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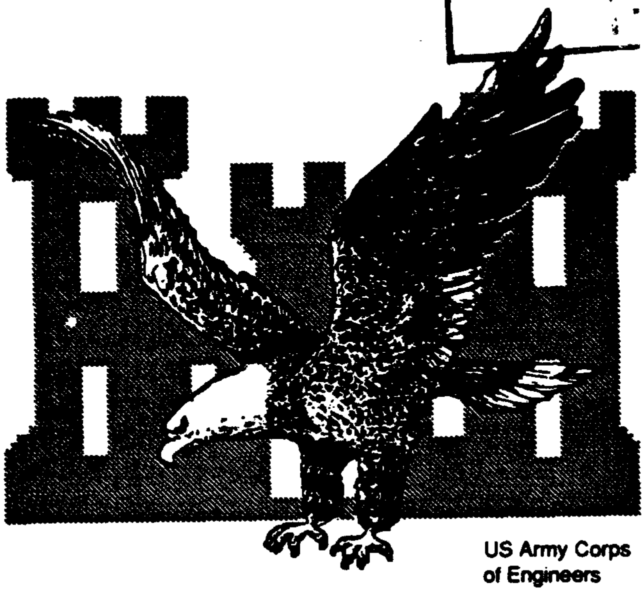
U S A T H A M A

U.S. Army Toxic and Hazardous Materials Agency


US Army Corps
of Engineers

PROCEEDINGS FOR THE

14th Annual Army Environmental R&D Symposium

Hosted By:
United States Army
Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, Maryland

14-16 November 1989
Ft. Magruder Inn and
Conference Center
Williamsburg, Virginia

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Symposium conducted as a useful means of technology exchange for the Army's Environmental R&D Program. This annual event involves key personnel from all pertinent Federal agencies and provides a forum where users and developers are kept abreast of latest state-of-the-art technologies. This report provides proceedings from the symposium.

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FOREWORD

This symposium is a significant means of technology exchange for the Army's R&D program. It is designed to facilitate developer/user interface by joint participation. This annual event involves key personnel from all pertinent Federal agencies and provides a forum where users and developers are kept abreast of latest state-of-the-art technologies and are given the opportunity to benefit from the perspectives of senior DOD leadership.

Because the number of abstracts received exceeded the spaces available for presentation at the symposium, these proceedings contain papers which were not presented at the symposium, as well as those that were presented. The papers enclosed in these proceedings were provided by their authors. Some papers presented at the symposium are not included in these proceedings due to authors' personal or professional reasons. All papers were reviewed and edited by USATHAMA personnel to prevent the disclosure of proprietary information and programmatic/funding information not allowed to be disseminated in compliance with competitive procurement policies.

THE SECRETARY OF DEFENSE
WASHINGTON, THE DISTRICT OF COLUMBIA

10 OCT 1989

MEMORANDUM FOR SECRETARIES OF THE MILITARY DEPARTMENTS

SUBJECT: Environmental Management Policy

This Administration wants the United States to be the world leader in addressing environmental problems and I want the Department of Defense to be the Federal leader in agency environmental compliance and protection.

Federal facilities, including military bases, must meet environmental standards. Congress has repeatedly expressed a similar sentiment. As the largest Federal agency, the Department of Defense has a great responsibility to meet this challenge. It must be a command priority at all levels. We must demonstrate commitment with accountability for responding to the Nation's environmental agenda. I want every command to be an environmental standard by which Federal agencies are judged.

The first priority of our environmental policy must be to integrate and budget environmental considerations into our activities and operations. This will decrease our future liabilities and costs for our people. The effort begins and ends with our people. We need the right people at the right place with the right training.

It is also extremely important that we communicate clearly what we are doing to address our environmental concerns. We need to work harder at telling our environmental success stories and solving our problems in an open, cooperative way with the public and also appropriate regulatory authorities. The universal recognition of effective DoD environmental compliance and stewardship activities is the surest way to maintain our access to the air, land, and water we need to maintain and improve our mission capability.

