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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

Warburg respirometric techniques were used to study the toxicity and biodegradability of a hydrazine wastewater treated with chlorine gas and ultraviolet radiation. The contrived wastewater, containing 500 ppm each of neat hydrazine, monomethyl hydrazine, unsymmetrical dimethylhydrazine, and dimethyl nitrosamine, was representative of those to be generated at the Rocky Mountain Arsenal Blend Facility.

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## 20. ABSTRACT (Concluded)

Stock culture organisms reared on milk solids and trickling filter slimes from a full-scale secondary plant were investigated using both standard substrates and the contrived wastewater. Biodegradation data showed that substrate inhibition does not occur with either the stock culture organisms or the trickling filter slimes. The data confirmed that the contrived wastewater does not inhibit those organisms tested and showed, in fact, that the wastewater itself can be recovered as oxygen uptake. The wastewater exerted an oxygen demand of approximately 150 mg/l in the presence of 875 mg/l volatile trickling filter solids.

Pretreatment with a bench-scale strong base ion exchange column had no effect on the uptake of standard substrate by trickling filter organisms significantly reduced the toxicity to the stock culture organisms.

Activated carbon pretreatment data suggested that no chlorinated hydrocarbons or incomplete oxidation products were formed during the UV-chlorinolysis process. Cumulative oxygen uptakes for these samples were very comparable in both the toxicity and biodegradation protocols. Stock culture organisms responded with a three-fold increase in cumulative oxygen uptake, whereas the filter organisms showed no significant change in degradation.

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#### PREFACE

This report was prepared by Captains Anthony M. Wachinski and Jay A. Farmwald based on in-house research conducted at the Civil and Environmental Engineering Development Office (CEEDO), Detachment 1, Headquarters, Armament Development and Test Center (HQ ADTC), Tyndall Air Force Base (AFB), Florida, from December 1978 to February 1979. CEEDO became the Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, Florida 32403 on 1 February 1979.

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

In August 1978, IIT Research Institute (IITRI) was tasked with developing design data for a system to treat hydrazine-laden wastewater generated by the Air Force Logistics Command (AFLC) Blend Facility at the Rocky Mountain Arsenal (RMA). Facility currently discharges 1000 to 2000 gallons of wastewater a day to a holding pond; there it is treated with calcium hypochlorite and ultimately discharged to a nearby lake. Concern over neat hydraxine (HZ), unsymmetrical dimethylhydrazine (UDMH), and dimethyl nitrosamine (DMNA) in the holding pond effluent prompted the Colorado Department of Health, Water Pollution Control Commission, to rule the present treatment system unsatisfactory. A system proposed by IITRI would incorporate ultraviolet (UV) catalyzed chlorine to treat the wastewater. Residual chlorine would be neutralized with sodium thiosulfate, the effluent being discharged to the RMA trickling filter plant and ultimately to a receiving stream.

On 31 October 1978, IITRI requested that the Air Force Engineering and Services Center, Division of Environics (AFESC/RDV) evaluate the toxicity of the chlorinated wastewater and comment on the possible effects of the effluent on the RMA trickling filter. The approach formulated by RDV involved classic Warburg Respirometer techniques coupled with an evaluation of ion exchange and activated carbon as pretreatment alternatives. This report summarizes data from these studies and their interpretation.

#### SECTION II

#### METHODS AND MATERIALS

## 1. WASTE CHARACTERIZATION

General. The wastewater obtained from IITRI originally contained 500 parts per million (ppm) HZ, 500 ppm UDMH, 100 ppm DMNA, and 500 ppm monomethylhydrazine (MMH). This synthetic wastewater had been batch treated in a 12-liter glass reactor at a radiation level of 0.9 watt/liter. The experiment was performed at pH 5. Chlorine was added to the reactor at a low flow rate to allow pH control to + 0.1 pH unit. The UV light was placed in the reactor from the start of the experiment. IITRI had reported that the MMH, UDMH, and HZ reacted rapidly with the chlorine, keeping residual chlorine below detectable levels in the reactor throughout the first phase of the experiment. When these three compounds were consumed, the chlorine concentration began to increase. The chlorine concentration was then brought to 500 ppm and held at that level for several hours. After the run the pH was adjusted to 7, residual chlorine removed with sodium thiosulfate, and capillary gas chromatography (Reference 1) analyses performed to verify the complete oxidation of the hydrazines and DMNA.

Using procedures outlined in <u>Standard Methods</u> (Reference 2), the treated wastewater was characterized in this laboratory as outlined in Table 1. Chemical Oxygen Demand (COD) analyses were performed, but results were erratic due to high chloride and sulfate concentrations. The COD was estimated to be 450 milligrams per liter (mg/ $\ell$ ).

b. Chlorination End Products. The stoichiometry associated with the chlorinolysis of HZ, MMH, UDMH and NDMA predicts

methanol, nitrogen gas, and hydrochloric acid as the only reaction products. However, it is known that several alternative mechanisms may proceed under certain conditions which involve more than one electron transfer and can lead to the formation of ammonia and methane. These compounds, in the presence of excess chlorine, could lead to the formation of certain chlorinated hydrocarbons and amines, including CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, NH<sub>2</sub>Cl, NHCl<sub>2</sub>, and NCl<sub>3</sub> (the most undesirable since it is explosive). The other compounds in the treated effluent prompted IITRI to conduct capillary gas chromatography (GC) analyses (Reference 1) on the wastewater. All of the compounds in question were found to be below detectable limits.

c. <u>Incomplete Oxidation Products</u>. Recent gas chromatography mass spectrometry (GC-MS)\* work on the hydrazine fuels in our Environmental Sciences Branch has shown that the products associated with the incomplete chlorination of these fuels are quite numerous. A summary of those compounds identified to date is presented in Table 2.

None of these compounds were detected in the treated IITRI sample, using GC-MS, indicating that the oxidation had gone to completion.

## 2. WARBURG TECHNIQUE

The Warburg used in this study was a Precision Scientific rotary apparatus with 18 manometer stations. A shaking rate of 130 strokes per minute was used with a shaking stroke of four centimeters. The constant-temperature bath was maintained at

<sup>\*</sup>Finnigan 3200 coupled to a System 150 data system.

25°C. Manometers were open-end U-tubes calibrated from 0 to 30 cm in one-millimeter (mm) increments. Unity oil, specific gravity 1.000 was used as manometer fluid. Each manometer was equipped with an adjustable fluid reservoir for maintaining the system at constant volume. Respirometer flasks were conical, borosilicate glass-vessels with side-arm and centerwell. Each flask-manometer couple was calibrated using a Gilmont® calibrator, as described by Yamaguchi (Reference 3). All experiments were conducted with 0.2 ml of 10 percent KOH in the center well. Folded 2 cm² strips of Whatman #1 filter paper were also placed in the center wells to enhance CO2 absorption. The other flask components were as described in subsections 4d and 4e.

TABLE 1. ANALYSIS OF RMA TREATED WASTEWATER

Parameter	Concentration (mg/l)
Total Solids (TS)	10,790
Total Volatile Solids (TVS)	2,670
Total Suspended Solids (TSS)	10
Total Kjeldahl Nitrogen (TKN)	4.5
Ammonia Nitrogen (NH <sub>3</sub> -N)	9
Sulfates (SO <sub>4</sub> )	58
Chlorides (Cl)	5,250
Total Alkalinity (MO)	10 (as CaCO <sub>3</sub> )
Нф	6.8

# TABLE 2. PRODUCTS EXPECTED FROM THE INCOMPLETE CHLORINATION OF HYDRAZINE FUELS

Hydrazones:

Formaldehyde (FH)

Formaldehyde monomethyl (FMH)
Formaldehyde dimethyl (FDH)
Acetaldehyde dimethyl (ADH)

Polymeric FMH, FDH

Amines:

Dimethyl Trimethyl

Others:

Ammonia
Azomethane
Formaldazine
Dimethylforamide

Detramethyltetrazene

Acetaldehyde 1-methyl - 1,2,4-triazole

#### 3. CULTURES

a. Stock Culture. A stock culture of heterotrophic bacteria was maintained in a fill-and-draw, Plexiglas® reactor, 660 mm high and 152 mm in diameter, containing a liquid volume of 10%. Mixing and aeration were by diffused air at a rate of 0.0019 m³/min (0.067 cfm). Waste sludge was removed daily to maintain a Solids Retention Time (SRT) of nine days. The inorganic nutrients in the feed are shown in Table 3; Carnation® dry milk was provided as the sole carbon source at a COD of 600 mg/%. Phosphorous, potassium, and buffer capacity were provided through the addition of 4 grams (gm) K2HPO4 and 2 gm KH2PO4 per liter of feed.

