



NRL/MR/6180--98-8141

Evaluation of the Effects of AFFF Inputs to the VIP Biological Nutrient Removal Process and Pass-through Toxicity—Phase IA

MUIDE ERTEN-UNAL
S. PARANJAPÉ
GARY C. SCHAFFRAN

*Old Dominion University
Department of Civil and Environmental Engineering
Norfolk, Virginia*

F.W. WILLIAMS

*Navy Technology Center for Safety and Survivability
Chemistry Division*

February 27, 1998



A000864

Approved for public release; distribution unlimited.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE February 27, 1998	3. REPORT TYPE AND DATES COVERED Phase IA Study, Sept. 1996-Sept. 1997		
4. TITLE AND SUBTITLE Evaluation of the Effects of AFFF Inputs to the VIP Biological Nutrient Removal Process and Pass-through Toxicity—Phase IA		5. FUNDING NUMBERS Prob. No. 61-M393-X7 Grant No.: N00014-96-1-G021 PR-Number: 61-2330-96 Disbursing Code: N68342 AGO Code: N66020 CAGE Code: 50075		
6. AUTHOR(S) Mujde Erten-Unal, S. Paranjape, Gary C. Schafran, and F.W. Williams		8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6180-98-8141		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Old Dominion University, Department of Civil & Environmental Eng. KH 135, Norfolk, VA 23529-0241		9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE A		
13. ABSTRACT (Maximum 200 words) This report discusses the results of a bench scale study conducted to evaluate the potential inhibitory effects of untreated AFFF wastewater to the Virginia Initiative Plant (VIP) biological nutrient removal process. A bench-scale study was conducted to evaluate the potential inhibitory effects of untreated AFFF wastewater to the nitrification process of the Virginia Initiative Plant biological nutrient removal system. Under this testing, bench-safe reactors simulating the nitrification process were loaded at various AFFF concentrations and the influence on the process performance was evaluated. The purpose of this effort was to determine the level of AFFF that could be incorporated into the influent of a biological nutrient removal process without causing inhibitory effects. The results of the nitrification inhibition study showed that the AFFF concentrations tested in the range between 10 ppm to 60 ppm did not show any significant inhibition to biological nitrification. The effluent from each reactor did not exhibit any pass-through toxicity as well. <i>50,000 gal H₂O for each 3 gal AFFF conc = 60 ppm AFFF conc</i>				
14. SUBJECT TERMS Environment AFFF Wastewater Nitrification		15. NUMBER OF PAGES 53 16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

CONTENTS

1.0	INTRODUCTION	1
1.1	Overview	1
1.2	Study Objectives	4
2.0	METHODS AND MATERIALS	5
2.1	Reference Reactor Operation	5
2.2	Analytical Methods	7
2.3	BNR Inhibition Batch Assays	8
2.4	Toxicity Pass-Through Testing	10
3.0	RESULTS	11
3.1	AFFF Waste Characterization	11
3.2	Reference Reactor Performance	11
3.3	Range Finding Test Results	17
3.4	BNR Inhibition Batch Assays	17
3.4.1	Inhibition Test at 60 ppm AFFF Concentration	20
3.4.2	Inhibition Test at 50 ppm AFFF Concentration	20
3.4.3	Inhibition Test at 30 ppm AFFF Concentration	25
3.4.4	Inhibition Test at 10 ppm AFFF Concentration	25
3.5	Toxicity Pass-Through Testing	25
4.0	DISCUSSION	35
5.0	CONCLUSION	41
	REFERENCES	44

TABLES

Table 2-1. Organic and inorganic synthetic wastewater constituents	6
Table 3-1. Chemical/Parameter Specific Measurements	12
Table 3-2. Weekly Performance of the reference reactor during the course of the study	14
Table 3-3a. Nitrite nitrogen concentration variation during different stages	16
Table 3-3b. Nitrate nitrogen concentration variation during different stages	16
Table 3-3c. Orthophosphate concentration variation during different stages	16
Table 3-4. Range finding test reactor components	18
Table 3-5. Range finding inhibition test results	19
Table 3-6. BNR Inhibition reactor components: 60 ppm AFFF	21
Table 3-7. Nitrification inhibition at 60 ppm	22
Table 3-8. BNR Inhibition reactor components: 50 ppm AFFF	24
Table 3-9. Nitrification inhibition at 50 ppm	26
Table 3-10. BNR Inhibition reactor components: 30 ppm AFFF	28
Table 3-11. Nitrification inhibition at 30 ppm	28
Table 3-12. BNR Inhibition reactor components: 10 ppm AFFF	31
Table 3-13. Nitrification inhibition at 10 ppm	32
Table 3-14. Summary of acute toxicity test results	34

Figures

Figure 2-1. BNR Inhibition Batch Assays	9
Figure 3-1. Specific oxygen uptake rates (SOUR's) during the feed stage for 60 ppm AFFF (A-control, B-inhibition)	23
Figure 3-2. Specific oxygen uptake rates (SOUR's) during the aerobic stage for 60 ppm AFFF (A-control, B-inhibition)	23
Figure 3-3. Specific oxygen uptake rates (SOUR's) during the aerobic stage for 50 ppm AFFF (A-control, B-inhibition)	27
Figure 3-4. Specific oxygen uptake rates (SOUR's) during the feed stage for 30 ppm AFFF (A-control, B-inhibition)	30
Figure 3-5. Specific oxygen uptake rates (SOUR's) during the aerobic stage for 30 ppm AFFF (A-control, B-inhibition)	30
Figure 3-6. Specific oxygen uptake rates (SOUR's) during the feed stage for 10 ppm AFFF (A-control, B-inhibition)	33
Figure 3-7. Specific oxygen uptake rates (SOUR's) during the aerobic stage for 10 ppm AFFF (A-control, B-inhibition)	33
Figure 4-1. AFFF inhibition study range finding test results	36
Figure 4-2a. Average ammonia concentrations for control reactors	38
Figure 4-2b. Average ammonia concentrations for inhibition reactors	38
Figure 4-3. Average ammonia nitrogen removal rates for the inhibition reactors	39
Figure 4-4a. Average COD removal rates for the control reactors	40
Figure 4-4b. Average COD removal rates for the inhibition reactors	40
Figure 4-5a. Average inorganic fluoride concentration for controls	42
Figure 4-5b. Average inorganic fluoride measurements as a function of reaction time	42
Figure 4-6. Fluoride released as a function of AFFF dose for inhibition reactors	43

Abstract

The U.S. Navy utilizes a surfactant in fire fighting water that improves the ability to control petroleum-based fires. This surfactant is currently manufactured by up to five companies and is commonly referred to as AFFF (aqueous film-forming foam) conforming to military specifications Mil-F-24385F. Present concerns over inhibitory effects of AFFF wastewater have resulted in the prohibition of its disposal to the Hampton Roads Sanitation District (HRSD), Hampton Roads VA collection system where it would eventually enter one of the biological wastewater treatment plants operated by the District. HRSD is particularly concerned with how AFFF wastewater might interfere with biological nutrient removal (BNR) processes at its Virginia Initiative Plant (VIP). The Navy does not discharge to that plant but HRSD wants to check the impact on the VIP process because it is more sensitive than a conventional activated sludge processes used by other HRSD Plants in which the Navy discharges to and HRSD plans to upgrade all of their plants to the VIP process eventually.

HRSD has indicated that compatibility of AFFF wastewater with the BNR process must be demonstrated prior to granting the necessary permit to discharge AFFF wastewater to the wastewater collection system leading to their plants. Previous studies were performed using surrogate AFFF compounds (AFFF-S), however, they did not address actual AFFF discharges. The overall objective of this program was to study the impact of AFFF wastewater to a biological nutrient removal process and determine whether pass-through toxicity occurs in the effluent of a biological process receiving wastewater containing AFFF.

A bench-scale study was conducted to evaluate the potential inhibitory effects of untreated AFFF wastewater to the nitrification process of the VIP BNR. In order to maintain a continuous supply of uniform nitrifying microorganisms to the bench-scale reactors, a fill-and-draw type batch reference reactor was operated continuously at the Civil and Environmental Engineering Laboratory at Old Dominion University. The reactor was operated sequentially in aerobic feed, anaerobic, aerobic, settle and decant phases. Feed aeration, mixing, and decant were all controlled by a programmable controller. After a specified settling period, supernatant (effluent) from the reactor was withdrawn by a solenoid valve and collected in a sample bottle for analysis.

Nitrification inhibition was assessed in series for untreated AFFF wastewater using a batch assay procedure. Inhibition tests were performed with different concentrations of AFFF and controls using six, 6-liter batch reactors. The inhibition reactors were operated following the same sequential cycle of the reference reactor. The degree of ammonia oxidation in reactors receiving a loading of AFFF wastewater was compared to the degree of oxidation in control reactors receiving similar volumes of tap water. Toxicity pass-through testing was also performed to determine maximum loadings of the untreated AFFF wastewater that would not cause toxicity in the effluent from a BNR process. Acute toxicity of the effluent to *Mysidopsis bahia* (mysid shrimp) and *Cyprinodon variegatus* (sheepshead minnow) have been examined in toxicity testing of both control and AFFF-loaded inhibition reactors.

The results of the nitrification inhibition study showed that the AFFF concentrations tested in the range between 10 ppm to 60 ppm did not show any significant inhibition to biological nitrification. The intensity of foaming in the reactors increased with the increasing AFFF concentrations and the loss of solids from the reactors was associated with the foaming density. At AFFF concentrations between 10 ppm to 50 ppm, the loss of solids increased. However, at 60 ppm, the foaming was so much denser that it did not allow solids carryover from the reactors. Uninhibited nitrification was also observed among the reactors that had excessive foaming. There was significant chemical oxygen demand (COD) removal observed for each AFFF concentration tested as well. However, the percent COD removal in the inhibition reactors was less than that of the control reactors. While the percent COD removal decreased with increasing AFFF concentration, the amount of COD removed actually increased (on a mg/L basis). This observation is a direct result of the addition of COD associated with the AFFF. The acute toxicity test results showed that the effluent from each inhibition reactor did not exhibit any pass-through toxicity.

Fluoride measurements were also conducted on control samples and the AFFF wastewater samples during the inhibition testing to examine fluoride release. A linear relationship was observed up to 50 ppm AFFF which signified that organo-fluoride compounds were being decomposed in proportion to the AFFF concentration. The low release of fluoride for the 60 ppm AFFF wastewater suggested some interference in fluoride release due to the inhibition of the microorganisms that were capable of decomposing these compounds or evidence of selective substrate utilization where microorganism were consuming other preferable compounds before selecting organo-fluoride compounds.

Overall, the results of this study indicated that AFFF solutions discharged into the wastewater at concentrations 60 ppm or below did not exhibit any inhibitory effect to biological nitrification and pass through toxicity.

Evaluation of the Effects of AFFF Inputs on the VIP Biological Nutrient Removal Process and Pass-Through Toxicity - Phase IA

1.0 INTRODUCTION

1.1 Overview

The US Navy utilizes a surfactant in fire fighting water that improves the ability to control petroleum-based fires. The surfactant, which is widely used by the Navy including facilities in the Hampton Roads region, Hampton Roads VA, is currently manufactured by up to five companies and is commonly referred to as AFFF (aqueous film-forming foam) conforming to military specifications Mil-F-24385F. The AFFF chemical makeup is not well known and likely varies among manufacturers and between batches. The US Navy is exploring a number of options that include disposal of the fire fighting water to wastewater collections systems where the components of AFFF wastewater would be removed biologically.

Current disposal of fire fighting water that includes AFFF wastewater has been limited by concerns for the environmental/toxic effects associated with AFFF. Disposal of the fire fighting foam to sanitary sewers has been considered as an option, however, concern for the potential toxic or inhibitory effects associated with AFFF wastewater have generally led to a ban on introduction of AFFF to wastewater collection systems.

Several studies have been performed on the disposal and treatment of AFFF surrogate (AFFF-S) wastewater using surfactants such as CalsoftL-40 (Pilot Chemical Co.), DRFS (Dominion Restoration Inc.), Micro Blazeout (Verde Environmental), and Silv-Ex (Ansul Fire Protection). Bench-scale anaerobic and aerobic reactors were used to investigate the potential inhibition of the AFFF surrogates to nitrification, denitrification, and phosphorus release and uptake in a biological nutrient removal (BNR) process [1,2]. These effects were investigated for both untreated and pretreated AFFF-S wastewater. The results showed that pretreating a wastewater containing AFFF-S allowed for complete nitrification and denitrification and untreated or pretreated wastewater did

not have any adverse effect on denitrification and phosphorus release. The use of coagulants such as alum, ferric chloride, calcium chloride, and cationic polymers also have been observed to be capable of reducing the organic content of AFFF [1,2,3,4].

Treatability studies have also been conducted with a high-purity oxygen activated sludge system. The results showed that acceptable levels of biological treatment could be obtained with untreated firefighting wastewater containing 3% AFFF diluted by a factor of 100. The use of dissolved air flotation treatment on the firefighting wastewater further reduced the dilution ratio needed for acceptable effluent quality from the biological process [5,6].

