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Technical Memorandum
TM-2246-ENV

TREATMENT AND DISPOSAL OF NAVAL AQUEOUS FILM FORMING FOAM (AFFF) FIREFIGHTING WASTEWATER

by

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January 1997

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EXECUTIVE SUMMARY

The current Aqueous Film Forming Foam (AFFF) has been proven to be a vital component of the fire protection of Naval aviation and other assets. However, there is concern about the potential environmental harm when AFFF constituents spread to the environment or are discharged to wastewater treatment plants. In the past two decades, Department of Defense (DoD) has devoted considerable resources towards treatment and disposal of AFFF wastewater. This report reviews and summarizes the past work that has been performed along with highlighting current and future research and development in the areas of treatment and disposal of the AFFF wastewater.

The Navy conducted a comprehensive study on AFFF treatment including chemical coagulation, clarification, carbon adsorption, chemical oxidation, air stripping, and biological treatment and concluded that none of the methods performed well enough to provide an effluent suitable for discharge to a receiving stream.

The use of an ultra-filtration/reverse osmosis (UF/RO) system is recommended for treating the AFFF wastewater. Since the Navy's initial study of UF/RO systems in 1980, commercial water and wastewater treatment system vendors have further developed the UF/RO systems for the treatment of AFFF wastewater. The UF/RO systems now can provide percent removal efficiencies of AFFF constituents ranging from 96 to 99%. Also, by purchasing a mobile unit, the treatment system can be utilized by multiple Navy bases, thereby minimizing the capital cost of the system.

The continued development of the AFFF separator by Naval Facilities Engineering Service Center (NFESC) is also recommended. The overall test results of NFESC prototype AFFF separator are highly encouraging. The test showed that the separator not only reduces the AFFF surfactants from typical firefighting wastewater, but also reduces the other pollutants in the waste as measured by BOD_5, COD, VPH, BTEX, and TPH.

In the long term, the Air Force (AF) sponsored research to find a more environmentally benign AFFF formulation should continue to be supported.

1.0 INTRODUCTION

Currently, Aqueous Film Forming Foam (AFFF) is the most effective firefighting foam available for extinguishing liquid hydrocarbon fires. Because of its effectiveness, it became a vital component of the naval aviation fire protection system. In fact, the U. S. Navy is one of the world's largest consumers of AFFF.

The Navy uses AFFF to suppress combustible and flammable liquid fuel fires resulting from aviation and shipboard accidents and battle-induced damage. The Naval Air Systems Command (NAVAIR) uses AFFF in aircraft hangar deluge systems and in ships flight deck sprinkler systems. The Naval Sea Systems Command (NAVSEA) requires AFFF to protect surface ships and submarine machinery spaces. The Naval Facilities Engineering Command (NAVFAC) specifies AFFF sprinklers for shore-side hangars and other flammable liquid hazards. The Navy also conducts a comprehensive firefighting training program, which requires large amounts of AFFF to extinguish simulated fires. In addition, AFFF is widely used by the Department of Defense (DoD) and the civilian sector in aircraft crash fire rescue (CFR) vehicles.

Despite its wide use and effectiveness, AFFF poses an environmental concern and raises questions about its long term continued use because of its resistance to biodegradation, its high Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), its toxicity due to constituent butyl carbitol, and extreme foaming capacity. The U. S. Environmental Protection Agency (EPA) has highlighted a potential problem with AFFF by listing glycol ethers, common solvent constituents in AFFF, as a hazardous air pollutant under the 1990 Clean Air Act Amendment. Although currently there is no annual reporting requirements for discharging AFFF into the environment, the trend is clearly toward stricter regulation of the chemicals in AFFF and of the emission of AFFF to the environment. In fact, the Hampton Roads Sanitation District (HRSD) at Norfolk, Virginia prohibits the discharge of AFFF into its plant. Other industrial wastewater treatment plants (IWTP) in the Maryland and Virginia area also restrict the discharge of AFFF into their local wastewater stream [1].

This report reviews and summarizes the past work that has been performed and highlights future research and development in the areas of treatment and disposal of the AFFF wastewater. The general objective of the studies in this area has been to develop a practicable physical-chemical treatment system capable of producing effluent quality to meet federal, state, and local requirements for situations ranging from discharge to biological treatment plants of varying size to direct release into the environment.

2.0 CHARACTERISTICS OF NAVAL AQUEOUS FILM FORMING FOAM (AFFF) FIREFIGHTING WASTEWATER

2.1 AQUEOUS FILM FORMING FOAM (AFFF)

AFFF, originally called "light water™", was first developed by Minnesota Mining and Manufacturing Company (3M) and the Naval Research Laboratory (NRL) in 1964. The purpose of its development was to improve the knockdown and extinguish times of liquid hydrocarbon fires over traditional protein and fluoroprotein based foams.

By adding an aqueous film, AFFF revolutionized flammable liquid firefighting. This rapidly spreading film provided faster knockdown of the fire than traditional foams because it attacked all three facets of the fire triangles: fuel, oxygen, and heat. The aqueous film floats on and rapidly spreads across the flammable liquid forming a physical separation between the fuel source and the oxygen source [2].

The foam formed by the AFFF application also cools the covered area by allowing the water contained in the foam to drain onto the sprayed surfaces. Additionally, the film also suppresses the escape of volatile vapors reducing the risk from possible recurrence of fire [2 and 3]. Because of the inherent low surface tension of AFFF in solution, it possesses the ability to reform the aqueous film around any object which may disturb or break the film. This "self healing" property, which was not present in any other previously developed foam, aids the firefighter in preventing occurrence of flashbacks and reduces the need to continuously apply the foam [3 and 4]. Because of its effectiveness, AFFF is used extensively in the fire protection systems of military aircraft hangars, naval vessels, and CFR vehicles of airport fire departments.

2.2 CHEMICAL COMPOSITION OF AFFF CONCENTRATES

AFFF used by the Navy is manufactured based on a performance military specification (MILSPEC), MIL-F-24385F [5]. The following AFFF products meet and/or exceed the MILSPEC and are currently on the Qualified Products List, QPL-24385-9:

Minnesota Mining and Manufacturing Company (3M)
- FC-199, FC-200, FC-203, AND FC-206

Ansul Company (ANSUL)
- K74-100

National Foam Systems, Inc. (AOW, Aer-O-Water)
- AOW-3 AND AOW-6

AFFF is commonly available in 1%, 3%, and 6% concentrate solutions. The difference between the three different concentrations is the strength of the surfactants. The surfactants in the 3% concentrate are twice as strong as those in the 6% concentrate [6]. Although the exact chemical make ups of the above AFFF concentrates are not known due to the propriety regulations, the typical composition of AFFF includes water, fluoroalkyl surfactants, non-fluorinated surfactants and butyl carbitol. Table 2-1, extracted from 3M's Material Safety Data Sheet (MSDS) on the 3% and 6% product concentrations, lists the percent by weight of each specific chemical constituent of the AFFF concentrates [6].

Table 2-1: Composition of 3M's Aqueous Film Forming Foams

Composition in Percent by Weight	FC-203 (3%)	FC-206 (6%)
Water	69.0-71.0	78.0-81.0
2-(2-Butoxyethoxy) Ethanol [butyl carbitol]	19.0-21.0	9.5-10.5
Urea	---	3.0-7.0
Alkyl Sulfate Salts	4.0-6.0	1.0-5.0
Amphoteric Fluoroalkylamide Derivative	1.0-5.0	1.0-2.0
Triethanolamine	0.5-1.5	0.1-1.0
Perfluoroalkyl Sulfonate Salts	0.5-1.5	---
Methyl-1H-Benzotriazole	0.0-0.1	0.0-0.1

Note: The above table was developed from Reference 6.

Although the concentrates are sold as 1%, 3%, and 6% concentrates, the chemical composition of AFFF solutions prepared from them are quite similar for a given manufacturer. AFFF solutions are prepared by diluting AFFF concentrates with water, using a suitable proportioning device. For example, 97 gallons of water is diluted with three gallons of 3% AFFF concentrate to achieve its usage form. The composition of the usage solution is >99% water, <1% non-fluorinated surfactant and butyl carbitol, and <0.3% fluorinated surfactant [9].

The flouroalkyl component of AFFF is the most important and expensive constituent in the chemical formulation [11 and 14]. The flouroalkyl surfactant molecule is characterized by a stable fluorocarbon tail and a solubilizing group Z, i.e., CF3(CF2)—Z. The solubilizing group can be organic or inorganic, anionic, cationic or nonionic, amphoteric, water soluble or oil soluble [6 and 7]. The performance of the fluorocarbon tail with the Z surfactant substituent is enhanced by the non-fluorinated surfactant and the foam booster (e.g. butyl carbitol sometimes referred to as the foam solvent). The fluoroalkyl component is used to form a tough, mobile, rapidly spreading, and readily healing vapor barrier. It contributes to the low surface tension and therefore rapid spread of the AFFF solutions. It also is significantly resistant to thermal, chemical, electrical and biological attacks with good resistance to radiation. Because of its resistance to degradation, the fluoroalkyl component of AFFF is an environmental concern.