We must be fully committed to do our part to meet the worldwide environmental challenge and I know I can count on your support to ensure that we are successful in that effort.

Dick Cheney

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SPECIAL TOPICS IN ENVIRONMENTAL QUALITY

ADDITIONAL PAPERS

THE SECRETARY'S CHALLENGE

LAST YEAR I CHALLENGED YOU TO "MAKE A DIFFERENCE" IN YOUR RESEARCH EFFORTS BY ENSURING THAT YOUR RESEARCH AND DEVELOPMENT PROGRAMS WERE CONSISTENT WITH THE OBJECTIVES OF EFFICIENTLY CLEANING UP THE ENVIRONMENT AND MITIGATING POLLUTION FROM DOD OPERATIONS. AMONG OTHER THINGS I TALKED ABOUT WAS THE IMPORTANCE OF FOCUSING ON THE PURPOSE FOR YOUR EFFORTS, OF MAKING SURE YOUR WORK WAS TIMELY AND USEFUL, AND OF INTERFACING WITH THE LOGISTICAL AND INDUSTRIAL COMMUNITIES. DOING THESE THINGS, I NOTED, WOULD MAKE A DIFFERENCE.

THIS YEAR, MORE THAN EVER, IT IS IMPORTANT TO RENEW THIS COMMITMENT BECAUSE SECRETARY CHENEY HAS ISSUED US A CHALLENGE THAT CANNOT BE IGNORED.

SPECIFICALLY, ON OCTOBER 10 OF THIS YEAR, THE SECRETARY ISSUED A MEMORANDUM FOR THE SECRETARIES OF THE MILITARY DEPARTMENTS ABOUT ENVIRONMENTAL MANAGEMENT POLICY. IN IT, HE NOTED THAT THE ADMINISTRATION WANTS THE UNITED STATES TO BE THE WORLD LEADER IN ADDRESSING ENVIRONMENTAL PROBLEMS. HE THEN CHALLENGED US TO BE THE FEDERAL LEADER IN AGENCY ENVIRONMENTAL COMPLIANCE AND PROTECTION.

THIS SYMPOSIUM CONTRIBUTES SIGNIFICANTLY TO DEPARTMENT OF DEFENSE LEADERSHIP IN ENVIRONMENTAL PROTECTION. WE ALL KNOW THAT

Opening Remarks to the 14th Annual Army Environmental R&D Symposium
Fort Magruder Inn, Williamsburg VA 14 November 1989

RESEARCH AND DEVELOPMENT FOCUSES ON THE FUTURE. HOW SUCCESSFUL IT IS - HOW SUCCESSFUL YOU ARE - IN FINDING ANSWERS TO OUR ENVIRONMENTAL PROBLEMS WILL INFLUENCE TO A GREAT EXTENT HOW SUCCESSFUL THE DEPARTMENT WILL BE IN PROTECTING OUR FUTURE ENVIRONMENT. OF COURSE THE SYMPOSIUM BY ITSELF RESULTS IN LITTLE TANGIBLE BENEFITS TO THE DEPARTMENT. RATHER, IT IS WHAT IS LEARNED HERE AND APPLIED TO OUR PROBLEMS WHICH PRODUCES RESULTS.

IN THAT SPIRIT, I WOULD LIKE TO ELABORATE A LITTLE ON THE SEVERAL POINTS MADE BY SECRETARY CHENEY IN HIS MEMO AND SHARE THEM WITH YOU USING SOME RHETORICAL QUESTIONS RELATED TO YOUR RESEARCH AND DEVELOPMENT EFFORTS. I'D LIKE YOU TO KEEP THESE QUESTIONS IN MIND AS YOU ATTEND THIS CONFERENCE AND WHEN, HOPEFULLY, YOU TAKE ADVANTAGE OF WHAT WILL BE PRESENTED THESE NEXT COUPLE DAYS.

