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**PROCEEDINGS OF THE SECOND  
CONFERENCE ON THE ENVIRONMENTAL  
EFFECTS OF EXPLOSIVES AND  
EXPLOSIONS (13-14 OCTOBER 1976)**

BY GEORGE A. YOUNG

RESEARCH AND TECHNOLOGY DEPARTMENT

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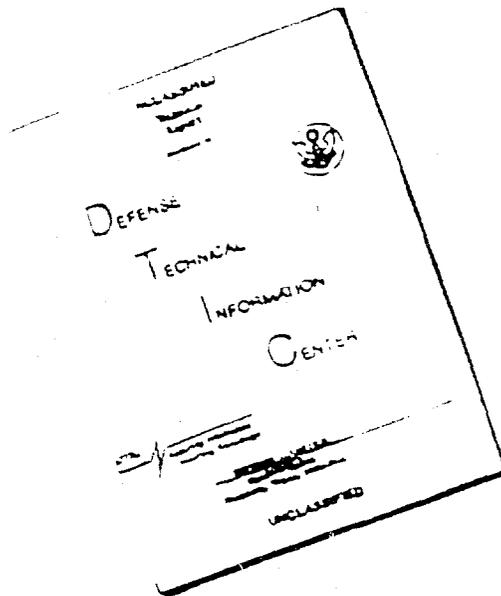
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U.S. ARMY DARCOM RESEARCH AND DEVELOPMENT  
ENVIRONMENTAL QUALITY PROGRAM

Allen E. Hilsmeier  
Edgewood Arsenal

The purpose of the briefing is to acquaint you with DARCOM's R&D Environmental Quality Program. DARCOM is responsible for materiel acquisition for DA which includes manufacture, test, use, disposal and pollution abatement aspects associated with these operations.

Our objective is to comply with the several environmental laws and regulations. With regard to water pollution abatement, DARCOM will use existing off-the-shelf or modified techniques to meet 1977 requirements. Our R&D Program has milestones to meet the 1983 requirement. With regard to air and solids pollution abatement, these requirements are handled on a case-by-case basis and for each site.

Our program is limited at this time to 6.2 funds although our Lead Laboratory charter includes 6.1 and 6.3 program activity. Our milestones call for completion of the 6.2 effort for our on-going work units by 1980. At that time, pilot studies will be done with manufacturing technology funds and the optimum approach will be selected for final incorporation into the operation.

DARCOM's policy and first priority is to eliminate pollution at the source by either recycling, recovering waste products or redesign of the process. If this is not feasible, we will then treat the waste and control the discharge to within environmental standards.

The DARCOM R&D Environmental Quality Program is built around the Lead Laboratory concept. This concept means that technical personnel contribute to management decisions by recommending which work units should be supported, at what level, priorities of work, direction of program, etc.

We have a technical advisory board which is comprised of DARCOM organizations participating in the studies and two outside consultants. It has been most effective in providing guidance to meet DARCOM pollution abatement objectives.

The overall program is organized by priorities and technology thrust areas. The first technology area, elimination, refers to recycle, recover or redesign of the process and is our first priority.

The second area, reduction, refers to physical, chemical or biological treatment to reduce pollution concentrations to acceptable levels.

The third area, control, refers to characterizing and monitoring the effluent to verify the treatment procedures.

Our first priority is munition waste elimination studies. We have two studies in this area.

1. Self-contained selliting - The current sodium sulfite process for purification of TNT creates a multitude of pollutants. The Red Water is currently evaporated to 60% concentration and sold. This is energy consuming and if the market is ever terminated, the army would have a voluminous amount of pollutants to dispose of.

We are studying the use of ammonium sulfite and magnesium sulfite as alternatives to the current process. Both techniques can be at least partially recycled and any residual pollutants can be more easily disposed of. With regard to the  $MgSO_4$  technique, which is the most promising, the  $MgO$  can be recycled. Also, a market exists for residual  $MgSO_3$  as a fertilizer supplement; thus this presents the possibility that at certain production levels, calcination back to the oxide might not be necessary.

2. Isotriol Recovery - This process is not currently in use because the waste products, called isotriol, are too formidable. If abatement techniques can be demonstrated, then this would become a viable alternative to the current production process.

3. Liquid Crystal Test for Brass Cartridge Cases - The current quality control test using mercury is polluting due to vapors and spills. We propose to use liquid crystals on a darkened cartridge case. We heat the case which is immersed in a cholesteric liquid crystal. The temperature gradient across a cracked surface will be displayed by a change in color. This work should be completed this year.

Our second priority is Munition Waste Reduction Studies. We have several studies ongoing in this area.

1. Biodegradation of Nitroglycerine - Bio pilot plant studies at RAAP are for single base propellants and pretreated NG.

An activated sludge system was found to be unstable due to the type of waste composition and loading rates. A rotating bio disc system was found stable with BOD and COD concentrations (400mg/l) being removed at 94 and 85% respectively and therefore acceptable (11 mg/l BOD; 58 mg/l COD).

An aerated waste stabilization (dispersed growth) system is also highly efficient and could be an alternative at RAAP.

2. Fluidized Bed Denitrification - The purpose of this work unit is to compare three systems for biodenitrification of high nitrate wastes  
(a) Fluidized bed (b) Stirred or mixed vessel (c) Fixed bed.

The stirred vessel system is the easiest to maintain, most stable and most efficient to operate but has the disadvantage of a longer detention time (10 fold) for reaction. It is 99.6% efficient in 36 hours vs 3 hours for other two systems. It is also less demanding in energy and less hardware needed.

The work will continue at least for this year because recent laboratory findings show that stability and efficiency can be improved for the fluidized bed by altering its design.

3. Carbon Energy for Bionitrification - This work should provide an economic carbon source for bionitrification processes. It will replace the use of expensive methanol. The use of sewage sludge for a carbon supplement was shown to be unfeasible since 27-30 pounds of sludge is needed to equal one pound of methanol. Waste dairy wheys are now being studied for their applicability.

4. Bioconversion of Waste Discharge - This is a new start for FY77. For the NG and single base propellant waste streams at RAAP, there are many compounds not intended for biotreatment such as TNT, DNT, RDX, HMX, waxes, phenols plasticizers, trinitroresorcinol, etc. They enter the bioplant, nevertheless. We need to know what bioconversion takes place, if any, what intermediates are formed and what are the consequent hazards from the byproducts.

5. Biodegradability of RDX/HMX - Here we want to determine the biodegradation, if any, of RDX and HMX. This is an adjunct to the Navy studies and is an attempt to determine conclusively, that the explosive indeed undergoes complete biodegradation. The presence of tagged C-14 in cellular or metabolic protein, lipid or carbohydrate fractions would indicate that ultimate biodegradation has occurred. Absence of C-14 would of course indicate no or incomplete biodegradation.

6. Toxicant Build-up in Sludge - If we go to the biodegradation system, as it appears we will, for RAAP, we need to know what other pollutants, other than those we are treating, could kill the microorganisms and shut down the system. This is a corollary to the bioconversion work where we determine if new toxicants are created as a result of the bio process. The work will study changes in microbial population and the usual BOD, COD, SS, and TCC.

7. Carbon Regeneration - The purpose of this work is to determine the mechanism whereby TNT and RDX are adsorbed on activated carbon and to apply this understanding to the development of a carbon regeneration process. The development of an effective and economically feasible regeneration process is being pursued by three methods (a) removal of

irreversibly adsorbed derivatives of TNT by chemical reaction (b) Identification of the nature of the surface sites which leads to chemical interaction with TNT and (c) pre-treatment of the charcoal surface or TNT to prevent the formation of the TNT/surface complex.

8. Economic Analysis of Resin vs Carbon- There are conflicting reports, about the technical feasibility and costs associated with the use of resin or carbon or both in series for the treatment of energetic material. The purpose here is to do a paper study of all the claims and determine which technique, i.e., resin or carbon, or combination of techniques would be the optimum system for a munition waste streams.

9. Physical Treatment Systems - Various physical-chemical processes have been studied for the separation of nitro cellulose from wastewater. These include: (a) coagulation filtration (b) pre-coat filtration and (c) convention multimedia filtration. In the first process, we add a cationic polyelectrolyte to water and then filter the waste. In the second technique, pre-coat, the filter is coated with a cationic polyelectrolyte. Unfortunately, neither of these two techniques were effective. Therefore, the third method, multimedia filtration was employed, i.e., mix, flocculate and settle out the solids and filter the supernatant. This technique resulted in a 94 + % turbidity removal and a 46% COD removal. It also has application for the alcohol rectification and metal finishing operations.

10. Foam Separation - The purpose of this work is to remove TNT and its photodecomposition products from aqueous solutions by the addition of surfactants. The TNT is actually precipitated out rather than the expected collection at the gas-liquid interface and forming a foam. We hope to recycle the surfactant but this has not been successful yet.

In order to measure the extent of removal, pink water containing C-14 TNT was used. The radioactive pink water was reacted with the surfactant and the supernatant was counted for residual radioactivity with very little found. Thus, neither TNT nor derivatives remain in solution after reacting with the surfactant.

Our third priority is:

#### 1. Characterization

The purpose of this work is to establish methods of analysis optimizing accuracy, precision and sensitivity for the characterization of explosives, byproducts and other related pollutants in air and wastes effluents generated at AAP's.

We begun our study at Volunteer AAP using their wastewater.

## 2. Instrumentation

We are now field testing a differentiating nitric and sulfuric acid ambient and stack monitor. The sensitivity is in ppm or less. We are also developing a conductivity, organic nitrate and total organic carbon -contoc- monitor for AAP effluents. Last we are seeking new monitoring concepts to meet the very low proposed standards generated by OTSG for TNT, RDX/HMX, DNT, WP, Pink Water.

## 3. Correlation of BOD, COD and TOC

The purpose of this work is twofold (a) Determine the oxygen demand from energetic waste streams and (b) Recommend to EPA the appropriate oxygen demand parameters to be incorporated in effluent guidelines for AAP's.

We have currently analyzed COD values with laboratory samples containing pure energetics. The BOD analysis has encountered difficulties due to the bio-toxic nature of energetic materials. Acclimated seed materials are being developed which will be resistant to the energetic wastes. TOC work is about to start.

## 4. Ecological Surveys

The Army Surgeon General has developed interim environmental standards for several military unique pollutants. But they can't afford to develop standards for all the pollutants which are discharged from AAP's. This work fills in that void. It generally analyzes the ecosystem around the AAP to determine its current condition and after pollution abatement measures are incorporated, the degree and rate of recovery. Aquatic vertebrates and invertebrates are analyzed along with species number, type and diversity.

In summary, DARCOM is involved with solving pollution problems associated with the manufacture and LAP of energetic material. We have not been involved in demilitarization and reclamation of energetic material from unserviceable munitions. We have relied on the Navy for this effort. We seek your advice regarding what role you see us playing, if any, in your demil program.

MUNITION WASTE REDUCTION STUDIES FY 77

PHYSICAL/CHEMICAL

CARBON REGENERATION  
EVALUATION OF POWDERED CARBON  
ECONOMIC ANALYSIS OF RESIN VS CARBON  
PHYSICAL TREATMENT SYSTEMS  
FOAM SEPARATION

OCT 76

SLIDE 1

MUNITION WASTE REDUCTION STUDIES FY 77

BIOLOGICAL

BIODEGRADATION OF NITROGLYCERINE  
FLUIDIZED BED DENITRIFICATION  
CARBON ENERGY FOR BIODENITRIFICATION  
BIOCONVERSION OF WASTE DISCHARGE  
BIODEGRADABILITY OF TAGGED RDX/HMX  
SOIL DEGRADATION OF ENERGETICS  
TOXICANT BUILD-UP IN SLUDGE

OCT 76

SLIDE 2

MUNITION WASTE CONTROL STUDIES FY 77

CHARACTERIZATION OF ENERGETIC MATERIAL  
INSTRUMENTATION DEVELOPMENT  
CORRELATION OF BOD, COD AND TOC  
ECOLOGICAL SURVEYS  
ECOLOGY DATA METHODS  
SYSTEMS ANALYSIS OF MANUFACTURING OPERATIONS

OCT 76

SLIDE 3

MAMMALIAN TOXICOLOGICAL EVALUATION OF WASTEWATERS  
 RESULTING FROM THE MANUFACTURE OF PRIMERS<sup>a/</sup>

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Introduction

Chemical characterization and animal toxicity studies on five desensitized primers, four wastewaters from primer production and one desensitization "Blank" were performed. These samples were:

<u>Number</u>	<u>Name</u>
1	Desensitized Pure Tetrazene
2	Desensitized Pure Lead Styphnate
3	Desensitized Primer Mixture FA 956
4	Desensitized Pure PETN (pentaerythritol tetranitrate)
5	Desensitized Pure Trinitroresorcinol (TNR)
6	Desensitization Blank
7	Tetrazene Wastewater
8	Primer Mixture FA 956 Wastewater
9	Lead Styphnate Wastewater
10	TNR Wastewater

The wastewaters were from Lake City Army Ammunition Plant, Independence, Missouri. Desensitized samples of pure primers were included to help decide whether observed toxicity was due to primer desensitization products or other products in the waste stream such as primer synthesis intermediates. Samples 2, 3, 4, 5, 6, 8, 9 and 10

<sup>a/</sup> This work was supported by the U.S. Army Medical Bioengineering Research and Development Command, Washington, DC, 20314, under Contract No. DAMD-17-74-4073.

were desensitized by adding atomized aluminum, adjusting pH to about 13 with sodium hydroxide pellets, and heating to about 90°C with steam for an hour. Samples 1 and 7 were desensitized by heating to about 90° for 1 hour.

### Chemical Characterization

#### A. Methods

The high-pressure liquid chromatographic conditions were: Instrument-Waters Associates Model 220, Detector-Schoeffel 770 variable wavelength, column 2 ft x 1/8 in.

Porasil AX, Solvent: (a) linear program 100% CH<sub>3</sub>CN to 60% H<sub>2</sub>O in 30 min with detector at 254 nm; and (b) isocratic 3% H<sub>2</sub>O in CH<sub>3</sub>CN with detector at 235 nm.

The gas chromatograph conditions were: Instrument - Bendix 2500 with flame ionization detector, column 6 ft x 1/4 in. with: (a) 3% OV-1 on Gas Chrom Q; and (b) 5% OV-17 on Anakrom ABS, flow rate - 50 cc N<sub>2</sub>/min, column T° to 130°, Injection T° to 200°, Detector T° to 200°.

#### B. Results

High-pressure liquid chromatography and thin-layer chromatography (Table 1) were most useful in characterizing the organic compounds present in the various samples. Complex chromatographic patterns were observed in most cases. Gas chromatography was useful only in assaying for pentaerythritol tetranitrate. The original organic compounds (i.e., primers) were present in trace quantities or entirely absent from Samples 1, 2, 5, 6, 7,

TABLE 1

THIN-LAYER CHROMATOGRAPHY SYSTEMS

<u>Sample No.</u>	<u>Plate</u>	<u>Solvent</u>	<u>Visualization Agent</u>
1	Silica gel F-254	95% Ethanol/conc. $\text{NH}_4\text{OH}$ (4:1)	a,b
2	Silica gel F-254	Acetone saturated with ammonium acetate	a,c
	Cellulose F-254	95% Ethanol/conc. $\text{NH}_4\text{OH}$ (4:1)	a,c
3	Silica gel F-254	Acetone saturated with ammonium acetate	a,c
	Silica gel F-254	Cyclohexane/Acetone (1:1)	a,c
4	Silica gel F-254	Cyclohexane/Acetone (1:1)	a,c
5	Silica gel F-254	Acetone saturated with ammonium acetate	a,c
6	Silica gel F-254	Acetone saturated with ammonium acetate	a,c
7	Silica gel F-254	95% Ethanol/conc. $\text{NH}_4\text{OH}$ (4:1)	a,b
	Silica gel F-254	Methanol chloroform (1:1)	a,b
8	Silica gel F-254	Acetone saturated with ammonium acetate	a,b
9	Silica gel F-254	Acetone saturated with ammonium acetate	a,b
10	Silica gel F-254	Acetone saturated with ammonium acetate	a,b

a/ UV light-254 nm

b/ Ninhydrin spray.

c/ 2% diphenylamine in ethanol plus 360 nm light for 5 min.

8, 9 and 10. PETN was found in the precipitates of Sample 3 (< 0.1% by dry weight) and Sample 4 (12% by dry weight).

The metal content of the lead styphnate and FA 956 mixture samples was determined by atomic absorption and is given in Table 2. Study of the water drainage system of Lake City AAP suggests the solutions of all samples will be diluted by a factor of about 1,000 before leaving the plant boundary.

Three lots of tetrazene wastes (No. 7) were received. The first lot was not used due to a very low dissolved solids content. When toxicity data indicated the second lot of tetrazene wastewater to have significant toxicity, the third lot was fractionated by silica gel column chromatography to give purified samples for toxicity tests. Two compounds were isolated in sufficient concentration for toxicity tests. Infrared spectra indicated one of the compounds (Fraction 47-55L) contains an azide group while the other (Fraction 57-63L) did not, however, both were toxic to animals. One of the minor fractionated components was found to be explosive when scratched with a metal spatula.

#### Toxicity Testing

##### A. Methods

The various materials were neutralized with acetic acid or sodium hydroxide and evaporated to about 100 mg/ml. The acute toxicity of these extracts to laboratory animals was then determined using standard methods.

TABLE 2

METAL CONTENT

<u>Metal</u>	<u>Sample 2</u>		<u>Sample 3</u>	
	<u>% in Supernatant</u>	<u>% in Precipitate</u>	<u>% in Supernatant</u>	<u>% in Precipitate</u>
Lead	0.0049	59.4	0.003	9.3
Barium	0.00002	< 0.0096	0.024	0.43
Antimony	< 0.00025	0.04	0.003	9.45
Aluminum	0.9	3.35	1.0	24.8

	<u>Sample 8</u>		<u>Sample 9</u>
	<u>% in Supernatant</u>	<u>% in Precipitate</u>	<u>% in Homogenous Sample</u>
Lead	0.0025	4.4	0.0075
Barium	0.0007	1.55	0.0002
Antimony	0.003	0.48	0.0005
Aluminum	0.08	51.2	0.09

The primary skin and eye irritation were determined with the Draize procedure<sup>1/</sup> using six white New Zealand rabbits per compound. The lethality after a single oral dose was determined in male and female rats (Albino Rats, CD Strain) and male mice (Albino Swiss Mice, CD-1 Strain, Charles River Laboratories). Animals were observed for 14 days and the median lethal dose (LD<sub>50</sub>) calculated, on the basis of solids content, by the probit method. The maximum dose used was 5 g/kg (50 ml/kg), since larger volumes might cause stomach rupture.

### B. Results

Results of the irritation tests are shown in Table 3. Desensitized pure tetrazene was mildly irritating to skin; all other samples non-irritating to skin and eyes.

Median lethal doses of the various materials are shown in Table 4. The desensitized pure tetrazene and primer mixture FA 956 were moderately toxic to rats, but nontoxic to mice at the highest dose tested. All animals died either on the first day after dosing, with no remarkable symptoms, or survived the entire holding period. There was insufficient desensitized tetrazene wastewater solids from the first lot to permit any testing. The second lot yielded enough for an estimated LD<sub>50</sub> in female rats similar to that of the pure tetrazene. However, the third lot was an order of magnitude more toxic, with LD<sub>50</sub>'s ranging from 0.3 to 0.8 g/kg in rats and mice. Differences between the sexes of mice were not significant, but the preparation was more toxic to female rats than to male rats or mice. This presumably reflects known metabolic differences between the sexes in laboratory rats.

TABLE 3

PRIMARY SKIN AND EYE IRRITATION IN NEW ZEALAND WHITE RABBITS TREATED WITH  
DESENSITIZED PRIMER COMPOUNDS OR EXTRACTS OF PRIMER WASTEWATERS

<u>Number</u>	<u>Compound</u>		<u>Irritation Scores</u>	
	<u>Name</u>		<u>Skin<sup>a/</sup></u>	<u>Eye</u>
1	Desensitized Pure Tetrazene		0.25	negative
2	Desensitized Pure Lead Styphnate		0.16	negative
3	Desensitized Primer Mixture FA 956		0.16	negative
4	Desensitized Pure PETN		0.00	negative
5	Desensitized Pure Trinitro- resorcinol (TNR)		0.00	negative
6	Desensitization Blank		0.08	negative.
7	Tetrazene Wastewater		0.00	negative
8	Primer Mixture FA 956 Wastewater		0.00	negative
9	Lead Styphnate Wastewater		0.12	negative
10	TNR Wastewater		0.08	negative

<sup>a/</sup> > 0.2, mild; > 2.5, moderate; > 5.0 severe.

TABLE 4

ACUTE ORAL LD<sub>50</sub>'S IN RATS AND MICE OF DESSENSITIZED PRIME  
COMPOUNDS OR EXTRACTS OF PRIMER WASTEWATERS

Number	Name	Rat (g solids/kg body weight)		Mouse (g solids/kg body weight)	
		Male	Female	Male	Female
1	Desensitized Pure Tetracene	3.40 (3.28-3.55) <sup>a/</sup>	3.30 (3.12-3.44)	> 5.0	b/ ND
2	Desensitized Pure Lead Styphmate	> 5.0	> 5.0	> 5.0	ND
3	Desensitized Primer Mixture FA 956	4.84 (4.62-5.19)	3.95 (3.85-4.04)	> 5.0	ND
4	Desensitized Pure FHTM	> 5.0	> 5.0	> 5.0	ND
5	Desensitized Pure Triafltro- resorcinol (TMR)	> 5.0	> 5.0	> 5.0	ND
6	Desensitization Blank	> 5.0	> 5.0	> 5.0	ND
7	Tetracene Wastewater, Lot 2 Lot 3	ND	est. 3.5	ND	ND
8	Primer Mixture FA 956 Wastewater	0.622 (0.568-0.664)	0.311 (0.262-0.371)	0.711 (0.589-0.845)	0.805 (0.705-0.975)
9	Lead Styphmate Wastewater	> 5.0	> 5.0	> 5.0	ND
10	TMR Wastewater	> 5.0	> 5.0	> 5.0	ND

a/ 95% Confidence Limits.

b/ Not determined.

Each of two fractions of the tetrazene wastewater was given to four mice at a dose of 0.5 g/kg; the same dose of the unfractionated preparation killed none of the 10 mice dosed. Two mice given Fraction 47-55L and one given Fraction 57-63L died within an hour of dosing; the others survived. From this and the abundance of the fractions it is probable that these two individual components represent much of the toxicity of the tetrazene wastewater.

Summary

Except for the tetrazene wastewater (discussed below), all priming compounds had little acute toxicity. However, lead accumulates in animals and many repeated small doses are as toxic as a few large doses. The only other inherently toxic component is antimony, an arsenic-like toxic metal. It is probable that the observed lethal effects of the primer mixture FA 956 were due solely to its lead and antimony content.

The desensitized tetrazene itself has moderate toxicity. However, certain lots of the tetrazene wastewater (Lot 3) are significantly toxic. This variability is unexplained, but is presumably due to qualitative or quantitative variation in the chemical desensitized wastewater.

REFERENCE

1. Draize, J. H., Dermal Toxicity, pp. 46-59 in Appraisal of the Safety of Chemicals in Foods, Drugs and Cosmetics, Association of Food and Drug Officials of the United States, Washington, D.C. (1955).

## STUDIES ON BACTERIAL DEGRADATION OF ORDNANCE WASTES\*

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Janet Coffey, and John Blecka

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Biodegradation of three Naval ordnance chemicals was attempted under laboratory conditions using a strain of Pseudomonas aeruginosa isolated from TNT waste ponds. Partial degradation of picric acid and Otto fuel II was achieved under anaerobic conditions; negative results were obtained with Noset A. The results provide evidence that these materials are very likely to be persistent environmental contaminants.

## INTRODUCTION

Recent passage of the Toxic Substances Control Act of 1976 (1) as well as Navy policies regarding environmental protection and enhancement (2) require the Navy to be familiar with the environmental toxicology of chemicals currently in use, as well as newly developed or adopted materials about which little toxicological information is available. One primary area of investigation regarding organic chemicals is their degree of susceptibility to biodegradation (by microorganisms) under environmental conditions. Three Naval materials under study in our laboratory have been the ordnance chemical picric acid (2,4,6-trinitrophenol), and the propellants Otto fuel II and Noset A. The major constituent of Otto fuel II is propylene glycol dinitrate (PGDN) and of Noset A is triethylene glycol dinitrate (TGDN).

Concern over picric acid, PGDN and TGDN as environmental pollutants is warranted considering reports in the literature concerning the toxic effects of these and similar organic nitrogen compounds. Breakdown products very similar to picric acid obtained from 2,4,6-trinitrotoluene (TNT) were shown in our laboratory to be mutagenic agents by means of the Ames mutagenic assay (3). PGDN and TGDN have been shown to cause methemoglobinemia in mammals. Of these two compounds PGDN has been reported to be two to five times more lethal in rats than is TGDN (4).

The molecular structure of picric acid suggested that biodegradation of picric acid would most likely be by reduction of one of the nitro groups forming 2,4-dinitrophenol or 2,6-dinitrophenol. Biodegradation of PGDN and TGDN was expected to occur by reduction of nitrate groups and result in the formation of propylene glycol and triethylene glycol. These compounds could then readily serve as substrates for many bacteria and be metabolized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The microbial reduction of nitro groups is an anaerobic process involving the enzyme systems nitrate and nitrite reductase (5). Therefore attempts to biodegrade these compounds were carried out employing anaerobic conditions.

\* This work was sponsored by the Naval Medical Research and Development Command, Code 474.

## METHODS AND MATERIALS

The bacterial species used in this investigation has been identified in our laboratory as Pseudomonas aeruginosa (6). Prior to the use of this organism, we were unable to isolate picric acid utilizers from activated sludge, garden soil, compost, and estuarine sediments. Experiments were conducted by incubation of the bacteria in a mineral salts medium containing the ordnance chemicals in solution.

Medium: The medium used in all investigations contained 0.05%  $K_2HPO_4$ , 0.02%  $MgSO_4 \cdot 7H_2O$  (7) and a 0.1% (v/v) nitrogen free trace element mix (8) all dissolved in distilled water. In order to degrade picric acid we found it necessary to supplement the medium with 0.1% yeast extract (Difco). Addition of yeast extract to the medium was continued in experiments with Otto fuel and Noset A. The initial concentration of picric acid in the medium was 0.1% whereas the initial concentration of Otto fuel II and Noset A was 0.5%. Undissolved components of the propellants (such as the stabilizer, N-dibutyl sebacate) were removed from media by filtration through a 0.5 cm bed of celite (Johns-Manville Co.). All media were autoclaved for 15 min at 121 C. Before inoculation, the pH of the media was adjusted to 6.5 by dropwise addition of 12 N HCL.

Incubation: Attempts to degrade picric acid, Otto fuel and Noset A were carried out in a 4 liter Virtis Laboratory fermentor at ambient temperature (25°C) and agitation of 200 rpm. Initial media volume was 3 liters. Oxygen in the medium was depleted by continuous bubbling of oil-free argon through the fermentor jar. Pure cultures of Pseudomonas aeruginosa were grown out in nutrient broth for 24 hours, and then removed from the medium by centrifugation. The cells were resuspended in 25 ml basal salt medium and added to the fermentor. Picric acid, Otto fuel and Noset A media were each incubated for 30 days after inoculation with Pseudomonas aeruginosa. A viable cell count employing the spread plate technique was conducted during each experiment to monitor the growth of the bacteria.

Analysis: Thin layer chromatography (TLC) coupled with a Photovolt photo-densitometer was used to determine depletion of the organic nitrogen compounds and presence of degradation products. Quantitation of these compounds was accomplished by comparison with known standards. Samples were periodically taken from the fermentor and filtered through a Millipore filter to remove microbial growth, before extraction and spotting on TLC plates.

Picric acid concentration was determined by extracting 10 ml of medium with 2 ml methyl ethyl ketone saturated with NaCl. Four microliters of the extracted solution were spotted on TLC plates (Quantum Industries) and migrated 10 cm in 50:50:1 benzene-acetone-glacial acetic acid. Plates were scanned photodensitometrically using a UV lamp to quantitate the picric acid.

To visualize degradation products, 10 ml medium were extracted with 5 ml of methyl ethyl ketone. Five microliters of the extract were spotted on Silica gel G plates (ANALTECH) and migrated three times with intermittent drying, a distance of 10 cm in 19:1 benzene-acetone.

In the Otto fuel and Noset A test systems the media were analyzed for depletion of PGDN and TGDN. These media were extracted with ethyl acetate, spotted on silica gel G plates and migrated twice, with intermittent drying, a distance of 10 cm in 3:1 hexane-benzene. Visualization of PGDN and TGDN was accomplished by

spraying the plates with a 1% solution of diphenyl amine in ethanol and developing under a UV lamp for 1 minute. Plates were scanned photodensitometrically to quantitate depletion of dinitrates.

In all analyses, determinations were carried out in triplicate, and the results were averaged.

## RESULTS AND DISCUSSION

The optimum pH for degradation of organic nitrogen compounds by a soil bacterium has been shown to range from 6.0 to 7.0 (7). The initial pH in each of our test systems was 6.5. After 0 days incubation of picric acid and Otto fuel, the pH steadily dropped to 6.3 and 6.14, respectively. However, the pH in the Noset A incubation system rose to 8.5. The reason for this increase in pH is unknown at the present time. Growth curve analyses of the test systems showed a 1 to 2 log increase in cells during the first 24 hr incubation, after which counts remained fairly constant throughout the 30 day incubation period. Cells were viable in each test system at the level of  $10^7$  to  $10^8$  cells/ml.

In the picric acid system, biodegradation was evidenced by a color change in the medium from yellow to brown. Under TLC analysis, the  $R_f$  value of picric acid was 0.17, while analysis of the degraded solution showed the presence of a compound with an  $R_f$  value of 0.47. We tentatively have identified this compound as picramic acid (4-amino-2,6-dinitrophenol). Quantitative assay of this process is illustrated in Fig. 1, which shows the degradation product appearing after approximately 11 days incubation. An anomalous decrease in concentration of picric acid between day 0 to day 1 may have been due to adsorption of picric acid to the fermentor, or to the bacterial cells which were filtered from the medium prior to analysis. A 25% loss in picric acid occurred over the 30 day incubation period. The amount of picramic acid detected in the medium represented only a 2% conversion of the picric acid to picramic acid. The loss in picric acid occurred either through complete mineralization, or by incorporation of picric acid into the bacterial cells which were removed from the medium before analysis. Further analysis is required to determine how much picric acid may be incorporated by a given bacterial cell biomass.

In the Otto fuel system, Figure 2, the apparent increase in the concentration of PGDN is due to the presence of di-n-butyl sebacate in the test medium. Initial samples, up to 12 days, do not represent the actual concentration of PGDN in the medium since some of this compound was dissolved in sebacate. When samples were filtered through a Millipore filter the sebacate containing PGDN was removed along with the bacteria. After 12 days incubation, the di-n-butyl-sebacate was microbially degraded to free the PGDN.

From day 12 to day 26 PGDN decreased in the medium by 80%. We were unable to demonstrate the presence of breakdown products, such as propylene glycol, in this test system. Considering that propylene glycol is a readily usable substrate for many microorganisms, it is possible that this compound if present, was depleted to undetectable quantities by the bacteria. A bacteria-free control system demonstrated less than 0.016% loss by evaporation over 30 day incubation period. Therefore the possibility of loss of PGDN by vaporization was ruled out. As with picric acid, it is not known how much PGDN was lost from the system by removal of the bacterial cells prior to analysis.

Following day 26, analysis of samples on days 28 and 30 show a consecutive increase of approximately 50 µg/ml in the concentration of PGDN. Whether this secondary increase is due to physical or biological parameters cannot be known without further research.

In the Noxet A system, which had incubation conditions identical with those of Otto fuel and picric acid, we were unable to detect any depletion of the TGDN. Further experimentation with longer incubation periods and other bacterial species will be required to ascertain whether TGDN is biodegradable.

#### CONCLUSIONS

Prior investigations in this area have been extremely limited. It is generally conceded that extended acclimation periods are required before microbial utilization of organic nitrogen compounds will occur, and as yet, no one has reported complete metabolism of these types of molecules. Considering these facts, and the results obtained in this investigation, detoxification by microorganisms should not be considered as a practical solution to the problem of eliminating waste effluents containing organic nitrogen compounds.

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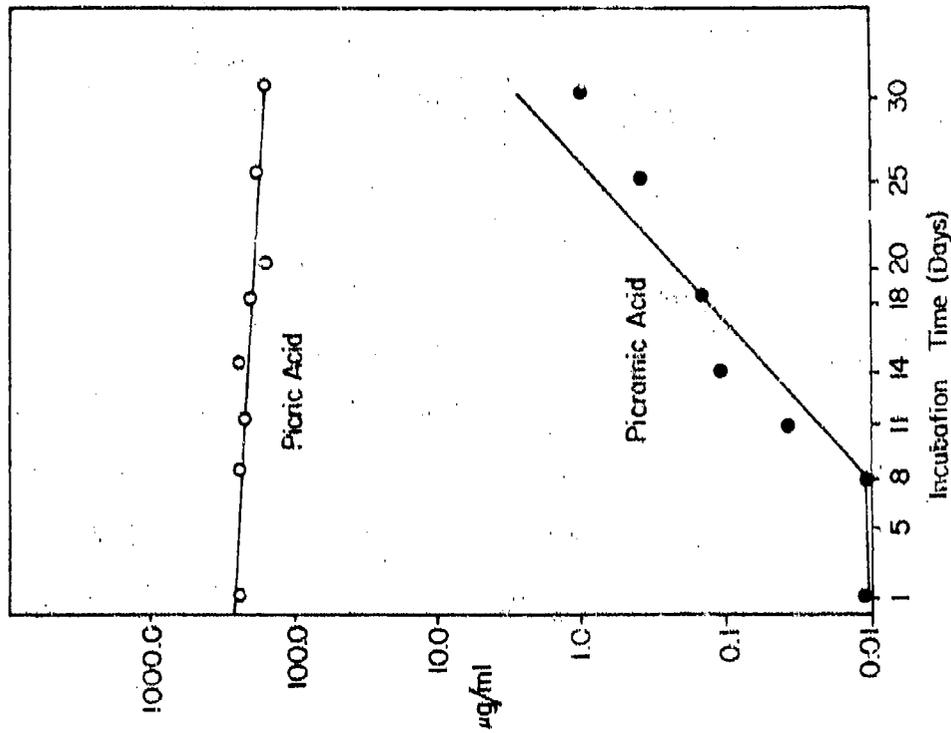


FIG. 1 MICROBIAL CONVERSION OF PICRIC ACID TO PICRAMIC ACID IN BASAL SALTS-YEAST EXTRACT MEDIUM

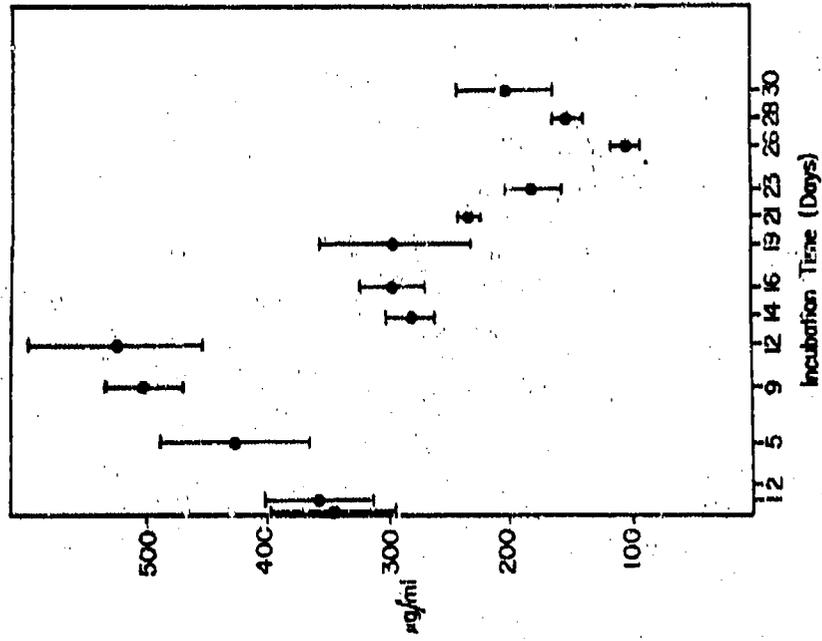


FIG. 2 MICROBIAL DEPLETION OF PROPYLENE GLYCOL DINITRATE IN BASAL SALTS-YEAST EXTRACT MEDIUM

## BIODEGRADATION OF TNT : PROGRESS REPORT

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Currently under investigation at NSWC is a feasibility study of using microorganisms to convert waste TNT and other nitroaromatic compounds into molecular species that can be completely metabolized to CO<sub>2</sub>, H<sub>2</sub>O, and NH<sub>3</sub> or into biologically altered compounds that have no adverse effects on the ecology. The extraction of 2-amino and 4-amino dinitrotoluenes as well as nitrite and nitrate ions from the stream waters near the bomb loading facility at NAD, McAlester, indicated the possibility of using biological as well as photolytic means to degrade dissolved TNT in waste water.