The use of chemical pretreatment with dissolved air flotation (DAF) provided consistent removal of chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), and firefighting surfactants [7]. Overall, the use of coagulation, flocculation, and clarification aided in the reduction of organics prior to discharge to a BNR process. Upon chemical pretreatment and using aerobic and anaerobic sequencing batch reactors, it was found that an acceptable effluent that is amenable to an aquatic stream could be processed [8, 9, 10]. Additional studies were performed to determine the biodegradability of AFFF wastewater. Some of the additional work included the use of wastewater containing actual fire fighting water and AFFF. However, detailed testing on the effects of actual AFFF wastewater on biological nutrient removal was not performed in these studies [11, 12]. The biodegradability of commonly used AFFF surrogates which have been used in training activities were evaluated on bench-scale, continuous-feed activated sludge processes [13, 14, 15]. The AFFF dose that was fed to the reactor increased gradually from 100 ppm to 250 ppm. The results exhibited very good BOD and COD removal rates, however, nitrification was inhibited with increasing AFFF concentrations.

Present concerns over inhibitory effects of AFFF wastewater have resulted in the prohibition of its disposal to the Hampton Roads Sanitation District (HRSD) collection system where it would eventually enter one of the biological wastewater treatment plants operated by the District. HRSD is particularly concerned with how AFFF wastewater might interfere with biological nutrient removal processes at its Virginia Initiative Plant (VIP). The Navy does not discharge to that plant but HRSD wants to check the impact on the VIP process because it is more sensitive than a conventional activated sludge processes used by the Army Base, Atlantic, and Chez-Eliz Plants in which the Navy

discharges. HRSD plans to upgrade all of their plants to the VIP process eventually. The VIP plant incorporates biological nitrogen, phosphorous, and organic matter (BOD/COD) removal through a sequential series of anaerobic, anoxic, and oxic reactors. Nitrogen removal occurs through microbially-mediated nitrification and denitrification and phosphorous removal occurs through enhanced uptake by poly P bacteria. It is well known that the nitrification and denitrification processes can be inhibited in the presence of various chemicals and Poly P bacteria have been observed to be inhibited by H_2S and 2,4-dinitrophenol. Because of the sensitivity of these microbial processes to inhibition, it is important to characterize the relationship between concentrations of various chemicals and the rates of conversion of nitrogen, phosphorous, and organic substrate.

HRSD has indicated that compatibility of AFFF wastewater with the BNR process must be demonstrated prior to granting the necessary permit to discharge AFFF wastewater to the wastewater collection system leading to their plants. Toxicity pass-through potential of AFFF is also another concern to HRSD. The US Navy at Naval base Norfolk, VA previously supported two studies [1,2] to investigate the impact of AFFF on the BNR process in support of their request to dispose of AFFF to the wastewater collection system. The study methodologies in these two studies, including the use of a reference reactor and inhibition testing with sequencing batch reactors operating on cycles of aerobic feed, anaerobic react, and settling were approved by HRSD. However, instead of using AFFF that is utilized by the Navy, surrogate AFFF compounds (AFFF-S) were used. The two studies by CH2m Hill Co. were performed using AFFF-S for the sole purpose of identifying the need for pretreatment and/or obtaining authority to construct and discharge AFFF-S wastewater to HRSD from the new fire training school at Fleet Training Center (FTC), Norfolk VA. Neither study was intended to address AFFF discharges. The current study is required to determine the level at which AFFF causes process inhibition or pass through toxicity so that discharge permits can be modified to allow the non-routine discharge of AFFF from sources other than the fire training school at FTC Norfolk VA (i.e., hangar fire protection systems and fire truck testing). The results were not accepted by HRSD since the AFFF solution used by the Navy was not tested. This situation lead to the current study which involved directly evaluating the impact of AFFF (as used by the Navy) on a BNR process.

A bench-scale study was conducted to evaluate the potential inhibitory effects of untreated AFFF wastewater to the nitrification process of the VIP BNR. Under this testing, bench-scale reactors simulating the nitrification process were loaded at various AFFF concentrations and the influence on the process performance was evaluated. The purpose of this effort was to determine the level of AFFF that could be incorporated into the influent of a biological nutrient removal process without causing inhibitory effects. Toxicity pass-through testing was also performed to determine maximum loadings of the untreated AFFF wastewater that would not cause toxicity in the effluent from a BNR process.

1.2 Study Objectives

The overall objective of this work was to study the impact of AFFF wastewater to a biological nutrient removal process and determine whether pass-through toxicity occurs in the effluent of a biological process receiving wastewater containing AFFF. Specific objectives of this study include:

- Determine the relationship between AFFF concentrations (i.e. % full strength, fluoro-organic compounds, butyl carbitol concentration) in influent wastewater and the degree of inhibition of nitrogen, phosphorous, and COD removal under a variety of operating conditions similar to those of the VIP plant;
- Identify conversion/removal through biological treatment of specific components of the AFFF surfactant (see analytical methods below);
- Measure the acute toxicity of the treatment reactors' effluent to *Mysidopsis bahia* (mysid shrimp) and *Cyprinodon variegatus* (sheepshead minnow) to assess the possibility of toxicity pass through in a process similar to the VIP process;
- Determine the chemical/parameter specific concentrations of the AFFF wastewater effluent quality with respect to parameters specified in HRSD industrial pretreatment guidelines. Also document appropriate findings from a treatment and aesthetic standpoint.

2.0 METHODS AND MATERIALS

2.1 Reference Reactor Operation

In order to maintain a continuous supply of uniform nitrifying microorganisms, a fill-and-draw type batch reference reactor was used at the Civil and Environmental Engineering laboratory at Old Dominion University. The reference reactor consisted of a 30-gallon polyethylene tank containing a hexagonal-shaped poly vinyl chloride (PVC) air diffuser and a rapid mixer. It was initially seeded with mixed liquor suspended solids (MLSS) collected from the secondary clarifiers at the VIP plant. The solids were allowed to settle and the supernatant was decanted. The reactor was then fed over the duration of the study with a synthetic feed solution comprised of organic and inorganic compounds necessary to support a healthy population of nitrifying, denitrifying and phosphorus removing bacteria. This feed was the same composition used in a previous study of AFFF-S[2]. Table 2-1 shows the organic and inorganic constituents used for preparing the feed solution. Some changes to the feed composition were made during the study and these changes are mentioned in subsequent sections. The reactor was fed this solution throughout the feed stage with a peristaltic pump. The reactor was operated sequentially in aerobic feed, anaerobic, aerobic, and settle and decant phases. Feed aeration, mixing and decant were all controlled by a programmable controller.

Air supply was adjusted to maintain 4 mg/l of dissolved oxygen (DO) in the reactor during the feed and aeration stages. A submersible DO probe with a DO meter was continuously used to monitor the DO concentration in the reactor. The feed tank consisted of a 30 gallon polyethylene tank which was placed in a refrigerator at 4°C. The feed tank was refrigerated to limit bacterial growth in the feed tank. The reactor was operated in a cyclical mode for a period of sixteen hours for each cycle. Operation of each cycle comprised of 4-hour feed with aeration, 4-hour anaerobic, 4-hour aerobic, 4-hour settle and a two-minute decant period. During each cycle, 7.5 gallons of feed was supplied and the same amount was decanted as supernatant. The total volume in the reactor was 24 gallons. The feed and supernatant were collected and analyzed for COD and ammonia nitrogen (NH₃-N) twice per week. The reactor was also monitored for MLSS and sludge volume index (SVI) twice per week. The COD analyses was favored over BOD as it gave very fast and repeatable results.

Table 2-1: Organic and inorganic synthetic wastewater constituents

Organic Feed Stock				
Constituent	Ref. Conc. g/L*	Conc/CH2M mg/L*	Grams for 30 gal soln	Grams per Gal.
Beef Extract	9.0730	56.9784	16.1748	0.5392
Bactopeptone	13.1960	82.8709	23.5250	0.7842
Urea	2.4740	15.5367	4.4105	0.1470
KH ₂ PO ₄	4.7420	29.7798	8.4537	0.2818
K ₂ HPO ₄	1.8560	11.6557	3.3088	0.1103
(NH ₄) ₂ CO ₃	9.3610	58.7871	16.6882	0.5563
NaHCO ₃	13.7330	86.2432	24.4823	0.8161
Na ₂ CO ₃	38.4760	241.6293	68.5925	2.2864
CH ₃ COOH	9.5710	60.1059	17.0626	0.5688

Inorganic Feed Stock				
Constituent	Ref. Con g/L*	Conc/CH2M mg/L*	Grams for 30 gal soln	Grams per Gal.
MgSO ₄	18.804	23.693	6.7259	0.2242
CaCl ₂ ·2H ₂ O	4.9500	6.2370	1.7705	0.0590
NaCl	82.50	103.95	29.5088	0.9836
FeSO ₄	2.0630	2.5994	0.7379	0.0246
MnSO ₄ ·H ₂ O	0.0186	0.0234	0.0066	0.0002
CuSO ₄	0.0012	0.0015	0.0004	0.0000
Na ₂ MoO ₄ ·2H ₂ O	0.0007	0.0008	0.0002	0.0000
ZnSO ₄ ·7H ₂ O	0.0193	0.0243	0.0069	0.0002

* - Concentrations obtained from a previous study, done by CH2M HILL.

However the BOD:COD ratio was periodically checked for both the feed and the supernatant in order to evaluate the stability of the ratio.

2.2 Analytical Methods

The analytical methods employed in this study for evaluating the effects of AFFF wastewater inputs on biological treatment performance consisted of procedures as prescribed by the United States Environmental Protection Agency (USEPA) [16] or in Standard Methods [17]. All chemicals used were reagent grade or better and all quality assurance/quality control procedures were followed as closely as possible.

Measurements of organic strength were determined through carbonaceous five day BOD ($CBOD_5$), COD, and total organic carbon (TOC) measurements. $CBOD_5$ (determined with a nitrification inhibitor added to BOD bottles) were measured to eliminate potential interferences that nitrification could have on the evaluation of organics removal with the BOD test. $CBOD_5$, COD, and TOC analyses were determined using filtered samples on reactor effluent and filtered and unfiltered samples in the influent. Samples were filtered through a glass fiber filter to eliminate microorganisms and other particulate materials that are not related to the organic components of the AFFF or the dissolved organic compounds that are in the wastewater before AFFF introduction. Since the AFFF components are water soluble and will be dissolved in solution, filtration should not directly interfere with their accurate detection. Measurements of total suspended and volatile suspended solids (TSS and VSS, respectively) were used to determine organic solids loading, reactor MLSS concentrations, and non-settleable TSS concentrations in reactor effluent. In order to reduce variability of TSS and VSS data, the tests were performed on the same days that solids concentrations feeding into the reactor. The nitrogen series were determined by three different analytical techniques. Persulfate digestion followed by ammonia analysis by ion selective electrode was utilized to determine total Kjeldahl nitrogen (TKN) concentrations, ammonia concentrations were measured by ion selective electrode without sample digestion, and nitrate and nitrite concentrations were determined on filtered samples using ion chromatography. Orthophosphate was similarly determined using ion chromatography.

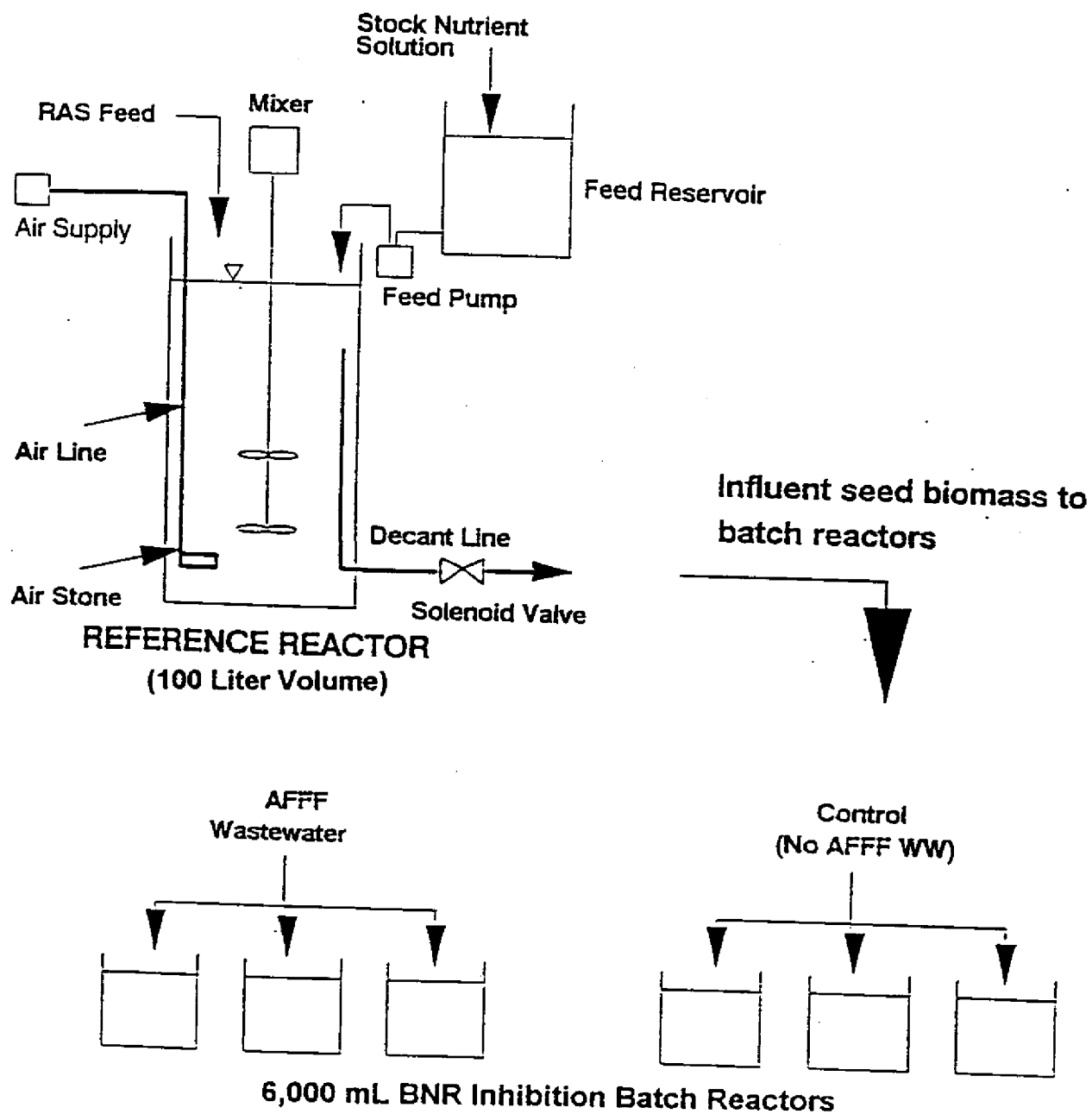
As part of this study, butyl carbitol, a major component of AFFF, is also being analyzed by ion chromatography utilizing electrochemical detection. Decomposition of fluoro-organic compounds are being evaluated by ion chromatography through determination of inorganic fluoride directly and inorganic fluoride following persulfate digestion. The change in fluoride concentration between pre- and post- digestion will give an indication of the amount of fluoride that is tied up in organic compounds.

