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TECHNICAL MEMORANDUM

title: DISPOSAL OF WASTEWATER CONTAINING AQUEOUS FILM FORMING FOAM (AFFF)

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CIVIL ENGINEERING LABORATORY

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INTRODUCTION

The firefighting training program for Naval personnel includes field exercises involving the extinguishing of large oil fires which are burned on the surface of water pools. A 6% concentration solution of a chemical compound named "Aqueous Film Forming Foam" (AFFF), or frequently referred to as "Light Water", is used alone or in combination with Purple K. Powder (PKP, potassium bicarbonate) to extinguish the fire. Wastewater generated from such firefighting exercises contains residual fuel oil and gasoline, AFFF, PKP and miscellaneous combustion products. All of these constituents, especially AFFF, have imposed upon the receiving environment a certain degree of toxicity/pollution effect. Another source of wastewater containing AFFF is generated by shipboard AFFF firefighting system testing. Naval industrial activities must test the shipboard system after it is installed, modified or repaired to ensure that the minimum concentration of AFFF in the output mixture is 3.5% (the optimum is 6%). The foam is generated for one minute at flow rates of 95 to 250 gallons per minute before a sample is taken to measure AFFF concentration. The water used for making foam can be fresh water, salt water or bilge water. AFFF firefighting equipment is tested aboard Naval ships located in thirty-three ports in CONUS and Hawaii and in six Naval shipyards servicing surface ships. Approximately 90% of the AFFF discharged is produced at Naval shore installations in the following ten locations.(1)

NS, San Diego, CA
NS, Norfolk, VA
NSY, Charleston, SC
NSY, Honolulu, HI
NSY, Philadelphia, PA
NS, Mayport, FL
Amphibious Base, Norfolk, VA
NSY, Long Beach, CA
NSY, Bremerton, WA
NAS, Alameda, CA

Another possible generation source of AFFF-laden wastewater is aircraft hangars, where the facility is equipped with an automated AFFF spraying and flooding system for extinguishing fires. In view of the need for disposing of firefighting training/testing wastewater that will be acceptable under local and Federal guidelines, the Civil Engineering Laboratory (CIVENGRLAB) has been tasked by the Naval Facilities Engineering Command (NAVFACENGCOM) to develop AFFF-laden wastewater treatment and disposal techniques. As industries (including DOD) and municipalities have been moving toward compliance with July 1977 requirements, the control of toxic (such as AFFF) and hazardous pollutants has become an immediate challenge confronting the progress of the nation's environmental protection efforts. The only real solution to the control of these harmful pollutants is through containment, reuse and recycling. This is more than just an axiom of pollution control; it is prudent economics. We must recapture the resources lost in industrial production and reuse them if we are to continue as a thriving industrial community. Most recently, the passage of the Resource Conservation Recovery Act (PL94-580) established recovery and reuse of wastes as a principal requirement of environmental protection methods. Therefore, recovery and reuse of AFFF will be considered as a most desirable disposal option. This report presents a summary of information currently available relevant to AFFF, and the RDT&E program plan to be executed by CIVENGRLAB.

BACKGROUND

The fire extinguishing agent, AFFF (MIL-F-24385) is characterized by a stable fluorocarbon tail and a solubilizing group Z, $CF_3(CF_2)$---Z. The solubilizing group can be organic or inorganic, anionic, cationic, nonionic, amphoteric, water soluble and/or oil soluble. The fluorocarbon tail (with surfactant) has exceptional resistance to thermal, chemical, electrical and biological attack with good resistance to radiation. Laboratory analysis of one type of AFFF liquid concentrate (FC-200) revealed a chemical oxygen demand (COD) of 730,000 mg/l, total organic carbon (TOC) of 235,000 mg/l, surfactants (as MBAS) 3,020 mg/l and fluoride 3,680 mg/l.[2]

The pollutional effects of the AFFF-laden wastewater may be divided into two major categories: (a) adversely affecting the performance of biological treatment processes, and (b) toxifying aquatic/marine environment.

AFFF is purchased under a performance specification prepared by the Naval Research Laboratory (NRL). The chemical formulation is proprietary. NRL is reviewing the specifications periodically for the purpose of adding biodegradability and toxicity standards. However, there is no particular indication that an effective firefighting agent could be produced in the near future that would meet treatability and environmental quality standards. Through a thorough literature search, it was found that there is no standard analytical procedure for measuring AFFF concentration. Instead, COD and BOD measurements have been used to represent AFFF concentration in the wastewater. Additionally, there is neither a discharge standard for AFFF concentration in the treated effluents, not is there an effective treatment method available. AFFF is known to be toxic to oyster larva about 100 mg/l and to fish about 1,000 mg/l. There is no conclusive evidence as to the limiting concentration for biological treatment systems under conditions of continuous feeding and/or shock loading. Dilution has been the only process for disposal of AFFF contaminated wastewater, and recovery and reuse technology for AFFF is not available. Also, there are no human health effect standards for AFFF.