2.3 ENVIRONMENTAL TOXICOLOGY

The MIL-F-24385 has limitations for AFFF toxicity, Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) as shown in Table 2-2. The MILSPEC requires AFFF toxicity testing in accordance with American Society for Testing and Materials, ASTM E729, *Standard Practice for Conducting Acute Toxicity Tests with Fish, Microinvertebrates and Amphibians* using dynamic procedures with the Killiefish (Fondulus hecteroclitus)[5].

Table 2-2: MIL-F-24385 Environmental Impact Requirement

	Type 3 (3%)	Type 6 (6%)
Toxicity, LC_{50} [(a)], mg/l, minimum	500	1000
COD, mg/l, maximum	1000K	500K
$\frac{BOD_{20}}{COD}$, minimum	0.65	0.65

Notes: (a) The above table was developed from Reference 5.
(b) LC_{50} = Median lethal concentration.

As indicated in Table 2-2, the LC_{50} limit for 3% AFFF concentrate is 500 mg/l and for 6% AFFF, 1000 mg/l. Based on the fish toxicity rating scale by U. S. Fish & Wild Life Service and EPA, which is given in Table 2-3 [11], both 3% and 6% AFFF meeting MILSPEC would be regarded as practically non-toxic to aquatic life.

Table 2-3: Fish Toxicity Rating Scales

	U. S. Fish & Wildlife Service	U. S. EPA
Aquatic LC_{50} (ppm)	**Relative Toxicity**	**Category**
<0.01	Super Toxic	Very Highly Toxic
0.01-0.1	Extremely Toxic	Very Highly Toxic
0.1-1	Highly Toxic	Highly Toxic
1-10	Moderately Toxic	Moderately Toxic
10-100	Slightly Toxic	Slightly Toxic
100-1000	Practically Non-toxic	Practically Non-toxic
>1000	Relatively Harmless	--------

Note: The above table was developed from Reference 11.

3M conducted several toxicology tests on its currently produced AFFF concentrate products. First, 3M performed plant bioassay toxicity tests using six plant species exposed to the Alcohol-Type Concentrate (ATC) AFFF formulation. This type of AFFF is used to extinguish polar liquid fires. The results of the study are shown in Table 2-4.

The median concentration of FC-600 that inhibits various plant physiological processes in the population of test species is as low as 0.16 % FC-600 with many plants showing adverse growth effects at concentrations well below the usage concentrations of AFFF. The usage concentration of AFFF is typically 3% or 6% and average wastewater concentration is 1.8 % [13]. Although AFFF wastewater many times runs off over land, there have been no documented cases of severe plant kills [11]. This result could be due to the fact that the toxicological effects of AFFF on vegetation are chronic rather than acute.

Table 2-4: Summary of Plant Bioassay Toxicity Data for 3M's FC-600 AFFF Formulation
(Values in the table represent the median value of the percent concentration of FC-600 that inhibits the specified response variable in the test populations. When estimated, the 95% confidence interval is presented in parentheses.)

	Plant Emergence Tests		Early Plant Growth Tests			
			Root Exposure[a]		Foliar Exposure[b]	
Plants	Germination	Root Elongation	Shoot Length	Shoot Weight	Shoot Length	Shoot Weight
Corn	>6	0.80 (0.6-1.0)	>6	>6	>6	>6
Oats	2.6 (2.4-2.8)	0.16 (.11-.71)	3.5 (3.4-3.6)	4.3	>6	>6
Perennial Rye Grass	1.8 (1.6-2.0)	0.26 (.20-.50)	>6	4.0 (3.1-5.3)	>6	>6
Soybeans	5.2 (4.7-6.1)	0.31 (.20-.50)	3.2 (2.4-4.3)	2.4 (1.5-4.0)	>6	3.0 (3.2-4.1)
Cucumber	>6	0.20 (.12-.30)	3.2 (2.5-4.1)	2.2 (2.0-4.3)	>6	5.8 (5.3-6.1)
Tomato	4.2 (3.5-5.0)	0.25 (.19-.33)		1.3 (1.1-1.5)	>6	5.2 (4.3-6.9)

(a) Plants were grown in pots containing 210 +/- 10g soil (dry weight) and irrigated with 50 ml of varied dilution of FC-600. No damage occurred from the bottom of the pots.
(b) Plants were grown in pots containing 210 +/- 10g soil (dry weight) and 25ml of varied dilution of FC-600 were applied to the plant leaves.

3M also conducted aquatic toxicology tests on its FC-203 (3%) and FC-206 (6%) AFFF formulations. The results of the study are shown below in Table 2-5 [9].

Table 2-5: Summary of Aquatic Toxicology Data for 3M's 3% and 6% AFFF Formulations
(All values are in mg AFFF/L unless noted in (b). When estimated, 95% confidence intervals are presented in parentheses.)

Test System	Metric [a]	FC-203 (3%)	FC-206 (6%)
Fat Head Minnows	Static 96-hr LC_{50}	>1000	>1000
Water Flea	Static 48-hr EC_{50}	>1000	>1000
Atlantic Oyster Larvae [b]	Static 48-hr LC_{50}		100-240
Conventional Activated Sludge [b]			200-1000
Microtox	5-min EC_{50} 15-min EC_{50} 30-min EC_{50}	>1000 890 (730-1000) 680 (610-750)	470 (420-520) 360 (330-390) 280 (260-300)

(a) LC_{50} = Median lethal concentration
EC_{50} = Median effective concentration immobilizing tested population
IC_{50} = Median inhibitory concentration reducing growth for test population
(b) Range provided in the literature measured in ppm (volume/volume)

Tests of AFFF toxicity to microorganisms were accomplished by 3M using the standard Beckman Microtox system, which utilizes a luminescent bacterium as the bioassay organism. The metabolism of the luminescent bacterium is influenced by low levels of toxicity, producing a change in the intensity of the bacterium's light output which can be measured (approximately one million bacteria per light unit) [14]. The photoluminescence of the bacterium used in this bioassay is inhibited by concentrations of AFFF in the range of approximately 250 - >1000 mg/l. The microbes and oyster larvae were more sensitive to the AFFF than the higher order aquatic life. This could indicate that AFFF wastewater may have a toxic effect on the microorganisms used in the wastewater treatment.

In addition, 3M conducted toxicology studies with FC-203 (the 3% concentrate) on lab rats and rabbits to assess the acute oral toxicity, acute dermal toxicity, and primary ocular irritation AFFF concentrates has on mammals [4 and 9]. Extremely high doses of AFFF concentrate, far exceeding the usage concentrations, were used during the testing. The results are the following:

- The acute oral toxicity tests indicated that AFFF was practically non-toxic orally under the conditions of the study.
- The test species showed some irritation on the skin in the area where the AFFF concentrate was applied during the dermal toxicity test. However, the overall results of the study were that AFFF was practically non-toxic dermally under the conditions of the study.
- The test species showed some irritation in the eye that the AFFF concentrate was applied to during the primary irritation test.
- No deaths of the tested species occurred during the studied.

As a result, the MSDS from 3M recommends eye and skin protection while handling the AFFF concentrate products [6].

2.4 BIODEGRADATION

It is generally agreed that chemical mixtures are readily biodegradable when the ratio of their 20-day BOD to their COD is greater than 0.5 [1]. Therefore, it is expected per Table 2-2 that all AFFF concentrates with MILSPEC requirements will fully biodegrade over time.

The Product Environmental Data sheets from 3M provide information on the biodegradation capacity of the various components of their AFFF formulation. The butyl carbitol™ component of AFFF has a BOD_{20}/COD ratio of 85%. The majority of the surfactant components are biodegradable with BOD_{20}/COD ratio between 74-94%.

It is expected that all hydrocarbon and hydrocarbon portions of fluorocarbon surfactants will fully biodegrade over time. However, it is accepted that the residual fluorinated carbon portions of the surfactants will not biodegrade once the hydrophilic, non-fluorinated end of the surfactant is biodegraded. The possible fates of the fluorocarbon constituent in the sewage treatment process include adsorption on to the microbial solids or passage out of the system in the IWTP effluent. It is noted in the 3M Product Environmental Data sheet that regardless of the fate of the non-biodegradable materials the concentrations will be very low and should be of low toxicity. [9]

2.5 AFFF WASTEWATER CHARACTERISTICS

The following are the characteristics of AFFF wastewater generated by the Navy Fire Fighting School at Norfolk, Virginia [12 and 13]:

Table 2-6: AFFF Wastewater Characteristics

Parameters	Range
pH (units)	6-7
Oil and Grease (mg/l)	15-2,000
BOD (mg/l)	700-2,000
COD (mg/l)	2,000-4,000
Total Suspended Solids (mg/l)	10-200
Surfactant (mg/l)	20-40

Note: The above table was developed from Reference 12.