2.3 BNR Inhibition Batch Assays

Nitrification inhibition was assessed in a series of batch experiments with AFFF-laden wastewater. Inhibition tests were performed using six, 6-liter batch reactors of which three were controls (no AFFF added) and three were a single desired concentration of AFFF as shown in Figure 2-1. Uniform seed biomass of approximately 4,000 mg/L was obtained from the reference reactor for each batch reactor. Approximately 2,000 mL of the appropriate organic and inorganic nutrients were added from the stock nutrient tank and stock (undiluted) AFFF was added in sufficient volume to the nutrient broth to obtain the test AFFF concentration needed. Each batch reactor was equipped with an air supply source, an air stone, and a mixer. After the uniform seed biomass was added to each reactor, the air was turned on and the feed stock solution was introduced manually at 0, 30, 60, and 90 minutes during the two hour fill cycle. The reactors were mixed and aerated during the feed cycle and dissolved oxygen was monitored to insure adequate aeration. At the end of this cycle, samples were withdrawn and the reactors were covered with lids to achieve anaerobic conditions. Mixing was continued throughout this cycle to maintain the biomass in suspension.

At the end of the two hour anaerobic cycle another sample was withdrawn from each reactor, air was turned on and the lids were removed. Aeration and mixing were continued for another two hours, and additional samples were taken at the end of the aerobic cycle. Finally, the reactor contents were allowed to settle for two hours and samples taken from the supernatant were removed during the decant cycle. Each sample from the reactors was analyzed for pH, TKN, ammonia, NO_3^- , NO_2^- , orthophosphate, COD, BOD, TSS, VSS, TDS, and alkalinity. Comparisons were made between the controls which did not contain any AFFF and the reactors dosed with AFFF.

Figure 2-1: BNR Inhibitor Batch Assays



The degree of ammonia oxidation in beakers receiving a loading of AFFF wastewater was compared to the degree of oxidation in control reactors that did not contain any AFFF. All samples were held for less than 48 hours prior to analytical testing. While performing the inhibition batch assay experiments, dissolved oxygen concentrations were determined during the feed and aeration cycles. This was done by measuring the dissolved oxygen depletion of a mixed liquor sample taken from each reactor into a BOD bottle for a period of five minutes. Oxygen uptake rates (OUR) were measured and the respiration rates were determined by specific oxygen uptake rate (SOUR) measurements; $SOUR = OUR/MLVSS$ (mixed liquor volatile suspended solids). This procedure provided an indication of the effects of the untreated AFFF wastewater on the microorganisms.

2.4 Toxicity Pass-Through Testing

Toxicity pass-through testing was performed on the inhibition reactors (controls and AFFF-dosed) to estimate what the maximum concentration of AFFF to the BNR process would be without causing effluent toxicity. The acute toxicity pass-through tests were performed using the procedures outlined by the USEPA [18]. At the end of the BNR inhibition batch aeration period, the mixed liquor was allowed to settle and clarified supernatant was decanted from each reactor and filtered through a coarse glass fiber filter. This filter is of the same type that is used for suspended solids analysis with 10 micrometer nominal size and without organic binder. Prior to use, the glass fiber filters were rinsed thoroughly by passing high-purity, deionized distilled water through the filter. The filtration apparatus was rinsed between each sample aliquot using 10 percent HNO_3 , acetone and high purity water. The filter toxicity was also checked by testing filtered dilution water.

Toxicity samples were submitted to a qualified bioassay laboratory, Reed and Associates, Newport News VA, for acute toxicity testing using *M. bahia* and *C. variegatus* following the current EPA procedures. It was ensured that the laboratory would perform a standard reference toxicant test on a regular basis and develop accompanying quality control charts. All samples were held for less than 48 hours prior to use in testing.

3.0 RESULTS

The results of this study include AFFF waste characterization, initial range finding tests, inhibition tests and toxicity pass-through. Each result will be described in the following sections.

3.1 AFFF Waste Characterization

The AFFF compound used in this study is manufactured by the 3M Company. The name of the compound is FC-203CE LightwaterTM brand Aqueous Film Forming Foam. Before analyzing for the priority pollutants, the manufacturer of the AFFF was contacted and a letter from the Company was obtained specifying the levels of different compounds that may be present in the AFFF.

Most of the priority pollutants were either claimed not to be intentionally added, or known to be present according to 3M Company.

Among the chemical specific measurements required by HRSD, BOD₅ is reported as 0.091 g/g, and COD is reported as 0.740g/g in the MSDS data. The pH value was measured as 8.0 at 77°F. The TSS, TKN, TOC and alkalinity measurements were not specification requirements for AFFF, therefore, they were measured in the Environmental Engineering laboratory of ODU along with the fluoride concentration.

Of the pesticides and PCBs, the compound Tolyl triazole (CAS# 29385-43-1) is stated to be present at 0.05 percent as shown in the MSDS. Butyl carbitol, (CAS# 112-34-5) is also present as diethylene glycol butyl ether at 30 percent by volume. The surfactant component of AFFF is a trade secret and was not disclosed by the 3M Company. Table 3-1 shows a summary of the chemical/parameter specific measurements determined in the laboratory for some parameters and specified by the 3M Company for most of the remaining parameters.

3.2 Reference Reactor Performance

The reference reactor was operated for 16 weeks and monitored for MLSS, MLVSS, SVI, COD, ammonia nitrogen, and TKN on a semi-weekly basis (Table 3-2). Collection of influent and effluent (supernatant) samples and the mixed-liquor allowed calculation of COD and ammonia removal as well as the food-to-microorganisms (F/M) ratio.

Table 3-1
Chemical/Parameter-Specific Measurements

Parameter	Concentration
BOD ₅	0.091 g/g
COD	0.740 g/g
TSS, EPA 160.2	<5 mg/L
Cl ₂ residual	Not intentionally added or known to be present by the manufacturer
pH, conventional	8.0 at 77°C
Total Phosphorus	Not intentionally added or known to be present by the manufacturer
TKN, EPA 351.2-1 thru -5	<0.5 mg/L
Chlorides, Standard Methods 4500.B	1 mg/L
TOC, Standard Methods	156,000 mg/L
NH ₃ ,	Not intentionally added or known to be present by the manufacturer
Alkalinity, standard Methods 2320.B	520 mg/l as CaCO ₃
TDS	Not intentionally added or known to be present by the manufacturer
Metals	Not intentionally added or known to be present by the manufacturer
Cyanide, by distillation	Not intentionally added or known to be present by the manufacturer
Pesticides and PCB's	Tolyl Triazole, 0.05% by volume
Volatile Organics	Butyl Carbitol, 30% by volume
Semi-volatile Organics	Not intentionally added or known to be present by the manufacturer
Acrolein	Not intentionally added or known to be present by the manufacturer
Acrylonitrile	Not intentionally added or known to be present by the manufacturer

1,2-Diphenylhydrazine	Not intentionally added or known to be present by the manufacturer
Arochlor 1252	Not intentionally added or known to be present by the manufacturer
Arochlor 1262	Not intentionally added or known to be present by the manufacturer
2,3,7,8-Tetrachlorodibenzo-p-dioxin	Not intentionally added or known to be present by the manufacturer
Methyl ethyl ketone	Not intentionally added or known to be present by the manufacturer
Methyl isobutyl ketone	Not intentionally added or known to be present by the manufacturer
Xylenes	Not intentionally added or known to be present by the manufacturer
Acetone	Not intentionally added or known to be present by the manufacturer
Surfactant	Trade secret (not disclosed)
Fluorohydrocarbons	Not intentionally added or known to be present by the manufacturer
Fluoride	May be present
Butyl Carbitol	30% by volume; method for direct measurement still under development

Table 3-2. Weekly Performance of the Reference Reactor during the course of the study

Week	MLSS	MLVSS	COD mg/l		% COD	SVI	NH3-N mg/l		TKN mg/l		F/M	Organic Load
	mg/l	mg/l	Feed	Super.	removal		Feed	Super.	Feed	Super.		mg/l/day
1	4060	3451	376	26	93.0	~~	6.4	0.2	33.3	1.9	0.03	169.0
	3940	3349	476	5	98.9	~~	22.5	0.2	34.2	4.0	0.04	214.3
2	3824	3250	495	24	95.2	~~	26.2	0.1	53.2	1.0	0.05	222.6
	3736	3175	~~	~~	~~	145.0	23.2	0.2	55.4	2.8	~~	
3	3636	3090	452	26	94.2	156.0	25.2	0.2	46.0	0.1	0.04	203.6
	2600	2210	478	22	95.4	~~	36.6	0.1	101.6	1.8	0.06	214.9
4	2768	2352	468	10	97.8	~~	20.4	0.0	48.4	0.1	0.06	210.7
	2908	2471	~~	~~	~~	~~	32.0	0.0	59.3	0.2	~~	
5	3024	2570	442	5	98.9	212.0	27.1	0.1	222.8	1.6	0.05	198.8
	3240	2754	672	39	94.1	~~	37.8	0.3	202.8	2.7	0.07	302.5
6	3323	2824	672	32	95.3	265.0	~~	~~	~~	~~	0.07	302.4
	3436	2920	974	18	98.1	258.0	~~	~~	~~	~~	0.10	438.3
7	2412	2050	968	77	92.1	344.0	~~	~~	~~	~~	0.14	435.5
	2956	2512	1421	9	99.4	314.0	26.0	0.1	144.6	2.9	0.17	639.6
8	3200	2720	~~	~~	~~	296.0	22.1	0.1	73.3	4.1	~~	
	3600	3060	~~	~~	~~	>400	29.0	0.4	312.5	2.1	~~	
9	2964	2519	807	76	90.5	>400	~~	~~	~~	~~	0.10	363.2
	2924	2485	971	151	84.5	>400	~	~~	~~	~~	0.12	437.1
10	3280	2788	1416	~~	~~	>400	58.3	15.3	995.1	57.9	0.15	637.2
	3024	2570	2250	156	93.1	>400	92.2	14.9	977.6	87.0	0.26	1012.4
11	3000	2550	1188	82	93.1	300.0	117.6	41.0	1245.4	87.0	0.14	534.7
	2668	2267	1231	55	95.5	292.0	80.9	0.2	977.6	8.5	0.16	553.8
12	2740	2248	1251	58	95.4	302.0	28.3	0.3	~~	~~	0.17	563.0
	2900	2420	1338	95	92.9	279.0	~~	~~	~~	~~	0.17	601.9
13	3220	2676	~~	~~	~~	~~	10.6	0.2	323.7	8.8	~~	
	2456	1976	~~	~~	~~	325.0	~~	~~	~~	~~	~~	
14	2704	2408	1300	90	93.1	332.0	35.7	0.4	413.9	6.2	0.16	585.0
	2160	1916	1300	90	93.1	~~	~~	~~	~~	~~	0.20	585.0
15	2372	2092	1400	100	92.9	379.0	30.3	0.3	454.5	6.4	0.20	630.0
	1740	1604	1200	90	92.5	>400	~~	~~	~~	~~	0.22	540.0
Average	2975	2454	989	59	94.2		37.5	3.6	338.7	14.3	0.14	445.1
	Average VSS--82.4%				note: ~~ = Data not available							

The average COD removal was approximately 95% while removal for ammonia-nitrogen averaged 90%. Throughout most of Phase 1A, the reference reactor exhibited good nitrification with > 98% ammonia removal. However, a sharp increase in the feed ammonia concentration occurred in the 10th and 11th week carried over to the supernatant indicating that significant nitrification inhibition occurred. Inhibition may have been caused by the elevated ammonia concentrations as high ammonia concentrations can be toxic to the nitrifying bacteria and inhibit the nitrification process. To overcome this problem the feed organic strength was reduced. The SVI values of the reactor increased significantly after five weeks of continuous operation. One of the reasons for this was thought to be aeration during the feed cycle and low nutrient loading to the reactor. To correct this problem, an unsuccessful attempt was made by adding hydrogen peroxide at 60 mg/l.

