaporator condensate by ion exchange for ammonia recovery were included in the system. Communication with the system operator (Reference 14) revealed that the evaporator system worked; however, it required considerable maintenance and was difficult to operate. Close pH control and daily caustic cleaning are practiced. The condensate was found to be contaminated with high levels of ammonia, acetate and sulfides. Thus, the ion exchange system had to be abandoned. Peroxide treatment and two-stage air stripping are now used, followed by two-stage reverse osmosis on the distillate.

Washwater, treated in a two-stage R.O. system is pretreated by pH adjustment and filtration. The evaporator solids are discharged to a pond, silver is recovered from the sludge, and the residue is hauled to a hazardous waste disposal site. Two to three experienced personnel are normally involved in the operation and maintenance of the system.

B. SUMMARY

The overwhelming majority of photoprocessing installations may satisfactorily dispose of wastewater into adequately sized municipal wastewater treatment systems. There has been little emphasis on developing separate treatment systems for these wastes, and, as a result, little information exists on the practical application of available treatment technologies to photographic wastewater. EPA's guidelines indicate that pretreatment for silver, cyanide and hexavalent chromium removal may be required before treatment of the conventional pollutants. The nonconventional pollutants may or may not be of concern, depending upon specific circumstances such as water quality requirements. Some studies involving conceptual designs, bench scale testing, and, to a much lesser degree, pilot scale development of treatment systems, have applied general knowledge of available treatment technologies to photoprocessing wastes. Generally, these studies conclude that additional study is required on the specific waste streams. Little information is available on achieving specific effluent concentrations other than for results expected with silver, cyanide and hexavalent chrome. One generally accepted principle, however, appears to be the segregation of the concentrated chemical solutions from the high volume washwaters prior to treatment and disposal. The treatment process technologies considered in this study are aimed at the specific contaminants in the wastes.

Regarding the deployment of the WS430-B, site-specific circumstances will, to a large degree, determine the treatment system needed. The first choice would be to discharge the total waste to a local sanitary or industrial waste treatment plant of adequate size. Equalization may be required to avoid upsets from slug loads. Truck hauling of the concentrated solutions to treatment plants within a reasonable distance, and onsite treatment of washwater would probably rank second. In the absence of available facilities, and/or the need to pretreat prior to discharge to such facilities, an onsite treatment system would be required. The basic objective of these studies is to develop the conceptual design of onsite treatment systems which will result in compliance with stipulated effluent levels.

SECTION III

ALTERNATIVE TREATMENT TECHNOLOGIES

Several unit treatment processes for photoprocessing wastewaters were considered for the bench-scale testing program. Waste characteristics, treatment objectives and information gleaned from other work discussed in the previous section were utilized in a preliminary screening evaluation prior to actual bench-scale testing. The following discusses the unit operations and the selection of those which were tested in the bench-scale studies. (Similar discussions were also presented in the waste characterization report.) Table 7 indicates the pollutants in the WS430-B total wastewater and washwater which are of concern with the three levels of treatment specified in the work scope for this project. The treatment technologies were selected to address these specific pollutants.

A. PRECIPITATION

Chemical reactions to precipitate specific elements are generally used to remove heavy metals such as silver, cadmium, mercury and chromium. Various chemicals such as sulfides, hydroxides, hydrides and organic materials can be used to precipitate the metals. The wastes can also contain high levels of iron and aluminum which will precipitate from solution and will thus have an impact on any precipitation scheme. These elements may also present some problems if present in a discharge to a stream.

Standard jar test techniques were used to evaluate the effectiveness of chemical precipitation. These involved incremental additions of chemical precipitants and pH adjustment to determine optimum conditions for forming a settleable precipitate.

B. SETTLING

Settling involves providing relatively quiescent conditions to permit suspended solids in the waste to settle out by gravity. These wastes do not contain high levels of suspended solids; however, precipitation would result in suspended solid levels which could be removed by settling. Jar tests provide screening information on the settleability of suspended solids and the effectiveness of polymers as settling aids.

C. CHEMICAL OXIDATION

Chemical oxidation involves the addition of strong oxidizing agents to the wastewater to react with oxidizable constitutents, thereby reducing the oxygen demand. The photoprocessing wastes contain inorganics, such as sulfides and thiosulfate, as well as organic components which exert a chemical oxygen demand. Oxidants typically utilized are hydrogen peroxide, chlorine and ozone. The use of ultraviolet light in conjunction with the oxidizing chemicals catalyzes oxidation reactions of certain organics, increasing the rate of COD reduction or converting the organics to more easily removable compounds by subsequent treatment. As noted in the previous section, oxidation of acetic acid, a major constituent of the wastewater, has not been found to be particularly successful. Certain studies (Reference 15) under carefully controlled laboratory conditions have shown some success; however, the reaction rate was quite low. Use of chlorine to destroy ammonia nitrogen (breakpoint chlorination) is a potential treatment for ammonia removal, although large quantities of chlorine are required. Jar tests are typically used to determine chlorine requirements. The effectiveness of chemical oxidation, primarily for inorganic COD reduction, was evaluated, using hydrogen peroxide. UV/peroxide oxidation was also tested in a special reactor cell on the total wastewater.

D. ELECTROLYTIC OXIDATION

Reduction of organics by electrolytic processes has been tested for sewage in sea water and reported in the literature. The process requires a solution high in TDS, particularly chloride and/or bromide salts. The electrical current releases free chlorine or bromine. Hypochlorous and hydrobromous acids are formed which react with and oxidize organics. This oxidation mechanism is similar to chemical oxidation with chlorine. The high ammonia content of the waste would present similar oxidant demand problems for this process. Additionally, the relatively low TDS of the wastewater may necessitate the addition of chloride salts. This would reduce the acceptabilty of the treated wastes with respect to TDS. The potential use of electrolytic oxidation for the total waste flow, even to meet Level 3 requirements, appeared limited; it was also judged impractical for the separated washwater. Thus, the process was not considered for bench-scale work.

E. CARBON ADSORPTION

Carbon adsorption is used to remove organics and small quantities of heavy metals from waste streams. Generally, it is most applicable as a final treatment or polishing step for organics which cannot be more easily and economically removed by other treatment technologies. Although activated carbon has a high adsorption capacity for many organics, it is quite poor for adsorbing the short chain polar organic acids, such as acetic acid, which comprises a significantly large portion of the photoprocessing waste load. Carbon isotherms were run on the total and washwater wastes to evaluate COD reduction by carbon adsorption. Limited carbon column studies were also conducted on washwater samples.

F. REVERSE OSMOSIS

Reverse osmosis (R.O.) is a volume reduction process, typically producing a concentrated stream of 3-5 percent total dissolved solids. It can reject a high percentage of salts, including the ammonium ion, heavy metals and various organics. Since the fix and developer are already highly concentrated (10-12 percent), only the washwater would be considered for R.O. treatment. Washwater samples were sent to a manufacturer for testing to determine salt and organics rejection, measure the level of concentration in both the product and reject waters, and develop an R.O. system design for maximum water recovery and concentration of contaminants for subsequent disposal.

G. ELECTRODIALYSIS

This process is similar to reverse osmosis; however, the driving force is application of an electrical current across the membrane. Thus, ions could be separated from nonionic organics. If the ammonium ion is separated from the organics, electrodialysis may simply produce two contaminated waste streams requiring further treatment. Our assessment indicated that electrodialysis would not be suitable for this application and this was not further pursued.

H. EVAPORATION

Evaporation is used to reduce the volume of a wastewater stream. A concentrated brine or slurry is produced, containing the dissolved solids. A condensate stream containing the water removed, and some portion of volatile compounds present in the wastewater, is also produced. Evaporation is a costly, high maintenance, energy intensive process; however, it is well known and widely used in various industrial processes. One such system, previously discussed, is used to treat photoprocessing wastewaters.

Since total dissolved solids are of significant concern with respect to Level 1 and Level 2 requirements for the total waste stream, evaporation was considered. A contaminated condensate stream requiring treatment would be produced. Use of evaporation could not be justified economically on the total waste stream, since separation of the concentrated fix and developer streams is quite simple.

Detailed evaporation tests were not included in the bench scale evaluations. Manufacturers can conduct pilot tests to determine fouling tendencies and condensate characteristics. Such tests were not included in the scope of this study; however, a simple boiling test was conducted to determine potential volatile losses to the condensate. The experience of the previously cited reference on use of evaporation and manufacturers' information was relied upon in considering this technology.

I. AIR STRIPPING/DISTILLATION

Large quantities of air or steam can be used in a stripping column to remove molecular ammonia (gaseous) from a waste stream. The removal of ammonia is dependent upon the un-ionized form which is a function of both pH and temperature. At a pH of 7.5, typical for the washwater and the total waste, less than 1 percent of the ammonia is un-ionized. For this process to be effective, the pH of the water must be raised to the 11-12 range, where approximately 100 percent of the ammonia is in the un-ionized form. The chemical used to increase pH is also of concern. Use of lime, which has been tried in a number of tertiary treatment systems on municipal and industrial wastewaters could result in precipitating voluminous quantities of sludge in the form of calcium sulfate from the wastewater, thereby causing a disposal problem. However, the use of caustic, (sodium hydroxide) a more costly chemical, would not produce as much sludge. Use of a distillation column with steam can produce a concentrated ammonia distillate which can be neutralized with an acid (HNO_3), and the salt could be subsequently utilized as a fertilizer. An air stripping tower discharging to the atmosphere would disperse the ammonia and would need to be sized to minimize odor problems. Cold weather operation would need to be considered since efficiency would be reduced. The possibility of a second adsorption unit to adsorb ammonia with a dilute acid solution may be considered in such a case.

J. BIOLOGICAL TREATMENT

The biological treatability of photoprocessing waste has been amply demonstrated; however, information on actual performance and effluent concentrations is limited. Two bench-scale biological activated sludge units were operated for 3 weeks on simulated samples of total waste and washwater, following air stripping for ammonia removal. The biological system reduces the COD and BOD from both organic and inorganic materials, and produces a sludge requiring disposal. When acclimated, these systems are also capable of reducing the ammonia concentration by nitrification to quite low levels, typically less than 2 mg/l. For this type of mobile installation, the reliability of biological treatment may be questioned. Waste flows and quantities are variable, and significant startup time would be required unless sufficient biological sludge seed can be obtained. By utilizing equilization and feeding controlled quantities of a fix solution, a constant baseline feed for a biological wastewater system could be made available; thus, the potential problems due to intermittent flow may be overcome. With nitrification occurring, pH buffering chemicals may be required to maintain optimum pH.

SECTION IV

BENCH SCALE TREATABILITY STUDIES

A. INTRODUCTION

Laboratory bench scale studies were conducted at HydroQual's laboratory, General Testing Corporation, in Hackensack, New Jersey. Screening and treatabilty tests were conducted on simulated wastewaters which were generated from fix and developer samples provided by the Air Force. Preparation of the simulated total discharge samples was based on the projected effluent characterization of the USAF WS430-B PPIF Facility presented in Section I of this report. Fix and developer solutions were mixed in appropriate proportion with local tap water. Washwater samples were simulated by dilution of fix with tap water, based on the estimated fix carryover rates (discussed previously in Section I).

Treatment technologies which may be feasible for the WS430-B application were discussed in Section III. Those which were selected for bench-scale testing are:

1. chemical precipitation/settling
2. chemical oxidation
3. air stripping
4. carbon adsorption
5. reverse osmosis
6. biological treatment
7. evaporation

The purpose of the bench scale studies was to investigate the ability of these technologies to reduce wastewater contaminants to the specified levels shown in Table 4.

1. Test Wastewater Samples

Table 8 presents analyses of the total discharge samples used in the laboratory bench scale tests. Aliquots of fix and developer were added to local tap water in proportions based on the maximum production levels estimated in the wastewater characterization report. Spent fix from the 11CN Versamat® (after silver recovery by iron replacement) was added in the ratio 32 ml/l tap water. Developer was added at a rate of 36 ml/l.

The resultant COD averaged 6470 mg/l, which is approximately 12 percent less than the 7404 mg/l that was projected as the maximum concentration in Table 4. The ammonia concentration averaged 920 mg/l, significantly less than the 2204 mg/l projected as maximum. This discrepancy was previously discussed; the sample which was originally analyzed and subsequently used for calculation of the maximum ammonia concentration (Table 4) had a concentration nearly twice the ammonia concentration of several subsequent samples. It is felt that the lower concentrations are more representative of the actual waste conditions. Other constituents, similar to the COD measurements, were reasonably consistent with the projected maximum wastewater characteristics.

Table 8 also presents analyses of the simulated washwater samples used in the bench-scale tests. Two dilutions were used to represent carryover of fix into a continuous washwater flow under maximum production conditions. The results were generally consistent with the maximum projected washwater concentrations shown in Table 6, again with the exception of ammonia.

TABLE 8. ANALYSES OF SIMULATED WASTE WATER SAMPLES

I - Total Discharge

Batch No.	COD (mg/l)	TOC (mg/l)	NH_3 (mg/l)	TS (mg/l)	BOD (mg/l)	SO_3 (mg/l)	Fe (mg/l)	Cd (mg/l)	Cr (mg/l)	Ag (mg/l)	Al (mg/l)	pH
1	6884	1312	1000	9374	-	2070	140	0.3	-	0.5	-	7.7
2	6695	1434	-	-	-	2330	130	-	-	0.7	70	7.8
3	6800	-	898	-	-	2160	178	-	-	0.19	54	7.9
4	5802	1340	867	6744	-	1776	-	-	-	-	-	7.9
5	6560	1440	916	-	-	2350	-	-	-	-	-	-
6	6720	1440	-	-	4307	-	-	-	-	-	-	-
7	5975	-	-	-	-	-	185	0.10	0.11	0.20	-	-
8	6400	-	- -	-	2125	-	-	-	-	-	7.8	
9	6400	-	- -	-	2160	-	0.11	2.75	0.15	-	7.9	

(1) - 11CN fix after silver recovery by iron replacement; 11CN developer.
(2) - estimated from fix and developer concentrations.

II - Washwater

Batch No.	Fix Source	ml/l Tapwater	COD (mg/l)	TOC (mg/l)	NH_3-N (mg/l)	TKN (mg/l)	BOD (mg/l)	SO_3 (mg/l)	Fe (mg/l)	Cd (mg/l)	Cr (mg/l)	Ag (mg/l)	Al (mg/l)	pH
1	11CN(1)	4.1	490	44	96	-	-	165	28	<.02	<.05	<.04	-	6.0
2	11CN(1)	4.2	482	62	150	237	-	182	28	<.01	<.05	-	-	6.1
3	11CN(1)	4.1	396	81	-	-	149	-	-	-	-	-	-	-
4	11CN(1)	5.7	554	84	132	-	-	215	-	-	-	-	-	6.1
5	1140(2)	6.0	551(3)	-	-	-	-	301	-	<.02	<.06	9.5	28	6.1
6	11CN(2)	4.25	404	51.5	146	-	-	240	<.01(3)	-	-	10.4	7	4.5

(1)-Fix after silver recovery by Fe exchange (2)-Fix before silver recovery (3)-Estimated from fix concentration

B. ACID-BASE TITRATIONS

Treatment processes may require pH adjustment to achieve optimum results, and, subsequently, adjustment to meet effluent requirements. To determine chemical quantities required to achieve various pH values, acid and base titration curves were developed for each of the waste streams. The results are presented in Figure 1. The developer solution is basic and the fix is acidic. Combining these with washwater to simulate the total discharge results in a neutral to slightly alkaline pH. The washwater pH is acid because of the carryover of the acidic fix solution. Approximately 0.03 equivalents of base per liter (or 10 pounds caustic/1000 gallons) were required to raise the wastewater pH to a level of 11.5 to 12. Approximately 0.12 equivalents of base per liter (or 40 pounds caustic/1000 gallons) were required for the total discharge. The relatively flat sections of the titration curves for fix and total discharge illustrate the high bufffering capacity due to ammonia.

The adjustment of pH back to the neutral range, pH 7 to 8, after ammonia stripping, required approximately 0.005 and 0.03 equivalents of acid per liter (2.3 and 10 pounds of sulfuric acid/1000 gallons) for the washwater and total discharge, respectively.

C. CHEMICAL PRECIPITATION, COAGULATION, FLOCCULATION

1. Procedures

Jar test procedures were used to evaluate precipitation, coagulation and flocculation of heavy metals in the simulated wastewaters. A six-place Phipps-Bird variable speed mixer was

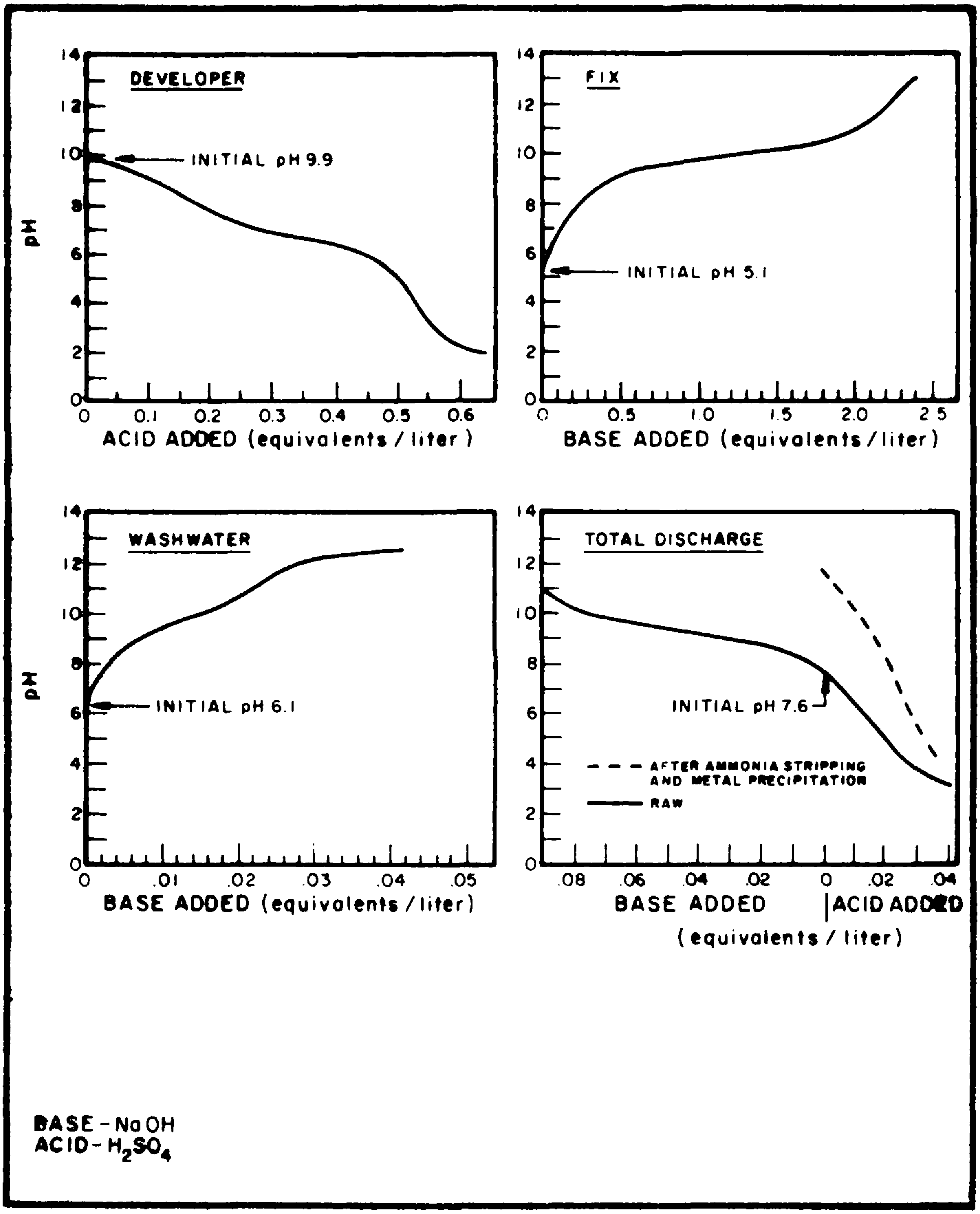


Figure 1. Titration Curves of Photochemical Solutions and Simulated Wastewater

used with 0.5 and 1.0 liter samples. Typically, samples were mixed rapidly for 1-2 minutes after the addition of appropriate chemicals (sodium hydroxide, lime, borohydride, etc.). The speed was then reduced to a slow mix for approximately 3 minutes to enhance flocculation of the coagulated material. Mixing was stopped and the floc was then allowed to settle for 30 minutes. Observations of floc appearance, size, settleability, and supernatant clarity were recorded during the test. After the 30-minute settling period, sludge volume was noted, and selected samples of supernatant were taken for analysis.

2. Total Discharge-Metals Precipitation

Appendix 2 contains the data tables for the bench tests which are discussed as follows. The initial precipitation tests on total raw waste discharge samples used caustic, borohydride, and lime and were tested at dosages which were required to raise the pH to 10. In Test 1, no significant precipitate was produced with the caustic alone or with the combined austic and sodium borohydride; however, lime addition resulted in a significant precipitate, which settled to about 1/3 the original volume. Soluble iron was reduced with the lime; soluble silver was reduced in all cases. Cadmium was not significantly affected, nor was there any significant COD reduction. Fifteen to 20 percent sulfite reduction was observed. The second test evaluated the effect of increasing pH. Iron and aluminum were not significantly affected up to pH 12. Soluble silver concentrations were lowered at the pH levels tested. Total suspended solids increased to about 200 mg/l with the chemical addition.

In Test 3, a sample of the total discharge was initially treated by distillation to remove ammonia which may have been interfering with metals reduction. The sample was raised to pH 11.8 with caustic which produced a precipitate. Analysis of the filtered supernatant indicated that iron and silver were reduced significantly; however, aluminum was not precipitated. The pH was adjusted to 9 and to 7 and samples were again analyzed for metals. Lower iron levels were achieved; the silver and aluminum levels remained about the same. Settling of each pH-adjusted sample resulted in total suspended solids levels below 20 mg/l in the supernatant.

Test series 4 and 5 concentrated on the use of lime on the total discharge, and the addition of an anionic polymer (American Cyanamid 535A®) to enhance flocculation and settling of precipitates. The data from these tests can be found in Table A2-2. In Test 4 a lime dosage of approximately 1 gm/l with polymer at about 2 mg/l (Jar 14) was found to produce the best settling floc and a reasonably clear supernatant. Several iron analyses indicated that the minimum iron level which could be achieved was in the range of 17-27 mg/l. The use of caustic to initially raise the pH to 9 and then adding the lime with polymer (Jars 7-12) did not result in a significant floc, and the settled supernatant was cloudy.