MEETING ENVIRONMENTAL STANDARDS. HOW DO THE RESEARCH, DEVELOPMENT AND DEMONSTRATION PROJECTS TO BE REPORTED HERE HELP THE FIELD MEET THEIR ENVIRONMENTAL REQUIREMENTS? OR CONVERSELY, HOW CAN YOU TAKE ADVANTAGE OF THEM TO MEET STANDARDS QUICKER, EASIER OR LESS EXPENSIVELY? WHAT IS THE PURPOSE OF THE RESEARCH EFFORT AND HOW DOES IT APPLY TO OUR ENVIRONMENTAL PROBLEMS? IF THE ANSWER IS NOT EVIDENT, YOU MUST QUESTION ITS UTILITY AND FIND OUT WHAT IS MISSING. SECRETARY CHENEY NOTED THAT, AS THE LARGEST FEDERAL AGENCY, THE DEPARTMENT OF DEFENSE HAS A SPECIAL RESPONSIBILITY TO MEET ENVIRONMENTAL STANDARDS AND THAT CONGRESS HAD REPEATEDLY EXPRESSED A SIMILAR SENTIMENT. THE SECRETARY

STATED THAT MEETING ENVIRONMENTAL STANDARDS MUST BE A COMMAND PRIORITY. IS IT YOUR COMMAND'S PRIORITY? ENVIRONMENTAL STANDARDS ARE THE TANGIBLE FORM OF OUR GOVERNMENT'S AND THIS DEPARTMENT'S CONCERN FOR THE HEALTH AND WELFARE OF ITS PEOPLE. THAT, OF COURSE, IS THE MOST BASIC REASON FOR OUR EFFORTS.

INTEGRATING AND BUDGETING ENVIRONMENTAL CONSIDERATIONS. THIS IS PERHAPS OUR MOST DIFFICULT CHALLENGE. RESEARCHERS: WHAT PLANNING HAVE YOU DONE TO HAVE A REASONABLE CHANCE OF CARRYING YOUR EFFORTS TO FRUITION, OR TO A POINT WHERE AN IMPORTANT GO - NO GO DECISION CAN BE MADE ABOUT THEIR MERITS? ARE YOU PLANNING NOW FOR THE NEXT STEPS YOU MAY HAVE TO TAKE A YEAR FROM NOW? I REFER HERE ESPECIALLY TO THE STEPS NEEDED FOR THE SUSTENANCE OF YOUR RESEARCH. WHO IS YOUR CUSTOMER AND DO YOU UNDERSTAND HIS REQUIREMENT? ARE YOU FAMILIAR WITH (OR KNOW SOMEONE WHO IS FAMILIAR WITH) THE BUREAUCRATIC PROCEDURES SO NECESSARY TO OBTAIN THE RESOURCES YOU NEED TO CONTINUE? DO YOU HAVE A SOUND JUSTIFICATION FOR CONTINUING AND ARE YOUR EFFORTS TIMELY? WHO KNOWS IT? DO I KNOW IT? CONVERSELY, FOR YOU WHO HOPE TO BENEFIT FROM THESE RESEARCH EFFORTS: HOW MUCH THOUGHT HAVE YOU GIVEN TO THE REQUIREMENTS AND MEANS TO INTEGRATE THE RESEARCH AND DEMONSTRATION RESULTS INTO REAL TIME APPLICATIONS WHICH MAKE THE REAL DIFFERENCE IN OUR ACTIVITIES AND OPERATIONS? SECRETARY CHENEY SAID THAT WE MUST DEMONSTRATE COMMITMENT AND ACCOUNTABILITY FOR RESPONDING TO THE NATION'S ENVIRONMENTAL AGENDA. HOW ACCOUNTABLE ARE YOU? ONLY WHEN WE IDENTIFY AND

APPLY, IN SOME FASHION, THE RESULTS OF RESEARCH EFFORTS TO REAL WORLD PROBLEMS IS THAT DIFFERENCE DEMONSTRATED. THE SECRETARY FEELS STRONGLY THAT SUCCESSFULLY BUDGETING AND INTEGRATING ENVIRONMENTAL CONSIDERATIONS INTO DOD ACTIVITIES AND OPERATIONS IS VERY IMPORTANT. HE SAID IT WAS THE FIRST PRIORITY OF HIS ENVIRONMENTAL POLICY.