The NSWC experiments consisted of (a) batch studies, (b) continuous culture studies, (c) Carbon-14 experiments, and (d) the design and operation of a pilot scale ditch facility.

The results of several large scale batch runs indicated that TNT supplemented with corn steep nutrient could be effectively biodegraded utilizing the activated sludge organisms acquired from a near-by sewage disposal plant. The rate of TNT biodegradation was found to be identical to the rate obtained with a pure pseudomonas bacterial strain isolated from the contaminated TNT streams at NAD, McAlester.

The 2-amino and 4-amino dinitrotoluenes and the 2,4-diamino and 2,6-diamino nitrotoluenes formed in the TNT biodegradation process were also found to be biodegradable, although at a slower rate than TNT, so that high levels of these materials would not build-up in the environment due to the discharge of effluent containing an acceptable level of these intermediates. The mono-amines degrade to the diamines. The 2-amine degrades to both the 2,4 diamine and the 2,6 diamine isomers, while the 4-amine degrades to only the 2,4 diamine isomer. An evaluation of the toxicity and carcinogenicity of these amine products is currently under investigation. Figure 1 represents the degradation products of TNT which have been identified, isolated, and analyzed by a combination of thin layer and vapor phase chromatography.

Batch studies of TNT run aerobically and anaerobically over a 24 hr. period indicated that TNT is degraded to a greater extent in an aerobic system (99.5%) than in an anaerobic system (69%). The percent of amine products formed in the anaerobic system was almost three times that formed in the aerobic system.

Batch runs were also used to determine the effects of temperature and pH on TNT biodegradation. The resulting data showed that within the 5°-53°C temperature range, the TNT was 95-99% biodegraded with the usual distribution of amine products formed.

The results of the pH study showed that TNT was only 45% degraded in the pH range of 6.0-6.2, while in the ranges of 7.4-7.8 and 8.7-9.1, the % TNT biodegraded was 99% and 97% respectively. The 8.7-9.1 region cannot be considered useful for practical TNT degradation due to the noticeable build-up of amine products (~75%).

TNB and RDX were also tested for their biodegradability using the same batch system as that used for TNT. TNB was ~99.5% biodegradable after a 48 hr. incubation period. The only product identified by GC/MS was 3,5-dinitroaniline which was found in about a 2.5% yield. RDX was not biodegradable, although it did not inhibit the degradation of TNT in an RDX-TNT mixture.

Experiments were also conducted in a continuous culture laboratory scale activated sludge plant. Using this technique, we were able to study the relatively long term effects (3-4wks) of TNT degradation on a biological system as well as providing data for the pilot scale biodegradation facility. Experiments were designed to determine (a) the effect of various nutrient concentrations on TNT biodegradation and amine product formation, (b) the effect of two nutrients ( e.g. Black Strap Molasses, Corn Steep Liquor), and (c) the long term effects of anaerobic conditions on TNT degradation.

Optimum results for TNT degradation were achieved with a rapidly growing colony of bacteria. This was accomplished by adding enough supplemental nutrient so that the daily increase in the weight of the floc averaged 10-20%. A zero or low order floc growth rate reduced the efficiency of the biodegradation process and lead to increased concentrations of the aminodinitrotoluenes.

Nutrient substitution of BSM for CSL did not have a noticeable effect on either the rate of TNT degradation nor on the formation of the aminodinitrotoluenes which was comparable for both systems.

The results of relatively long term anaerobic conditions on TNT degradation in the CCP agreed with the data obtained from the batch studies, that of greater amine formation under anaerobic conditions. Varying the level of dissolved oxygen in the CCP had no significant effect on process efficiency provided that aerobic conditions were maintained. However, if the dissolved oxygen level decreased below 1ppm, the amount of aminodinitrotoluenes produced increased until under completely anaerobic conditions essentially all the degraded TNT was converted to these and other amine products.

Biodegradation experiments were also carried out using C-14 labelled TNT in order to determine the distribution of the C-14 activity and also to detect if C-14 CO<sub>2</sub> was being formed which would indicate aromatic ring cleavage.

The C-14 TNT was used in several batch-type biodegradation experiments in which all the materials, TNT, activated sludge organisms and corn steep nutrient were initially mixed together and aerated. Water and aqueous potassium hydroxide traps were provided to capture any volatile compounds and CO<sub>2</sub> which were then analyzed by scintillation counting techniques for C-14 activity.

Very little C-14 CO<sub>2</sub> or other volatile species were produced (< 0.5%) in the biological reaction after a 72 hr. incubation period. The benzene extract of the supernatant yielded the 2- and 4-aminodinitrotoluenes. These isomers accounted for the total activity found in the benzene extract. Approximately 40% of the activity remained in the aqueous phase after benzene extraction. This phase contained small quantities of extremely polar and/or high molecular weight material which has not yet been identified. No evidence was found in any of the C-14 experiments which indicated aromatic ring cleavage.

The batch, continuous culture, and C-14 experiments were conducted in support of the pilot plant facility in continuous operation at NSWC since November of 1973. This facility (Figure 2) has a 3,000 gal. capacity and was designed to biodegrade 0.5 lbs. of aqueous TNT per day. Dissolved TNT and nutrient are fed into the ditch at a rate of 2 gal./min. The cage rotor provides a dissolved oxygen content of 3-4 ppm, and moves the liquid and floc in the ditch at a rate of 1-foot per second. A 350 gal. settling tank is used to return the bacterial floc to the ditch. Data from a typical run are summarized in Figure 3.

1. 4-AMINO-2, 6-DINITROTOLUENE.
2. 2-AMINO-4, 6-DINITROTOLUENE.
3. 2, 4-DIAMINO-6-DINITROTOLUENE.
4. 2, 6-DIAMINO-4-NITROTOLUENE.
5. NITRITE ION.
6. NITRATE ION.
7. 3, 3', 5, 5'-TETRANITRO-4, 4'-DIMETHYLAZOXYBENZENE.
8. 3, 3', 5, 5'-TETRANITRO-2, 2'-DIMETHYLAZOXYBENZENE.
9. 3, 3', 5, 5'-TETRANITRO-2, 4'-NNO-DIMETHYLAZOXYBENZENE.
10. 3, 3', 5, 5'-TETRANITRO-2, 4'-NNO-DIMETHYLAZOXYBENZENE.
11. 4, 6-DINITRO-2-HYDROXYLAMINOTOLUENE.
12. 2, 6-DINITRO-4-HYDROXYLAMINOTOLUENE.

FIG. 1 INTERMEDIATE PRODUCTS OF  $\alpha$ -TNT BIODEGRADATION

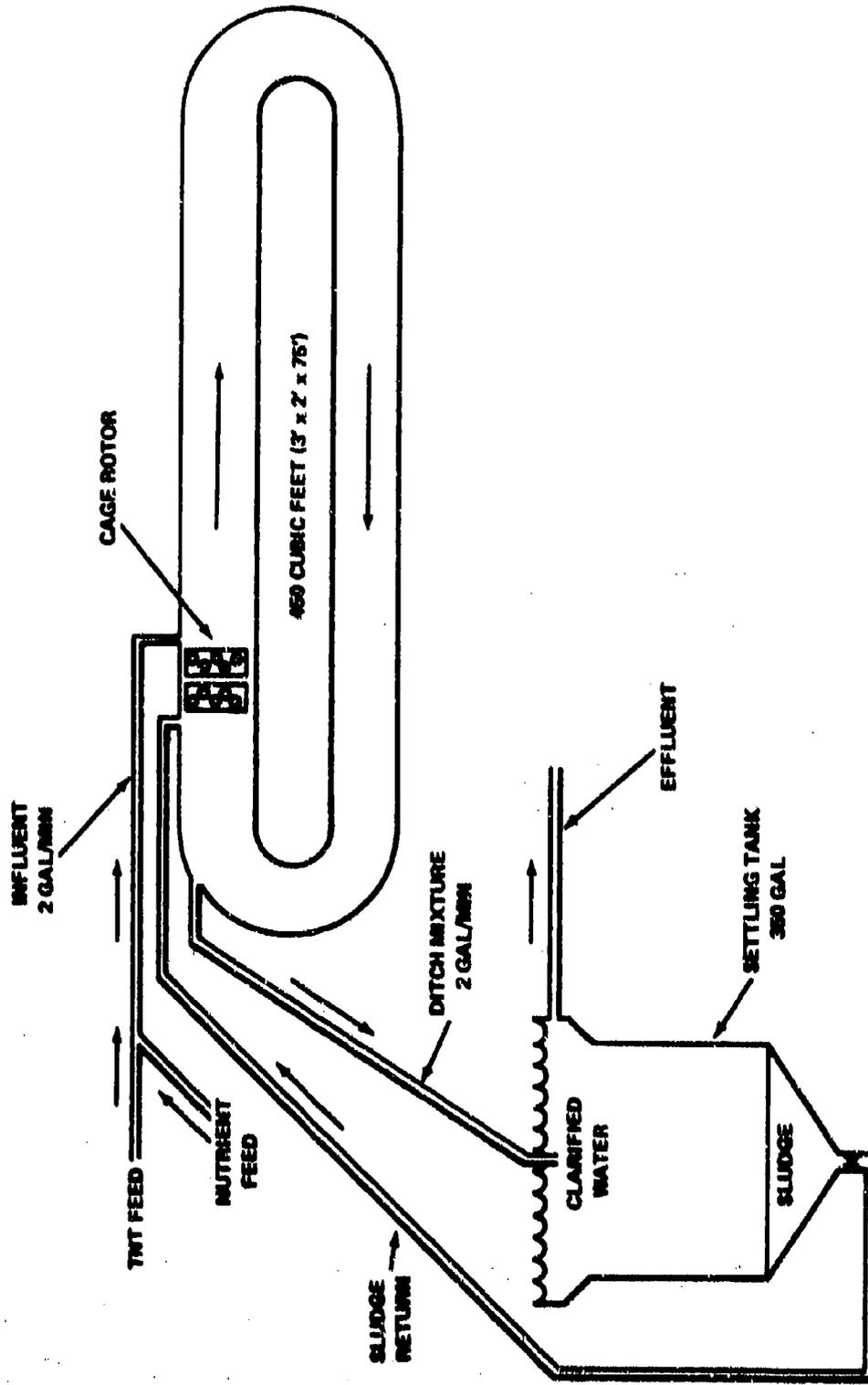


FIG. 2 RESEARCH PILOT PLANT FOR TREATMENT OF TNT WASTE WATER

**TOTAL TIME OF RUN 60 DAYS**

**PROCESS PARAMETERS**

**TNT FEED 173 gms / 24 hrs 15 ppm**

**RATIO OF NUTRIENT FEED TO TNT FEED ~ 100/1**

**FLOC CONCENTRATION 5-6 gms/liter**

**DITCH VOLUME 3000 gal**

**FEED RATE 2 gal/min**

**pH 7-8**

**DISSOLVED OXYGEN 7-8 ppm**

**PROCESS EFFLUENT**

**TNT NOT BIODEGRADED 0.09 gms/24 hrs 0.008 ppm**

**AMINODINITROTOLUENES 15.3 gms/24 hrs 1.35 ppm**

**SUSPENDED SOLIDS 570 gms/24 hrs ~ 50 ppm**

**EFFLUENT RATE 2 gal/min**

**% TNT BIODEGRADED 99.9%**

**% AMINE PRODUCTS FORMED 8.7%**

**FIG. 3 TNT BIODEGRADATION DITCH FACILITY**

## PHOTOLYTIC DECOMPOSITION OF RDX IN AQUEOUS SOLUTION

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### INTRODUCTION

The problems of decontaminating waste water containing dissolved RDX are different than those concerned with water contaminated with TNT. For example, RDX is not biodegradable as is TNT and RDX is not adsorbed as readily as TNT on charcoal or polymeric resins. This paper presents the results to date of on-going studies to show that photolysis is an attractive approach to treatment of RDX waste water.

### FLOW PHOTOLYSIS SYSTEM

Cursory experiments indicated that RDX in aqueous solution was rapidly destroyed by photolytic action when exposed to the full spectral output from a medium pressure mercury lamp (220 nm - 1367 nm). It was also found that if the spectral input to the RDX solution was limited to wavelengths greater than 280 nm by a pyrex filter the rate of RDX disappearance was greatly reduced.

To take advantage of this rapid destruction of RDX a laminar flow tray apparatus was designed and fabricated. Figure 1 shows a schematic diagram of the apparatus. A reverse water fall concept was used to achieve laminar flow characteristics. The solution entered at the bottom of the vertical section, flowed up into the flat tray section,

across the tray and exited through the three variable height drain tubes. The nominal dimensions of the tray section are 30 cm long, 14 cm wide and 4 cm deep. A 1200 watt medium pressure mercury lamp with an active length of 30 cm was centrally located immediately above the tray along its long dimension. A reflector cover the entire tray to maximize the light impinging on the RDX solution. Table 1 presents the results of runs made at several flow rates and solution depths of 0.5 cm and 1.0 cm.

TABLE 1  
RDX Removal by Photolysis in the Laminar Flow Tray

solution depth, cm	% RDX removed at various flow rates				initial RDX conc., ppm
	1000	1500	2000	2500	
0.5	99.9	99.8	98.7	96.9	22
1.0	99.9	99.9	98.6	96.9	39

The results in Table 1 show that RDX is rapidly destroyed by photolysis in a flow system. Efforts are underway to optimize the photolysis geometry to increase the efficiency of RDX removal.

#### PRODUCT ANALYSIS

Work on the flow photolysis system has been complemented by efforts to determine the photodecomposition products of RDX in aqueous solution and by attempts to understand the primary photochemical steps involved. These studies have been conducted using a static photolysis geometry.

Gas chromatographic analysis of a benzene extract of a photolysed solution show other peaks in addition to that due to residual RDX. The number and relative intensities of these peaks depend upon the extent of

photolysis, quality of light (i.e., with and without a pyrex filter) and the pH of the solution during photolysis. The compounds responsible for these peaks are all photo-unstable since they become undetectable when the RDX becomes undetectable.

Exposure of the RDX solution to the full spectral output of the lamp produces the largest number of the additional peaks. As many as seven peaks with retention times ( $R_t$ ) ranging from 0.2 min to 2.5 min ( $R_t = 3.5$  min for RDX) are observed. The presence of these peaks are independent of pH. In contrast, the peak at  $R_t = 2.5$  min is the only predominate one when the spectral input is limited to wavelengths greater than 280 nm and is present only when the pH of the solution is acidic.

The pH of RDX solutions made up in distilled water falls to values of 3.5 - 4.0 during photolysis with either unfiltered or pyrex filtered light. When the solutions are made up in tap water the pH remains near neutral. This buffering action is presumably due to the ions in tap water.

The compound giving the peak at  $R_t = 2.5$  min has been identified via gas chromatograph/mass spectrometric techniques as 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (mono-nitroso analog of RDX). Mass spectra of the other peaks imply similar type compounds but positive identifications have been hampered by the small amounts present and the lack of model compounds.

The absolute amounts of these compounds produced in the flow photolysis system is estimated to be very low. For example, at a flow rate of 2500 ml/min and a depth of 1.0 cm the amount of the mono-nitroso compound (it gives the most intense peak of all the compounds) is estimated to be less

than 0.5 ppm. This is less than 1.3 % of the initial RDX concentration.

Varying amounts of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{CH}_2\text{O}$  have been found as end products. Table 2 presents values of the mole ratios of these products to the moles of RDX photodecomposed by unfiltered light ( $\lambda > 220 \text{ nm}$ ) and pyrex filtered light ( $\lambda > 280 \text{ nm}$ ) at pH 7.

TABLE 2  
Mole Ratios of Products to RDX Photolyzed

Ratio $\lambda$	$\frac{\text{NO}_3^-}{\text{RDX}}$	$\frac{\text{NO}_2^-}{\text{RDX}}$	$\frac{\text{CH}_2\text{O}}{\text{RDX}}$
$>220 \text{ nm}$	0.01	2.4	0.8
$>280 \text{ nm}$	0.7	2.0	0.7

Although further work is required for a more complete product analysis the data acquired to date permit some speculation as to the primary photochemical steps taking place.

It is postulated that at wavelengths greater than 280 nm the primary photochemical step is the homolytic cleavage of the nitramine bond to give the  $\text{asayl}$  radical and  $\text{NO}_2$ . The interaction of  $\text{NO}_2$  and water provides a source of the observed nitrate and nitrite ions. Under acidic conditions (photolysis in distilled water solutions causes decrease in pH) the nitrite ion produces NO which can add to the  $\text{asayl}$  radical to give the observed mono-nitroso compound. When the photolysis is carried out in tap water where the pH remains near neutral the mono-nitroso compound is not observed since NO cannot be formed.

When the incident wavelengths extend down to 220 nm it is postulated that the predominant primary photochemical step is the cleavage of the

N-O bond of the nitro group to give the mono-nitroso compound directly. Thus, its formation would be independent of pH and this is what is observed. Additionally the mono-nitroso compound can undergo further N-O bond cleavage to give the di-nitroso analog of RDX. It is attractive to speculate that the additional peaks observed in the benzene extract are due to this and other similar type compounds. The very small amounts of nitrate ion found compared to that found for wavelengths greater than 280 nm lend support to the above hypothesis.

The presence of formaldehyde as a final product indicates that the ring is broken. The paths from the primary photochemical steps to final products is undoubtedly complex and is yet to be resolved. The formation of nitrite ion as nitrous acid must occur at some point since the pH of unbuffered solutions decrease asymptotically to approximately 4.

#### FUTURE EFFORT

In summary, the use of photolysis to degrade RDX in aqueous solution appears to be very promising. Additional work, both in terms of determining the most efficient photolysis geometry and completing the product analysis is required. Improvement on the present knowledge of the photochemistry is also desirable in order to be able to predict the effects of other solutes (e.g., TNT, added  $H_2O_2$ ,  $O_3$ ) on the photolysis rate of RDX. Work is in progress in these areas and results will be presented in future reports.

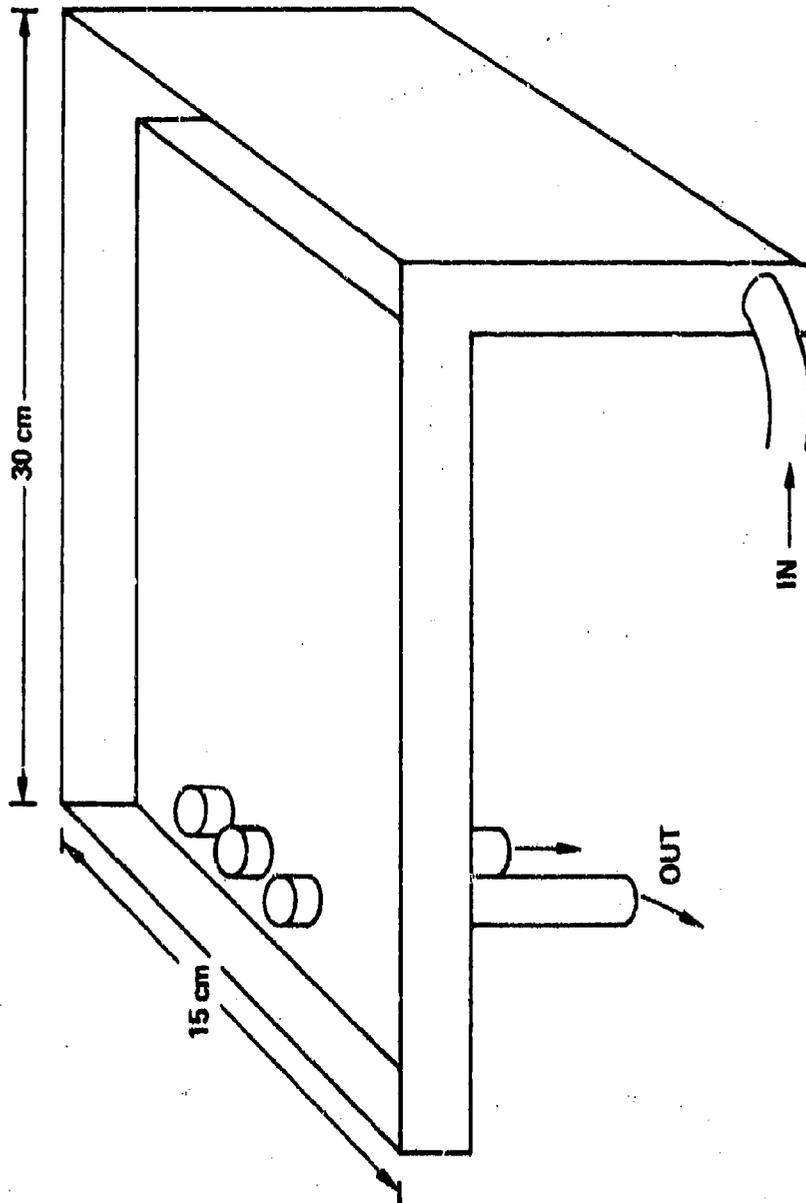


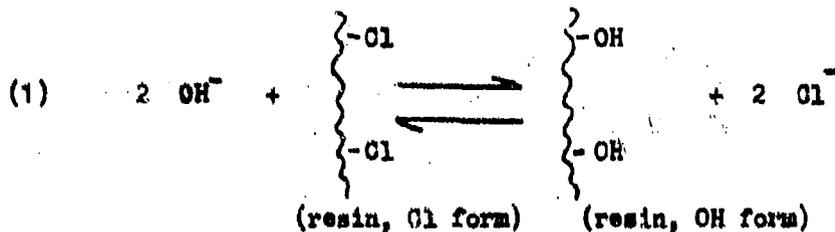
FIG. 1 LAMENAR FLOW TRAY

## ALKALINE HYDROLYSIS OF RDX ON ION-EXCHANGE RESINS, LABORATORY STUDY

John C. Hoffsommer, Donald A. Kubose, and Donald J. Glover

Although the basic hydrolysis of RDX in water produces a number of products including  $\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CH}_2\text{O}$ , and  $\text{HCOO}^-$ , the time required for 99% conversion is too slow to be practical as a decontamination procedure at a reasonable pH<sup>1</sup>. Since  $-d(\text{RDX})/dt = k_2(\text{OH}^-)(\text{RDX})$  where  $k_2 = 3.9 \times 10^{-3} \text{ l-mole}^{-1}\text{sec}^{-1}$  at 25.0°C, it can be calculated that 30% NaOH is required to reduce 45 ppm RDX to 0.45 ppm in 20 minutes, and at a pH of 12 (approximate pH of lime water) this same conversion requires approximately 14 days.

A relatively simple method to effectively increase the  $\text{OH}^-$  concentration was accomplished by passing aqueous RDX solutions through strongly basic ion-exchange resin columns. The basic resins studied were the styrene/divinylbenzene copolymer type with trimethylammonium hydroxide<sup>2</sup> or dimethylethanolammonium hydroxide<sup>3</sup> groups. The maximum number of moles of  $\text{OH}^-$  obtainable on the resin was found to be  $1.75 \times 10^{-3}$  moles  $\text{OH}^-/\text{gram}$  (equivalent to 1.22 mole  $\text{OH}^-/\text{liter}$ ) by passing 2 resin volumes of 1 M NaOH through the chloride form as shown schematically,

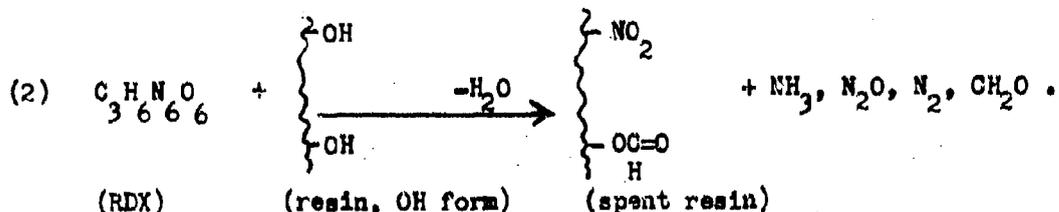


1 J. J. Hoffsommer, D. A. Kubose, and D. J. Glover, J. Phys. Chem., in press.

2 Amberlite 400 (Rohm & Haas Co., Philadelphia, Pa.).

3 Amberlite 410 (Rohm & Haas Co., Philadelphia, Pa.).

Hydrolysis of the RDX on the basic resin may be shown similarly,



Since three moles of  $\text{OH}^-$  are consumed for each mole of RDX hydrolyzed, the following expression may be written for the maximum number of resin volumes,  $\text{RV}_{\text{max}}$ , that may be theoretically treated,

$$(3) \quad \text{RV}_{\text{max}} = \text{RL}_{\text{OH}} / (3)(M) \quad , \quad \text{where } \text{RL}_{\text{OH}} \text{ is resin}$$

hydroxide loading factor expressed in moles  $\text{OH}^-$ /liter of resin, and  $M$  is the molar concentration of the RDX solution. At the maximum  $\text{RL}_{\text{OH}}$  for the resin, 1.22 moles  $\text{OH}^-$ /liter, used to treat a  $2.0 \times 10^{-4}$  M (45 ppm) RDX aqueous solution,  $\text{RV}_{\text{max}}$  is calculated to be  $2.0 \times 10^3$  resin volumes. From (3) the actual volume of water treated,  $V_{\text{Lmax}}$ , becomes  $V_{\text{R}} \times \text{RV}_{\text{max}}$ , where  $V_{\text{R}}$  is the actual resin volume.

Figure 1 shows the RDX resin break-through curve for the hydrolysis of RDX on 5.16 grams of 400 Amberlite resin containing  $2.04 \times 10^{-3}$  moles of  $\text{OH}^-$  ( $\text{RL}_{\text{OH}} = 0.278$ ) with an RDX feed concentration of  $1.98 \times 10^{-4}$  M (44 ppm). At 56%  $\text{RV}_{\text{max}}$  (1.7 liters) the effluent RDX concentration was  $\cong 0.5$  ppm ( $\cong 2 \times 10^{-6}$  M). In another experiment where  $\text{RL}_{\text{OH}} = 1.22$ , the effluent RDX  $\cong 0.5$  ppm at 54%  $\text{RV}_{\text{max}}$  (15.8 liters) and verifies (3). In other words, at a point where  $55 \pm 2\%$  of the available  $\text{OH}^-$  groups have been reacted or displaced, we may expect an RDX effluent bleed of approximately 0.5 ppm.

Since tap water contains varying amounts of anions (notably  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ ) reaction and displacement of  $\text{OH}^-$  ion from the basic resin is expected.

Table 1 shows the RDX resin break-through effluent bleeds for 9 cycles for the hydrolysis of RDX in tap water on Amberlite 410 resin. Figure 2 shows the extent of  $\text{OH}^-$  displacement from the basic 410 resin by area tap water. After approximately 50% of the total available  $\text{OH}^-$  has been displaced, the  $\text{OH}^-$  replacement markedly decreases. An additional 25% of the total  $\text{OH}^-$  was determined by NaCl displacement to remain on the resin. The other 25% of the total  $\text{OH}^-$  is presumed to be mainly consumed in the neutralization reaction with bicarbonate ion:  $\text{OH}^- + \text{HCO}_3^- = \text{H}_2\text{O} + \text{CO}_3^{2-}$ . Since the molar concentration of  $\text{HCO}_3^-$  was determined to be  $1.13 \times 10^{-3}$  M (or 69 ppm) by acid titration with methyl orange indicator,  $1.80 \times 10^{-3}$  moles of  $\text{OH}^-$  (22.5% of total) would be expected to be consumed by this neutralization reaction.

Regeneration of the spent resin was accomplished by the passage of 2 resin volumes of 1 M HCl through the resin, followed by water rinsing, then 2 resin volumes of 1 M NaOH. The HCl treatment was necessary to dissolve insoluble hydroxides and carbonates which accumulated over several cycles and were found to clog the resin. For large scale hydrolyses it was necessary to include urea in the HCl to prevent the formation of nitrous acid. The regeneration step is shown schematically,



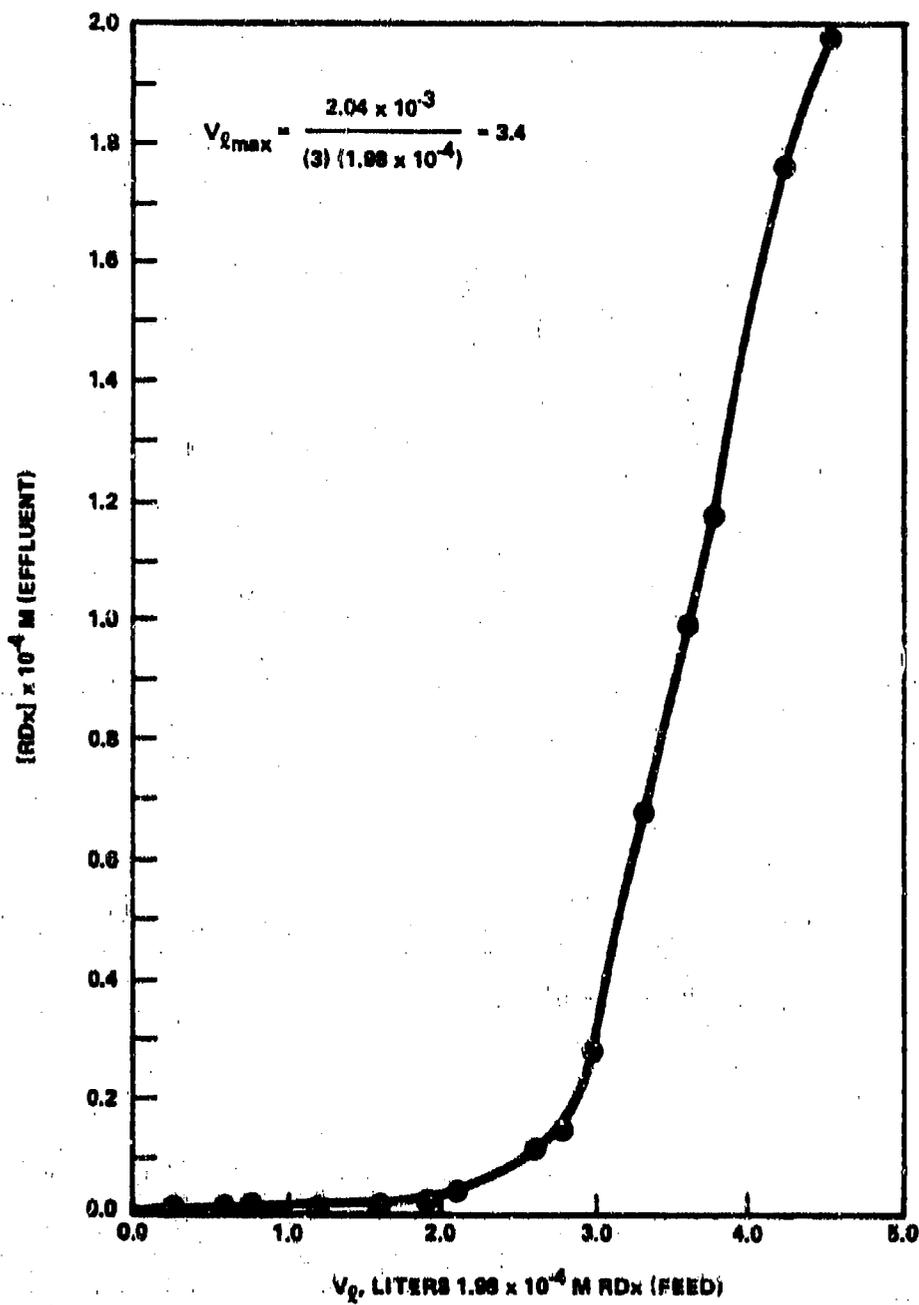


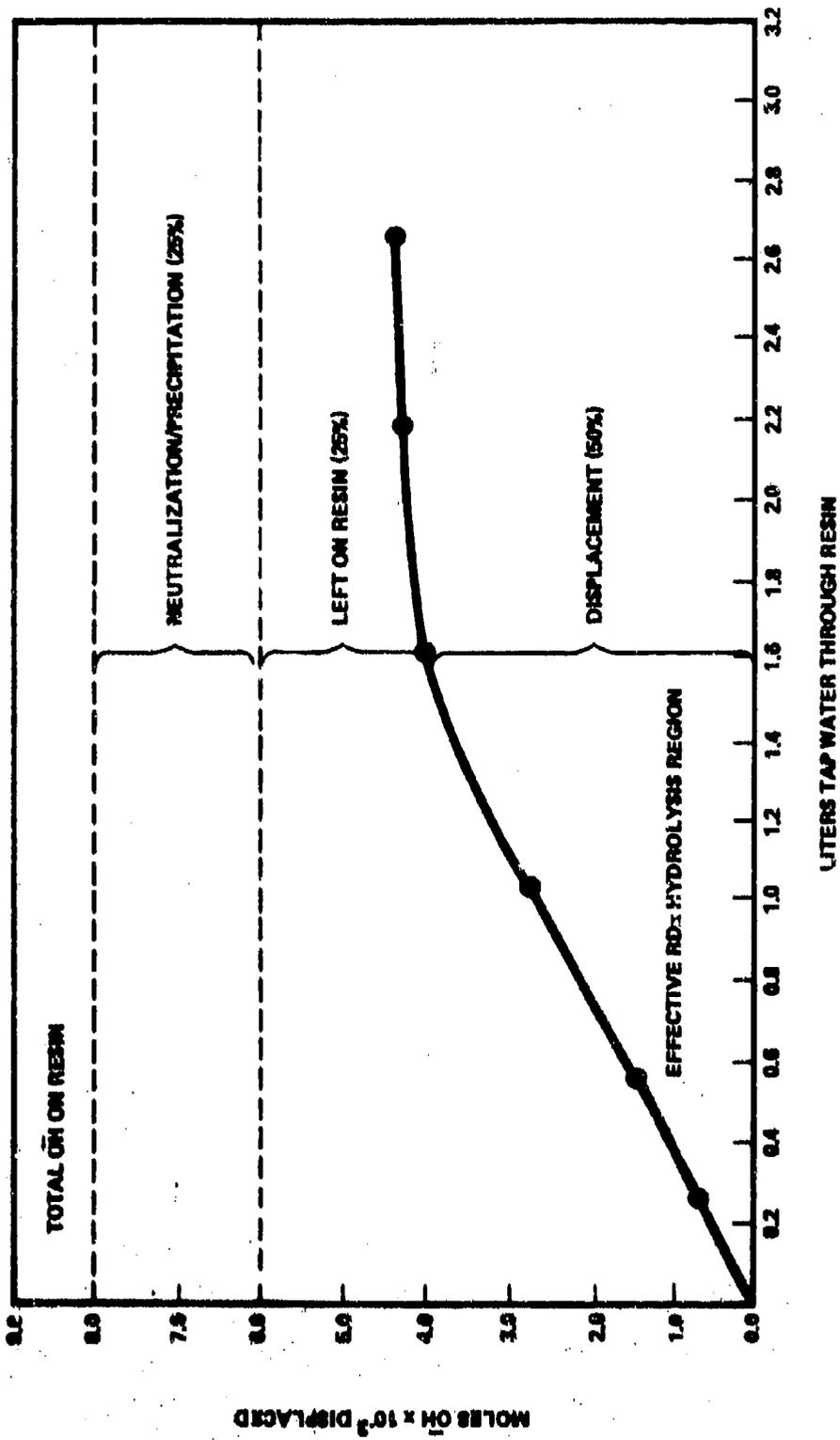
FIG. 1 HYDROLYSIS OF RDX WITH BASIC 400 RESIN IN DISTILLED WATER.