TABLE 3. INORGANIC SALTS USED FOR THE GROWTH OF STOCK CULTURE

Source	Mineral	Concentration	n of Mineral in Feed
		mg/	mg/mg COD
FeC13.6H20	Fe*	6	1x10-2
MgSO4.7H20	Mg*	3	5x10-3
NH4CP	N	36	0.06
CaC <sub>1</sub>	Ca	3	5x10 <sup>-3</sup>
MnCl <sub>2</sub> .4H <sub>2</sub> 0	Mn	0.06	1 x 1 0 - 4
Na <sub>2</sub> MoO <sub>4</sub> .2H <sub>2</sub> O	Мо	0.006	1x10-5
CuSo4.5H20	Cu	0.06	1 x 1 0 - 4
ZnCl <sub>2</sub>	Zn	0.09	1.5x10 <sup>-4</sup>
CoC1 <sub>2</sub> .6H <sub>2</sub> 0	Со	0.06	1 x 1 0 - 4

<sup>\*</sup>Iron, magnesium, and nitrogen solutions were made up at concentrations such that daily additions of 10 mls affected the desired concentrations. All other trace nutrients listed were available from one stock solution, 10 mgs of which were added daily to the feed.

Feeding was accomplished once every 24 hours according to a procedure by Joel and Grady (Reference 4).

- (1) The air to the reactor was stopped for one minute and the reactor volume adjusted to 10% with deionized water to replace evaporation losses.
- (2) The air was turned back on, and the reactor was allowed to mix. Samples were removed for mixed liquor volatile suspended solids (MLVSS) and soluble COD analyses.
- (3) A volume of mixed liquor appropriate to maintain the SRT at the desired value was removed from each reactor. This volume was adjusted to account for solids lost in the supernatant on the preceding day.
- (4) The air was stopped again for 30 minutes, and the solids were allowed to settle.
- (5) The supernatant was decanted down to the 5% mark in each reactor and samples removed for Volatile Suspended Solids (VSS) determination.
- (6) Five liters of feed solution were added to each reactor, and the air was started again.

In studies using these organisms, cells were withdrawn from the reactor, washed three times in distilled water, and resuspended in a small volume of distilled water. A mixed liquor volatile suspended solids test was performed according to the 14th edition of <u>Standard Methods</u> and the cell suspension adjusted to 2000 mg/L with additional distilled water.

b. Trickling Filter Organisms. For the second group of Warburg studies, trickling filter organisms from the Tyndall Air Force Base trickling filter plant were used. Use of these organisms represented a conservative approach in that the trickling filter slime was used in a dispersed growth environment.

The slime was scraped from the rock media, blended in a Waring blender at the lowest setting for one minute; and aerated for 24 hours without substrate before use. The cells were washed three times in a pH 7.4 phosphate buffer (Table 4) and resuspended in a buffer/inorganic salts medium (Table 5). An MLVSS test was performed, and the suspension was adjusted to 875 mgl.

TABLE 4. PHOSPHATE BUFFER COMPOSITION

Constituent	Concentration (gm/1)
KH2F04	8.5
K2HFO4	21.75
Na <sub>2</sub> FPO <sub>4</sub> .7H <sub>2</sub> O	33.4
NH4C1	1.7

TABLE 5. BUFFER/INORGANIC SALTS MEDIUM

Constituent	Volume/Liter	Reference
Phosphate Buffer	2.5 m <b>l</b>	Table 4
Stock Fe Solution	0.5 m <b>g</b>	Table 3
Stock Mg Solution	0.5 m <b>£</b>	Table 3
Stock N Solution	0.5 m£	Table 3
Stock Trace Nutrient Solution	0.5 m2	Table 3

## 4. EXPERIMENTAL WORK

A. General. A waste stream containing 500 ppm HZ, 500 ppm MMH, 500 ppm UDMH, and 100 ppm DMNA could, assuming complete oxidation to methanol, contribute a waste load of 1450 mg/£ COD after chlorination. For a flow of 2000 gallons per day, this represents an additional 24 pounds of COD per day to the RMA trickling filter which currently treats from 0.06 to 0.1 million gallons per day (mgd) of domestic wastewater. As the current influent Biochemical Oxygen Demand (BOD5) is only 20 mg/£, the blend facility discharge would essentially double the present organic loading. However, because the plant is operating at less than 0.01 percent of its design capacity, the limiting factor will most probably be associated with total dissolved solids and/or the presence of any toxic organics produced during chlorinolysis, not COD loading.

- b. Pretreatment. Since the chlorinated wastewater is high in chlorides, i.e., over 5000 mg/k, several aliquots of the original sample were passed through a bench-scale, strong-base ion exchange column packed with Amberlite® IRA-938 resin (hydroxyl cycle). An analysis on these effluents confirmed that all chlorides had been removed. These samples were then used in both the toxicity and biodegradation experiments described below. While analysis of the wastewater indicated that methanol was the only major reaction product, several samples were passed through a bed of Calgon F-300 activated carbon at 0.15 gpm/ft2 prior to the collection of oxygen uptake data. Because most of the potential reaction products discussed thus far should adsorb to some degree ard since not all of the partial oxidation products have been identified to date, carbon pretreatment would serve as a rough, screening technique in evaluating the effects of organics (if any) in the chlorinated wastewater. These treated samples were used in the two standard protocols established.
- c. <u>Warburg</u>. Two standard Warburg techniques were used in this study; one was designed to evaluate waste toxicity, and one was designed specifically for biodegradability.

In the first technique, sample flasks were set up containing microorganisms, a known concentration of standard substrate (milk or sodium acetate) and wastewater. By comparing uptake in these flasks with the uptake in substrate only, it was possible to make inferences about the effects of the particular wastewater sample on standard substrate degradation.

In the second protocol, flasks containing only microorganisms and wastewater were used. A standard carbon source was not incorporated into the flasks to insure that all oxygen uptake above endogenous was due to microbial degradation of the wastewater sample. Note, however, that a limited number of compounds have been shown to stimulate oxygen uptake even though they are not utilized for energy or synthesis (Reference 5).

- d. Stock Culture Studies. The various components in the Warburg flasks for the stock culture studies were as summarized in Table 6. All runs were made with a thermobarometer flask containing 3.2 mls of distilled water and two endogenous flasks containing 2 mls of distilled water and 1 ml of stock culture cells. Those flasks calling for standard substrate (milk) were made up with an initial food (Milk-COD) to microorganism ratio (7/M) of 0.3 equal to that in the fill and draw reactor. All flasks had an inorganic-salts to microorganism ratio equal to that in the fill and draw reactor.
- e. Filter Organism Studies. All runs were made with a thermobarometer flask containing 4.2 mls of phosphate buffer and two endogenous flasks containing 2 mls of distilled water, 1 ml of the buffer/salts medium and 1 ml of cells. Those flasks calling for standard substrate (sodium acetate) were prepared with an initial COD-to-microorganism ratio of 0.3, a high estimate of the organic loading at RMA (0.06) based on a uniform slime thickness of 2 mm. As each flask was made up to 4.0 mls, dilution of the wastewater samples was very conservative (1:4) compared to expected dilutions at RMA (1:30)\*. Table 7 summarizes the matrix established for these experiments.