Lime precipitation, however, produced a considerable volume of sludge. The settled sludge was 10 - 20 percent, by volume, of the original waste. In Test 5, higher lime dosages were evaluated and the polymer dosage level was optimized. A fast-settling floc and a clear supernatant were achieved at a lime dosage of 3 gm/l and greater. On this sample, the sludge produced was 10 to 15 percent by volume. Soluble iron was reduced to approximately 10 mg/l; analysis for silver on two samples indicated that the 0.1 mg/l Level 2 criteria were achieved.

In Test 6, the total discharge was pretreated by ammonia stripping. The waste was adjusted to pH 11.0 with caustic and air stripped. The resulting wastewater ammonia concentration was 10 mg/l and the pH was 9.5. A lime dosage of 0.8 gm/l with 2 mg/l polymer produced a settleable precipitate and minimum supernatant turbidity. Analyses of the filtered supernatants indicated cadmium and silver concentrations below Level 3 criteria, while chromium concentrations were below Level 1 criteria.

a. Summary

Caustic addition to the total discharge produced a light precipitate and poorly settleable floc; lime addition resulted in a heavy precipitate which, aided with polymers, settled to a volume in the range of 5 to 15 percent of the initial sample volume. Silver and cadmium, initially in relatively low concentrations in the waste, were generally reduced below Level 3 criteria, and approached Level 2. Chromium was reduced below Level 1 criteria. Iron, which is primarily from the silver recovery system on the 11CN Versamat®, was precipitated, yielding supernatant levels of 15-25 mg/l. Aluminum was not affected significantly by lime treatment. Iron and aluminum are not specified in the effluent criteria goals, although either or both may be of concern in a discharge to a receiving water.

3. Washwater Metals Precipitation

Two tests were conducted on an 11CN washwater sample (made up with fix after silver recovery) treated with caustic (Table A2-4). The caustic dosage was adequate to precipitate metals. Silver, cadmium, and chromium, initially present in the washwater samples were all below the limit of detectability and essentially meet Level 1 criteria; it is not known if the metals were affected by the caustic addition. Iron is in the sample since the washwater was made up using the 11CN fix solution normally discharged following silver recovery by iron exchange.

Jar Test 3 was conducted on a washwater sample. After it had been treated with caustic and air stripped, it yielded an ammonia concentration of 40 mg/l. Sulfuric acid was used to adjust pH and polymer was added to aid in flocculation. The washwater contained significant suspended solids after air stripping. Good flocculation and settling were achieved at a pH of 8.7 and a polymer dosage of 0.5 mg/l. Supernatant silver was measured below the Level 1 concentration and the iron concentration of the filtered supernatant was in the range of 1 to 4 mg/l. COD was not affected by chemical precipitation.

In Jar Test Series 4 an 1140 washwater sample was tested after air stripping. This sample contained a higher silver concentration, since the recirculated fix (after electrolytic recovery) was used to make up the simulated washwater. The air-stripped sample pH was adjusted to 9 and 10, and varying amounts of polymer were added. The best results occurred at a pH of 10 and polymer dosages of 0.2 to 1 mg/l. Low levels of cadmium and chromium were achieved; however, a significant concentration of silver remained. These results were inconsistent with previous results regarding the precipitation of silver.

Polymer and a proprietary solution, EPS® (MacDermid Co.), was used in Test 5 to determine its effect on silver removal. EPS, a dithiocarbamate, is used in the electroplating industry to assist in precipitation of heavy metals. The sample tested was 1140 washwater after pH adjustment and air stripping. Cadmium and chromium levels were both low, however; residual silver after settling and after filtration exceeded criteria Level 3, indicating that precipitation of the silver was not completely successful (Table B-6).

a. Summary

As indicated in Table 7, cadmium and chromium are not of concern in the washwater; however, silver is of concern. The washwater after ammonia stripping contains a precipitate which can be coagulated with polymer and settled. The data indicate that the low levels of silver required for Level 3 could not be met with polymer coagulation or the addition of the EPS solution, although previous jar test results on the total wastewater indicated that caustic and lime treatment could reduce silver in the clarified supernatant to Level 2 criteria (0.1 mg/l).

D. CHEMICAL OXIDATION

2. Procedures

Chemical oxidation was evaluated using jar test procedures with the six-place Phipps-Bird mixer. Each sample was dosed with oxidant and mixed slowly. When the oxidant was depleted (indicated by KI/Starch Spot Test) select samples were drawn for analysis. In the case of breakpoint chlorination, free residual chlorine was measured by the DPD-FAS method.

UV catalyzed chemical oxidation was also investigated, using the laboratory batch reactor shown in Figure 2. It is an all glass, jacketed resin kettle with a liquid capacity of 3 liters. A quartz well was inserted in the middle of the reactor to hold a 100-watt, high pressure mercury arc lamp (Canrad-Hanovia Inc.). A 3-liter sample was treated with the appropriate oxidant under ultraviolet irradiation. Samples were drawn with time and selectively analyzed for oxidant residual, SO_3, COD, TOC, NH_3-N and TKN.

Oxidation by simple aeration was tested by vigorously aerating a 2-liter sample. Samples were drawn with time and analyzed for sulfite. Data tables may be found in Appendix B. The following discusses the results of the bench scale tests.

2. Aeration

The reduction of sulfite and thiosulfate (measured as sulfite (SO_3)) by aeration was slow. After an initial reduction of 10 percent in the first 20 minutes, further reduction proceeded at a slow rate with only 18.3-percent reduction noted after 4 hours and 20 minutes of aeration. It was concluded from this test that

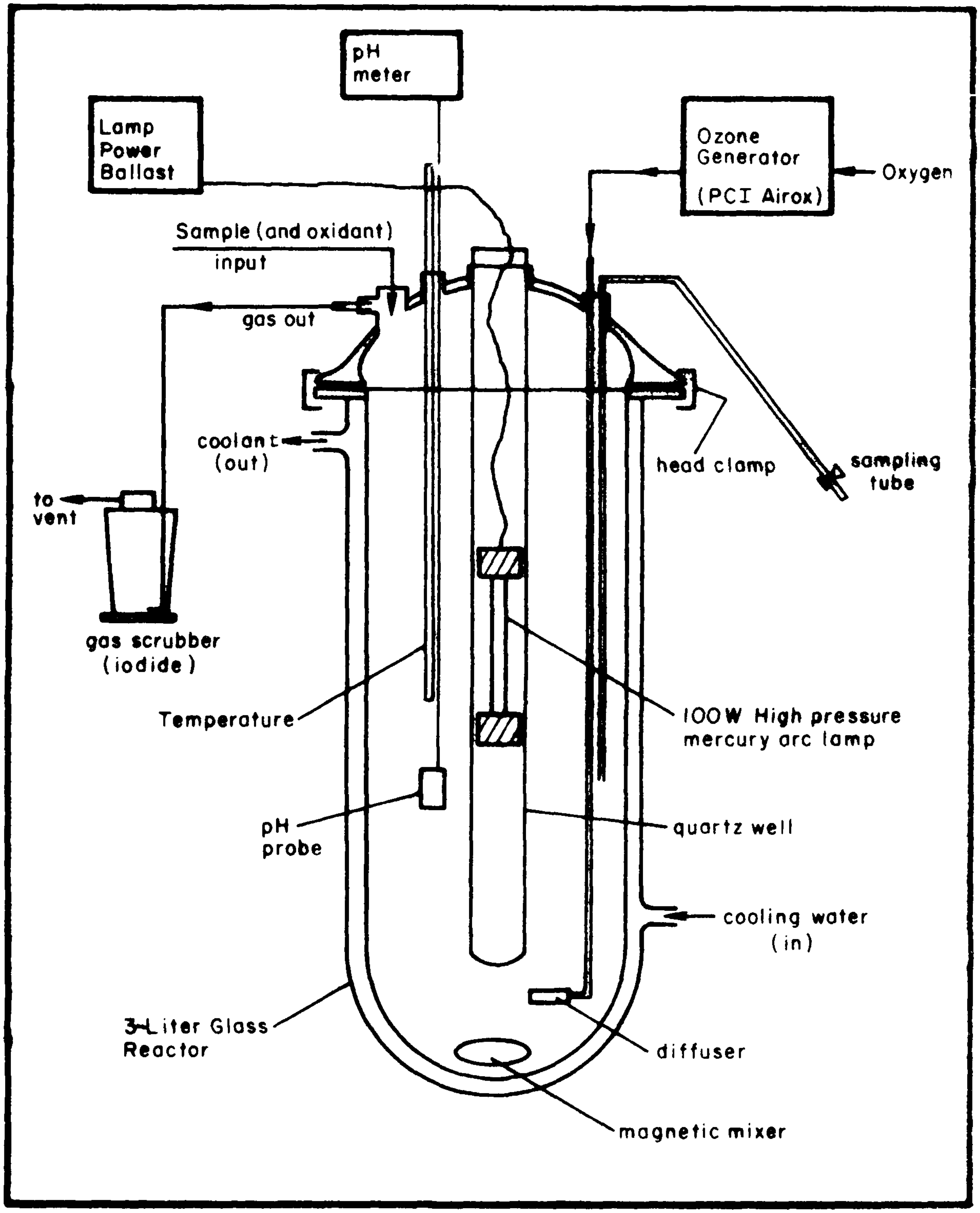


Figure 2. Schematic of Lab Scale Chemical Reactor

simple aeration of the total discharge to oxidize sulfite was not effective and would not be practical.

3. Hydrogen Peroxide

Hydrogen peroxide is an effective oxidizing agent. Sulfite is oxidized to sulfate rapidly in an acid solution, and more slowly in alkaline solutions. Thiosulfate, on the other hand, is oxidized to sulfate in an alkaline solution.

a. Total Discharge

Seven jar tests were run to evaluate hydrogen peroxide for the treatment of the total discharge. These results, Tables B-8 - B-11, are graphically displayed on Figure 3. The results indicate that the sulfite was oxidized, yielding an overall COD reduction of approximately 20 percent. The observed percent removal lies between the stoichiometric requirements for sulfite and thiosulfate, and indicates that approximately one-third of the measured SO_3 is sulfite and two-thirds is thiosulfate. A ratio of 1 to 1.2 parts hydrogen peroxide to measured sulfite was required to achieve 100-percent reduction of the sulfite, plus thiosulfate (measured as sulfite).

Similar tests were conducted on the simulated washwater; the results are presented in Figure 3, Table B-9. The observed removals, in this case, were typically lower than would be predicted from the theoretical thiosulfate requirements. Note that thiosulfate is used in the fix and is carried over to the washwater, while sulfite is used in the developer. A COD reduction of 15 to 20 percent was achieved with peroxide oxidation and up to 100-percent reduction of the sulfite plus thiosulfate (measured as sulfite) was achieved. A ratio of 1.7 to 1.9 hydrogen peroxide to SO_3 was required.

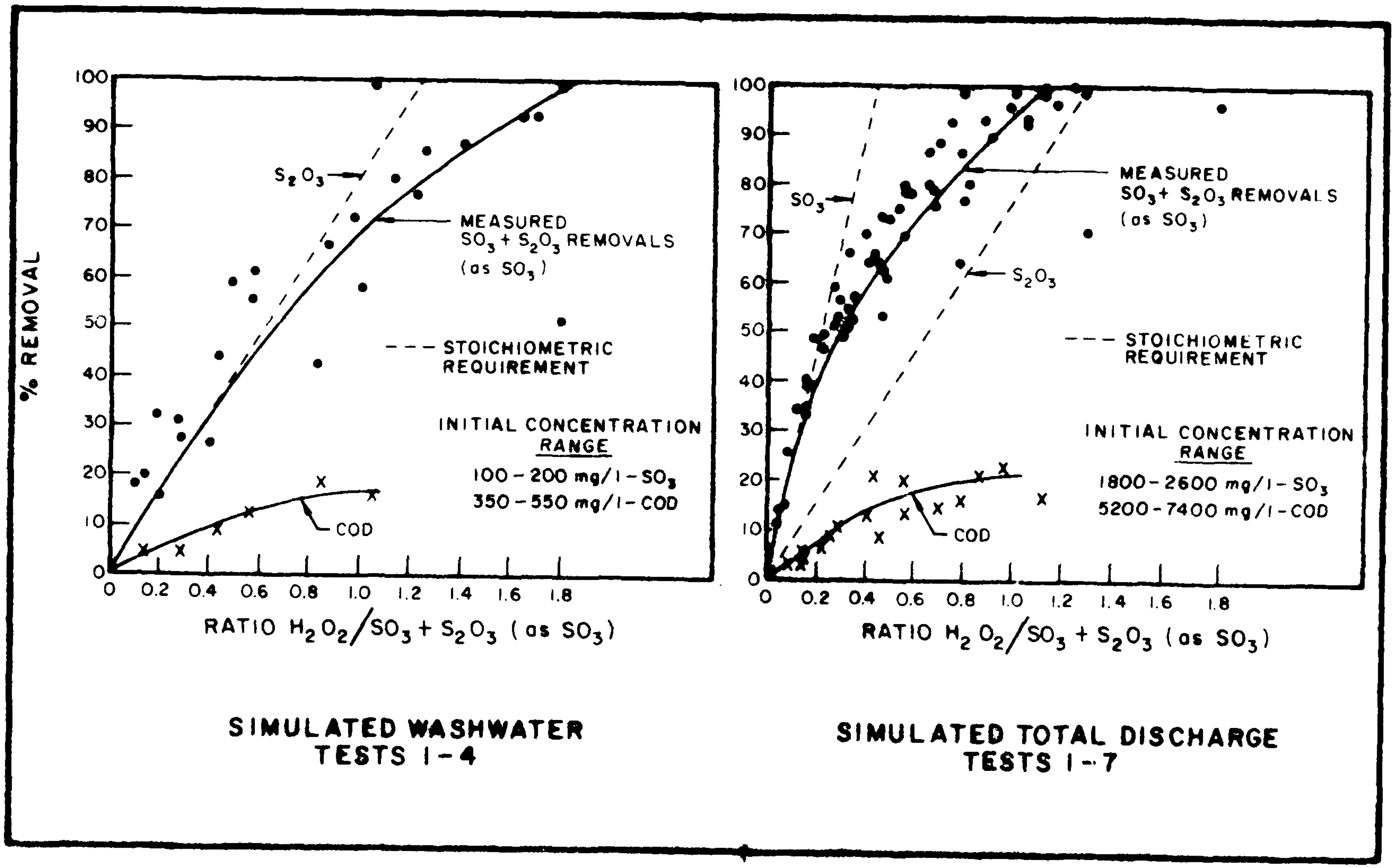


Figure 3. Hydrogen Peroxide Oxidation of Simulated Wastewaters

Figure 4 illustrates the time of reaction for hydrogen peroxide oxidation at various peroxide dosage levels. The data are presented in Tables B-10 and B-11. In the total discharge there was generally a rapid, initial reduction in the total measured $S_2O_3 + SO_3$ concentration. In the washwater, the rate of oxidation of total measured $S_2O_3 + SO_3$ was slower, reflecting the proportionally higher thiosulfate concentration, which apparently reacts more slowly than sulfite. In the total discharge and washwater tests, when the dosage added was in excess of that stoichiometrically required, 100-percent reduction was achieved. A reaction time of 20 to 40 minutes was indicated for the total waste. The washwater sample, after ammonia air stripping required 90 to 120 minutes to achieve complete removal; however, most removal was accomplished within 50 to 60 minutes.

4. Chlorine Oxidation

Chlorine oxidation was evaluated on both the total discharge and on the washwater. Chlorine was added incrementally, until a residual equal to that added (breakpoint) was observed. Sulfite, ammonia and COD were measured. Data are included in tables in Appendix B.

a. Total Discharge

Two test runs were performed on the total discharge. In Test 1, the pH was maintained at a constant pH. The pH was allowed to decrease with the addition of chlorine in Test 2. In both cases,

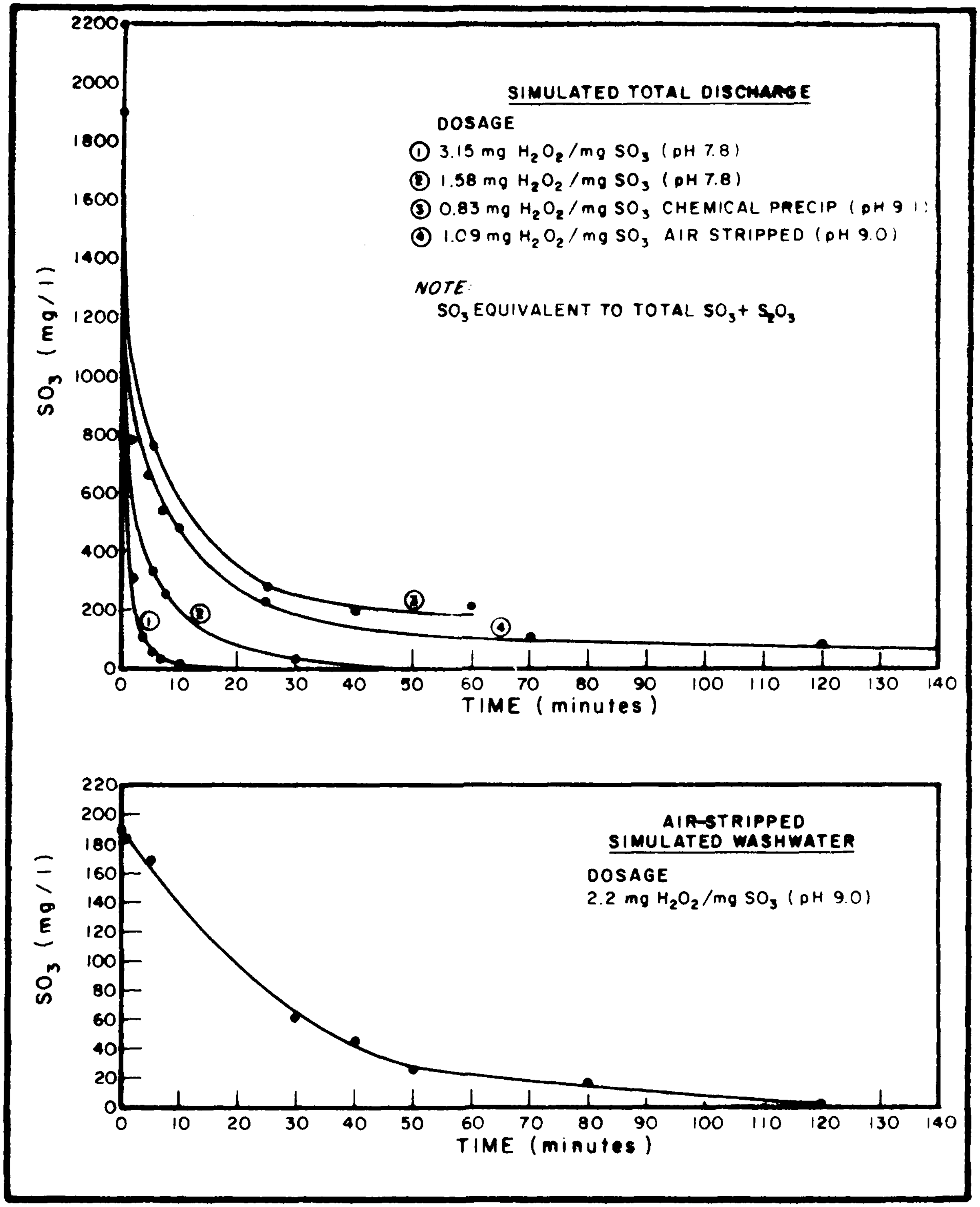


Figure 4. Peroxide Oxidation Reaction Time Tests

the samples had been pretreated by ammonia stripping and peroxide oxidation (sulfite removal). The primary intent was to remove the residual ammonia by breakpoint chlorination.

The results of Test 2 are shown in Figure 5. Residual sulfite was fully oxidized at a dosage of approximately 1000 mg/l. Residual ammonia was not completely oxidized until a dosage of approximately 2800 mg/l chlorine was reached. An overall COD reduction of about 28 percent in Test 1 and 34 percent in Test 2 was observed. Normally a ratio of 8 to 10 parts chlorine per part ammonia is required to oxidize the ammonia to nitrogen. Thus, for the initial 20 mg/l ammonia (as nitrogen), approximately 200 mg/l chlorine would be required. The oxidation of the initial 76 mg/l of combined sulfite and thiosulfate would theoretically require 70 to 90 mg/l of chlorine. The overall consumption of approximately 1000 mg/l chlorine shows a chlorine demand from other organic substances in the wastewater. The COD was reduced by 1460 mg/l in Test 2, and a chlorine-to-COD-removed ratio of about 1.8 was observed at the chlorine breakpoint. Although ammonia was oxidized, as was a portion of the COD, the high dosage of chlorine necessary to achieve these removals requires the addition of alkalinity to maintain pH. This will result in a significant increase in total dissolved solids in the effluent.