TRAINING. THE SECRETARY'S MEMORANDUM TALKS ABOUT NEEDING THE RIGHT PEOPLE AT THE RIGHT PLACE WITH THE RIGHT TRAINING. CERTAINLY, THIS TECHNICAL TRANSFER SYMPOSIUM IS AN EXAMPLE OF TRYING TO GET THE RIGHT PEOPLE TO THE RIGHT PLACE. ARE ALL THE RIGHT PEOPLE HERE OR ARE WE JUST "PREACHING TO THE CHOIR"? JUST AS IMPORTANT IS THE QUESTION, IS THIS ALL THERE IS? DON'T BE COMPLACENT AND LET YOUR TECH TRANSFER EFFORTS END HERE. AGAIN SUCCESSFUL TECH TRANSFER MEANS EXACTLY THAT: TECHNOLOGY DEVELOPED MUST BE TRANSFERRED ALL THE WAY TO THE APPLICATIONS FOR WHICH IT IS INTENDED FOR TRANSFER TO BE CONSIDERED SUCCESSFUL. UNTIL THAT TIME THE SECRETARY'S CHALLENGE TO ENVIRONMENTAL LEADERSHIP REMAINS A GOAL - A DESIRE - AND NOT THE REALITY WE MUST MAKE IT.

COMMUNICATIONS. SECRETARY CHENEY SAID IT WAS EXTREMELY IMPORTANT THAT WE COMMUNICATE CLEARLY WHAT WE ARE DOING TO ADDRESS OUR ENVIRONMENTAL CONCERNS. HE SAID THAT WE HAVE TO WORK HARDER AT TELLING OUR ENVIRONMENTAL SUCCESS STORIES. CERTAINLY, THIS IS RELATED TO THE TECHNOLOGY TRANSFER THAT IS OCCURRING HERE WHICH I JUST NOTED. BUT IT IS BROADER THAN THAT. HOW MANY PERSONS

OUTSIDE OF DOD AND ITS IMMEDIATE CONTRACTORS ARE HERE? HOW MANY WERE INVITED? WHAT CAN WE LEARN FROM THEM AND WHAT OPPORTUNITIES ARE WE MISSING BY NOT TELLING THEM OUR SUCCESS STORIES? THESE QUESTIONS APPLY NOT ONLY HERE, BUT TO ALL OUR EFFORTS. WE NEED TO SOLVE OUR PROBLEMS AND AIR OUR SUCCESSES IN AN OPEN, COOPERATIVE WAY WITH THE PUBLIC AND THE APPROPRIATE REGULATORY AUTHORITIES. THE REASON IS SIMPLE AND WAS ARTICULATED IN THE SECRETARY'S MEMO. IT IS BECAUSE *RECOGNITION* OF OUR ENVIRONMENTAL COMPLIANCE AND STEWARDSHIP ACTIVITIES IS THE SUREST WAY TO MAINTAIN OUR ACCESS TO THE AIR, LAND, AND WATER WE NEED FOR OUR DEFENSE READINESS REQUIREMENTS. THERE'S AN OLD QUESTION: "IF A TREE FALLS IN THE FOREST AND NO ONE IS THERE, DOES IT MAKE ANY NOISE?" IF WE HAVE A GOOD PROGRAM AND WE DON'T TELL ANYONE, HOW WILL THEY KNOW?