<sup>\*</sup>Based on low domestic flow of 0.06 MGD and high blend facility discharge of 2000 gallons per second (gpd).

TABLE 6. STOCK CULTURE FLASK MATRIX

Flask No.	Date	Components
4:5	8 Dec	1 mg cells
		1 mg Carnation® milk feed with
		inorganic salts
		1 mg distilled water
6:7	8 Dec	1 mg cells
		1 ml Carnation® milk feed with
		inorganic salts
		1 ml IITRI wastewater
8:9	8 Dec	1 ml cells
		1 ml Carnation® milk feed with
		inorganic salts
		1 ml IITRI wastewater with chlorides
		removed (pH 12)
14:15	8 Pec	1 mg cells
		1 ml Carnation® milk feed with
		inorganic salts
		1 ml of IITRI wastewater treated with
		activated carbon
14:15	19 Jan	1 m2 cells
		1 m£ Carnation® milk feed with
		inorganic salts
		1 mg of HITRI wastewater with chlor-
		ides removed (pH7)
8:9	19 Jan	1 mt cells
		1 mg IITRI wastewater
		1 ml inorganic salts
10:11	19 Jan	1 mg cells
		1 ml IITRI wastewater with chlorides
		removed (pH 7)
		1 ml inorganic salts
12:13	19 Jan	1 mL cells
		1 ml inorganic salts
		1 ml 1178f wastewater treated with
		antivated carbon 12
		# 6.

TABLE 7. FILTER ORGANISM FLASK MATRIX

Flask No.	Date	<u>Components</u>
6:7	2 Jan	l mg cells in buffer
		1 mg inorganic salts
		1 ml sodium acetate
		1 m@ distilled water
10:11	2 Jan	l me cells in buffer
		1 mg inorganic salts
		1 m 2 sodium acetate
		1 m@ IITRI wastewater
16	2 Jan	1 m@ cells in buffer
		l ml inorganic salts
		1 m & sodium acetate
		1 ml IITRI wastewater treated with
		activated carbon
12:13	2 Jan	1 mg cells in buffer
		1 me inorganic salts
		1 m g sodium acetate
		l mg IITRI wastewater minus chlorides
		(pH7.0)
4:5	2 Jan	1 m 2 cells in buffer
		l mg inorganic salts
		1 m g IITRI wastewater
	_	1 mg distilled water
8:9	2 Jan	1 mg cells in buffer
		1 m & inorganic salts
		1 m & IITRI wastewater minus chlorides
		(pH 7.0)
3 lt 3 m	O . To	1 m & distilled water
14:15	2 Jan	1 ml cells in buffer
		1 m & IIMEL west event on threated with
		1 m l IITRI wastewater treated with activated carbon
		1 m l distilled water

#### SECTION III

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#### RECTLES AND DISCUSSION

#### 1. TOXICITY

a. Stock Culture Organisms. The effect of chlorinolysis wastewater (referred to as IITRI wastewater) on the respiration of stock culture organisms is shown in Figure 1. Each point has been corrected for endogenous respiration and represents the mean of duplicate flasks. The raw data have been summarized in Appendix A.

The Carnation® milk shows a cumulative oxygen uptake of 235µl expected based on a measured COD of (0.036 mg COD/mg milk solids). All of the milk and approximately 50 µl of HTRI wastewater, were recovered as oxygen uptake, for the sample containing both milk and wastewater, indicating that the chlorinolysis effluent did not inhibit these organisms with respect to standard substrate oxidation.

b. <u>Trickling filter Organisms</u>. Figure 2 shows that the IITRI wastewater exhibited no toxic effects on the respiration of trickling filter organisms. However, a lag period of about 24 hours occurred before any significant oxygen utilization was observed.

Many reasons can be postulated for such a response. A lower concentration of trickling filter organisms was used in these experiments, i.e., 875 mg/L versus 2000 mg/L for the stock culture runs. Furthermore, the trickling filter organisms which are normally found in a fixed-film environment were operating in a dispersed growth mode. One important aspect of the oxygen progression shown in Figure 2 is the higher oxygen uptake (105µL) attributed to the IITRI wastewater in the presence of trickling filter organisms than the stock culture organisms (50µL).

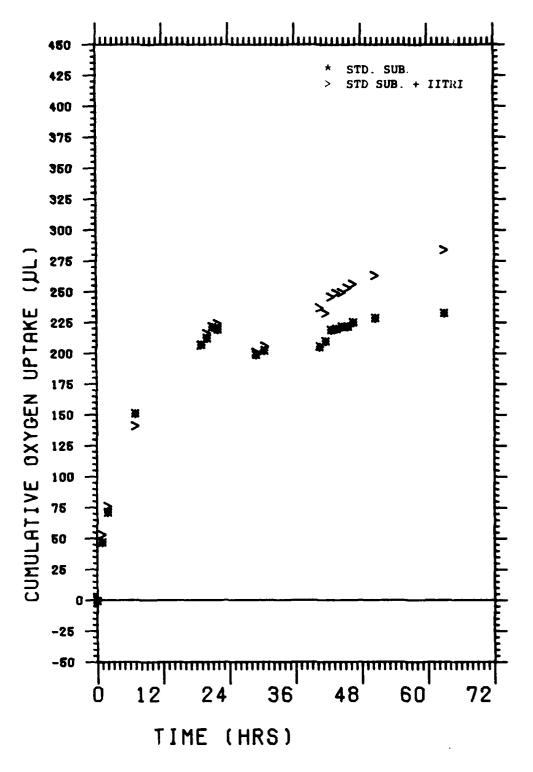


Figure 1. The Effect of IITRI Wastewater on the Respiration of Stock Culture Organisms

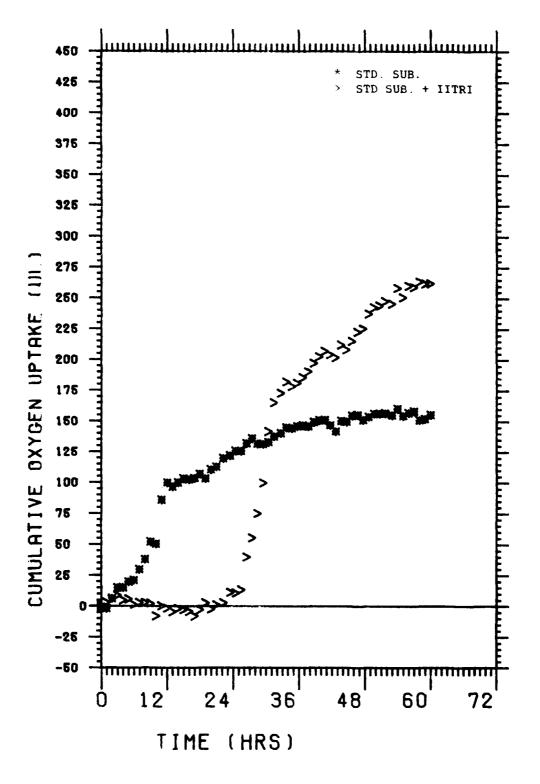


Figure 2. Effects of IPERL Wastewater on the Respiration of Trickling-Filter Organisms

The filter organisms were better able to degrade the wastewater following an initial acclimation period. If total oxygen uptake per milligram of volatile suspended solids (VSS) is computed, this difference is more evident, i.e.,  $120\mu$  /mg filter VSS and 25  $\mu$  /mg stock VSS. From these studies, it appears that the chlorinolysis effluent is not toxic and appears to be biodegradable by nonacclimated organisms. However, the effluent itself is better degraded by trickling filter slime by a factor of 5 compared to stock culture organisms.