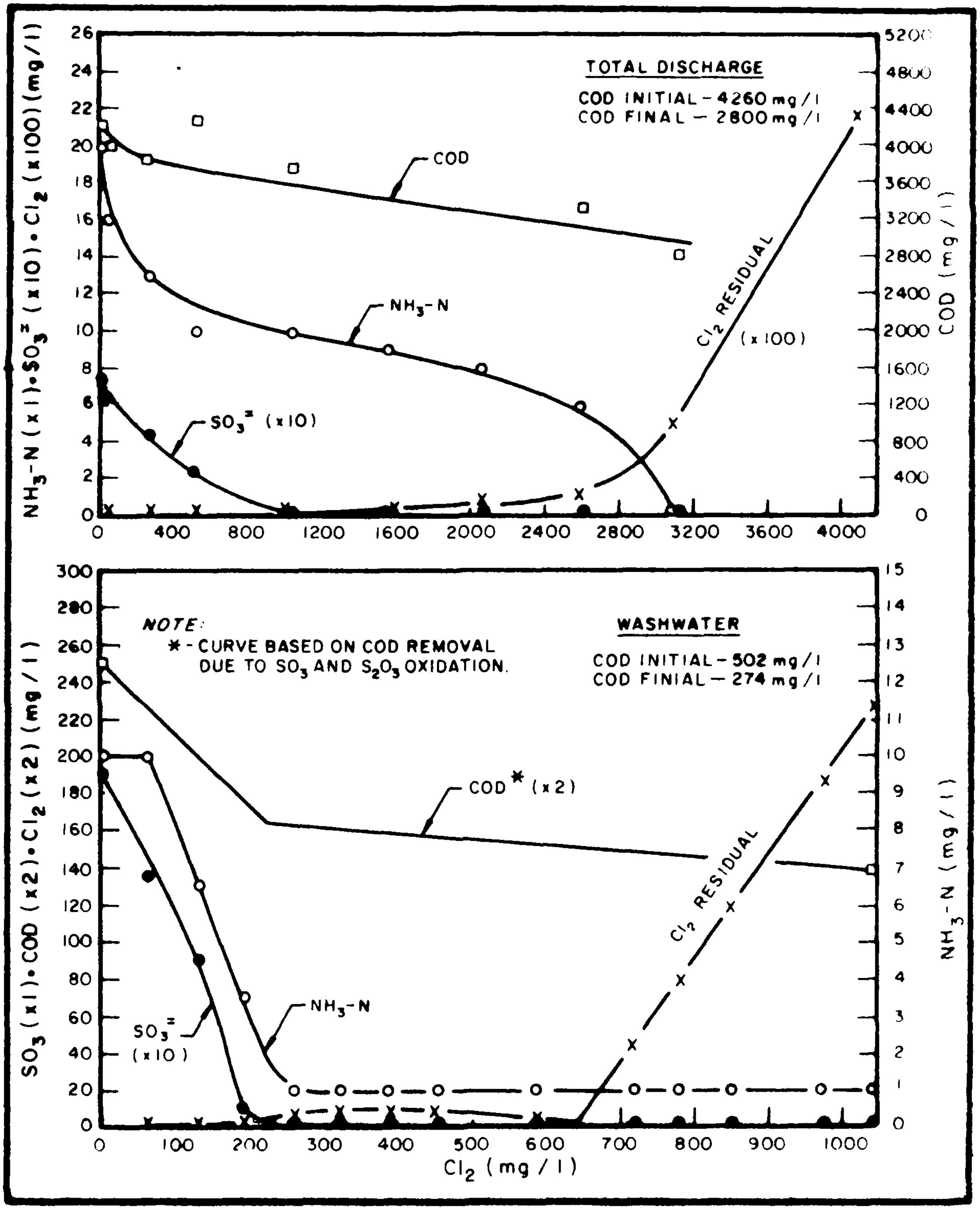


Figure 5. Breakpoint Chlorination of Simulated Wastewaters

b. Washwater

Results of breakpoint chlorination on a simulated washwater sample are also displayed in Figure 5. The test sample was pretreated by air stripping, peroxide oxidation, and metals precipitation. Approximately 600 to 650 mg/l chlorine were required to achieve the breakpoint dosage. Ammonia was oxidized to less than 1 mg/l, and sulfite was completely removed. COD reduction was 45 to 67 percent in the two test runs. As shown in Figure 5 (results of Test 1) ammonia appeared to be oxidized to less than 1 mg/l, at a dosage which was approximately 40 percent of that required to achieve breakpoint. In Test 2, however, ammonia was not reduced until about 80 percent of the breakpoint dosage was achieved. In Test 1, allowing for the ammonia and sulfite chlorine demand, a ratio of 1.9 mg chlorine demand per milligram COD removed is calculated; in Test 2, the ratio was about 1.2, using the estimated initial COD value.

These tests indicate that chlorine oxidation of the washwater can produce an ammonia concentration which will meet effluent criteria Levels 1, 2 and 3, although, high chlorine dosages are required. COD concentrations after chlorine oxidation met Level 3 requirements, but did not meet those of Levels 1 or 2.

5. UV Catalyzed Chemical Oxidation

To determine if ultraviolet light (UV) would enhance the oxidation of organics by chlorine, a UV chlorination test was performed on the simulated washwater. The results are shown in Figure 6. Sulfite and ammonia nitrogen were oxidized completely. COD results are somewhat variable because of the residual chlorine levels which had to be neutralized. An overall COD reduction of approximately 48 percent was achieved; effluent COD concentrations did not meet Level 1 or 2 criteria. Total organic carbon (TOC) reduction was approximately 27 percent; most of the COD reduction was likely due to inorganic COD demand.

This test indicates that the use of UV to assist chlorine oxidation may slightly increase COD removals over simple chlorination; the final COD level, however, was still greater than the criteria for Levels 1 and 2.

A UV/peroxide test was also conducted. Sulfite was reduced; however, it was judged from the low rate of peroxide depletion, that very little, if any, further reduction of COD was accomplished. This is consistent with the findings discussed in Section 3, namely, that UV was not effective in oxidizing the acetate ion. As a result, UV/peroxide oxidation was not pursued further.

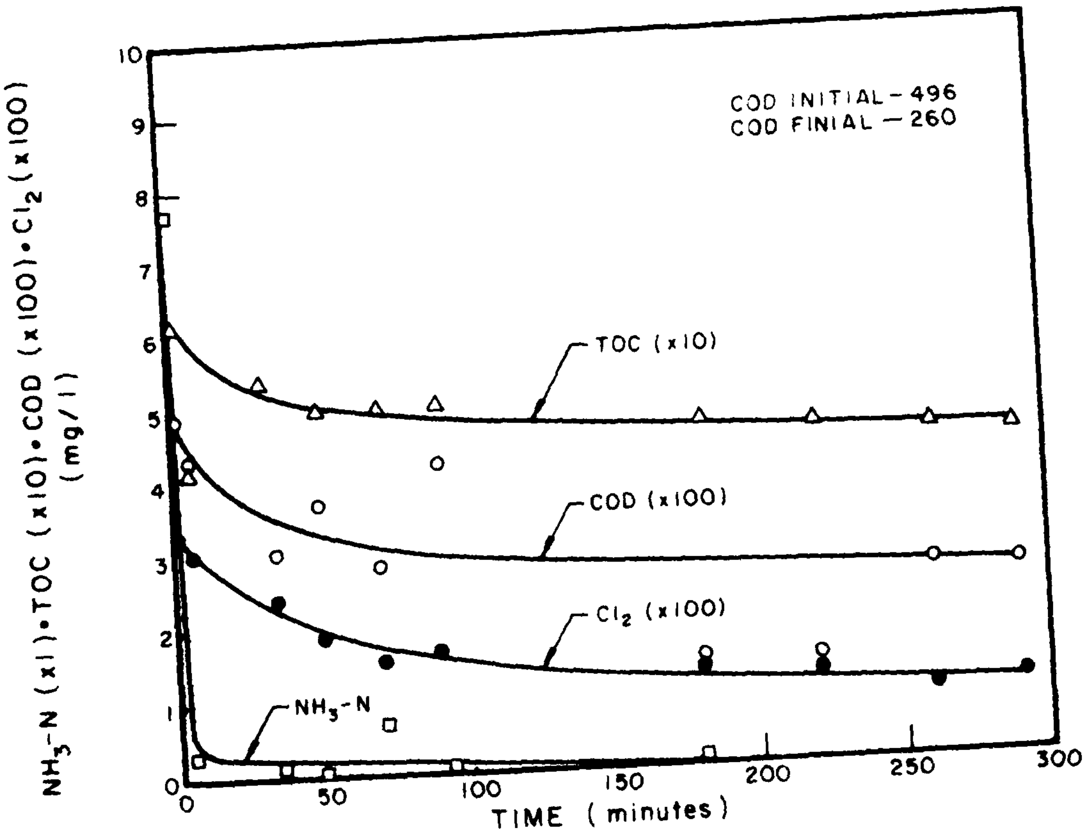


Figure 6. UV Catalyzed Chlorine Oxidation of Simulated Washwater

E. AIR STRIPPING

1. Procedures

Ammonia stripping was investigated with the use of the laboratory bench scale apparatus shown in Figure 7. The apparatus consisted of a 5-inch diameter plastic column filled to 2 feet with 1-inch pall rings. The column was operated in a countercurrent mode. The sample was fed through a distribution plate at the top of the column and air was blown upward through the bottom of the column. Air and liquid flows were measured and an Orion® Selective Ion Ammonia Electrode continuously monitored the NH_3-N. Feed samples were mixed and adjusted to pH levels of 11 to 12.5 with caustic. Ammonia is essentially all in the un-ionized state at this pH. Tests were typically run until greater than 85 percent ammonia removal was achieved. Air stripping tests were run either in a batch mode, or in a continuous mode.

The results of the air stripping tests are summarized in Table 9 and graphically displayed in Figure 8. Individual test data are presented in Appendix B. The results indicate that ammonia can be removed from wastewaters by air stripping. The volume of air required to achieve 90-percent removal is generally consistent with theoretical air requirements (based on Henry's Law), 250 to 300 cf/gal for 90-percent removal. Full scale data on municipal wastewaters stripped in a 24-foot cooling tower show greater than 90-percent ammonia removal at air rates of 400 to 500 cf/gal (Reference 16).

Figure 9 illustrates ammonia removals with each pass; a pass in this case is 2 feet in height. A first order mechanism is indicated; that is, for a given set of conditions (ie. air flow, liquid flow, pH and temperature) the removal rate depends on the

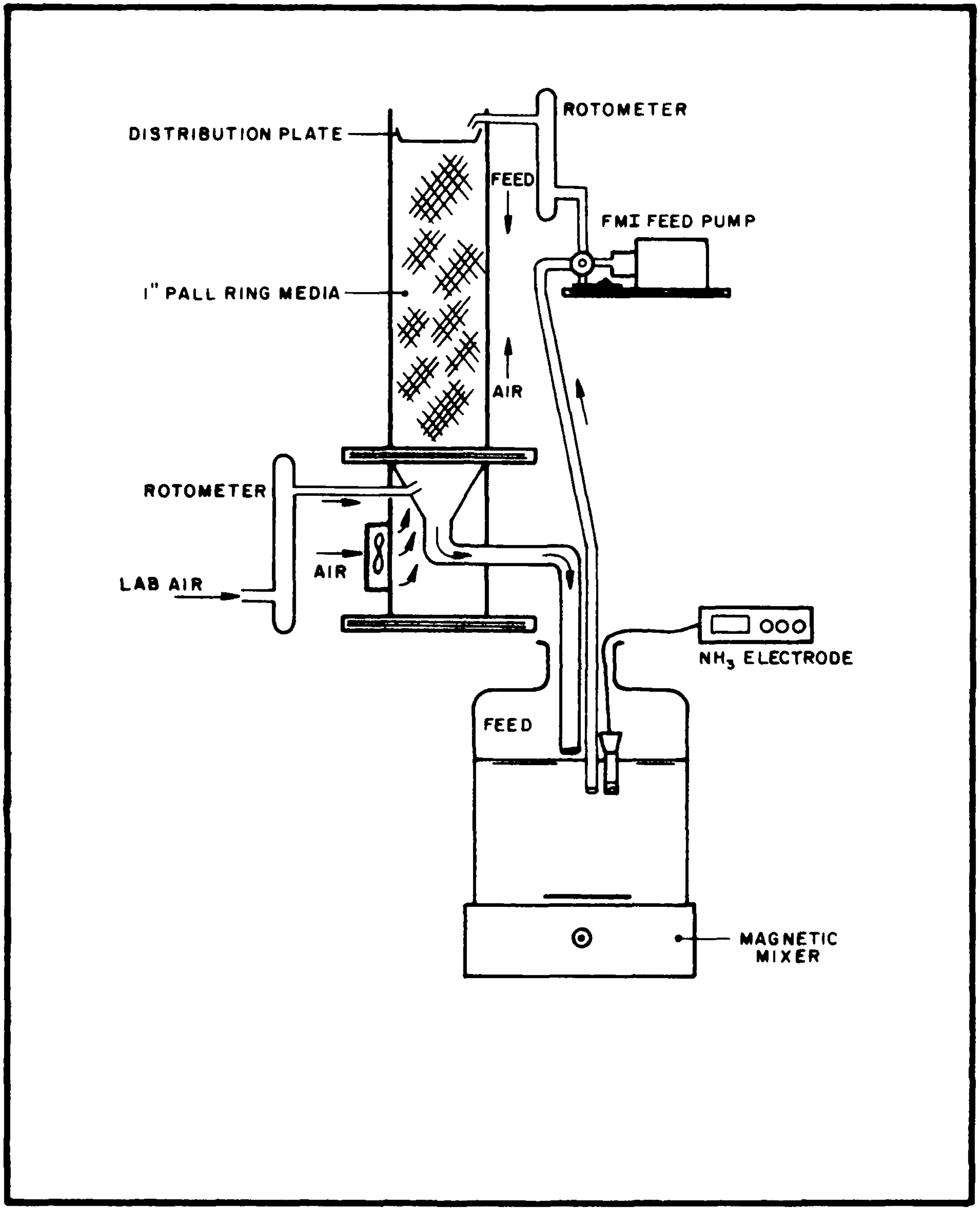


Figure 7. Ammonia Stripping – Laboratory Apparatus

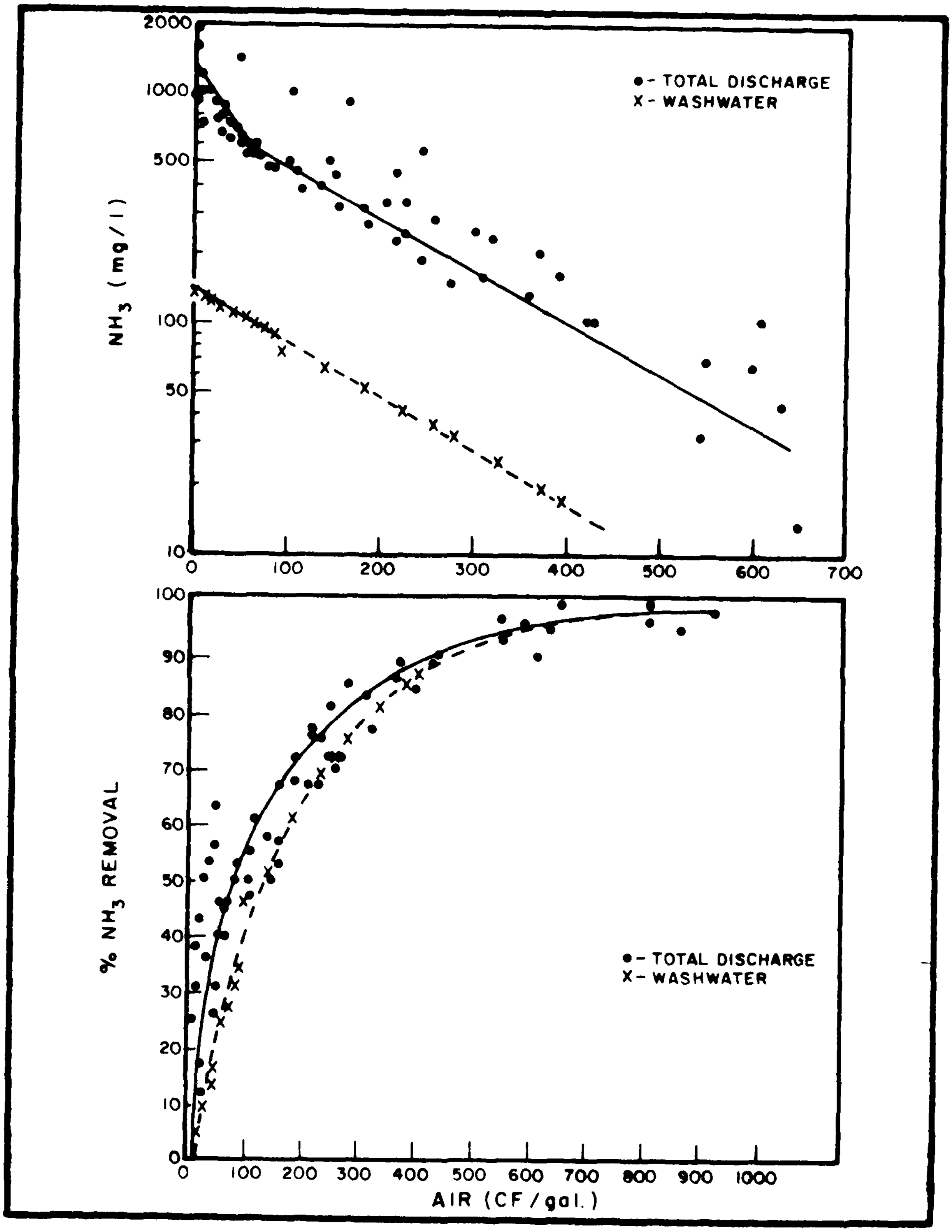


Figure 8. Air Stripping of Simulated Wastewaters

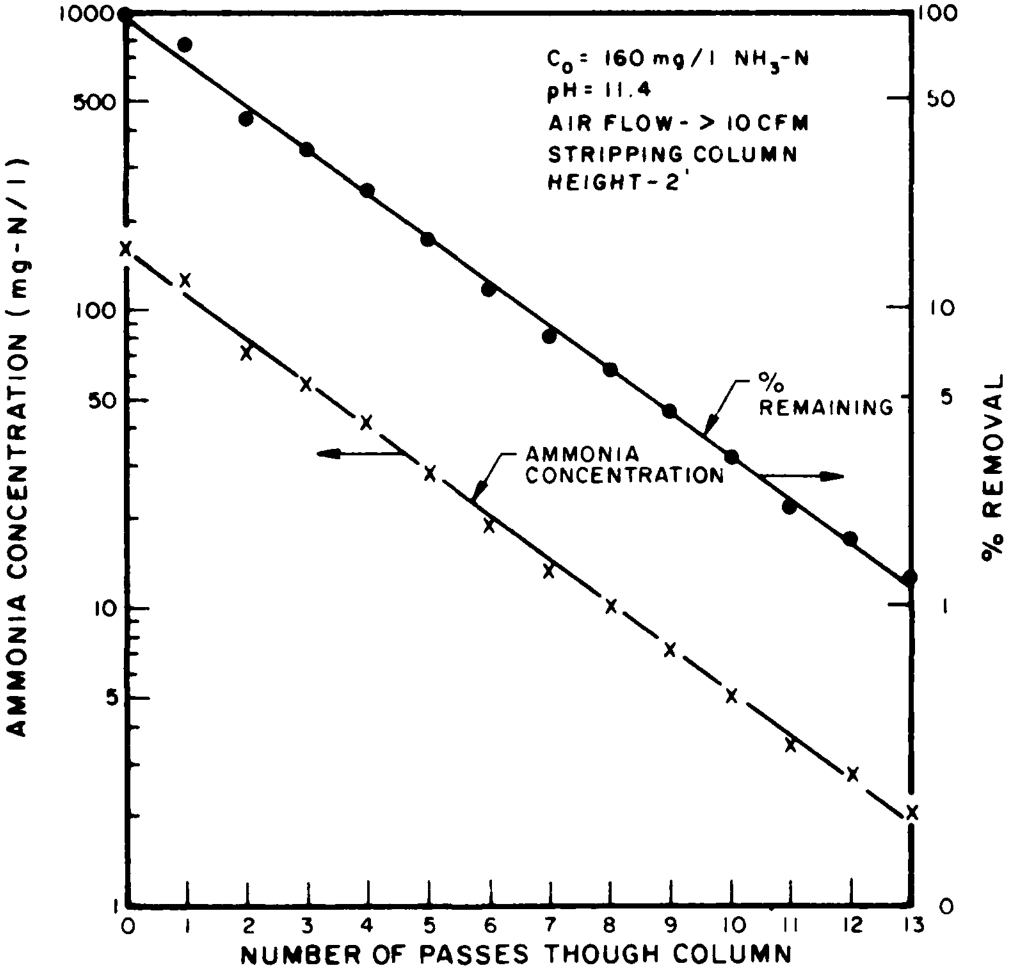


Figure 9. Air Stripping of Washwater Sample

TABLE 9. SUMMARY OF AIR-STRIPPING TESTS

Runs 1 - 7, 10; Total discharge
Runs 8, 9, 11; Washwater

Run No.	Type[(1)]	Liquid Rate (l/min)	Air Rate (cfm)	Total Air (cf)	Initial NH_3-N (mg/l)	Final NH_3-N (mg/l)	NH_3-N Removed (%)
1	R	0.1	.6	318	1,100	220	80
2	R	0.1	.9	916	1,900	35	98
3	R	0.1	.5	648	1,000	13	99
4	R	0.1	2	1,337	1,000	15	99
5	B	0.5	0.5	45	1,600	600	63
6	B	0.5	1	272	1,000	148	85
7	R	0.5	1.5	627	955	44	95
8	R	0.5	2	393	134	17	87
9	B	0.5	>10	>936	160	2	99
10	R	0.5	>10	>8400	~1000	~10	99
11	R	0.5	>10	>840	86	3.5	96

(1) R - Continuous recirculation
B - batch runs

residual concentration. As shown in Figure 9, the progressively higher levels of ammonia removal which could be achieved required proportionally greater air-to-liquid ratios. Thus, while air stripping is effective, there will be practical and economical limits to the final ammonia concentrations which can be achieved.

In summary, the results of the bench scale air stripping tests show that Level 3 criteria of 10 mg/l NH_3-N (90-95 percent removal) can be achieved in a practical operation; further treatment (chlorine oxidation, biological nitrification) would probably be required to meet the Level 1 and 2 criteria of 1 and 2 mg/l ammonia nitrogen, respectively.

F. CARBON ADSORPTION

Carbon adsorption for the removal of COD was investigated by the development of carbon isotherms and with carbon column breakthrough tests. Isotherms were developed by contacting a series of samples with incremental doses of pulverized activated carbon. One-hundred milliliter samples were placed in 150 ml ground glass stoppered bottles with selected weights of pulverized granular activated carbon (150-325 mesh) which had been washed several times in distilled water and dried at 103° C. The samples were continously shaken for approximately 20 hours at 20°C, and then removed and filtered through 0.45-micron membrane filters. The filtrates were analyzed for COD and TOC. Samples had been pretreated with hydrogen peroxide and/or chlorine to oxidize the inorganic fraction of the chemical COD. Total discharge samples were also tested at two pH levels, to determine pH effects.

Carbon column breakthrough tests were conducted using the bench scale column apparatus illustrated in Figure 10. Virgin granular activated carbon was prewashed in distilled water and dried at 103° C. A preweighed portion of carbon was transferred to the column and backwashed with tap water to removing gas and fines. The carbon was allowed to settle, and the bed depth was measured. Influent was applied to the column through a metering pump at approximately 1 gpm/sf. Grab samples were drawn with time until the influent was depleted. The influent samples had been pretreated by ammonia stripping, metals precipitation, peroxide oxidation and breakpoint chlorination. Effluent samples were analyzed for COD.