CIVENGRLAB will concentrate its efforts in the problem areas identified above, with the cooperation of U.S. Air Force, the only other Department of Defense agency that is a user of the material. A literature search summary addressing this subject is presented in the following discussion section.

DISCUSSION

1. Characteristics and Composition of AFFF Concentrate - One of the major AFFF producers is Minnesota Mining and Manufacturing Company (3M). Their product is designated by FC-NOS, such as FC-206. Characteristics of AFFF concentrate manufactured by 3M and others by National Foam Systems, Inc. (trade mark AOW), and Ansul Co. (trade mark ANSUL), are summarized in the table on the next page.

In June 1976, a Qualified Products List (QPL-24385-9) of products qualified under military specification (MIL-F-24385) for AFFF was published. There are five products in the list. ANSUL AFFF (NRL Report C05-19(74), FC-200 (NRL Report 61C05-19 (529)), FC-200 (NRL Report 61C05-19 (536)), FC-206 (NRL Report C05-19 (187)) and Aer-O-Water 6 (NRL Report

AFFF Agent	Specific Gravity	PH	COD mg/1	BOD mg/1	Sulfactant mg/1asMBAS	Fluoride mg/1	Ethylene Glycol	Diethylene Glycol Monobutyl Ether	Wate
AOW-3	1.062	7.8	500,000	161,000 (5-day) 354,000 (30-day)	80,000 (as active agents)	5,000	10%	10%	72%
AOW-6	1.031	7.9	350,000	135,000 (5-day) 300,000 (30-day)	80,000 (as active agents)	2,500	10%	10%	72%
FC-199	1.02	4.6	550,000	180,000 (5-day) 300,000 (ultimate)	-	-	-	-	-
FC-200	0.989	7.6	730,000	50,000 (5-day) 510,000 (ultimate)	3,020	3,680	-	39%	59%
FC-203	-	-	870,000		-	-	-	-	-
FC-206	1.02	7.8	500,000	210,000 (5-day) 420,000 (ultimate)	- 41,000	14,000 (as Fluorine) 2% as Fluo- carbon		- 27%	- 70%
ANSUL K74-100	1.015	7.9	210,000	54,400 (5-day) 159,000 (20-day)	80,000 (as active agents)	5,000	-	-	92

C05-19 (358) and (189A)). The six percent AFFF solution can be made with either fresh, bilge, or sea water. In the case of sea water, the wastewater will have an additional adverse effect caused by the sea water on a biological wastewater treatment process due to the high concentrations of chloride and sulfur.

2. Characterisitics of Firefighting Training School Wastewater - As mentioned previously, the firefighting training school wastewater will contain dissolved, free and emulsified fuel oil and gasoline, AFFF, PKP and a variety of dissolved and suspended combustion products. A Navy contract study[3] reveals the wastewater characteristics as follows:

Parameter	NS Norfolk, VA Bilge Water	Synthetic Composite Wastewater *
pH	4.2	7.0
Total Suspended Matter (mg/l)	76	15
Oil and Grease (Freon Extractables (mg/l)	1120	325
Chemical Oxygen Demand (COD, mg/l)		
Total	8800	2190
Filtered	5800	1590

*One volume of bilge water + four volumes of dilution water + 1,000 ppm AFFF ÷ 100 mg/l PKP. This synthetic wastewater was used by the contractor (Engineering Science, Inc.) for physical-chemical treatability studies.

3. Quantity of Firefighting School Wastewater - AFFF concentrates used in the Navy amount to 5 - 20 gallons/week at Naval Air Stations and 20 - 125 gallons/week at firefighting schools. Total wastewater quantity from each exercise may range from 2,000 to 50,000 gallons. At Naval Air Stations, fires (pan fires) are generally set on or about ground surface, while at firefighting schools they are set on water pools. Therefore, the quantity of wastewater from air station exercises is much less than those from firefighting schools and quite frequently they are discharged to storm drainage and/or allowed to percolate into the ground. Ground water contamination from this type of practice is yet to be defined. A Waterspray Smoke Control System (WSS) is commonly used in firefighting training facilities.[3] This practice produces extra wastewater containing combustion by-products, particulates, soot, gas, etc. Such transient loadings can adversely affect the performance of treatment processes.

4. Treatability Studies

A. Preliminary Treatment

(1) A gravity-type oil-water separator (such as API-type separators) is generally employed to separate free oil, foam and settle-

able solids from the firefighting school wastewater.

(2) An equalization basin is used to adjust excessive hydraulic and load fluctuations of the influent to the treatment facility, since transient loadings can adversely affect the performance of any treatment process.

B. Physical-Chemical Treatment

(1) pH Adjustment - It was reported[5] that oil emulsion was readily broken down by sulfuric acid acidification to a pH of about 4.5 from two wastewater samples. One sample contained "Light Water" AFFF plus a trace of protein foam and the other sample contained protein foam only. However, Engineering Science, Inc., experienced failure in this pH adjustment technique, when pH was reduced to as low as 1.5.