TABLE 1 HYDROLYSIS OF RDX ON 410 RESIN IN TAP WATER.

CYCLE	RESIN VOLS	EFFLUENT % THEORETICAL	
		ppm RDX	RESIN VOLS <sup>(1)</sup>
1	200 <sup>(2)</sup>	< 0.3	8.7
2	400	< 0.1	17.5
3	342	< 0.5	14.9
4	392	< 0.3	17.1
5	321	< 0.5	14.0
6	336	< 0.3	14.6
7	292	< 0.5	12.7
8	385	< 0.2	16.8
9	342	< 0.5	14.9

$$(1) = \frac{\text{MOLES OH}}{(3) \text{ (RDX)}} \times \frac{1}{V_R} = 2294; (18,886 \text{ GALLONS/CUBIC FT.})$$

(2) = 1,496 GALLONS/CUBIC FT. OF RESIN

FIG. 2 DISPLACEMENT OF OH<sup>-</sup> ION FROM BASIC 410 RESIN BY TAP WATER.

REMOVAL AND DISPOSAL OF RDX FROM WATER: LARGE-SCALE BASIC RESIN SYSTEM

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A companion paper has described laboratory scale studies of the use of a strongly basic ion exchange resin for the adsorption and destruction of RDX dissolved in water. The parameters of flow rate, resin regeneration, resin loading, etc., were examined on small amounts of resin, usually less than 10 grams. The work reported here describes a scale up of the laboratory studies to approximately 3200 grams (1.6 cu. ft.) of the resin.

RDX Column

A major concern in the scale up was the generation of thousands of gallons of RDX contaminated water. The concept used was to pass water through a column of RDX. This idea was used in the laboratory studies and with relatively slow flow rates (1-2 ml/min) produced water containing 40 - 50 ppm RDX. The RDX column used in the scale up work consisted of RDX held in a pyrex pipe nominally 7.5 cm ID and 13 cm long fitted with polyvinyl chloride (PVC) end pieces. These end pieces had concentric and radial grooves, the latter leading to a central take-off hole, to provide laminar flow through the RDX. A 10 micron stainless steel screen on the bottom end piece prevented particulate RDX from leaving the column. The pyrex-PVC assembly was sandwiched between two steel plates and secured by bolts. RDX concentrations of 25-30 ppm were obtained at flow rates of 8 l/min and increased to 40-50 ppm at flow rates of 3 l/min. "Channelling" of the RDX in the column was corrected by shaking the columns to relevel the RDX.

### Resin Column

The design of the column used to contain the Amberlite 410 basic anion exchange resin (Rohm and Haas Co., Philadelphia, Pa.) is similar to that used for the RDX column. The resin column was made of PVC pipe 28 cm ID and 120 cm long. The PVC end pieces had the same system of concentric and radial grooves to provide laminar flow. A 10 micron stainless steel screen prevented loss of resin.

### Plumbing

A schematic of the overall plumbing system is shown in Figure 1. The incoming tap water, filtered through a coarse (100 micron) and fine (10 micron) set of filters, can be directed through the RDX column or, if desired, directly to the resin column for flushing purposes after passing through the flow meter and total volume meter. A sampling outlet located between the two meters allows samples of the RDX contaminated water to be taken for assay. The two three-way valves on the resin column are plumbed such that the incoming water can be directed downflow or upflow through the resin. The flow when RDX is being degraded is downflow. The incoming water, after being filtered, can also be directed to the regeneration tanks. The regeneration solutions are pumped from the tanks and passed upflow through the resin column via the three-way valves.

### System Operation

The RDX is handled at all times in a water slurry. The RDX columns are loaded by disconnecting the water lines to the columns and removing the top steel plate and end piece. The amount of RDX put in each column is approximately 1 lb. The PVC end piece and steel plate are put back on after cleaning up any spilled RDX and the water lines are reconnected.

The resin column is loaded in much the same manner.

To begin a run the water is turned on and the appropriate valves opened or closed to allow the water to pass through the RDX columns, pass downflow through the resin column and exit out the effluent pipe. The flow rate is monitored and the RDX columns releveled when the channelling becomes too great. Samples of the input RDX feed and resin column effluent are taken at various time intervals and assayed for RDX content. The length of a cycle, i.e., the number of resin volumes input before the RDX concentration in the effluent reaches 0.5 ppm, was examined as a function of flow rate and regeneration parameters. Regeneration of the spent resin to the hydroxide form was accomplished by use of HCl, NaCl and NaOH, in that order. In some instances the NaCl was omitted. Urea (dissolved in the HCl) was used to convert the nitrous acid which is formed from acidification of  $\text{NO}_2^-$ , a product adsorbed on the resin, to  $\text{N}_2$  and  $\text{CO}_2$ . In one cycle NaCl was used first to displace the  $\text{NO}_2^-$  prior to addition of HCl and the urea was not used.

#### Results

Figure 2 presents the data obtained for eight cycles. The number of resin volumes of RDX contaminated water passed until the effluent reached a RDX concentration of 0.5 ppm is listed in the second column. As can be seen the parameter which most affects the performance of the resin is the amount of hydroxide ion used in the regeneration of the resin. These results are in agreement with those obtained on a laboratory scale and demonstrate that the resin process can be scaled up.

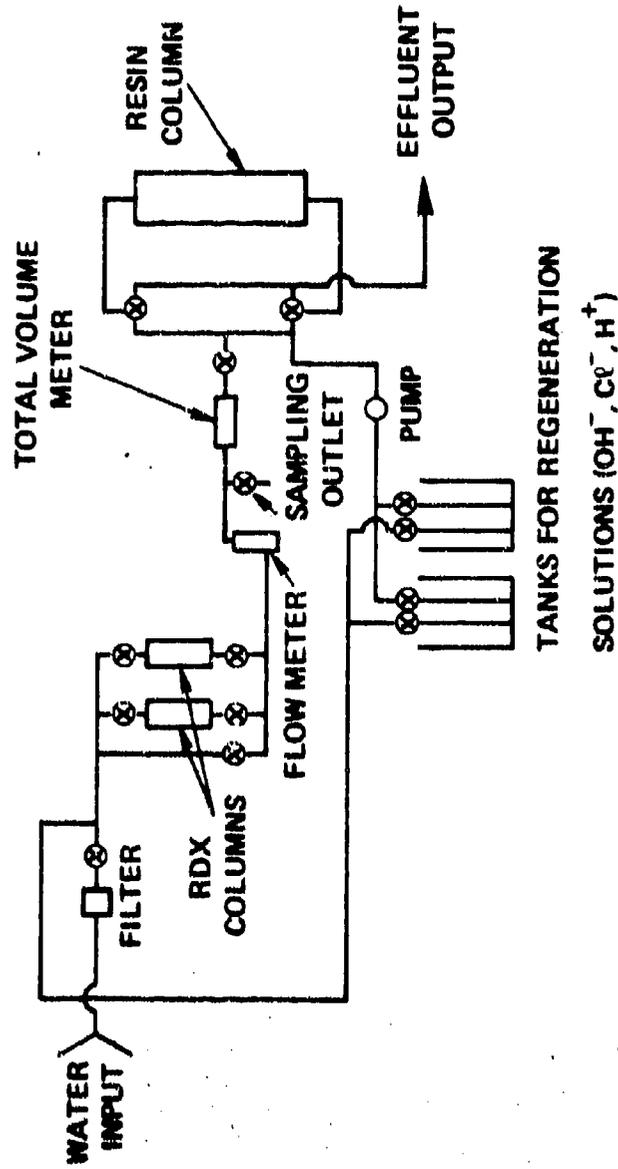


FIG. 1 SCHEMATIC PLUMBING DIAGRAM

CYCLE	RESIN VOLUMES AT 0.5 ppm	AVERAGE FLOW RATE, l/min	MOLES REAGENT			
			NaOH	NaCl	HCl	UREA
1	190	7-7½	194	NONE	NONE	NONE
2	205	5-5½	180	113	25	1.7
3	160	7-8	180	113	25	1.7
4	175	5½-6	180	NONE	121	1.7
5	178	3-3½	136	NONE	90	1.7
6	145	3-3½	90	NONE	90	1.7
7	170	3½-4	112	113	90	1.7
8	185	3-3½	180	180	23	NONE

200 RESIN VOLUMES = 9000 LITERS; 1 RESIN VOLUME = 45 LITERS (1.6 cu. ft.)

FIG. 2 RESIN BREAK-THROUGH/REGENERATION PARAMETERS

## CARBON REGENERATION

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Introduction

Carbon adsorption treatment of pink wastewater (TNT/RDX) is being used at the Load-Assembly-Packaging Divisions of Joliet, Iowa, Kansas and Tooele Army Ammunition Plants. The practice, to date, of disposing of the TNT/RDX-saturated carbon is by incineration which is potentially hazardous and costly. Alternative methods of handling the pink wastewater problem are under current investigation. IAAP is studying thermal regeneration of carbon and Natick Laboratories, polymer resin adsorption. The economics of both methods are being evaluated for a decision on adoption. A method having the adsorptive capacity of carbon which can be regenerated on column without disassembly by elution techniques would be considered the ideal solution to the problem. This latter approach is the basis of the study being conducted at Picatinny Arsenal. The first phase of this study which deals with the determination of the mechanism by which TNT is adsorbed on carbon is the subject of this presentation.

TNT Adsorption

Since TNT replaces RDX from the adsorbed state and TNT remains strongly bound to the carbon surface, the study of the process of carbon degeneration was initially confined to TNT. For this, adsorption isotherms of aqueous solutions of TNT (130 ppm) on FS300 were determined concurrently with surface area determinations using argon adsorption at  $-196^{\circ}\text{C}$ .

The adsorption of TNT on carbon was studied as a function of pH, temperature and particle size. Adsorption was found to be significantly dependent upon particle size and hence diffusion, but independent of pH and temperature. The independence of pH is indicative of a non ionic process of adsorption. Because the thermodynamics of adsorption and diffusion are diametrically opposing in that adsorption decreases and diffusion rates increase with increasing temperature, the observed independence of TNT adsorption as a function of temperature is explained.

The strong dependence of TNT adsorption on diffusion is illustrated in Figure 1. At approximately two hours, the fine carbon adsorbs TNT to its saturation level, the medium to 60% capacity and coarse (as received) to 15% capacity. This demonstrates the importance of minimizing the path the TNT must traverse to interact with the available internal surface. It should be noted that the observed capacities are independent of the different geometric surface areas of the respective particle sizes. Although the geometric surface areas (calculated), .003, .008, and .08  $\text{cm}^2/\text{g}$  of the coarse, medium and fine particles differ by orders of magnitude, the corresponding percent differences with respect to the total surface area of  $1000 \text{ M}^2/\text{g}$  is infinitesimal, viz.,  $8 \times 10^{-7}$ ,  $8 \times 10^{-8}$  and  $3 \times 10^{-8}$  percentages.

Deactivation of Carbon

The progressive deactivation of FS300 was determined as a function of adsorption/desorption cycles (Figure 2). Adsorption was performed in the usual manner from aqueous solution and desorption with acetone. The specific adsorption of the three carbons decreases (deactivation) with similar proportionality constants. However, the deactivation of the medium and fine carbons relative to

the coarse (0.3g TNT/g Carbon) requires three cycles for the medium with a total capacity of 1.1g TNT, and four cycles for the fine with a total capacity of 2.0g TNT/g Carbon.

The material balance of eluted TNT and retained TNT by the carbon, together with the associated attrition of surface area is presented in Table I. As the retained TNT accumulates, the surface area deteriorates and correspondingly less TNT adsorbs with each successive cycle. The total of TNT retained and removed with each cycle remains fairly constant. It can be inferred from the data that in the process of the TNT being strongly bound to the surface, pores are successively blocked precluding the elution of otherwise reversibly bound TNT. The question of how the TNT is strongly bound to the carbon surface was addressed by the application of the ESCA (Electron Spectroscopy Chemical Analysis) technique which is uniquely suited for surface-adsorbent analysis.

TABLE I  
DEACTIVATION OF COARSE FS300<sup>4</sup> BY TNT ADSORPTION

NO. CYCLE	SP.ADN. (gTNT/gC)	SP.DES. <sup>1</sup> (gTNT/gC)	$\Sigma S_A^2$ (M <sup>2</sup> /g)	CUMMULATIVE <sup>3</sup> RETAINED SP.ADN.	TOTAL SP.ADN. (SP.ADN. + CUM.RET.SP.ADN.)
1	.36	.24	890	.12	
2	.29	.27	818	.14	.41
3	.25	.21	701	.18	.39
4	.15	.14	570	.19	.33
5	.14	.08	541	.25	.33

<sup>1</sup>By Acetone Elution: <sup>2</sup>Surface Area After Desorption: <sup>3</sup>After Acetone Elution:

<sup>4</sup> $\Sigma S_A = 1098M^2/g$

VC

#### Mechanism of TNT Adsorption

Since explosives contain nitrogen in distinct oxidation states which, when subjected to chemical interaction undergo changes in their oxidation states, the electron spectra generated by ESCA reflect the various changes induced. TNT contains nitrogen in one oxidation state, N<sup>+3</sup> of the nitrogen dioxide functional group. The electron spectrum should therefore contain only one peak at 405.6 ev. Instead, the electron spectrum shown in Figure 3 depicts two additional peaks of nitrogen in lower oxidation states at 401 and 400 ev. The assignments of N<sup>+1</sup> and N<sup>-1</sup> could be indicative of a nitroso and secondary amine nitrogens, respectively. The significance of this spectrum is the unequivocal evidence of TNT having undergone chemical reactivity with the carbon surface. This TNT-carbon surface reaction complex was further substantiated by infrared and mass spectrometric analyses.

#### Conclusions

The process of deactivation of carbon by TNT involves both physically and chemically adsorbed TNT in the micro and meso porous internal surface area structure. The chemisorbed TNT plugs up the pore openings thereby precluding the elution of reversibly physisorbed TNT. Diffusion plays an important role in the irreversible adsorption of TNT. The slower the diffusion rate, the greater the residence time and the greater the degree of chemical reactivity of TNT with the carbon surface.

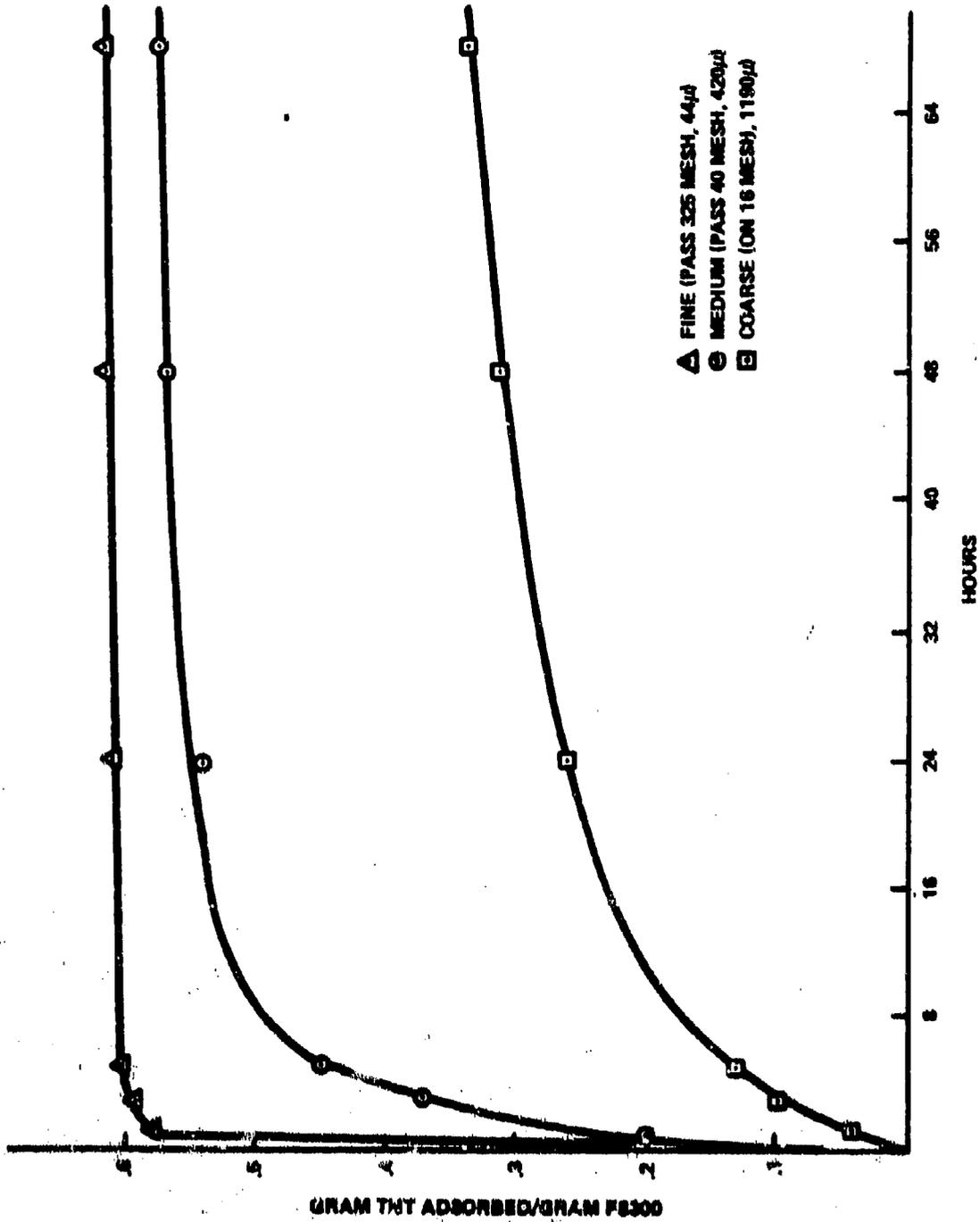


FIG. 1 EFFECT ON ADSORPTION RATE OF TNT BY PARTICLE SIZE OF F8300

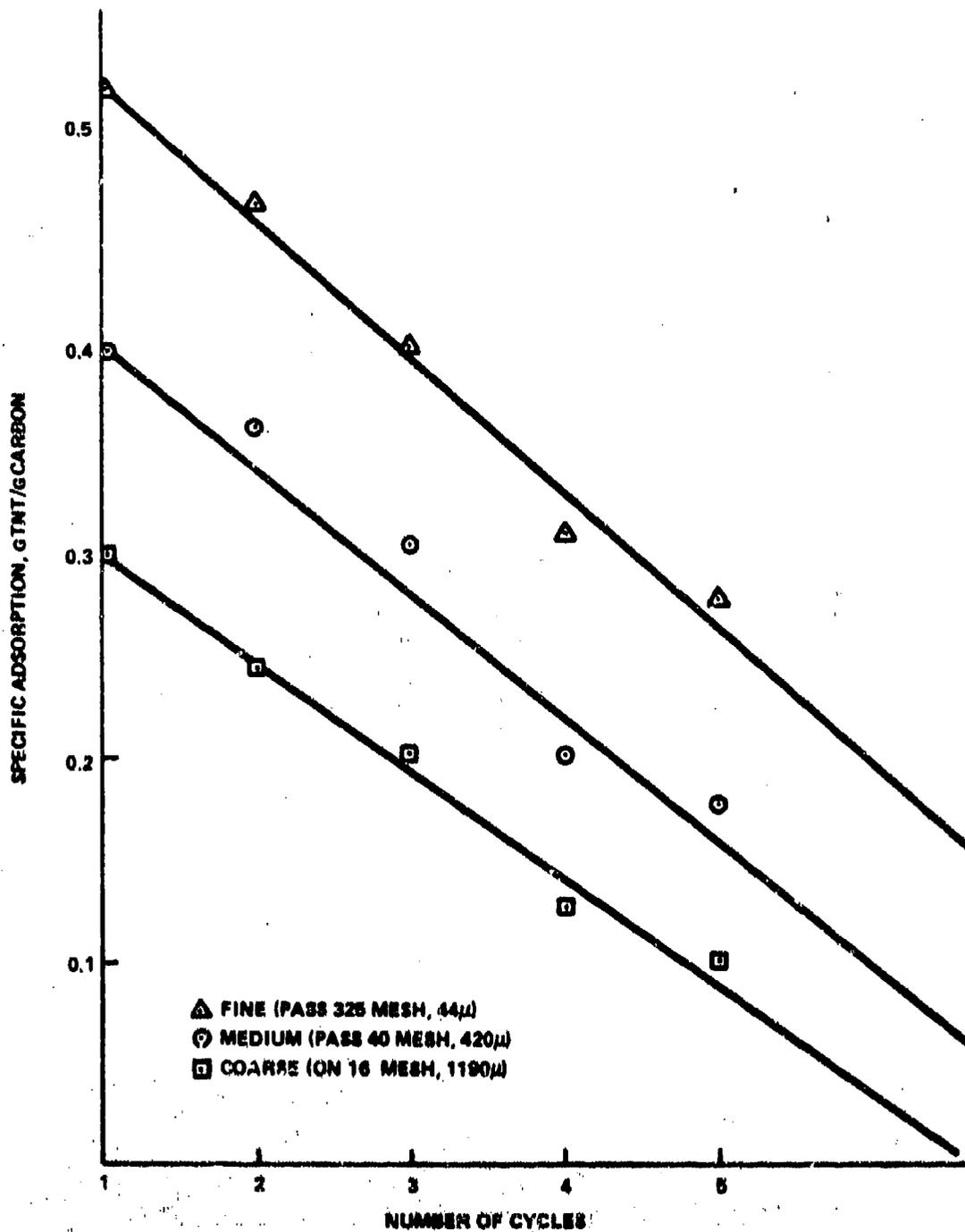


FIG. 2 DEACTIVATION OF F8300 AS A FUNCTION OF ADSORPTION/DESORPTION CYCLE AND PARTICLE SIZE

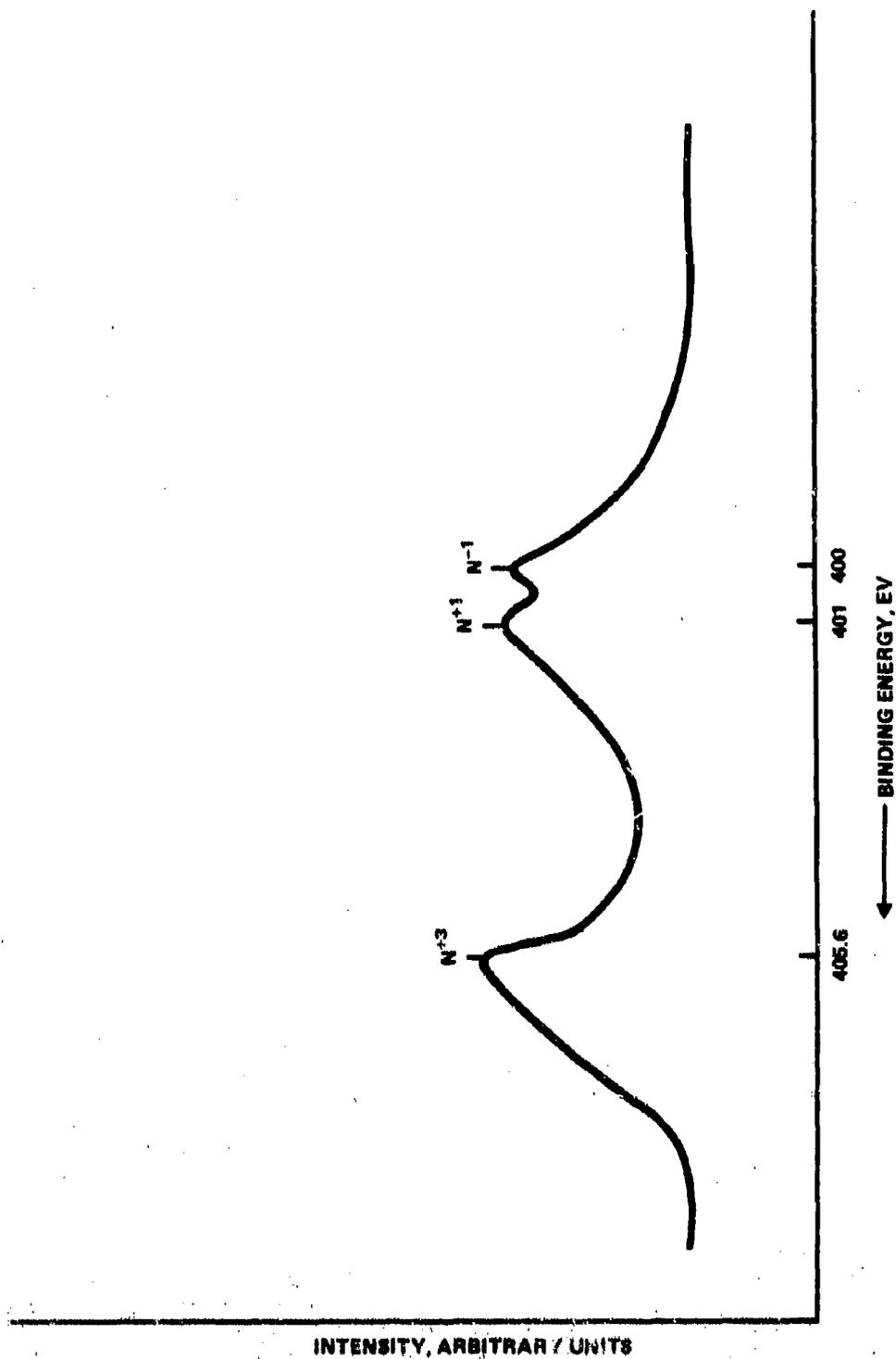


FIG.3 STRONGLY ADSORBED TNT ON CHARCOAL, FS300

## IMPROVED PROCEDURES FOR PURIFYING TNT

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Crude TNT must be purified for military use. Since World War I, the almost universal practice has involved purification by treatment with aqueous sodium sulfite ("sellite"). The resulting waste liquor ("red water") has entailed a serious disposal problem. A portion of it has in the past been sold to paper companies, but this is no longer possible. It is now concentrated and then incinerated to crude sodium sulfate. Unfortunately there has been no use for it, and it has accumulated steadily at the TNT plants.

A recent approach to recovery of this sodium sulfate for reuse as sodium sulfite has involved the following reactions:

- (1)  $\text{Na}_2\text{SO}_4 + 2 \text{C} + \text{Na}_2\text{S} + 2 \text{CO}_2$
- (2)  $\text{Na}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{S}$
- (3)  $\text{H}_2\text{S} + 3 \text{O} + \text{SO}_2 + \text{H}_2\text{O}$
- (4)  $\text{Na}_2\text{CO}_3 + \text{SO}_2 + \text{Na}_2\text{SO}_3 + \text{CO}_2$

Adding the above equations, we have:



All of the above reactions have been used commercially in the past; the most recent application has been the Tampella Process used in the Finnish paper industry. This procedure is complicated and quite energy intensive.

It occurred to us that waste water recovery might be simpler if other sulfites were used. Since no literature was found on the purification of TNT with sulfites other than sodium, we screened five of them (ammonium, magnesium, calcium, zinc and cadmium). Only the first two appeared interesting; they will be discussed in turn. Initial work was done by the writer and V.I. Siele at Picatinny. Followup studies aimed toward plant operation, being made at Radford Army Ammunition Plant by C.D. Chandler, Jr., G.R. Gibson, and R. Mundy, are still in progress.

#### Use of Ammonium Sulfite

It was found that vigorous agitation of molten crude TNT with aqueous ammonium sulfite (0.1 lb., anhydrous basis, per 1.0 lb. crude TNT) at 85-90°C removed the impurities and gave a purified TNT of satisfactory set point. When using sodium sulfite, this reaction can be run in an open beaker. Use of this

procedure with ammonium sulfite was unsatisfactory, since ammonia was lost, the pH dropped, and an unsatisfactory product resulted. This problem was overcome by operating with a flask and reflux condenser. It was also noted that the mode of mixing was important. Satisfactory results were obtained by mixing the reagents at room temperature, followed by heating to 85°C, or by dropwise addition of the sulfite to an agitated mixture of molten TNT and water preheated to 85°. Pouring the sulfite solution into the preheated TNT - water mixture at 85° led to a mild exothermic reaction with a temperature rise to 90-95°, and an unacceptable product. All samples of TNT purified by this procedure were colored yellow, resulting from the formation of small amounts of 3- and 5-amino-2,4-dinitrotoluenes by side reactions. It was noted that these compounds were not found when solid TNT was ground in a ball mill with aqueous ammonium sulfite.

Followup studies at Radford led to the conclusion that the process appeared suitable for large-scale use on a batch basis (simulating incremental addition of sulfite), but not on a continuous basis (involving rapid mixing). As noted above, rapid mixing greatly favors the formation of aminodinitrotoluenes, thereby lowering the set point. It was found that the amino compounds could be removed by melt-washing with 70% sulfuric acid, but incorporation of this extra step was concluded to be impractical in plant operation. Since all future American TNT production and purification will involve continuous operation, the ammonium sulfite process is therefore not of interest until better control of the side reactions is achieved.

The ammonium sulfite process has advantages which suggest that further study is warranted. A better yield of purified TNT is obtained than with sellite, and it is a cheaper process to operate. The raw materials (ammonia and sulfur dioxide) are already available at the TNT plants. Most important, the red water contains no metal ions, and the Radford engineers believe that it can probably be disposed of by simply mixing it with the spent sulfuric acid from the nitration. A separate recovery step is thus completely eliminated. In the acid recovery plant, all of the sulfur values of the ammonium sulfite would be recovered, and the ammonia values would be converted to nitrogen.

#### Use of Magnesium Sulfite

Purification with magnesium sulfite was effected in a similar manner, except that a more dilute solution was used because of its low water solubility. Four pounds of sulfite (anhydrous) are required per 100 lbs. crude TNT. Yields from magnesium sulfite purification are higher than those obtained with sellite. Current selliting practice involves overtreatment, with an estimated loss of about 8% of 2,4,6-TNT; this loss would not be incurred with magnesium sulfite. Even with optimum use of sellite, as proposed by Radford, the magnesium process would show a yield advantage of 1 1/2%. A yield increase is of considerable economic importance, since it is estimated that at full mobilization production, an increase of 1% results in a saving of \$1,000,000 per year.

Unlike the ammonium sulfite process, the magnesium process is not complicated by side reactions, and yields a product of high purity. Continuous selliting induces the formation of small amounts of hexanitrobiphenyl and methyl pentanitrodiphenylmethane. Work at Radford has shown that these materials are detrimental to random crystallization, which may lead to undesirable cracks and voids in the shell fillings. These materials are not formed with magnesium sulfite.

Magnesium process red water would be calcined back to magnesium oxide by the following reactions:



It will be noted that magnesium sulfate behaves entirely differently from sodium sulfate (Equation (1)) upon heating with carbon, since the former is converted to the oxide, which can be directly reconverted to the sulfite for reuse. The carbon already present in the waste liquor may be sufficient without supplement. In any case, the carbon requirement for Reaction (6), is only 1/4 that of Reaction (1). Reaction (6) is already in widespread commercial use in the paper industry, and for the scrubbing of power plant flue gas. We have made contacts in both areas; these are expected to provide data and assistance in implementing scaleup of the red water recovery step of the magnesium process.

The ammonium sulfite purification process is disclosed in US Patent 3,956,409 (May 1976); a patent is pending on the magnesium process.

#### Conclusions

Ammonium and magnesium sulfites are superior to sodium sulfite for purifying TNT with respect to ease of red water disposal and yield of TNT. The ammonium process requires no special red water disposal step, but is not now suitable for continuous operation. The magnesium process yields a purer TNT than either of the other two processes, and is currently under study toward possible future plant-scale use.

PHYSICO-CHEMICO UNIT PROCESSES FOR PURIFICATION  
OF EXPLOSIVE PLANT EFFLUENTS

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ABSTRACT

The U.S. Army owns 17 Army Ammunition Plants (AAP) engaged in the manufacture or loading of propellants or explosives. Liquid waste effluents from these plants must be purified to meet new and stringent discharge standards. Various physico-chemico water purification unit processes are already known to be effective, or merit investigation.

THE RELATIONSHIP BETWEEN FISH SIZE AND  
THEIR RESPONSE TO UNDERWATER BLAST

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The major objectives of this study were (1) to assess the tolerance of several species of fish to various levels of underwater blast and (2) to use these data to develop a method for predicting the hazard to fish for untested underwater blast exposure conditions. Secondary objectives were (1) to determine if there was any difference in blast tolerance between fish with ducted swimbladders and those with nonducted swimbladders, and (2) to confirm the assumption that overpressure impulse is the best parameter for evaluating the response of fish to underwater blast.

Previous studies have demonstrated that, when an animal is exposed to either airblast or underwater blast, the most serious injuries occur to the gas-containing organs and their surrounding tissues. In particular, the swimbladder is the target organ in fish, except for those species which have no swimbladder and are very resistant to underwater shock. The airblast studies have indicated that, for a short-duration blast wave, the level of injury in a given animal is primarily a function of the overpressure impulse, and that the impulse required to produce a given level of injury divided by the cube root of the animal's body mass tends to be approximately constant, at least for similar species of mammals.

Of the eight species of fish tested five had ducted swimbladders (physostomes) and three had nonducted swimbladders (physoclists). The ducted-bladder species were top minnows (Gambusia affinis), goldfish (Carrasius auratus), carp (Cyprinus carpio), rainbow trout (Salmo gairdneri), and channel catfish (Ictalurus punctatus). The nonducted-bladder species were guppies (Lebistes reticulatus), bluegills (Lepomis macrochirus), and large mouth bass (Micropterus salmoides). The major difference between the two types of fish was the presence of a pneumatic duct connection between the bladder and the gut in the physostomes and the lack of one in the physoclists. Because small and large specimens were available within five of the species, a total of 13 body weight groups was utilized. The average body weights ranged from 0.02 to 744 g.

All tests were conducted in a freshwater pond. The surface dimensions were 220 x 150 ft with a 30-ft-deep, 100- x 30-ft central portion. The test pond was described in Reference 1.

1. Yelverton, J. T., D. R. Richmond, W. Hicks, K. Saunders and E. R. Fletcher, "The Relationship Between Fish Size and Their Response to Underwater Blast" Technical Report, DNA 3677T, Defense Nuclear Agency, Washington, D. C., June 18, 1975.

The explosive charges used throughout this study were bare, 1-lb spheres of pentolite with 3/16-inch detonator wells. DuPont E-99 electric blasting caps were used to initiate the charges.

There were four channels of pressure-time instrumentation. The methods and equipment used for measuring and recording the blast waves were basically the same as those described in References 2 and 3.

Most of the fish were tested in cages which consisted of cylindrical wire frames covered with small diameter nylon or plastic mesh. The cages were constructed to fit the individual species so that they could be held at an exact depth. The mesh covering ranged in size from 1/4 to 7/8 inch. The largest mesh that would keep the fish from escaping was used in order to minimize the amount of material that could possibly shield the fish from the underwater shock. A majority of the fish were tested one per cage and oriented side-on to the charge. The small bluegills and the small goldfish were tested 5 or 10 per cage. The cages were suspended from the center of the rigging that spanned the pond. The rigging consisted of a grid system that could be raised or lowered to the desired depth by an electrically operated winch on the bank. Top minnows and guppies which averaged less than 0.5 g in body weight were not confined but were released from a dip net beneath the water surface 1 sec before detonation and retrieved within 1 to 2 sec afterward with a dip net.