Figure 11 presents the carbon isotherms developed for the total discharge and washwaters. The data are also presented in

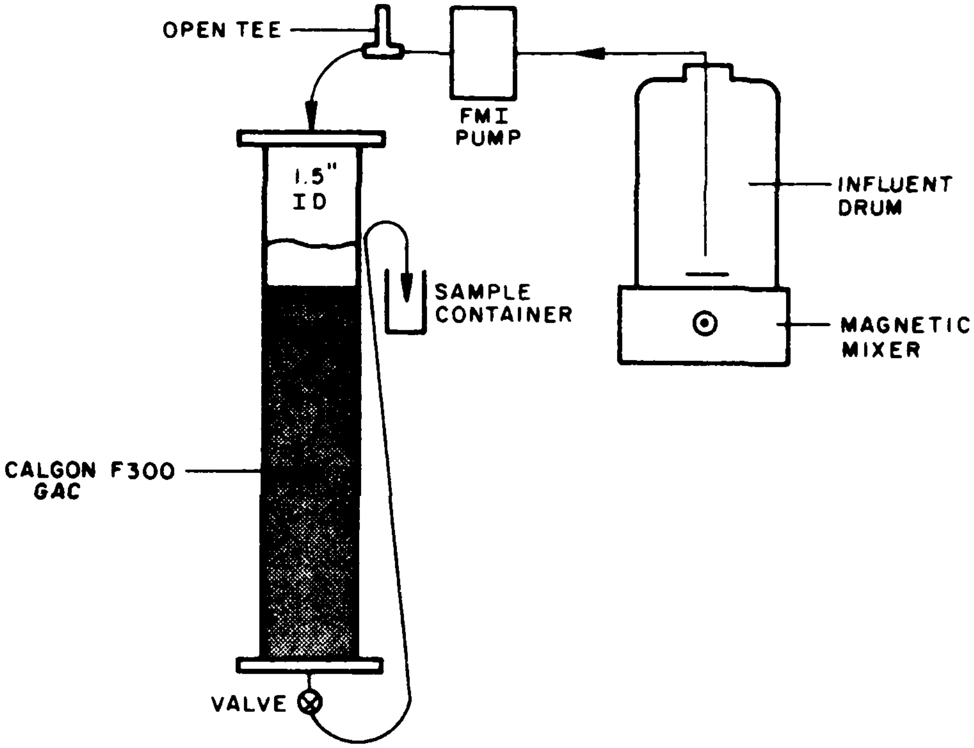


Figure 10. Bench Scale Carbon Column

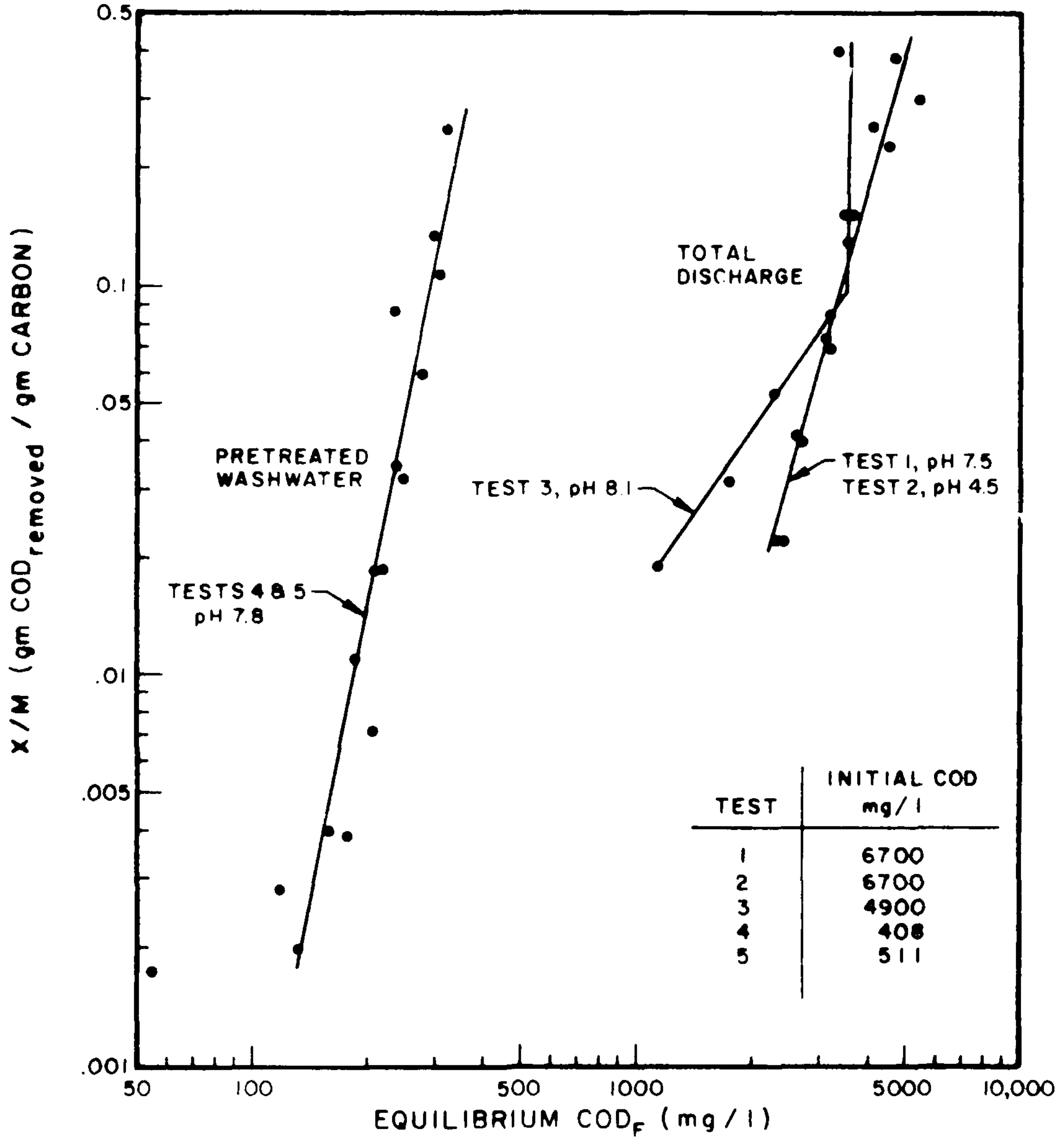


Figure 11. Carbon Isotherms on Simulated Wastewaters

Appendix B. Tests 1 and 2 were performed on the total discharge sample with no pretreatment; the sample pH was adjusted to 4.5 for Test 2. Both samples yielded similar isotherm curves. The steepness of the isotherm curves is indicative of poor adsorption; equilibrium COD values greater than 2000 mg/l were measured in the filtrate at a relatively high carbon requirement.

Tests 4 and 5 were conducted on washwater samples which had been pretreated by ammonia stripping, peroxide oxidation and chlorination. The test 4 sample had been dechlorinated, while the test 5 sample had a 3 mg/l Cl_2 residual. Both samples exhibited similar isotherm curves. The curves were quite steep, again indicating relatively poor adsorption of COD. At the maximum dosage of 20 gm carbon per 100 mls, COD was reduced 86 percent and 74 percent, respectively, in Tests 4 and 5. Test 4 yielded a COD of 56 mg/l while the Test 5 filtrate COD was 133 mg/l.

The results of the isotherm analyses for the total discharge indicate that the required effluent criteria could not be practically achieved. The isotherms developed on the washwater indicated that carbon adsorption may be applicable to reduce COD levels after pretreatment for oxidation of the inorganic COD fraction. Thus, two carbon column breakthrough tests were run on the washwater to obtain preliminary information on column performance and design requirements. The results of the breakthrough studies are displayed in Figure 12.

The 1 foot of carbon provided 9 minutes detention and the 2 feet of carbon provided 18 minutes detention. COD breakthrough was relatively quick. Breakthrough at 100 mg/l, COD Level 2 criteria occurred shortly after displacement of the clean water in the 1-foot column, and after only about two displacements of the carbon empty bed volume with waste in the 2-foot column.

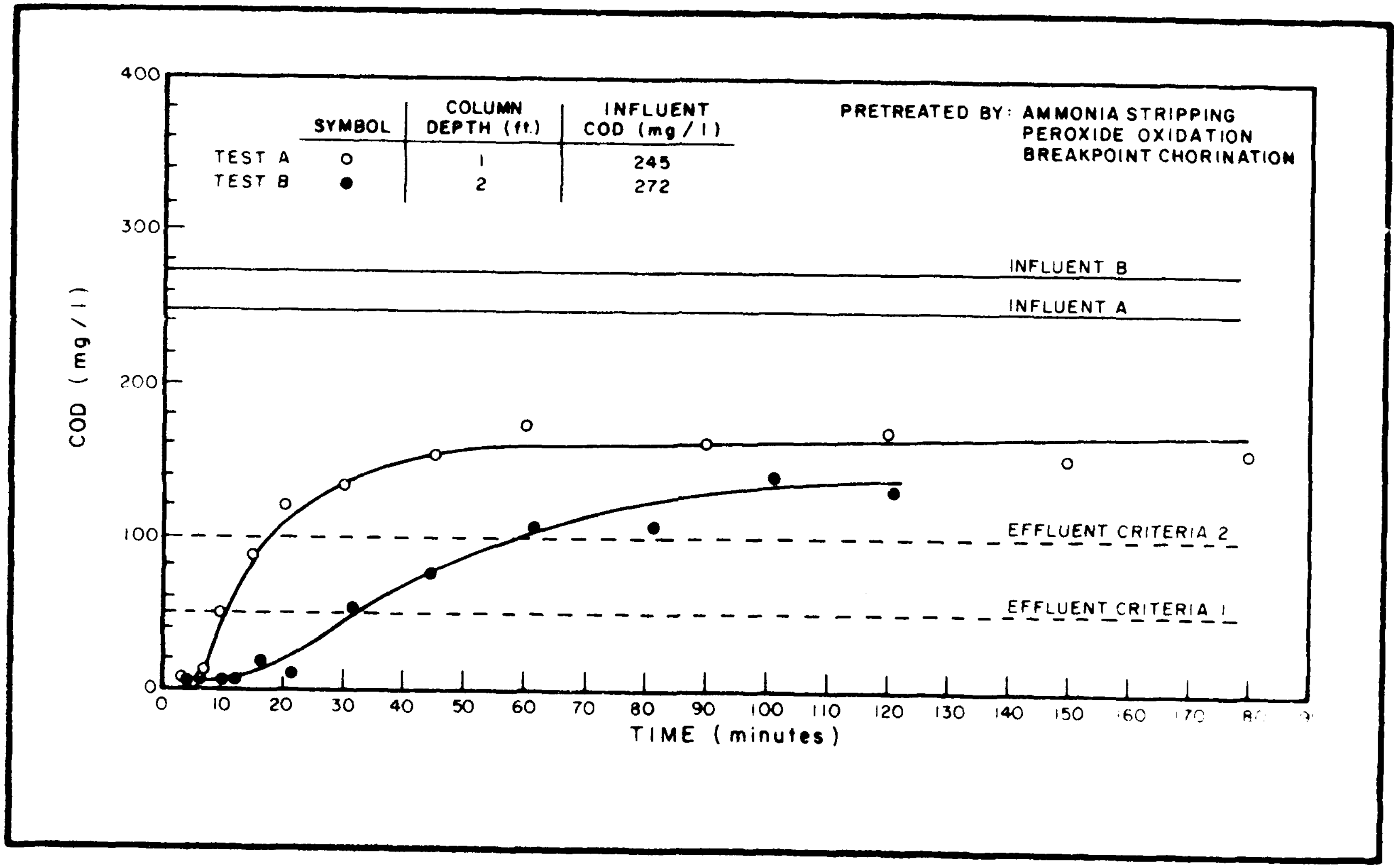


Figure 12. Carbon Column Breakthrough Tests Simulated Washwater

Both tests show similar results with effluents greater than the required effluent criteria after relatively short periods. Neither test lasted long enough for carbon to become saturated; thus, neither curve reached the influent COD during the test period, indicating that a fraction of the COD is adsorbed. This fraction of removable COD was about 36 percent in Test A and 51 percent in Test B. These results indicate that to achieve the required effluent criteria Levels 1 and 2, very large quantities of carbon (very deep beds) would be needed.

Low molecular weight materials, such as acetic acid, do not adsorb well to activated carbon. The poor adsorption seen in the isotherm test and the rapid COD breakthrough in the column runs precluded further consideration of activated carbon treatment.

G. REVERSE OSMOSIS

This technology, as previously discussed, has been applied to photoprocessing wastewater to remove and concentrate contaminants, and to permit recycling of the treated water. The technology would not be applicable to the total discharge, since the reject (brine) concentration would typically be less than the concentrations of the fix and developer solutions. These can be easily separated from the wastewater by simple stream segregation.

Several companies manufacture reverse osmosis systems and maintain the special testing facilities required to determine performance of applicable membranes on a specific wastewater. Osmonics, Inc., of Minnetonka, Minnesota, a manufacturer with a system presently in use on a photoprocessing wastewater was contacted to conduct screening studies on a simulated wastewater sample. A sample of fix was collected by the Air Force from the 11CN facility at Shaw AFB, and shipped to Osmonics. This sample (see Table 3) was diluted with demineralized tap water to simulate washwater concentration. Several runs were conducted on two membranes and at several pH levels. Samples of the feed, permeate and concentrate streams were collected during each test run, and sent by Osmonics to our laboratory for analysis.

Five runs were conducted; the results are summarized in Table 10. The report submitted by Osmonics, Inc. is presented in Appendix C. Based on conductivity and refractometer measurements, Osmonics indicated that Run 2 yielded the best results. Approximately 97 percent rejection of ionized species was measured. The data in Table 10 indicate both Run 1 and Run 2 gave good results. At the higher pH levels, as might be expected, ammonia is less ionized and therefore passes though the

TABLE 10. ANALYSES OF SAMPLES GENERATED BY OSMONICS, INC., RO WASHWATER EVALUATION

	FIX	FEED				PERMEATE					CONCENTRATE			
Run No.		1	2	3	4	1	2	3	4	5	2	3	4	5
pH	4.5	4.5	8.3	10.0	10.2	5.2	9.1	10.0	10.4	10.3	8.3	10.0	10.25	9.7
SO_3	56,600	240	214	202	212	5	3	3	4	3	235	235	223	210
COD	82,800	404	-	-	-	62	15	27	27	15	427	458	415	1440
NH_3-N	32,500	146	-	-	-	7.4	21.6	100	98	16	-	-	-	86
TDS	135,857	520	-	-	-	<1	<1	85	160	150	-	-	-	47,000
SO_4	-	60	-	-	-	-	-	-	-	7	-	-	-	835
TOC	5555	51.5	-	-	-	23.5	7.0	7.0	7.0	6.0	63	70	59	539
Al	2300	7.1	-	-	-	-	-	-	-	0.2	-	-	-	22.0
Cd	2.03	-	-	-	-	-	-	-	-	<.025	-	-	-	.05
Cr	0.27	-	-	-	-	-	-	-	-	<.05	-	-	-	<.05
Fe	2.49	-	-	-	-	-	-	-	-	.05	-	-	-	.19
Ag	2040	10.4	-	-	-	.04	.06	.02	-	0.06	13.2	12.8	12.6	43
Zn	0.45	-	-	-	-				-	<.01	-	-	-	<.01

Feed Sample 4.25 ml/l of spent fix solution diluted with R.O. demineralized water. pH adjusted with caustic for samples 2, 3, 4 and 5

Note - No sample run 1 concentrate
Feed 4 used for Runs 4 and 5

Run No.	1	2	3	4	5
Membrane type	97CA	97CA	97CA	PAC	PAC
Percent Recovery	10%	10%	10%		75%
Operating pressure		400 psig average			

membrane. Ammonia is completely ionized at a pH below about 6.5 to 7. An ammonia removal of 95 percent was achieved at a feed pH of 4.5 (Run 1). This is likely the most efficient removal which may be expected with one stage. The COD rejection averaged 95 percent in all runs except No. 1. Acetic acid will pass through cellulose acetate membranes, while the sodium salt of acetic acid is rejected; thus, at the lower pH, equilibrium would favor acetic acid, explaining the higher COD in the permeate on Run 1. A pH of approximately 7 would be optimum for both COD and ammonia removal.

Test 5, run at a high pH, indicated that the waste could be highly concentrated (almost 100 times based on dissolved solids measurement) without observable operational problems. The low ammonia result in Run 5 may be attributed, in part, to losses during the test from volatilization and not rejection by the membrane, (an ammonia odor was noticed during the test). Ammonia would essentially be all molecular at pH 10.2, and Test 4 results indicated high passage of ammonia with the same membrane. As shown by the analysis, COD and heavy metals effluent criteria can be met on the simulated washwater and significant ammonia reduction (95 percent) can be accomplished at low pH. A two-stage system would reduce the ammonia concentrations to below the 1 and 2 mg/l criteria of Levels 1 and 2, respectively.

Osmonics observed no fouling of the membranes and pure water permeate flow rates were restored with a post-test water flush. Osmonics expressed some concern, however, with potential fouling from iron precipitation, and the possible need for iron pretreatment. The actual level of iron in the washwater, however, was considerably less than that estimated (based on a washwater simulated using fix solution after passing an iron/silver recovery exchange unit); thus, it is not felt that iron would cause any significant problem at the concentration of less than .01 mg/l calculated from the actual fix concentration.

In their report, Osmonics recommended an Osmonics R.O. Process Evaluation Unit (15,000) to further test various membranes, and to obtain longer term data. Subsequent conversations with Osmonics indicated that a full-scale prototype system could be sized on the basis of these tests.

In summary, reverse osmosis is a feasible treatment system for the washwater. A design can be developed to produce an effluent meeting Level 1 criteria for all components. The concentrate stream from the system comprising about 2 percent of the washwater flow will require subsequent disposal. System maintenance includes flushing and cleaning the membranes periodically, preserving the membranes if not in use for long periods, usually with formaldehyde, and membrane replacement when flux rates deteriorate below required capacities. Adjustment of the pH may be required to optimize both COD and ammonia removals. Filtration may also be necessary as a precautionary measure to remove any fine suspended solids prior to the reverse osmosis system.

H. BIOLOGICAL TREATMENT

1. Procedures

As previously discussed, the biological treatment of photoprocessing wastes, usually in a municipal treatment system, is the most common method of disposal of these wastes. A possible approach to onsite biological treatment was considered. A screening study was conducted to obtain information on performance and the effluent levels of contaminants which might be achieved by biological treatment of the total discharge and the washwaters. For this screening study, it was decided to pretreat by air stripping for ammonia reduction and to assess biological treatment for final ammonia removal by nitrification, to the criteria required for Levels 1 and 2.

The studies were conducted in laboratory activated sludge units which consisted of 6-liter aeration reactors and a 1-liter settling unit , as illustrated in Figure 13. Settled sludge was recycled back to the reactor by pumps at approximately 60-minute intervals. Wastewater was pumped to the aeration units on a continuous basis, after an initial acclimation (batch-fed) period. A nitrifying activated sludge was obtained as seed to start the system. The unit was fed at a COD loading rate of approximately 0.3 gms COD/gm total mixed liquor solids. Wastewater flows were 1 ml/min to the total discharge unit, and 10 ml/min to the washwater unit. The waste had adequate ammonia for biological treatment; it was necessary, however, to add phosphorous as a nutrient for biological growth. Approximately 1 mg of phosphorus was added for each 100 mg of COD.

The units were started in early (7/2) July and fed on a batch basis for 1 week to allow for acclimation. Ammonia in the feed

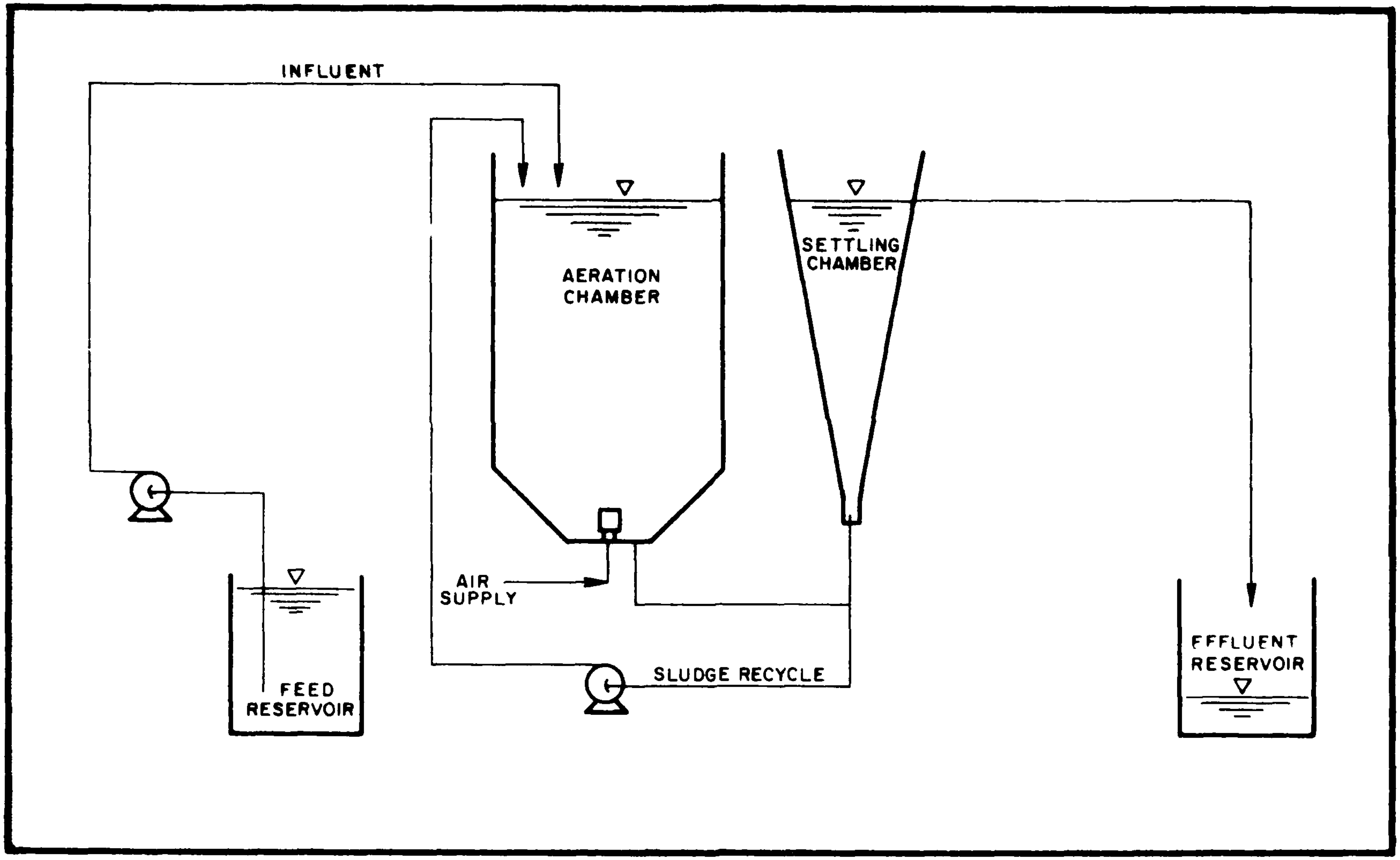


Figure 13. Schematic of Typical Laboratory Biological System

was 35 to 40 mg/l and spot checks of effluent ammonia indicated good ammonia removals in both units.