As indicated by Table 2-6, AFFF wastewaters vary widely in concentration. The AFFF wastewater sometimes contains dissolved, free, and emulsified fuel oil and gasoline, PKP (a dry material termed "Purple-K-Powder" or otherwise known as potassium bicarbonate powder), a variety of dissolved and suspended combustion products, and water (being either freshwater, bilge water, or saltwater). In a firefighting situation, the AFFF wastewater generated will contain PKP, residual petroleum products (both free product and emulsified oils), along with combustion by-products (particulates, soot, gas).

2.6 AFFF WASTEWATER DISPOSAL AND TREATMENT CONCERNS

AFFF wastewater may be collected during firefighting, system testing and maintenance of the hangar deluge systems, or firefighting training exercises. In any event, unless special precautions are taken, AFFF wastewater can eventually be discharged to a sewage treatment plant and cause plant upsets and other problems including law suits.

First, AFFF wastewater has higher BOD content than typical IWTP influent. Therefore, without proper dilution, there is a high possibility the AFFF wastewater will cause "shock loading" to the biological system of the plant.

Second, if not pre-treated by an oil/water separator, associated products, such as fuels, oils, and combustion by-products, found in AFFF wastewater will add to its toxicity and kill the biomass, disrupting the biological treatment operation of an IWTP. AFFF solutions have a tendency to emulsify hydrocarbon fuels and some polar fuels which are only slightly soluble in water. Water soluble polar fuels will mix with AFFF solutions. The formation of emulsions will upset the operation of fuel/water separators and potentially cause the carryover of fuel into the waste stream [21].

Third and the most noticeable adverse effect of AFFF wastewater to an IWTP is the foaming that occurs during the aeration phase of the treatment process. Because of the high strength of the surfactants, AFFF wastewater can foam even in dilute solutions. This can cause aesthetic problems in rivers and streams, and both aesthetic and operational problems in sewers and wastewater treatment systems. The bubbles of AFFF trap the activated sludge used to treat the water in the system and bring it to the surface. If the foam removes too much of the activated sludge, the wastewater treatment system may not operate properly. Other wastes passing through will be incompletely processed until activated sludge concentration again accumulates.

As a result of these factors, IWTPs may operate outside water quality permit limits regulated by local environmental agencies. In extreme case, local authorities may severely restrict or prohibit the discharge of AFFF wastewater into the local wastewater stream. This is currently the case with the Hampton Roads Sanitation District (HRSD), which is located adjacent to the Norfolk Naval Station, Virginia. Treatment plant upsets have reportedly occurred as a result of firefighting training school AFFF use and AFFF system discharge tests from aircraft carriers.

To prevent shock loading and foaming in the IWTPs, foam manufacturers and foam users recommend dilution of foam solution before AFFF wastewater enters the treatment plant. The National Fire Protection Association (NFPA) recommends that the concentration of AFFF solution in the plant influent should not exceed 1,700 parts per million (588 gallons of plant influent per gallon of AFFF solution). 3M recommends a dilution of the 3% AFFF product in the aeration basin of the IWTP down to a concentration less than 50 ppm [9]. According to the 3M Product Environmental Data sheet, a dilution rate of 1:180 would be required to get the active ingredients in the 3% AFFF usage solution down to 50 ppm in the worst case scenario. This worst case assumes there is no dilution of the product during application. At this dilution rate, a release of 1,000 gallons of AFFF wastewater would require 180,000 gallons of dilution water. Although the dilution is a recommended treatment process for AFFF wastewater, it is time consuming and inefficient, especially when a single event in a typical hangar can release up to 30,000 gallons of AFFF solution.

3.0 ENVIRONMENTAL REGULATIONS AND GUIDANCE

3.1 ENVIRONMENTAL PROTECTION AGENCY (EPA) REGULATIONS

3.1.1 EPCRA Section 313 Reporting Requirement

Section 313 of Emergency Planning and Community Right-to-Know (EPCRA) requires owners or operators of manufacturing facilities that manufacture, process, or otherwise use designated toxic chemicals, in amounts exceeding specific threshold quantities, to report annually their emissions to the environment of such chemicals. The specific threshold quantity for total glycol ether usage is 10,000 pounds per year for a facility that "otherwise used" the listed chemical; it is 25,000 pounds per year for a facility that manufactured, imported, or processed the listed chemical [17].

On July 6, 1993, the EPA proposed to redefine the glycol ethers category on the list of toxic chemicals subject to reporting under EPCRA. The EPA believed that existing glycol ether category was overly broad and included substances that traditionally have not been considered glycol ethers. **On July 5, 1994, the EPA published the final rule for the EPCRA amendment. It states, "this redefinition of the glycol ethers category, which is based on EPA's review of available human health data on short chain length glycol ethers, eliminates the EPCRA section 313 reporting requirements for those glycol ethers known as surfactant ethers [18]."**

3.1.2 Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)

Title III, Section 112, of the 1990 Clean Air Act Amendments, lists glycol ethers as a hazardous air pollutants (HAPS) [16]. The butyl carbitol (ethanol, 2-,2-butoxyethoxy) constituent of AFFF is part of the large family of glycol ethers. EPA issued a proposed rule on, 22 October 1993, adding five hazardous air pollutants that are classified as broad generic categories of substances (among these were glycol ethers) to the CERCLA. This proposed rule amended the designation, reportable quantities (RQ) and notification requirements of these families of chemicals under CERCLA. There were no fines or penalties imposed by the rule for having a release. However, it mandated reports of glycol ethers releases to the EPA National Response Center.

At the time of publishing the proposed rule, the EPA had not finalized an RQ for glycol ethers. Therefore, the statutory RQ of one pound, equivalent to 15 gallons of AFFF solution, was set [19]. **But, on June 12, 1995, the EPA dropped this reporting requirement.** However, CERCLA continues to apply to release of all compounds in the glycol ethers category even if reporting is not required. Parties responsible for release of glycol ethers are liable for costs associated with the clean up and any natural resource damage resulting from the release [20].

3.2 NATIONAL FIRE PROTECTION ASSOCIATION (NFPA) STANDARD 11, APPENDIX E - FOAM ENVIRONMENTAL ISSUES

The NFPA established the Environmental Task Group on Foam Environmental Issues on August 1994. The main objective of the Task Group was to develop a "white paper" for distribution to foam users that provides general information on the areas of potential environmental impact:

- The Clean Air Act reporting requirements for the release of glycol ethers
- The handling of foam after use, the potential need for containment and disposal
- The persistence of fluorocarbon surfactants in the environment.

The NFPA issued the paper entitled "Foam Environmental Issues" in March 1996 as an Appendix E to NFPA Standard 11, *Low Expansion Foam and Combined Agent System.* The paper provides guideline for coping with environmental impacts and coping with issues of foam use that may be under regulation or restriction. The paper also provides information sources which may be consulted for more detailed information, product specific information, and current regulatory status information. The goal of the paper is not to limit or restrict the use of firefighting foam, but to provide information to end users to allow foam to be used in an environmentally responsible manner [21].

4.0 TREATMENT METHODS FOR AFFF WASTEWATER

Because of the adverse effect to the operation of sewage treatment plants, a number of treatment methods for AFFF wastewater have been previously studied. The methods include chemical coagulation and flocculation (precipitation), clarification, carbon adsorption, chemical oxidation, air stripping, biological treatment, and ultra filtration/reverse osmosis (UF/RO) treatment. The following sections detail the findings and analysis of each treatment technique.

4.1 CHEMICAL COAGULATION, FLOCCULATION AND CLARIFICATION

The use of chemical coagulation allows for dilute oil emulsions to be clarified or broken by the addition of soluble metal-salts. The coagulant assisted in the lowering of organics by reducing the content of oils, fuels, soot, and other organic products found in the wastewater. Both Alum and ferric chloride were investigated as coagulants with various types of cationic, anionic, and nonionic organic polymers. The studies found that the Alum coagulation to be the most beneficial in treating AFFF wastewater [8, 12, 22, and 23].

Upon coagulation and flocculation of the wastewater, the developed floc needs to be removed prior to further processing. The use of a dissolved-air-floatation (DAF) process may be the most beneficial for removing the floc present. This process involves air saturation of pressurized influent, with the release of the pressure in either a circular or rectangular tank (at atmosphere pressure) creating a myriad of minute bubbles that float the suspended and oily particles to the surface. The layer of solids floating on the water surface is removed by mechanical skimming, while the underflow represents the clarified effluent. The results showed that the use of a chemical pretreatment with DAF provides consistent removal of COD (28%), BOD (59%), TSS (75%), Oil and Grease (66%), and surfactant (26%). Table 4-1 summarizes the results [8, 12, 22, and 23].