Most of the tests were conducted with the fish at 1-ft depths and with the charges detonated at 10-ft depths. The impulse and peak pressure were varied by changing the slant range between the fish and the charge. Small carp were also tested at 0.17- and 10-ft depths with the charges at 10 ft and the slant range varied. The top minnows and guppies were at 0.25-ft depths. One series of tests was conducted with small bluegills in which the charge and fish depths were varied but the slant range was held constant. This made it possible to vary the surface cut-off time, and thus the impulse dose, while keeping the peak pressure constant.

By plotting the probit of mortality versus the logarithm of the impulse, it was determined that the dose-response data for each species of fish fell approximately along a straight line. For this reason, a probit regression analysis was run on each set of data to obtain an equation in the form of  $y = a + b \log_{10}(x)$  where  $y$  was the percent mortality in probit units and  $x$  was the logarithm of the impulse. In general, the probit slopes,  $b$ , for one species exposed at several depths or the slopes for large or small specimens of a species were not significantly different. In these instances a parallel probit

2. Richmond, D. R., J. T. Yelverton and E. R. Fletcher, "Far-Field Underwater-Blast Injuries Produced by Small Charges," Technical Progress Report, DNA 3081T, Defense Nuclear Agency, Washington, D. C., July 1, 1973.
3. Yelverton, J. T., D. R. Richmond, E. R. Fletcher and R. K. Jones, "Safe Distances from Underwater Explosions for Mammals and Birds," Technical Progress Report, DNA 3114T, Defense Nuclear Agency, Washington, D. C., April 1973.

analysis was used resulting in a common slope for the various regression lines. The probit equations as well as the impulses for 1-, 50-, and 99-percent mortality (including confidence limits) computed from the equations are presented in Table 1.

The assumption that impulse was the damage parameter was confirmed in tests wherein one species of fish was exposed at three different depths. Carp were tested at depths of 0.17, 1, and 10 ft, respectively. As seen in Table 1, the individual LD<sub>50</sub> impulse values were not significantly different: 27.4 psi·msec for carp at 0.17 ft, 23.5 psi·msec for carp at 1 ft, and 26.2 psi·msec for those at 10 ft. In contrast, the corresponding peak pressures associated with these LD<sub>50</sub> impulses varied considerably: 810 psi at 0.17 ft, 335 psi at 1 ft, and 176 psi at 10 ft.

That the peak pressure was not the damage parameter was also demonstrated in tests with small bluegill. They were placed at increasing depths but at a constant slant range from the explosive charge (Table 1). The peak pressure remained at 182 psi. In those instances, the impulse and mortality increased with the depth of the fish.

Figure 1 is a log-log plot of LD<sub>50</sub> impulse versus body weight taken from the data in Table 1. A linear regression was obtained using all of the data points, and the regression line and equation are given in the figure. As can be seen, there was no detectable difference between the ducted and nonducted fish in that the data for both types fall close to the line. The figure also demonstrates that the larger the fish, the larger the impulse required to produce 50-percent mortality. This was true both within a species and between species. Further the slope of the line is near the predicted value of 1/3.

Considering the data for all eight species and thirteen body-weight groups, the impulse required to produce 1-percent mortality was 0.55 times the LD<sub>50</sub> impulse, on the average. This factor was used to derive the 1-percent mortality line in Figure 1. In a similar manner, the largest impulse at which no injuries were produced was determined to be 0.20 times the LD<sub>50</sub> impulse, on the average. This factor was used to derive the no-injuries line in Figure 1.

The data presented in this report and in Reference 1 can be used to predict ranges from underwater explosions at which fish will be killed and to predict ranges where there would be no-injuries. It should be emphasized that these data should only be used to predict fish response under conditions analogous to those of this experiment; that is, for underwater-blast waves having steep fronts and short durations typical of those recorded in free water and near the surface. There is uncertainty in predicting fish response at long ranges from very large explosions because of the difficulty in forecasting the impulse. At long ranges, the wave shape can be altered by such things as water temperature gradients.

TABLE 1  
RESULTS OF PROBIT ANALYSIS

Species	Depth of Fish, ft	Number of Fish	Mean Body Weight, g	Impulse, psi-msec			Probit Equation
				LD <sub>1</sub>	LD <sub>50</sub>	LD <sub>99</sub>	
<b>PERCIFORMES:</b>							
Top Minnow ( <i>Gambusia affinis</i> )	0.25	225	0.47	1.3 (0.9-1.6)	3.4 (3.0-3.8)	6.9 (7.1-12.6)	$y = 3.089 + 8.516 \log x$
Small Goldfish ( <i>Carassius auratus</i> )	1	60	1.4	3.0 (1.8-4.1)	6.2 (5.0-7.3)	12.5 (9.6-25.2)	$y = -0.976 + 7.887 \log x$
Small Channel Catfish ( <i>Ictalurus punctatus</i> )	1	60	106	17.6 (4.4-25.2)	33.3 (27.4-43.1)	63.0 (46.0-208)	$y = -7.781 + 8.398 \log x$
Small Carp ( <i>Cyprinus carpio</i> )	0.17	60	149	19.0 (6.0-22.8)	27.4 (24.2-31.7)	39.5 (32.2-112)	$y = -16.119 + 14.686 \log x$
	1	60	117	16.7 (10.2-19.2)	23.2 (21.2-25.2)	32.1 (29.0-51.4)	$y = -16.440 + 15.644 \log x$
	10	75	113	14.9 (4.0-16.0)	26.2 (23.5-31.2)	46.2 (32.5-102) <sup>a</sup>	$y = -8.395 + 9.445 \log x$
Rainbow Trout ( <i>Salmo gairdneri</i> )	1	60	145	12.3 (3.0-15.4)	20.7 (17.8-30.7)	35.0 (27.0-208) <sup>b</sup>	$y = -8.436 + 10.207 \log x$
Large Goldfish ( <i>Carassius auratus</i> )	1	6	245	13.0	26.5	52.5	$y = -5.786 + 7.887 \log x$
Large Channel Catfish ( <i>Ictalurus punctatus</i> )	1	18	326	19.5	36.8	66.7	$y = -8.148 + 8.398 \log x$
Large Carp ( <i>Cyprinus carpio</i> )	1	12	744	35.1	49.5	66.7	$y = -21.811 + 15.644 \log x$
<b>PERCIFORMES:</b>							
Guppy Fry ( <i>Gambusia affinis</i> )	0.25	75	0.02	0.7	1.7	4.6	$y = 3.687 + 8.516 \log x$
Guppy Adult ( <i>Gambusia affinis</i> )	0.25	36	0.13	1.0	2.7	7.2	$y = 2.803 + 8.516 \log x$
Small Bluegill ( <i>Lepomis macrochirus</i> )	1, 2.7, 2.5 <sup>b</sup>	40	1.4	4.2 (2.0-5.1)	6.7 (5.0-7.4)	10.4 (8.0-14.2)	$y = -5.063 + 12.174 \log x$
Large Bluegill ( <i>Lepomis macrochirus</i> )	1	40	68	17.7 (14.1-19.0)	20.7 (19.6-21.9)	24.3 (22.7-30.2)	$y = -20.078 + 34.231 \log x$
Large Mouth Black Bass ( <i>Micropetrus salmoides</i> )	1	4	148	15.8	26.5	37.3	$y = -17.266 + 15.644 \log x$

1-15 charges detected at 10-ft depths

<sup>a</sup> 80-percent confidence limits

<sup>b</sup> 95-percent confidence limits

All others were 68-percent confidence limits

<sup>c</sup> Slant range held constant

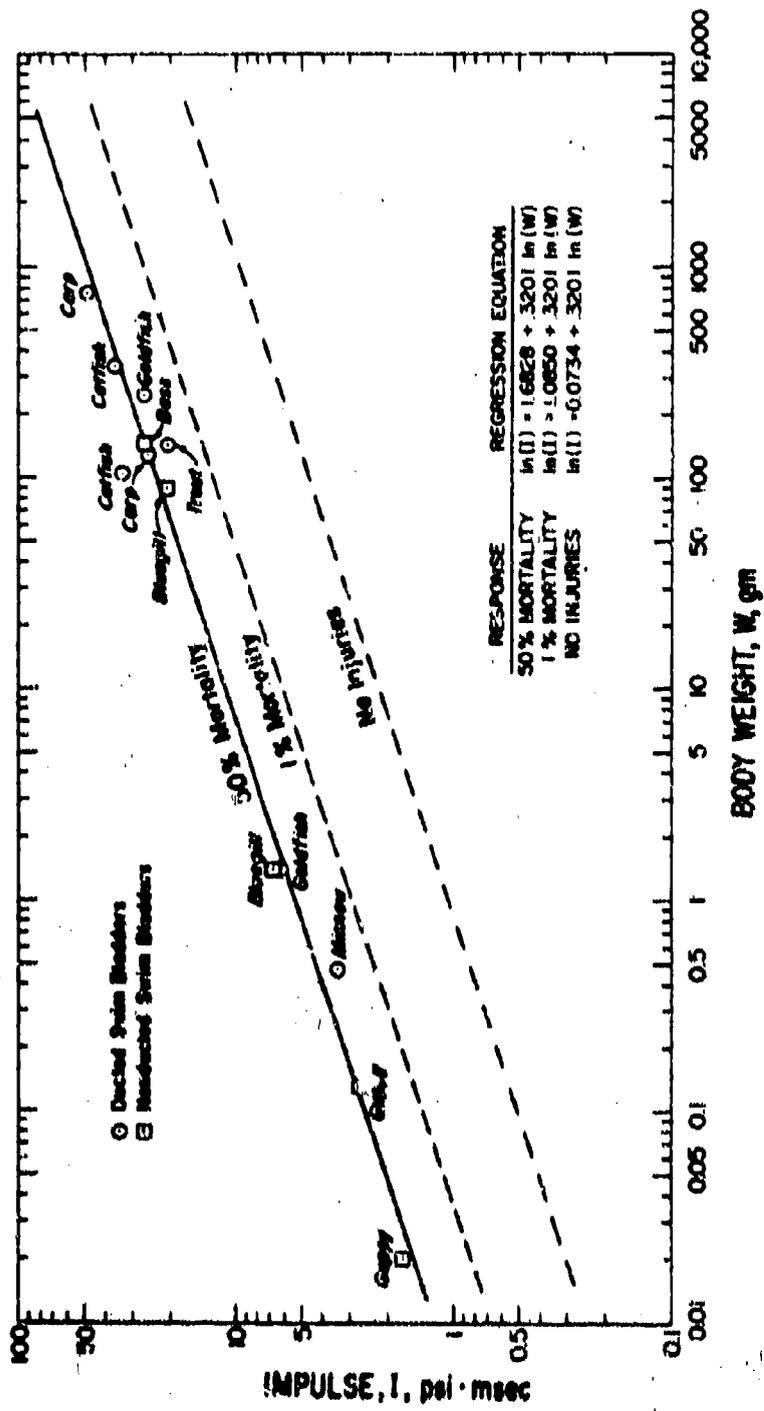


FIG. 1 RESPONSE OF FISH TO UNDERWATER BLAST AS A FUNCTION OF IMPULSE AND BODY WEIGHT

ENVIRONMENTAL ASSESSMENT OF THE USE OF EXPLOSIVES  
FOR SELECTIVE REMOVAL OF EELGRASS (*ZOSTERA MARINA*).

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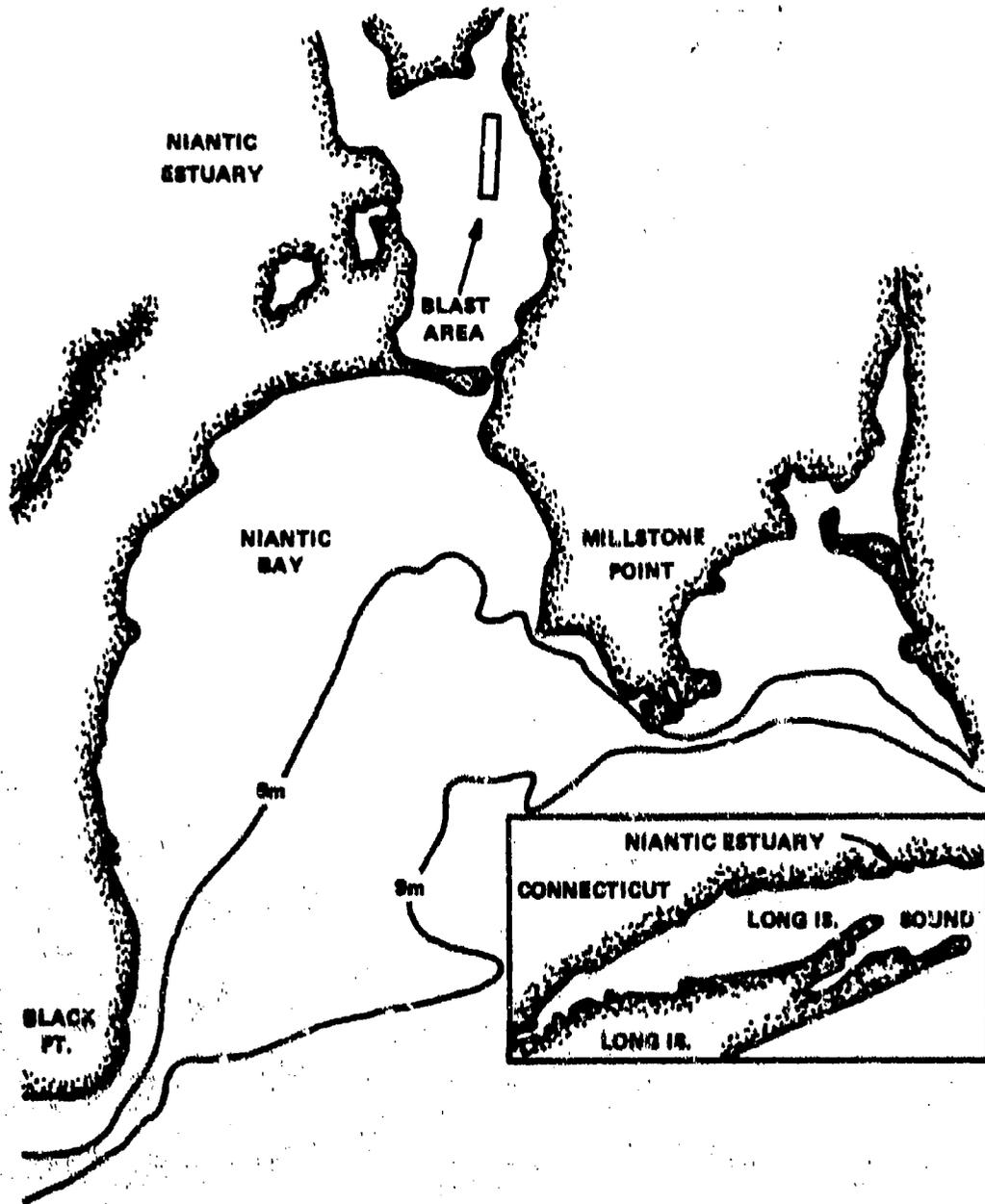
ABSTRACT

Data were obtained regarding the biological and physical impacts associated with using explosives as a herbicide for eelgrass (*Zostera marina*). Removal of the rooted marine vegetation from an area approximately 122 meters wide and 550 meters long within Niantic Estuary at Waterford, Connecticut has been proposed in an attempt to improve water quality and containment of egg and larval stages of the Bay Scallop (*Argopectens irradians*). Creation of a channel through dense stands of eelgrass should reestablish a persistent tidal eddy in the inner estuary which would improve dissolved oxygen levels and allow more complete habitation of the embayment. Relying on a physical model and in situ-generated information from both the private and public sectors it has been concluded that such an attempt, with proper constraints, should be allowed.

INTRODUCTION

During the 1930's, eelgrass (*Zostera marina*) was subjected to a wasting disease that caused extensive dieoffs of this rooted marine vegetation.<sup>1</sup> The thallus structures of eelgrass had been found to be a primary location of bay scallop (*Argopectens irradians*) larval setting prior to their establishment on the bottom within these vegetated areas.<sup>2</sup> It was, therefore, expected that as the eelgrass beds died out bay scallop populations would decrease. This expectation was realized along the coastline with the possible single exception of the Niantic Estuary.<sup>3</sup> Located in Connecticut's eastern-most New London County, Niantic Estuary is almost entirely land-locked, is relatively shallow, and has minimal freshwater input, (Figure 1). Nutrients are supplied to the area primarily from upland runoff and a tidal prism that cycles approximately 51 percent of the estuary's low water volume. However, the residence time for a water particle from the northern area

1. Stevens, N.E., H.R. Ellis and R.B. Stevens. Wasting and Recovery of *Zostera marina* on the Atlantic Coast of the United States. Plant Disease Reporter, 34: 357-362.
2. Thayer, G.W. and H.W. Stuart. 1974. The Bay Scallop makes its Bed of Seagrass. Mar. Fisher. Rev. 36 7: 27-30.
3. Marshall, N. 1960. Studies of the Niantic River, Connecticut with Special Reference to the Bay Scallop, *Argopecten irradians*. Limnol. Oceanogr. 5: 86-105.



of the estuary is approximately 27 days. This is quite long for the small size of the water body, but the restrictive opening and resulting poor flushing characteristics of the outer bay area cause such a drawn out exchange.<sup>4</sup> The reduction in plant biomass induced by the eelgrass disease allowed, within the area, a more thorough flushing and creation of a tidal gyre in the upper reaches. The gyre appears to have acted as a passive maintenance system for larval bay scallops while providing a more thorough mixing of waters in this upper estuary region. Marshall's 1960 discussion of this situation describes the scallops as setting on red algae in the absence of eelgrass within the estuary. Apparently the algae served as a suitable substitute for the destroyed eelgrass. As eelgrass reestablished itself along the coastline it also revegetated the estuary and had, by the early 1960's, extensively reduced the tidally-generated gyre's persistence and mixing capabilities. During this same period bay scallop production suffered a serious decline. Compounding the reduction in numbers of juveniles the area experienced a series of concurrently occurring harsh winters which had caused the almost complete exclusion of bay scallops from the area.<sup>5</sup>

#### INVOLVEMENT

In 1973, a local marine contractor, who had been experimenting with small charge blasting to remove eelgrass, was offered the opportunity of using his technique to remove the grass from a North-South band along the central area of the estuary. The National Marine Fisheries Service's involvement was stimulated by the uniqueness of those efforts and the need for U.S. Department of the Army permits to perform this activity. Our initial concern was that the area selected for defoliation had not been chosen properly and that little coordinated effort was being made to insure environmental protection of the area's resources. A literature review was undertaken in an attempt to begin to remedy these shortcomings. The review revealed that the U.S. Coast Guard Academy had a functional hydraulic model of the area and had performed extensive oceanographic sampling therein. In view of their previous involvement, and although the model had not been verified, the Coast Guard was asked to perform a series of model runs using simulated eelgrass in an attempt to identify the extent of grass removal needed to reestablish the tidal gyre. From those studies it was concluded that an 18 acre band approximately 550 meters long by 122 meters wide should be defoliated if the gyre was to be reestablished with a relatively high level of confidence and persistence.<sup>6</sup>

Concurrent with the Coast Guard's modeling activities, the contractor demonstrated his technique with in situ observations being performed on the detonation of single and multiple charges as well as a weighted length of detonation cord alone. Prior

4. Kollmeyer, R.C. A Study of the Niantic River Estuary, Niantic, Connecticut. Report No. RDCGA18. Office of Research and Development, U.S. Coast Guard Headquarters. Wash., D.C. pp78.
5. Gaucher, T.A. and V. Lee. 1972. Progress Report on the Program to Revitalize the Bay Scallop in the Niantic River Estuary. Prepared for: Waterford-East Lyme Shellfish Commission, Waterford-East Lyme, Connecticut. pp35.
6. Kollmeyer, R.C. 1974-75. Results of Modeling Letters to Regional Director, National Marine Fisheries Service.

to electrically triggering the charges the contractor used even smaller charges (fireworks) in an effort to frighten finfish from the blast area. Those in situ observations, performed immediately after the blasting, attempted to quantify the extent of biological perturbation experienced following each blast technique.

#### DISCUSSION

It was found that the physical impact on the substrate was a small, approximately 45 cm diameter by 15 to 20 cm deep crater. Finfish impacts were quantified by diver and surface collecting efforts. It was noted that some stunned or killed fish, even though equipped with swim bladders, failed to surface as a result of entrapment in the eelgrass fronds and/or heavy predation by attracted American eels (Anguilla rostrata). The 1 to 3 meters of water depth in much of the estuary appears to, along with seasonality, limit the size of the finfish using the area during lower tidal stages. This was verified by the finding that the finfish most impacted during experimental blasting were predominately juvenile (0 or 1 year class) Atlantic silversides (Menidia menidia), rainbow smelt (Osmerus mordax), Sticklebacks (Family GASTEROSTEIDAE), tomcod (Microgadus tomcod), and blackfish (Tautoga onitis).

Initial counts of eelgrass density ranged from 80 to 140 stalks per square meter, with some rockweed (Fucus sp) and the green algae Codium sp interspersed. Our biological appraisal results appear to support those described by the Chesapeake Biological Laboratory (1948), Brown and Smith (1972) and Young (1973).<sup>7,8,9</sup> Relying on the data generated by those investigations and the more recent work of Gaspin (1975), it was concluded that minimization of water depths and areal coverage would do much to minimize the extent of biological perturbation.<sup>10</sup> Follow-up studies on those initial blasts have indicated that most soft-bodied invertebrates within close proximity to the blast crater suffered extensive mortality. It should be noted that this substrate is generally a silt/sand composition, typical of eelgrass stands.<sup>11</sup>

7. \_\_\_\_\_, 1948. Effects of Underwater Explosions on Oysters, Crabs and Fish. Publication No. 70, Chesapeake Biological Laboratory for the State of Maryland, Board of Natural Resources, Dept. of Research and Education. pp43
8. Brown, C.L. and R.H. Smith. 1972. Effects of Underwater Demolition on the Environment in a small tropical marine cove. NUSC Technical Report 4459, Naval Underwater Systems Center. pp18
9. Young, G.A. 1973. Guidelines For Evaluating the Environmental Effects of Underwater Explosion Test. Explosions Research Dept., Underwater Explosions Division, Naval Ordnance Laboratory, White Oak, Silver Spring, Md. pp91
10. Gaspin, J.B. 1975. Experimental Investigations of the Effects of Underwater Explosions on Swimbladder Fish, 1; 1973 Chesapeake Bay Tests. Naval Surface Weapons Center, White Oak, Silver Spring, Md. pp40
11. Marshall, N. and K. Lukas. 1970. Preliminary Observations on the Properties of Bottom Sediments with and without Eelgrass, Zostera marina Cover. In: Proceedings of the National Shellfisheries Assn. 60: 107-111.

The hard shelled invertebrates, such as quohog (Mercenaria mercenaria), channeled whelk (Busycon canaliculatum), bay scallops (Argopectens irradians), and hermit crab (Pagurus sp) were apparently, in both the short and long-term, unaffected by the blasts unless directly beneath or in extremely close proximity to the point of detonation. In that approximately 0.25 square meter area total mortality was observed, but recolonization by opportunistic species was well advanced within a two week period. During the next eight weeks the eelgrass experienced a remarkable orderly dieback. In no instance was the disappearance less than complete along an expanding circle of defoliation. In the case of the single charged detonations the circular defoliation had a final diameter of approximately seven to eight meters. The chain or string detonations created overlapping rings of impact ultimately clearing a rectangular area approximately 40 meters long and 7 to 8 meters wide. The detonation cord created a similar impact but the final zone of influence was limited to approximately 2 to 4 meters of total width. Removal was restricted to eelgrass, with Codium and rockweed thriving in the defoliated areas following eight weeks. The cause of this orderly species-specific defoliation is hypothesized as being the result of a disruption of the cellular structures within the rhizomes. The disruption could also have stimulated biological attacks on these structures. Such conditions represent one possible explanation for the extensiveness of the dieoff, since initial cell rupture did not appear as widespread in area as the dieoffs ultimately covered. As the cellular destruction radiated outward the thallus structures separated in a manner reminiscent of normal exfoliation during the late autumn or winter period. Examination of the rhizomes, however, clearly indicated cell wall failure internally while the epidermal fibers continued to hold the structure together.

To assess the physical and biological impact of the removal, a pre and post activity monitoring program has been established. In situ sampling and a literature review of area finfish resources was also used in an attempt to identify the most appropriate time frame for this activity. The monitoring program relies heavily on water quality parameters as indicators of the effectiveness of the effort. Using temperature data collected at three points concurrently with dissolved oxygen levels it is hoped that following the removal scheduled for October 15th through December 15th, 1976, clear evidence will be obtained regarding the effectiveness of this potentially useful technique.

The restrictions which have been incorporated within the Department of the Army permit for this activity include:

1. Two full years of monitoring
2. Blasting will not encompass more than  $\frac{1}{4}$  acre per shot and only after adequate precautions have been taken.
3. Blasting will occur between October 15th and December 15th and during the lower half of each tidal cycle.

4. Monitoring stations will be at the head and foot of the blast area with a third being in the area of the gyre's appearance.
5. Collections will be at least duplicates of surface and bottom recordings.
6. Results are to be presented at least bi-annually to the involved groups.

From these stipulations it is our hope that the environmental impact of the total effort can be assessed for this site and applied to other locales when or if eelgrass removal is deemed necessary or desirable.

## UNDERWATER EXPLOSION LEVELS EVALUATED BY SWIMMER

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Introduction

In 1969 an underwater test facility was constructed specifically to study biological effects produced by underwater blasts. Experiments were conducted to determine the ranges from small charges that were lethal, injurious, or noninjurious to several species of mammals, birds, and fish. It was reasonably well established that the impulse (integral pdt) in the underwater-blast wave was the parameter that governed biological damage.

The results of one study demonstrated that large animals were not injured at impulse levels of 2 psi·msec (Ref. 1). During that study a swimmer evaluated the 2 psi·msec underwater-blast level. Based on the results of that study, minimum stand-off ranges for unprotected swimmers near underwater explosions were compiled (Ref. 2). Because the 2 psi·msec criterion was based on one set of underwater-blast exposure conditions, namely, swimmer with head above the surface and a small charge at a 10-ft depth of burst, the criterion had definite constraints. The criterion applied to an underwater blast having a simple exponential waveform. It did not apply to distorted, double, or repeated pulses. These pulses could be expected when charges were detonated on the bottom, encountered near reflecting surfaces, or from multiple bursts. The criterion was limited to operations in deep, open water; swimmer within 10 ft of the surface; charges smaller than 50 lb; charge depths of 30 ft or less; and impulse levels of 2 psi·msec with associated peak pressures limited to 50 psi.

The purpose of this report is to present additional data on impulse levels sustained by a swimmer in configurations which removed most of the above constraints. The following conditions were evaluated: underwater blasts from charges larger than 50 lb, underwater blasts from charges fired at depths greater than 30 ft, underwater blasts with high peak pressures, and nonexponential waveforms

1. Richmond, D. R., J. T. Yelverton, and E. R. Fletcher, "Far-Field Underwater-Blast Injuries Produced by Small Charges," Technical Progress Report, DNA-3081T, Department of Defense, Defense Nuclear Agency, Washington, D. C., 1 July 1973.
2. Christian, E. A. and C. J. Aronson, "Minimum Allowable Standoff Ranges for Swimmers Operating Near Underwater Explosions," pp. 1477-1501, Vol. II, Minutes of the Fifteenth Explosives Safety Seminar, 18-20 September 1973, San Francisco, California, Department of Defense Explosives Safety Board, Washington, D. C.

generated by bottom reflections. In addition, reflections near an obstacle were tested. Finally, the effects of underwater explosions on the ears were evaluated.

## Results

Series 1: 1-Lb Charges, 10-Ft Depth of Burst. This series was the initial test to evaluate impulse levels of 2 psi·msec and above from 1-lb charges fired at 10-ft depths of burst. This configuration corresponded to the one commonly used with animal specimens. The peak pressures were on the order of 100 psi. The subject was standing, neck deep, facing the charge, in the southeast corner of the test pond except on Shot 193 when he was treading water beneath the center of the east rigging. The charges were placed along the main axis of the pond that ran from east to west.

The sensations produced by the underwater blasts along with the pressure-time parameters for Series 1 appear in Table 1. Only slight pings were felt at the lower abdomen at impulse levels ranging from 1.9 to 3.0 psi·msec. These levels were tolerable and did not produce any discomfort. At impulse levels above 3 psi·msec, a transient, stinging sensation over the entire front body surface was evident, but was also tolerable.

Series 2: Open Water Tests. These tests were to assess impulse levels of near 2 psi·msec from larger charges in open water with some detonations at greater depths. Six tests were run: three in a large bay where the water was 150 ft deep and the bottom was of muddy organic material, and three in a river where the water was 25 ft deep and the bottom was sandy. As usual, the swimmer was facing the charge, wearing swim trunks only (no life jacket), and was treading water.

Since the depth-of-burst was fairly deep on the first three firings in water 150 ft deep, the peak pressures associated with the impulses were near 100 psi. In the tests conducted in the water 25 ft deep, the peak pressures were near 50-60 psi. Pressure-time patterns were not recorded adjacent to the swimmer during the open water tests, they were calculated.

Only minimal sensations were experienced by the swimmer during the open water tests (Table 1). These were slight pings and thump-like sensations felt at the lower abdomen or pelvic region. There were no sensations felt at the thorax. None of the sensations produced any discomfort.

Series 3: Impulses With High Peak Pressures. These tests were to evaluate the effects of impulses with high peak pressures. High peak pressures were obtained by placing the charges at shallow depths of burst (1 ft). The subject was standing, neck deep, in the southeast corner of the pond and the charges were placed along the main axis of the pond. One exception was on Shot 7E, 9/6/73, when the 0.5-lb charge was 45 ft from the southeast corner on a line toward the northwest corner.

Only a slight thump at the pelvic region was experienced by the subject from a 2.6-lb charge detonated at a range of 81 ft. The impulse was 1.1 psi·msec and the peak pressure was 218 psi with a cut-off time of 0.005 msec, Table 1.

Series 4: Evaluation of Sound from Underwater Blast. These tests were to determine whether or not the sound heard from an underwater-blast wave having an impulse of 2 psi·msec would be acceptable. The plan was to have the swimmer's ears at a 1-ft depth and decrease the range of the charge until an impulse of 2 psi·msec was reached or tinnitus (ringing in the ears) was experienced. The swimmer wore the upper half of a wet suit during these tests.

Preliminary tests involved the use of blasting caps as the explosive source. The subject was beneath the main rigging, upright in the water, facing the charge with ears at a 1-ft depth. The blasting caps were detonated at 10-ft depths to the east of the main rigging. Distances from the charge ranged from 100 to 25 ft with the highest impulse being 1.3 psi·msec with a corresponding peak pressure of 52 psi.

As seen in Table 1, none of the sound levels associated with impulses ranging from 0.28 to 1.3 psi·msec were uncomfortable to the subject. The sounds heard were about the same as from a small pistol, 10 ft away, fired in air.

Next, 0.5-lb pentolite charges were detonated at 10-ft depths with the swimmer at the southeast corner of the pond. The subject faced the charge with ears at a 1-ft depth. The charges were suspended from a line extending from the southeast corner to the northwest corner of the pond.

No tinnitus or discomfort was experienced during the 0.5-lb charge firings. There was never any pressure felt at or inside the subject's ears. The sound was similar to that heard from the blasting caps.

Series 5: Underwater Blast Near a Reflector. Series 5 tests were to obtain information on the effects of underwater blasts near an obstacle or reflecting surface. The reflecting surface was a 4- by 8-ft steel plate, 5/8-in-thick, which was hung from a large raft located toward the west end of the test pond. The plate was perpendicular to the main axis of the pond with its upper margin 6 in above the water surface. Two tests were run. On the first test (41A) the subject was upright in the water, head out of the water, with his right shoulder against the steel plate. On the second test (41B) he was in a supine position, 1 ft from the reflecting plate with head out of the water.

Table 1 shows the results obtained with the subject against and at 1 ft from the reflecting plate with 1-lb charges detonated at a range of 130 ft with a 5-ft depth of burst. As anticipated, only weak pings were felt from the direct wave and its reflection from the reflecting plate. However, a moderate blow at the base of the spine was delivered by the reflection from the bottom or from the west bank of the pond. This was different and more intense than the other sensations experienced on prior tests. This moderate blow to the lower spine was also encountered on the second shot of this series when the subject was horizontal to the surface and 1 ft from the reflecting plate.

Series 6: Wet Suit. Two tests were conducted to determine what influence a wet suit might have on the sensations produced by the underwater blast. The wet suit was 3/8 in. thick. The subject wore both the top and bottom portions of the wet suit. He was standing in

the southeast corner of the pond, neck deep, 115 ft from a 1-lb charge detonated at a 10-ft depth.

Table 1 shows the results obtained when the swimmer, clad in a wet suit, received an impulse of 3 psi·msec. The wet suit reduced the blast sensations from what was felt with swim trunks only. On the first shot, 31A, the lower leg portion of the wet suit was unzipped and a transient sting was felt on the uncovered portion of the body. On the following shot, 31B, the wet suit was zipped closed and there was a noticeable reduction in the effect. The sting sensation was reduced to a weak thump.

Bottom Reflections. The bottom reflections measured on some of the tests were characterized by a finite rise to the peak pressure that occurred about midway in the wave. The peak pressures were considerably less than in the direct shocks but the impulses were larger because the durations were longer by a factor of about 10.

The peak pressures in the reflected waves ranged from between 15 and 38 psi and, in one case, 98 psi. Impulse values recorded at 1-ft depths ranged from 2.5 to 8.7 psi·msec--durations were on the order of tenths of milliseconds. Usually, there were several such bottom reflections on a record, but only the larger ones were selected to compute the impulse.

In most instances, the bottom reflections did not add to the sensations reported in Table 1, an exception was during Series 5.

### Discussion

The present study has provided information that permits the lifting of some of the constraints on the application of the minimal allowable stand-off ranges described in the introduction of this report.

To begin with, the sensations experienced from the detonation of larger charges in deep, open water, including some with burst depths greater than 30 ft, were mild and indistinguishable from those received from small charges in the test pond facility.

Distorted wave shapes from the bottom reflections having impulses well above 2 psi·msec, but with lower peak pressures than in the direct wave, were experienced and found, for the most part, not to produce any discomfort. Many of the pressure-time recordings showed that the bottom reflections were actually a series of repeated pulses. Since the multiple reflections did not produce discomfort, it can be assumed that any individual wave in this series would not produce discomfort.

Double pulses that totaled 2 psi·msec, consisting of incident and reflected waves, were evaluated when the swimmer was against or near an obstacle. This was found to have no undesirable effect.

In regard to the constraint on the peak pressure allowable with an impulse of 2 psi·msec, there was but limited pertinent data from the present study.

The data suggest that peak pressures up to 100 psi, associated with waves having impulses of 2 psi·msec, would be tolerable to a swimmer with head out of the water. The highest peak pressure, with an impulse of 2 psi·msec, evaluated on the ears was 71 psi.

For practical reasons it must be remembered that in order to get low impulses and high peak pressures the charge and swimmer

must be very near the surface. In an actual situation, this becomes dangerous because small differences in the depth of burst or depth of swimmer that cannot be easily controlled would greatly increase the blast effect.

According to the information in Reference 1, one would not expect any lesions from underwater blasts in large animals subjected to impulses of less than 10 psi·msec. Above 10 psi·msec, small areas of contusions on the lining of the gastrointestinal track begin to occur along with petechial lung hemorrhages. The incidence and severity of these lesions increased with greater impulse levels.