## c. Pretreatment

(1) <u>Carbon</u>. Figure 3 shows little difference (with respect to stock culture oxygen uptake) between raw IITRI samples and those treated with activated carbon.

These data confirm that chlorination of the wastewater was complete and that no partial oxidation or chlorinated end products were present in the samples tested.

As would be expected from the stock culture data, treating the wastewater with carbon had no impact on the uptake curve for filter organisms. The results are summarized in Figure 4.

(2) <u>Ion Exchange</u>. Pretreatment with ion exchange to remove the high concentration of chlorides significantly reduced the toxicity of the chlorinolysis effluent to the stock culture organisms as shown in Figure 5.

The mean total oxygen uptake for the Carnation® with treated IITRI wastewater samples was 400 µl (170 µl of uptake attributed to the IITRI wastewater). This represents a three-fold increase in uptake over the sample containing the high concentration of chlorides. The observed advantages associated with the reduced osmotic pressure may well be realized through dilution of the blend facility effluent at the RMA filter with the domestic flow.

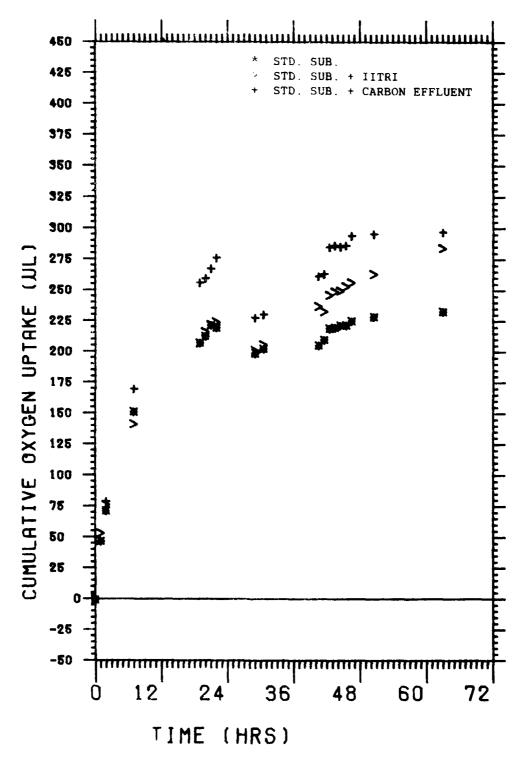


Figure 7. The Effect of Activated Carbon Pretreatment on the Toxicity of IITRI Wastewater to Stock Culture Organisms

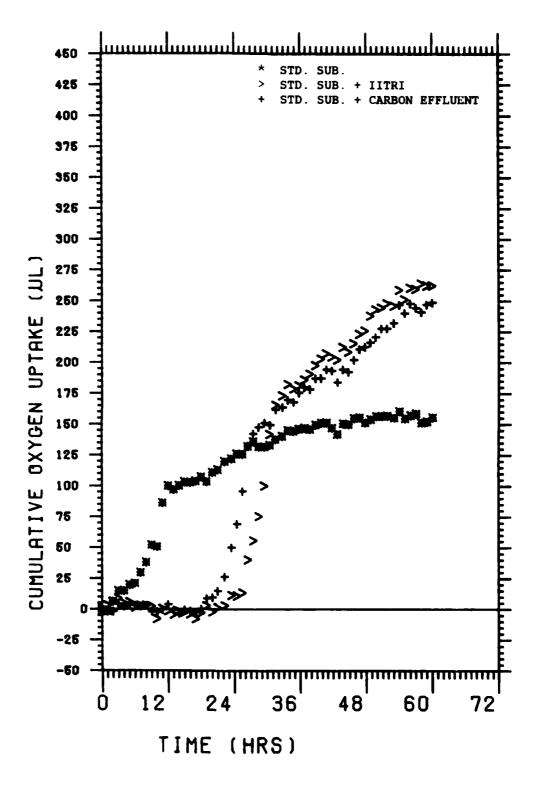


Figure 4. The Effects of Activated Carbon Pretreatment on the Toxicity of IITRI Wastewater to Trickling Filter Organisms

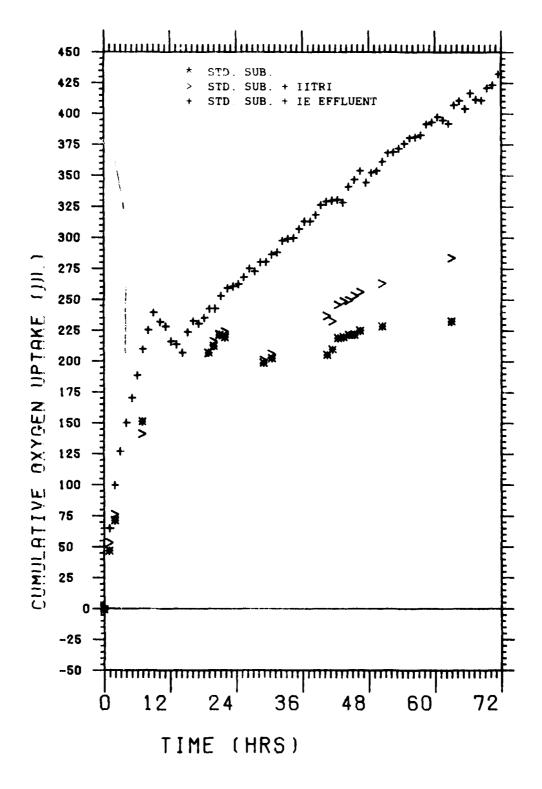


Figure 5. The Effect of Ion Exchange Pretreatment on the Toxicity of IITRI to Stock Culture Organisms

Figure 6 demonstrates the need to adjust the pH from 12 back into the biological range following pretreatment with strong base resin. The negative oxygen uptake indicates no microbial activity.

Ion exchange pretreatment had little effect on the uptake of standard substrate by filter organisms as shown in Figure 7.

The difference between stock and filter organism response to elevated osmotic pressure as demonstrated in these experiments is attributed to population dynamics. As biological principles would predict, the more specialized milk grown population was less tolerant to such an environmental change than the more heterogenous filter population.

#### 2. BIODEGRADABILITY

a. Stock Culture Organisms. Figure 8 illustrates the biodegradability of the ITTRI wastewaters by stock culture organisms. The cumulative uptake of 75 µl for the chlorinolysis effluent compares well with that value of 50 µl reported in the toxicity section.

Cumulative oxygen uptake values observed for the IITRI carbon column effluent also agree with the values obtained by difference using the Carnation® dry milk. IITRI wastewater treated with carbon gave a cumulative oxygen uptake value of 65  $\mu$ l with microorganisms only and 70  $\mu$ l when calculated by difference.

Pretreatment with ion exchange had a pronounced effect on the biodegradability of the wastewater, indicating that degradation can be increased by a factor of nearly 3 in the absence of TDS. Again the cumulative uptake shown in Figure 8 for this sample, 250 µl (357 mg/ BOD), correlates well with the 200 µl observed

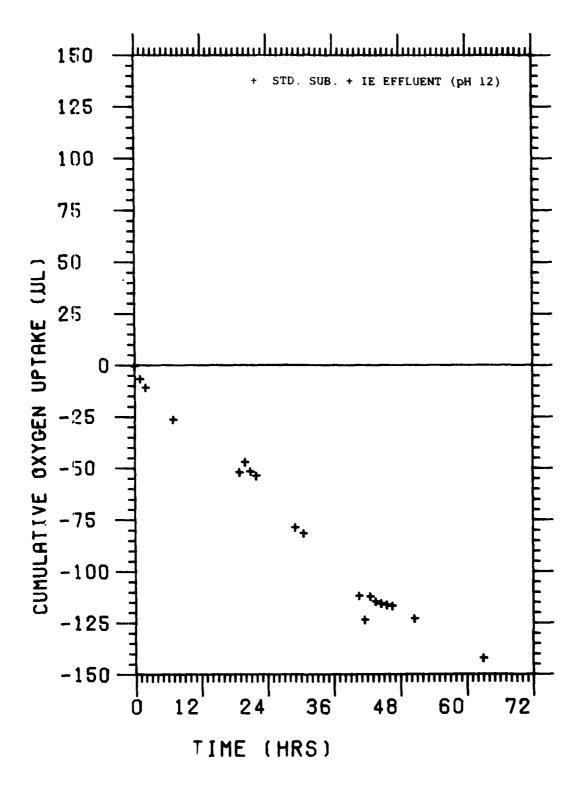


Figure 6. The Effect of Ion Exchange Pretreatment Without pH Adjustment on the Toxicity of IITRI Wastewater to Stock Culture Organisms