COMMITMENT THE SECRETARY CALLED UPON ALL OF US TO BE FULLY COMMITTED TO MEET OUR WORLDWIDE CHALLENGE OF ENVIRONMENTAL COMPLIANCE AND PROTECTION. HE SAID HE HAD CONFIDENCE IN US TO BE SUCCESSFUL IN OUR EFFORTS. HOW COMMITTED ARE YOU? DO YOU DESERVE HIS CONFIDENCE? IF NOT, WHAT ARE YOU DOING HERE? IF WE ARE TO BE SUCCESSFUL, WE WILL NEED NOT WORDS BUT ACTIONS. MORE THAN ACTIONS, WE WILL NEED APPLICATIONS. AND MORE THAN APPLICATIONS, WE WILL NEED SUCCESSFUL RESULTS WHICH DEMONSTRATE OUR LEADERSHIP IN ENVIRONMENTAL COMPLIANCE AND PROTECTION.

[PAUSE]

I TOLD YOU LAST YEAR THAT I BELIEVED YOUR WORK IS ESSENTIAL FOR THE LONG TERM SUCCESS OF THE DOD ENVIRONMENTAL PROGRAM. THIS IS TRUE MORE THAN EVER. I SUPPORT THIS PROGRAM. OUR ENVIRONMENTAL COMPLIANCE REQUIREMENTS AND CLEANUP ACTIVITIES WILL ONLY ACCELERATE IN THE FUTURE. YOUR TALENTS, YOUR INITIATIVES, YOUR SKILLS ARE NEEDED TO ADDRESS THE MANY PROBLEMS WE WILL ENCOUNTER ALONG THE WAY. PLEASE KEEP IN MIND, HOWEVER, THAT WE DON'T HAVE THE LUXURY OF DOING RESEARCH SOLELY FOR CURIOSITY'S SAKE - AND I EMPHASIZE THE WORD "SOLELY". YOU MUST ALWAYS QUESTION WHY YOU ARE MAKING THE EFFORT AND FOR WHOM. YOU MUST ALWAYS QUESTION WHAT BENEFIT YOU HOPE TO DERIVE AND ITS ULTIMATE UTILITY. YOU MUST SEARCH OUT WHAT ALREADY HAS BEEN DONE BECAUSE WE CANNOT AFFORD TO DO "FUN" PROJECTS OR TO REINVENT THE WHEEL. UNLESS YOU CAN PROVIDE SOUND JUSTIFICATION FOR YOUR EFFORTS UP THE CHAIN OF COMMAND, YOU WILL HAVE DIFFICULTY IN THIS AGE OF AN AUSTERE BUDGET GETTING WHAT YOU WANT. PERHAPS MOST IMPORTANTLY, YOU MUST BE SMART ENOUGH TO REALIZE THAT UNLESS YOU PLAN AHEAD AND INVOLVE OUR LOGISTICAL AND FINANCIAL COLLEAGUES, YOUR CHANCES FOR SEEING YOUR EFFORTS SOLVE DOD ENVIRONMENTAL PROBLEMS ARE NIL. IN A WORD, YOU MUST INSIST ON A QUALITY PROGRAM AND THAT MEANS PRACTICING TOTAL QUALITY MANAGEMENT.