After 1 week, continuous feed was started to the units and new feed samples were made up. These samples were pretreated by peroxide oxidation, air stripped at a pH of 11.5, and treated with polymer to settle suspended solids. The pH in the washwater unit dropped to 3.5 over a weekend, effectively killing the unit. A new seed was obtained and the unit was restarted. Thereafter, the alkalinity of the feed was adjusted by the addition of sodium bicarbonate to maintain an appropriate pH in the mixed liquor. The detention time in the washwater unit averaged approximately 12 hours at an F/M ratio of 0.27 COD/MLSS. COD removals on the order of 87 percent were achieved; the effluent concentration met the Level 1 criteria of 50 mg/l. Effluent BOD's were less than 15 mg/l, effluent ammonia was less than 1 mg/l, and sulfide was completely oxidized. Heavy metals were low and met Level 1 criteria.

As previously indicated in the total discharge unit, ammonia nitrogen removal was observed during startup under batch feed conditions. During continuous feed, little nitrification was achieved. Effluent COD reduction reached 73 percent; the effluent COD concentration averaged 1218 mg/l, much above the Level 3 criteria of 500 mg/l. At the end of the study, the unit was aerated for 2 days with no feed to determine if a lower effluent COD could be produced; however, there was minimal reduction beyond that achieved when the unit was receiving a continuous flow. Heavy metals met Level 3 criteria and, except for cadmium and copper, generally met Level 1 criteria.

The biological treatability tests indicated the feasibility of using biological treatment on the washwater to meet proposed effluent criteria. Effective pH and alkalinity control are critical to maintain treatment and a nitrifying microorganism population. Although fairly good COD and BOD removals were achieved on the total wastewater, the results indicate that the proposed effluent criteria, even at Level 3, cannot be met by biological treatment. This level of removal, however, might be considered in specific cases for pretreatment prior to discharge to a local sanitary treatment plant.

I. EVAPORATION

The total dissolved solids concentration in the discharge exceeds both Level 1 and Level 2 criteria. Evaporation, as previously discussed, could remove dissolved solids to meet these criteria. The operation is costly and energy intensive; thus, since the highly concentrated fix and developer solutions can easily be separated from the washwater, evaporation should only be considered for these solutions.

During evaporation, volatile material in the waste will be driven off. Ammonia and acetic acid would be expected to vaporize, as well as some sulfur dioxide from the breakdown of sulfur compounds in the waste at evaporation temperatures. Several manufacturers of evaporation equipment were contacted. Large pilot scale tests to evaluate evaporation were recommended; however, these were beyond the scope of this project. A previous report studied evaporation for the fix and developer (Reference 10) and some information on the use of an evaporator at a photoprocessing installation was obtained, (Reference 14) and discussed in Section II.

A sample of the total discharge was evaporated in a laboratory distillation apparatus to determine the potential extent of contaminant carryout. The water vapor condensate was collected and analyzed for COD and ammonia. Test data indicated that approximately 80 percent of the COD and 97 percent of the ammonia were driven off from the total waste; 30 percent COD and 10 percent ammonia were in the condensate, with the rest lost to atmosphere. This test result and other information gathered (Reference 14) on the evaporation of photoprocessing wastes, indicated that the condensate from an evaporation system would require further treatment prior to discharge.

SECTION V

TREATMENT SYSTEM - CONCEPTUAL DESIGN

A. INTRODUCTION

The wastewater characterization study defined the flows and constituents in the wastewaters discharged by a WS430-B photoprocessing facility. Specific contaminants were identified (Section I, Table 7) which would have to be removed or reduced to meet three effluent quality goals established by the Air Force (Table 4). Treatment technologies currently available were researched, and information was reviewed to determine the potential application of these processes to treatment of the photoprocessing wastewaters. There was little direct information on actual performance results of the applicable treatment technologies, since most photoprocessing wastes are simply discharged to a sanitary sewerage system for treatment. Bench scale studies were run on simulated samples of the wastewaters to determine the effectiveness of various unit processes in yielding effluents which would comply with the criteria. Both the total discharge and the washwater were studied. Alternative treatment systems were considered and evaluated on the basis of performance, ability to meet Air Force requirements of mobility, ease of operation and maintenance by unskilled personnel, and cost.

B. TREATMENT OF THE TOTAL DISCHARGE

1. Summary of Test Results - Alternatives

The initial objective of this study was to develop the conceptual design for end-of-the-pipe treatment of the total WS-430B discharge. As had been discussed in Section I, the total discharge dissolved solids concentration exceeds Level [illegible] mg/l) and Level 2 ([illegible] mg/l) criteria by a wide margin; [illegible] it does meet the Level 3 (15,000 mg/l) criterion. [illegible] dissolved solids [illegible] mostly inorganic salts which [illegible] constitute a residue for disposal [illegible] removed from the [illegible] waste stream. Alternatives considered to meet the Level [illegible] TDS criteria include evaporation, reverse osmosis, [illegible] segregation of the fix and developer solutions from the [illegible] waste flow.

Evaporation is a relatively costly operation. The size of the system and the capital and operating costs are directly proportional to the volume of water to be evaporated. Evaporation will produce two streams requiring further handling. The concentrated slurry would contain 30 to 40 percent total solids (depending upon the system selected); the condensate stream, which would constitute the total discharge after treatment by evaporation, would contain volatilized materials such as ammonia, sulfur dioxide and organics (acetic acid) which would require subsequent treatment. The slurry constituting from 1 to 2 percent of the total flow would require further handling and ultimate disposal. As indicated in Section [illegible], evaporation of photo processing waste requires skilled operation and has considerable maintenance requirements.

Reverse osmosis can separate dissolved minerals from a feed stream, producing a relatively clean permeate and a concentrated brine. Depending upon the system configuration and pressure used (typically 40[illegible]-8[illegible] psi), the concentrate stream would contain from 2 to [illegible] percent dissolved solids. For the total discharge, a concentrate stream from an R.O. system would constitute from 7 to [illegible]4 percent of the total waste flow and would require further handling and disposal. The permeate [illegible] (assuming a multiple-stage system) would be suitable for discharge, since it would meet all effluent criteria levels. An R.O. system requires some skill in operation and maintenance, although it would probably meet the Air Force's objective.

The third alternative, separation of fix and developer solutions from the total waste flow, can be easily and economically accomplished. These concentrated solutions (8 to 12 percent solids, by weight) comprise less than 5 percent of the total flow and contain over 90 percent of the total dissolved solids. The removal of these streams from the total flow would result in a total discharge which would meet all criteria levels for total dissolved solids. Further treatment would be required to meet other criteria. These solutions, removed from the total wastewater, would be equivalent to a treatment system residue, and would require further handling and ultimate disposal.

2. Comparison of Alternatives for Total Discharge Treatment

A comparison of the three alternatives results in the obvious conclusion that the fix and developer should be separated from the total waste stream to meet Levels 1 and 2 dissolved solids criteria. Although the solutions are greater in volume than a concentrated slurry from evaporation, there are minimal capital costs and essentially no operating costs involved. Furthermore, this avoids an evaporation system relatively difficult to operate and maintain.

Reverse osmosis treatment of the washwaters alone (having segregated the fix and developer solutions) would be more economical than R.O. treatment of the total waste. R.O. can typically achieve a reject concentration of 5 - 10 percent, which is less than the initial levels in the fix and developer. Thus, R.O. should be applied only to the washwater.

As indicated [illegible] meet Level 3 discharge [illegible] Level 3 ammonia, chemical oxygen demand, [illegible]. Treatability tests on the total wastewater [illegible] could be reduced to Level 3 criteria, [illegible] at an elevated pH. Chemical [illegible] addition to the total discharge, after ammonia stripping, indicated that Level 3 criteria could also be [illegible] silver; significant quantities of sludge were produced, however, which would require subsequent disposal. Carbon adsorption and biological treatment did not reduce the total [illegible] concentration to the Level 3 limit of 500 mg/l.

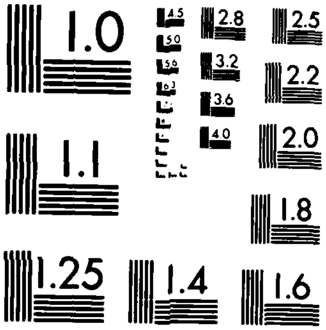
Based on these findings, onsite, end-of-the-pipe treatment of the total discharge for the mobile photoprocessing facility would not be feasible to meet Level 3 effluent goals. Separation of the concentrated fix and developer solutions from the total discharge is required as the first step in an onsite treatment system. The remaining discharge is the washwater, which as shown in Table 7, would require treatment to meet COD, ammonia and silver criteria.

C. TREATMENT OF THE WASHWATER

1. Summary of Test Results

The washwater will constitute the total discharge after the fix and developer solutions are separated and collected for disposal. The [illegible] indicated that the washwater, contaminated with fix and developer, could be effectively treated to meet the effluent criteria for Level 3. As shown in [illegible] and [illegible]

AD-A128 231 PHOTOGRAPHIC PROCESSING INTERPRETATION FACILITY 2/2
WASTEWATER CONCEPTUAL TREATMENT DESIGN(U) HYDROQUAL INC
MAHWAH NJ E J DONOVAN ET AL. MAR 83 AFESC/ESL-TR-82-42
UNCLASSIFIED F08635-81-C-0143 F/G 13/2 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

requirements at Level 3; however, treatment is required to meet Levels 1 and 2 for COD, and Levels 1, 2 and 3 for ammonia and for silver.

Ammonia can be successfully air stripped from the washwater. Achieving the Level 1 and 2 criteria will be considerably more difficult than Level 3, because of required high recirculation rates. Ammonia can also be oxidized by chlorination, although dosages exceeding theoretical requirements were required because of other chlorine-demanding substances present in the wastes. Ammonia can also be successfully removed by reverse osmosis. A two-stage system would be required to meet Levels 1 and 2. Level 1 ammonia criteria were also achieved by biological treatment, after air stripping to about Level 3 concentrations.

Jar tests using lime and caustic on various samples of both the total discharge and the washwater yielded variable and inconsistent results with respect to final effluent silver concentrations. Tests on samples after air stripping for ammonia removal did not reduce silver concentrations below Level 3 (1 mg/l). Based on literature references (Reference 1), chemical precipitation has been shown to reduce silver to Level 2 concentrations (0.2 mg/l) on photoprocessing wastes; however, Level 1 (0.1 mg/l) would be expected to only be marginally achieved. Reference data and reverse osmosis test indicate that a silver concentration of 0.1 mg/l (Level 1) can be met by R.O. treatment of the washwater.

Level 1 and 2 COD requirements (50 mg/l, and 100 mg/l, respectively), could be met by both biological treatment and reverse osmosis. Oxidation with hydrogen peroxide or chlorine did not reduce the COD concentrations to below Level 2 requirements.

2. Washwater Treatment Alternatives

Based upon the results of the bench tests and a review of other work discussed in Section II, the following alternative process schemes for washwater treatment are possible.

a. Washwater Treatment System - Alternative 1

- Collection and equalization of washwater discharge;
- pH adjustment to 11.5 and air stripping for ammonia removal;
- pH adjustment and chemical precipitation, settling for silver removal;
- Biological treatment for COD removal and residual ammonia nitrification;
- Filtration for final removal of suspended solids (silver precipitate);
- Chlorination capability for final ammonia oxidation when nitrification efficiency is low (cold temperatures, system startup);
- Sludge (chemical precipitate, excess biological solids) collection and storage;
- Solids dewatering for disposal.

b. Washwater Treatment System - Alternative 2

- Collection and equalization of washwater discharge;
- pH adjustment to 6.5-7.5 to optimize subsequent R.O. performance;
- Filtration through a 5-micron filter;
- Two - stage reverse osmosis system;
- Single stage R.O. for concentration of reject from the two-stage R.O. system;
- Concentrate disposal with the fix and developer.

Alternative 1 would be expected to meet all effluent criteria to Level 1 with the possible exception of silver. However, Alternative 1 was not eliminated on this basis, since there is evidence that with a greater degree of process optimization Level 2 (0.2 mg/l) could be consistently achieved, and possibly Level 1.

Alternative 2 would meet all effluent criteria of Level 1. Note that the controlling design parameter, ammonia, can be reduced to below 10 mg/l a single-stage R.O. unit; thus, to meet only Level 3, a single-stage reverse osmosis system would be adequate.

c. Washwater Treatment System - Alternative 3
To meet Level 3 only

- Collection and equalization of washwater discharge
- pH adjustment to 11.5 and air stripping for ammonia removal;
- pH adjustment and chemical addition, settling for silver removal;
- Filtration for suspended solids removal;
- Chlorination capability for final ammonia oxidation as required;
- Sludge collection, storage and solids dewatering for disposal.

2. Comparison of Alternatives for Washwater Treatment

A comparison of Alternatives 1 and 2 under the criterion that a system must be "operable, portable and maintainable by unskilled personnel at a "remote site" would clearly indicate Alternative 2 as the [illegible] choice. Alternative 1 is far more complex than Alternative 2 and will require a high skill level to operate and maintain the various process parameters (ph, alkalinity, nutrients, chlorine residuals, etc.) within acceptable limits. Additionally, because of the nature of the wastewater discharge (intermittent and variable in quantity and strength), variable performance of the biological system may be expected and may require a supplemental feed (e.g. spent developer solution) to maintain viability during periods of low or no production. Startup of a biological system would require transport of a viable nitrifying activated sludge or acclimation and development of a biomass, (which may take several weeks) prior to achieving acceptable treatment. This alone may possibly eliminate the practical application of this treatment scheme (i.e. biological) to many situations. Additionally, the disposal of a biological sludge may present added difficulty in cases where simple land disposal is not possible.

Alternative 2 is a physical-chemical system and is relatively compact. The effluent quality from this system would be more constistent and superior in quality to that of Alternative 1. Thus, the potential of effluent reuse at a water-short location is available with reverse osmosis. Additionally, a reverse osmosis system can be quickly put into operation and lends itself easily to intermittent operation.

Minor pH adjustment of the wastewater may be required, depending on the alkalinity of the water supply used and carry-over of fix to the washwater. Collection and equalization need only be large enough to provide a reasonably continuous feed to the treatment system. Some skill is required, however, in the operation and maintenance of the filter and R.O. systems, which require periodic (i.e., weekly, or monthly) flushing, cleaning, filter cartridge replacement, and, on a long term basis, replacement of membrane modules. The handling of a waste brine solution of about 2 percent of the original wastewater volume is required with this system. This brine would have a concentration of approximately 2.5 percent dissolved solids. Combining the brine with the spent fix and developer solutions for disposal is proposed.

Alternative 3 would only be applicable in cases where Level 3 requirements are imposed; however, the requirements with respect to operation and maintenance, except for biological treatment, would be the same as discussed under Alternative 1.

Preliminary cost estimates for each of the three alternatives are summarized as follows:

	Alternative 1 Physical-Chem Biological	Alternative 2 Reverse Osmosis	Alternative 3 Physical-Chemical (Level 3 only)
Capital	$102,500	$125,000	$85,000
Annual Operating	32,500	13,000	30,500

These estimates could range considerably and do not include the transport modules or sludge disposal. Alternative 2 appears to have a significant operating cost advantage, while (within the level of accuracy of these estimates) there is little significant difference in capital cost among the alternatives.

Based on these considerations, Alternative 2, incorporating reverse osmosis, is recommended for onsite treatment of the washwaters, when required by the installation location.

4. Recommended Onsite Treatment System

Figure 14 is a schematic diagram of the recommended onsite wastewater treatment system for the WS-430 B facility. The system includes collection of the fix and developer solutions, and the washwater into separate collection tanks. The washwater would be treated by reverse osmosis to meet required treatment levels. The R.O. concentrate would be combined with the fix and developer solutions and disposed of by one of several possible alternatives, determinable only by an assessment and evaluation of the various factors involved in the deployment of the facility. Major factors are the site location, production schedules, length of campaign,and locally available options.

D. SIZING OF TREATMENT SYSTEM

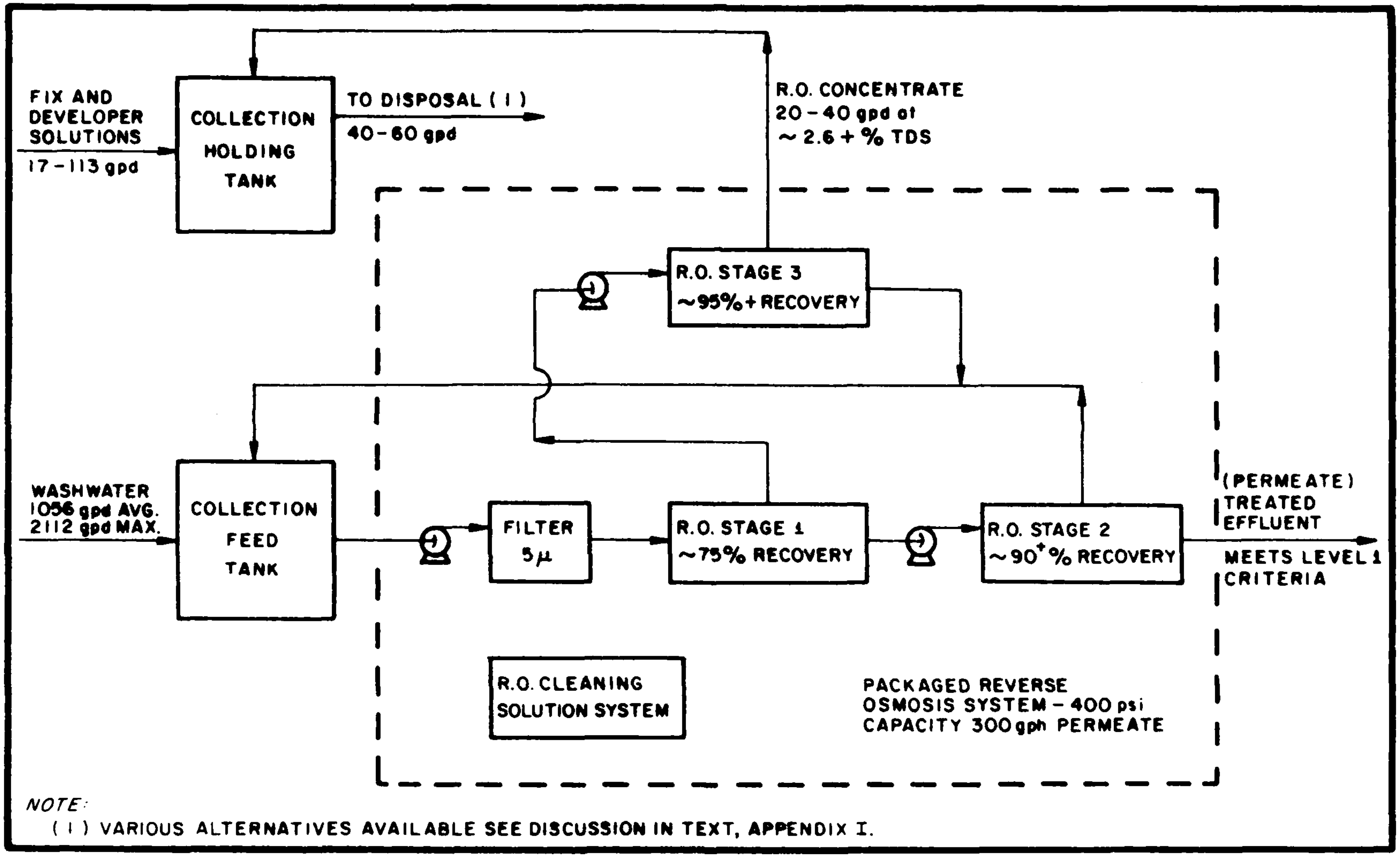
1. Fix, Developer, and R.O. Concentrate Collection and Holding Tank

The volume required would depend on the method selected to package and transport the waste residue (Tanks, drums, tank truck etc.). A minimum size to provide 5 days capacity at average volumes would be about 200 gallons. For maximum production, 5 days capacity would be about 800 gallons. For cost estimating purposes assume an 800-gallon tank with transfer pump rated for approximately 25 gpm at a 25-foot head.

2. Washwater Collection and Feed Tank

Volume (gallons/day) for the 1140 system):

Average - 1050 gallons/8 hours
Maximum - 2100 gallons/8 hours



NOTE:
(1) VARIOUS ALTERNATIVES AVAILABLE SEE DISCUSSION IN TEXT, APPENDIX I.

Figure 14. Conceptual Design Schematic Treatment System for WS 430B Facility

Provide sufficient storage at average flow to permit the R.O. system to be down for 1 day; and for 16-hour operation at maximum flow.

Volume required - 1000 gallons

3. Reverse Osmosis System

Size the system to permit processing the maximum washwater flow in an 8-hour shift. Capacity of permeate production is 300 gph.

Expected Brine flows at 2 percent of permeate production

Average	20 gpd
Maximum	40 gpd

Example: Osmonics, Inc.,

- Packaged system, including a prefilter, 5-micron dual cartridge type;
- Two-stage system for permeate;
- Single-stage recirculation system for concentrate; to concentrate residual for disposal to 2 percent of the volume of final permeate.

E. PRELIMINARY COST ESTIMATE FOR RECOMMENDED TREATMENT SYSTEM

1. Capital Costs

Collection Tanks	
800 gallon with transfer pump	$5,000
1,000 gallon with mixer and chemical feed system	7,000

Reverse Osmosis packaged system 2 stages + 1 stage concentrate including pumps, prefilters - skid-mounted	68,000
Piping and electrical	10,000
Engineering, detailed design/construction	40,000
Total	$130,000

Note that this is a preliminary order-of-magnitude estimate based on equipment budget costs. Range is ± 35 percent with a probability of 80 percent.

2. Annual Operating Costs

Labor - operator 2 hours/day	6,500
Maintenance and membrane replacement	5,000
Chemicals	1,000
Power	500
Total Annual Cost	$13,000

Note that the cost to transport and dispose of concentrated residue is not included.

F. RESIDUAL DISPOSAL

A concentrated residue consisting of the fix and developer solutions and the brine concentrate from R.O. treatment would require final disposal. The actual total volume will depend upon the type of system used (11CN or 1140) and production levels. The following illustrates the design volume for disposal which includes fix and developer and R.O. brine (estimated as 2 percent of the washwater flow):

Production Level	Gallons per Day 11CN System	1140 System
Average	36	38
Maximum	98	155

1. Residual Disposal Alternative Studies

A study commissioned by the Air Force (Reference 6) in 1971 developed and sized an evaporation system incorporating vapor compression evaporation and scraped surface jacketed kettles to produce an 80-percent solids slurry from photoprocessing wastes. The system developed for the concentrate involved extrusion into bricks, drying, coating with asphalt, and transportation to disposal. The system was sized for an average production of 165,000 feet of film daily (about 43 times the average production of the individual WS-430 B facilities). A further study (Reference 10) investigated recovery of the chemicals from the evaporated photowastes, and concluded that recovery of major chemicals is feasible, and could be economically justified. A residual of approximately 10 percent of the chemical would still remain for ultimate disposal. Further pilot plant studies were recommended to evaluate the proposed recovery system.