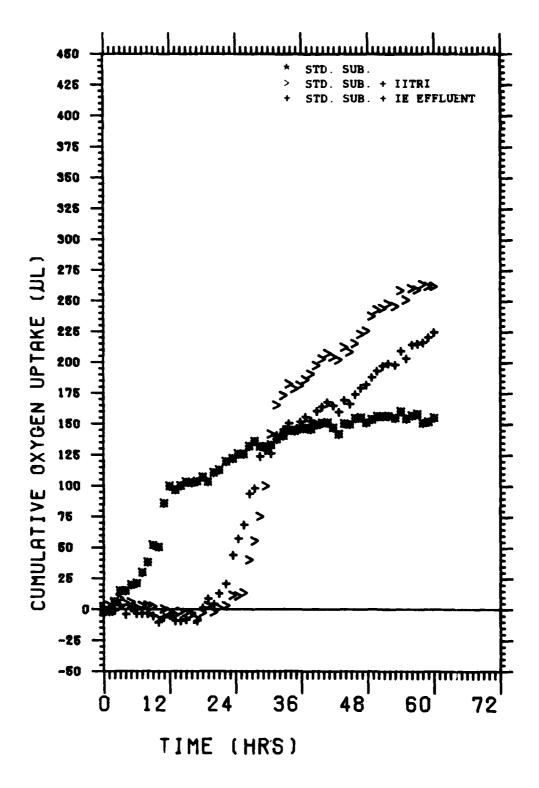


Figure 7. The Effect of Ion Pretreatment on the Toxicity of IITRI Wastewater to Trickling Filter Organisms

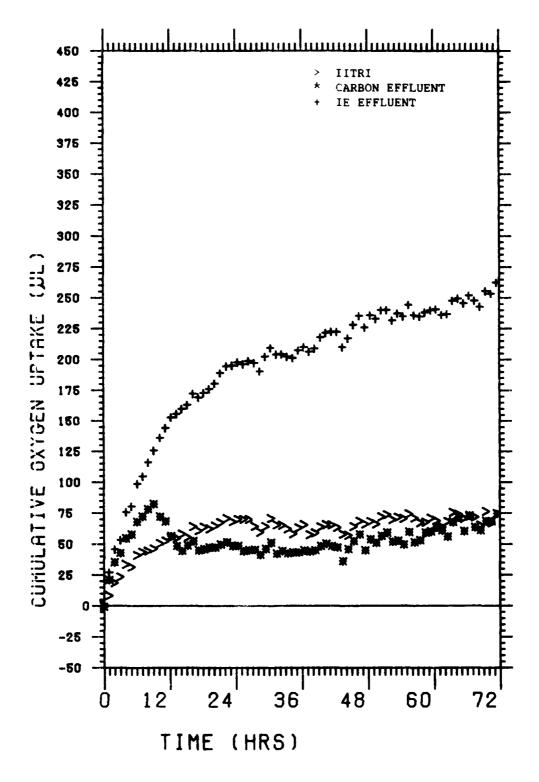


Figure 8. Biodegradability of IITRI Wastewaters by Stock Culture Organisms

during the toxicity experiments. It is obvious from these and previous data that the high concentration of chlorides is inhibitory to the stock culture organisms.

b. Trickling Filter Organisms. The data in Figure 9 confirm that pretreatment with activated carbon and ion exchange have no effect on the biodegradability of the IITRI wastewater by filter organisms. It is degradable but the required acclimation period of some 24 hours is again evident.

This lag time should not present operational problems in a continous flow trickling filter plant once steady state is achieved. The mean cumulative uptake for all three samples,  $100\mu$  correlates very well with values obtained by difference during the toxicity experiments (mean = 97  $\mu$ L).

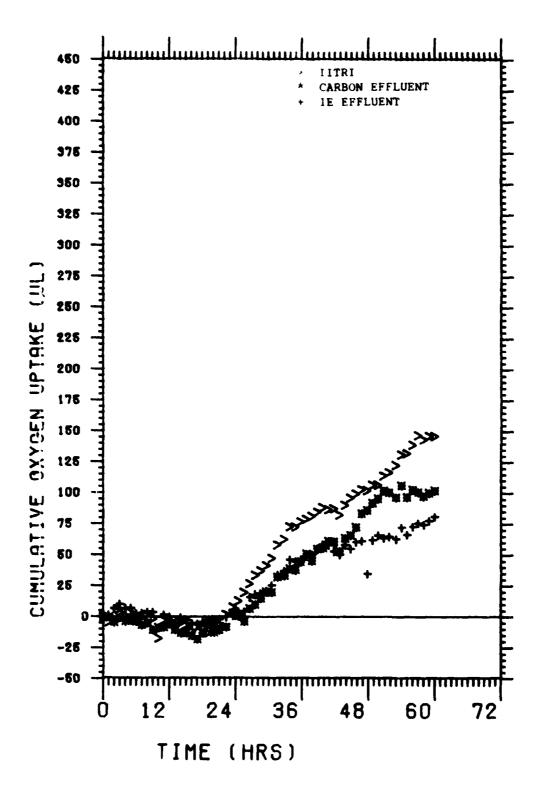


Figure 9. Biodegradability of IITRI Wastewater by Trickling Filter Organisms

#### SECTION IV

#### SUMMARY

Investigations involving standard substrates and untreated IITRI wastewater indicated that substrate inhibition does not occur in either stock cultures or trickling filter slimes. Unlike the stock culture organisms, trickling filter biomass consistently required some 24 hours to acclimate to all forms of the wastewater. This phenomenon has been attibuted to the protocol employed, i.e., these slimes were evaluated in a dispersed growth environment and maintained on unfamiliar (yet very degradable) substrate (NaAc). However, under steady-state conditions (continous blend facility discharge), this observed lag should pose no operational problems after an initial acclimation period.

Biodegradation data confirmed that IITRI wastewater does not inhibit those organisms tested and showed, in fact, that the waste itself can be recovered, to some extent, as oxygen uptake. On a per mg VSS basis, the trickling filter biomass is better able to degrade the wastewater by a factor of 5.

Activated carbon pretreatment data suggest that no chlorinate i hydrocarbons or incomplete oxidation products were formed during the UV-chlorinolysis process. Cummulative oxygen uptakes for these samples were very comparable in both the toxicity and biodegradation protocols. Ion exchange pretreatment significantly reduced dissolved solids. The stock culture organisms responded with a three-fold increase in cumulative oxygen uptake whereas the filter organisms showed no significant change in degradation.

These trends are well illustrated in Table 8 which is a summary of 60-hour, oxygen-uptake values for the experimental matrix. These values, which were easily calculated using the conversion 1  $\mu$ L/0.00143 mg 0<sub>2</sub> (assuming standard temperature and pressure), were determined both directly (biodegradation protocol) and by difference (toxicity protocol).