Reference 1 also gives information on dog eardrum rupture resulting from 1-lb charges fired at 10-ft depths of burst wherein dogs were tested right-side-on with ears 1 ft deep. There were no eardrums ruptured in three animals at an impulse of 12.4 psi·msec with an associated peak pressure of 215 psi (range, 60 ft). One out of 11 (9%) eardrums were ruptured at an impulse of 19.2 psi·msec and an associated peak pressure of 292 psi (range, 45 ft). There were 8 out of 22 (36%) eardrums ruptured at impulses of 20-23 psi·msec and a peak pressure of 307-328 psi (range, 40 ft).

These data give some indication of the margin between injurious and noninjurious underwater-blast levels and those experienced in the present study which spanned the comfort-discomfort range for unprotected swimmers.

TABLE 1  
UNDERWATER BLAST PARAMETERS EVALUATED BY SWIMMER

Series Date (Shot No.)	Experimental Conditions	Charge Weight, lb	Charge Depth, ft	Water Depth, Ft	Horizontal Range, ft	Peak Pressure, psi	Impulse, psi·msec	Cut-Off Time, msec	Remarks
<b>SERIES I</b> 7-24-73 (192)	Standing SE Corner, Hook Deep	1	10	20 <sup>a</sup> (9)	133	73	1.9	0.027	Slight ping only; no reflections.
7-25-73 (194)	Near Center of Boat Span, Hook Deep			30 (13)	130	88	2.4	0.033	Felt ping and slight abdominal pressure; no reflections.
8-21-73 (14)	Standing SE Corner, Hook Deep			30 (24)	120	84	3.0	0.038	Ping on elick sensation only; no pressure; no reflections.
8-22-73 (13)	Standing SE Corner, Hook Deep			30 (9)	115	101	3.3	0.036	Moderate stings from incident and reflected waves; no pressure.
8-19-73 (10)	Standing SE Corner, Hook Deep			30 (8)	100	118	4.4	0.049	Strong stings from incident and reflected waves; no pressure.
<b>SERIES II</b> 8-15-73 (1)	Treading Water, Hook Deep	1	20	150 (150)	100	37	2.3	0.044	Multiple, very slight pings or clicks.
8-23-73 (2)		8	40	150 (150)	300	37	2.4	0.044	Multiple, very slight pings.
7-26-73 (3)		84	70	150 (150)	870	48	1.8	0.034	Single, very slight ping plus vibrations from vessel.
8-9-73 (1)		100	25	35 (33)	400	111	2.3	0.031	Multiple, very slight pings.
8-9-73 (2)		100	10	35 (23)	450-500	126-112	1.3-0.9	0.009-0.008	Single, mild thump at pelvic region.
8-9-73 (3)		100	25	25 (23)	600	114	2.0	0.018	Single, mild thump, lower abdomen.

TABLE 1 (Continued)  
UNDERWATER BLAST PARAMETERS EVALUATED BY SWIMMER

Series Date (Shot No.)	Experimental Conditions	Charge Weight, Lb	Charge Depth, Ft	Water Depth, Ft	Horizontal Range, Ft	Peak Pressure, psi	Impulse, psi-msec	Cut-Off Time, msec	Remarks
<b>Series B</b>									
8-1-73 (75)	Standing SE Corner, Neck Deep	0.5	1	25 (2)	45	225	2.0	0.009	Strong shock on feet; nothing on trunk. Wore top of wet suit.
8-4-73 (4)		1.0	1	30 (3)	57	180	0.7	0.005	Slight sting on front surface.
8-31-73 (3)		2.0	1	30 (3)	81	214	1.1	0.005	Slight thump in pelvis region.
<b>Series C</b>									
8-1-73 (1)	Upright in Water, Ears 1 Ft Deep	0.0014	10	15 (30)	100	12	0.2	0.042	Exposed left ear. Single sound like the crack of a small pistol fired in air. No tinnitus. Felt nothing else.
8-4-73 (2)				30 (30)	75	10	0.4	0.050	Same as above.
8-4-73 (3)				30 (30)	50	25	0.7	0.003	Same as above.
8-8-73 (1)				30 (30)	45	32	0.0	0.102	Same as above.
8-1-73 (2)				30 (30)	30	44	1.1	0.123	Same as above.
8-3-73 (2)				30 (30)	25	52	1.2	0.154	Sound a little more intense; not uncomfortable; no tinnitus. Felt weak shock on face.
8-8-73 (7A)	Standing SE Corner, Ears 1 Ft Deep	0.5	10	25 (3)	175	48	1.1	0.024	Exposed left ear. Heard two cracks; felt clicks on legs but not at ears; no tinnitus.
8-8-73 (7B)				30 (3)	130	50	1.5	0.028	Same as above.
8-8-73 (7C)				30 (3)	175	71	2.1	0.024	Same as above.
8-8-73 (7D)				30 (3)	125	71	2.1	0.024	Exposed both ears. Same as above.
<b>Series D</b>									
8-1-73 (21A)	Upright in Water, Neck Deep, Right Side Against Reflector Plate	1	8	15 (30)	130	53	0.9	0.060	Slight pings from direct wave and reflection from plate. Moderate blow to lower spine from bottom reflections.
8-8-73 (41B)	Supine, Parallel to Reflector; 1 Ft Deep and 1 Ft from Reflector Plate			15 (30)	130	77 <sup>b</sup> (73)	1.0 (0.60)	0.014 (0.012)	Same as above.
<b>Series E</b>									
8-1-73 (22A)	Standing SE Corner, Neck Deep, Wearing Wet Suit	1	10	30 (15)	150	110	3.0	0.028	Weak thumps front of thighs and abdomen (less than in absence of wet suit). Stings on bare ankles. No other sensations.
8-1-73 (22B)				30 (15)		110	3.0	0.028	Same as above. No stings on covered ankles, only weak thump.

Pressure-time parameters for 1 ft depths:  
<sup>a</sup> water depth at charge (water depth at swimmer)  
<sup>b</sup> direct shock (reflected shock)

NAVAL SURFACE WEAPONS CENTER EXPERIMENTS ON  
FISH DAMAGE BY UNDERWATER EXPLOSIONSby Joel B. Gaspin  
Naval Surface Weapons Center

Here at the Naval Surface Weapons Center (NSWC) we are in the business of detonating underwater explosions. We do this to conduct research on explosion phenomena as well as in the testing of warheads and weapon systems. Of course we are required to consider the adverse environmental effects of this work. One of the major effects is damage done to the local fish population. We have been studying the effects of underwater explosions on swimbladder fish (which include most fish with sport or commercial value) with the aim of predicting and controlling the damage done by our operations. Since becoming involved in this work, we have become aware of other groups, in the private sector as well as state and federal government, who are doing demolition, construction, seismic exploration at sea and various other operations using underwater explosions. These groups share our need to predict and control fish damage. In order to make these predictions, we need to know the pressure waveform put out into the water by the explosion, a bio-response theory to calculate the damage done to a fish by this pressure wave, and a population estimate (species and density). In this talk I will describe the experimental work we have done as part of developing and validating a bio-response theory. In order to validate the theory we need explosion pressure-time data at a given position, an evaluation of the damage done to a fish at that position, and a measure of the swimbladder volume (one of the parameters in the bio-response theory). NSWC, in association with the Chesapeake Biological Laboratory (CBL) of the University of Maryland, performed two large-scale field programs to gather pressure-time and fish damage data (swimbladder volumes were measured in a laboratory effort at CBL).

## Slide 1

The first set of tests was performed in the Summer of 1973 in 150-foot of water in the Chesapeake Bay. Fish were placed in plastic mesh cages at various distances and depths from underwater explosions. The horizontal extent of this setup was up to about 1000 feet. The pressures in the water at each cage position were recorded and each specimen was dissected and its damage evaluated. The swimbladder fish used were white perch and spot, with hogchokers as a non-swimbladder control. Explosive charges from 1 to 70 pounds were used. Eleven shots were fired in this series. The major limitation was that, due to local seasonal conditions, there was insufficient dissolved oxygen to support fish life below about 20-feet. In order to gather deeper data, and to include more species, a second test series was performed in the Spring of 1975.

## Slide 2

The test design was similar to the 1973 series, except that the cage and pressure gage array was configured vertically, with fish placed at depths from 5 to 100-feet, at a single horizontal range from

the charge, on each shot, of 40 to 300 feet. In addition to the species used in the 1973 series, we used toadfish, white catfish, bluefish, croaker, menhaden, blueback herring and striped killifish. Six explosive shots, with charge weights of 1.25 and 70 pounds, were fired in this series.

#### Slide 3

After each shot, the fish specimens were retrieved and dissected, and the damage evaluated in terms of the five numerical categories. Fish damaged at level 2 would be unlikely to survive in the wild, as they would be subject to selective predation. If kept in a holding tank, away from predators, damaged fish which were not killed by the explosion, showed a remarkable ability to survive and heal their wounds.

#### Slide 4

Before we look at a sample of the pressure-time data, let's see what pressure pulses the fish would be exposed to. The first pulse to reach the fish is the direct shock wave, which travels a direct path to the point of observation. Next, the surface reflection of the direct shock arrives. The positive shock wave undergoes a 180° phase shift upon reflection at the water surface, and is transmitted as a negative pressure wave. The third arrival is the bottom reflected shock wave. This may be either positive or negative, depending on bottom type and experimental geometry. In our tests, the bottom reflection was usually negative.

#### Slide 5

Here is the output of one pressure gage recorded on tape at two gain settings. The low-gain record is used to get the details of the direct shock wave. The high-gain record is set to overload on the direct shock wave, and is used to study the details of the lower secondary pressures. On the left of the low-gain record we see the direct shock arrival as a near-instantaneous rise to a peak pressure, followed by a slowly decaying, roughly exponential tail. The surface reflection arrival is marked by an abrupt drop to below ambient hydrostatic pressure. The details of the surface reflected waveform are best studied on the high gain record. After a time, the pressure returns to ambient. Later, the negative bottom reflection arrives. It is the aim of our bio-response theory to relate the observed damage in the test specimens to the details of this type of pressure record through a calculation of the dynamical motion of the swimbladder under explosive pressure loading.

#### Slide 6

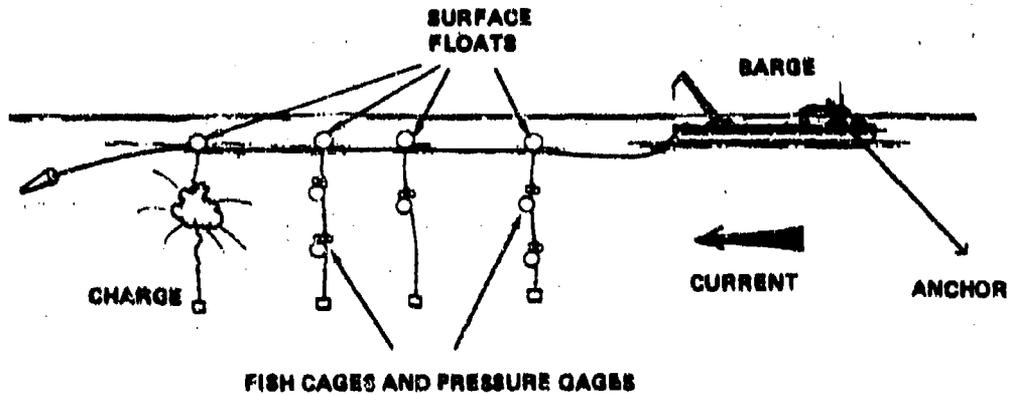
This table summarizes the scope of the data set collected from our two field-test programs. This comprises the results of seventeen explosive shots. The indicated ranges of variables for charge weights and depths, and fish depths and horizontal ranges have been reasonably thoroughly covered. We have about 270 high quality, broad band recordings of the pressure waveforms at fish cage locations. These recordings are either on magnetic tape or oscilloscope camera records. We also have the numerical

evaluation of damage to about 2600 specimens which were dissected. In the next talk, John Goertner will discuss the model of the dynamical motion of the swimbladder, and the correlations between the pressure-time and biological data.

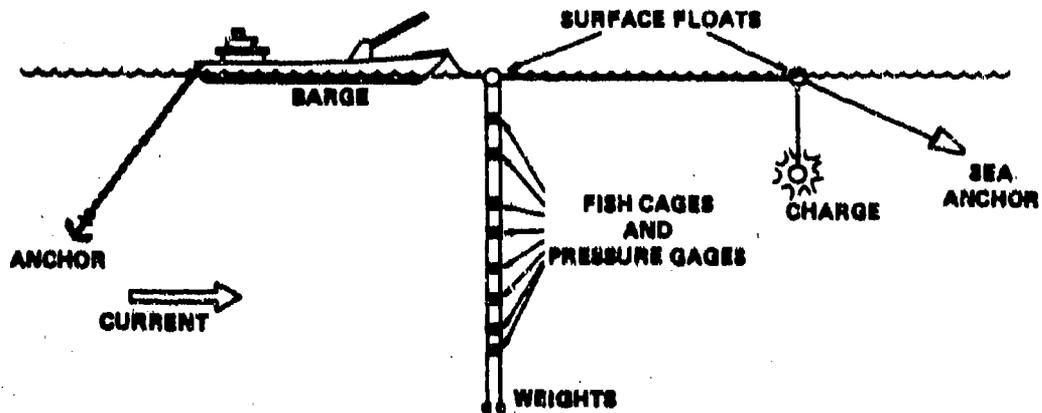
The complete details of these test series are given in the following two references:

Joel B. Gaspin, "Experimental Investigations of the Effects of Underwater Explosions on Swimbladder Fish, I: 1973 Chesapeake Bay Tests," NSWC/WOL/TR 75-58, 20 June 1975.

Joel B. Gaspin, Martin L. Wiley and Craig B. Peters, "Experimental Investigations of the Effects of Underwater Explosions on Swimbladder Fish, II: 1975 Chesapeake Bay Tests," NSWC/WOL/TR 76-61, 21 September 1976



SLIDE 1 1973 CHESAPEAKE BAY TESTS



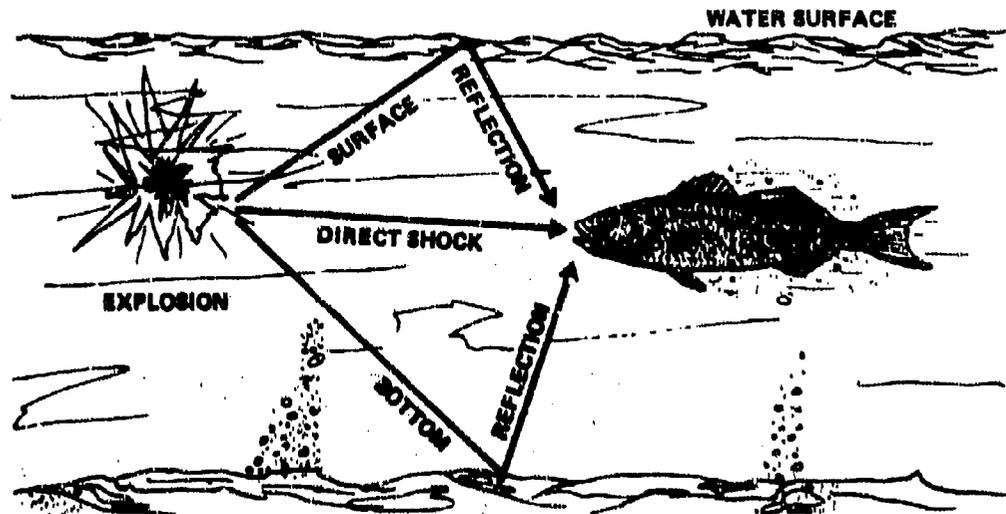
SLIDE 2 1975 CHESAPEAKE BAY TESTS

**DAMAGE LEVELS**

- 0 NO DAMAGE**
- 1 LIGHT HEMORRHAGING**
- 2 WIDESPREAD HEMORRHAGING, SOME KIDNEY DAMAGE**
- 3 BURST SWIM BLADDER, INTERNAL ORGAN DAMAGE, GROSS KIDNEY DAMAGE**
- 4 BODY WALL PARTIALLY BREACHED, BURST SWIM BLADDER, GROSS INTERNAL ORGAN DAMAGE**

**SLIDE 3**

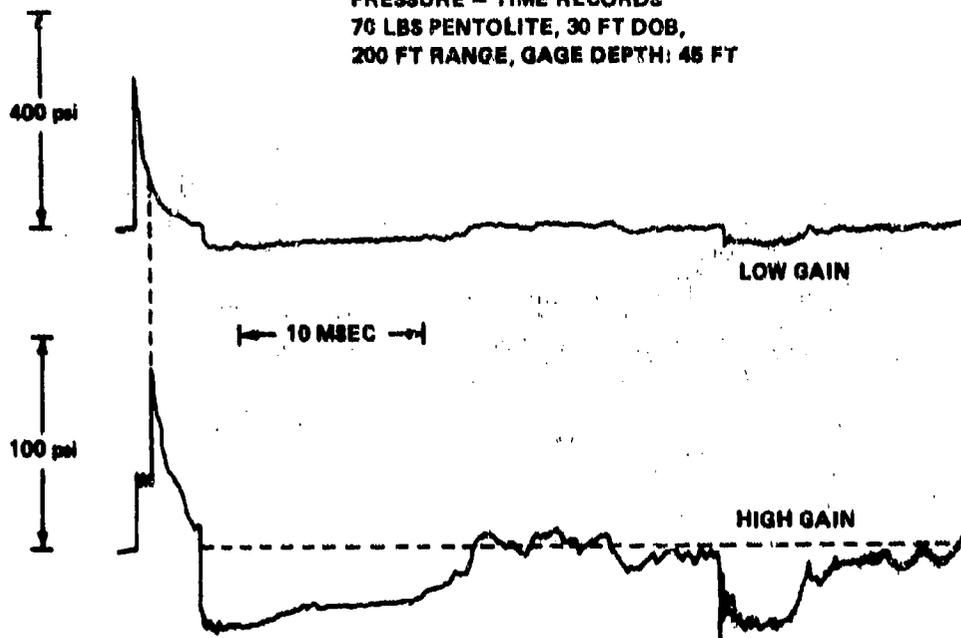
**PRESSURE WAVES**



**SLIDE 4**

NSWC/WOL/TR 77-36

**PRESSURE - TIME RECORDS  
76 LBS PENTOLITE, 30 FT DOB,  
200 FT RANGE, GAGE DEPTH: 45 FT**



SLIDE 5

**DATA SUMMARY**

**CHARGE WEIGHTS: 1 - 72 POUNDS**

**CHARGE DEPTHS: 5 - 70 FEET**

**FISH DEPTHS: 5 - 100 FEET**

**FISH RANGES: 40 - 700 FEET**

**FISH DAMAGE DATA: ~2000 SPECIMENS DISSECTED, 6 SPECIES**

**PRESSURE-TIME DATA: ~270 RECORDS**

SLIDE 6

## DYNAMICAL MODEL FOR EXPLOSION INJURY TO FISH

John F. Coartner  
Naval Surface Weapons Center

To interpret the results of the Chesapeake Bay Tests described in the preceding paper by Gaspin we hypothesized a damage mechanism (Figure 1). This hypothesis was that the fishes' internal injuries can be related to dynamical oscillations of its gas-filled swim bladder in response to the pressure field from the underwater explosion.

In this work we represented the swim bladder (Figure 2) by a spherical bubble of air and calculated its response to the changing outside pressure due to the underwater explosion. This response--a sequence of radial oscillations--was calculated using the classical hydrodynamic theory for inviscid flow. (For these calculations we used the work of Kennard (1943) and Snay and Christian (1952).)

Figure 3 is a sketch showing the air bubble response to a square-step positive pressure followed by a constant negative pressure. The tension or negative pressure is analogous to what happens in the underwater explosion when the rarefaction reflected from the water surface arrives at the fish. The case on the left shows the negative pressure arriving at the time of an expansion causing the minimum amount of radius overshoot at negative pressure. On the right is the case where the negative pressure arrives at the instant of a compression causing the maximum amount of radius overshoot at negative pressure. These two cases are the extremes of this resonance phenomenon. The same resonance phenomenon occurs in underwater explosions with the arrival of the surface reflection.

Figure 4 shows the calculated response to an underwater explosion pressure wave. Below the pressure-time traces, we show the relative sizes of the spherical bubble at its successive extrema. The first compression--radius designated by  $A_{MIN}$ --is always the smallest. The largest radius,  $A_{MAX}$ , generally occurs during the final expansion. From the ratio  $A_{MAX}/A_{MIN}$ , we form the damage parameter,  $100 \text{ LOG}_E (A_{MAX}/A_{MIN})$ , for explosion injury to fish.

Figure 5 was reproduced from Yelverton, Richmond, et al (1975) and was also used to describe the results of their experiments in their paper given at this Conference.

Figure 6 was derived from Figure 5 by making use of the experimentally observed line slopes of 1/3 to define the Impulse Damage Parameter  $= 80 \text{ LOG}_E (I/M^{1/3})$ , where I is the impulse in psi-msec of the positive portion of the pressure wave and M is the mass in grams of the fish.

The value, 80, of the arbitrary constant was calculated to correspond to the value, 100, in the Bladder Oscillation Parameter  $= 100 \text{ LOG}_E (A_{MAX}/A_{MIN})$  the damage parameter refined in Figure 4. The curve is the cumulative logistic probability function with mean and variability parameter fitted to the Lovelace Foundation results shown in Figure 5.

Level 3 injuries consist of severe hemorrhaging throughout the body cavity, gross kidney damage, and the gas bladder is usually burst. Level 3 injury has been shown to correspond to the visible fish-kill on underwater explosion tests; and corresponds approximately to the 24-hr mortality used by the Lovelace Foundation (Figure 7).

Results for 1500 Spot and White Perch from the 1973 and 1975 Chesapeake Bay Explosion Tests are shown plotted in Figure 8 as a function of the Impulse Damage Parameter. Each data point represents the average of from 5 to 20 fish. The plot shows that the Impulse Damage Parameter does not describe this data.

Figure 9 is identical to Figure 8 except that data points where the bladder response calculation showed more than one cycle to have occurred during the positive phase have been removed. Thus, the Impulse Damage Parameter describes those cases where the charge and/or the fish were at shallow enough depth so that only one or less cycles of oscillation occurred before surface reflection. The curve is the averaged curve from Figure 6—the Lovelace Foundation result. It also describes this data.

Figure 10 shows all of the Spot and White Perch level 3 injury data from the Chesapeake Bay Explosion Tests plotted as a function of this calculated damage parameter. The Bladder Oscillation Parameter derived from the dynamical response of the swimbladder describes the complete set of results for Spot and White Perch from these tests.

Figure 11 is identical to Figure 10 except that the White Perch data have been removed leaving only the results for some 700 Spot. The curve shows the Cumulative Logistic Probability Function,

$$p = \frac{1}{1 + \text{EXP}[-0.055(Z-125)]}, \text{ which was fitted analytically to this}$$

data. The curve passes the chi square test of goodness of fit at the 5% significance level. For the present we plan to use this curve to represent all of our Spot and White Perch data from these tests for the purpose of making fish-kill predictions.

Figure 12 is identical to Figure 10 except that the curve fitted to the Spot data (Figure 11) has been added.

When the charge and/or the fish are sufficiently shallow so that one or less cycles of bladder oscillation occur during the positive phase of the pressure wave we may use either or both the Impulse Damage Parameter and the Bladder Oscillation Parameter to describe the kill probability (Figure 13). When the geometry of the explosion is deeper and more than one cycle of oscillation occurs as in Figure 4, only the Bladder Oscillation Parameter applies.

The curves shown in Figure 14 are calculated from the Bladder Oscillation Parameter using the cumulative probability function described in Figure 11. The "Bladder Radius" is the spherical bubble radius used for the dynamical response calculation. The "Rockfish Length" is the

estimated size of a Rockfish (Striped Bass) corresponding to the effective bladder radius.

The calculated curves for the kill probability are a complex function of the fishes' depth in the water column. They also change in a complex manner for different sized fish. The "hump" in the kill-probability curves for the two larger fish is due to the resonance which occurs when the surface reflection arrives during the first compression of the swim bladder. Thus, the surface reflection protects these larger fish at shallow depths, but does them in at the resonance depth.

Figure 15 shows the regions of greater than 10%, 50% and 90% kill predicted by our results for 8.5" White Perch for 70 lbs pentolite at 30 ft depth. This plot gives further evidence of the strong dependence of the kill probability on the fishes' depth. Also, regions of less than 50% kill--since they encompass a tremendous volume of water--make a major contribution to the total number of fish killed by an underwater explosion. In order to predict the total fish-kill it is necessary to sum-up or integrate the product of kill probability and fish density (number of fish per unit volume) over the region surrounding the explosion.

In summary, the kill probability is determined by the dynamical oscillations of the fishes' swim bladder. This dynamical response can be calculated from the underwater explosion pressure-time function.

#### References

- Goertner, J. F., "Dynamical Model for Explosion Injury to Fish", NSWC/WOL/TR in preparation
- Kennard, E. H., 1943, "Radial Motion of Water Surrounding a Sphere of Gas in Relation to Pressure Waves", published in Vol. II of "Underwater Explosion Research", Office of Naval Research, 1950.
- Snay, H. G., and Christian, E. A., 1952, "Underwater Explosion Phenomena: The Parameters of a Non-Migrating Bubble Oscillating in an Incompressible Medium", NAVORD Report 2437
- Yalverton, J. T., et al, 1975, "The Relationship between Fish Size and their Response to Underwater Blast", Lovelace Foundation, DNA Report 3677T.

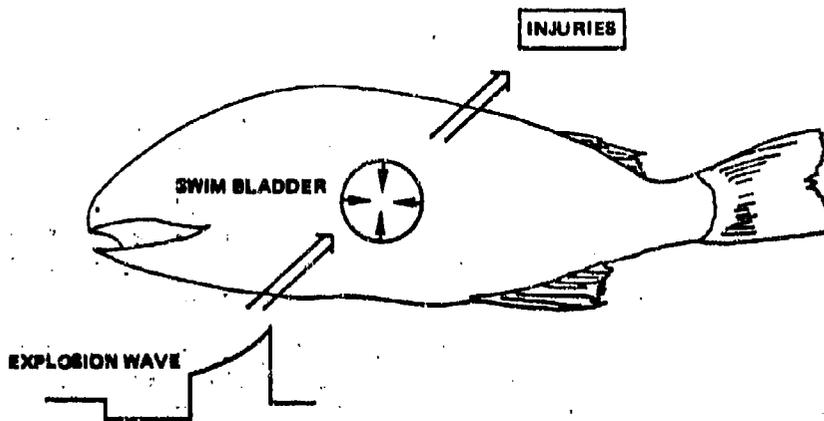


FIG. 1 DAMAGE MECHANISM.

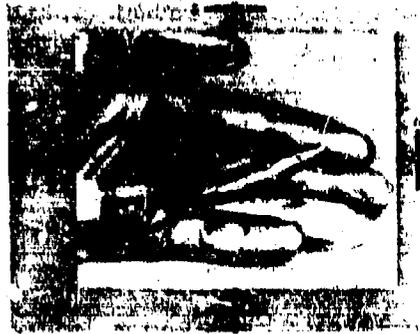


FIG. 2 SWIM BLADDER REMOVED FROM SPOT.

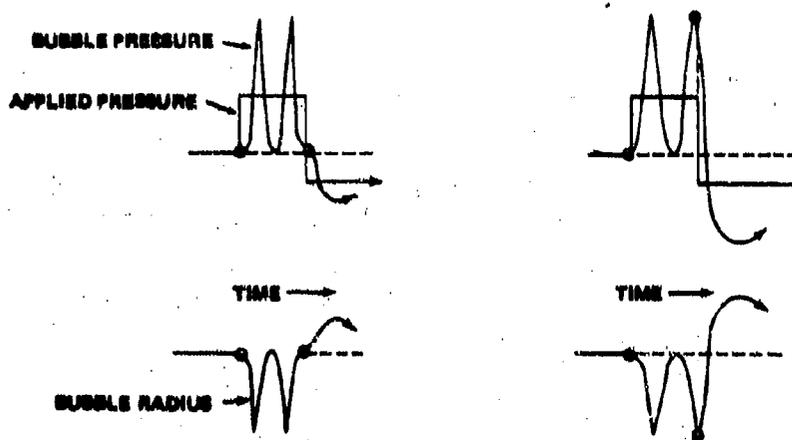


FIG. 3 AIR BUBBLE RESPONSE TO COMPRESSION FOLLOWED BY TENSION.

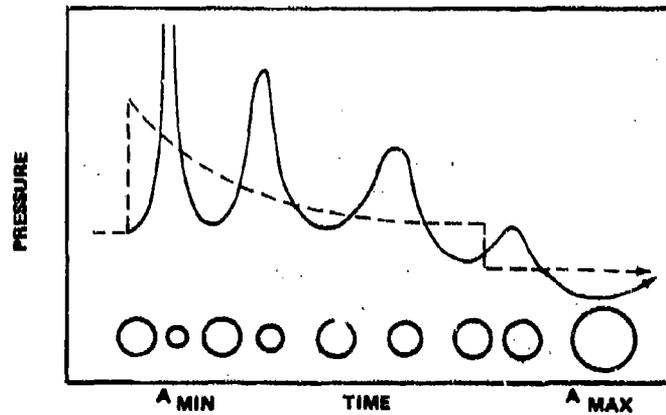


FIG. 4 SWIM BLADDER RESPONSE TO EXPLOSION WAVE.

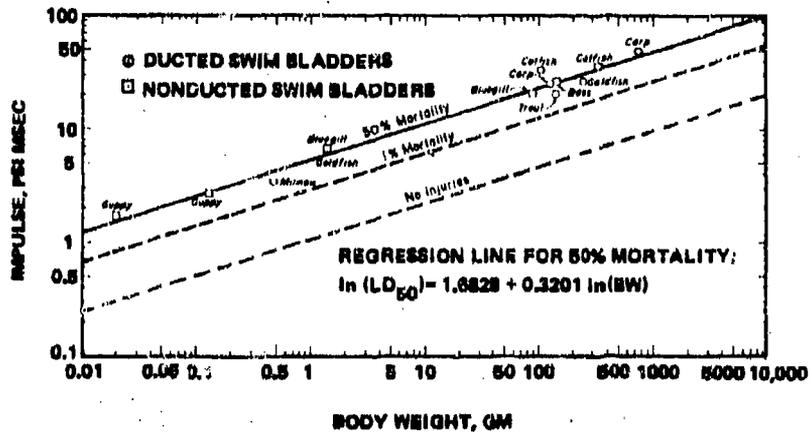


FIG. 5 RESPONSE OF FISH TO UNDERWATER BLAST AS A FUNCTION OF IMPULSE AND BODY WEIGHT.

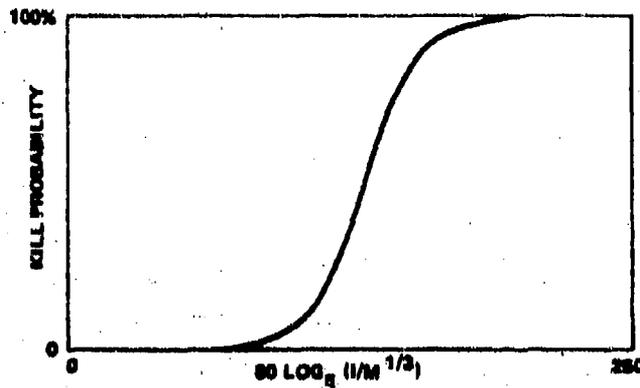
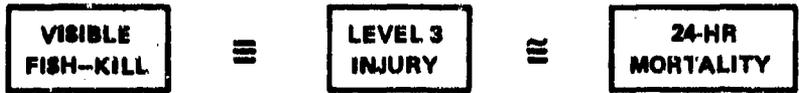


FIG. 6 KILL PROBABILITY AS A FUNCTION OF THE IMPULSE DAMAGE PARAMETER.



- SEVERE HEMORRHAGING
- GROSS KIDNEY DAMAGE
- GAS BLADDER BURST

FIG. 7 DESCRIPTION OF LEVEL 3 INJURY.

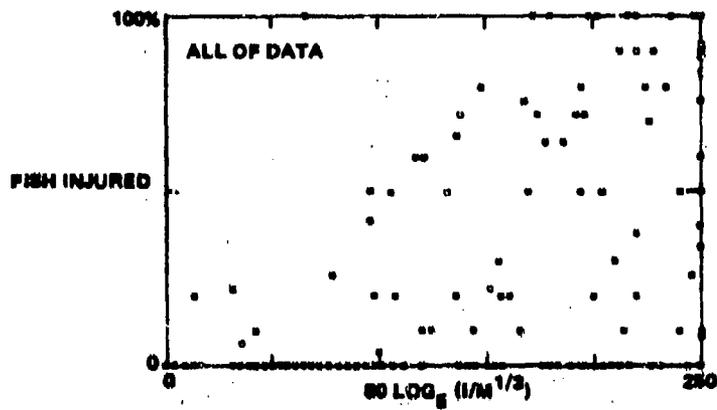


FIG. 8 LEVEL 3 INJURIES VS. IMPULSE DAMAGE PARAMETER.

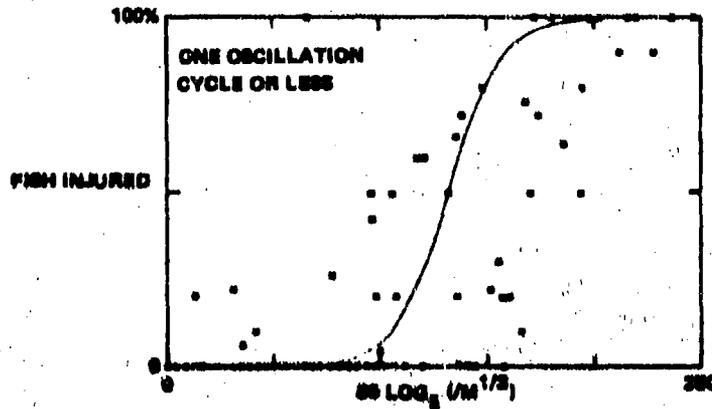


FIG. 9 LEVEL 3 INJURIES VS. IMPULSE DAMAGE PARAMETER.

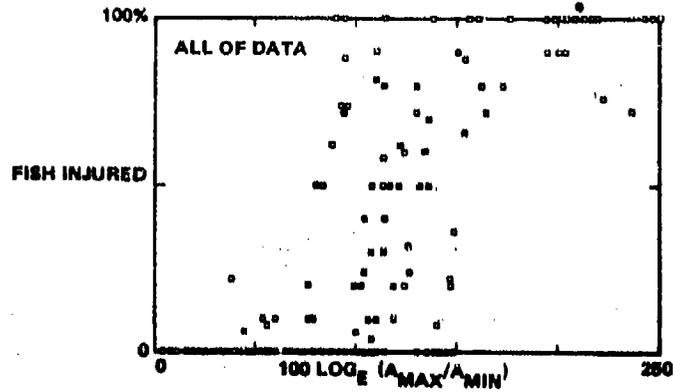


FIG. 10 LEVEL 3 INJURIES VS. BLADDER OSCILLATION PARAMETER.

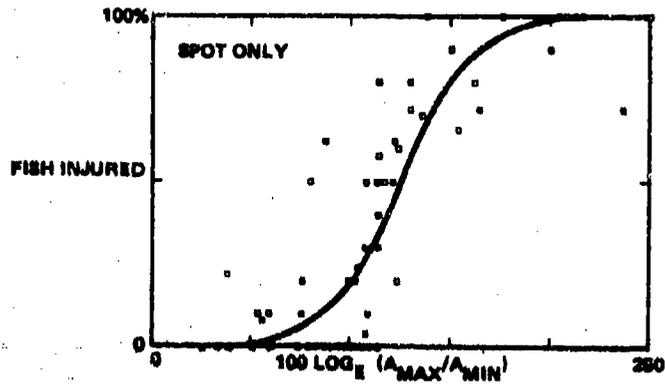


FIG. 11 LEVEL 3 INJURIES VS. BLADDER OSCILLATION PARAMETER.