A study in 1972 (Reference 9) considered alternatives for disposal of evaporated residual from photoprocessing wastes, which included encapsulation, direct disposal to a land fill or a salt sink, recovery of chemicals, reuse by industry, reuse on film, and conversion to glass. The report concluded disposal to a suitable landfill or salt sink was the simplest and least costly recommended method of disposal. A further Air Force study in 1979 (Reference 11) evaluated incorporation of the concentrated photo wastes (before evaporation) into ceramic materials suitable for disposal to a Class 3 landfill. A portable system was sized in addition to a large 10-ton per week photowaste handling system. The ceramics were felt to be products which could be used as insulation materials. No recommendation for implementation or further evaluation was made.

With respect to the mobile WS430 B facilities, onsite handling of the residuals by one of the above techniques does not appear to be feasible. The various evaporation, drying, and encapsulation technologies are substantial in cost and size, and require significant operating skill. The trade-off between transport of the total residue for disposal and onsite handling (for example, by evaporation, condensate treatment, and final residue disposal) involves the consideration of feasibility, available operating personnel, and economics. For purposes of comparison, a conceptual design for an onsite residual handling system to concentrate residuals to a smaller volume for ultimate dispoal offsite was developed, and is presented in Appendix A.

A simple, imperviously lined, and protected evaporation pond could be constructed for long-term storage and liquid evaporation of the concentrated wastes at facilities where it is determined to be feasible. Solar evaporation rates would have to exceed local precipitation; temporary covers may also be required in certain areas. Ultimate disposal of the solid residual would still be required. Alternatives might include removal and transport to a chemical recovery plant, to a secure permanent disposal site or final closure of the pond in an environmentally acceptable manner. Sizing of the pond would be relatively simple and would be based on the planned duration of the campaign at the location. Ponds could also be built in stages when duration of the campaign at a specific location is undeterminable, and suitable long-term solutions are not readily available.

Other alternatives for disposal of the concentrates involve transport to offsite facilities. The cost to transport the concentrates offsite would have to be considered and compared to onsite alternatives. Since a decision depends upon many factors, most of which are specific to each site, a generalized recommendation is not possible.

Offsite facilities may include a large biological treatment facility, a hazardous waste disposal facility, or a chemical recovery facility. These facilities may be publicly or privately owned or actually built by the Air Force specifically to deal with the photoprocessing waste residuals from several WS430 B facilities within a reasonable transport range.

In summary, residual disposal from waste treatment operations remains a difficult problem. Simple to complex solutions, based upon varying degrees of cost effectiveness and feasibility, environmental problems and site-specific factors, must all be compared and evaluated to arrive at a satisfactory solution for any given disposal situation. With respect to the WS430 B there simply is no single optimum solution available which would be applicable to all cases. Those presented in this and other studies provide an array of alternatives which can be considered for each given location. A review of these studies indicates that the most desirable solution from cost, simplicity and environmental acceptability, would involve disposal of the concentrate in an adequately sized municipal treatment system.

Where this is not feasible because of distance and transport costs, further evaluation of available alternatives becomes necessary.

2. Alternatives to an Onsite Treatment System

Discharge of the total waste stream to an adequately sized treatment plant, as discussed previously, would be preferred to onsite treatment. However, when this is not possible, separate collection and handling of the concentrated solutions may permit direct discharge of the washwater to a local facility and therefore, should be considered for each deployment site.

A second alternative at suitable sites is land disposal of the washwater. The potential deployment of the WS430 B to remote sites would imply that large tracts of land may be available for spray disposal. Based on a typical ammonia nitrogen application rate to grassland of 100 pounds/acre/year, about 12 acres would be required for disposal of the washwater at maximum production and about 2 acres would be required at average production. No recommended limits for silver application to land were cited (Reference 17); however, using the maximum recommended cadmium application rate of 8 pounds/acre/year for silver, and an average silver concentration in the washwater of 5 mg/1, about 1 acre per year of application would be required at average washwater flow. Land disposal is site-specific; thus, requirements for each site would have to be developed. The need for a storage pond for holding during inclement weather would have to be determined, as well as the potential for runoff and the specific application system to be used. Land disposal, however, would eliminate the need for the treatment system on the washwater, and would reduce the residual concentrates which would have to be handled.

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APPENDIX A

ONSITE EVAPORATION OF RESIDUAL CONCENTRATED WASTE

APPENDIX A

ONSITE EVAPORATION OF RESIDUAL CONCENTRATED WASTE

A. INTRODUCTION

An evaporation system for onsite reduction of the residue volume consisting of the fix, developer and R.O.concentrate was considered in this study. Such a system would not be recommended if a more feasible alternative were available. Since these alternatives are all site-specific, a direct comparison is not possible. An onsite evaporation system would simply reduce the volume of residue which would require subsequent disposal. Thus, the decision to incorporate a mobile evaporation system with the WS430-B facility would have to be made on the basis of its location, the cost to transport the total residual volume to an acceptable disposal system, and the disposal of the solids from evaporation,either onsite or offsite.

Figure A-1 schematically presents the elements required for the evaporation of the fix and developer solutions and the brine from the washwater treatment system. The evaporation system produces a condensate which is contaminated with ammonia, volatile organics,and sulfur compounds. As such, it will require further treatment.

The effectiveness and potential problems, however, of treating ths condensate by pH adjustment and air stripping or steam distillation could not be defined in this study. The evaporator condensate ammonia concentration is estimated at 2 - 4 percent by weight. The effect of dispersing the ammonia from

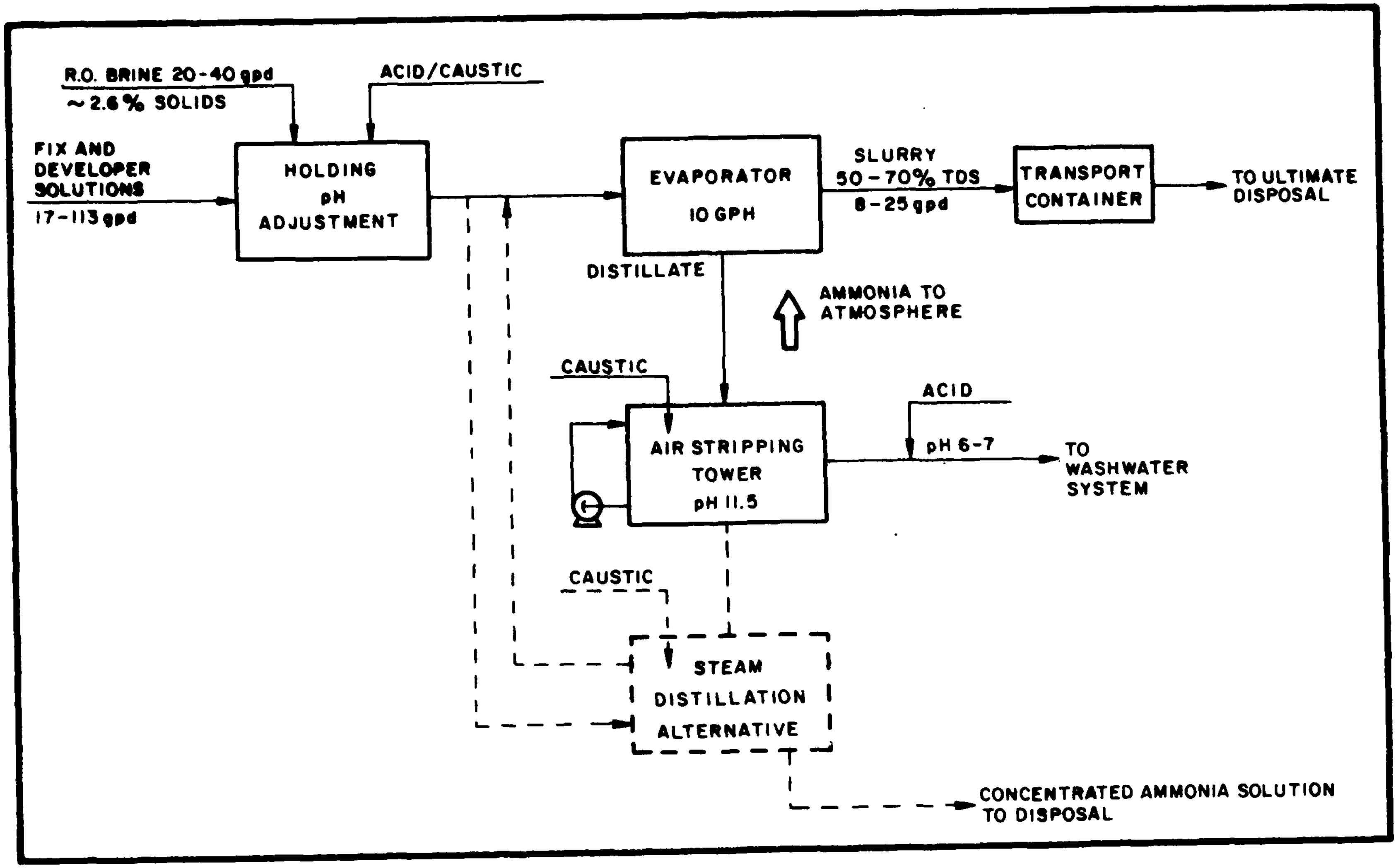

Figure A-1. Conceptual Design Schematic for Fix and Developer and R.O. Concentrate Evaporation System this concentrated solution to the atmosphere by air stripping is of concern. Undoubtedly, odor will be significant; however, the location of the facility in a remote area may not require any special handling, other than adequate dispersion to the atmosphere, so as not to cause facility personnel discomfort during operation of the stripping system. If ammonia cannot be dispensed to the atmosphere because of local regulations or odor problems, distillation would be reqired to extract the ammonia into a more concentrated solution prior to evaporation. Either system would be complex, requiring skilled operation and maintenance, and, thereby, would not meet the project's stated goal concerning the ease of operation and maintenance for a mobile treatment system. Preliminary order-of-magnitude capital and operating costs were estimated for this system and are shown in Table A-1.

B. SIZING OF ONSITE EVAPORATION SYSTEM FOR CONCENTRATED RESIDUE

1. Evaporator

An evaporator would be sized to process the maximum expected volume, 155 gallons, in 16 hours. Selection would be based on standard equipment sizes.

Examples:

- AquaChem Inc.; packaged, single-effect evaporator with a capacity of 10 gallons/hour

- Artisan Industries, Inc.; Rototherm E, 5-square foot unit Capacity of 200 pounds/hour.

2. Evaporator Condensate Air Stripping Tower

Condensate volume max 150 gallons/day
Recirculate over small packaged cooling tower, with excess air, to minimize ammonia odors and facilitate dispersion to atmosphere; caustic feed to adjust pH to >11.5 required for air stripping. Assume manual caustic addition to recycle sump.

Example: Process Construction Inc.; Delta Tower T-101
Air flow 5000 cfm; includes a 6-foot diameter, 4-foot deep sump (800 gal); 1.5-horsepower fan.

3. Alternate Distillation System

In cases where dispersion of ammonia to atmosphere is not feasible because of potential odor problems, or regulations, a closed stripping system would be required. This system would handle the residual solution before evaporation to conserve energy (heating).

A preassembled, skid-mounted system, including heat exchanger, stripping column, pumps and instrumentation, electrical heater, and adsorbing column, would be recommended.

Example:
200 gallons/day ammonia packaged distillation system, APV Equipment Inc.; Tonawanda, New York

4. Slurry Disposal

Estimated final concentration of the residue is 60 percent TDS. The volume would average approximately 10 gallons/day with a maximum of 30 gallons/day.

Drum, ship to ultimate disposal (e.g., secure landfill, chemical recovery etc.), or construct an onsite secure land fill for disposal.

5. Condensate

The condensate after ammonia stripping would contain some contaminants and would be discharged to the washwater treatment system after pH adjustment for final treatment. Note further evaluation of the effect of this stream on performance of the recommended washwater system is required.

TABLE A-1. PRELIMINARY COST ESTIMATE - ONSITE EVAPORATION SYSTEM FOR FIX AND DEVELOPER AND R.O. CONCENTRATE

System	Capital Costs
Evaporation system; 10 gph including electric boiler	$160,000
Air stripping tower, 800 gal sump, recirculation pump, chemical feed tank and pump	$8,000
Alternate distillation system ($40,000 - $60,000)	
Piping and electrical allowance -	50,000
Engineering detail design/construction allowance	50,000
Total	$268,000

Note - preliminary order-of-magnitude estimate based on equipment budget estimates
range ± 35 percent
probability 80 percent

- Mobile housing not included. System skid-mounted ready for piping and electrical connections.

TABLE A-1 (CONCLUDED)

	Annual Cost[1]
Labor - Full time operator/maintenance	$25,000
Maintenance Materials and Supplies at 10% of equipment cost	17,000
Power - 110 kw	25,000
Chemicals - Caustic/Acid	2,000
Total	$69,000

[1] Disposal of 2000-4000 gal of 60% slurry/year not included in annual costs.

APPENDIX B

BENCH TREATABILITY TEST DATA TABLES

TABLE B-1. METALS PRECIPITATION JAR TESTS - TOTAL DISCHARGE

Test No.	Treatment	Dosage	pH	Supernatant Concentrations Fe (mg/l)	Ag (mg/l)	Cd (mg/l)	Al (mg/l)
1	None	-	7.8	140	0.5	0.3	-
	NaOH	.052 eq/l	10	230	0.1	0.5	-
	NaOH/BH_4	.05 eq/l 50 mg/l BH_4^+	10	220	0.2	0.4	-
	lime	.076 eq/l	10	11	0.15	0.4	-
2	None	-	7.45	130	0.7	-	70
	NaOH	.084 eq/l	10.5	100	0.14	-	54
	NaOH	.096 eq/l	11.8	98	0.12	-	33
	NaOH	.108 eq/l	12.0	106	0.1	-	33
3	None	-	7.8	178	0.19	-	54
	NaOH *	.095 eq/l	11.8	36	0.07	-	55
	H_2SO_4*	.009 eq/l	9.0	9.5	0.04	-	61
	H_2SO_4	.017 eq/l	7.0	10.2	0.04	-	63

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* Treatment was after ammonia distillation of sample, analysis done on filtered sample.

TABLE B-2. METALS PRECIPITATION JAR TESTS WITH LIME AND POLYMER - TOTAL DISCHARGE

Test 4 Batch 7 Total Discharge
Fe (mg/l): 185
Cd (mg/l): 0.10
Cr (mg/l): 0.11
Sample Volume: 500 ml

Jar No.	1	2	3	4	5	6
Initial pH	7.8	7.8	7.8	7.8	7.8	7.8
Lime (gm/l)	0.2	0.3	0.4	0.6	0.8	1.0
Polymer (mg/l)	4	4	4	4	4	4
Sludge Vol. (mls)	0	0	10	25-50	75	100
Sludge Obs.	Very Fine	Very Fine	Very Fine	Fine	Fine	Fluffy
Supt. Obs.	Cloudy	Cloudy	Cloudy	Cloudy	Slightly Transparent	Transparent

Jar No.	7	8	9	10	11	12
Initial pH	9.0	9.0	9.0	9.0	9.0	9.0
Lime (gm/l)	0.1	0.2	0.3	0.4	0.6	1.0
Polymer (mg/l)	4	4	4	4	4	4
Sludge Vol. (mls)	<10	<10	<10	<10	<10	<10
Sludge Obs.	Stringy	Stringy	Fine	Fine	Fine	Fine
Supt Obs	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy
Supt pH	-	-	-	-	-	-
Fe (mg/l)	-	-	-	-	-	-

Test 4 (continued)

Jar No.	13	14	15	16
Initial pH	7.8	7.8	7.8	7.8
Lime (gm/l)	1.0	1.0	1.0	1.0
Polymer (mg/l)	1	2	4	6
Sludge Vol (mls)	250	100	100	100
Sludge Obs	Fine	Large	Fine	Fine
Supt Obs	Cloudy	Transparent	Transparent	Transparent
Fe (mg/l)	24	17	21	27

TABLE B-2. METALS PRECIPITATION JAR TESTS WITH LIME AND POLYMER - TOTAL DISCHARGE (CONCLUDED)

Test 5 Batch 8 total discharge
Sample Volume: 1 liter

Jar No.	1	2	3	4	5	6
Initial pH	7.8	7.8	7.8	7.8	7.8	7.8
Lime (gm/l)	1	1.25	1.5	2	2.5	5
Polymer (mg/l)	3	3	3	3	3	3
Sludge Vol. (mls)	0	0	150	125	100	100
Sludge Obs.	Slow	Slow	Fast	Fastest	Fast	Fast
Supt. Obs.	Cloudy	Cloudy	Transparent	Transparent	Transparent	Cloudy
Supt. pH	-	-	9.3	9.45	9.7	12.0
Fe (mg/l)	-	-	13.3	8.5	9.0	8.2

Jar No.	7	8	9	10	11	12
Initial pH	7.8	7.8	7.8	7.8	7.8	7.8
Lime (gm/l)	2	2	2	2	2	2
Polymer (mg/l)	0.5	1	2	3	4	5
Sludge Vol (mls)	250	200	125	100	100	125-150
Sludge Obs.	Fine/Slow	Fine/Slow	Fine/Slow	Fine/Slow	Medium/Quick	Medium/Quick
Supt. Obs.	Suspended Fines	Suspended Fines	Clear	Clear	Clear	CLear
Supt pH	9.4	9.4	9.4	9.4	9.4	9.4
Fe (mg/l)	-	12.9	9.6	10.9	10	10.4
Ag (mg/l)	-	-	0.10	-	0.10	-

Sludge Obs. - Relative observation of floc settling.
Supt. Obs. - Relative observation of clarity of supernatant after settling

TABLE B-3. METALS PRECIPITATION JAR TEST - TOTAL DISCHARGE - PRETREATED BY AMMONIA STRIPPING

Test 6 Batch 9 Total Discharge - Pretreated by Ammonia Stripping

Initial Concentration

Cd (mg/l) -	0.10
Cr (mg/l) -	0.08
Ag (mg/l) -	0.20
Sample Volume:	500 ml

Jar No.	1	2	3	4	5	6
Initial pH	9.5	9.5	9.5	9.5	9.5	9.5
Lime (gm/l)	0.4	0.8	1.2	1.6	2.0	2.4
Polymer (mg/l)	2	2	2	2	2	2
Sludge Vol.	0	75	75	75	100	75
Sludge Obs.	None	Fine	Fine	Fine	Fine	Fine
Supt. Turbidity (NTU)	82	26	77	120	140	100
Supt pH	10.9	11.6	11.85	12.05	12.1	12.2
Ag (mg/l)	0.23	0.21	0.20	0.20	-	-
Cd (mg/l)	0.12	0.09	0.09	0.08	-	-
Cr (mg/l)	0.12	0.08	0.05	0.05	-	-

TABLE B-4. METALS PRECIPITATION JAR TESTS-(WASHWATER)

Test No.	Treatment	Dosage (mg/l)	pH	Fe (mg/l)	Ag (mg/l)	Cd (mg/l)	Cr^{tot} (mg/l)
1	None	-	6.0	28	<.04	<.02	-
	NaOH	1268	12.0	6.3	<.04	<.02	-
2	None	-	6.1	28	-	<.02	<.05
	NaOH	1280	12.4	3.8	-	<.02	<.05

TABLE B-5. METALS PRECIPITATION JAR TESTS - WASHWATER PRETREATED BY AMMONIA STRIPPING

Test 3

Initial Concentrations

NH_3-N:	40 mg/l	
	Alk:	1240 mg/l as $CaCO_3$
	pH:	11.8
	Fe (mg/l):	34
	Ag (mg/l):	.04
	COD (mg/l):	564

Jar No.	1	2	3	4	5	6
H_2SO_4(as mg/l $CaCO_3$)	0	800	670	970	870	850
pH	11.8	9.4	10.1	6.0	6.2	8.7
Polymer (mg/l)	0.5	1.0	0.5	0.5	0.5	0.5
Sludge Obs	Fair	Clumpy	Good	Fine	Fair	Good
Supt Obs	pin floc	clear	clear	pin floc	pin floc	clear
Fe (mg/l)	5.5	5.7	2.7	3.71	7.5	5.2
Fe Filtered (mg/l)	-	-	1	3.2	-	3.7
Ag (mg/l)	-	-	<.03	-	-	.03
COD (mg/l)	557	557	549	-	-	549
Supt SS (mg/l)	134	113	126	132	108	92

TABLE B-5. METALS PRECIPITATION JAR TESTS - WASHWATER PRETREATED BY AMMONIA STRIPPING (CONCLUDED)

Test 4 Batch 5

Initial Concentrations

Al (mg/l):	28
Cd (mg/l):	<.02
Cr (mg/l):	<.06
Ag (mg/l):	9.5

Jar No.	1	2	3	4	5
pH	9	9	9	10	10
Polymer (mg/l)	1	2	3	1	2
Turbidity (NTU)	4.2	3.5	5.2	2.0	2.9
Sludge Obs	Fine	Fine	Fine	Large	Fine
Al (mg/l)	-	-	-	12 (13.3)	-
Cd (mg/l)	-	-	-	<.02(<.02)	-
Cr (mg/l)	-	-	-	<.06(<.06)	-
Ag (mg/l)	-	-	-	9.8(5.4)	-

Jar No.	6	7	8	9	10
pH	10	9	9	10	10
Polymer (mg/l)	3	.5	.2	.5	.2
Turbidity (NTU)	4.2	4.1	6.8	2.7	2.6
Sludge Obs.	Fine	Fine	Fine	Large	Large
Cd (mg/l)	-	-	-	<.02	-
Cr (mg/l)	-	-	-	<.06	-
Ag (mg/l)	-	-	-	6.7	-

Note: Values in ( ) are on filtered samples

TABLE B-6. METAL PRECIPITATION JAR TESTS— WASHWATER PRETREATED BY AMMONIA STRIPPING

Test 5 Batch 6

Initial Concentrations

Al (mg/l):	28
Cd (mg/l):	<.02
Cr (mg/l):	<.06
Ag (mg/l):	9.5

Jar No.	1	2	3	4	5
pH initial	10	1	10	10	10
Polymer (mg/l)	1	1	1	1	1
EPS* (mls/l)	2	6	10	14	.2
pH final	9.9	9.9	9.9	9.9	9.9
Turbidity	3.5	3.7	10	7	2.1
Ag (mg/l)	1.57(.21)	-	-	-	-
Cd (mg/l)	<.02(<.02)	-	-	-	-
Cr (mg/l)	<.06(<.06)	-	-	-	-
Al (mg/l)	11.2(10.8)	-	-	-	-