TABLE 8. SIXTY-HOUR OXYGEN UPTAKE SUMMARY

			STOCK CULTURE			FILTER ORGANISMS	ANISMS	
	Toxicity Protocol	tocol	Degradation Protocol	Protocol	Toxicity Protocol	Protocol	Degradation Exeterol	: Frote sol
	Substandard	Std. Sub.	: :		Standard	Std. Sub.		
Pretreatment		0	Waste Waste (mgO $_2/\ell/$ mg vss)	Waste (mg02/8/mg vss)		plus waste	Waste Maste (mg0 2 / 2 / 2 / 2 / 2 / 2 / 2 / 2 / 2 / 2	Waste (moo. 9/m mis)
NONE	230	280	0.036	0.050	155	260	0.172	0.237
CARBON	230	300	0.050	0.046	155	250	0.155	C. 163
ION EXCHANGE	230	400	0.122	0.172	155	255	0.114	2,131

#### SECTION V

#### CONCLUSIONS

- 1. UV-chlorinolysis of a solution containing 500 ppm each Hz, MMH, UDMH, and DMNA produced an effluent which was not toxic to stock culture or trickling filter heterotrophic organisms.
- 2. The wastewater itself exerts an oxygen demand of approximately 150 mg/L in the presence of 875 mg/L volatile trickling filter sclids. Ion exchange pretreatment did not significantly change this value.
- 3. In the presence of a milk solids-reared, dispersed growth stock culture (2000 mg/L MLVSS), ion exchange pretreatment reduced TDS such that cummulative oxygen demand values were increased from 90 mg/L to 335 mg/L.
- 4. Current flows at RMA should insure sufficient dilution such that actual chlorinated effluent/organism ratios will be 7 to 8 times lower than those investigated here.
- 5. Carbon adsorption pretreatment had little effect on toxicity and degradability of the wastewater, indicating that chlorinated organics, amines, and/or incomplete oxidation products were not formed in the effluent studied.

#### SECTION VI

#### REFERENCES

- 1. Koch, Roger, "Wastewater Treatment System for Hydrazine Fuel Mixing Facility at Rocky Mountain Arsenal" IIT/Research Institute, Chicago, IL, November 1978.
- 2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, Washington DC 1975.
- 3. Yamaguchi, M. et al, "Anal. Biochemistry" Vol 16, 1966.
- 4. Joel, Arnon R., and C. P. L. Grady III, "Inhibition of Nitrification Effects on Aniline After Biodegradation," Journal Water Pollution Control Federation, May 1977.
- 5. Umbriet, W. W. and J. F. Stauffer, <u>Manometric Techniques</u>, 5th edition, Burgess Publishing Co., Minneapolis 1972.

## APPENDIX A

STOCK CULTURE
DUPLICATE FLASK DATA

## AVERAGE CORRECTED WARBURG DATA

## SAMPLES AVERAGED: Carnation Carnation

Reference of the man	FI ASK	1995 • • Z n	
1 - 1 - 1 1 + 1	Proposition of the Control of the Co	+ [ β α σ = 5 πρ ( Δε ε = 5π) Μ ( π ( )	OF STATE OF THE ST
1000 - 1000 000 000 000 000 000 000 000	1000 1000	り・0 つか・0 161・3 161・3 260・1 270・1 240 -1 240 -1 24	0.) 47.4 71.9 151.7 207.5 213.0 220.1 159.5 210.7 210.7 220.6 220.7 220.
5 (1 7 (1 5 3 1) ()	176.3	232.4 235.7	233.5

## SAMPLES AVERAGED: Carnation® + IITRI/Carnation® + IITRI

6 14 - 34 (	1.77	K MINA NY I	
7 - 15 T 1 - 1 - 1 - 1 - 1	F1 454 5 12-1445 5174 (111_)	FLAST / HETARE SUM	AVEHAGE UPTAKE SUM (UL)
1.00 1.00 2.00 7.00 7.00 23.00 23.00 23.00 23.00 23.00 23.00 23.00 23.00 23.00 24.00	1.0 71.5 71.5 134.5 134.5 145.6 213.6 213.6 213.6 213.6	0.0 73.8 79.1 140.1 214.9 230.5 230.5 230.6 210.6 214.9 243.3	0.0 52.5 75.3 140.3 205.8 215.4 221.1 223.3 200.1 205.1 236.3 232.1
4 / 5 7 7 7 7 4 3 5 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	11/10/ 11/10/10/10/10/10/10/10/10/10/10/10/10/1	2 m n • m 2 m l • d 2 m l • m 2 m 4 • d 2 m f • m 2 d • m 2 d • m	ረ45.3 248.2 248.5 252.5 255.6 252.5 241.3

SAMPLES AVERAGED: Carnation® + IITRI-C1s/Carnation® + IITRI-C1s

111 - 11 C No.	19/0 FLASK	N(17. H/ 4	
1101	FLASE S UPTAKE SUM (UL)	FLASK 9 OPTAKE SOM (UL)	AVERAGE UPTAKE SUM (UL)
1.00 1.00	0.0 -1.0 -1.0 -1.0 -1.0 -4.0 -4.0 -4.0 -4.0 -1.0 -	0.0 -11.4 -15.1 -32.8 -56.7 -51.5 -56.7 -56.8 -83.4 -127.0 -126.0 -126.0 -128.5 -126.0 -126.2 -126.2 -126.2 -126.2	0.03 -10.00 -20.00 -51.00 -51.00 -53.00 -780 -780 -1121.00 -1121.00 -115.00 -116.00 -116.00 -116.00 -116.00 -116.00
43.06	-115.6	-164.8	-141.7

SAMPLES AVERAGED: Carnation® + IITRI CCE Carnation® + IITRI CCE

Dalt-DEC 4.	1974 FLASK	NU3.14/15	
1+51 11*** (-05)	TLANK 14 CHIAKE SUM (UL)	FLASK 15 DETAKE SUM (UE)	AVERAGE UPTAKE SUM (IJL)
3.00 1.00 2.00 7.00 13.00 20.00 21.00 22.00 23.00 23.00 41.50 41.50 43.50 44.50 44.50 45.50 46.50	0793100700700000000000000000000000000000	0.00 77.00 77.00 17.	47.0.4 47.0.4 170.6 170.6 170.6 170.6 170.6 17.6 17.6 17.6 17.6 17.6 17.6 17.6 17
+ A to go	294 (1)	301.8	296.3 297.9

## SAMPLES AVERAGED: IITRI-C1S/IITRI-C1S

OATE-JAN 19.	1414 FLASK	MOS.10/11	
TEST TIME (HKS)	FLASK 10 UPTAKE SUM (UL)	FLASK 11 HPTAKE SUM (UL)	AVENAGE UPTOFF Street
00008888855555555555555555555555555555	0020457828410895652491620406788 09414973566768895652491620406788 112367682823657468282365744788 1123111111111111111111111111111111111	090 •••0 •••0 •••0 ••57 ••57 ••57 ••57 ••64 ••65 ••64 ••67 ••64 •	0.46.46.7.06.1.18.6.7.0.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4
31.42 32.42 33.42 34.42	202.2 203.6 201.7 199.7	207.2 206.6 204.7 204.5	204 • / 205 • 1 203 • 2 202 • 1
35.42 36.42	206.0 209.5	210.6 212.3	208.3 210.9

# SAMPLES AVERAGED: IITRI-Cls/IITRI-Cls (Continued)

56.50       233.1       240.3       235.5         57.50       230.3       241.1       235.5         58.50       233.8       244.5       235.5         59.50       236.4       245.2       244.6         60.50       236.3       246.9       241.2         61.50       231.8       242.4       237.3         62.50       232.5       243.1       237.3         63.50       242.3       254.6       24r.         64.50       243.3       257.3       250.6         65.50       244.2       251.6       245.6         66.50       244.9       260.6       254.6         67.50       242.6       254.6       246.6         68.50       242.6       250.5       242.6         68.50       236.6       250.5       242.6	25732091130780072717728518534865
66.50 244.9 250.5 252 67.50 242.6 254.6 24c. 68.50 236.6 250.5 24c. 69.50 249.4 263.2 255. 70.50 246.3 261.9 254. 71.50 255.5 270.9 263.	<b>.</b> l