The initial F/M ratios in the reference reactor were very low. However, by gradually increasing the COD of the feed solution, the F/M ratios were increased. The purpose of increasing the F/M ratio was to simulate the VIP process that operates under an F/M ratio of approximately 0.22. As noted earlier, the reactor did not exactly simulate the VIP process. Aeration of the reactor during the fill stage caused the reactor to cycle from aerobic to anoxic to aerobic before settling. In contrast, the VIP process consists of an anaerobic, anoxic, aerobic sequence of conditions. The operation of the reference reactor under these conditions did not allow for P removal. Phosphorus removal is best achieved by having anaerobic and/or anoxic conditions preceding the aerobic cycle allowing poly P bacteria to become established. To assess the phosphorus removal and nitrate production in the reactor, the supernatant was analyzed by ion chromatography periodically and the results are tabulated in Tables 3-3 a, b, and c. As can be seen from these results phosphorus removal did not occur. Nitrite was generally low and it was observed on one occasion (February 18) to accumulate during aerobic periods indicating not all of the ammonia was oxidized to nitrate. Nitrate concentrations were high throughout the study due to the high concentration of TKN in the feed wastewater. Nitrate was removed during the anaerobic (anoxic) stage but the lack of organic matter during this stage most likely limited nitrate removal.

The reactor was also monitored for pH during the different stages of operation. The pH of the feed solution was maintained at approximately 6.7 with a bicarbonate alkalinity of approximately 300-400 mg/l as calcium carbonate. The pH during the various cycles ranged from 7.5 to 7.8. The

Table 3-3a: Nitrite Nitrogen concentration variation during different stages

Sample	Nitrite (NO ₂ ⁻ -N) mg/l		2/7/97	2/18/97
	1/16/97	1/23/97		
Feedstock	0.0	0.0	0.0	0.7
Start-of-Feeding	0.0	0.0	1.4	2.7
Middle-of-Feeding	0.0	0.0	0.6	0.7
End-of-Feeding	1.1	0.0	1.6	3.1
Middle-of-Anaerobic	1.1	0.0	1.5	0.7
End-of-Anaerobic	1.0	0.0	0.0	0.7
Middle-of-Aerobic	0.0	0.0	0.0	2.9
End-of-Aerobic	0.0	0.0	~~	3.5
Middle-of-Settling	0.0	0.0	~~	3.2
Supernatant	0.0	0.0	0.0	3.2

Table 3-3b: Nitrate Nitrogen concentration variation during different stages

Sample	Nitrate (NO ₃ ⁻ -N) mg/l		2/7/97	2/18/97
	1/16/97	1/23/97		
Feedstock	0.9	0.9	0.8	0.7
Start-of-Feeding	46.6	49.4	54.3	94.6
Middle-of-Feeding	44.6	43.0	33.9	83.1
End-of-Feeding	48.1	43.2	57.2	82.8
Middle-of-Anaerobic	46.2	41.8	53.2	76.5
End-of-Anaerobic	43.8	40.2	53.6	75.8
Middle-of-Aerobic	45.9	48.3	56.2	86.5
End-of-Aerobic	47.9	49.7	~~	101.8
Middle-of-Settling	48.3	49.7	~~	101.5
Supernatant	47.4	49.9	57.7	101.5

Table 3-3c: Orthophosphate concentration variation during different stages

Sample	PO ₄ -P mg/l		2/7/97	2/18/97
	1/16/97	1/23/97		
Feedstock	20.6	21.9	24.3	34.1
Start-of-Feeding	20.0	22.7	25.6	27.5
Middle-of-Feeding	19.6	22.4	22.9	27.2
End-of-Feeding	19.1	20.4	23.3	26.0
Middle-of-Anaerobic	19.0	20.9	22.9	25.4
End-of-Anaerobic	18.6	20.9	22.9	25.7
Middle-of-Aerobic	20.5	21.9	23.7	26.1
End-of-Aerobic	19.3	22.3	~~	26.8
Middle-of-Settling	19.5	22.2	~~	27.0
Supernatant	19.4	23.0	24.1	27.1

alkalinity of the supernatant was about 100-150 mg/l as calcium carbonate. Alkalinity of the feed was sufficient to provide good nitrification throughout this phase of the study. The DO concentration was also continuously monitored during the different stages of the reactor operation. The average DO values ranged between 4.5 to 5.5 mg/L during the feed stage; 0.15 to 0.10 mg/L during the anaerobic stage; and 5.5 to 6.0 mg/L during the aeration stage of the reactor operation. The DO was adjusted by changing the flow of air which was measured with the help of a flow meter, attached to the air supply line.

3.3 Range Finding Test Results

At the beginning of the study, it was proposed that AFFF wastewater concentrations be tested at concentrations that might be expected for a worst-case scenario. The worst-case scenario was stipulated by HRSD and was identified as the highest discharge from a Navy hangar occurring at the lowest hourly flow through HRSD's Chesapeake-Elizabeth plant. Consideration of greater dilution factors would be a cause for the District to require containment and subsequent controlled discharge.

The results of preliminary tests that were conducted at the worst case concentration indicated that the motility of microorganisms were affected significantly. Therefore, the range finding tests were performed at lower concentrations of AFFF solutions than the worst-case concentration. Initially, a set of BNR inhibition batch assays were performed with different concentrations of AFFF wastewater in order to determine a range that may be inhibitory to the nitrification process. This range aided in narrowing the span of concentrations to be tested in the further biological nutrient removal inhibition evaluation tests. The concentrations of AFFF used were 1,050 ppm, 105 ppm, 60 ppm, 10.5 ppm, 1.05 ppm and a control. The reactor components for each AFFF concentration and the control are summarized in Table 3-4. The results indicated that nitrification inhibition occurred at AFFF concentrations of 60 ppm, 105 ppm, and 1,050 ppm in the feed wastewater. The results of range finding tests with respect to ammonia nitrogen and COD removal rates are shown in Table 3-5.

3.4 BNR Inhibition Batch Assays

After determining a specific range of AFFF wastewater that exhibited inhibitory effects to the biological nutrient removal process, four concentrations of AFFF were tested in addition to paired

TABLE 3-4 — Range Finding Test Reactor Components

PARAMETER	CONTROL REACTORS			INHIBITION REACTORS		
	A ₁	A ₂	A ₃	B ₁	B ₂	B ₃
Total Reaction Volume (mL)	6,000	6,000	6,000	6,000	6,000	6,000
Batch MLSS (mg/L)	2,560	2,560	2,560	2,560	2,560	2,560
Seed Biomass Volume (ml)	4,000	4,000	4,000	4,000	4,000	4,000
Effective Wastewater (feed & AFFF) Volume (ml)	2,000	2,000	2,000	2,000	2,000	2,000
AFFF Concentration (ppm)	0	1,050	1,050	1,050	1,050	1,050
AFFF Volume for the simulated wastewater (ml)	0.0	70.0	7.0	4.0	0.70	0.07
Volume of synthetic Feed Solution for the simulated wastewater (mL)	3,000	1,930	1,993	1,996	1,999.3	1,999.93

TABLE 3-5 — Range Finding Inhibition Test Results

Reactor	AFFF ppm	Initial* NH ₃ -N mg/L	Final NH ₃ -N mg/L	% Removal	Initial* NO ₃ -N mg/L	Final NO ₃ -N mg/L	Initial COD mg/L	Final COD mg/L	COD Removal %
Feedstock	0								
Reference Reactor	0								
Control	0	8.4	0.1	98.8	29.7	36.9	171	22.0	87.1
AFFF-1	1.05	13.7	1.2	91.2	19.7	34.8	181	44.5	75.4
AFFF-2	10.5	7.5	0.2	97.3	30.6	39.7	267	97.0	63.7
AFFF-3	60	5.2	3.7	28.8	31.6	36.5	718	504.5	29.7
AFFF-4	105	8.1	7.7	4.9	28.9	32.3	1128	827.0	26.7
AFFF-5	1050	13.7	23.8	-73.7	6.0	7.4	9738	3919.5	**

* Initial Values correspond to the measurements taken at the end of feeding stage.

** The COD vials used measured between the ranges 0 to 900 mg/L. Dilutions were not made due to very high levels of COD at this concentration.

controls. During each inhibition testing, one set of triplicate reactors (6-liter volume) were used as control which did not include any AFFF wastewater exposure. The remaining three reactors were used for one specific AFFF concentration. The inhibition concentrations that were tested include 10 ppm, 30 ppm, 50 ppm, and 60 ppm of AFFF in the feed wastewater and mixed liquor from the reference reactor. The results of each concentration tested will be described separately in the following sections.

3.4.1 Inhibition Test at 60 ppm AFFF Concentration

Triplicate reactors for control and 60 ppm AFFF concentration were set up to observe nitrification inhibition. The conditions of this inhibition test are summarized in Table 3-6. During the testing, significant foaming occurred with the 60 ppm AFFF concentration as compared to the controls however, solids washout were not significant. A thick layer of foam was formed on top of the inhibition reactors which prevented the loss of solids. The ammonia nitrogen removal rates ranged between 97 to 98 percent as shown in Table 3-7. There was no significant nitrification inhibition as compared to the control reactors. The COD removal rates were higher for the AFFF-dosed inhibition reactors ranging between 92 and 95 percent. This higher removal reflects the higher initial COD concentration associated with the AFFF. Oxygen uptake rates (OUR) and SOUR were measured during the inhibition testing. The air supply to each reactor was monitored during the aerated feed and aerobic stage with a submersible dissolved oxygen probe to ensure that appropriate amount of dissolved oxygen was provided. The results indicated a lower oxygen uptake with the inhibition reactors at 60 ppm AFFF concentration and are shown in Figures 3-1 and 3-2.

3.4.2 Inhibition Test at 50 ppm AFFF Concentration

At 50 ppm AFFF concentration, significant foaming and solids removal from solution were observed. The foam was “lighter” and there was no layered foam as observed in the reactors as seen with the higher 60 ppm AFFF concentration. The solids loss was the most intense of all the inhibition tests as shown in Table 3-8 along with the reactor components. The nitrification inhibition results indicated ammonia nitrogen removal rates ranging from 94 to 96 percent for the control reactors. Nitrification was not inhibited in the inhibition reactors as compared to the controls. The COD

TABLE 3-6—BNR Inhibition Reactor 60 ppm AFFF Components

PARAMETER	CONTROL REACTORS			INHIBITION REACTORS		
	A ₁	A ₂	A ₃	B ₁	B ₂	B ₃
Total Reaction Volume (mL)	6,000	6,000	6,000	6,000	6,000	6,000
Batch MLSS (mg/L)	2,540	2,513	2,567	2,353	2,280	2,253
Batch MLVSS (mg/L)	2,387	2,347	2,413	2,207	2,120	2,120
Seed Biomass Volume (ml)	4,000	4,000	4,000	4,000	4,000	4,000
Effective wastewater (feed & AFFF) Volume, ml	2,000	2,000	2,000	2,000	2,000	2,000
AFFF Concentration (ppm)	0	0	0	60	60	60
AFFF Volume for the simulated wastewater (mL)	0.0	0.0	0.0	4.0	4.0	4.0
Volume of Synthetic Feed Solution for the simulated wastewater (mL)	2,000	2,000	2,000	1,996	1,996	1,996

TABLE 3-7 — Nitrification Inhibition at 60 ppm

Reactor	AFFF ppm	*Initial NH ₃ - N mg/L	Final NH ₃ - N mg/L	% Removal	*Initial NO ₃ - N mg/L	Final NO ₃ - N mg/L	Initial COD mg/L	Final COD mg/L	COD Removal %
Feedstock	0	30.3	---	---	0.9	---	1931		
Reference Reactor Decant	0	0.3	---	---	103.5	---	127		
Control (A1)	0	8.2	0.21	97.44	70.9	87.8	343	37	89
Control (A2)	0	7.8	0.14	98.21	67.8	87.7	343	37	89
Control (A3)	0	6.9	0.17	97.54	68.6	89.7	343	48	86
AFFF (B1)	60	10.0	0.27	97.30	60.8	84.5	1206.**	97	92
AFFF (B2)	60	10.4	0.23	97.79	58.0	82.5	1206.**	67	95
AFFF (B3)	60	8.5	0.19	97.76	61.0	86.3	1206.**	67	95

* Initial values correspond to the measurements taken at the end of feeding stage.

** Corresponds to the total COD which includes: Reference Reactor decant COD = 127 mg/L, Feedstock COD=1,931 mg/L and AFFF COD = 5,180 mg/L.