The use of a coagulation, flocculation, and clarification is warranted to aid in the reduction of foam effects to biological nutrient removal (BNR) of a biological treatment plant.

Table 4-1: Coagulation, Flocculation, and Dissolved Air Floatation Clarification Results of AFFF Wastewater

Wastewater Composition	BOD (mg/l)			COD (mg/l)			Oil and Grease (mg/l)			TSS (mg/l)			Surfactant MBAS (mg/l)			pH (unit)	
	INF	EFF	%	INF	EFF	%	INF	EFF	%	INF	EFF	%	INF	EFF	%	INF	EFF
No Chemical	1100	840	24	3264	2448	25	1877	207	89	160	92	42	21.2	16.5	22	7.3	7.15
Alum Only	1648	1009	39	2597	1945	25	108	15	86	14	8	43	28	16	43	6.35	6.08
Alum/Cationic	1410	685	51	2906	1614	38	15	7	56	73	10	75	32	16	45	6.4	5.8
Alum/SEAR	725	535	26	3891	2827	32	43	19	57	120	27	69	36	34	4	6.7	6.1
Alum/Nonionic	2132	413	68	3196	2406	22	169	9.9	86	134	22	82	32	25	22	6.6	6.0
Average	1480	614	59	3227	2208	28	91	12.3	66	157	16	75	31	23	26	6.6	6.0

Notes: (a) SEAR – Southeast Applied Research
(b) The above table was developed from Reference 12.
(c) % represents percent removal.

4.2 CARBON ADSORPTION

The use of carbon adsorption as a treatment mechanism for removing AFFF products from wastewater was studied by the Naval Civil Engineering Laboratory (NCEL) in 1979. This study showed that activated carbon adsorption provided good removal efficiency (above 90% COD reduction) of AFFF products from the waste stream [38]. However, the carbon adsorption technique involved excessive costs (over $600K for a system which treats 10,000 gallons per day) [38]. These costs included both acquisition of a large quantity of carbon and problems with disposal or regeneration of the spent carbon. A 5-gallon FC-206 concentrate used in firefighting training may require about 66.25 pounds of NUCHAR WV-L carbon to adsorb the AFFF products and produce an effluent acceptable to an IWTP. It requires about 1,325 pounds of carbon to adsorb the AFFF products and produce an effluent that contains a trace amount of AFFF products (7 mg/l as COD). [38]

4.3 CHEMICAL OXIDATION

Chemical oxidation using chlorine was found grossly inefficient in reducing the AFFF components from the wastewater. It was further discovered that a large chlorine residual remained in the wastewater following treatment. Another method utilized potassium permanganate for oxidation purpose. Similar to the chlorine oxidation, minimal COD reduction (<14%) was observed. The summary of the chlorine oxidation and permanganate oxidation processes are shown in Table 4-2 below [8, 12, and 22]:

Table 4-2: Chlorine and Potassium Permanganate Oxidation of AFFF Wastewater

Chlorine Dosage (mg/l)	Total Chlorine Residual (mg/l)	COD (mg/l)	Potassium Permanganate Dosage (mg/l)	COD (mg/l)
0	0	681	0	494
0.18	0.2	---	20	482
0.36	0.3	---	60	478
0.72	0.8	---	100	470
1.44	1.6	---	140	447
2.16	2.2	---	180	431
21.6	20	---	220	423
26.3	30	665		
52.6	50	657		
78.9	80	638		
105.2	100	638		
131.5	140	630		

Note: The above table was developed from References 12 and 22.

4.4 AIR STRIPPING

NCEL conducted a study to see if COD reduction would be achieved by air stripping the more volatile components from the AFFF wastewater. It was on the study that no significant COD reduction was achieved through direct oxidation with air or through air stripping. Only a 10 % reduction in COD was observed after twenty hours of aeration, most of which can attributed to stripping [8, 12, and 22].

4.5 ANAEROBIC BIOLOGICAL TREATMENT SYSTEM

The anaerobic biological treatment was selected to control the foaming of the AFFF wastewater, which is a common problem in aerobic treatment systems. The two-stage anaerobic biological filter treatment system consisted of two packed columns followed by an aerobic lagoon. The initial column is packed with Raschig rings that were covered with a bacterial film. This first column provides roughing and partial breakdown of the wastewater before it is sent to a second column packed with fluidized granular activated carbon. The second column is used for further biological breakdown and toxicity reduction. The effluent from the two column anaerobic system (first stage) is sent to aerobic lagoons (second stage) for further reduction in COD. Results of the study shows 50 % reduction in COD in the first stage with a 90 % reduction in the AFFF foaming agents (surfactants) and glycol. The second stage provides a further reduction of 40 % COD with no foaming problems. Additionally, it is shown that the methane production in the first stage provided a sufficient amount of energy to power the aeration of second stage [25 and 26].

4.6 BACTERIAL SPORE PRETREATMENT

Wright Laboratory Fire Research Group of Tyndall Air Force Base (AFB) developed a pretreatment technique for AFFF wastewater. The technique is based on microbiological digestion of most of the compounds of AFFF. Bacterial spores were chosen because of their almost unlimited shelf life. In their vegetative state, the bacteria can facultate to use the components of AFFF and soluble fuel residues as food. When added to AFFF wastes along with the proper inorganic nutrients and aeration, approximately 90 % reduction occurred and the glycol ether, in particular, was reduced to a level undetectable by the EPA gas chromatographic method [29].

Air Force recommends the following site specific actions to eliminate foam solution [29]:

Crash Site: Overspray the area with bacterial spore solution (100 gallons of 1% spore solution per 1000 gallons of AFFF solution) to enhance the breakdown of both the fuel and foam on the runway and soil surfaces. Spray inorganic nutrients over the area at a rate of 50 gallons of liquid 10-34-0 fertilizer solution (1/2%) per 1000 gallons of AFFF solution. Reapply fertilizer solution after seven days to further enhance the microbial breakdown.

Foam Water Runoff: Dilute the firefighting wastewater by 100:1 with fresh water. This should be applied to the contained water. Wastewater that has entered a body of water should have fresh water applied immediately to commence the dilution process. Wastewater entering any storm runoff piping should alert response personnel to place oil absorbing floats to trap the fuel and oil at the discharge and begin pumping fresh water at the outfall to commence foam dilution.

Contained Waters: Dilute the wastewater 10:1 with fresh water. Treat the solution with a bacterial spore concentrate at a rate of 100 gallons per 100,000 gallons of contained water. Add inorganic nutrients at a rate of 50 gallons of 10-34-0 liquid fertilizer per 100,000 gallons of wastewater to accelerate the growth of the organisms. Repeat the fertilizer application after seven days. The solution must also be aerated at a rate of 1200 CFM per 100,000 gallons of contained water in order to sustain the organism population. This process will result in elimination of 90 % of AFFF within 20 days. The resultant can then be processed through a sewer treatment plant without the need for metering.

Firefighting Training Facility: All wastewater at the facility is contained by the lined fire pit. This wastewater then needs to be processed through oil water separator to remove up to 95 % of fuel for reuse in other burns. The concentrated foam solution is then kept in a holding pond. Introduce spore concentrate or a bacteria solution at a rate of 50 gallons of concentrate per 50,000 gallons of contained water. Feed with inorganic nutrients at a rate of 25 gallons of 10-34-0 liquid fertilizer per 50,000 gallons of contained water. Repeat after seven days to accelerate organism growth. After twenty days, this treatment process will result in the elimination of 90 % of the AFFF. Follow-up with straight discharge to a sewer treatment plant for final disposal. For maintenance purposes, five gallons of spore concentrate along with fertilizer should be added weekly to the holding ponds.

4.7 ULTRA-FILTRATION (UF) AND REVERSE OSMOSIS (RO)

NCEL conducted research to demonstrate the feasibility of recovery of AFFF active ingredients with UF and RO in 1980 [30 and 31]. The results of the study are listed below:

- The combined UF/RO recovery system has been demonstrated viable and technically adequate through laboratory and field tests.
- Laboratory tests showed that with a 1:5 ratio of recovered AFFF-freshwater mixture, fires can be satisfactorily extinguished.
- Field tests show that recovered AFFF can meet the 15 second standard for extinguishing a 5 gallon fire.
- AFFF recovered and reused five times has the same effect as commercial grade AFFF in extinguishing fire.

RO and UF processes are similar in that hydraulic pressure is used as the driving force, and a synthetic semi-permeable membrane is employed as the separating medium. These processes are unique in that they do not involve a chemical change or any interfacial transfer. The schematic diagram in Figure 1 graphically illustrates the UF/RO treatment process for AFFF wastewater.