## SAMPLES AVERAGED: IITRI/IITRI

DATE-JAN 14.	1474 FLASK	NO5. H/ 4	
TEST	FLASK H	FEASK F	AVE KASE
TIME	UPTAKE SUM	UPTAKE SUM	BPTARE SITA
(MMS)	(UL)	(DL)	(UE)
35.42	63.2	61.7	62.5
36.42	66.4	63.2	54.8
37.42	58.5	55.3	56.4

## SAMPLES AVERAGED: IITRI/IITRI (Continued)

3H.42	59 <b>.</b> 0	57.5	58.3
39.42	64.0 65.7 66.3 63.5	p2.4	63.4
40.42	65.7	64.1 63.1 61.9	647
41.42	66.3	63.1	64-7
41.42 42.42 43.42	63.5	61.9	52.7 57.3
43.47	58.9	22.6	5 <b>7.</b> 3
44.42	58.1	54.4	56.5
45.42	58.1 65.3	62.0	63.7
46-50	69.5	66.2	56.5 63.7 67.7
47.50	68.8	62.0 62.0 62.0	65.4
48.50	71.1	64.3	67.7
49-50	70.6	60.4 65.3	65.7
50.50	77.3	65.3	71.5
47.50 48.50 49.50 50.50 51.50	70.6 77.3 80.7	65.3	65.7 71.3 73.0 65.0
52.50	19.2	รีย์ สี	69.0
ร์ริโร์ดั	82.0	59 <b>.</b> 8	70.9
52.50 53.50 54.50 55.50 56.50	82.0 80.1 83.0	59.6	64.7
55.5ŭ	หรือ	64.2	73.5
56.50	79.8	60.9	70.5
57.50	75.1	รียั•ีด์	66.6
รู้ชี•รี้ง	74.8	59.3	67.1
50 • 50 60 • 60	77 1	หลัง	70.2
59.50 60.50	77.1 75.0 69.0 72.8 78.5	63.3 61.2 56.9	ก็ยู้.โ
61 60	43°0	24.5	63.0
61.50	73 4	50° 4	63.0 57.5
62.50	70 6	62.4	74
63.50	76.5	71.4	74.9 73.3
64.50	76.0 71.8 73.6 73.9	70.6	70.0
65.50 56.50	73.4	58.1	71.7
00.00	73.0	69.9	71.6
n/ • n/	(3.7	68 • 4	64 h
68.50	57.2	5 <u>1.8</u>	64.5 75.7
69.50	72.6	18.9	66 4
70.50	61.4	65.8	66.3
71.50	74.3	73.9	74.1

## SAMPLES AVERAGED: IITRI-C1s (pH7)/IITRI-C1s (pH7)

DATE-JAN 194	14/4 FLASK	NU5.14/15	
TFST TTM= (MMS)	FLASK 14 UPTAKE SUM (UL)	FLASK 15 UPTAKE SUM (UL)	АУЕНАОЕ ПРТАКЕ 511m (JL)
00008888888888888888888888888888888888	(UL) 0.45 9360 777.131.62.94350 1037.631.632.6445.68 1136.6363445.68 1136.63636445.68 1136.63636445.68 1136.63636445.68 1136.63636445.68 1136.6366448 1136.6366448 1136.636448 1136.6366488 1136.6366488 1136.6366488 1136.6366488 1136.6366488 1136.6366488 1136.6366488	0.72 45553 37 45553 37 45553 37 45553 37 45553 37 45553 37 45553 37 4577 937 86 67 20 6512127 147 86 67 20 6512127 22 22 22 22 22 22 22 22 22 22 22 22 2	(III) 10000000000000000000000000000000000
28.442 29.442 31.442 33.442 33.442	298.1 298.4 304.5 305.8 315.8 317.5	263.8 264.2 270.2 270.7 281.0 282.7 282.4	/81.0 /81.3 /87.3 /87.1 /98.4 /100.1

## SAMPLES AVERAGED: | IITRI-Cls (pH7)/IITRI-Cls (pH7) (Continued)

44 ( )	3.36	3000	4.6.
35.42	325.4	240.2	307.⊀
36.42	332.6	245.5	314.1
37.42	333.5	ع من ذ	314.0
31442	333.5	294.5	31400
3H.42	337.9	300.6	314.7
34.42	345.1	309.4	321.0
40 43	344.7		ن د د د
40.42	340.	311.5	329.4
41.42	344.5	312.0	330.0
42.42	350.3	312.7	331.5
43.42	349.9	308.5	ລິລີເລື່ອ
43.45	347.7	307.63	324.5
44.42	361.7	321.9	341.H
45.42	367.3	327.5	347.4
46.50	373.7	335.5	354 · h
40.0			
47.50	364.3	326∙5	345.0
48.50	372.3	334.0	353.6
49.50	375.8	333.8	367. 0
4 7 6 10	3(3.0		354.4
50.50	384.4	334.1	362.0
51.50	392.1	346.2	364.7
52.50	361 1		364
	391.0	344.5	364.0
53.50	393.4	351•4	372.0
54.50	397.9	355•2	376.5
55.50	404.5	358.2	
22.50			341.3
56.50	403.3	300.4	341.n
57.50	405.9	361.1	343.5
58.50	414.8	369°9	342.3
	712.9	37767	3,78 • 3
54.50	415.6	372.4	344.
50.50	420.9	375.8	394.7
61.50	418.2	373.1	395.5
6.7 6.0	7,12,5	270 2	363
65•20	415.3	370.2	342.7
63.50	430.6	345•1	407.7
64.50	435.2	387.9	411.5
22.27	737 5	365 1	
65.50	427.7	382.1	41)4.7
66 <b>.</b> 50	442.2	342.4	417.5
67.50	436.3	388.5	412.4
	735.3		
68.50	435.7	384.5	411.4
69.50	444.7	349.0	421.7
70.50	444.1	399.4	474.2
	458.2	40H.4	(33
71.50	<b>4</b> 70 • €	4 U M • 4	433.5

## SAMPLES AVERAGED: | IITRI CCE/IITRI CCE

++1 PAL-140	19/9 FLASK	NU3-17/11	
1-5T 11MF (m-5)	FLASK 12 UPTAKE SUM (UL)	FLASK 13 OPTAKE SOM (OL)	CH )
) • 0 0 1 • 0 0 2 • 0 0 3 • 0 0	U.0 23.8 37.4 44.4 57.2	() • () 1 • () 3 • () 4 3 • () 5 3 • ()	7) • 71 ~ 1 • 7 4 ~ 6 • 7 9 h • 9
7.08 7.08 7.08 4.08 4.08	50.6 71.7 74.3 80.4 85.7	56.4 55.4 71.7 71.6 40.4	65.1 96.5 73.0 79.0 83.5
1 - 25 11 - 25 12 - 25 13 - 25 14 - 25	74.5 70.8 59.7 49.5 45.9	11.5 67.7 54.9 48.8 44.8	73.4 ny.2 n/.3 44.3
10.25 10.25 17.25 18.25 18.25	52.1 54.9 47.5 47.9	+7.1 71.7 44.1 46.1 46.4	47.5 53.3 45.7 46.5 46.1
20 • 25 21 • 25 22 • 42 23 • 42 24 • 42	52.6 54.2 57.0 55.9 55.0	43.6 40.8 47.7 42.9 43.8	4 M . 1 5 (1 . 5 5 c . 1 4 7 . 4 4 9 . 4
25.42 25.42 27.42 24.44 24.44	49.1 50.d 50.2 45.7 52.7	41.7 41.1 42.3 38.9 41.0	45 • 1 45 • 7 45 • 7 47 • 0 45 • 0
3 1.47 3 .42 37.42 31.47 34.42	りは・ソ 4お・9 4お・6 4ち・7 4お・4	45.2 37.1 41.9 49.0 39.8	45.1 45.3 45.1 44.1
34.42 34.42 34.42 34.42	4 % • 2 5 1 • 0 5 0 • 1 5 1 • 0 5 6 • 4	3H • 7 • 0 • 5 39 • 5 • 0 • 2 • 1 • 9	45 - 7 44 - 8 45 - 6 45 - 6