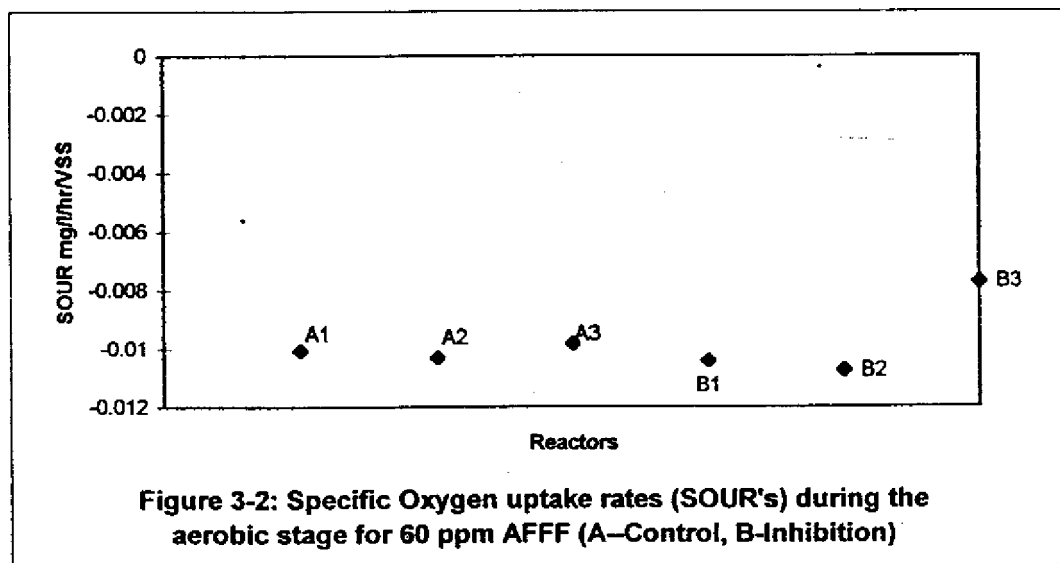
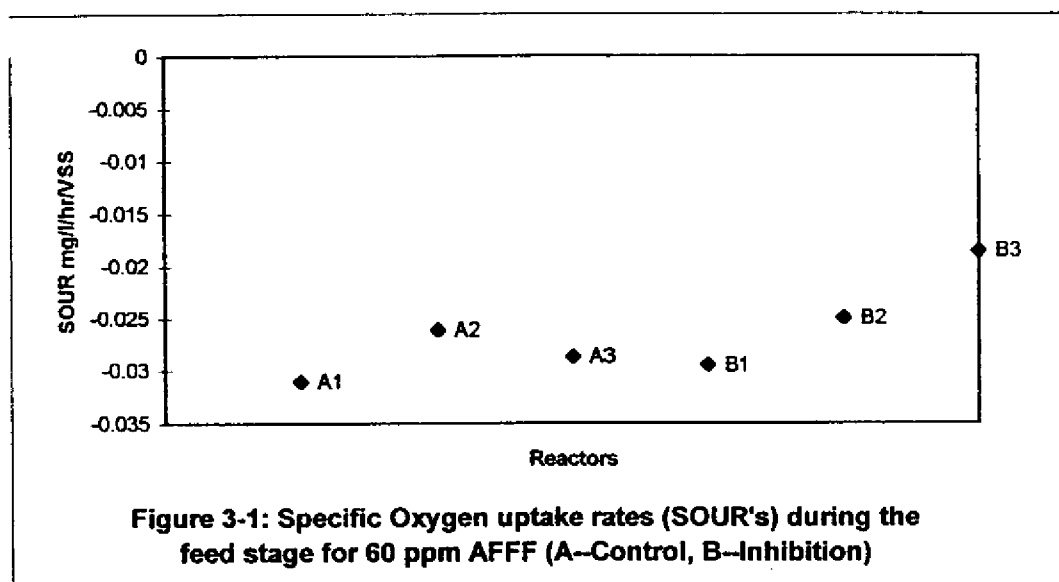


TABLE 3-8—BNR Inhibition Reactor Components: 50 ppm AFFF

PARAMETER	CONTROL REACTORS			INHIBITION REACTORS		
	A ₁	A ₂	A ₃	B ₁	B ₂	B ₃
Total Reaction Volume (mL)	6,000	6,000	6,000	6,000	6,000	6,000
Batch MLSS (mg/L)	2,713	2,653	2,680	1,693	1,106	1,213
Batch MLVSS (mg/L)						
Seed Biomass Volume (ml)	4,000	4,000	4,000	4,000	4,000	4,000
Effective wastewater (feed & AFFF) Volume, ml	2,000	2,000	2,000	2,000	2,000	2,000
AFFF Concentration (ppm)	0	0	0	50	50	50
AFFF Volume for the simulated wastewater (mL)	0.0	0.0	0.0	3.3	3.3	3.3
Volume of Synthetic Feed Solution for the simulated wastewater (mL)	2,000	2,000	2,000	1,997	1,997	1,997

removal rates were significantly lower in inhibition reactors than the control reactors which are shown in Table 3-9. The dissolved oxygen measurements during the aerobic stage are also presented in Figures 3-3.

3.4.3 *Inhibition Test at 30 ppm AFFF Concentration*

The reactor components for this inhibition test are shown in Table 3-10. Loss of solids was also observed in this test in the inhibition reactors as compared to the control reactors potentially due to the nature of the foam formed with this AFFF concentration. The results showed no significant nitrification inhibition. The COD removal rates ranged between 75 to 77 percent in the inhibition reactors and 87 to 90 percent in the control reactors as shown in Table 3-11. The oxygen uptake rates in terms of SOURs are also shown in Figures 3-4 and 3-5.

3.4.4 *Inhibition Test at 10 ppm AFFF Concentration*

Significantly less foaming and loss of solids were observed with the 10 ppm AFFF concentration. The reactor components and volumes are shown in Table 3-12. Most of the nitrification has already occurred during the aerated feed stage with the ammonia nitrogen concentrations being less than 0.2 mg/L for the control reactors. Even though the ammonia nitrogen removal rates were lower (between 10 and 45 %) for the control reactors, the effluent ammonia nitrogen values were also less than 0.1 mg/L as shown in Table 3-13. The COD removal for the inhibition reactors were not significantly different than the control reactors possibly due to the low COD of AFFF at the lower concentrations tested. The SOUR measurements during the feed and aerobic stages are shown in Figures 3-6 and 3-7.

3.5 Toxicity Pass-Through Testing

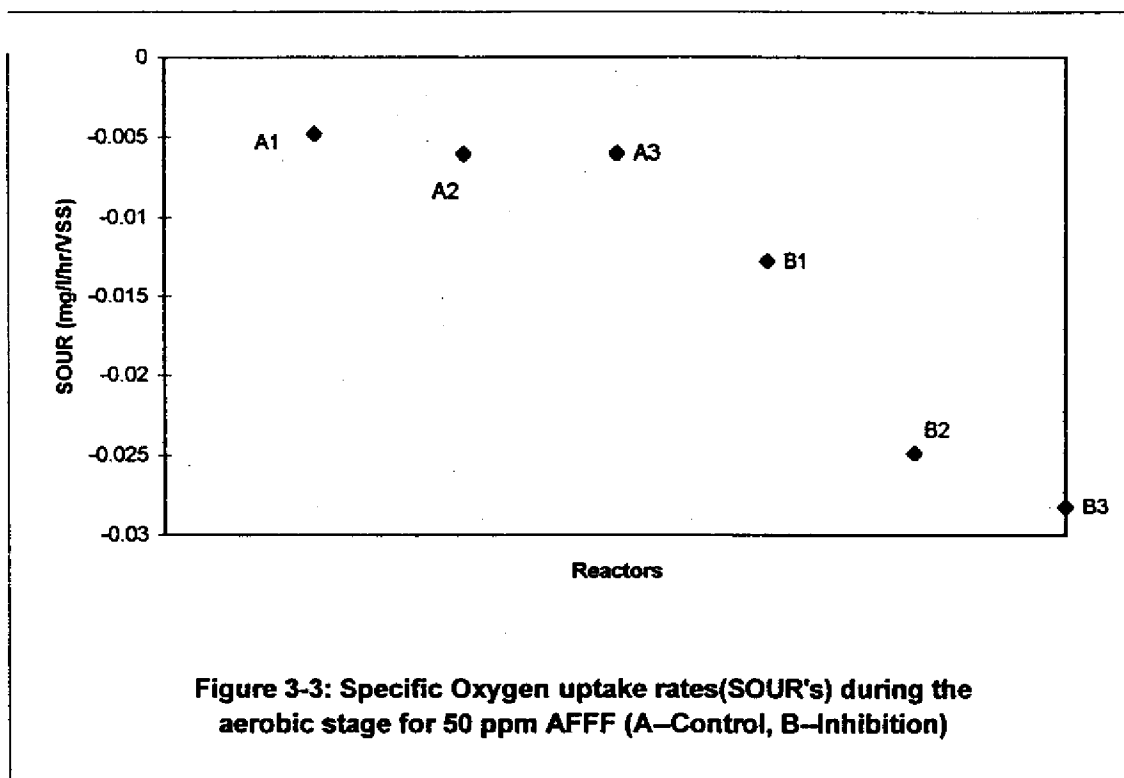
The results of the plant toxicity pass-through tests conducted with the mysid shrimp and sheepshead minnows did not exhibit any pass-through toxicity. The response measured during the acute toxicity tests was survival over the exposure period. The toxicity test results for the samples collected at the end of each inhibition testing from the reactors with and without AFFF had LC_{50} values greater than 100 percent for both test organisms as shown in Table 3-14. The only sample that

TABLE 3-9 — Nitrification Inhibition at 50 ppm

Reactor	AFFF ppm	*Initial NH ₃ - N mg/L	Final NH ₃ - N mg/L	% Removal	*Initial NO ₃ - N mg/L	Final NO ₃ - N mg/L	Initial COD mg/L	Final COD mg/L	COD Removal %
Feedstock	0	29.73	---	---	0.7		997		
Reference Reactor Decant	0	0.94	---	---	105.7		79		
Control (A1)	0	3.23	0.19	94.12	82.8	93.1	367	24.1	93.4
Control (A2)	0	2.74	0.19	93.10	84.0	85.6	367	43.2	88.2
Control (A3)	0	3.81	0.15	96.06	84.6	86.1	367	38.4	89.5
AFFF (B1)	50	9.68	0.20	97.93	82.9	96.3	976	315.3	67.7
AFFF (B2)	50	11.88	0.64	94.61	75.6	90.7	976	332.0	66.0
AFFF (B3)	50	11.40	0.09	99.21	77.7	95.5	976	327.2	66.5

* Initial values correspond to the measurements taken at the end of feeding stage.

** Corresponds to the total COD which includes RR decant COD = 79 mg/L, Feedstock COD = 997 mg/L and AFFF COD = 4320 mg/L



Note: The SOUR's are calculated by using VSS, which were calculated by taking the average TSS:VSS ratio for the reference reactor, since they were not actually measured.

TABLE 3-10—BNR Inhibition Reactor Components: 30 ppm AFFF

PARAMETER	CONTROL REACTORS			INHIBITION REACTORS		
	A ₁	A ₂	A ₃	B ₁	B ₂	B ₃
Total Reaction Volume (mL)	6,000	6,000	6,000	6,000	6,000	6,000
Batch MLSS* (mg/L)	2,787	2,760	3,300	2,140	2,560	2,400
Batch MLVSS* (mg/L)	2,573	2,293	2,753	1,927	2,300	2,193
Seed Biomass Volume (ml)	4,000	4,000	4,000	4,000	4,000	4,000
Effective wastewater (feed & AFFF) Volume, ml	2,000	2,000	2,000	2,000	2,000	2,000
AFFF Concentration (ppm)	0	0	0	30	30	30
AFFF Volume for the simulated wastewater (mL)	0.0	0.0	0.0	2.0	2.0	2.0
Volume of Synthetic Feed Solution for the simulated wastewater (mL)	2,000	2,000	2,000	1,998	1,998	1,998

* Reference reactor MLSS = 3,760 mg/L and MLVSS = 3,296 mg/L

TABLE 3-11 — Nitrification Inhibition at 30 ppm

Reactor	AFFF ppm	*Initial NH ₃ - N mg/L	Final NH ₃ - N mg/L	% Removal	*Initial NO ₃ - N mg/L	Final NO ₃ - N mg/L	Initial COD mg/L	Final COD mg/L	COD Removal %
Feedstock	0	35.71			0.0		2675		
Reference Reactor Decant	0	0.39			88.2		380		
Control (A1)	0	6.6	0.30	95.4	69.2	84.5	509	66.8	86.9
Control (A2)	0	7.1	0.32	95.5	67.7	84.4	509	61.8	87.9
Control (A3)	0	7.4	0.31	95.8	65.9	83.8	509	51.8	89.8
AFFF (B1)	30	10.7	0.42	96.1	63.5	84.9	948**	232	75.5
AFFF (B2)	30	11.6	0.69	94.0	61.5	79.8	948**	249	73.7
AFFF (B3)	30	10.7	0.66	93.8	63.4	83.7	948**	217	77.1

* Initial values correspond to the measurements taken at the end of the feeding stage.