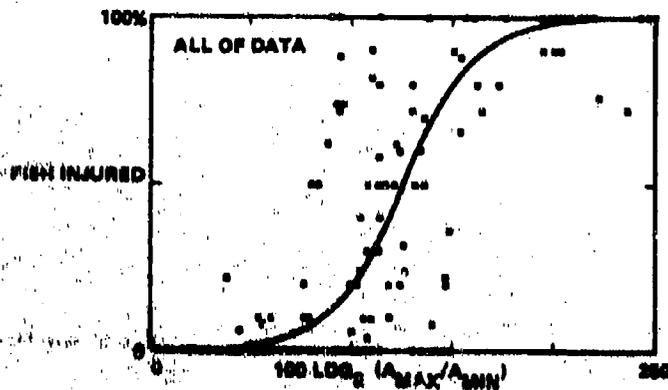


FIG. 12 LEVEL 3 INJURIES VS. BLADDER OSCILLATION PARAMETER.

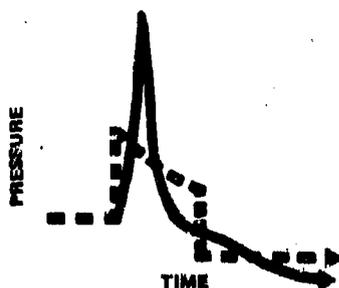


FIG. 13 SWIM BLADDER RESPONSE TO EXPLOSION WAVE OF SHORT DURATION.

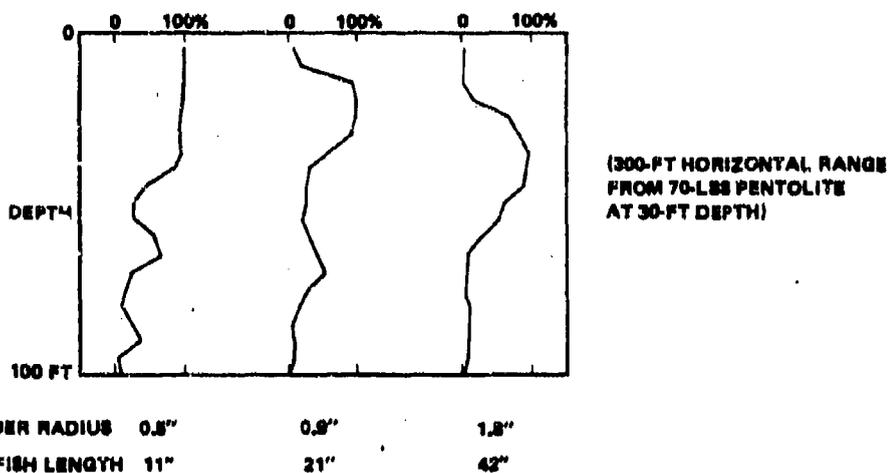


FIG. 14 KILL PROBABILITY AS A FUNCTION OF DEPTH FOR DIFFERENT SIZED SWIM BLADDERS.

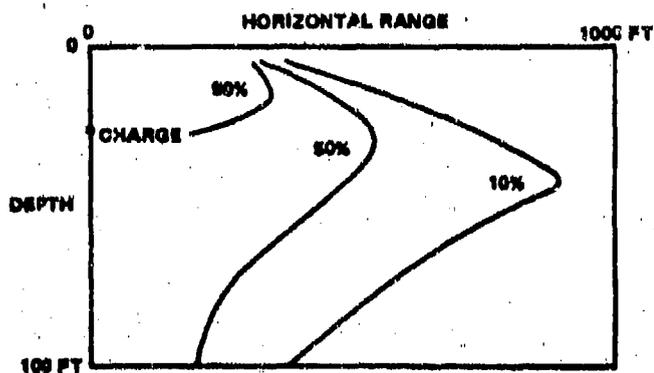


FIG. 15 KILL PROBABILITY CONTOURS: 70 LBS PENTOLITE AT 30 FT DEPTH, 8.5" WHITE PERCH.

The Ability of some Chesapeake Bay Fishes  
to Compensate for Changes in Pressure

Martin L. Wiley and Greig B. Peters

Chesapeake Biological Laboratory, Solomons, Maryland

Experiments on white perch (Morone americana) and spot (Leiostomus xanthurus) were conducted in a pressure chamber to determine the rates at which the fish could equilibrate to changes in hydrostatic pressure by secretion into or resorption of gas from the swimbladder. The equilibration rate of white perch in response to increases in pressure, rises with increasing temperature, but equilibration to reductions in pressure is less dependent on temperature. Spot of all sizes equilibrate to increasing pressure at the same rate, up to the equivalent of 11 meters depth. At greater pressure, the largest spot equilibrate at a greater rate than smaller fish.

In both species, the rate of equilibration falls as the depth (pressure) increases, but the resorption rates in both are independent of depth (Fig. 1). For example, at 18°C, white perch can equilibrate to a descent (secretion of gas) of 3.6 meters in 24 hours, and resorb the amount of gas generated in that time in 3.5 hours. Spot can equilibrate to a descent (secretion of gas) of 11.2 meters in 24 hours and resorb the amount of gas generated in that time in 1 hour.

White perch maintain near near-neutral buoyancy but quickly lose their balance as the pressure is increased to the equivalent of 8 meters depth, soon become exhausted by the struggle to remain upright, and apparently cease to secrete gas into the swimbladder. Spot, in contrast, respond to pressure increases of up to 3 atmospheres (= 30 meters depth) by slightly increasing the rate of pectoral fin beat but show no signs of stress.

Observations on fish caught at various depths by trawl revealed that several estuarine species were generally negatively buoyant and quite variable in the depth to which they were acclimated (Table 1, Figs. 2, 3). Benthic species were the most negatively buoyant, but they exhibited less interspecific variation than the species that remain above the bottom. The activity of fish can have a great influence on the buoyancy they maintain. White perch were the least active during winter and were more neutrally buoyant than in spring or summer. The swimbladder damage exhibited by trawled fish was dependent on both the buoyancy that the fish maintained before capture and the tolerance of the swimbladder to excessive internal pressures (Figs. 4, 5). Both of these conditions appear to be species specific. The species sampled are not expected to suffer swimbladder damage when collected from depths of 9 meters or less. Frequency of damage to fish caught at greater depths is dependent on the species and the depth at which individuals had recently been acclimated.

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Table 1. Species of fish for which buoyancy was determined. - means that the species was always negatively buoyant, ± indicates that the species was usually neutrally buoyant, and ? denotes species for which insufficient data were obtained to be sure how to characterize them.

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<u>Species</u>	<u>Buoyancy</u>
Spot, <u>Leiostomus xanthurus</u>	-
Atlantic croaker, <u>Micropogon undulatus</u>	-
Weakfish, <u>Cynoscion regalis</u>	-
Striped killifish, <u>Fundulus majalis</u>	-
Oyster toadfish, <u>Opsanus tau</u>	-
White catfish, <u>Ictalurus catus</u>	-
Brown bullhead, <u>Ictalurus nebulosus</u>	-

Table 1 (Cont'd.)

<u>Species</u>	<u>Buoyancy</u>
Atlantic silverside, <u>Menidia menidia</u>	-
Bluefish, <u>Fomatomus saltatrix</u>	-
Bay anchovy, <u>Anchoa mitchilli</u>	-
Spotted hake, <u>Urophycis regius</u>	-
Black sea bass, <u>Centropristis striata</u>	-
Pinfish, <u>Lagodon rhomboides</u>	-
Silver perch, <u>Bairdiella chrysur</u>	-?
Atlantic menhaden, <u>Brevoortia tyrannus</u>	+
Blueback herring, <u>Alosa aestivalis</u>	+
White perch, <u>Morone americana</u>	+
Mummichog, <u>Fundulus heteroclitus</u>	+
Sheepshead minnow, <u>Cyprinodon variegatus</u>	+
Red hake, <u>Urophycis chuss</u>	!+

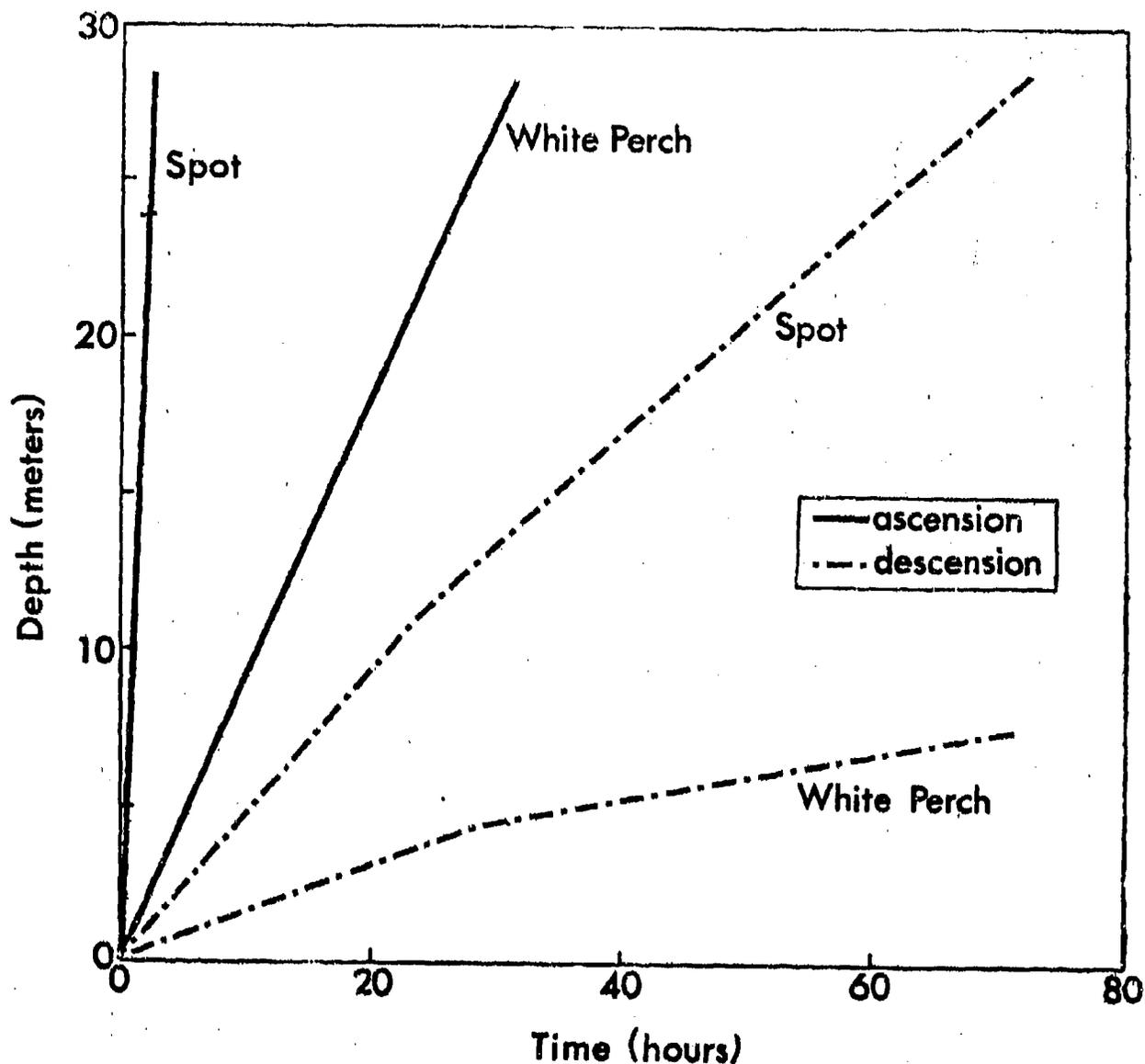


Fig. 1. Predicted compensation curves for white perch and spot weighing 82 g at an acclimation temperature of 18°C. Both ascent and descent curves are shown. Zero coincides to the surface for the descent curve, but because equilibration to negative pressure is independent of depth, the ascent curve may be interpreted as distance from any initial depth.

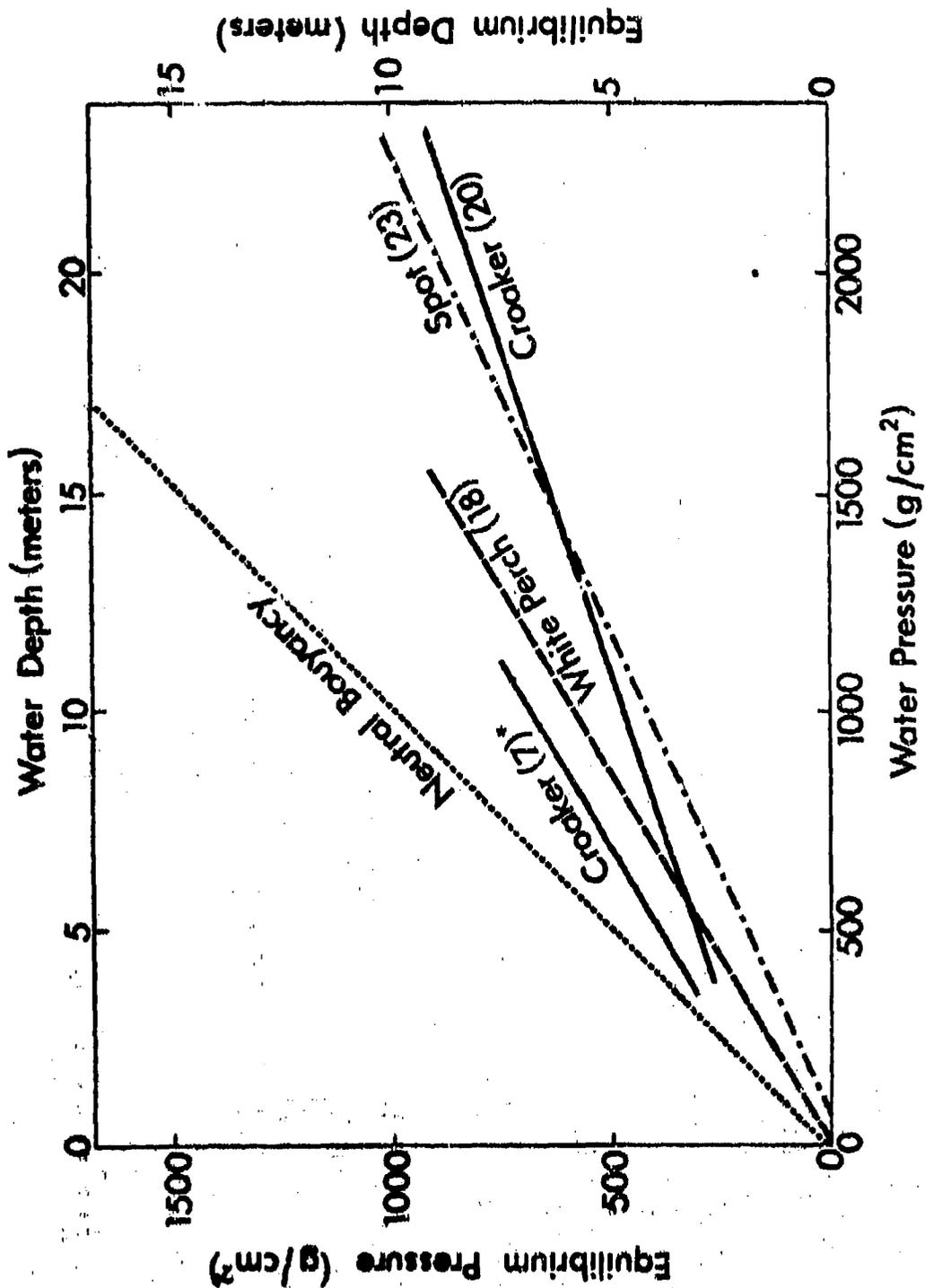


Fig. 2. Least squares regressions of equilibrium pressures of white perch, spot, and Atlantic croaker as a function of the pressure at depth of capture. Lines are calculated from sample means. The line marked by \* is calculated from samples of Atlantic croakers which contained no damaged swimbladders. Number of samples is in parentheses. Correlation coefficients (r) for croaker, croaker\*, white perch, and spot regression lines are 0.763, 0.983, 0.844, and 0.733, respectively.

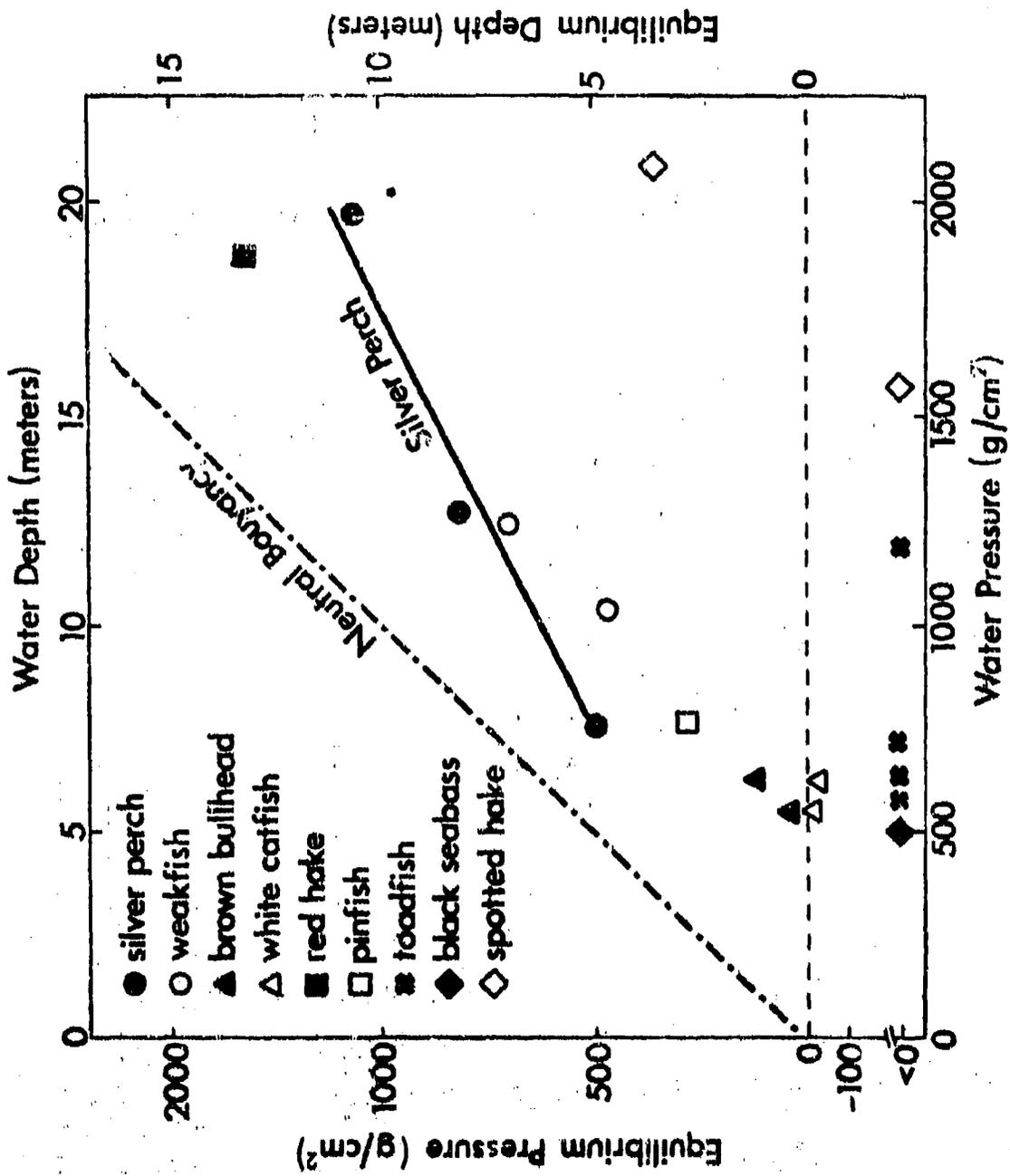


Fig. 3. Equilibrium pressure of several fish species as a function of the pressure at depth of collection. Each point represents a group mean.  $r = 0.992$  for the silver perch regression line.

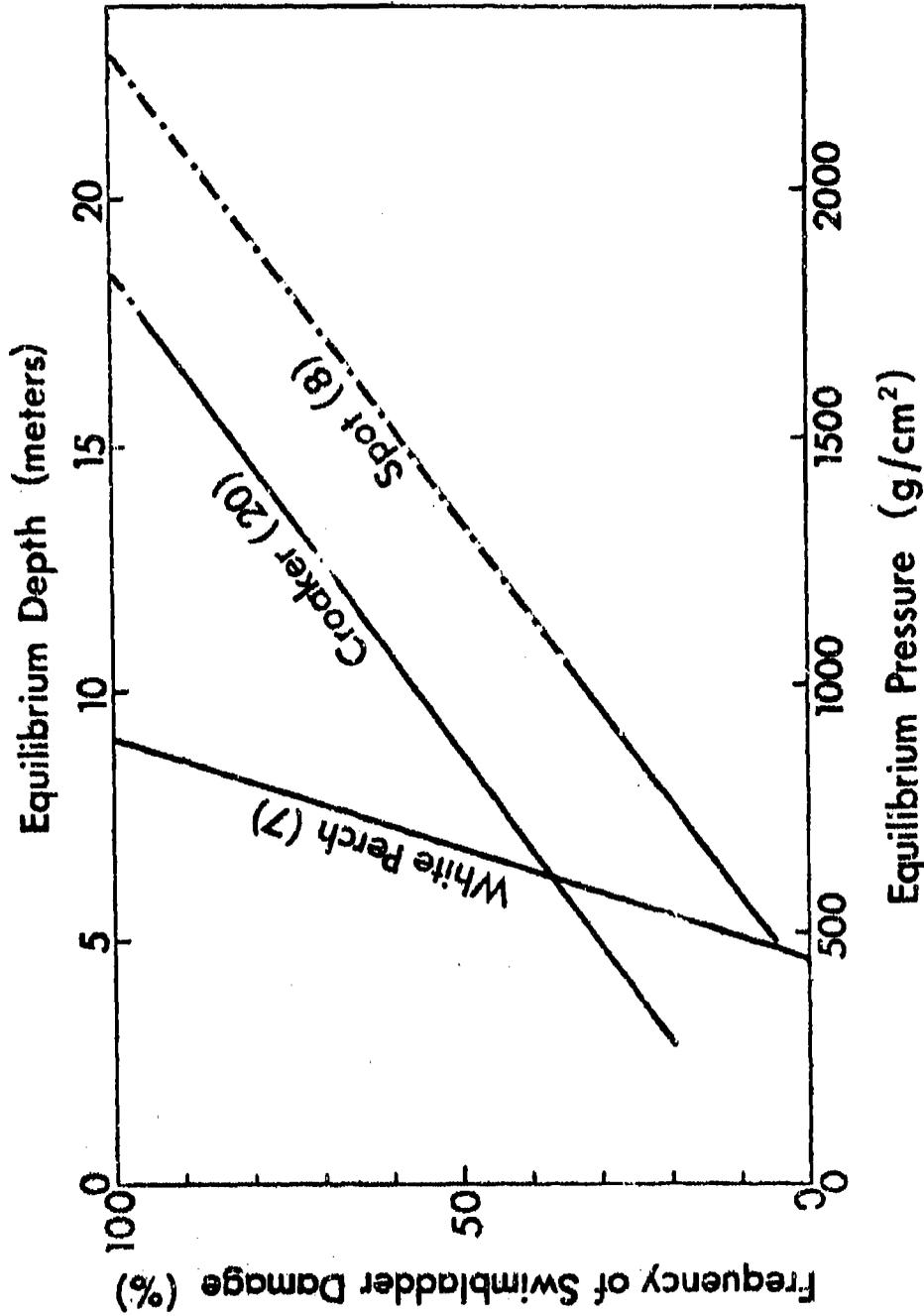


Fig. 4. Frequency (in percent) of swimbladder damage as a function of the equilibrium pressure that was maintained by trawl-captured white perch, spot, and Atlantic croaker. Regression lines are calculated from sample means (number of samples in parentheses). Correlation coefficients (r) are 0.984 for white perch, 0.573 for Atlantic croaker, and 0.621 for spot. Dashed segments of the lines are interpolations beyond the actual pressure readings.

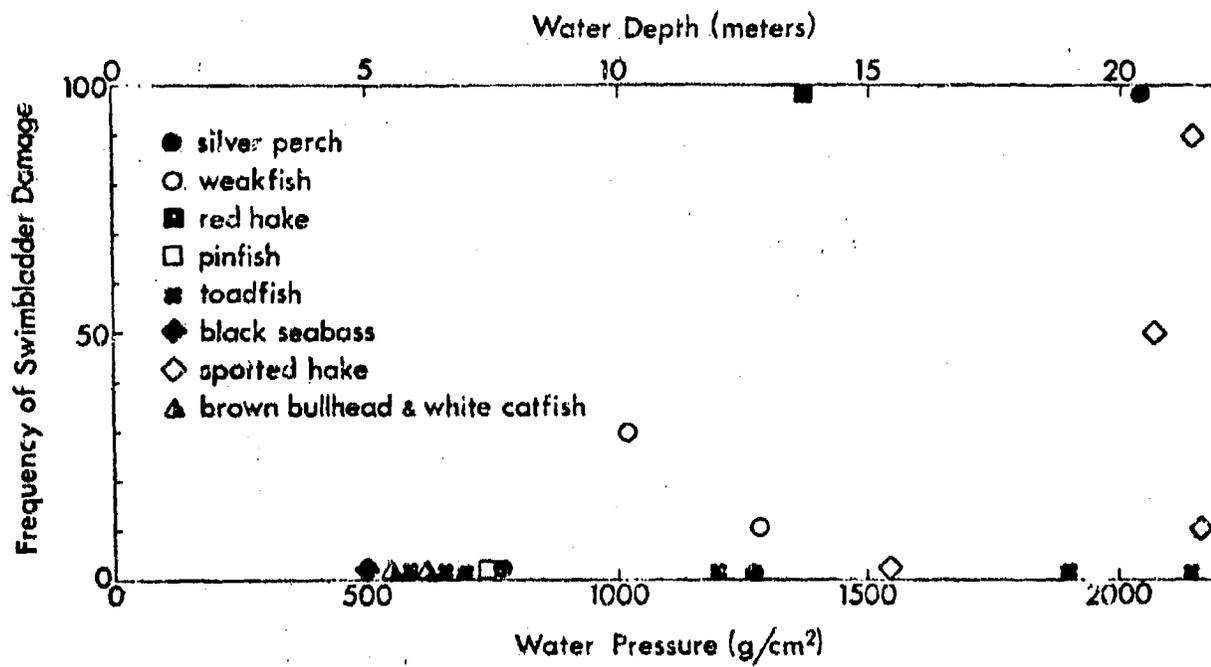


Fig. 5. Frequency (in percent) of swimbladder damage for several fish species as a function of the pressure at the depth of collection. Each point represents a group mean.

ROYAL ARMAMENT RESEARCH AND DEVELOPMENT ESTABLISHMENT  
FORT HALSTED, SEVENOAKS, KENT, UK.

The Reduction of Noise Levels from Explosive Test Facilities Using Aqueous Foams

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Abstract

The test firing of explosive charges can apply a particular strain to people living close to a munition research facility because of the noise of explosions and their unexpected and transient character. Recent investigations have shown that substantial reductions in both noise and blast can be achieved by using high expansion aqueous foam as an explosion muffler.

This paper describes experiments aimed at comparing external noise levels when foam was used to muffle explosions in two RARDE firing chambers with normal levels. Sound level measurements were made on the dB(A) scale to give as close an approximation to the response of the human ear as possible. The foam, with an expansion ratio of about 300:1, was produced by a Turbex generator supplied by Angus Fire Armour Ltd. To provide base line data, spherical explosive charges weighing between 0.02Kg and 0.34Kg were detonated in the centre of each chamber. A second series of firings were then carried out with explosive charges covered to a depth of 2.5 metres with high expansion aqueous foam. In the smaller chamber charge weights ranged from 0.05Kg to 0.5Kg and in the larger from 0.05Kg to 2.5Kg. In both cases 60 m<sup>3</sup> of foam was required to fill the chamber to a depth of 2.5 metres and this was generated in 30 seconds. Every charge fired, irrespective of weight collapsed the foam entirely, leaving only a small amount of foam and puddles of water. The additional time required when using foam over that normally taken to set up and detonate the charge was 5 minutes. In the event of a misfire it was demonstrated that 60 m<sup>3</sup> of foam would be collapsed in 10 minutes using 10 litres of 5% aqueous solution of an anti-foam agent dispensed from a knapsack-mounted garden spray.

Impulsive noise levels measured with the monitoring equipment were plotted for charges detonated in air and under foam. Comparison of the curves showed that firing the charges under 2.5 metres of foam reduced noise levels by at least 20 dB(A) over the full range of charge weights examined. This represents an approximate 10-fold reduction in sound pressure.

The cost of the foam generating equipment used in these trials was £500 and the cost of the foam compound was about £2 for each firing. Provided a commercially produced fire-fighting compound is used there should be no health hazard and in the UK a Home Office specification precludes the use of a material which is not completely biodegradable.

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**SUMMARY**

Substantial noise reduction from explosive charges fired in bomb chamber test facilities has been achieved by covering the charges with high expansion aqueous foam produced by a commercially available fire-fighting generator. The capital cost and running expenses of the equipment contribute little to the expense of firing. The 10 to 20 fold reduction of noise level is achieved at the cost of a few minutes extra time while the foam is emplaced, without any health hazard and with little damage to the environment. In the event of a misfire the foam may be removed safely and swiftly with the aid of a commercially available spray.

## 1. INTRODUCTION

Increasing emphasis is being placed on the reduction of 'noise pollution' in the environment. Noise in this context can be defined as unwanted sound, but the degree of 'unwantedness' is, however, a complex relationship between the make up of the sound and its psychological and physiological effects. These effects may range from moderate annoyance to impairment of hearing from sustained exposure to high noise levels. Environmental quietness is not only desirable solely from the annoyance and health viewpoint, but also from an economic stand-point. In general, people do not like to live in the immediate vicinity of an airport, or close to roads with heavy traffic and this can be reflected in the value of adjacent property.

The test firing of explosive charges can also apply a particular strain to people living close to a munition research facility because of the noise of explosions and their unexpected and transient character. Further, the damage to property which may be caused by overpressure effects is a constant worry.

Public opinion has in general led to this Establishment reducing the weight of explosive charges fired in bomb chambers. For instance, in Woolwich a chamber capable of withstanding the detonation of 3.5 Kg charges is currently only used for 0.3 Kg charges. Resort has been made to fixing larger charges in remote areas which is not cost effective.

Recently a considerable amount of work has been done in evaluating high expansion aqueous foam as an explosion muffler. Substantial reductions in both blast and noise levels have been observed. This paper describes some experiments which were aimed at comparing the noise levels obtained when foam was used to muffle explosions in two RARDE bomb chambers with the levels without foam.

## 2. ACOUSTIC NOISE MEASUREMENTS

The quantity normally measured when dealing with acoustic noise is the Root Mean Square Sound Pressure. The average adult human ear can detect sounds corresponding to a lower threshold pressure of  $2 \times 10^{-4}$   $\mu\text{bar}$  ( $2 \times 10^{-5} \text{ Nm}^{-2}$ ) at a frequency of 1000Hz. At pressures in excess of about 1000  $\mu\text{bar}$  ( $100 \text{ Nm}^{-2}$ ) perception is accompanied by physical pain and severe physiological damage can result from prolonged exposure to sound intensities of this order. As sound power is related to the square of the sound pressure, and the hearing mechanism responds to changes in sound power in a relative rather than an absolute manner, a convenient scale for sound measurement is the decibel (db) scale, defined as

$$\text{Sound level (db)} = 10 \log \left( \frac{p^2}{p_1^2} \right) = 20 \log \frac{p}{p_1}$$

where  $p$  is the sound pressure being measured and  $p_1$  the reference sound pressure (normally taken to be  $2 \times 10^{-4}$   $\mu\text{bar}$ ). Table 1 shows the relationship between sound pressure, sound level and commonly encountered environmental noise conditions.

## 3. NOISE CRITERIA

While it is possible to define absolutely the concept of loudness of a sound, the notion of annoyance is more difficult to specify. Psychoacoustical experiments however, suggest that a noise becomes more annoying as its intensity increases and

that high frequency noise is more disturbing than that of low frequency. Thus, a meter to measure noise as opposed to sound must take account of both the loudness and the frequency range of the noise. This is done most simply by using the internationally accepted frequency weighting networks; designated A, B or C, in the noise measuring instrument. These frequency weighting networks ensure that the sound level meter is more affected by certain designated frequency ranges, and it is generally accepted that frequency network A gives a fair approximation to the response of the human ear. Measurements of sound pressure levels determined using frequency weighting network A are designated dB(A).

#### 4. EXPERIMENTAL

##### 4.1 Description of test chambers

Two different firing chambers were used. The small chamber, whose ground plan and immediate surroundings are shown in Fig.1, is built from reinforced concrete and is totally enclosed except for an aperture 2 metres wide and 2.2 metres high at one end. The blast from an explosive firing vents through this aperture and is deflected by a wall. The explosive limit is 0.34 Kg (0.75 lb).

The large chamber (Fig.2) is built of reinforced concrete with the upper portion formed from overlapping air-spaced girders. This chamber was built for an explosive limit of 3.62 Kg (8 lbs) but in recent years this has been reduced to 0.34 Kg (0.75 lb) because of complaints from a neighbouring industrial estate.

The positions of the noise measuring microphone relative to the test chambers are shown by an X in Figs.1 and 2.

##### 4.2 Noise measurement of firings without muffling

Spherical plastic explosive (PE4) charges weighing between 0.02 Kg and 0.34 Kg were detonated in the centre of each chamber. In the small chamber (Fig.1) the charges were placed on a steel plate on the floor while charges fired in the large chamber (Fig.2) were de-coupled 0.25 m from the floor by suspending them from the roof.

The noise generated was, in each case, measured by a Bruel & Kjaer Impulse Sound Level meter, Type 2607 using a 25.4 mm condenser microphone set to record the maximum transient impulsive sound level with the 'A' frequency weighting network.

##### 4.3 Noise measurement of foam muffled firings

A second series of firings were carried out with the explosive charges covered to a depth of 2.5 metres with high expansion aqueous foam. In the small chamber charge weights ranged from 0.05 Kg to 0.5 Kg, in the larger one between 0.05 Kg and 2.5 Kg.

The foam was produced from a Turbex generator supplied by Angus Fire Armour Ltd. and was found to have an expansion ratio of around 300:1. Each chamber was filled to the required depth by sealing the entrance with polythene sheeting leaving a one metre gap at the bottom. This gap enabled a 1.2 metre diameter polythene ducting from the generator to be introduced diagonally through the entrance to the chamber (Fig.3). As soon as the foam was generated the ducting inflated, sealing against the polythene sheeting and preventing the escape of foam under the plastic (Fig.3). In both cases about 60m<sup>3</sup> of foam was required to fill the chamber to a

depth of 2½ metres and this was generated in about 30 seconds. The additional time required using foam over that normally taken to set up and detonate the charge was about 5 minutes.

Every charge fired, irrespective of weight, collapsed the foam entirely, leaving little foam and puddles of water. Very little water and no foam remained on the chamber walls and ceiling.

High expansion foam has a sufficiently high electrical resistance to be considered non-conducting and there was no indication of the foam shorting out the electrical firing systems used in the trials.

In the event of a misfire it would be necessary to clear the foam from the vicinity of the charge. It has been demonstrated that 60m<sup>3</sup> of foam can be collapsed in under 10 minutes using 10 litres of a 5% aqueous solution of an antifoam agent such as Nalfluc N71D5 dispensed from a knapsack-mounted garden spray.