The UF unit, installed in series with an RO unit, is used primarily for clarification of AFFF wastewater. UF membranes are selected with a porosity that permits passage of the AFFF ingredients and rejects the bulk of the suspended solids, unburned fuel, soot, and debris resulting from fire extinguishment. The UF reject is returned to a feed water tank and recirculated until the original water volume had been reduced by at least 90 %. The remaining 10 % is a concentrated mixture of unburned fuel, suspended solids, and some AFFF. Disposal is accomplished through incineration or dry lagooning. The permeate from the UF unit is then used as feed water to the RO unit.

The RO membranes effectively dewater the UF permeate and separate the AFFF ingredients from the feed wastewater. The RO permeate is a high quality effluent suitable for reuse as a water source or suitable for discharge to a sewer system. The RO reject contains AFFF plus some water.

Both the UF and RO units each recover, as permeate, approximately 90 % of the initial feed water. Overall it was estimated that approximately 72% of the AFFF was recovered by the UF/RO system [30]. The recovered AFFF and recycled wastewater were utilized to extinguish test fires in order to see if they met military specifications. The results of the testing were satisfactory except that slightly longer extinguishing times were required.

Since the Navy's initial study, commercial water and wastewater treatment system vendors have further developed and improved the UF/RO systems for the treatment of AFFF wastewater. The performance characteristics from the product literature of a leading UF/RO treatment manufacturer are shown in Table 4-3. The characteristics of the RO concentrate and permeate show similar performance to the results found in the Navy study completed in 1980. The RO concentrate showed high levels of TDS and TOC, indicating that the AFFF product was removed from the wastewater. The permeate showed levels of TOC that would definitely be acceptable for sanitary sewer release and possibly surface water release. The product water recovery from the manufacturer's UF system is approximately 95% and 85% for the RO system for a total treatment system product water recovery of 80%. According to the manufacturer, the recovered AFFF concentrate from the RO system has been reconcentrated with virgin AFFF and it passed all functional test specified by the AFFF MILSPEC [4].

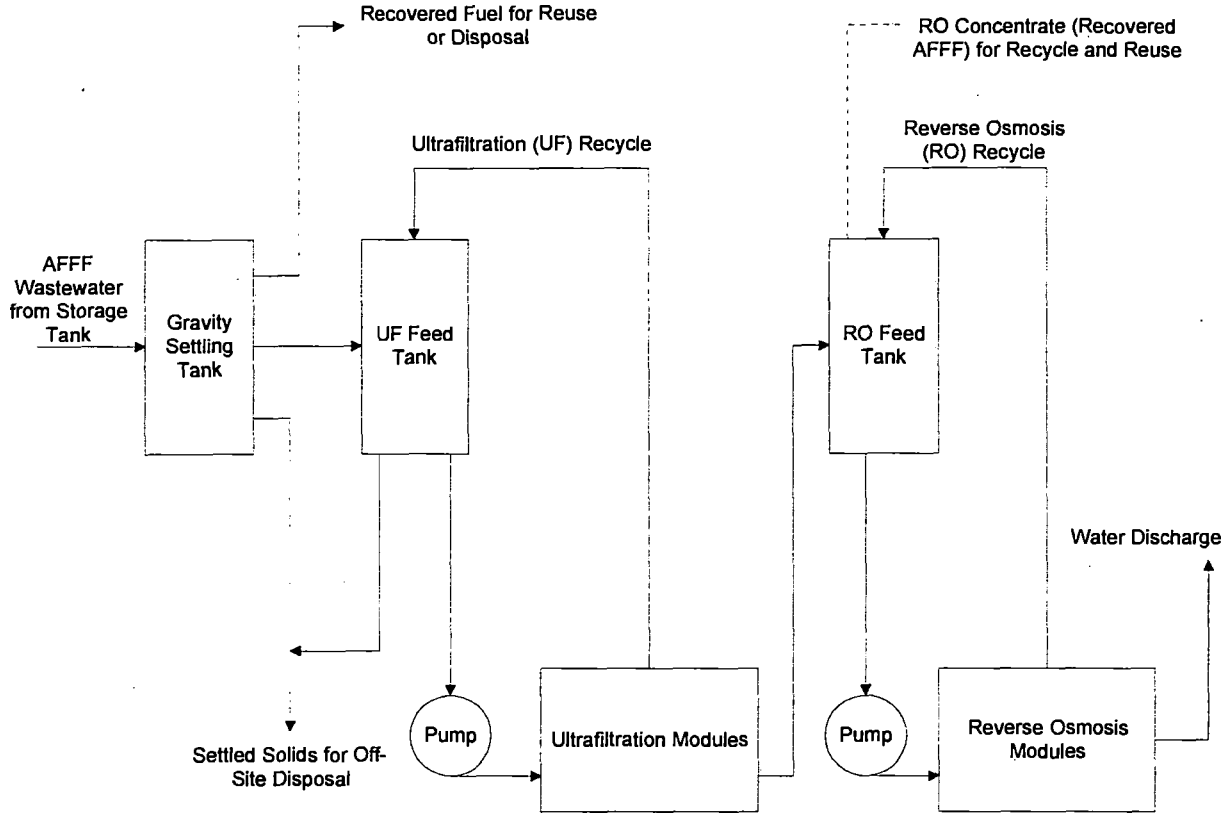


Figure 1: Schematic Diagram of UF/RO Treatment of AFFF Wastewater

Table 4-3: Performance Parameters

(Test Results of Zenon Environmental System Inc. Ultra-Filtration/Reverse Osmosis System on AFFF Wastewater from Canadian Navy Fire Fighting School)

Parameter (mg/L)	UF Feed	UF Conc.	UF Perm.	UF % Removal	RO Conc.	RO Perm.	Typical Sanitary	Typical Storm
TSS	120	582	0.0	100.0	0.0	0.0	350	15
TDS	2593	--	2214	14.6	18540	--	--	--
BOD	2400	--	180	25.0	--	25	300	--
TOC	1912	2150	1677	12.3	13187	25	--	--
Oil & Grease	1570	--	793	49.5	--	3	15	15

TDS – Total Dissolved Solids
TOC – Total Organic Carbon
Adapted from Zenon Environmental System Inc. Product Literature, 845 Harrington Court, Burlington, Ontario, Canada L7N3P3, 1994.

UF/RO systems can process the AFFF wastewater at a rate ranging from 1 gpm to 200 gpm. A small unit costs approximately $70,000. There is an additional cost for membrane preservative fluid that would be required to be maintained in the system during pressing down time [4 and 39]. Operating costs would include utilities, chemicals for preserving and cleaning the system, labor for operation and maintenance and membrane replacement [7]. The life of the system is estimated to be approximately 10 years with the UF membrane having a life of about 1 year and RO membrane lasting about 3 years [4]. There would also be cost associated with testing the permeates prior to release to the environment. Additionally, approximately a week of training would be required for operators of the system. The unit cost ranges from $0.007 -$0.052 per gallon [7]. Unit cost would vary with the size of the system and the amount of use of the system.

5.0 CURRENT AND FUTURE RESEARCH

5.1 AFFF SEPARATOR

Naval Facilities Engineering Service Center (NFESC) sought an economical way to separate AFFF concentrate from the wastewater at the firefighting training facilities. The project resulted in a proof-of-principle device that lowers the AFFF concentrate in wastewater solutions [32].

The basic concept of the separator design is to use air bubbles to create foam. Water alone cannot form a bubble, but the surfactants in the AFFF allow a foam to form. The foam should be rich in surfactants compared with the average water solution. This effectively concentrates the surfactants into the foam which can be subsequently removed by mechanical means. The method was shown to be capable of separating the surfactants from AFFF solutions down to a concentration of 1000 ppm, or lower, of surfactants [32 and 33].

One of the major concerns with this separation technique is the verification of the AFFF concentration remaining in the solution. NFESC developed a simple test that can be performed in the field that would correlate with the AFFF concentration. The method developed is based on drain times since the AFFF MILSPEC requires that drain time be determined for all AFFF solutions. The drain time is defined as the amount of time required for a specific amount of generated foam to return to a specific amount of liquid. Drain time is measured using 2.54 cm (1 in) diameter by 10.2 cm (4 in) high test tube with a screw cap. The tube is filled with 5.2 cm (2 in) of solution and shaken 50 times. The time to reduce 90 % of the foam back to liquid is recorded.

The drain time results were correlated with a property of the AFFF that could be accurately be measured--surface tension. It is believed that as the drain time decreases, the amount of fluorocarbon surfactant in the solution decreases. In order to verify this, a series of surface tension tests were conducted on the same solutions used in the drain time tests. The objective of these tests was to determine the surface tension of solutions that had varying concentrations of AFFF concentrate. This would also evaluate the concentration of the fluorocarbon surfactant since its concentration is in the same ratio as that of surfactant to concentrate in all of the solutions since the surfactant is responsible for the decrease in surface tension. These results could then be compared to the drain time measurements to verify their efficacy. The results were in excellent agreement and provide a good measure of the relative decrease in the amount of AFFF in the solution.