(2) Chemical Coagulation - Diluted oil emulsions can be clarified or broken by the addition of soluble heavy-metal salts in the presence of sufficient alkalinity to form a precipitate which is then conditioned by flocculation and removed by some type of clarification process. A study[4] revealed that the addition of 120 mg/l alum and 0.1 - 0.3 mg/l of polymer (American Cyanamid 835A or Calgon WT 3000) to the synthetic wastewater as described previously, was effective in coagulating the emulsified-oil content in the wastewater. It was also observed that wastewater alkalinity was insufficient to resist pH depression during coagulation, and the addition of sodium hydroxide was required for pH control.

(3) Clarification - Sedimentation, filtration and air flotation are generally used techniques for removing flocs resulting from chemical coagulation and flocculation processing of wastewater. The air flotation method is particularly useful for removing flocs which exhibit poor settling characteristics such as those observed in firefighting school wastewater treatment. Experience has shown[4] that when a recycle ratio of 33% and a 3 gpm/ft^2 overflow rate were used, a good clarification was obtained for chemically treated synthetic wastewater. The quantity of float was 2 - 3% of the wastewater volume and the solids content of the float was calculated at 5% by weight. An interesting finding obtained in this experience was that both FC-206 and AOW-6 showed an "oil" contribution of approximately 100 mg per ml of AFFF concentrate.

(4) Advanced Oil/Water Separation System - CIVENGRLAB has been developing a three-stage oil/water separation system for Naval shore installation application. The system consists of an improved gravity parallel plate separator, an ultrasonic backwashable, self-cleaning coalescer, and a carbon adsorption bed. With bilge oily wastewater containing about 900 mg/l to 20% of oil, the first-stage parallel plate is able to remove down to less than 100 mg/l (even to 15 mg/l), and the second-stage coalescer further reduces the oil concentration to below 10 mg/l. A two-stage system of this type is being tested at NS Mare Island, CA, to determine cost-effectiveness, especially in the reduction of the coalescer element costs. The last-stage carbon would absorb free oil from 10 mg/l or below to about 1 mg/l and remove solubles. This developmental system appears to have a high application potential to firefighting school wastewater.

(5) Carbon Adsorption - Four commercial activated carbons, Westvaco Nuchar WV-G and WV-1, Calgon Filtrasorb 400, and ICI America Hydrodarco 3000 were used by Engineering Science, Inc.[4] to conduct adsorption isotherm of AFFF by the carbon. It was concluded that their findings confirmed those reported by the Air Force,[6] that virtually all of the COD due to FC-206 (in demineralized water) would be removed by carbon adsorption, but only 70% removal of AOW-6. That is because diethylene glycol monobutyl ether, the major constituent of FC-206, is readily adsorbed by carbon; while AOW-6 contains about 50% of ethylene glycol that makes it difficult to be adsorbed by the carbon. However, when AFFF synthetic wastewater was tested, both showed very poor carbon adsorption efficiency. It was reasoned that this was caused by using bilge water to make the synthetic wastewater, since bilge water demonstrated a poor adsorption characteristic in subsequent experiments. The same study group performed experiments using carbon column for adsorbing FC-206 and AOW-6 in a pretreated synthetic waste (COD 1400 mg/l), and found that roughly 1000 mg/l of the waste COD content was not removed. Carbon columns were operated at a loading rate of 2.3 gpm/ft^2 and a detention time of 10 minutes for each column or 40 minutes total for four columns in series.

(6) Chlorine Oxidation - Carbon-treated AOW-6 synthetic waste that had 681 mg/l COD was oxidized for two hours with chlorine ranging from 0.18 mg/l to 131.5 mg/l. The overall COD reduction was less than 8% in all chlorine dosages tried and the high residual chlorine concentration in the tested samples indicated the chlorine oxidation process was totally inefficient.

(7) Permanganate Oxidation - Permanganate oxidation followed the same procedure as that used in chlorine oxidation. Dosages ranged from 20 to 220 mg/l and the COD reduction rate was below 14%. Again, a general resistance of AOW-6 to oxidation by chemicals was indicated.

(8) Air Stripping - Air stripping of volatile components in the waste was tested. Only a 10% reduction in COD was observed after 20 hours of aeration.

(9) Combined Physical Chemical Treatment Process - Two synthetic wastewaters containing FC-206 and AOW-6 respectively were subjected to treatability studies comprising chemical coagulation and dissolved air flotation (DAF) and clarification (first-stage). Carbon adsorption (second-stage) was then used to treat the chemical coagulation and DAF effluent. It was found that the first-stage process could remove 36% COD (from 2190 mg/l down to 1400 mg/l) and the second-stage, 14% COD. The second-stage effluent still contained more than 600 mg/l COD. Therefore, it was concluded that additional treatment would be required to meet toxicological requirements.

C. Biological Treatment

The Air Force performed four biodegradability and toxicity studies respectively for AER-O-Water (AOW) 3 and 6[7], FC-200[2], FC-206[8], and ANSUL K74-100[9] AFFF. Results from these studies are summarized in the table following (excluding toxicity data, which will be tabulated and reported later).