## 5. RESULTS

Impulsive noise levels were measured with the monitoring equipment at the points marked X in Figs.1 and 2 for charges detonated in air and under foam. The data are plotted in Figs.4 and 5. Comparison of the 2 curves in Fig.4 shows that firing charges under 2.5 metres of foam reduced noise levels by at least 20 dB over the full range of charge weights examined. Fig.5 shows a similar reduction for the larger chamber using 2.5 m of foam.

A clear picture of the reduction in sound pressure achieved can be seen in Figs.6 and 7, where this parameter has been plotted for varying charge weights with and without foam. In both cases, the sound pressure increased much more slowly with charge weight when the charge is covered with foam. It is particularly interesting to compare the sound pressure from 500 gms of explosive detonated under foam with that from 25 gms of explosive detonated in the open air in the smaller chamber. The charge overlaid with foam gives a sound pressure only 1/5th of that from the unmuffled charge even though the charge weight involved is 20 times higher.

## 6. DISCUSSION

These results clearly indicate that foam can be used to reduce the noise level from the explosive charge weights normally used in the HARDE bomb chambers. Moreover, the option is available to increase the explosive charge weight that might be fired in any test facility without exceeding an agreed acceptable noise level. Without decoupling the charge from the foam muffler this technique would not, of course, be suitable for experiments involving high speed photography.

The additional time required to generate enough foam to carry out trials muffled in this way is hardly significant. The bomb chamber was filled in less than 30 seconds. In most cases, the preparations required to prevent the foam from flowing out of the entrance of the chamber will cause the major increase in time. This will vary with the design of the chamber but the polythene sheeting is largely undamaged by the foam muffled explosion and if necessary could be replaced in 2 or 3 minutes. The total additional preparation time for the firings with foam detailed in this memorandum averaged 5 to 10 minutes. Most of the foam disappeared during the firing and very little was left to interfere with later firings.

The cost of foam generating equipment varies according to its mode of operation and the rate of foam production. The Angus Fire Armour Turbex generator could be installed as a fixture; it is powered solely by water pressure. A single foam generator produces about 200m<sup>3</sup>/min of foam using approximately 300 litres/min of water and 5 litres/min of foam compound. The generator costs £500 and the foam compound used about £2.00 for 5 litres.

The most inconvenient characteristic from the operators standpoint is the fact that the wet conditions can lead to inconvenience but even this can be minimised by suitable clothing.

There should be no health hazard provided a commercially produced fire-fighting compound is used which meets Home Office Fire Departments' specification JCDD/28. In fact, in addition to noise and blast reduction, the foam seemed to reduce the level of fumes from the detonation of the charges. After an explosion most of the solids comprising the smoke from the charge, eg carbon, were trapped in the water layer under the low expansion foam left on the chamber floor.

The Home Office specification also precludes the use of any material in British foam compounds other than those which are completely biodegradable. The diluted foam compound can, therefore, be adequately broken down in a normal sewage treatment works and does not present a pollution problem.

#### 7. OTHER USES OF FOAM FOR NOISE AND BLAST REDUCTION

Muffling an explosion by means of aqueous foam seems to have little or no effect on the performance of a charge in contact with a target. This suggests that foam muffling may have wider applications. Many more of the techniques for using explosives for cutting, boring and welding etc could be used closer to public places if their noise and extraneous blast effects could be reduced. However, it is important to remember that foam has no effect on decreasing the velocity of fragments from an explosion.

#### 8. CONCLUSIONS

High expansion aqueous foam produced by commercially available fire-fighting generators has been shown to reduce the noise levels from explosive charges fired in bomb chamber test facilities by 20 dB over a range of charge weights up to 2.5 Kg. This represents an approximate 10-fold reduction in sound pressure. The initial capital cost of equipment is about £500, but the additional cost for each foam covered firing from expendable items is only about £2. After the firing most of the foam is evaporated apart from a thin layer of low expansion foam on the floor of the facility.

SOUND PRESSURE IN dbf	SOUND LEVEL IN db	ENVIRONMENTAL CONDITIONS
1 mber	140	THRESHOLD OF PAIN
100 $\mu$ ber	130	PNEUMATIC DRILL
10 $\mu$ ber	120	LOUD AUTOMOBILE HORN (DISTANCE 1m)
1 $\mu$ ber	110	
	100	
	90	INSIDE A MOTOR BUS
	80	
	70	CONVERSATIONAL SPEECH
0.1 $\mu$ ber	60	
0.01 $\mu$ ber	50	LIVING ROOM, SUBURBAN AREA
	40	
	30	BEDROOM AT NIGHT
0.001 $\mu$ ber	20	
	10	
0.0002 $\mu$ ber	0	THRESHOLD OF HEARING

TABLE 1 THE RELATIONSHIP BETWEEN SOUND PRESSURE,  
DECIBELS AND SOME COMMONLY ENCOUNTERED  
ENVIRONMENTAL NOISE CONDITIONS.

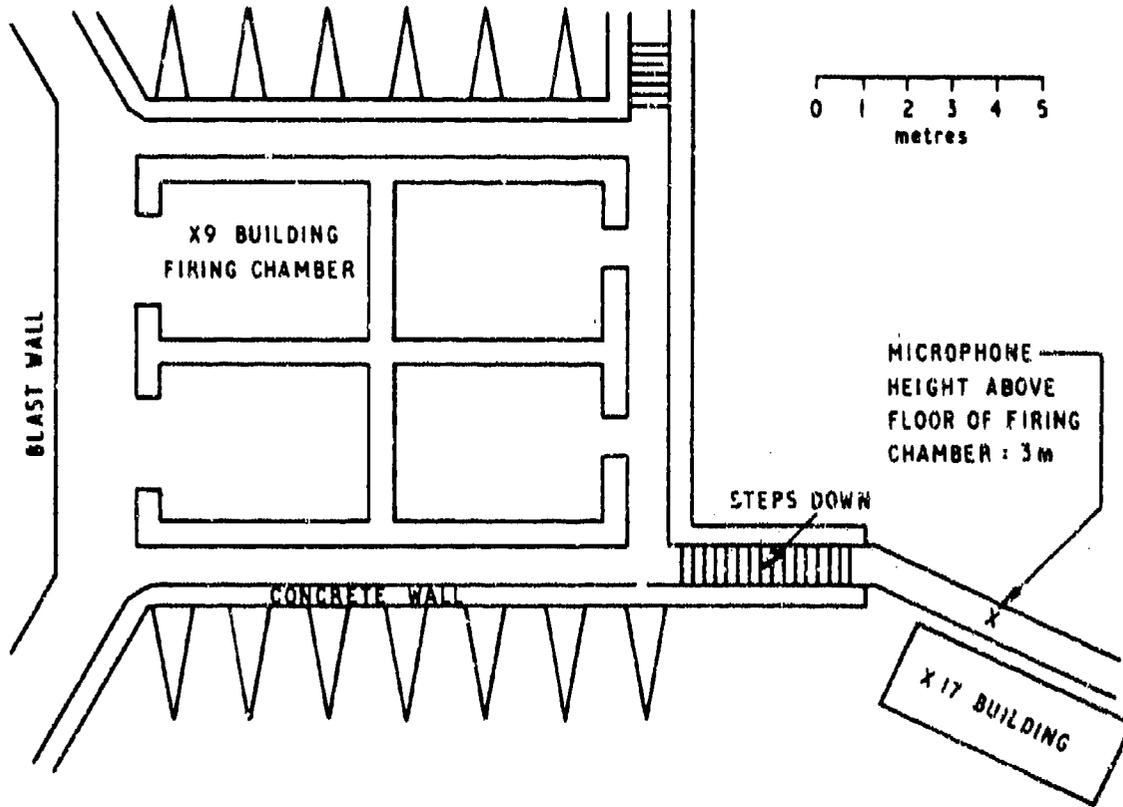


FIG. 1 PLAN OF SMALL FIRING CHAMBER AND MICROPHONE POSITION FOR SOUND LEVEL MEASUREMENTS

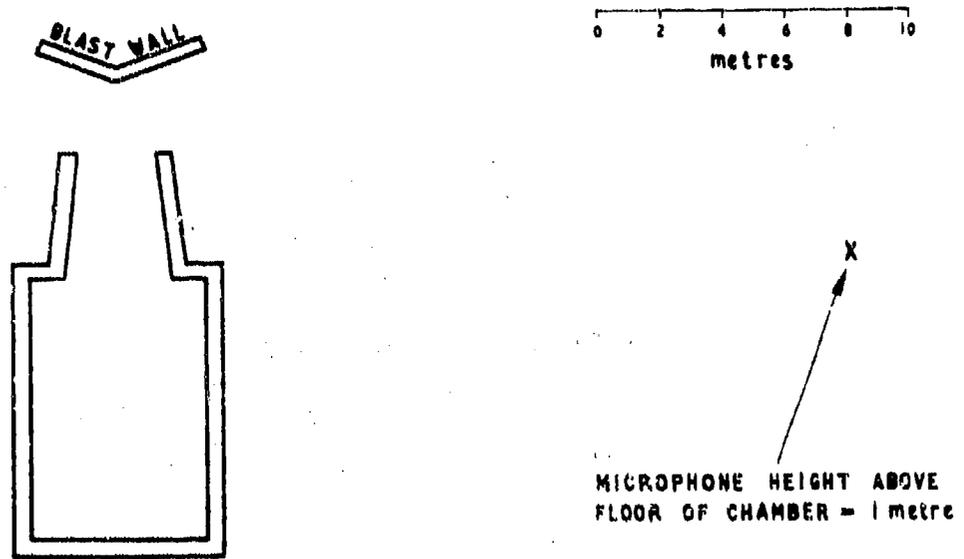


FIG. 2 PLAN OF LARGE CHAMBER AND MICROPHONE POSITION  
FOR SOUND LEVEL MEASUREMENTS



FIG. 3(a) ENTRANCE TO SMALL CHAMBER  
BEFORE FILLING WITH FOAM

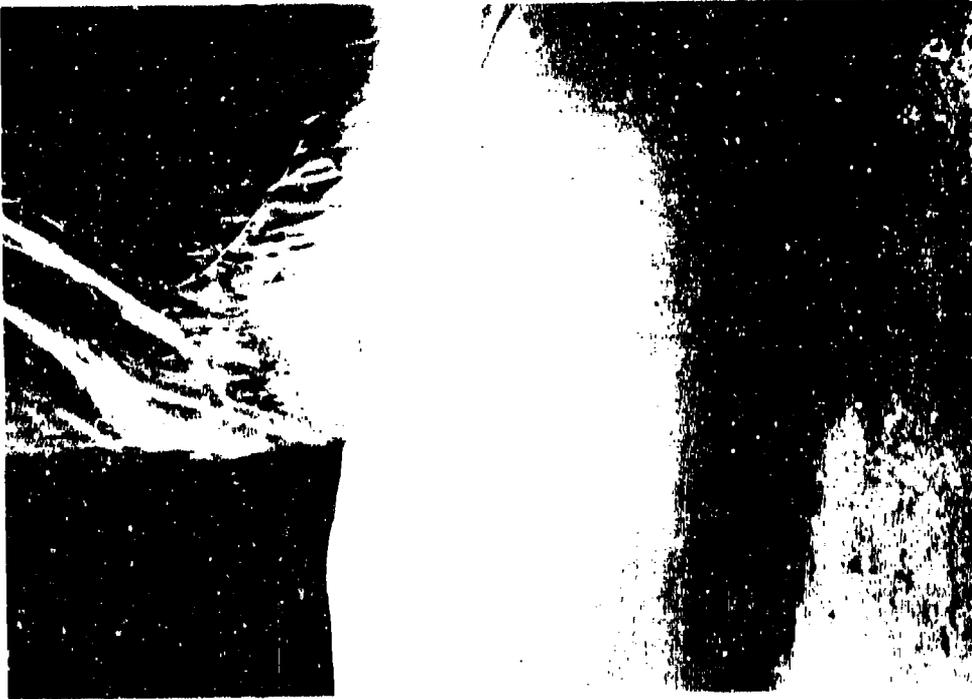


FIG. 3(b) ENTRANCE TO SMALL CHAMBER  
FILLING WITH FOAM

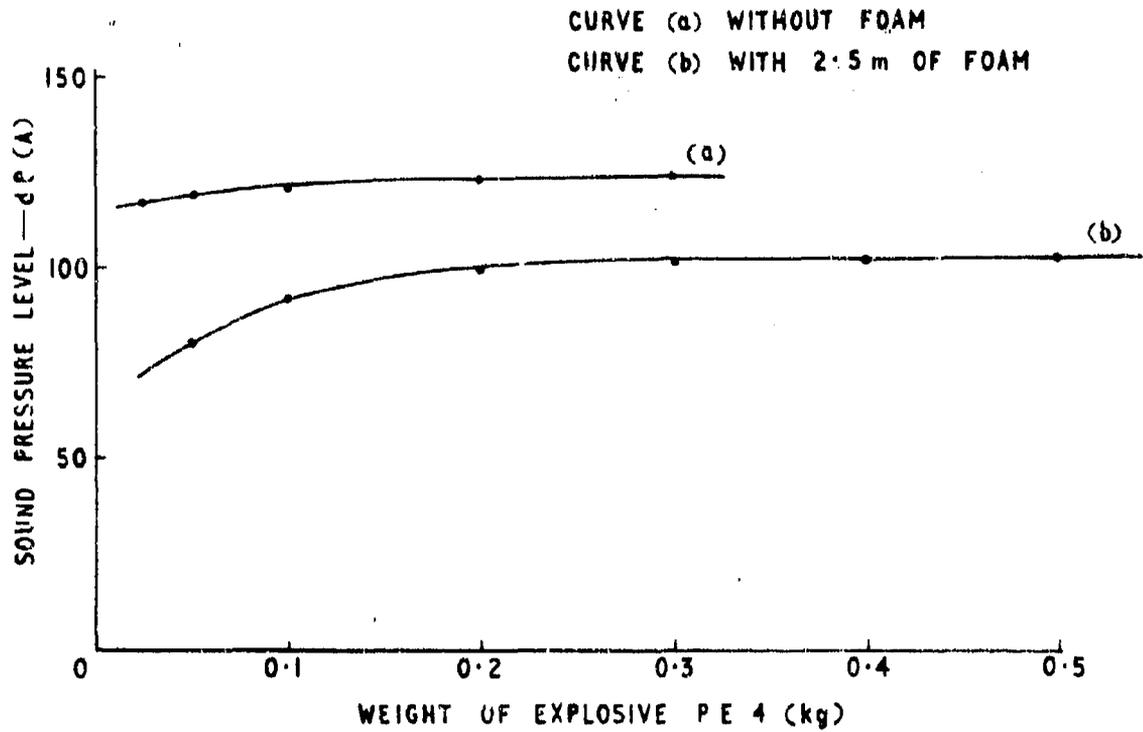


FIG. 4 PLOT OF SOUND PRESSURE LEVEL AGAINST CHARGE WEIGHT FOR SMALL CHAMBER

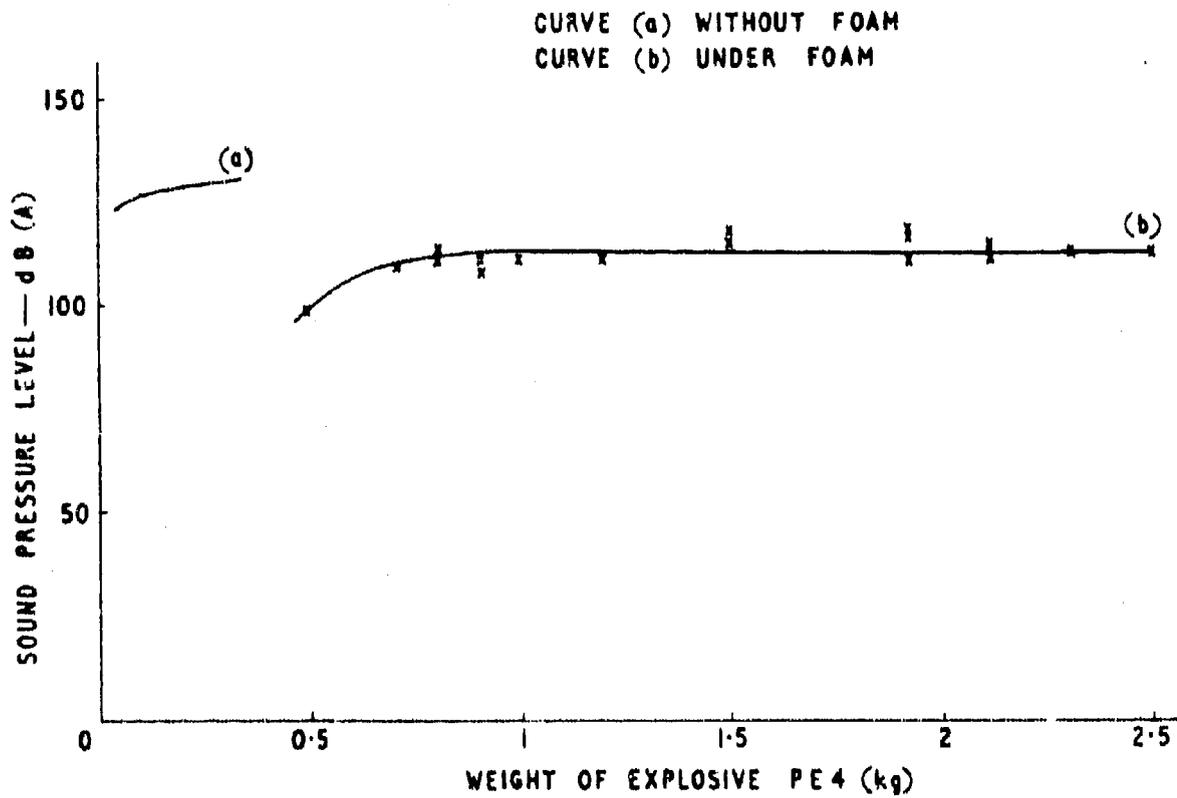


FIG. 5 PLOT OF SOUND PRESSURE LEVEL AGAINST CHARGE WEIGHT FOR LARGE CHAMBER

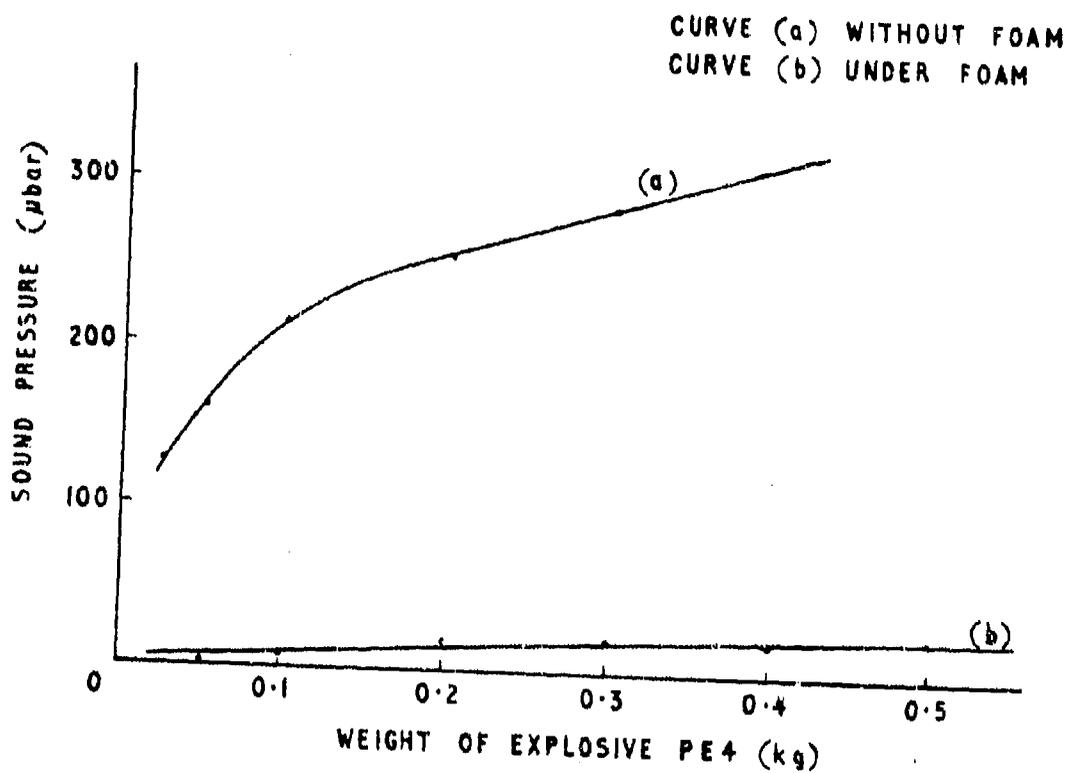


FIG. 8 PLOT OF SOUND PRESSURE AGAINST  
CHARGE WEIGHT FOR SMALL CHAMBER

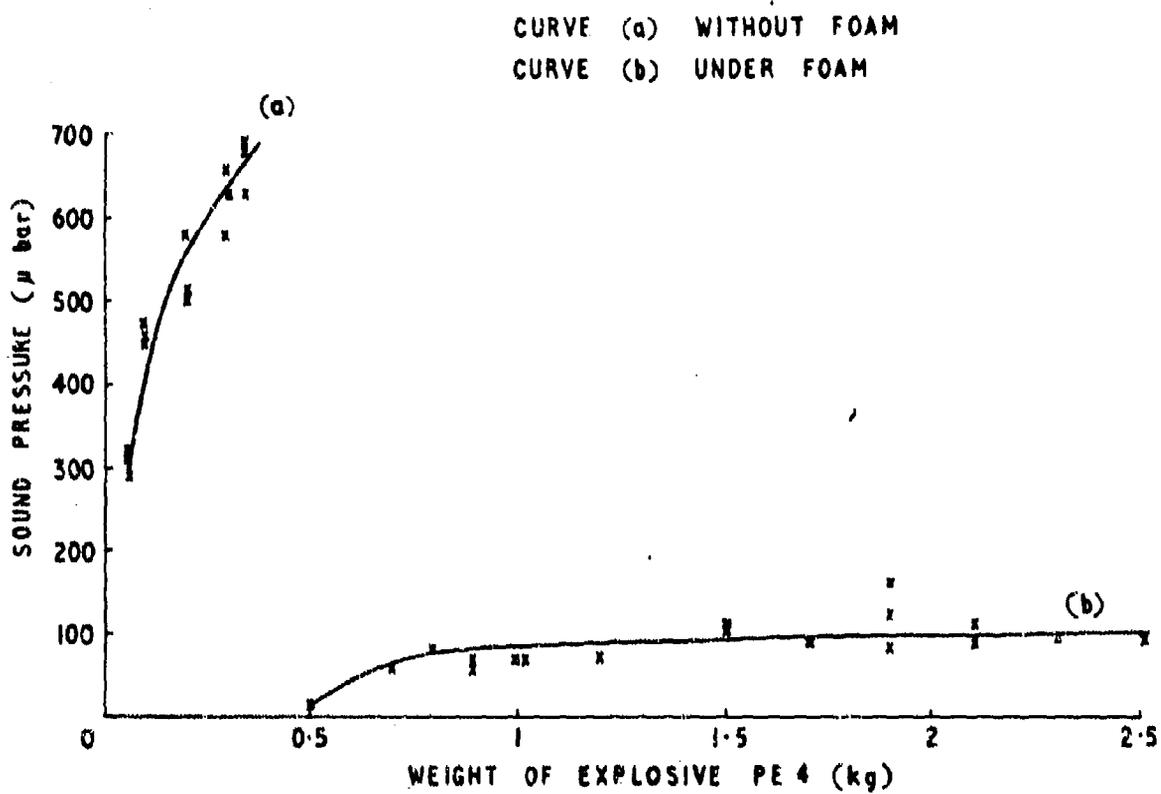


FIG. 7 PLOT OF SOUND PRESSURE AGAINST  
CHARGE WEIGHT FOR LARGE CHAMBER

NOISE ABATEMENT FOR DEMOLITION OPERATIONS

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ABSTRACT

Project Description: Detonation of explosives is performed under the auspices of LEAD's demilitarization mission. Under established procedures explosives are placed at ground level and covered with a five foot mound of loose earth. Shock waves propagating from a 25 pound explosive charge detonated in this manner are sufficient in magnitude to create a nuisance noise in surrounding communities. Utilization of an earth auger to bore holes, up to 12 feet deep, permits the detonation of individual charges up to 380 pounds with no undesirable effects on the environment. This method of operation provides for a productivity increase in excess of 600%, eliminated 95% of cleanup efforts after detonation, and shows an estimated annual net savings of \$1,442,338.02.

The procedure has been approved for demilitarization operations by the Joint Conventional Ammunition Program, Demil and Disposal Task Group, the US Army Materiel and Readiness Command Safety Office, and the Department of Defense Explosives Safety Board.

ENVIRONMENTAL ASSESSMENT OF EXPLOSIVE DEMOLITION DISPOSAL  
OPERATIONS AT FORT PICKETT, VIRGINIA

By

M. M. Swisdak, Jr.  
and  
G. A. Young

In early 1974, the Naval Weapons Station, Yorktown, Virginia, asked the Naval Surface Weapons Center, White Oak Laboratory, to conduct a study of the environmental effects produced by the explosive demolition of unserviceable munitions at the then Camp Pickett, Virginia. This talk presents the results of that study.

During the period from 1961 to 1969, NWS, Yorktown, occasionally used the impact area facilities at Camp Pickett for the disposal of Naval munitions. From 1970 to 1972, there was a gradual increase in the disposal operations, with the following weights detonated: 1970 - 68 metric tons, 1971 - 372 tons, and 1972 - 803 tons. During the period from 8 January to 31 March 1973, munitions with a shipping weight of 2700 tons, including 1630 tons previously prepared for deep sea disposal, were disposed of by detonation at Camp Pickett by NWS personnel. Disposal operations were discontinued in April 1973.

On 30 January 1974, it was determined that 2.25 million kilograms (shipping weight) of unserviceable ammunition was awaiting disposal at Yorktown. This included 401,087 kg of explosive. The rate of accumulation at NWS, Yorktown, was estimated to be 91,000 kilograms shipping weight per month.

Current items on hand at NWS requiring disposal by detonation or burning include small arms, bombs and warheads, boosters, mine cases, grenades, depth charges, propelling charges, fuzes and primers, gun cartridges, projectiles, cartridge actuated devices, igniters, exploders, fittings, rockets, rocket motors, signals, flares, pyrotechnics, and demolition material.

Fort Pickett is located in southern Virginia, approximately 70 kilometers southwest of Richmond.

The mission of Fort Pickett is to provide training in armor and artillery for reserve components and active forces of the armed services. The total land area is about 18,200 hectares. Of this, about 7,300 hectares are used as tank and artillery firing ranges during training exercises. The disposal site is in Impact Area 3, which is about 1400 hectares in size. Although the boundaries cannot be precisely defined, the area of the land used previously for disposal is about 8 hectares.

As an integral part of this assessment, alternative methods to the proposed action of explosive demolition at Fort Pickett

were also evaluated. These included: (1) open burning, (2) incineration, (3) washout--water or steam, (4) detonation at NWS, Yorktown, (5) detonation at locations other than Fort Pickett, and (6) deep water dumping. The problems associated with each of these methods are discussed below.

#### (1) Open Burning

Most of the items requiring disposal can be burned in the open. However, open burning produces gases such as carbon monoxide, oxides of nitrogen, and other pollutants, some of which are possibly unknown. Because of state and federal laws, this method has been greatly reduced in recent years, and it can be used to handle only small quantities of munitions. It will most likely be phased out when other methods become operational.

#### (2) Incineration

Controlled incineration is confined to small arms, primers, detonators, fuzes, illuminating signals, and other small items. The potential products of combustion and reaction of these include nitrogen oxides, sulfur oxides, phosgene gas, ozone, lead vapor, cadmium vapor, mercury vapor, ammonia, hydrochloric acid, sulfuric acid, hydrogen sulfide, carbon monoxide and particles containing magnesium, aluminum, lead, copper, phosphates, potassium, barium, strontium and antimony. It is, therefore, essential that scrubbers and precipitators be developed to remove the effluent gases and particulate matter. Some devices have been tested, but evaluation is continuing and the system is not yet operational with the pollution control equipment installed. In any case, it could not handle the backlog of large items of unserviceable ordnance.

Incineration at sea on a specially designed ship is also feasible, but no such ships have been built as yet for munition disposal.

#### (3) Washout - Water or Steam

The explosives in mines and projectiles can sometimes be removed by the use of hot water or steam jets. After washout, the material can be sold or reworked for use in new Navy weapons. A pilot production plant is being built at Yorktown to establish criteria for proposed production plants. However, many of the items in the NWS, Yorktown, inventory are unsafe for washout in the pilot plant or are in small quantities which cannot be handled on an economic basis.

#### (4) Detonation at NWS, Yorktown

Some disposal of munitions takes place at NWS, Yorktown, at the present time. However, only 22 Kg of explosive can be detonated at one time in the existing demolition pit. A new disposal area, that will have 45 detonating holes, has been proposed. This will have an allowable limit of 70 Kg per hole.

If this is completed during FY 1976, it will help to dispose of incoming ordnance. However, it will not be ready in time to handle the existing backlog.

(5) Detonation at Locations other than Fort Pickett

Other locations for possible detonation of unserviceable munitions include the Naval Ammunition Depots at Crane, Indiana, and Hawthorne, Nevada. However, shipment to Camp Pickett is by truck and is relatively inexpensive. Shipment to Crane or Hawthorne would require careful loading in freight cars and would cost more for shipping and would involve additional handling costs. A cost analysis prepared at NWS, Yorktown, in January 1974 shows an estimated saving of \$622,505 by using Camp Pickett instead of Crane.

(6) Deep Water Dumping

The deep water dump procedure involves the loading of unserviceable and obsolete munitions on a surplus cargo ship, which is then towed to a deep ocean disposal site and either scuttled or detonated. The latter procedure is preferred for safety considerations and because the detonation products are less hazardous than the components of the ordnance. Deep water disposal was halted in 1970 and is against current policy. Nevertheless, it has been shown that the past Deep Water Dumps did not have any permanent, irreversible effects on the environment, and it is conceivable that this method could be reinstated. However, it would require possibly two years to follow the administrative procedures leading to the acquisition of a permit from the EPA and to then prepare a ship. This method could not solve the current problem of disposing of the existing, and growing, backlog.

The items which were given the largest consideration in this study were: (1) air quality, (2) water quality, (3) sound control, and (4) land use. Each of these will be discussed in more detail.

(1) Air Quality

The effects of surface and buried explosions on the quality of the air include the formation of a cloud of dust and the ejection of explosion products to the air. Metal fragments and clods of soil may also be blown into the air, but this is considered to affect the surrounding land, not the quality of the air.

The magnitude of these effects depend on the nature of the soil, the depth of burial, and the weight of explosive.

From available data, it is evident that burial is highly effective in reducing the ejected dust.

When a non-homogeneous mixture of munitions is buried, the ejection of explosion products is less than from a surface burst. Solid explosion products will probably be retained in the soil while the gases will doubtless escape rapidly, unless the explosion is at camouflet depth. In this case, the gases will probably slowly filter to the surface.

The quantity of importance is the concentration reached in air. At an explosion site, the atmospheric concentrations for shallow underwater explosions of TNT possibly reach 522 ppm for carbon monoxide, 42.5 ppm for ammonia, and 5.30 ppm for hydrogen cyanide. The cloud is carried downwind and is rapidly diluted by atmospheric turbulence. Very similar effects occur with underground explosions.

For example, it has been estimated that the concentrations of carbon monoxide, ammonia, and hydrogen cyanide are reduced to 50 ppm, 4 ppm, and 0.5 ppm respectively at a distance of 550 feet from a 1000-lb underwater explosion. The threshold limit values (TLV) for these gases are 50 ppm for carbon monoxide, 50 ppm for ammonia, and 10 ppm for hydrogen cyanide. As the TLV is a condition to which industrial workers may be exposed daily during an 8-hour day, 40-hour week, without adverse effect, no hazard can be anticipated from the explosion gases from explosives weighing 450 kg or less.

For safety, the disposal team would remain at greater distances. In addition, the effect is transient, not continuous. As the distance from the disposal site in area 3 to the nearest point on the boundary of the military reservation is 3.6 kilometers, no effect on air quality would be visible or detectable to the public.

## (2) Water Quality

To document the effect of explosive demolition operations in Impact Area 3 of Fort Pickett on the quality of water in the surrounding area, water and soil samples were collected from nearby streams, water standing in craters, and in nearby lakes. These samples were collected after a series of controlled firings (to be discussed later) had been completed. These samples were analyzed for TNT, lead, and mercury. The latter are the metals of major concern, as the more common ordnance metals are not considered to be hazardous. For example, concentrations of iron up to 0.3 ppm and concentrations of copper up to 0.2 ppm are permissible in public water supply.

The results of these analyses are presented in Figure 1.

Twelve water samples and eight soil samples were collected at Camp Pickett on 3-4 September 1974 and were analyzed for TNT

concentrations at the Naval Mine Engineering Facility, Yorktown, Virginia. The water samples showed less than 0.1 ppm except for three readings of 0.1 ppm in samples obtained from artillery and demolition holes in the impact area. The soil samples had less than 0.01% TNT except for one taken in a demolition hole that had been used just prior to the time of sampling. This sample contained 0.6% of TNT.

The water samples are the most important, as they help to show if dissolved materials are getting into the local water supply. However, except for one reading of 0.1 ppm, those taken in drainage ditches and the creek show levels less than 0.1 ppm, and in three cases, show no measurable TNT.

The Army Ammunition Procurement and Supply (APSA) interim guideline for the discharge of ordnance compounds from ammunition plants in waste-water is 0.5 ppm for TNT and other nitrocompounds. The amount of TNT entering Birch Creek is well below this level.

A total of 24 water samples was collected to be analyzed for lead and mercury. The first 12 were taken on 26 November 1974 and the second on 11 December 1974. All of the samples had lead concentrations less than 0.05 ppm. In the case of mercury, the highest measured concentration was 0.008 ppm. One sample had 0.004 ppm, while two showed 0.003 ppm, 17 had 0.002 ppm, two had 0.001 ppm, and one had no mercury, giving an overall average of about 0.002 ppm.

As these values are all well below the maximum allowable limit of 0.05 ppm for both lead and mercury in public water supply sources, there is no hazard to the public from these metals that can be attributed to the disposal operations in area 3 at Camp Pickett.

### (3) Sound Control

It was felt from the start of this study that this item, sound control, would be the most difficult to complete satisfactorily. Discussions with the residents living around Fort Pickett and with members of the administrative staff at the base indicated that many complaints had been registered during previous disposal operations. The majority of the complaints came from the vicinity of the town of Rawlings, located about 11 kilometers from the firing site. Additional complaints were said to have been received from the towns of Alberta, McKenney, Victoria, and Burkeville. (Figure 2)

A preliminary aerial survey conducted in May indicated that the geology of the area could be contributing to the problem. There are three granite quarries located in the area at: (1) Rawlings, (2) Fort Pickett, and (3) Burkeville. The quarries in Rawlings and Burkeville are both active and in production. Visits to these sites and discussions with the quarry managers indicated that a granite ridge did run between Rawlings and Burkeville. They also indicated that they did extensive blasting

within the quarries (up to 400 kilograms of explosive per delay, with several delays being fired in a string), with no complaints registered from their neighbors. The manager of the quarry at Burkeville also stated that Hercules Powder Company made routine, periodic seismic measurements (ground motion) and had never detected any vibration levels that could cause annoyance or damage to structures.

The noise generated by explosive demolition operations at Fort Pickett was studied in a series of experimental firings. All of the charges were cylinders with a length to diameter ratio of 1/1. The charges were either TNT or Composition C-4. One charge was detonated on the surface, one three meters above the surface, and the remainder either in open holes or buried. Instrumentation consisted of microphones with their associated electronics, ground motion gages, magnetic tape recorders, and sound pressure level recorders. Measurements were made at 3 locations (Figure 3).