Jar No.	6	7	8	9
pH	10	11.2	5.2	10
Polymer (mg/l)	1	1	1	1
EPS* (mg/l)	1	1	2	2
Turbidity	1.2	1.0	1.0	1.0
Cd (mg/l)	<.02	<.02	<.02(<.02)	<.02(<.02)
Cr (mg/l)	<.06	<.06	<.06(<.06)	<.06(<.06)
Ag (mg/l)	6.6	6.4	2.24(1.56)	1.86(1.64)

* - 100 x dilution of stock EPS

Note - Values in ( ) are on filtered samples

TABLE B-7. OXIDATION BY AERATION - TOTAL DISCHARGE

Test 1

Batch 1
Sample Volume: 2 liters
pH: 10.0

Time (min)	SO_3 (mg/l)	SO_3 (%) Removed
0	1945	0
10	1890	2.8
20	1750	10.0
25	1740	10.5
32	1740	10.5
45	1680	13.6
65	1680	13.6
120	1650	15.0
260	1590	18.3

TABLE B-8. HYDROGEN PEROXIDE OXIDATION JAR TESTS - TOTAL DISCHARGE

Test 1 No Pretreatment

H_2O_2 Dose (mg/l)	0	300	600	900	1200	1500	1800	2100	2400
SO_3 (mg/l)	1900	1140	920	720	460	375	70	12.5	7
pH		8.4		7.8		6.4		5.7	5.6
H_2O_2/SO_3	0	.16	.32	.47	.63	.79	.95	1.11	1.26
% Removal SO_3	0	40	52	62	76	80	96	99.3	99.6

Test 2 No Pretreatment

H_2O_2 Dose (mg/l)	0	300	600	900	1200	1500
SO_3 (mg/l)	2260	1460	1100	795	680	500
COD (mg/l)	7400	7173	6695	6375	5898	-
H_2O_2/SO_3	0	.133	.265	.398	.531	.644
% Removal SO_3	0	35.4	57.3	64.8	69.9	77.9
% Removal COD	0	3.1	9.5	13.8	20.3	-

Test 3 No Pretreatment

H_2O_2 Dose (mg/l)	0	300	600	900	1500	2500	3500
SO_3 (mg/l)	1950	1180	1010	910	710	580	40
pH	7.6	8.5	8.5	8.4	8.3	8.0	-
H_2O_2/SO_3	0	.154	.308	.462	.769	1.28	1.79
% Removal SO_3	0	39.5	48.2	53.3	63.9	70.3	97.9

Test 4 No Pretreatment

H_2O_2 Dose (mg/l)	0	150	300	450	600	750	900	1050
SO_3 (mg/l)	2350	2000	1550	1200	975	80	700	648
H_2O_2/SO_3	0	.06	.13	.19	.26	.32	.38	.45
% Removal/SO_3	0	15	34	49	59	66	70	73

TABLE B-8. HYDROGEN PEROXIDE OXIDATION JAR TESTS— TOTAL DISCHARGE (CONCLUDED)

Test 4 (continued)

H_2O_2 Dose (mg/l)	1200	1350	1500	1800	2100	2400	2700	2850
SO_3 (mg/l)	580	520	460	305	265	175	100	5
H_2O_2/SO_3	.51	.57	.64	.76	.89	1.02	1.15	1.21
% Removal SO_3	75	78	80	87	89	93	96	99.8

Test 5 No Pretreatment

H_2O_2 Dose (mg/l)	0	150	300	450	600	675	750	900
SO_3 (mg/l)	2125	1825	1375	1125	1000	980	920	730
H_2O_2/SO_3	0	.071	.141	.212	.282	.318	.353	.424
% Removal SO_3	0	14.1	35.3	47.1	52.9	53.9	56.7	65.6
H_2O_2 Dose (mg/l)	1050	1125	1350	1500	1650	1725		
SO_3 (mg/l)	560	430	280	140	50	25		
H_2O_2/SO_3	.494	.529	.635	.706	.776	.812		
% Removal SO_3	73.6	79.8	86.8	93.4	97.6	98.8		

Test 6 No Pretreatment pH 7.9

H_2O_2 Dose (mg/l)	0	60	180	300	450	600	900	1200	1500	1800	2100
SO_3 (mg/l)	2160	1910	1600	1450	1080	940	770	476	265	147	20
COD (mg/l)	5279	4742	5117	4992	4928	4730	4181	4555	4493	4181	4077
H_2O_2/SO_3	0	.03	.08	.14	.21	.28	.42	.56	.69	.83	.97
% Removal SO_3	0	11.6	26	33	50	56.5	64	78	88	93	99
% Removal COD	0	10.1	3.1	5.4	6.6	10.4	20.8	13.7	14.9	20.8	22.8

Test 7 Pretreatment by Ammonia Stripping and Polymer/Lime Metals Precipitation pH 9.0

H_2O_2 Dose (mg/l)	0	300	600	900	1500	2100	3000
SO_3 (mg/l)	1917	1170	940	770	460	43	0
COD (mg/l)	5279	5018	-	4809	4469	4443	-
H_2O_2/SO_3	0	.156	.313	.470	.782	1.10	1.56
% Removal SO_3	0	39	51	60	76	98	100
% Removal COD	0	4.9	-	8.9	15.3	15.8	-

TABLE B-9. HYDROGEN PEROXIDE OXIDATION JAR TESTS WASHWATER

Test 1 Batch 1 No Pretreatment

H_2O_2 Dose (mg/l)	0	16	32	48	79	95	174
SO_3 (mg/l)	165	136	113	121	70	65	3
COD (mg/l)	490	-	-	-	-	-	408
H_2O_2/SO_3	0	.100	.194	.291	.490	.576	1.05
% Removal SO_3	0	18	32	27	58	61	98
T Removal COD	0	-	-	-	-	-	16.7

Test 2 Batch 4 No Pretreatment

H_2O_2 Dose (mg/l)	0	30	60	90	120	180	210	240	270	300	360
SO_3 (mg/l)	215	172	148	120	95	70	61	44	29	27	14
COD (mg/l)	540	518	518	490	475	439	-	-	-	-	-
pH	8.1	8.15	8.2	8.2	8.15	8.1	8.0	8.0	7.9	7.8	7.5
H_2O_2/SO_3	0	.14	.28	.42	.56	.84	.98	1.12	1.26	1.40	1.67
% Removal SO_3	0	20	31	44	56	67	72	80	86	87	93
T Removal COD	0	4.1	4.1	9.3	12.0	18.7	-	-	-	-	-

Test 3 Batch 5 Pretreated by Ammonia Stripping and Metals precipitation by polymer addition

H_2O_2 Dose (mg/l)	0	60	120	240	300	360	480
SO_3 (mg/l)	295	250	217	170	125	70	30
pH	9.9	-	-	-	-	-	-
H_2O_2/SO_3	0	.20	.40	.81	1.0	1.22	1.63
% Removal SO_3	0	15	26.4	42.4	51.6	76	90

TABLE B-10. HYDROGEN PEROXIDE OXIDATION TOTAL DISCHARGE

Test 1 Batch 1 pH 7.8

H_2O_2 Dose: 6000 mg/l; 3.15 mg H_2O_2/mg SO_3

Time (min)	SO_3 (mg/l)
0	1900
2	310
3	110
5	55
7	35
10	18

Test 2 Batch 1 pH 7.8

H_2O_2 Dose: 3000 mg/l; 1.58 mg H_2O_2/mg SO_3

Time (min)	SO_3 mg/l
0	1900
5	338
7	255
30	17

Test 3 Batch 8 pH 9.1 Pretreatment by polymer/lime metals precipitation.

H_2O_2 Dose: 1734 mg/l or .83 mg H_21_2/mg SO_3

Time (min)	SO_3 (mg/l)
0	2150
5	750
15	400
25	280
40	195
60	205

TABLE B-10. HYDROGEN PEROXIDE OXIDATION - TOTAL DISCHARGE (CONCLUDED)

Test 4 Batch 9 pH 9.0 Pretreatment by polymer/lime
metals precipitation and ammonia stripping.
H_2O_2 Dose: 2076 mg/l or 1.09 mg H_2O_2/mg SO_3

Time (min)	SO_3 = (mg/l)
0	1900
1.5	780
4	660
6.5	535
9.5	480
24.5	225
70	103
120	96
150	75
204	77

TABLE B-11. HYDROGEN PEROXIDE OXIDATION OF WASHWATER

Test 1 Batch 2 pH 9.0; Pretreatment by ammonia stripping

H_2O_2 Dose: 420 mg/l or 2.2 mg H_2O_2/mg SO_3

Time (min)	SO_3 (mg/l)
0	190
1	185
5	170
30	60
40	45
50	25
80	18
120	0

TABLE B-12. CHLORINE OXIDATION OF TOTAL DISCHARGE

Test 1 Batch 5 Pretreated by Ammonia Stripping and Peroxide Oxidation, pH maintained at 8.3

Cl_2 Dose (mg/l)	SO_3 (mg/l)	NH_3 (mg/l)	COD (mg/l)	Chemical Required to Maintain pH 8.3 (mg/l $CaCO_3$)
0	167	44	5040	
33	145	-	-	
99	130	33	-	
166	110	29	-	
265	85	32	-	7600
364	55	-	-	
464	40	32	-	6202
563	30	29	-	5000
663	20	28	-	
762	15	-	-	
861	5	29	-	7600
961	5	22	-	-
1093	0	18	-	10,000
1226	0	16.6	-	
1358	0	13.2	-	5000
1491	0	8.3	-	5000
1623	0	3.6	-	5000
1756	0	1.7	3600	-

Note: Total Alkalinity Consumed: 51,400 mg/l $CaCO_3$

TABLE B-13. BREAKPOINT CHLORINATION OF TOTAL DISCHARGE

Test 2 Batch 9 Total Discharge Pretreated by Ammonia Stripping, Metals Precipitation and Peroxide Oxidation

pH: 8.4
COD initial: 4260 mg/l

Cl_2 Dose (mg/l)	SO_3 (mg/l)	NH_3-N (mg/l)	COD (mg/l)	Cl_2 Residual (mg/l)	pH
0	76	20	4260	0	8.4
52	66	16	4103	0	8.2
260	46	13	3842	-	6.8
520	24	10	4280	0	5.3
1040	0	10	3840	5	3.5
1560	0	9	-	33	2.4
2080	0	8	-	75	-
2600	0	6	3320	108	1.7
3120	0	0	2800	453	1.9
4160	0	0	-	2160	3.3
5200	0	0	-	4248	6.1

TABLE B-14. BREAKPOINT CHLORINATION OF SIMULATED WASHWATER

Test 1 Batch 2 Pretreated by Ammonia Stripping
Initial pH: 8.3

Cl_2 Dose (cumulative) (mg/l)	SO_3 (mg/l)	NH_3-N (mg/l)	Cl_2 Residual (mg/l)	COD (mg/l)	TOC (mg/l)
0	190	10.0	0	502	62
65.5	135	10.0	0		
131.5	90	6.5	0		
197	10	3.5	0		
262.5	0	<1.0	12.5		
328	0	<1.0	17.5		
394	0	<1.0	14		
459.5	0	<1.0	16		
590.5	0	<1.0	5.5		
721.5	0	<1.0	85		
787.5	0	<1.0	156		
853	0	<1.0	234		
984.5	0	<1.0	372		
1050	0	<1.0	461	274	60

Test 2 Batch 5 Pretreated by Ammonia Stripping, Metals Precipitation and Peroxide Oxidation
Initial pH: 8.7

Cl_2 Dose (mg/l)	SO_3 (mg/l)	NH_3-N (mg/l)	Cl_2 Residual (mg/l)	COD (mg/l)
0	0	15	0	551 (est)
52	0	13	5	
91	0	13	6	
130	0	13	5	272
156	0	13	3	
182	0	13	3.6	
208	0	13	3	
260	0	8	0.1	238
312	0	8	0.1	
364	0	7	0.4	
416	0	6	1.5	
468	0	1	3	200
520	0	0	6	176
624	0	0	195	-
780	0	0	390	

TABLE B-15. CHLORINE/UV OXIDATION OF SIMULATED WASHWATER

Batch 2 Pretreated by Ammonia Stripping, pH Adjusted to 5.0 (after Cl_2 Dose)
Sample Volume: 3.0 liter
Chlorine Dose: 1040 mg/l Cl_2
U.V. Source: Conrad-Hanovia 7825-3 Immersion Lamp

Time (min)	Cl_2 Residual (mg/l)	pH	SO_3 (mg/l)	NH_3-N (mg/l)	COD (mg/l)	TKN (mg/l)	TOC (mg/l)
Initial	-		190	7.7	496	13	62
0	343	5.0	0	0.30	740	43	-
5	310	4.1	0	0.33	434	21	42
30	243	4.1	0	0.18	302	21	54
50	191	3.4	0	<.1	376	125	50
70	152	3.2	0	-	285	103	50
90	163	-	0	<.1	426	28	50
180	131	3.1	0	<.1	155	80	46.5
220	120	3.1	0	-	147	-	46
260	97	3.1	0	-	264	-	45
290	106	3.1	0	-	260	-	44

TABLE B-16. HYDROGEN PEROXIDE/UV OXIDATION OF TOTAL DISCHARGE

Test 1	Batch 2	
	Sample Volume:	3 liters
	H_2O_2 Dose:	Incremental
	pH initial:	7.6
	UV Source:	Conrad-Hanovia 7825-3 immersion/amp (11.49 watts radiated energy)

H_2O_2 Dose (mg/l)	pH	SO_3 (mg/l)	H_2O_2 Residual
0	7.6	1950	depleted
300	8.5	1180	depleted
600	8.5	1010	depleted
900	8.4	910	depleted
1500	8.3	710	depleted
2500	8.0	580	depleted
3500	5.4 (aft 1 hr)	40	present 5 hours

TABLE B-17. AMMONIA STRIPPING TESTS

Test 1	Batch 3	Total Discharge
Sample Volume	1.5 liters	
pH	12.3	
eg/l OH^-:	.133	
Waste flow:	100 ml/min	
Air Flow:	0.6 CFM	

Time	NH_3-N mg/l	CF gal	% Removal
0	1100	-	-
16	800	23	27
29	720	45	35
40	620	68	44
50	550	91	50
58	480	113	56
66	410	136	63
72	390	159	65
78	350	182	68
83	310	204	72
87	270	227	75
92	260	250	76
95	250	272	77
101	220	318	80

TABLE B-18. AMMONIA STRIPPING TESTS

Test 2	Batch 3	Total Discharge
	Sample Volume:	1.5 liters
	pH:	12.0
	eq/l OH^-	.113
	Waste Flow:	100 ml/min (0.24 gpm/sf)
	Air Flow:	0.9 CFM

Time (min)	NH_3-N (mg/l)	CF/gal	% Removal
0	1900	0	0
20	1400	45	26
44	1000	101	47
71	900	164	53
94	450	214	76
105	530	240	72
162	200	368	89
403	35	916	98

Test 3	Batch 3	Total Discharge
	Sample Volume:	1.5 liters
	pH:	12.0
	eq/l OH^-	.117
	Waste Flow:	100 mls/min (0.24 gpm/SF)
	Air Flow:	0.5 CFM

Time (min)	NH_3-N (mg/l)	CF/gal	% Removal
0	1000	0	0
24	880	30.3	12
54	600	68	40
86	450	108	55
113	500	144	50
180	330	227	67
204	280	257	72
249	230	315	77
309	160	391	84
344	100	434	90
428	33	540	97
484	64	598	96
514	13	648	99

TABLE B-19 AMMONIA STRIPPING TESTS

Test 4 Batch 3 Total Discharge
Sample Volume: 1.5 liters
pH: 12.3
eq/l OH^- 0.10
Waste Flow: 100 mls/min (0.24 gpm/SF)
Air Flow: 2 CFM

Time (min)	NH_3-N (mg/l)	CF/gal	% Removal
0	1000	0	0
10	600	51	40
20	500	101	50
30	430	151	57
40	330	202	67
50	300	252	70
120	100	606	90
170	56	858	95
235	18	1186	98
265	15	1337	99

Test 5 Batch 4 Total Discharge
Sample Volume: 2 liters
pH: 12.2
eq/l OH^- 0.1
Waste Flow: 500 mls/min (1.2 gpm/SF)
Air Flow: 0.5 CFM

Pass No.	NH_3-N (mg/l)	CF/gal	% Removal
0	1600	0	0
1	1200	3.8	25
3	1000	11	38
5	920	19	43
7	800	26	50
9	750	34	53
11	700	42	56
12	600	45	63

TABLE B-20. AMMONIA STRIPPING TESTS

Test 6 Batch 4 Total Discharge

Sample Volume:	2 liters
pH:	12.5
eq/l OH^-	.125
Waste Flow:	500 mls/min (1.2 gpm/SF)
Air Flow:	1 CFM

Pass No.	NH_3-N (mg/l)	CF/gal	% Removal	COD
0	1000 (885)	0	0	6193
1	755 (799)	8	25	-
3	695	23	31	-
5	649	38	36	-
7	541	53	46	-
9	540	68	46	-
11	477 (509)	83	53	5723
15	387	113	61	-
20	327	151	67	-
24	277	181	72	-
28	225	211	77	-
32	190	242	81	-
36	148 (127)	272	85	5566

Note - Values in ( ) are laboratory analytical values

Test 7 Batch 5 Total Discharge Pretreatment by Peroxide Oxidation

Sample Volume:	1.25 liters
pH:	12.5
eq/l OH^-	0.12
Waste Flow:	500 mls/min (1.2 gpm/SF)
Air Flow:	1.5 CFM

Time (min)	NH_3-N (mg/l)	CF/gal	% Removal
0	955	0	0
5	794	23	17
10	661	45	31
15	525	68	45
20	478	81	50
30	398	136	58
40	302	182	68
50	240	227	75
67	158	304	83
79	132	358	86
93	100	422	89
120	69	545	93
138	44	627	95

TABLE B-21. AMMONIA STRIPPING TESTS

Test 8	Batch 1	Washwater
	Sample Volume:	2 liters
	pH:	
	eq/l OH^-	
	Waste Flow:	500 mls/min (1.2 gpm/SF)
	Air Flow:	20 CFM

Time (min)	NH_3-N (mg/l)	CF/gal	% Removal
0	134	0	0
3	128	11.4	4.5
7	122	26.5	9
10	117	37.8	12.7
12	112	45.4	16.4
15	102	56.8	23.9
18	98	68	26.9
20	93	76	30.6
23	89	87	33.6
29	72	91	46.3
37	65	140	51.5
48	52	180	61.2
60	42	227	68.7
68	37	257	72.4
73	33	276	75.4
87	25	329	81.3
98	19	371	85.3
104	17 (16)	393	87.3

Note: ( ) Laboratory Analytical Values

TABLE B-22. AMMONIA STRIPPING TESTS

Test 9 Washwater

Sample Volume: 4 liters
pH: 11.3
eq/1 OH^- 0.023

Waste Flow: 525 mls/min (126 gpm/SF)
Air Flow:

Pass No.	NH_3-N (mg/l)	CF/gal	% Removal
0	160 (189)	-	0
1	125	72	22
2	72	144	55
3	56	215	65
4	42	288	74
5	28	360	83
6	19	432	88
7	13	504	92
8	10	576	94
9	7.2	648	96
10	5.0	720	97
11	3.4	792	98
12	2.7	864	98
13	2.0 (1.2)	936	99

Note - ( ) Laboratory Analytical Values

Test 10 Total Discharge

Sample Volume: 10 gal
pH 11.0
eg/1 OH^- .086
Waste Flow: 570 mls/min
Air Flow: 10 cfm estimated
Recirculated for approximately 14 hours
Final Ammonia N -10 mg/1
Initial Ammonia: 1000 g/1 estimated

Test 11 Washwater

Sample Volume: 10 gal
pH: 11.1
eg/1 OH^- .02
Waste Flow: 525 mls/min
Air Flow: 10 cfm estimated
Recirculated: 14 hours
Initial Ammonia: 86 g/1
Final Ammonia: 3.5 mg/1

TABLE B-23. CARBON ISOTHERM DATA - TOTAL DISCHARGE SAMPLES

Carbon: Pulverized Calgon Filtrasorb® 300 (150-325 mesh)

Test 1
Sample: Simulated Total Discharge pH 7.45

Carbon Dose (gm)	Sample Volume (mls)	COD (mg/l)	TOC (mg/l)	SO_3 (mg/l)	COD_r (mg/l)	X/M COD_r g/g Carbon
0	-	6700	1434	2330	-	-
0.5	100	5148	1308	1450	1552	0.31
1.0	100	4446	1086	1300	2254	0.23
2.0	100	3588	576	1250	3112	0.16
5.0	100	3042	561	1070	3608	0.073
10.0	100	2574	368	1050	4126	0.041
20.0	100	2340	297	980	4360	0.022

Test 2
Sample: Simulated Total Discharge pH 4.5

Carbon Dose (gm)	Sample Volume (mls)	COD (mg/l)	TOC (mg/l)	SO_3 (mg/l)	COD_r (mg/l)	X/M COD_r g/g Carbon
0	-	6700	1434	2330	-	-
0.5	100	4758	1145	1200	1942	0.39
1.0	100	4134	1029	1190	2566	0.26
2.0	100	3666	840	1140	3066	0.15
5.0	100	3276	846	1140	3424	0.069
10.0	100	2652	350	1140	4048	0.04
20.0	100	2340	257	860	4360	0.022

Test 3
Sample: Simulated Total Discharge Pretreated with H_2O_2 to oxidize SO_3 and S_2O_3. pH 8.1

Carbon Dose (gm)	Sample Volume (mls)	COD (mg/l)	TOC (mg/l)	SO_3 (mg/l)	COD_r (mg/l)	X/M COD_r g/g Carbon
0		4900				
0.5	100	3354	1272	270	1546	0.31
1.0	100	3588	1142	200	1312	0.13
2.0	100	3200	975	210	1700	0.085
5.0	100	2240	555	410	2660	0.053
10.0	100	1760	378	320	3140	0.031
20.0	100	1170	347	100	3730	0.019

TABLE B-24. CARBON ISOTHERM DATA – WASHWATER SAMPLES

Test 4

Sample: Simulated Washwater Pretreated by ammonia stripping, peroxide oxidation, breakpoint chlorination and dechlorination. pH 7.8

Carbon Dose (gm)	Sample Volume (mls)	COD (mg/l)	TOC (mg/l)	COD_r (mg/l)	X/M COD_r g/g Carbon
0		408			
0.1	100	301	57	107	0.107
0.2	100	231	59	177	0.089
0.5	100	235	54	173	0.035
1.0	100	220	58	188	0.019
2.0	100	188	47	220	0.011
5.0	100	176	52	232	0.005
10.0	100	120	22	288	0.003
20.0	100	56	23	352	0.0018

Test 5

Sample: Simulated Washwater Pretreated by ammonia stripping, peroxide oxidation and breakpoint chlorination to 3 mg/l Chlorine Residual. pH 7.8

Carbon Dose (gm)	Sample Volume (mls)	COD (mg/l)	TOC (mg/l)	COD_r (mg/l)	X/M COD_r g/g Carbon
0		511			
0.1	100	312	82	259	.259
0.2	100	293	82	278	.139
0.5	100	273	78	298	.0596
1.0	100	242	73	329	.0326
2.0	100	211	64	360	.018
5.0	100	211	76	360	.0072
10.0	100	166	56	411	.004
20.0	100	133	61	438	.0022

TABLE B-25. CARBON COLUMN BREAKTHROUGH TESTS - WASHWATER

Test A

Carbon: 195 gms Calgon Filtrasorb® 300

Sample: Simulated Washwater; Batch 4 at pH 7.0; after pretreatment by ammonia stripping; metals precipitation by polymer addition; peroxide oxidation; and breakpoint chlorination.