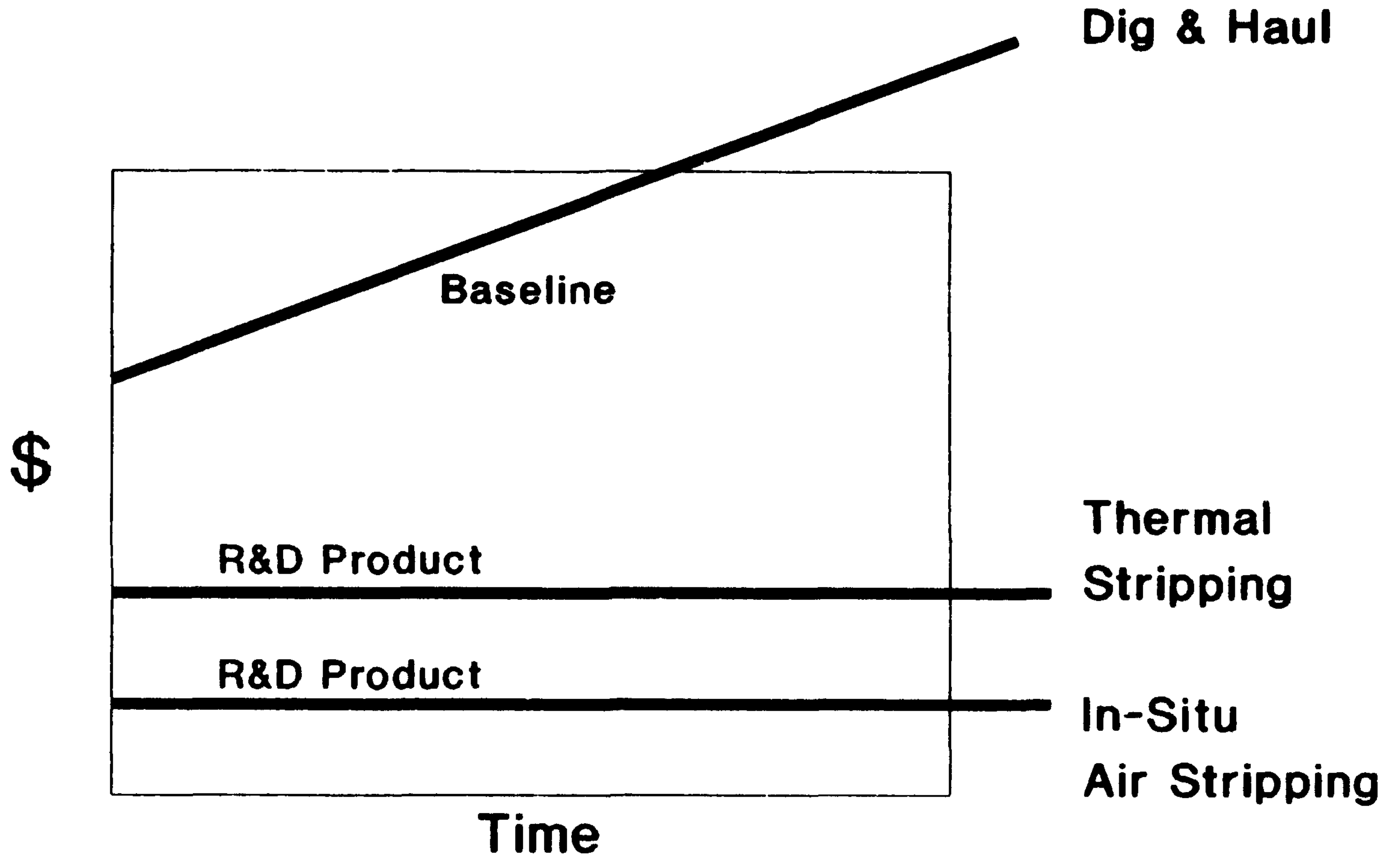
WHEN SECRETARY CHENEY GAVE US THE CHALLENGE TO MAKE DOD THE FEDERAL AGENCY LEADER IN ENVIRONMENTAL COMPLIANCE AND PROTECTION HE NOTED THAT THE EFFORT NEEDED TO ACCOMPLISH IT BEGINS AND ENDS WITH OUR PEOPLE. YOU ARE THOSE PEOPLE. ALL YOUR GOALS MUST

REFLECT HIS CHALLENGE AND YOU MUST NEVER LOOSE SIGHT OF WHY WE MAKE THE EFFORT. AGAIN I CHALLENGE YOU TO MAKE A DIFFERENCE: A DIFFERENCE IN HOW EFFECTIVELY AND READILY WE CAN MEET OUR ENVIRONMENTAL REQUIREMENTS THROUGH RESEARCH AND ITS APPLICATION TO ENVIRONMENTAL PROBLEMS. THAT'S QUALITY RESEARCH: YOU CAN DO NO LESS FOR THIS DEPARTMENT AND FOR THIS COUNTRY.