Figure 2 provides a graph showing the surface tension test results. As shown, the AFFF does lower the surface tension of water dramatically. At approximately 1000 ppm of AFFF concentrate, the surface tension curve becomes fairly flat and the concentration is not readily distinguishable above 1000 ppm. At concentrations less than 1000 ppm, the surface tension measurement is sensitive to AFFF concentration. Figure 3 provides a graph showing the surface tension versus concentration over the range of 0 to 2000 ppm. Figure 4 provides a graph

comparing the surface tension measurements with drain times for the various solutions. As shown, a good correlation between the two measurements does exist. This correlation thus provides an assurance that the drain time measurements can provide a reliable measurement for AFFF concentration above 1000 ppm. [32 and 33] All of these results, however, were obtained on 'standard' or pure AFFF-water solutions that would be typical from AFFF discharge tests, e.g., testing fire trucks.

In 1996, Naval Research Laboratory (NRL) conducted environmental and efficacy tests for AFFF separator developed by NFESC using actual firefighting wastewater. Two basic scenarios were evaluated: Standardized Fire Tests (AFFF MILSPEC Qualification Tests) and Actual Fire Events (Firefighter Training). Table 5-1 lists the results of the environmental tests.

Table 5-1: Percent Reductions between BEFORE and AFTER Samples

Sample captured for environmental testing just prior to running the AFFF Separator are labeled BEFORE. Samples taken after AFFF separation are labeled AFTER.

	MILSPEC TEST*	WASTEWATER*
TEST	**% REDUCTIONS**	**% REDUCTIONS**
Drain Time	82	72
BOD_5	78	21
COD	82	34
MBAS	72	70
TPH	NA	33
VPH	95	78
BTEX		
Benzene	99	71
Toluene	100	100
Ethybenzene	100	100
Xylenes	100	88

Note: (a) The above table was developed from Reference 33.
MILSPEC TEST – Wastewater resulted from QPL Tests.
WASTEWATER – Wastewater resulted from QPL Tests, Small-scale tests in the Burn Building, and Medium and Full-scale Tests.

The results of the tests are highly encouraging, such that continued development of the AFFF separator is recommended, as discussed below [33]:

1. The AFFF separator is able to reduce the AFFF surfactants for these typical firefighting wastewater tested. Typical contaminants such as petroleum fuels and volatile aromatic compounds do not have an adverse effect on the final surfactant reduction process or final concentration.

2. The AFFF separator is also reducing the volatile petroleum hydrocarbons and aromatic compounds through the aeration process. The results from all of the environmental tests indicated that the effluent from the AFFF separator is less polluting than the original wastewater as based on COD and BOD_5.