	Detention Time	Influent Feed	COD	BOD	
1. AOW-3	7.6 hrs.	50-2400 ppm (V/V)	94 down to 25 in 94 days Continuous Experiment	97 down to 66 in 94 days	Ethylene Glycol Not Biodegradable Plant Did Not Recover After 1700 ppm Feed
2. AOW-6	7.5 hrs.	50-2400 ppm (V/V)	86 down to 50 in 94 days	96 down to 74 in 94 days	Plant Did Not Recover After 1700 ppm Feed
3. FC-200	6-8 hrs.	50-250 ppm	89 down to 45 in 53 days	Maintained at 96 in 53 days	Efficiency Degraded After 100 ppm Feed
4. FC-206	6-8 hrs.	50-300 ppm (V/V)	Maintained 96 - 98	98 down to 96.5 in 51 days	Efficiency Degraded After 250 ppm Feed
5. ANSUL K74-100	6-8 hrs.	50-3500 ppm (V/V)		98 down to 75 in 98 days	Efficiency Degraded After 250 ppm Feed

All experiments were conducted under the following conditions:

(a) Using bench-scale, continuous feed activated sludge process

(b) Employing pure AFFF concentrate and synthetic sewage as feeding substrate

(c) Acclimating activated sludge with synthetic sewage before AFFF was gradually (dosage increased with time) fed to the process.

A summary table[9,10] which presents a comparison of concentrations of AFFF in synthetic sewage amenable to biological treatment is shown below:

AFFF Agents	Recommended For* Treatment, ppm V/V	Maximum to Sewage** Treatment Plant, ppm V/V
FC-199	25	250
FC-200	10	100
FC-206	20	200
AOW-3	150	1700
AOW-6	150	1700
ANSUL K74-100	25	250

*Based on reactions to microorganisms, aquatic life and safety factors (about 10% of maximum to sewage treatment plant concentration).

**Synthetic sewage used in the activated sludge pilot plant study consisted of glucose (160 mg/l), Peptone (160 ms/l), urea (28.6 mg/l), sodium bicarbonate (102 mg/l), potassium phosphate (32.5 mg/l) and tap water.

The Air Force study[9] also recommended the maximum concentration of AFFF for direct discharge to a stream containing aquatic life as follows:

AFFF Agents	Maximum Recommended Concentration, ppm V/V
FC-199	20
FC-200	5
FC-206	54
AOW-3	60
AOW-6	22.5
ANSUL K74-100	55

5. <u>Toxicity Studies</u> - The Air Force has performed toxicity studies along with their biodegradability studies.[1,7,8,9] The 3M Company[11] also performed some studies for their products. The newest military specification (MIL-F-24385A, issued in May 1977) for the fire extinguishing agent AFFF liquid concentrate calls for a new formula from manufacturers that will meet a toxicity standard of TL_{50} of not less than 1500 ppm when tested as specified in the Standard Marine Bioassay Procedure for Shipboard Chemicals. In this same specification, BOD_{20} and COD of AFFF liquid concentrate are not to exceed 500,000 ppm. This is the first time that NRL included environmental impact parameters in the specification. The new AFFF formula supposedly will be less toxic and more biodegradable than the old formula. Yet, the high BOD_{20} number indicates that high dilution rate and long detention time are still required for subjecting AFFF-laden waste to biological treatment process. Data collected from these studies are presented in the next table.

CIVENGRLAB Case Studies

A. Naval Station, Mayport, Florida

(1) Problem: In November 1975, 1,500 gallons of AFFF wastewater containing 8.46% of FC-206 concentrate (based on COD concentration measurement) were off-loaded for shore disposal from the aircraft carrier Saratoga, resulting from shipboard firefighting system testing. A 0.5 MGD activated sludge plant in the station was the best candidate disposal option for the AFFF wastewater at that moment. CEL was requested to provide assistance in disposing of the "pure" AFFF solution to the sewage treatment plant.

(2) Solution: Constrained by both time and available technology, the Air Force's recommended concentration for treatment, i.e., 20 ul/l of concentrate was used to dose the activated sludge plant at the grit chamber. This concentration is actually much less than the recommended maximum concentration of 54 ul/l for direct discharge to streams containing aquatic life.

The dosage was initiated at 50% feed strength, i.e., 10 ul/l, and increased to 100% in a one week time frame for Mayport's sewage treatment plant operation. Close monitoring of influent and effluent water quality was carried out because of the nature of this first time, full scale sewage treatment plant operation. Samples collected from the plant were analyzed for BOD, COD, SS, TS, detergent, DO and p .