## HAMPING AVORAGED: TITRI CCEZITTEI CCE (Continued)

41.46	<b>ጛሗ•</b> ዸ	43.7	51.
41.46	57.3	41.0	
42.42	56.3	39.9	44.1
43.42	43.3	30.5	36.7
	53.3	40.3	46.3
44.46	60.8	45.9	دُ وَ دُ
45.42	110 • f7	Z:	44.4
46.50	67.2	50.4	( m m
47.50	54•3	37.7	47.7
44.50	6ۥ3	47.2	54.1
44.50	<b>60.4</b>	43.4	51.7 57.1
50.50	65.4	48.7	7 ( • 1
51.50	67.7	52. <u>3</u>	70.0
52.50	54.3	45.7 45.0	24.2
53.50	65.5	45.0	つきゅう
54.50	57.3	43.6	ر • ر، • ب
55.50	64.4	51.9	50.0
56.50	59•i	45.2	56.7
ร์7ี.ร์งั	6๋โ.ห์	46.0	53.9
50 50	67.2	53.0	64.1
58.50	68.0	53.7	69.4
54.50	71 6	57 <b>°.</b> i	64.4
60.50	71.6	21.0	01.7
61.50	ê4•à	54.5	27.
06.50	62.4	51.5	57.5
63.50	74.2	63.0	6H • 7
54.50	7ក្.ក	65.g	76.5
65.50	67.6	54.7	51.2
66.50	80.5	67.3	74.9
67.50	71.0	57.7	64.3
6H.50	66.7	57.7 57.2	51.7
69.50	75.9	62.7	69.1
70.50	74.8	63.2	64.1
71.50	45.2	68.6	75.→
1.1 • J.//	76. € €	0	

# APPENDIX B TRICKLING FILTER ORGANISM DUPLICATE FLASK DATA

## AVERAGE CORRECTED WARBURG DATA

## SAMPLES AVERAGED- NA AC

	NA AL		
DATE-JAN 2.	1979 FLASK	NOS. 6/ 7	
TEST TIME (HRS)	FLASK 6 UPTAKE SUM (UL)	FLASK 7 UPTAKE SUM (UL)	AVERAGE UPTAKE SUM (UL)
00000000000000000000000000000000000000	0.66669275394067841589987203331406041072614404275354704471948033328976972126880285	05791467249466126025064143340942773869403206298838352350534901079243164102598939781266324335926688871337311661155557762589103	011886979849869055914869868975962949883828738632814612493193 0175501082160.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.

## AVERAGE CORRECTED WARBURG DATA

# SAMPLES AVERAGED- TITRI-CLS TITRI-CLS

DATE-JAN 2.	1979 FLASK	NOS. 8/ 9	
TRST	FLASK H	FLASK 9	AVERAGE
TIME	UPTAKE SUM	UPTAKE SUM	UPTARE SUM
(HRS)	(UL)	(UL)	(IIL)
00000000000000000000000000000000000000	0137610509998892520614835868001658155389945776067107044882960	084087275514209905749547647959468423878874624877196582295982	016399487706891763677296208080558394123410200417107713598471
	0160883444721211552321	028277334482-5-1454-2113558023858754794762984991364647205893	027177334482 3 1453121 1556992647757016994196125374543736582

## AVERAGE CURRECTED WARBURG DATA

## SAMPLES AVERAGED- NA AC+IITRI NA AC+IITRI

	VA ACTITUI		
PATE-JAN 2.	1979 FLASK	NOS.10/11	
TEST	FLASK 10	FLASK 11	AVERAGE
TIME	UPTAKE SUM	UPTAKE SUM	UPTAKE SUM
(HRS)	(UL)	(UL)	(UL)
00000000000000000000000000000000000000	003362554576673419530441392774388119646747280012446243598781	027089198453194386500694158953273513073581679579805198378820	040242733564315597520438275864275816300169480740126121488256
	05939187181652542=384786783762529977271186417227393036557765	01 31 7723557020116040635365126765493821619684227617192431868	025845 22181252348323 20029449142180507263118425723758098311
	11145704667777889909900011121202323233333	01 70 111111111111111111111111111111111	11111111112222222222222222222222222

## AVERAGE CORRECTED WARBURG DATA

## SAMPLES AVERAGED- NA AC+IITRI-CLS

		NΑ	AC+IIIHI-	-CLS
VAL-3TAC	2,	1979	FLASK	NOS.12/13

TEST	FLASK 12	FLASK 13	AVERAGE
TIME	UPTAKE SUM	UPTAKE SUM	UPTAKE SUM
(HRS)	(UL)	(UL)	(UL)
00000000000000000000000000000000000000	075696681615726886503590066491772908777039713873176772623238	02734976517395130479204874732332488746298895447508965498006d	0 81928777344844515941769356967093497564968834129032113352148
	0126241- 1032743 5763569389039093029207383906526549655664958	0-219-34578749215132326030975033491950656871084793363251486572	0 -331222449538872819531489484971615263148569948090456715
	- 112369039093111111111111111111111122222222222		124569922244555566666767888990910111222

AVERAGE CORRECTED WARBURG DATA

# SAMPLES AVERAGED- IITHICCE

DATE-JAN 2.	1979 FLASK	NOS.14/15	
TEST	FLASK 14	FLASK 15	AVERAGE
TIME	UPTAKE SUM	UPTAKE SUM	UPTAKE SUM
(HRS)	(UL)	(UL)	(UL)
00000000000000000000000000000000000000	067378982343140288762308505890908776052255956686699561667408	0245489241240611007333364805109834283824141557204610483101952	0.7.6468958783951244288037405800821985938608257440150572889720
	0121-12153-2254471612575226176128629322768706685099300175256	0-4-423874242690472622902875-44551084899167912025036944408479	0.3.2125397749224724107313706103498516566214463473631777731813
	1112223335555666677777678899099302222222222222222222222222222222		0.3.2125333334545456667888990090909090909090909090909090909090

# AVERAGE CORRECTED WARBURG DATA SAMPLES AVERAGED- IITRICCE+NA AC

DATE-JAN 2,	1979 FLASK	NOS.16/##	
TEST TIME (HRS)	FLASK 16 UPTAKE SUM (UL)	FLASK### UPTAKE SUM (UL)	AVERAGE UPTAKE SUM (UL)
00000000000000000000000000000000000000	009018909324625157175839145149164564029012822864053486760675 053433311 4 2 -11905700633810240861978854453213718827085157931445166766787889980111222234444444	000000000000000000000000000000000000000	009018909324625157175839145149164564029012822864053486760675 053433311 4 2 -11905700633381024056619788544532137188270885179 11257934445102408619788998137188270885179

## AVERAGE CORRECTED WARHUNG DATA

## SAMPLES AVERAGED- IITRI IITRI

DATE-JAN 2.	1979 FLASK	NOS. 4/ 5	
TEST TIME (HRS)	FLASK 4 UPTAKE SUM (UL)	FLASK 5 UPTAKE SUM (UL)	AVERA JE UPTAKE SUM (UL)
0000000000000000000000000000000000555555	034815097446978826811100766480825036572918092712467549750730 054414-1353254537126673741928472737037899409155099176866146 -1-1-1-1-1-112334456788899999900111121213344566146	037752562463312827023364334505762258950397624826110775676281 0526-11-1034768105577416306038717045716239815971270644407465 	036738889405645321467722090947748192261608853824884117663066 0535 211 2833657293366172862606712168047661958218635582186355362018635553620186355362018635536201863556201862018620186201862018620186201862018

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