No explosion noise above ambient background was recorded in Alberta, McKenney, Victoria, or Burkeville. The background noise changed with the time of day and local traffic conditions at each measurement site. Moreover, during wind gusts, the ambient background jumped even higher. As a result, no absolute number can be given for the background.

At the four close-in stations, the sound levels were below 90 decibels for all charges fired in a tamped hole within a crater. The maximum recorded level was 109.5 decibels at the closest station (3700 meters) for a shot in an open hole (Figure 4).

No detectable ground motion was recorded on any of the shots at any of the recording locations. As a check on the ground motion sensors, a "heel drop" test was performed at each location. In this test, a person stands near the gage, rises up on the balls of his feet and allows his weight to drop on his heels. The amplitude recorded here was over 5mm/sec at each station. Some representative noise and vibration thresholds are presented in Figure 5. Thus we can estimate that the ground motion generated by the explosions was at least a factor of 20 below that which could cause minor structural damage, such as plaster cracking.

#### (4) Land Use

As long as Camp Pickett remains in existence and retains its current mission, the entire impact area will be unsuitable for any other usage. In order to convert it to non-military use, it would be necessary to conduct a systematic and thorough inspection and to remove or destroy all dud ordnance. As the munition disposal area is within the impact area, there is no possibility of using it for any but ordnance-related activities by ordnance experts.

The direct effects of the explosions on the land include cratering and the deposit of metal fragments, solid explosion

products, and possibly undetonated explosive. Extensive operations doubtless lead to a removal of vegetation and erosion of the site.

In summary, the major effects are the cratering and erosion of the site. The littering with metal fragments is similar to that resulting from the use of the area as an impact range. Cratering is not irreversible, as the land could be leveled with bulldozers after a removal of dud ammunition. Other debris, such as packing containers, can be removed after each disposal operation.

There is no doubt that noise is generated by explosions, but the amount of distant noise that might be a nuisance to residents can be reduced by a careful consideration of atmospheric conditions and by charge burial.

For example, if air temperature increases with height in the lowest 1500 meters, the speed of sound will increase with height and sound rays will bend over and return to earth at some distance from the source. This channeling and focussing effect can cause exceptionally large noise at a distance of miles. With very large charges it could lead to window breakage. To avoid this possibility, tests should be conducted when weather conditions are good, that is, no low level temperature inversions and no fog.

In regard to burial, it is known that the air shock wave is reduced when an explosive charge is detonated at increasing depths in the ground. For example, if the depth of a 227 kg charge is increased from .3 meters to 2.4 meters, the peak pressure in the air is reduced by a factor of 16. The air shock becomes a sound wave at a distance and creates an impulse type of noise. The Occupational Safety and Health Act (OSHA) has set an impulse noise limit of 140 decibels, and a noise level of 90 decibels is considered to be loud but not harmful.

It is clear that the charge weights employed in the tests can be detonated without creating a nuisance to surrounding residents by the generation of excessive levels of sound. However, it is essential that they be at the bottom of a 3-meter pit and be covered with about 3 meters of soil. The report includes an estimated upper limit of 227 kg for detonation in this manner.

#### Summary:

It is clear that undesirable effects such as noise, fragmentation, dust, and ground shock can be held to acceptable levels by limiting explosive weights, burying of explosives, firing when the weather is not conducive to channeling or focussing of shock or sound waves, and by allowing an adequate time interval between detonations. The evidence indicates that the charge weight should not exceed 227 kilograms and that the explosive should be buried about 3 meters beneath the bottom of a 3-meter open pit.

FIGURE 1 CONCENTRATION OF MERCURY, TNT, AND LEAD IN WATER SAMPLES

CONSTITUENT	HIGH CONCENTRATION (ppm)	LOW CONCENTRATION (ppm)	AVERAGE CONCENTRATION (ppm)	MAXIMUM ALLOWABLE CONCENTRATION (ppm)
TNT	0.1	0.0	0.07	0.5
LEAD	< .05	< .05	< .05	.05
MERCURY	0.008	0.00	0.002	0.05

■ BURKEVILLE

■ BLACKSTONE

■ VICTORIA



■ ECHOLS' FARM

■ McKENNEY

■ RAWLINGS

■ MEASUREMENT LOCATION

\* FIRING SITE

■ ALBERTA

FIG. 2 CAMP PICKETT, VA., AND SURROUNDINGS

<b>LOCATION</b>	<b>DISTANCE (METERS)</b>
<b>BLDG. 3006</b>	<b>4300</b>
<b>ECHOLS' FARM</b>	<b>3700</b>
<b>RAWLINGS</b>	<b>11400</b>
<b>BLACKSTONE</b>	<b>12100</b>
<b>ALBERTA</b>	<b>20800</b>
<b>VICTORIA</b>	<b>33200</b>
<b>McKENNEY</b>	<b>18300</b>
<b>BURKEVILLE</b>	<b>36800</b>

**FIG. 3 MEASUREMENT LOCATIONS**

FIGURE 4 AIRBLAST DATA

SHOT NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13*
LOCATION													
Bldg. 3006	90	<90	<90	<90	<90	<90	<90	<90	<90	<90	<90	<90	<90
Rawlings	94	104.5	90.8	90.5	<90	<90	96	100	90	<90	<90	72	<70
Blackstone	90	<90	<90	<90	<90	<90	<90	<90	<90	<90	<90	<90	<90
Echols' Farm	ND	ND	ND	103	<90	<90	106	109.5	<90	<90	<90	<90	<90

Burkeville  
Victoria  
Alberta  
McKenney

No signals above background

ND No Data

\* three shots--15 seconds apart

<b>140 dB</b>	<b>THRESHOLD WINDOW DAMAGE</b>
<b>90 dB</b>	<b>NOISE 3 METERS FROM SLAM OF A CAR DOOR</b>
<b>70 -80 dB</b>	<b>TOWN TRAFFIC</b>
<b>50.8 mm/sec</b>	<b>PLASTER CRACKS</b>
<b>3 mm/sec</b>	<b>SAFE LIMIT OF VIBRATION FOR BUILDINGS (NO DAMAGE)</b>
<b>0.25 mm/sec</b>	<b>JUST PERCEPTIBLE -- EASILY BEARABLE</b>

**FIG. 5 NOISE AND VIBRATION THRESHOLDS**

## ENERGY PARTITIONING

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Abstract

Concrete blocks containing a known quantity of explosive have been tested underwater, to prevent secondary fragmentation, and in an explosive chamber - calorimeter system as part of an energy partitioning study. The portion of the total energy available that goes into creating new surface area, heating of the fragments, heating the reaction chamber, and the residual heat of the product gases and air has been determined.

Introduction

While explosives have been employed for blasting for over centuries, only limited theory has been developed and little experimental work performed to evaluate the partitioning of explosives energy in blasting processes. Three theories have been employed to evaluate the crushing energy: The Rittinger theory states that the energy is proportional to the new surface area formed and may be expressed as

$$E = K_r \left( \sum \text{pct}_i \left( \frac{1}{d_i} - \frac{100}{d_0} \right) \right).$$

The Kick theory states that the energy of crushing is proportional to the particle size reduction and is expressed as

$$E = K_k \left( \sum \text{pct}_i \log \left( \frac{1}{d_i} + 100 \log d_0 \right) \right).$$

Bond's third theory is a compromise between these two and is given by

$$E = K_b \left( \sum_1^{40} pct_1 (1/d_1^{1/2}) - (100/d_0^{1/2}) \right)$$

In these formulas E is energy, the K's are constant,  $d_1$  is particle size diameter of a given screen fraction, and  $d_0$  is the diameter of unbroken material. Bond's theory applies well to commercial crushing and grinding but does not take into account the energy required for creating very fine particles. Rittinger's (surface energy) theory is believed to be more nearly correct and was used in this study.

The available work from an explosive is given by:

$$A = \int_{P_4}^{P_3} p \, dv$$

where  $p_3$  is the pressure of the "explosion state" and  $p_4$  is the final pressure, usually atmospheric. This is often approximated closely by the heat of explosion in the explosion state, i.e., considering the explosion products to be at a density equal to that of the explosive and the chemical equilibria calculated accordingly. Either value can be determined by computer program.

The total energy of an explosive detonated under the above test conditions can be classified as follows:

- a. Surface energy of broken materials =  $H_a$
- b. Residual heat of gases and air =  $H_b$
- c. Residual heat of broken material =  $H_c$
- d. Residual heat of box =  $H_d$
- e. Compaction of specimen
- f. Elastic deformation of specimen
- g. Elastic deformation of box

- h. External shock and sound
- i. Formation of secondary chemical products

Of these categories items a thru d can be measured. Items e thru g will be included in the first four. The last two are considered negligible for the purposes of this study.

A heat balance may be set up as follows:

$$Q = A = H_a + H_b + H_c + H_d$$

where *A* is the total available chemical energy from the explosive.

### Experimental

Cylinders of very fine aggregate concrete (neet cement) were prepared containing small quantities of a permissible explosive and were cured under saturated lime water until they obtained their maximum strength. These test specimens (Fig. 1) were then suspended in an explosion chamber (Fig. 2) fitted with a quick release port by which the broken fragments could be dropped into a calorimeter (Fig. 3). Additional samples were anchored in a steel box filled with water for underwater fragmentation tests (Fig. 4).

### Results

Experiments were performed in the reaction chamber on specimens containing from 3 g to 40 g of explosive. The air temperature increase in the chamber and water temperature increase in the calorimeter ranged from 2.40 to 11.62 deg C and from 0.88 to 4.31 deg C, respectively, depending on the quantity of explosive used. The fragments were screened, the particle size distribution determined, and comparisons made with drop hammer results. Tests were conducted using the concrete cylinders containing 1, 2, 3, and 4 g of explosive, underwater, utilizing a fragment catcher to eliminate secondary breakage against the walls. The cumulative

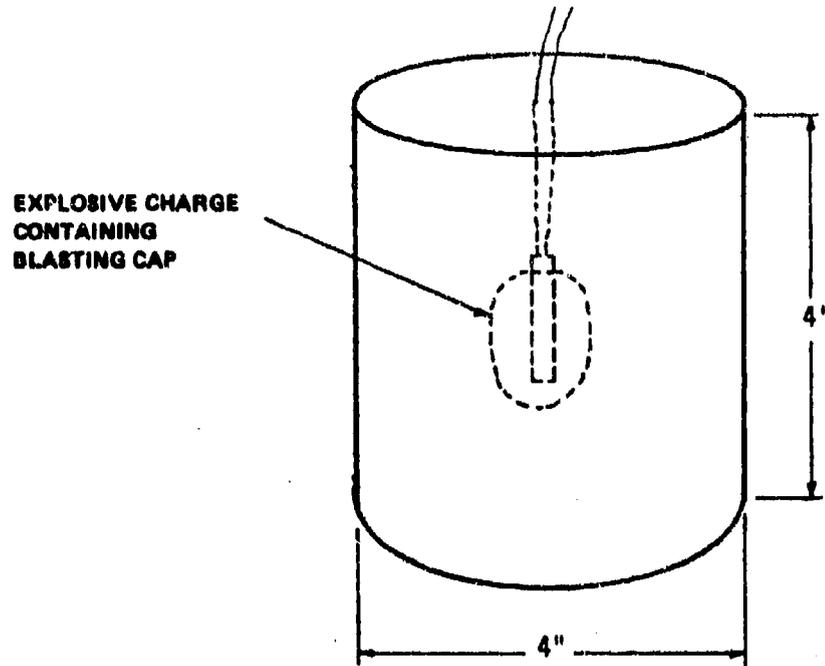


FIG. 1 CONCRETE TEST SPECIMEN

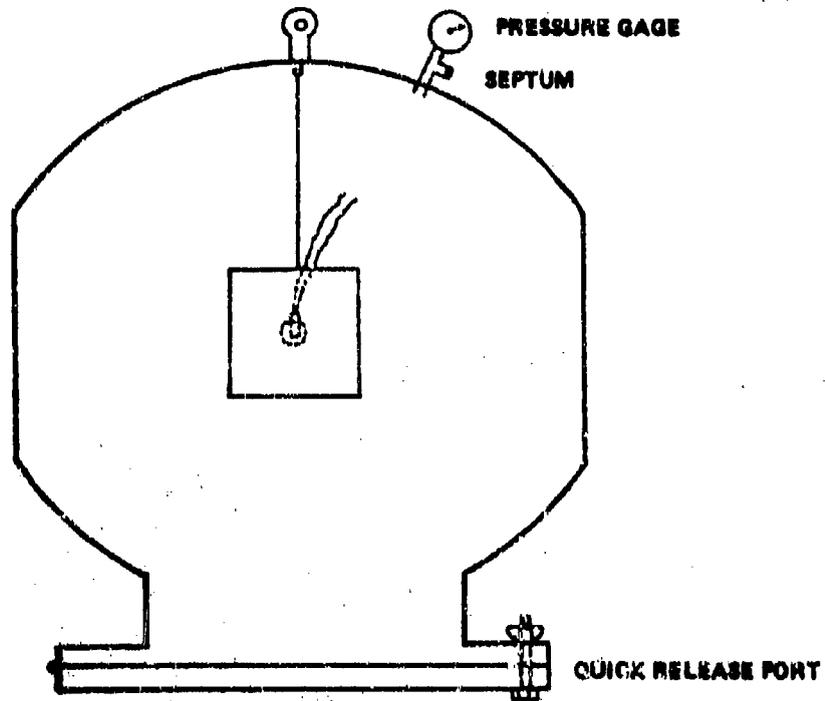


FIG. 2 EXPLOSION CHAMBER

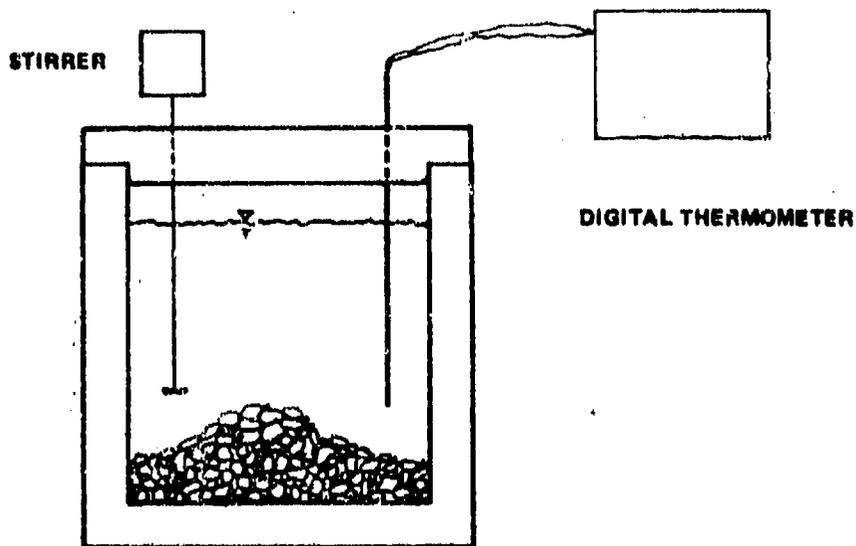
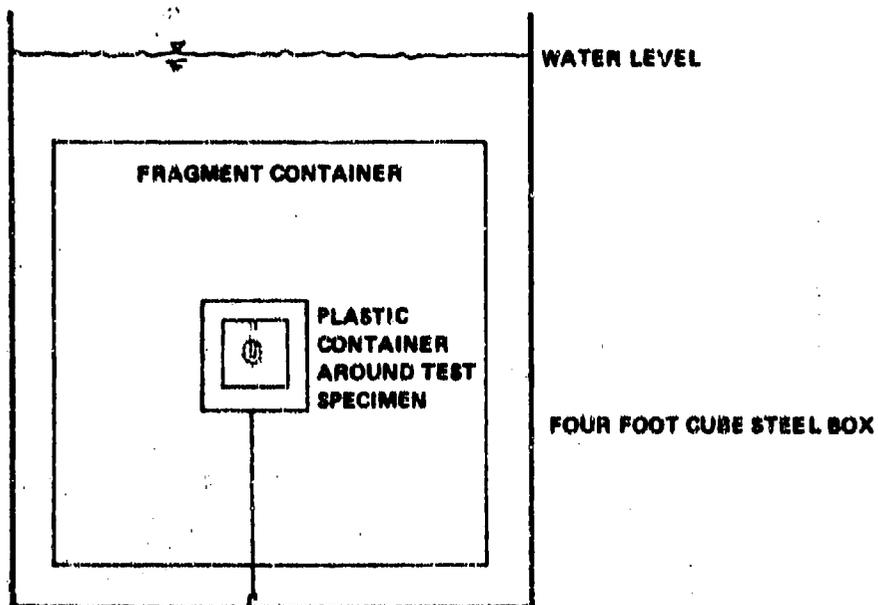


FIG. 3 CALORIMETER APPARATUS



SLIDE 4 UNDERWATER FRAGMENTATION TESTS

logarithmic diagram of screen analysis on the 5.3 m height drop hammer tests correlates with the results obtained from the 1 g, underwater tests (Fig. 5). The energy is essentially the same and the particle size distribution is similar. A computer program was utilized to calculate the energy.

Explosion product gases were analyzed on an A-700P Varian Gas Chromatograph. Two chambers were fabricated for confining the explosive effects and the product gases. One was 20.3 cm in diameter, 13.7 cm long, 2.5 cm wall thickness, and was designed for 3 g of explosive. The second chamber was 10.2 cm in diameter, 18.3 cm long, 1.3 cm wall thickness, and was designed for 1 g of explosive. The chambers were evacuated prior to initiation of the explosive and sampled by a hypodermic needle inserted through a septum. Connections were threaded in the end plates and had needle valves and a vacuum gage.

A theoretical computation was made based on the explosive composition and loading density to determine the detonation and explosion state temperature, pressure, heat of explosion, reaction products, and the detonation velocity. The theoretical gaseous concentrations compare with the results obtained from the Gas Chromatograph.

#### Summary

The heat of explosion ( $Q_3$ ) was calculated by use of the thermohydrodynamic detonation theory from known physical properties of the explosive;  $A$  is approximately equal to  $Q_3$ ;  $H_a$  was determined from calibrated drop hammer tests by comparison with the input energy to produce equivalent breakage and particle size distribution and from the underwater shots;  $H_b$  was found directly from reaction chamber measurements and calculated independently from gas chromatography results of the explosive gases, the two results being in agreement;  $H_c$  was measured experimentally in a calorimeter; and  $H_d$  was found by difference and approximated by two experimental values.

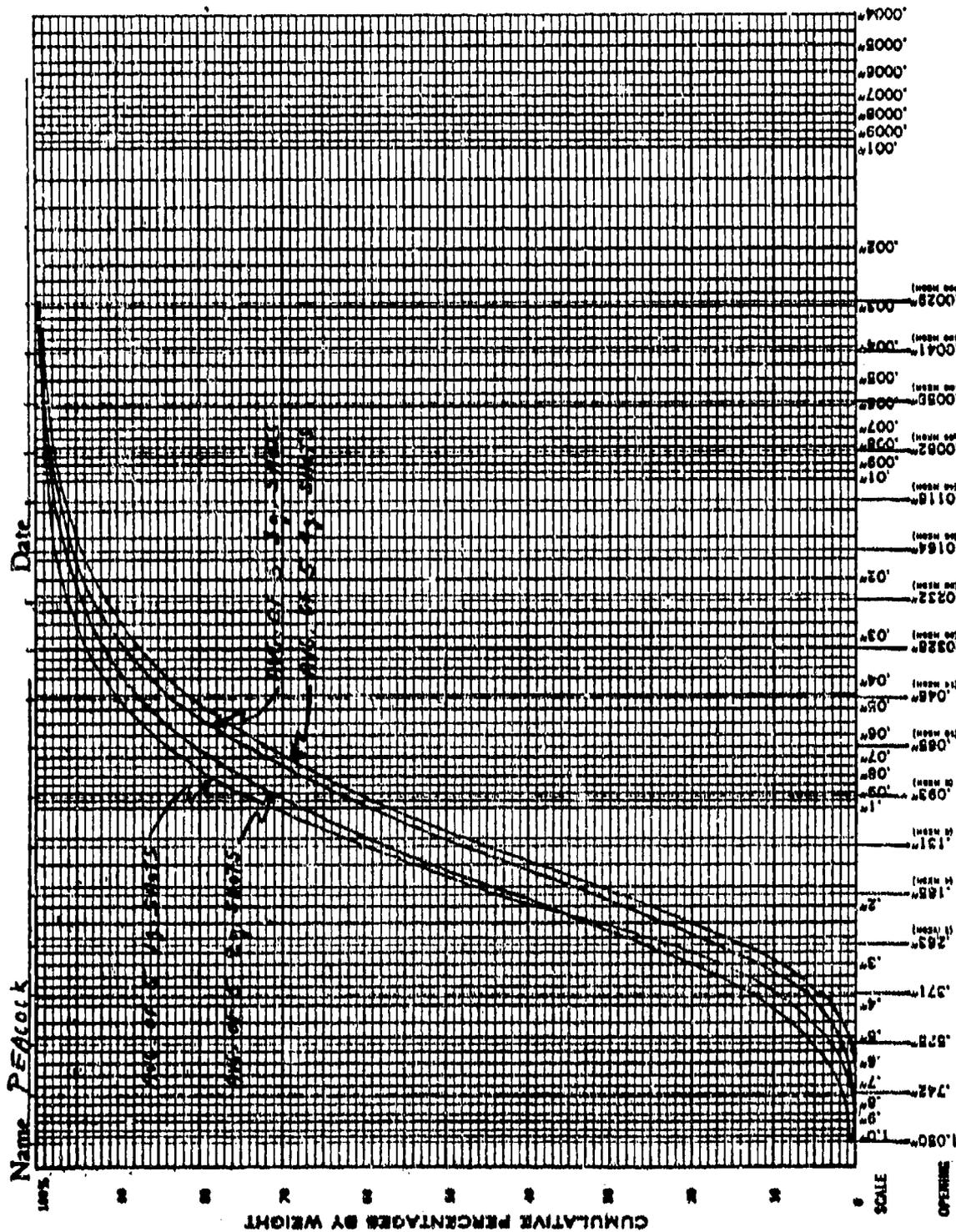


FIG. 5 CUMULATIVE LOGARITHMIC DIAGRAM OF SCREEN ANALYSIS ON SAMPLE OF AVERAGES OF 5 UNDERWATER SHOTS  
1G, 2G, 3G, AND 4G

<u>Q<sub>3</sub> or A (cal/g)</u>	<u>H<sub>a</sub></u>	<u>H<sub>b</sub></u>	<u>H<sub>c</sub></u>	<u>H<sub>d</sub></u>
896	652.2	64.8	117	62
100%	72.8%	7.2%	13.1%	6.9%

For the above completely confined explosive charge at least 72.8 percent of the explosive energy was transmitted to the confining solid (concrete) and converted to breakage energy. For surface energy determinations the concrete cylinder was free on all surfaces, suspended inside a plastic container underwater to prevent the fragments from impacting against the chamber walls causing further breakage.

This experiment illustrates dramatically why confined explosives are so effective in rock breakage.

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EXPLOSIVE WASHOUT UTILIZING DISSOLUTION

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## ABSTRACT

A field portable system for the dissolution of main charge explosives is being developed. Card gap tests showed that the dissolution process resulted in a desensitization of the high explosives. Detonations of saturated solvent containing excess explosive demonstrated that there was no solvent contribution to the detonation overpressure. The feasibility of dissolving just the explosive surrounding the booster and utilizing attenuating materials to prevent sympathetic detonation of the main charge as a result of booster detonation was demonstrated.

Discussion

Two approaches to explosive neutralization were initially considered: neutralization through chemical reactions and solvent dissolution.

Picatinny Arsenal performed a "state-of-the-art" paper study looking into the feasibility of using chemical neutralization reactions in a portable system. The study concluded that all neutralization reactions were too exothermic to be used on such a large scale and recommended that the dissolution approach be followed.

The dissolution technique has been selected for the present system design. The system consists of a storage tank, pumping unit(s), an injection unit, and a suitable solvent. The solvent impinges on the explosive surface through a hole in the ordnance case, is collected, and recycled until it becomes saturated with explosive. A diagram of the anticipated system layout is given in Figure 1. A filtering mechanism is required to remove particles of aluminum or undissolved explosive from the main stream in order to prevent damage to process pumps.

Work initially completed at the Naval Surface Weapons Center, (NAVSURFWPNCEN), White Oak included a study to select a suitable overall solvent for explosives. Factors considered in choosing a solvent were explosive solubility, cost, availability, convenience, melting point, boiling point, and the toxicity. Solubilities of standard military explosive (HMX, RDX, TNT, HNS, and DATB) were determined in various solvents from 25°C to 98°C. The solvents used were from various classes of compounds (acids, amides, amines, esters, ketones, nitriles, nitro compounds, etc.). Dimethylformamide (DMF) appeared to be the best choice for a general explosive solvent (reference 1). Table 1 reviews various properties including solubilities of some typical solvents.

The sensitizing or desensitizing effect of DMF on explosive in solution and slurry form were of concern to system development. A study was conducted by NAVSURFWPNCEN, White Oak to observe these effects. The NOL large scale gap test was used as a measure

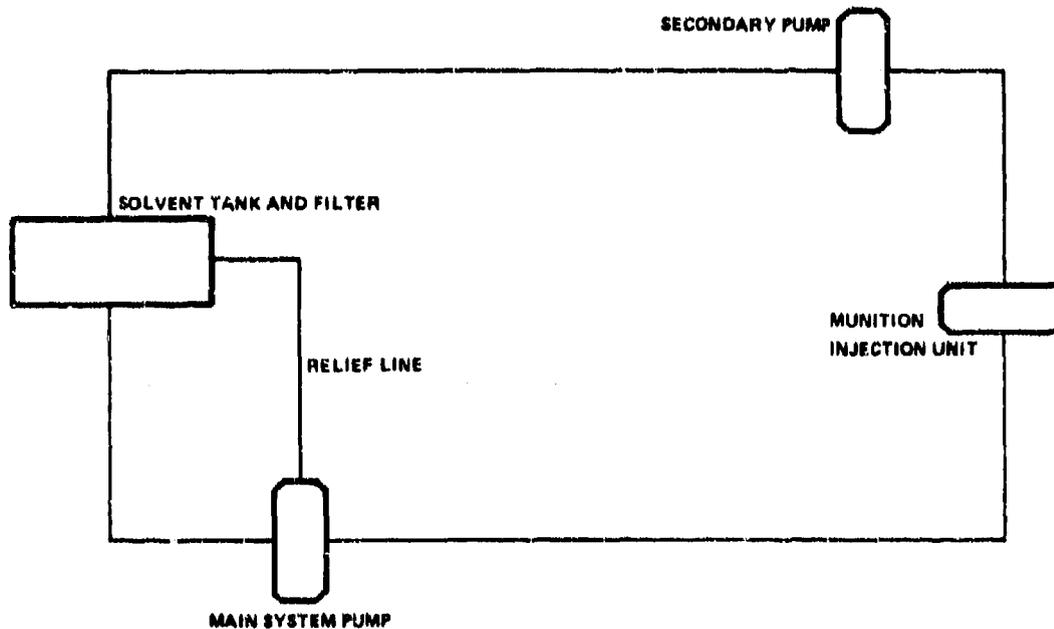


FIG. 1 FLOW DIAGRAM

of the sensitivities of several slurries of explosives and solvents. The large scale gap test is a donor/acceptor explosive train propagation test with the components separated by any number of standard thickness plastic cards. Card values refer to the distance between the donor and acceptor charges where one card corresponds to 0.01 inch separation. Higher card values describe more sensitive samples. A slurry of TNT and DMF containing a 50 percent excess of TNT over the amount required to give a saturated solution in DMF at 25°C (68 percent TNT by weight) failed to give a positive test (high order detonation perforating the witness plate) at 50 cards, whereas TNT at 65 percent theoretical maximum density (TMD) has a value of 282 cards. Similarly, a mixture of RDX and DMF containing a 50 percent excess of RDX over the amount required to give a saturated solution in DMF at 25°C (35 percent RDX by weight) did not give a positive test at 50 cards. RDX at 85 and 91 percent TMD yields values of 336 and 323 cards, respectively. It was concluded that by dis-

solving a sensitive high explosive in DMF a desensitized solution is produced

Table I

Solubilities of Explosives (g/100g) at 25°C after five minutes

SOLVENT	Melting Point °C	RDX	HMX	TNT	HNS	DATE	Ammonium Picrate
Dimethylsulfoxide (DMSO)	18	41	57	128	1.4	2.2	75
N-Methyl Pyrrolidone (NMP)	-21	40	Solvate	118	2.4	4.5	62
Dimethylformamide (DMF)	-60	37	Solvate		1.5	2.5	90
79.2% NMP							
20.8% DMSO	-30	41	Solvate	120	2.3	4.6	70
71.7% DMF							
28.3% DMSO	-30	39	Solvate	142	1.7	2.9	95
Butyrolactone	-42	14	12	--	0.4	0.8	--
Acetone	-94	8.2	2.8	--	0.1	0.4	--
Cyclohexanone	-47	7.7	1.0	--	1.1	--	--

Even though the solutions were less sensitive than the explosives themselves, the question arose whether the solvent would contribute to the explosive blast output. This information was needed for assessing possible damages resulting if an accidental explosion occurred during removal of high explosives from munitions with the DMF solvent or during the transportation and disposal of the contaminated solvent. The blast outputs from saturated solutions of TNT and DMF were measured and compared with overpressures from spherical charges of TNT. Two saturated DMF/TNT liquid charges were fired and free air blast outputs were recorded at varying distances. The first test was a 4480 gram saturated solution of DMF/TNT boosted with a 200 gram pentolite cylinder. A second test consisted of two plastic one gallon containers of saturated DMF/TNT solution taped together and boosted by a 500 gram pentolite cylinder. Results indicate that the saturated DMF/TNT solutions did not detonate high order; the blast output was approximately equivalent to that of the booster alone.

Three liquid charges containing saturated DMF/H-6 solution plus excess undissolved H-6 were fired. Two of the charges were contained in one gallon plastic cartons with 35 percent and 65 percent excess

undissolved RDX by weight. The third with a 35 percent excess undissolved H-6 was contained in a two gallon polyethylene bag. In these three tests all charges were boosted by 579 gram pentolite cylinders. The air blast output of the DMF/H-6 was approximately equivalent to the air blast of an equal amount of H-6. In none of the tests was there evidence that the DMF contributed to the detonation.

Two approaches for explosive washout are the complete and the partial dissolution of the main charge. Due to the greater time and solvent requirements of the complete washout method the partial main charge removal technique appeared more attractive. A test program has been run to determine the amount of explosive which must be removed from around the booster cup of a bomb in order to interrupt the explosive train. Mk 81 and 82 bomb sections have been modified and loaded with H-6 explosive to within varying distances of the booster. Figure 2 shows the test set-up. Two, three, four and five inch gaps were left between the booster cups and the main charges. 50/50 pentolite boosters of approximately 230 grams, drilled for insertion of blasting caps, were used to initiate the sections. The gaps in these initial tests were filled with various materials for blast and fragment attenuation. A length of det cord was inserted through a previously machined hole in the welded metal plates and placed across a lead witness block for evaluation after the test. The test involved inserting the blasting cap into the booster, firing the cap remotely, and observing whether a detonation occurred. Table 2 summarizes the tests performed. In no case was a high order detonation observed, as evidenced by the lead plates being unscarred.

Table 2. Partial Washout Feasibility Tests

<u>Bomb/Section</u>	<u>Booster/Main Charge Gap (in.)</u>	<u>Explosive Weight (lbs.)</u>	<u>Attenuating Material</u>
Mk 82/T	5	25	Sand
Mk 81/N	5	15	Air
Mk 81/N	4	17	Air
Mk 81/N	3	19	Air
Mk 82/T	2	35	Sand
Mk 81/T	2	27	DMF
Mk 82/T	2	35	Air
Mk 81/T	2	28	Air
Mk 81/T	2	26	Air*

\* Full explosive yield not realized by the booster.

No detonations were observed using 230 grams 50/50 pentolite boosters.

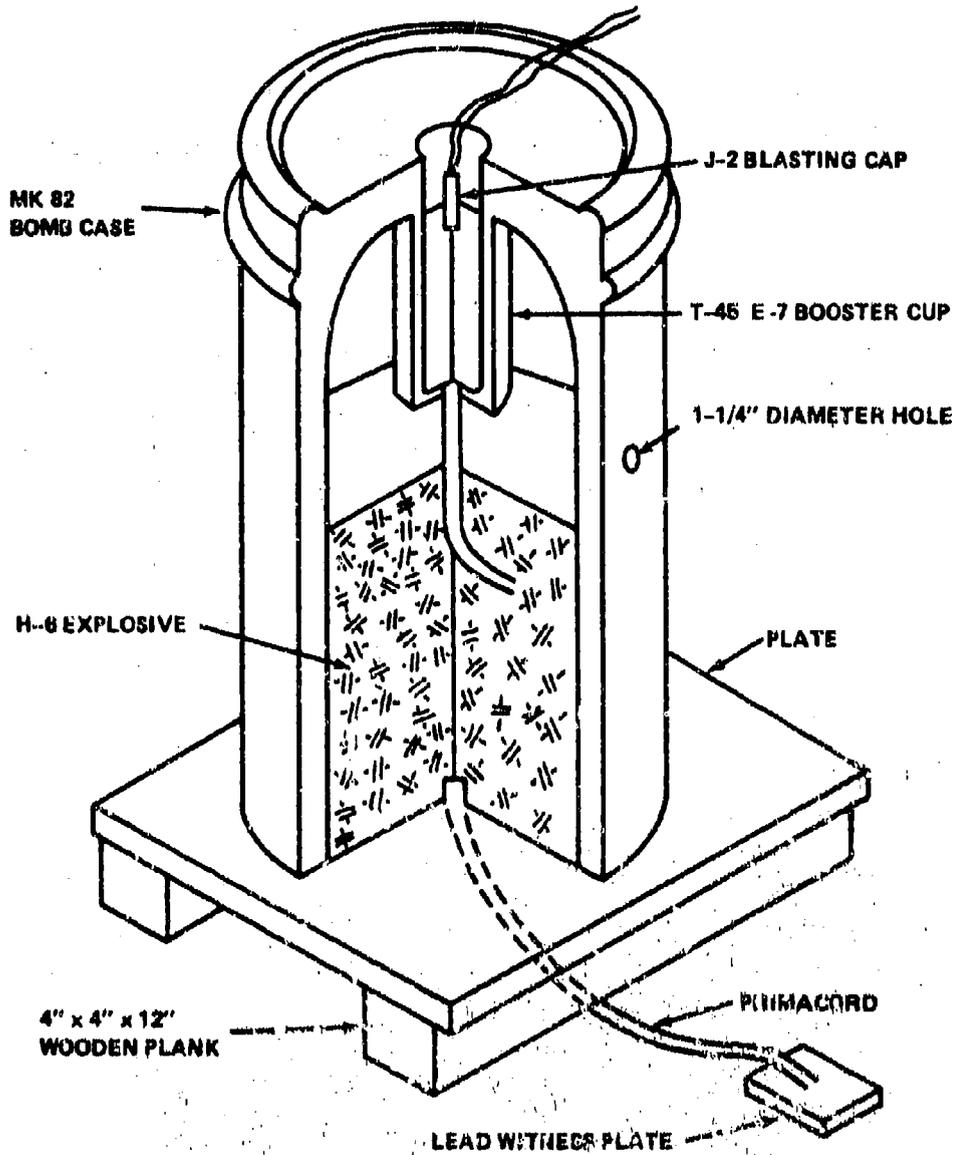


FIG. 2 CROSS-SECTION OF TEST SET-UP

The pentolite boosters were sufficient in each test to fracture the bomb casing, leaving large fragments spread over the test area within 100 yards of the initiation site.

### Conclusion

The dissolution process has been shown to be effective against all non-PEX type high explosives, reducing them to a desensitized solution of explosive and DMF. The DMF has demonstrated no contribution to explosive blast output when detonated in the solvated form. A partial main charge removal technique has been shown to be feasible.

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