The operation was discontinued after 6 days of initial operation, due to the noticeable increase in suspended solids in the plant effluent (according to the plant operator's observation). It was also noticed that the plant received a "slop" oil type waste during the same time period from some industrial operation on the base. The plant resumed AFFF waste feed two and one-half weeks after the initial feeding when the plant operator determined that the plant had completely recovered from the previous "shock" loading of AFFF waste. It took a total of 42 days to feed 1500 gallons of AFFF waste or 35.7 gallons per day average. This was about one-fifth the feed strength as originally planned. This Laboratory evaluated the analytical data supplied by Southern Analytical Laboratory for Mayport sewage treatment plant operation and concluded that there was no apparent and significant impact from feeding AFFF waste to the plantat the recommended dosage, 20 ul/l. The initial shock might be attributed to the unknown "slop oil" waste. A

TLm Concentrations (µl/1) for Tested Species

Test Species	AFFF Agents						
	FC-199	FC-200	FC-203	FC-206	AOW-3	AOW-6	ANSUL K74-100
Fresh Water Fish							
Fathead Minnows (Pimephales promelas)	398** (96 hrs)	97** (96 hrs)	1,900 (96 hrs)	3,000 (96 hrs)	600** (96 hrs)	225** (96 hrs)	1100 (96 hrs)**
	588** (48 hrs)	135** (48 hrs)		1,080** (96 hrs)	820** (48 hrs)	255** (48 hrs)	1425 (48 hrs)**
				1,810** (48 hrs)			
Rainbow Trout (Salmo Gairdneri)			1,300 (96 hrs)	1,800 (96 hrs)			
Marine Fish							
Mummichog (Fundulsheteroclitus)				1,820 static (96 hrs)			
Grass Shrimp (Palaemonetes-vulgaris)				280 static (96 hrs)			
Fiddler Crab (Uca Pugilator)				3,260 static (96 hrs)			
Atlantic Oyster Larvae (Crassostrea Virginica)				> 100 < 240 (48 hrs)			
Invertebrates							
Water Flea (Daphnia Magna)			1,600 (48 hrs)	5,850 (48 hrs)			
Scud (Gammarus Fasciatus)			1,100 (48 hrs)	5,170 (48 hrs)			
Algae							
Chlorella Pyrenoidosa			1:1,000*				
Phormidium Inundatum			1:1,000*				

*Exhibit Growth at Dilutions, **Air Force Study Result. Others are 3M Co. results.

data summary is presented below:

Parameter Measured	AFFF* Loading Rates	Influent (Grit Chamber) mg/1	Effluent (Secondary Clarifier) mg/1
BOD_5	20	85 - 150	8 - 13
	30	75 - 172	4 - 7
	40	133 - 226	12 - 18
COD	40	215 - 370	30 - 45
	60	190 - 470	20 - 35
	80	290 - 380	36 - 50
SS	20**	55 - 113	3 - 20
	30	58 - 207	9 - 23
	40	73 - 141	3 - 5

*AFFF loading rates are expressed in terms of the parameter measured.

**AFFF loading rates in SS were expressed as BOD_5 concentrations.

As shown in the data table, the plant effluent water quality met EPA secondary effluent standard, implemented since July 1977, for a monthly average of 30 mg/1 of both BOD_5 and SS.

A parallel study was performed at CEL using Arthur Bros. Co., Inc., B.O.D. Analyzer. Activated sludge as well as settled sewage was obtained from nearby Camarillo City Sewage Treatment Plant, California. The settled sewage containing 150 mg/1 BOD was fed to a 2 liter BOD Analyzer reactor, with a loading rate (F/M ratio) of 0.2 lb BOD/lb MLSS. AFFF waste obtained from NS Mayport containing 8.46% AFFF concentrate based on COD concentration measurement was used in feed with the settled sewage during the experiment. The experiment was conducted under intermittent feed conditions, and under a constant temperature of 20^{o}C. The experimental results are summaried on the following table.

It is difficult to derive a conclusion from the 4-day laboratory experiment. However, the results do not indicate a significant impact (using oxygen demand as an indicator) on the activated sludge until the concentration in the reactor reached between 15.77 and 38 ppm (V/V). The laboratory experiment resembles a field operation in terms of shock loading, i.e., not much time was provided for the activated sludge to become acclimatized or recover from shock. AFFF waste was not fed at night during the experimental period. The system, though shocked between concentrations of 38 and 624 ppm, maintained a fairly good performance in terms of oxygen uptake rates and effluent turbidity. It was observed that a certain amount of MLSS was lost via the effluent. This was evident from the sludge volume change. When the AFFF concentration increased from 624 ppm to 1250 ppm in 1 - 5 hours, the foam inside the reactor increased to an extent that no representative sample could be obtained for analysis. At high AFFF concentration (e.g., more than 1,000 ppm) the aeration reactor behaved as a flotational clarifier.

Cumulative Time, hrs	FC-206 Concentration Inside the Reactor, V/V ppm	Oxygen Demand, mg/l - hr	Effluent Turbidity, JTU	Sludge Vol Change % (After 30 mins Settling
0	0	18.07	-	0
25	0.85	13.3	18	0
26.5	1.63	15.3	9.5	+19
28	2.31	17.0	12	+76
29.5	2.93	18.6	8.2	+24
31	5.72	20.3	9.2	+ 8
46.5	0	15.0	10	0
48	6.0	15.0	10	0
49.5	7.17	16.3	5.9	+33
51	9.09	18	10	+43
52.5	11.70	19.3	7.6	+36
54	15.77	20.3	7.2	+36
69.5	0	10.3	12	0
71	38	10.3	8.2	-23
73.5	77	10.3	12	-50
75	155	11.97	10	-50
76.5	312	11.3	12	-50
78	624	16.63	12	-60
79.5	1250*	-	-	-

* Too much foam in the reactor to make any analyses.