FIGURE 2: SURFACE TENSION VS. CONCENTRATION FOR AFFF (6%) SOLUTIONS

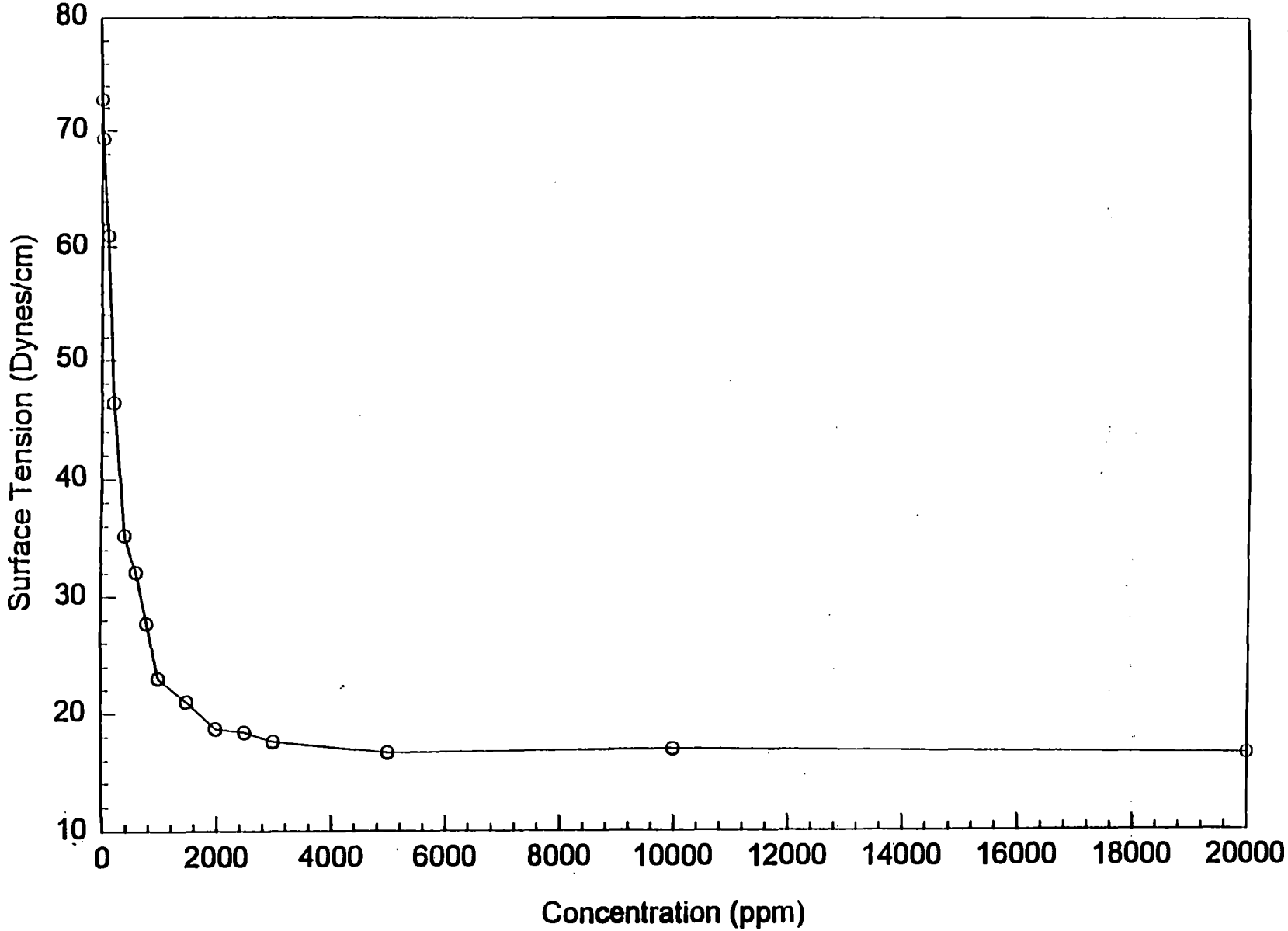


FIGURE 3: SURFACE TENSION VS. CONCENTRATION FOR AFFF (6%) SOLUTIONS

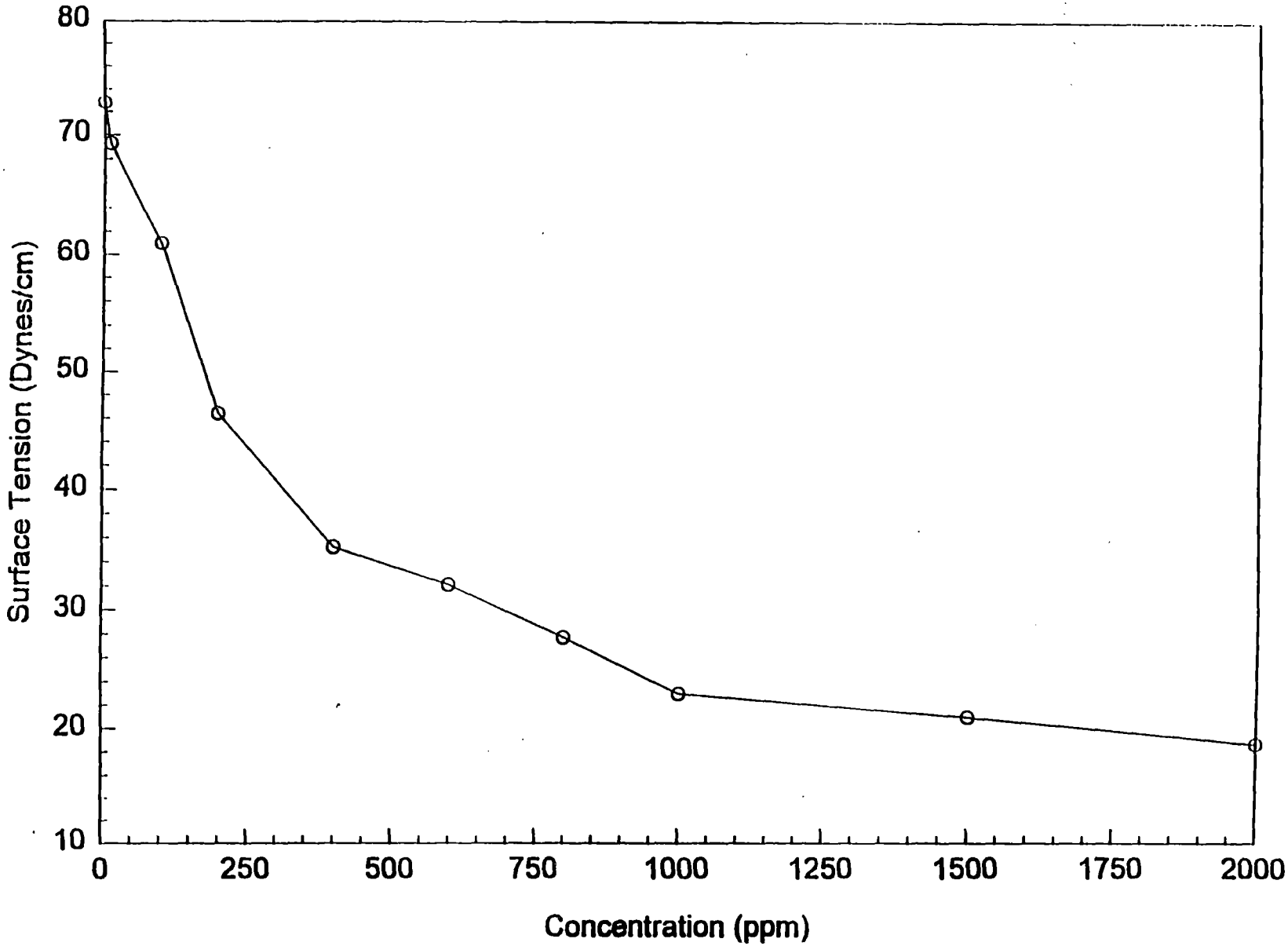
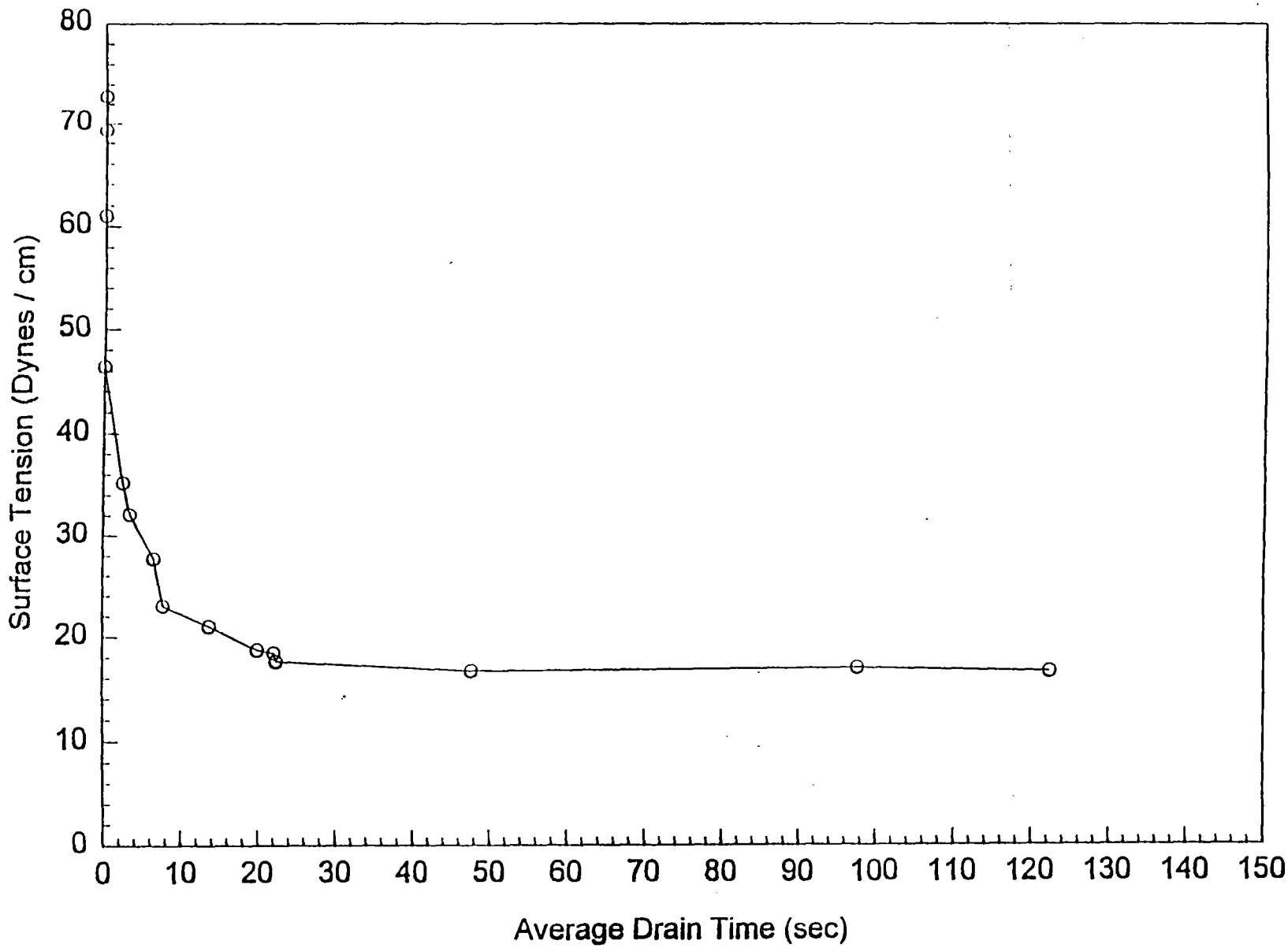


FIGURE 4: SURFACE TENSION VS. AVERAGE DRAIN TIME FOR AFFF (6%) SOLUTIONS



3. The BOD_5 test is not adequate to characterize the typical firefighting wastewater tested. A longer residence time is apparently needed for the bacteria to consume the organics. It is recommended that the BOD_{20} test be specified for all future testing.

4. The Methylene Blue Active Substances (MBAS) test alone does not adequately correlate to the AFFF concentrations as measured by drain time. The environmental test for Cobalt Thiocyanate Active Substances (CTAS) should also be included in any further testing.

5. At present, a study is being conducted to determine whether these wastewaters would be acceptable to the IWTPs at Chesapeake Beach Detachment (CBD) or HRSD as direct influent. The degree of dilution with other influent wastewaters will impact this decision. However, the separator is improving the wastewater and should assist in making these effluents acceptable.

5.2 LIQUID MEMBRANE SEPARATION

U. S. Air Force (AF) designated the Armstrong Laboratories to develop innovative treatment technologies to pretreat the AFFF wastewater before it is discharged to a storm or sanitary sewer. The Armstrong Laboratories is currently studying liquid membrane technologies to treat AFFF wastewater. The first phase would remove the hydrophobic components of AFFF using Membrane-Like-Material (MLM). MLM is a compound formed from a solvent, water and an extract of Athabasca bituman. MLM exists as non-permeable film, or membrane, separating oil and water into two distinct phases [34].

The MLM encapsulates the hydrophobic component of the solution in an extreme stable film allowing the encapsulated material to be physically removed from solution. The MLM does not form a compound with the encapsulated species and it promptly disassociates and releases the captured substance at the air to water interface. The process has been developed as a new technology to separate oily water mixtures such as sea water and oil, emulsified industrial laundry wastewater, metal finishing wastes, an other oily waste mixtures. The hydrophilic species in the AFFF wastewater would remain after this initial treatment. This include most of the BOD which is contained in the butyl carbitol and hydrocarbon surfactants and alkyl portion of the fluoroalkyl surfactant.

The second phase of treatment would remove the hydrophilic component using another liquid membrane treatment process termed Direct-Nucleate-Floatation (DNF). The DNF membrane substance forms a layer of bubbles, each with a chemical collection capability. The bubbles have a layer of charged collector ions on the surface and surrounded by a charged ion cloud. The organized bubble layer has a low permeability and has proven to be very reactive capturing heavy metals out of solution along with other species. Chemicals collected are added as molecular mono-layers to each bubble [34].

A lab scale test of this two phase processing, using a 3 % solution of AFFF, was accomplished. A simple shake test of the process effluent showed the foaming capacity was significantly reduced, with the water to foam interface being restored in 10 seconds.

5.3 AFFF REFORMULATION

In addition to new treatment technology development, AF has conducted a study to stimulate industry to develop a more environmentally acceptable AFFF product with the current products level of effectiveness. This research is being managed by the Wright Laboratories and Dynax Corporation, under the Small Business Innovative Research (SBIR) program [36].