** Corresponds to the total COD which includes Reference Reactor decant COD = 380 mg/L, Feedstock COD = 2675 mg/L, and AFFF COD = 2,630 mg/L

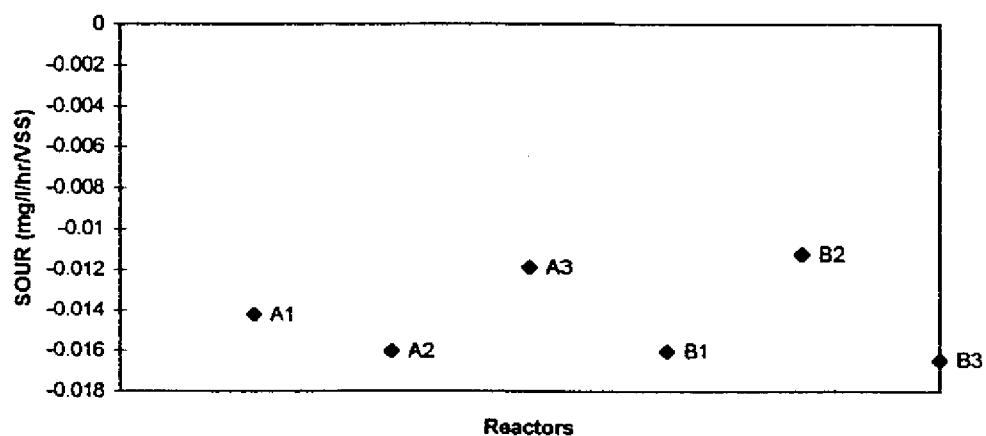


Figure 3-4: Specific Oxygen uptake rates (SOUR's) during the feed stage for 30 ppm AFFF (A—Control, B—Inhibition)

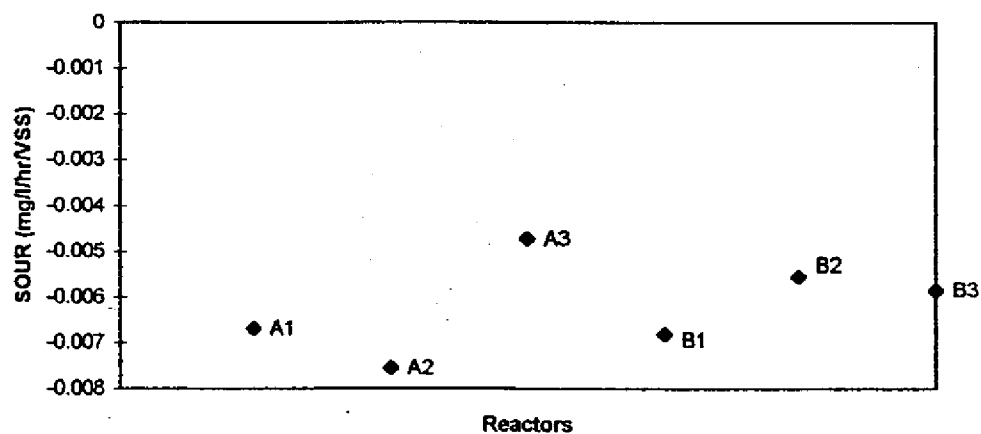


Figure 3-5: Specific Oxygen uptake rates (SOUR's) during the aerobic stage for 30 ppm AFFF (A—Control, B—Inhibition)

TABLE 3-12—BNR Inhibition Reactor Components: 10 ppm AFFF

PARAMETER	CONTROL REACTORS			INHIBITION REACTORS		
	A ₁	A ₂	A ₃	B ₁	B ₂	B ₃
Total Reaction Volume (mL)	6,000	6,000	6,000	6,000	6,000	6,000
Batch MLSS * (mg/L)	2,847	2,807	2,747	2,613	2,527	2,600
Batch MLVSS * (mg/L)	2,567	2,553	2,827	2,393	2,333	2,367
Seed Biomass Volume (ml)	4,000	4,000	4,000	4,000	4,000	4,000
Effective wastewater (feed & AFFF) Volume, ml	2,000	2,000	2,000	2,000	2,000	2,000
AFFF Concentration (ppm)	0	0	0	10	10	10
AFFF Volume for the simulated wastewater (mL)	0.0	0.0	0.0	0.7	0.7	0.7
Volume of Synthetic Feed Solution for the simulated wastewater (mL)	2,000	2,000	2,000	1,999	1,999	1,999

* Reference Reactor MLSS = 4,020 mg/L, MLVSS = 3,464 mg/L

TABLE 3-13 — Nitrification Inhibition at 10 ppm

Reactor	AFFF ppm	*Initial NH ₃ - N mg/L	Final NH ₃ - N mg/L	% Removal	*Initial NO ₃ - N mg/L	Final NO ₃ - N mg/L	Initial COD mg/L	Final COD mg/L	COD Removal %
Feedstock	0	10.61			0.0		2396		
Reference Reactor Decant	0	0.22			85.4		247		
Control (A1)	0	0.10	0.09	10.0	78.6	76.9	441	63.2	85.7
Control (A2)	0	0.14	0.09	35.7	79.8	76.0	441	55.3	87.4
Control (A3)	0	0.20	0.11	45.0	78.6	76.7	441	57.9	86.9
AFFF (B1)	10	1.05	0.08	92.4	69.4	76.2	596**	118	80.2
AFFF (B2)	10	0.62	0.11	82.3	73.4	79.4	596**	116	80.6
AFFF (B3)	10	0.92	0.12	87.0	72.2	76.4	596**	123	79.3

* Initial values correspond to the measurements taken at the end of feeding stage. (end of 2 hours)

** Corresponds to the total COD which includes Reference Reactor Decant = 2,396 mg/L, Feedstock COD = 247 mg/L and AFFF COD = 1,608 mg/L

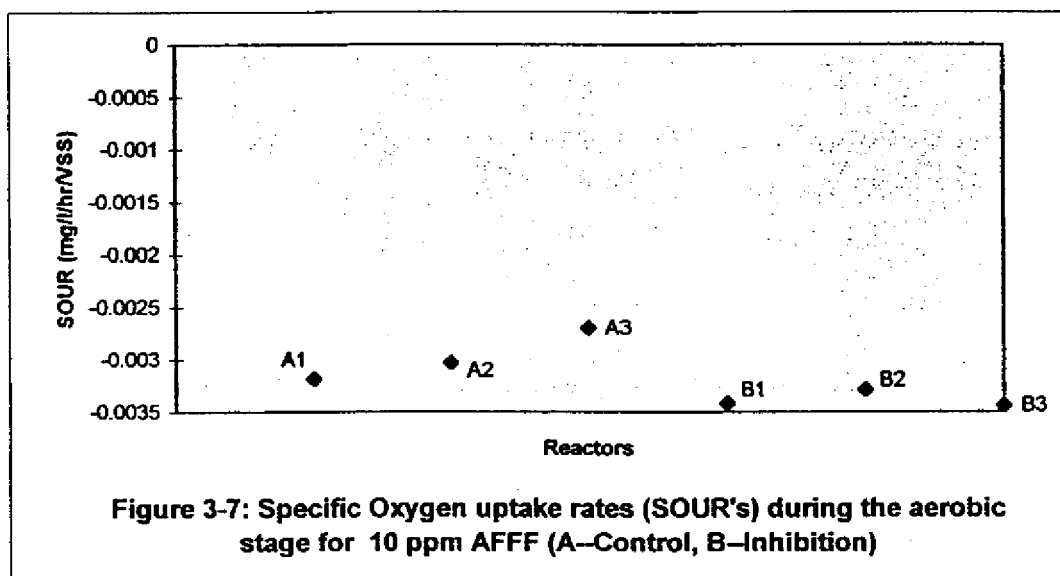
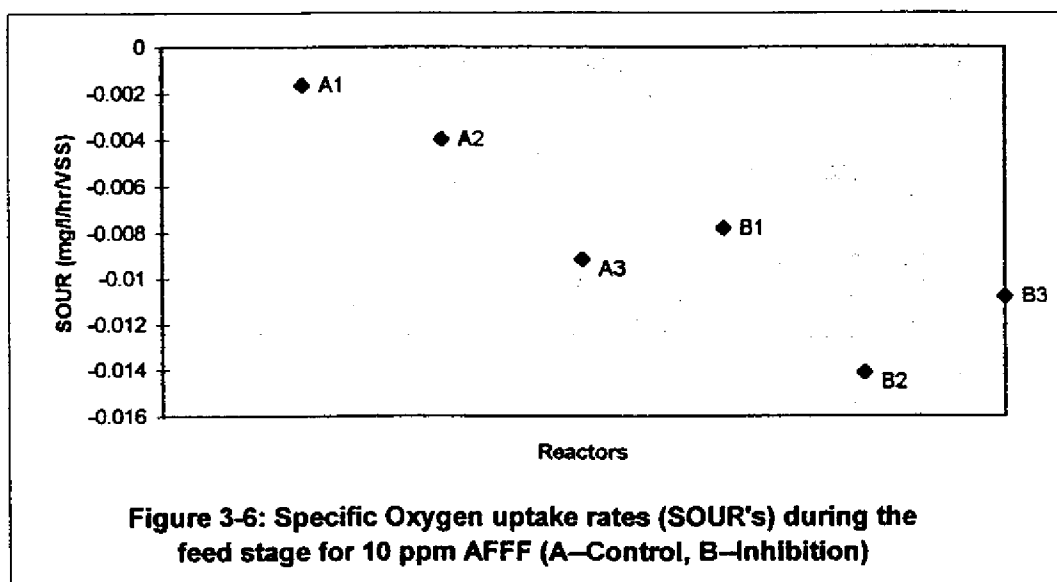


Table 3.14: Summary of the Toxicity Testing for the Inhibition tests

AFFF Conc.(ppm)	Date of test	Sample	LC50	
			Fathead Minnow	Mysid Shrimp
10	3/11/97	Feedstock	< 6.25	31
		R.R.Mix Liquor	>100	>100
		Control A1	>100	>100
		Control A2	>100	>100
		Control A3	>100	>100
		Inhibition B1	>100	>100
		Inhibition B2	>100	>100
		Inhibition B3	>100	>100
30	3/19/97	Feedstock	17.7	52
		R.R.Mix Liquor	>100	>100
		Control A1	>100	>100
		Control A2	>100	>100
		Control A3	>100	>100
		Inhibition B1	>100	>100
		Inhibition B2	>100	>100
		Inhibition B3	>100	>100
50	2/11/97	Feedstock	19.5	35
		R.R.Mix Liquor	>100	>100
		Control A1	>100	>100
		Control A2	>100	>100
		Control A3	>100	>100
		Inhibition B1	>100	>100
		Inhibition B2	>100	>100
		Inhibition B3	>100	>100
60	3/25/97	Feedstock	33	34
		R.R.Mix Liquor	>100	>100
		Control A1	>100	>100
		Control A2	>100	>100
		Control A3	>100	>100
		Inhibition B1	>100	>100
		Inhibition B2	>100	>100
		Inhibition B3	>100	>100

exhibited consistent toxicity was the influent feed to the reactors which was attributed to the high ammonia concentrations present in the feed mix which ranged from 30 to 35 mg/L of $\text{NH}_3\text{-N}$.

4.0 DISCUSSION

The results of the range-finding tests indicated that concentrations of AFFF higher than 60 ppm clearly exhibited significant potential to impact nitrification. For the lower AFFF concentrations in the range finding tests, the ammonia nitrogen concentrations in the supernatant were 0.1 mg/l for the control, 1.2 mg/L for 1.05 ppm AFFF solution, and 0.2 mg/L for 10.5 ppm AFFF solution indicating little or no inhibition as seen in Figure 4-1. For AFFF solutions of 60 ppm and above, significant nitrification inhibition occurred in the wastewater as compared to the control reactors. Note that the increasing ammonia concentrations at 1,050 ppm indicate conversion of organic nitrogen to ammonia occurred. Nitrate production rates were also in accordance with the ammonia removal rates, and an excellent mass balance on the nitrogen species was observed overall. During the range finding tests, the motility of microorganisms were also observed under the microscope for each AFFF concentration. There were no apparent changes observed between 1 and 60 ppm AFFF concentrations. However, at concentrations greater than 60 ppm AFFF, motility of microorganisms was impacted significantly. This observation is consistent with the nitrification inhibition results. Therefore, AFFF concentrations equal to and lower than 60 ppm were tested in the inhibition study to better delineate the effects of AFFF at concentrations approaching nitrification inhibition levels.

The COD removal rates decreased with increasing AFFF concentrations from as high as 87% in the control reactor to 27 % at the greatest AFFF concentration. While the percent COD removal decreased with increasing AFFF concentration, the amount of COD removed actually increased (on a mg/L basis). This observation is a direct result of the addition of COD associated with the AFFF. For example, the COD of 300 ppm AFFF solution (1% AFFF concentrate) was measured to be 8,200 mg/L. This additional COD contributed by the AFFF had the effect of increasing the initial COD of the wastewater as the AFFF concentrations increased.