B. Naval Station, Norfolk, Virginia (12)

(1) Problem: Hampton Roads Sanitation District (HRSD) in Norfolk, Virginia, receives Naval Station wastewater that includes waste generated by the firefighting school. HRSD requires the Navy to provide a satisfactory solution (pretreatment) to handle AFFF containing waste, so that both toxicity and treatability requirements will be met. HRSD plans to complete construction of its 15 MGD pure oxygen activated sludge plant (UNOX process) by 1980.

The Navy is requested by HRSD to pretreat the firefighting wastewater so that it will be compatible with an UNOX plant operation and will not contribute to HRSD effluent toxicity so as to exceed 0.01 of 48-hour TLm concentration using oyster larvae as the testing species.

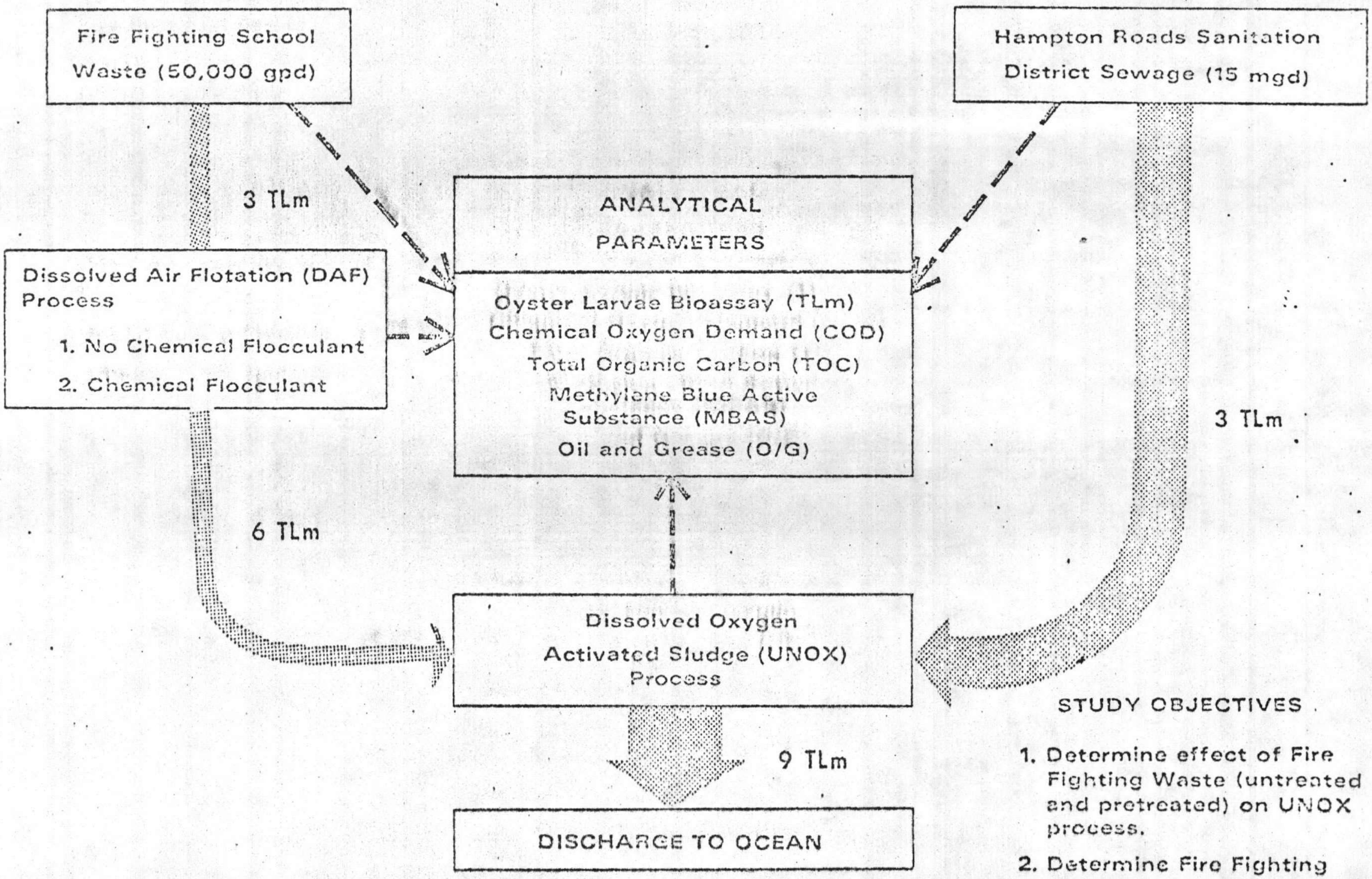
(2) Solution: The Civil Engineering Laboratory (CIVENGRLAB) assisted Atlantic Division (LANTDIV), Naval Facilities Engineering Command (NAVFACENGCOM) to conduct a field pilot treatability study. A flow diagram of the unit processes and number of samples to be collected for toxicity tests is shown on the following page. The study was divided into three parts, namely, (a) chemical coagulation, flocculation and dissolved air flotation (DAF), (b) UNOX process, and (c) Oyster larvae bioassay test. Four contractors were employed to conduct the assigned tasks. In addition, some in-house work was done by David W. Taylor Naval Ship R&D Center (NSRDC), Annapolis, MD. The performers and their assigned task are listed as follows:

Performers	Task
NSRDC Annapolis, MD and NRL, Washington, D.C.	Chemical coagulation/flocculation
Southeast Applied Research, New Orleans, LA	Chemical coagulation/flocculation
The Pielkenroad Separator Co. Houston, TX	Chemical coagulation/flocculation and DAF
Union Carbide Corp. Tonawanda, NY	UNOX Process
Bionomics (EG&G), Pensacola, FL	Oyster Larvae Bioassay

Field tests were conducted during October and November of 1977. However, to date, CIVENGRLAB has not received completed final reports from all contractors. A final report for this study will be drafted after receiving all reports from contractors. Based on limited information/data collected to date, some statements may be made as follows:

- Alum (60 - 120 ppm) appeared to be an effective coagulant for clarification of firefighting school wastewater. Alkali (45 - 80 ppm) has to be added for pH adjustment. Purifloc N-20 (Dow Chemical) and Magnifloc 835A (American Cyanamid) (3 ppm) in the presence of 60 - 120 ppm alum produced a compact floc. Zeta potential measurements were found effective in establishing the optimum dosage of coagulant and polymer as recommended by

FIRE FIGHTING SCHOOL, NORFOLK VA PILOT TREATABILITY STUDY



STUDY OBJECTIVES

1. Determine effect of Fire Fighting Waste (untreated and pretreated) on UNOX process.
2. Determine Fire Fighting Waste contribution to UNOX effluent toxicity.

Puricon, Inc., Bervyn, PA.

. Surefloc Process used for removal of surface active agents (surfactants), soil, oils and grease from laundry wastewater was tested for its treatability of AFFF wastewater. Sodium hydroxide was used to adjust the pH to above 9.3, then 200 - 700 ppm surefloc was added and followed by the addition of alum until the pH was down to between 5 to 6.5. Good flocs and clear supernatant were obtained. This process is not recommended due to the large amount of chemicals required according to Southeast Applied Research, New Orleans, LA.

. DAF Process proved to be effective in removing flocs generated from treatment of AFFF waste with 120 ppm alum and 3 ppm polymer. Results obtained from DAF pilot plant operation are summarized as follows:

Parameter Measured	Influent mg/1	Effluent mg/1	% Removal	DAF Float Material
BOD	713 - 4,070	151 - 1,009	13 - 89	2,474 - 20,350 mg/1
COD	2,064 - 5,180	1,489 - 4,094	16 - 60	13,670 - 119,923
Grease & Oil	12.6 - 1,877	2.3 - 207	36 - 95	4,146 - 42,836
TSS	14 - 316	6.5 - 92	2 - 96	8,240 - 58,880
Surfactants	31.7 - 50.8	21.8 - 47.2	11 - 58	107.6 - 1,970
pH	6.3 - 7.3	5.7 - 7.2	-	-

However, during pilot testing, it was found that a means for removing the foaming agent (or surfactant) in AFFF waste was necessary. Otherwise, the foaming problem alone in DAF effluent may rule out discharging it into sewers as concluded by The Pielkenroad Separator Company, Houston, Texas.

. UNOX Process testing was completed. Experimental results indicate that the process would effectively treat the firefighting school wastewater with 1:50 to 1:300 dilution (with sewage). The biomass was acclimatized with a gradual increase in the feeding of firefighting school wastewater and was able to recover from the few system upsets.

. Emryos of eastern oysters (crassostrea virginica) were used for the toxicity bioassay test. Results of the test were expressed as a 48-hour EC_{50} (the concentration of effluent estimated to be effective in preventing normal development of 50% of the exposed embryos). Test results are presented as follows.

Wastewater Source		48-hour EC_{50} ($\% = \frac{\text{Waste vol.}}{\text{Total vol.}}$)
Hampton Rd. Sanit. Dist.	- Raw Sewage	0.4%
Firefight School Waste	- Untreated	12.2%
Firefight School Waste	- Pretreat/ no chemicals	9.0%
Firefight School Waste	- Pretreat/ alum only	5.1%
Firefight School Waste	- Pretreat/ alum/cationic polymer	51. %
Firefight School Waste	- Pretreat/ surefloc/Sear's	4.1%
UNOX Effluent - 100:1 dilution/untreated		2.3%
UNOX Effluent - 50:1 dilution/pretreated		18.8%

It is interesting to note that the data indicated raw sewage was more toxic to oyster larvae than untreated or pretreated AFFF waste during the pilot plant study.