The initial stage (Phase I) of research at Wright Laboratories involves setting a baseline for the current firefighting foam market. This baseline established environmental and effectiveness data on over twenty five firefighting foam agents currently available. The foam agents were broken down into four groups: protein base, fluoroprotein base, hydrocarbon surfactant base, and AFFF. Six evaluation criteria were measured - solvent hazard potential, biodegradability of product, toxicity to fish and microorganism, extinguishment effectiveness, flame resistance, and impact on dispersing equipment [35 and 37].

Primary results show that AFFF is the most effective extinguishing agent using the criteria of application density versus extinguishing time and flame spread resistance versus time. A simple toxicity test on gold fish showed AFFF to be more toxic than protein based foams, equal in toxicity to fluoroprotein based foams and ten times less toxic than hydrocarbon surfactant based foams. AFFF was in the bottom quarter of the biodegradability test, with a BOD_5/COD ration of 8.4 which was over five times worse than the most biodegradable foam (ratio of 43.8) tested. These results document that no currently available foam is more effective than AFFF, while many are more biodegradable. To date, only two foams tested at Wright Laboratories have been forwarded to NAVSEA and passed the MILSPEC test and were incorporated into the QPL. Both these foams were similar to AFFF in chemistry and provided little environmental improvement over AFFF.[35 and 37]

The second stage (Phase II) of the research centers around the development of the next generation of AFFF. The objectives of this research are to maintain current MILSPEC AFFF performance, eliminate the glycol ether constituent (butyl carbitol), decrease the foaming capacity, reduce the fluorocarbon constituent, utilize more biodegradable hydrocarbon surfactants, and assess the feasibility of adding microorganism to the AFFF during application to aid in product degradation.

The research concentrated on mono-, di-, and tri-propylene glycol ethers as the replacement for butyl carbitol because these families of glycol ethers did not fall under the reporting requirements of EPCRA and have similar physical properties with good biodegradability [35 and 36]. Initial laboratory screening of the new solvents was accomplished by obtaining two foams listed QPL-24385-9 from each manufacturer. One foam contained butyl carbitol and the second foam was identical to the first but without butyl carbitol.

Various solvents were added to the foam without butyl carbitol and evaluated. Although results showed some promise for propylene glycol, the solvent did not change the surface and interfacial tension properties and suppress the flame spread like the foam containing butyl carbitol. The suspected cause of this performance problem was that some propylene glycol solvents evaluated had lower flash points that butyl carbitol and also had limited solubility in water. Also, some propylene solvents were slow to biodegrade and exceeded the MILSPEC toxicity limits. Consequently, pure propylene glycol solvents were eliminated from further testing and blends of propylene glycol solvents were prepared and evaluated.

Blending propylene glycol was accomplished to improved the flash point and solubility of the solvent. Laboratory testing demonstrated that the foams evaluated using the new solvent had firefighting performance similar to foams containing butyl carbitol. From the laboratory data, three of the most promising solvent blends were selected for medium scale evaluations, which were accomplished using foams containing blends of the propylene glycol solvents. Testing was accomplished using the MILSPEC with minor changes to make the fire more severe. These changes included using mo-gas in lieu of heptane in the 28 sq.ft. pan and keeping the burnback pan in the foam instead of removing it as stated in the MILSPEC.

All QPL foams were evaluated, showing that the new solvent blend works as good as, and in some instances better than the performance of the foam when compared to the same foam with butyl carbitol. Table 5-1 summarizes the test results [36].

Also, as a part of Phase II study, Wright Laboratories developed a new formulation which, in comparison with AFFFs listed on the QPL:

- contains no glycol ethers;
- utilizes 50 % less fluorocarbon surfactant;
- exhibits improved drain time and foam expansion;
- exhibits shorter extinguishment times and longer burnback resistance; and
- is less toxic to fish.

The details of this study will be published and distributed in December 1996 (to date, nothing has been published).

Table 5-2: 28 Square Feet Pan Fire Tests of 3% Foams				
Agent	**Extinguishment (Seconds)**		**Burnback (25%) (Seconds)**	
	Butyl Carbitol	**New Solvent**	**Butyl Carbitol**	**New Solvent**
3M Light Water				
Fresh Water, Full Strength	31	27	390	430
Salt Water, Full Strength	44	42	322	309
Fresh Water, Half Strength	72	42	275	320
Salt Water, Half Strength	47	42	315	298
Ansul Ansulite				
Fresh Water, Full Strength	35	39	347	409
Salt Water, Full Strength	32	35	406	465
Fresh Water, Half Strength	47	62	339	358
Salt Water, Half Strength	45	56	403	386
National Foam Aer-O-Water				
Fresh Water, Full Strength	34	34	376	405
Salt Water, Full Strength	40	39	393	380
Fresh Water, Half Strength	38	37	364	318
Salt Water, Half Strength	63	49	320	341
Angus Triol				
Fresh Water, Full Strength	57	43	336	389
Salt Water, Full Strength	39	46	365	388
Fresh Water, Half Strength	73	76	310	326
Salt Water, Half Strength	40	44	379	412

Note: The above table was developed from Reference 33.

6.0 CONCLUSION AND RECOMMENDATIONS

MILSPEC AFFF is still the most effective firefighting foam currently available and until a more environmentally benign alternative is formulated, it will continue to be widely used within the DoD and at civilian airports. Although the Air Force's current effort of changing the solvent and optimizing the fluorocarbon surfactant and additives in AFFF is quite promising, the new formulation will not be materialized within the next five years. There is an urgent requirement for a pollution prevention method to treat AFFF wastewater that will efficiently remove AFFF and auxiliary contaminants from aqueous streams and concentrate them for disposal in an economically and environmentally sound procedure.

The high BOD and COD, toxicity to bacteria in typical-usage concentration, and extreme foaming capacity of the current AFFF formulation makes disposal in an IWTP difficult. Also, it is suspected that some of the compounds used to create the highly effective characteristics of AFFF do not breakdown in the environment. Thus, the very elements that apparently make AFFF an effective agent have a detrimental, or at least an unknown, impact on the environment. Furthermore, the EPA regulations and current trend towards stricter regulation add an additional concern with respect to the use and disposal of this product. Based on these perceived problems, local authorities in Maryland and Virginia area severely restrict or prohibit the discharge of AFFF into the local wastewater stream.

DoD has devoted considerable resources towards treatment and disposal of AFFF wastewater in the past two decades. In 1978, the Navy conducted a comprehensive study on possible approaches for AFFF treatment including coagulation, clarification, carbon adsorption, chemical oxidation, air stripping, and biological treatment. In the study, the Navy concluded that none of the attempted treatment methods performed well enough to provide an effluent suitable for discharge to a receiving stream. There are two specific points appearing in this early Navy report that are still relevant today:

1. One disposal method for AFFF appears to be dilution with quantities of water and slow metering into a wastewater treatment plant so as to avoid system shock.

2. No good analytical method exists for measuring AFFF concentration. Prediction and monitoring of AFFF pollution control are not possible without appropriate analytical methods.

A different approach using membrane treatment was proposed and tested by the Navy in 1983. In the study, the Navy concluded that the ultra-filtration (UF)/reverse osmosis (RO) system is unfeasible due to high set-up and operational costs, as well as the unacceptable high levels of training required to operate the equipment. Since the Navy's initial study, the UF/RO system is further developed and improved by commercial vendors, thus, making the UF/RO system a preferred method over other treatment processes previously researched. The UF/RO systems now can provide percent removal efficiencies of AFFF constituents ranging from 96 to 99%. Also, by purchasing a mobile unit, the treatment system can be utilized by multiple Navy bases, thereby minimizing the capital cost of the system.

Naval Facilities Engineering Service Center (NFESC) undertook a study to find an easier, more economically sound way to separate AFFF from the wastewater generated by firefighting training facilities in 1995. This study focused on separating the AFFF from the wastewater by mechanical means. A prototype AFFF separator was developed and tested on actual firefighting wastewater. The study found that the presence of contaminants that would typically be found in firefighting wastes, such as petroleum hydrocarbons and aromatic compounds, do not have an adverse effect on the mechanism or the efficiency of the process. The test also showed that the separator not only reduces the AFFF surfactants from typical firefighting wastewater, but also reduces the other pollutants in the waste as measured by BOD_5, COD, VPH, BTEX, and TPH. The overall results are highly encouraging and continued development of the AFFF separator is recommended.

NFESC also developed an inexpensive, fairly reliable, small-scale field method to measure the relative concentration of AFFF solution. The drain time results were correlated against a property of the AFFF that could accurately measured, surface tension. The results were in excellent agreement and provide a good measure of the relative decrease in the amount of AFFF on the solution.

In the long term, the Air Force (AF) sponsored research to find a more environmentally benign AFFF formulation should continue to be supported.

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