The results of the nitrification inhibition study showed that the AFFF concentrations tested in the range between 10 ppm to 60 ppm did not show any significant inhibition to biological nitrification. The effluent from each reactor did not exhibit any pass-through toxicity. The intensity

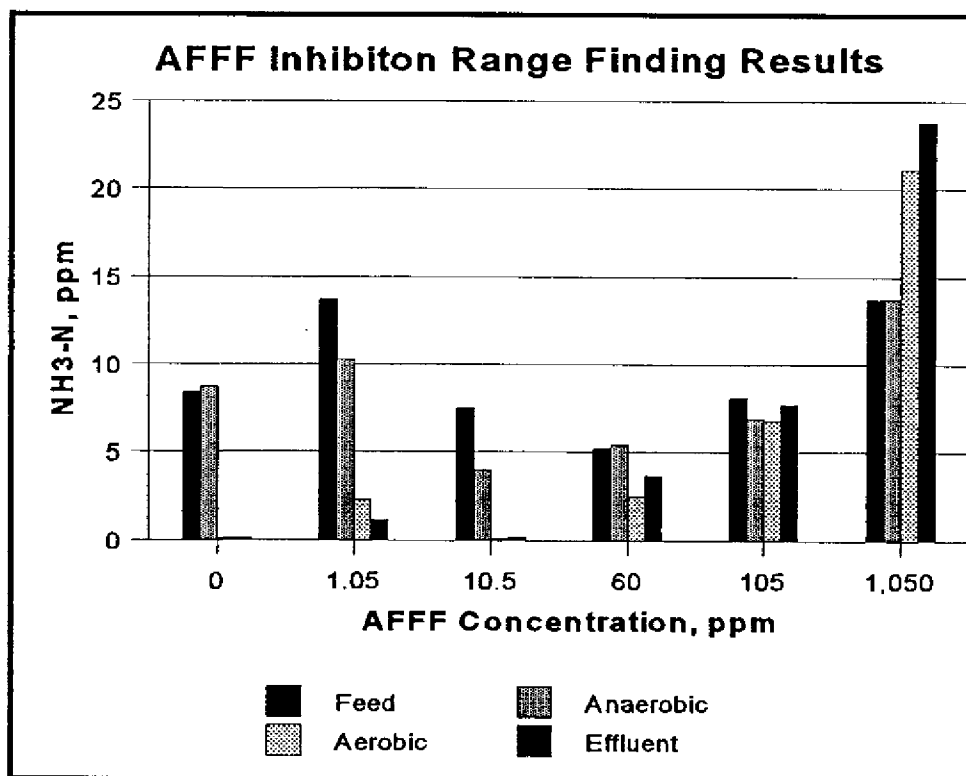


Figure 4-1. AFFF Inhibition Study Range Finding Results

of foaming increased with the increasing AFFF concentrations. The loss of solids from the reactors was associated with the foaming density which was in turn related to the amount of air supplied and bubble size formed in each reactor. At AFFF concentrations between 10 ppm to 50 ppm, the loss of solids increased. However, at 60 ppm, the foaming was so much denser that it did not allow solids carryover from the reactors. Uninhibited nitrification was also observed among the reactors that had excessive foaming. Some reductions in percent COD removal were seen as the AFFF concentrations increased. However, as indicated above these reactors actually removed more COD.

The results showed no significant nitrification inhibition for any of the AFFF concentrations tested as compared to the control reactors as shown in Figures 4-2a and 4-2b. It was observed that nitrification started to occur at the beginning of the aerated feed stage for all of the reactors and that significant ammonia removal occurred during this stage for both control and inhibition reactors at all AFFF concentrations tested. At the end of the anaerobic cycle, some of the ammonia nitrogen was released in all tests, possibly due to bacterial reduction of nitrates and nitrites or organic nitrogen conversion to ammonia. The ammonia nitrogen concentrations decreased significantly at the end of the aerobic cycle and in the effluent for each reactor, exhibiting no nitrification inhibition. The nitrate data for each inhibition test also supported the occurrence of nitrification in the reactors. The nitrification occurring in each reactor can also be seen in Figure 4-3 which shows the ammonia nitrogen removal during different stages for each AFFF concentration tested. The effluent from each reactor exhibited greater than 98 percent ammonia removal.

There was significant COD removal observed for each AFFF concentration tested as well. However, the percent COD removal in the inhibition reactors was less than that of the control reactors and the percent COD reduction decreased with increasing AFFF concentrations in the inhibition reactors. These results are shown in Figures 4-4a and 4-4b. During this study, there was an increase in the foaming in the inhibition reactors with increased AFFF concentrations. This foaming was specifically heavy during the aerated feed stage of the inhibition testing. The major influence on the reactor performance was the loss of solids (MLSS) at higher AFFF concentrations. This loss of solids removed microbical cells from solution and likely contributed to the lower percent COD removals. However, even at lower MLSS concentrations, the total amount of COD removed exceeded that of the controls.