CONCLUSIONS

Through a thorough literature review and knowledge gained via experiments and experience, the following conclusions can be drawn, relative to the treatment and disposal of wastewater containing AFFF generated from either firefighting school exercises or equipment testing on shipboard.

1. Coagulation of the AFFF-laden wastewater with alum and polymer may produce relatively clear supernatant, and floc may be suited to clarification by the dissolved-air flotation (DAF) process. However, this pretreated effluent may not meet sewer discharge criteria in terms of COD, grease and oil, surfactant/foam, and unknown toxicity potential.

2. Activated carbon treatment of the pretreated effluent (by chemical coagulation and DAF) does not provide adequate removal of the dissolved organic content (including AFFF, unburned fuel, and combustion products) to meet receiving stream discharging requirements.

3. Biodegradation capacity of nominal biological systems are very limited especially under overload and/or shock loading conditions.

4. Oxidation of AFFF with chlorine and potassium permanganate is not effective.

5. AFFF related problem areas identified through literature search and past experience are as follows:

a. AFFF is toxic to marine and aquatic life. Laboratory experiments also demonstrated that it would adversely affect biological treatment efficiency. There is no numeric discharge standard for AFFF concentrations in treated effluents at present. The actual treatability level of AFFF wastewaters in a biological treatment system has not been demonstrated or evaluated in the field. Bench scale testing employed pure AFFF instead of actual firefighting school wastewater, except the latest NS, Norfolk, VA study. There are no human health effect standards for AFFF. Establishment of toxicity guidelines or criteria is required.

b. There is no standard analytical method for measuring AFFF concentrations. Fluorocarbon, sulfactant, ethylene glycol, diethylene glycol monobutyl ether and water are the major constituents of 3M Company (FC-206, etc.) and National Foam System (AOW-3&6) products. These constituents all contribute to COD concentration. There is no precise breakdown composition percent for each constituent. Residual fuel and combustion products together with AFFF in firefighting school wastewater further complicates the COD concentration distribution. The biological breakdown of each constituent is yet to be determined. As stated previously, fluorocarbon has high resistance to biodegradation. Thus, biodegradation experiments performed in the past may represent only the biodegradation of constituents other than fluorocarbon. The change in the composition of constituents affecting toxicity and biodegradability needs better understanding. What are the synergistic effects ? Development of a standard analytical method for measurement of AFFF is necessary to predict and monitor AFFF pollution control.

c. There is no satisfactory and effective treatment method for AFFF waste. Physical - chemical process is less sensitive to shock loading, more consistant in performance and process operation can easily be automated. Development of a new effective treatment method should concentrate on the physical-chemical process rather than the biological process. However, water hyacinth may be effective in treating AFFF waste.

d. Firefighting school wastewater and shipboard AFFF waste may contain sea water and/or bilge water (if they are used for making 6% AFFF solution). The high chloride and sulfate concentrations in sea water would adversely affect the biodegradation process. Similarly, heavy metals and other toxic compounds in some bilge water can affect the biodegradation process as well. The use of sea water and bilge water should be eliminated, or future biodegradation and toxicity studies should include these parameters.

e. AFFF concentrate is an expensive material. Treatment of AFFF wastewater is complex. Therefore, reclamation and reuse of AFFF concentrate may prove to be the most cost/effective alternative.

f. When AFFF wastewater is allowed to percolate into the ground what is its impact on ground water? Disposal of floats or skimmings from a DAF system may create a significant effect on air pollution (via incineration), or ground water contamination (via sanitary landfill).

FUTURE WORK PLAN

CEL plans to execute the tasks described below (in their priority order with technical approaches to each task.

1. Development of an AFFF standard analytical method.
   1.1 Conduct chemical composition analysis.
   1.2 Perform analytical methods evaluation.
   1.3 Develop standard analytical procedure.

2. Establish toxicity criteria.
   2.1 Develop toxicity limit for biological waste treatment systems.
   2.2 Define toxicity limit for operational personnel.

3. Development of a cost-effective AFFF treatment alternative.
   3.1 Evaluate state-of-the-art physical-chemical treatment technology.
   3.2 Select best treatment alternative for development.
   3.3 Develop prototype model design criteria.

4. Disposal options.
   4.1 Evaluate cost-effective disposal options.
   4.2 Select disposal options that will best suit the selected treatment alternative.

5. Recovery and reuse.
   5.1 Establish pretreatment requirement.
   5.2 Evaluate concentration technology.
   5.3 Select best technology for development.
   5.4 Evaluate recovery technique in lab and field.

6. Environmental impact assessment.
   6.1 Evaluate air pollution potential.
   6.2 Evaluate soil adsorption and biodegradation capacity.
   6.3 Assess AFFF waste effect on soil micro-organisms and vegetation.
   6.4 Assess ground water contamination potential.

7. Develop new AFFF formula.
   7.1 Investigate AFFF constituent substitute - less toxic, easier to dispose of and more effective firefighting agent.
   7.2 Develop new AFFF formula for testing.
   7.3 Develop AFFF substitute for firefighting system/equipment testing.

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