Flow: 47 mls/min (1.01 gpm/sf)

Influent COD: 245 mg/l

Empty Column Detention Time: 8.6 min

Time (min)	COD (mg/l)
0-2	-
2-4	8
4-6	4
6-8	12
8-10	50
15	88
20	120
30	133
45	153
60	172
90	161
120	169
150	153
180	157

TABLE B-25. CARBON COLUMN BREAKTHROUGH TESTS - WASHWATER (CONCLUDED)

Test B

Carbon: 400 gms Calgon Filtrasorb® 300

Sample: Washwater at pH 6.8 after pretreatment by ammonia stripping, metals precipitation, peroxide oxidation and breakpoint chlorination.

Flow: 47 mls/min (1.01 gpm/sf)

Influent COD: 272 mg/l

Empty Column Detention Time: 18.8 min

Time (min)	COD (mg/l)
3-5	6
5-7	6
9-11	6
11-13	6
15-17	19
20-22	9
30-32	54
43-45	76
60-62	107
80-82	107
100-102	140
120-122	131

TABLE B-26. WASHWATER BIOLOGICAL TREATABILITY STUDY

		INFLUENT	EFFLUENT										
			7/19	7/20	7/21	7/22	7/23	7/25	7/26	7/27	7/28	7/29	7/30
Flow (mls/min)		10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Total detention time (days)		-	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	-	-
pH	influent	-	10.1	10.0	9.8	9.45	9.9	-	9.2	9.2	8.9	-	-
	effluent	-	6.95	7.75	8.2	7.4	7.6(1)	8.9	8.35(2)	8.45	8.5	-	-
Alkalinity	influent	-	420	400	390	370	460	-	540	580	604	-	-
	effluent	-	-	<80	70	90	108	-	190	300	368	-	-
(mg/l as $CaCO_3$)													
NH_3-N (mg/l)		20 (32)	<1.0	<1.0	<1.0	<1.0 (7.4)	<1.0	-	<1.0	<1.0 (9.7)	<1.0 (1.3)	-	-
NO_3-N (mg/l)(3)		0.62	-	-	-	12	-	-	-	18	14	-	-
COD (mg/l)		275	38	16	27	32	54	-	30	48	48	27	90
BOD (mg/l)		155	-	-	-	8	-	-	-	11	9	11	-
$SO_3^=$ (mg/l)		40	-	0	0	0	0	-	0	-	-	-	-
MLSS (mg/l)		-	2400	2467	2530	2830	2801	-	2608	2827	2345	-	-
MLVSS(mg/l)		-	1877	1927	2001	-	-	-	-	-	-	-	-
Loading g/COD/gMLSS		-	0.28	0.27	0.26	0.23	0.24	-	0.25	0.23	0.28	-	-
% Volatile		-	78.2	78.1	79.1	-	-	-	-	-	-	-	-
O_2 Uptake (mg/l/hr)		-	12	16.2	14	12	12	-	8.5	12		-	-
Cr (mg/l)		<.02	-	-	-	<.06	-	-	-	-	<.06	-	-
Cd (mg/l)		<.02	-	-	-	<.01	-	-	-	-	<.01	-	-
Cu (mg/l)		0.10	-	-	-	.15	-	-	-	-	0.14	-	-
Fe (mg/l)		0.28	-	-	-	<.05	-	-	-	-	0.06	-	-
Ag (mg/l)		<.02	-	-	-	<.02	-	-	-	-	<.02	-	-
TDS (mg/l)		-	-	-		2806	-	-	-	3256	-	-	-

(1) - Raised pH and alkalinity with NaOH on 7/23
(2) - Raised alkalinity with Na_2CO_3 on 7/26
(3) - Ammonia probe results; values in ( ) which are analytical values

TABLE B-27. TOTAL DISCHARGE BIOLOGICAL TREATABILITY STUDY

		INFLUENT	EFFLUENT										
			7/19	7/20	7/21	7/22	7/23	7/25	7/26	7/27	7/28	7/29	7/30
Flow (mls/min)		1.0	1.0	0.66 (1.25)	1.25	1.25	1.25	1.25	1.25	1.25	1.25		
Total detention	time days	14.9	4.9	7.4	3.9	3.9	3.9	3.9	3.9	3.9	3.9	-	-
pH	influent	-	8.7	8.7	8.75	8.5	9.5	-	10.0	10.0	10.0	-	-
	effluent	-	8.5	8.35	7.9	6.7	5.5	5.9	5.35	8.2	8.35	-	-
Alkalinity	influent	-	1200	1200	1040	900	1350	1740	2658(2)	2605	2678	-	-
	effluent												
(mg/l as $CaCO_3$)		-	-	560	322	82	18	-	22	426	510	-	-
NH_3-N (mg/l)		20	20	18	20	15	18	-	12	15	-	-	-
		(14)				(25)			(23)	(24)	-	(40)	-
NO_3-N (mg/l)		<.02	-	-	-	2.5	-	-	-	<.02	<.02	-	-
COD (mg/l)		4503	1465	1536	1355	1386	1188	-	816	911	1228	1128	1104
BOD (mg/l)		2387	-	-	-	415	-	-	-	115	52	81	-
SO_3 (mg/l)		160	-	15	-	10	10	-	5	-	-	-	-
MLSS (mg/l)			3200	3625	4186	4010	4025	-	4050	3930	-	-	-
MLVSS (mg/l)		2291	2577	2708	2708	-	-	-	-	-	-	-	-
Loading g COD/g MLSS		-	0.34	0.20	0.32	0.34	0.34	-	0.33	0.34	-	-	-
% Volatile		-	71.6	69.7	64.7	-	-	-	-	-	-	-	-
O_2 Uptake (mg/l/hr)			12	12.25	12	22.1	42.7	-	21.75	23	-	-	-
Cr (mg/l)		<.06	-	-	-	0.08	-	-	-	-	0.09	-	-
Cd (mg/l)		0.06	-	-	-	0.09	-	-	-	-	0.04	-	-
Cu (mg/l)		0.54	-	-	-	1.45	-	-	-	-	0.43	-	-
Fe (mg/l)		4.78	-	-	-	2.7	-	-	-	-	6.1	-	-
Ag (mg/l)		0.07	-	-	-	0.04	-	-	-	-	0.05	-	-
TDS (mg/l)		-	-	-	-	14326	-	-	-	23,064	-	-	-

(1) - raised pH and alkalinity with NaOH on 7/23

(2) - Raised alkalinity of feed further with Na_2CO_3 on 7/25 and 7/26

(3) - Ammonia data probe results except those values in ( ) which are analytical values

TABLE B-28. EVAPORATION OF TOTAL DISCHARGE

500 mls of total discharge were evaporated and 100 ml portions of condensate were collected for characterization.

Sample	Volume (mls)	pH	COD (mg/l)	TOC (mg/l)	NH_3-N (mg/l)
Total Disch	500	8.1	5802	1340	867
1st Cut	100	9.7	3606	1300	250
2nd Cut	100	8.9	2509	800	9.5
3rd Cut	100	7.0	2117	720	46
4th Cut	120	5.3	1803	640	46
Bottoms	75	5.5	8000	5000	147
Avg Distillate	-	-	2079	666	85

- pH increase in Cut #1 due to NH_3 coming over
- pH decrease after Cut #1 probably due to less NH_3 carryover and carryover of SO_2 and acetic acid.
- NH_3-N data will not balance because of losses to air.
- A higher volume for bottoms COD expected, probable loss to air of volatile COD.

APPENDIX C

OSMONICS REPORT ON REVERSE OSMOSIS TEST ON WASHWATER

NOTE: This Appendix contains a test report of a reverse osmosis test on washwater, performed by Osmonics, Inc., 5951 Clearwater Drive, Minnetonka, Minnesota, at the request of HydroQual, Inc. Photographic fixer concentrate used in the test was provided by USAF.

APPLICATION TEST REPORT

Company:	Hydro Qual, Inc.	Written By:	Gerard J. Gach
Address:	1 Lethbridge Plaza Mahwah, NJ 07430	Tested By:	Gerard J. Gach
		Date of Test:	11 Aug 82

SAMPLE IDENTIFICATION

We received two quarts of photographic fixer concentrate from the United States Air Force. This solution is used in the processing of film and photographic prints.

The concentrated fixer solution was diluted using a ratio of 4.25 ml fix/l of water at Osmonics. This dilution was performed at the request of Hydro Qual, Inc to simulate a wash water stream produced by the USAF. Reverse osmosis (RO) water was used for the dilution.

The wash water stream was reported to typically contain:

COD	600 mg/l
TOC	75 mg/l
NH_3-N	100-250 mg/l
SO_3	75 mg/l
$S_2O_3^=$	350 mg/l
$SO_4^=$	20 mg/l
Fe	30 mg/l
Cd	<0.02 mg/l
Ag_{+o+}	<0.04 mg/l
Cr	<0.05 mg/l
TDS	500 mg/l
TVS	250 mg/l
pH	6.1

Measured at Osmonics, the fixer concentrate had a refractometer reading of 27° Brix, a conductivity of 130,000 micromhos and a pH of 5.0. The solution was yellow, clear and had a distinct ammonia odor. The sample was packed in ice during shipment to Osmonics to prevent degradation of the solution.

After dilution the solution was measured at Osmonics to have a refractometer of 0.2° Brix, a conductivity of 1,700 micromhos and a pH of 4.50. The simulated wash water was a very faint yellow, clear and had a weak ammonia odor.

Cont/

ABSTRACT

Using an Osmonics RO system, the USAF would like to process their wash water stream to a 90%+ recovery while producing a permeate meeting one of the following criteria:

	Level 1	Level 2	Level 3
COD mg/l	50	100	500
NH_3-N mg/l	1	2	10
Ag mg/l	0.05	0.1	0.5
TS mg/l	1,500	3,000	15,000

The site for disposal of the permeate stream will depend upon which of the above criteria is met. Hydro Qual is considering evaporation of the concentrate stream.

The objective of this test was to process the diluted solution using Osmonics' lowest passage cellulose acetate (CA) and polyamide (PA-C) membrane to generate samples of permeate for analysis by Hydro Qual and to determine the compatibility of the wash water solution with SEPA® membranes. The diluted (pH 4.5) solution was first recirculated through an OSMO®-192T-97(CA) sepralator. The pH of the feed stream was then adjusted with NaOH to increase the ionization and, therefore, rejection of the NH_3 molecule, and again recirculated on the sepralator. The solution was also processed to 75% recovery using an OSMO-52(PA-C) sepralator. Data on operating pressure, flow rates, pH, refractometer readings and conductivity were recorded periodically throughout the tests. Samples of the RO dilution water, feed, concentrate and permeate of the solution tested, and the original concentrate fix solution were sent to Hydro Qual for analysis.

CONCLUSIONS

1.0 A clear, colorless permeate low in conductive solids with no measurable refractive solids was produced while recirculating the diluted fixer solution on OSMO-52(PA-C) and OSMO-192T-97(CA) sepralators.

  1.1 No fouling of the membranes was observed. The initial pure water permeate flow rates were restored with a post-test water flush.

  1.2 Some NH_3 may have been passed to the permeate stream as indicated by a weak ammonia odor in both the 97(CA)'s and PA-C's permeate streams.

Cont/

2.0 No measurable passage of refractive soldis occurred while processing the wash water to 75% recovery using the OSMO-52(PA-C) sepralator. Conductive solids passage also remained low throughout the concentration.

2.1 Conductive solids were concentrated higher than three-fold while refractive solids were concentrated higher than two-fold at 75% recovery.

2.2 The solution could have been processed to a higher recovery but time constraints prohibited further processing.

3.0 Further conclusions on the success of meeting the USAF's objectives can be drawn when Hydro Qual's analysis of the permeate samples is completed.

RECOMMENDATIONS

1.0 Hydro Qual should analyze the samples collected to determine if the USAF's effluent quality can be met using an Osmonics RO system.

2.0 A two-stage RO system should be considered to further reduce COD, NH_3-N, Ag, and TS if a one-stage RO system does not effect an effluent meeting the desired level of the USAF's criteria.

3.0 The molecular form which Fe exists in the wash water and its solubility should be defined by Hydro Qual. If the solubility limits of the Fe compound will not allow Hydro Qual's recovery objectives to be met (i.e. due to precipitation of Fe resulting in fouling of the membrane), an appropriate method of Fe removal prior to processing with RO is recommended.

4.0 If the analysis in Recommendation #1 indicates an effluent meeting the criteria set by the USAF can be met using SEPA RO membrane, an Osmonics RO Process Evaluation System (PES) unit containing the SEPA membrane producing the best quality permeate should be purchased to provide longer term testing and operational data.

PROCEDURE

The OSMO-192T-97(CA) and OSMO-52(PA-C) sepralators were checked on a standard salt solution for salt passage and flow rates. After testing, the sepralators were immediately rechecked for flow rate and salt passage. The flow rate and salt passage checks allow us to determine fouling effects, compaction or membrane deterioration which may have occurred during the tests.

Cont/

A PES/OSMO®-19-60-SSXXC machine was used for the tests. The flow to the machine from the feed tank was provided by a TONKAFLO® transfer pump. The flow path through the machine consisted of a 5 micron cartridge prefilter, two TONKAFLO centrifugal multi-stage pumps mounted in series, a tube inshell heat exchanger and a stainless steel pressure vessel containing one sepralator. All wetted parts in the system are stainless steel or plastic. The flow rate and pressure in the machine are controlled by valves on the concentrate and pump recycle lines. Panel mounted pressure gauges, flow meters and a thermometer monitor the operating parameters. Permeate flow rates were measured using timed volumetric methods.

Two hundred and forty two mls of the concentrated fixer solution were diluted with 15 gallons (56.8 l) of RO water (a 4.25 ml fix/l water dilution) and transferred to the feed tank. Data was taken while recirculating the permeate and concentrate through the OSMO-192T-97(CA) sepralator back to the feed tank to establish baseline operating conditions on the sample. After it was determined the system had reached equilibrium, permeate flow rates were timed using volumetric methods. Data on operating pressures, permeate rates, conductivity and refractometer readings were recorded periodically throughout the test. The feed solution was then adjusted with NaOH to pH's of 8.2 and 10.0 and processed using the above regimen. This data is recorded in Table #1.

The OSMO-52(PA-C) sepralator was then run using the same regimen with the feed adjusted to a pH of 10.0. The PA-C sepralator was also used to run the feed solution to 75% recovery (recovery is defined as the ratio of permeate volume to feed volume expressed as a percentage). Data for this test is recorded in Table #2. Samples of the feed, concentrate and permeate streams were collected periodically throughout the tests and sent to Hydro Qual for analysis.

DISCUSSION

The PA-C sepralator run on the diluted fixer solution showed no sign of fouling and returned to 100% of its initial pure water permeate rate with a post-test water flush. The decrease in permeate flow rate during the concentration can be contributed to an increase in osmotic pressure caused by increasing ionic and refractive solids concentration. Osmotic pressure reduces the effective pressure resulting in lower permeate flow rates.

Cont/

Using SEPA® RO membranes the greater the ionization of a dissolved solid, the greater the percent rejection of that solid. To maximize rejection of the NH_3 the pH of the fixer solution was adjusted to increase NH_3 ionization. Reduction of the NH_3-N concentration is a primary concern in producing an effluent meeting the USAF criteria. Some of the fixer solution's characteristic ammonia odor was detected in the 97(CA)'s and PA-C's permeate streams indicating some passage of the NH_3 occurred. Hydro Qual's analysis will verify the NH_3 passage.

After processing the pH adjusted solution, a slight increase in NaCl passage of the SEPA-97(CA) membrane was noted (see Table 1). Processing solutions with pH's greater than 8.0 tend to increase the rate of hydrolysis of the CA polymer. Hydrolysis destroys the ionic rejection characteristic of the CA membrane, increasing salt passage. It is probable that processing the solution at pH 10.0 caused slight hydrolysis and subsequently a slight increase in salt passage.

It can be seen from the data that the optimum passage (measured by conductivity) during this test occurred at pH 8.1. The probable hydrolysis noted occurred at pH 10.0, but no benefit was realized from operation at this pH. In fact, the conductivity in the permeate was more than twice as high as that at pH 4.5 and 8.1. This indicates that the optimum operating pH will be in a range which is compatible with CA membrane.

The PA-C membrane was chosen to concentrate the sample due to the polymer's superior stability while processing solutions with higher pH's. If it is determined a permeate meeting the USAF's criteria can best be achieved with a solution pH above 8.0, then the PA-C membrane should be considered for this application. Based on the data obtained at Osmonics, there is no indication that PA-C membrane has superior rejection characteristics to 97(CA) membrane. Hydro Qual's analysis will provide more information to compare the performance of the two membranes.

The molecular state which Fe exists in the wash water solution must be considered when processing to higher recoveries. If the solubility limits of the Fe complex are exceeded while concentrating the solution, precipitation of that complex will occur resulting in fouling of the membrane. Fouling will result in decreased permeate flow rates and possible damage to the membrane (see Recommendation #3).

Cont/

The results of this test are very encouraging. The data indicates a substantial reduction in dissolved and refractive solids can be effected while processing the wash water stream with SEPA® RO membrane. Concentration data also indicates the solution can be run to a high recovery. Hydro Qual's analysis of the permeate quality will determine which level of the USAF's separation objective have been met. If Hydro Qual concludes from their analysis that the objective can be obtained, an Osmonics RO system will provide a viable means to solve photographic fixer wash water discharge problems presently facing the USAF.

Written By ______________________
Gerard J. Gach
Appl. Devel. Engr.

Approved By David J Paulson
David J. Paulson
Supervisor R&D

GJG/gw
23 Aug 82

TABLE C-1. REVERSE OSMOSIS WITH AN OSMO 192T-97 (CA) SEPRALATOR

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Table #1

Reverse Osmosis With An OSMO®-192T-97(CA) Sepralator[1,2]

Elapsed Time (Min)	Permeate Flow[3] (gph)	Permeate Flow[3] (lph)	Temp (°F)	Temp (°C)	Conductivity (micromhos) Feed	Conductivity (micromhos) Conc	Conductivity (micromhos) Perm	Conductivity (micromhos) % Pass	Refractometer (°Brix) Feed	Refractometer (°Brix) Conc	Refractometer (°Brix) Perm	Refractometer (°Brix) % Pass	pH Feed	pH Conc	pH Perm	Sample No.
	Began recirculation (feed solution pH = 4.5)															
0	10.2	38.6	75	23.9	-	-	-	-	-	-	-	-	-	-	-	
9	10.4	39.4	78	25.6	1710	2040	78	4.2	0.2	0.2	0.0	00.0	4.5	4.5	3.3	1
17	10.6	40.1	80	26.7	1800	2050	77	4.0	-	-	-	-	-	-	-	
23	pH adjusted feed to 8.15															
27	10.6	40.1	80	26.7	2180	2440	74	3.2	0.2	0.2	0.0	00.0	8.15	8.15	8.20	
47	10.4	39.4	74	23.3	2080	2260	65	3.0	0.3	0.2	0.2	80.0	8.15	8.2	8.55	2
52	pH adjusted feed to 10.0															
57	10.3	40.0	73	22.8	-	-	-	-	-	-	-	-	-	-	-	
68	10.6	40.1	81	27.2	2260	2560	185	7.7	0.3	0.2	0.0	00.0	10.0	10.0	9.45	
72	10.9	41.3	82	27.8	2330	2560	185	7.6	0.3	0.2	0.0	00.0	10.0	10.0	9.45	3
Pre-Test NaCl Solution Check																
10	9.9	37.5	76	24.4	1870	1930	92	4.8								
Post-Test H_2O Flush and NaCl Solution Check																
20	10.8	40.9	76	24.4	1500	1650	86	5.5								

[1] 400 psig average operating pressure
[2] 1.5 gpm (5.7 lpm) concentrate flow
[3] Corrected to 77°F (25°C)

TABLE C-2. REVERSE OSMOSIS WITH AN OSMO -52 (PA-C) SEPRALATOR

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Table #2

Reverse Osmosis With An OSMO®-52(PA-C) Sepralator[1,2]

Elapsed Time (Min)	Rec (%)	Permeate Flow[3] (gph)	Permeate Flow[3] (lph)	Temp (°F)	Temp (°C)	Conductivity (micromhos) Feed	Conductivity (micromhos) Conc	Conductivity (micromhos) Perm	Conductivity (micromhos) % Pass	Conductivity (micromhos) Comp. Perm	Refractometer (°Brix) Feed	Refractometer (°Brix) Conc	Refractometer (°Brix) Perm	Refractometer (°Brix) % Pass	Refractometer (°Brix) Comp. Perm	pH Feed	pH Conc	pH Perm	pH Comp Perm	Sample No.
	Began recirculation (feed pH = 10.2)																			
0	-	2.7	10.2	85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
5	-	-	-	77	25.0	2100	2250	315	14.5	-	0.3	0.3	0.0	0.0	-	9.60	9.60	9.95	-	
	Began concentration																			
30	0	2.4	9.1	74	23.3	2350	2420	520	21.8	-	0.3	0.3	0.0	0.0	0.0	10.0	-	-	-	4
40	41.7	2.1	8.0	78	25.6	3800	3940	460	11.9	436	0.4	0.4	0.0	0.0	0.0	9.85	9.85	10.25	10.0	
110	66.7	2.1	8.0	77	25.0	5100	5180	446	8.7	418	0.6	0.6	0.0	0.0	0.0	-	-	-	-	
140	75.0	2.0	7.6	78	25.6	-	6950	450	6.5	412	-	0.7	0.0	0.0	0.0	-	9.75	10.0	10.1	5
Pre-Test NaCl Solution Check																				
-	-	2.0	7.6	-	-	-	-	-	8.7											
Post-Test H_2O Flush and NaCl Solution Check																				
-	-	2.4	9.1	-	-	-	-	-	3.4											

[1] 400 psig average operating pressure
[2] 1.0 gpm (3.8 lpm) concentrate flow
[3] Corrected to 77°F (25°C)