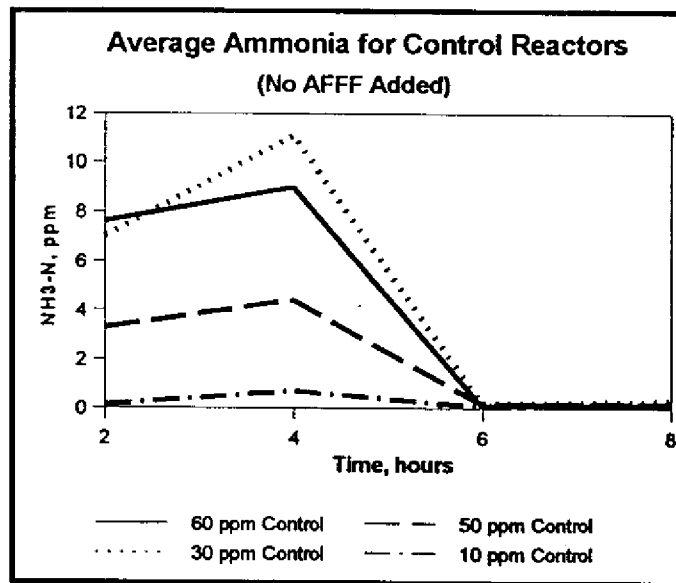


Figure 4-2a. Average Ammonia Concentrations for Control Reactors

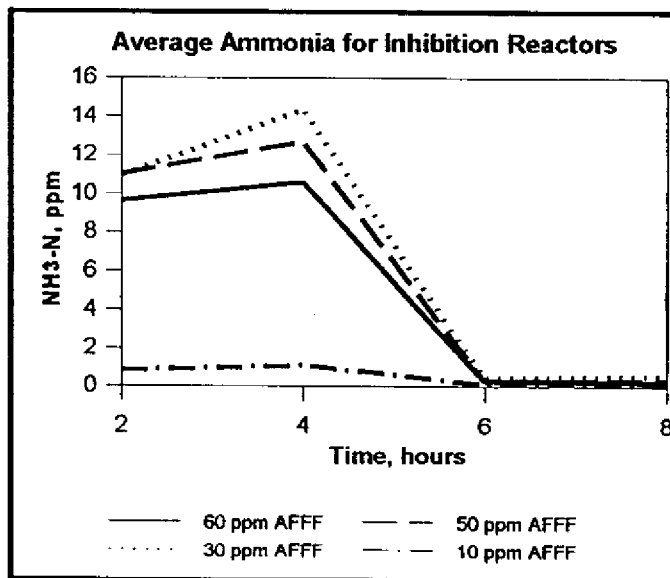


Figure 4-2b. Average Ammonia Concentrations for Inhibition Reactors

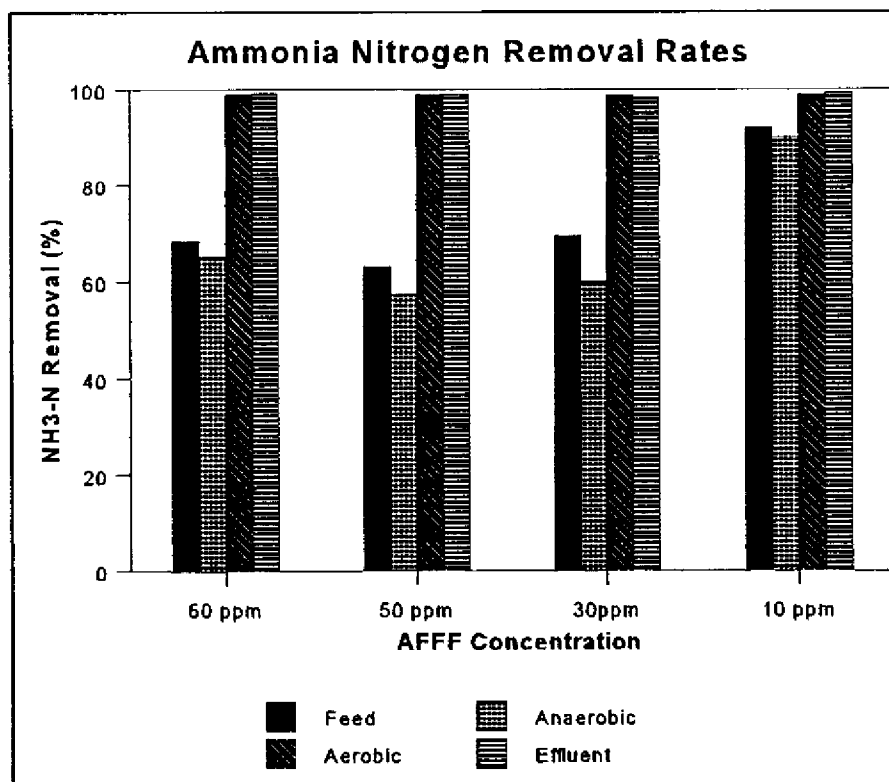


Figure 4-3. Average Ammonia Nitrogen Removal Rates for the Inhibition Reactors

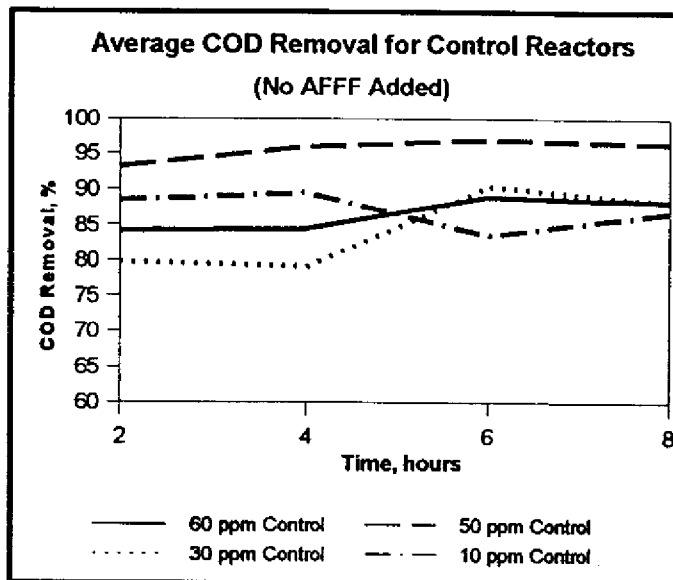


Figure 4-4a. Average COD Removal Rates for the Control Reactors

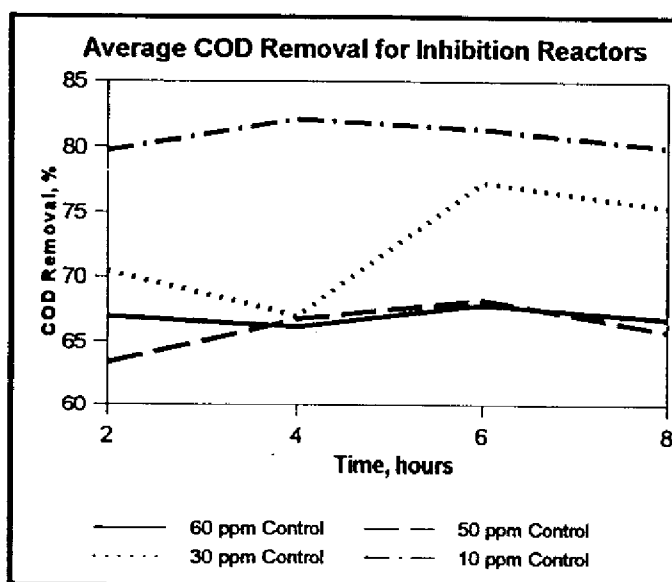


Figure 4-4b. Average COD Removal Rates for the Inhibition Reactors

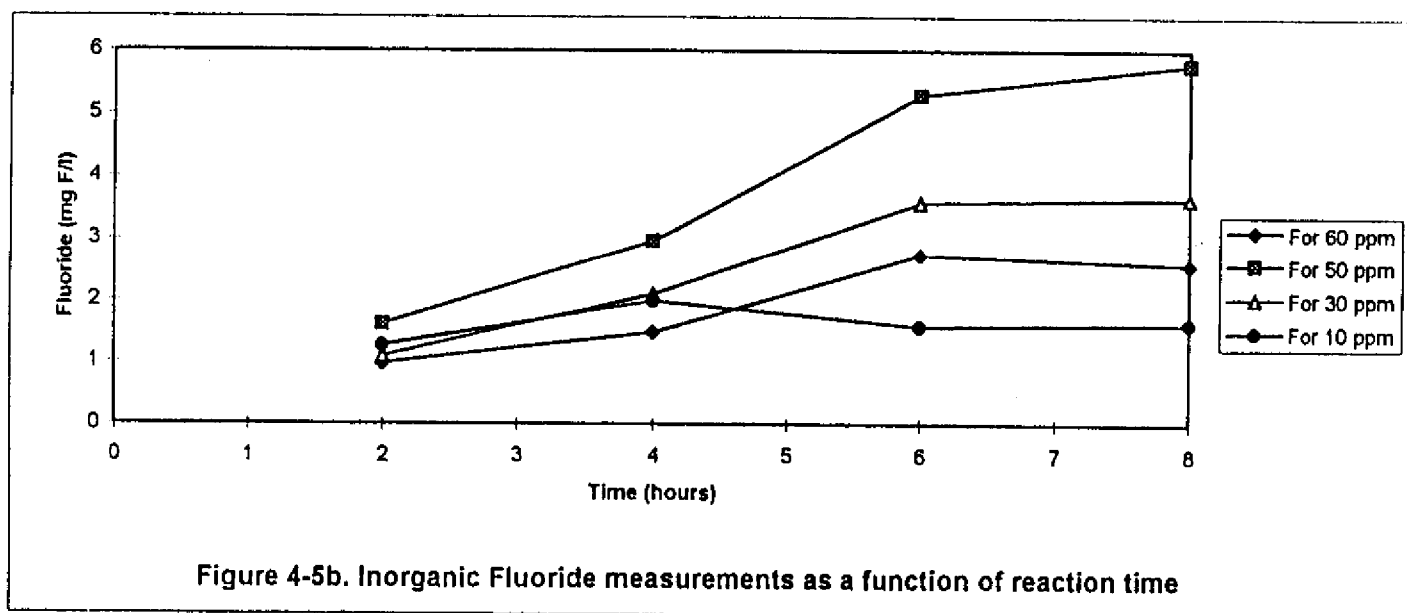
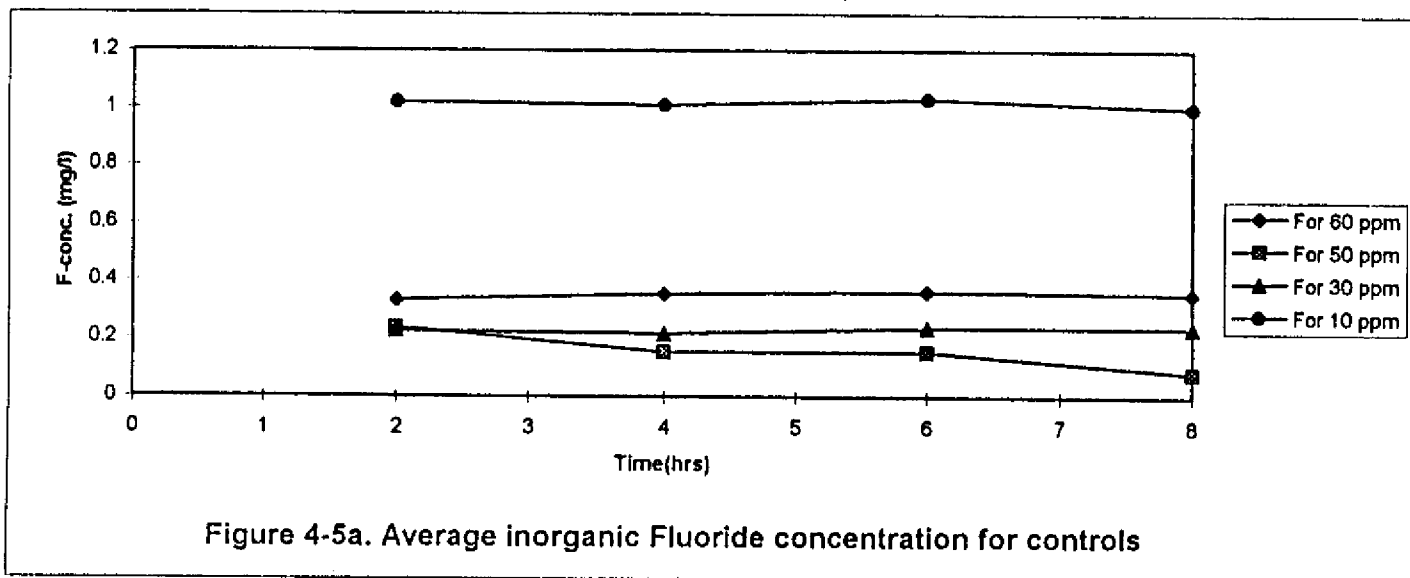
Organo-fluoride compounds are known to be a constituent of AFFF and it was suspected a priori that decomposition of the organo-fluoride compounds would likely occur resulting in accumulations of inorganic fluoride in solution. If this reaction occurs, then an increase in inorganic fluoride should be observed upon treatment of a water containing AFFF.

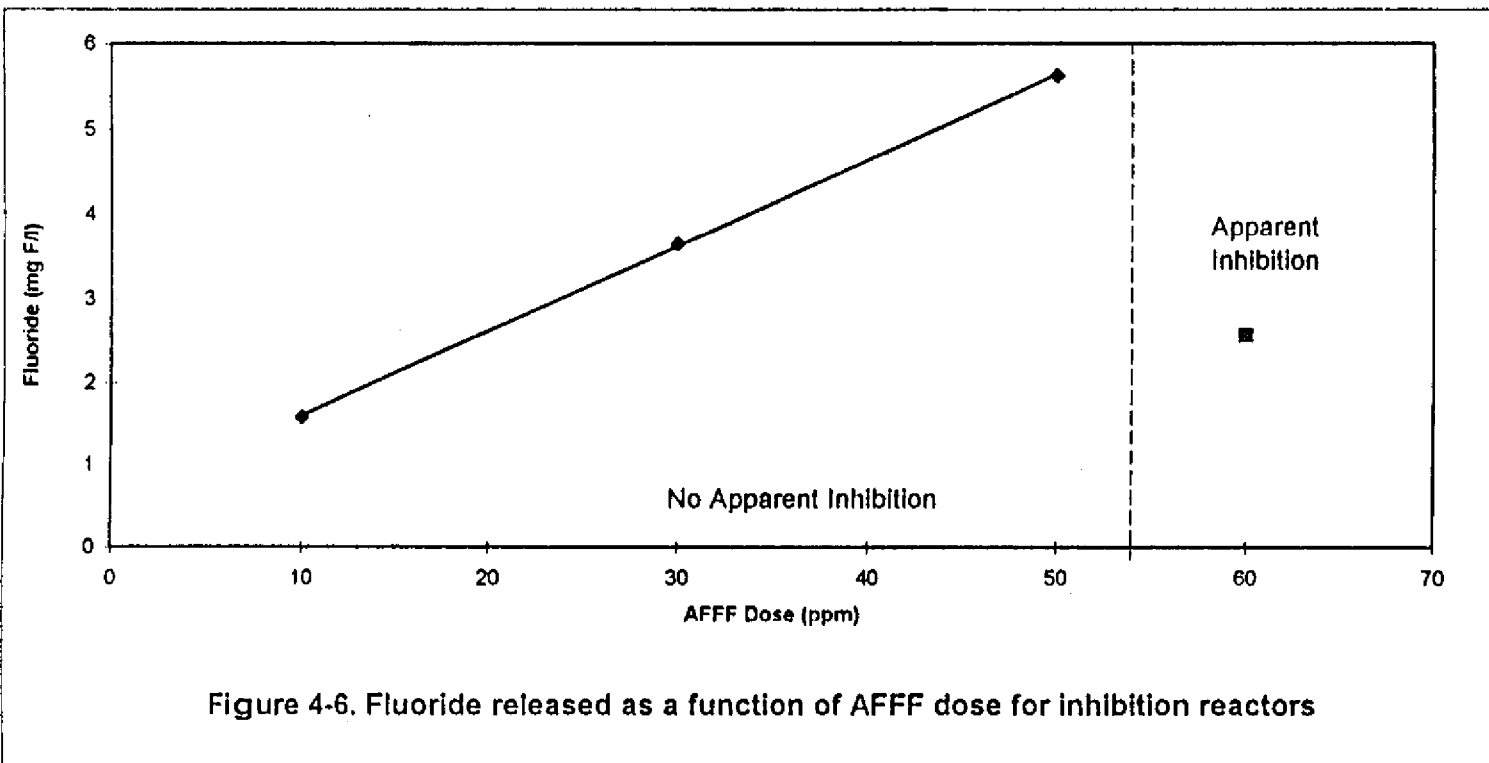
Fluoride measurements were conducted for controls and the AFFF wastewater at two-hour intervals and then examined for fluoride release. In the control samples, the fluoride concentrations remained essentially unchanged during the testing (Figure 4-5a) as expected with no organo fluoride compounds present. The fluoride measured for these samples reflects the “background” inorganic fluoride concentration and when subtracted from the fluoride concentrations measured for the AFFF-dosed wastewater (Figure 4-5b) will reflect the fluoride released from organic compounds (Figure 4-6). The linear relationship up to 50 ppm AFFF signifies that organo-fluoride compounds are being decomposed in proportion to the AFFF concentration. The low release of F for the 60 ppm AFFF wastewater suggests some interference in fluoride release. This interference may be an inhibition of the microorganisms that were capable of decomposing these compounds or evidence of selective substrate utilization (i.e. diauxic growth) where microorganism were consuming other preferable compounds before selecting organo-fluoride compounds.

5.0 CONCLUSIONS

The results of the nitrification inhibition study showed that the AFFF concentrations tested in the range between 10 ppm to 60 ppm did not show any inhibition to biological nitrification. The range finding tests indicated nitrification inhibition did occur above 60 ppm AFFF. Microscopic observations also showed significant impacts on the motility of microorganisms at concentrations greater than 60 ppm AFFF.

The reference reactor did not develop biological P removal due to the rapid consumption of COD during the aerobic feed stage. This occurrence most likely prevented significant production of acetate during anaerobic stage which is essential for developing poly P bacteria. It is likely that with an anaerobic feed cycle, the reactors would have exhibited P removal. Loss of biological solids from the reactors increased with increasing AFFF concentrations up to 50 ppm, however, at 60 ppm very little solids were lost from the reactors. The intensity of foaming increased with the increasing AFFF





concentrations however, uninhibited nitrification was also observed among the reactors that had excessive foaming. Some reductions in the percent COD removal were observed as the AFFF concentrations increased.

Fluoride release suggested that organo fluoride compounds decomposed up to 50 ppm and some inhibition was observed at 60 ppm. Acute toxicity test results showed that the effluent from each inhibition reactor did not exhibit any pass-through toxicity as well.

Overall, the results of Phase 1A study indicated that AFFF solutions discharged into the wastewater at concentrations 60 ppm or below did not exhibit any inhibitory effect to biological nitrification and pass through toxicity.

REFERENCES

1. CH₂M Hill Co; Wastewater Effluent Pilot Study for the Advanced Fire Fighting Training Facility, Naval contract N62470-91-R-6650, Atlantic Division, Naval Facilities Engineering Command, October 1992.
2. CH₂M Hill Co; Wastewater Treatability Final Report for the Advanced Fire Fighting Training Facility, Navy Contract N62470-91-C-6650, Atlantic Division, Naval Facilities Engineering Command, January 1995.
3. Chan, D. B., Disposal of Wastewater Containing Aqueous Film Forming Foam, Technical Memorandum No. M-54-78-06, Civil Engineering Laboratory, April 1978.
4. Chan, D.B., Pam Bingham; AFFF-laden Wastewater Treatment Technology Initiation Decision Report (IDR), Technical Memorandum No. TM-71-88-11, Naval Civil Engineering Laboratory, December 1988.
5. "Toxicity of Selected Effluents from the U.S. Navy Firefighting School, Norfolk, VA to Embryos of Eastern Oysters". Technical Report by EG&G, Atlantic Division, Naval Facilities Engineering Command, May 1978.
6. Union Carbide, Unox System Treatability Study Report, U.S. Navy Firefighting School, Naval Facilities Engineering Command, February 1978.

7. Engineering-Science Incorporated, Physical-Chemical Treatment from Navy Firefighting Schools, Contract No. N00025-74-C-0004, Naval Facilities Engineering Command, November 1986.
8. Saam, R., and Rakowski, P., Firefighting School Wastewater Study, Technical Memorandum No. 54-79-14, Civil Engineering Laboratory, June 1979.
9. Saam, R., Rakowski, P., and Aydlett, G., "Treatability of Firefighting School Wastewaters: U.S. Navy Compliance with POTW Pretreatment Requirements", Proceedings of the 34th Purdue Industrial Waste Conference, West Lafayette, Indiana, May 1979.
10. Thomas, J.F., and LeFebvre, E.E., "Biodegradability and Toxicity of FC-200 Aqueous Film Forming Foam", Report No. EHL(K) 74-3, USAF Environmental Health Laboratory, KellyAFB, Texas, 1973.
11. Grace and Associates Inc., "Engineering Investigation of Impact of AFFF on Wastewater Treatment Performance at Naval Air Station, Memphis, Millington, Tennessee", U.S. Navy Contract N62467-86-C-0351, Naval Facilities Engineering Command, November 1986.
12. Lefebvre, E.E., "Biodegradability and Toxicity of Light Water". Report No. EHL (K) 71-36, USAF Environmental Health Laboratory, November 1971.
13. Lefebvre, E.E., and Inmand, R.C., "Biodegradability and Toxicity of ANSUL K74-100, Aqueous Film Forming Foam", Report No. EHL(K) 75-3, USAF Environmental Health Laboratory, Kelly AFB, Texas, January 1975.
14. Lefebvre, E.E., and Inmand, R.C., "Biodegradability and Toxicity of Light water FC-206,, Aqueous Film Forming Foam", Report No. EHL(K) 74-26, USAF Environmental Health Laboratory, Kelly AFB, Texas, November 1974.
15. Lefebvre, E.E., and Thomas, J.F., "Biodegradability and Toxicity of AER-O-Water 3 and 6 Aqueous Film Forming Foam", Report No. EHL(K) 73-22, USAF Environmental Health Laboratory, Kelly AFB, Texas, December 1973.
16. Environmental Protection Agency, "Methods of Chemical Analyses of Water and Wastes", Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA 600/4-79-020, March 1979.

17. American Public Health Association, American Water Works Association, and Water Environment Federation, "Standard Methods for the Examination of Water and Wastewater", 19th Edition, Washington, DC, 1995.
18. Environmental Protection Agency, "Toxicity Reduction Evaluation Protocol for Municipal Wastewater Treatment Plants", April 1989.