MAKING THE DIFFERENCE

Army
Environmental
Research and Development

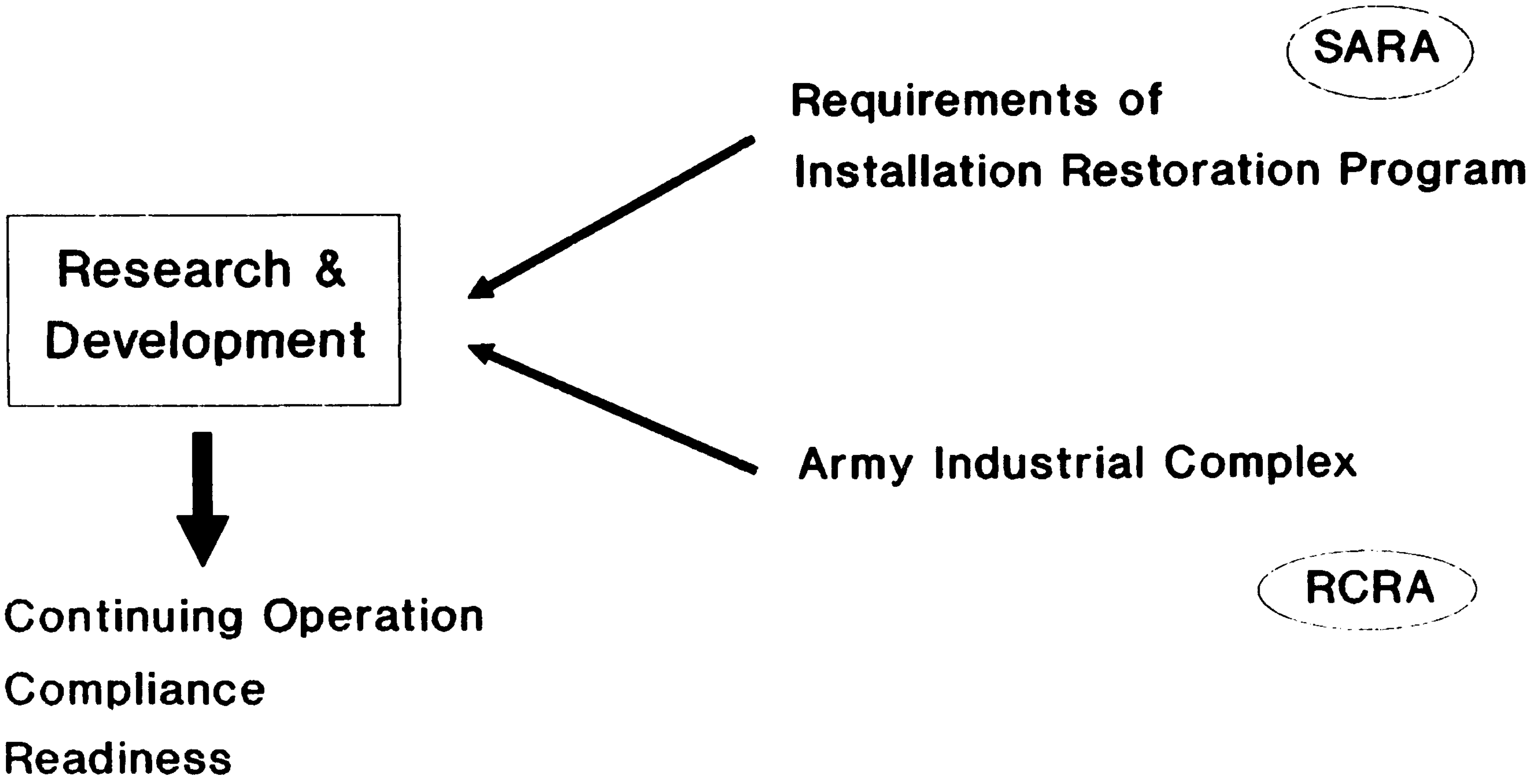
The Difference



Contaminated Soil Treatment

• Solvents •

ENVIRONMENTAL RESEARCH AND DEVELOPMENT



SARA

Requirements of
Installation Restoration Program

Army Industrial Complex

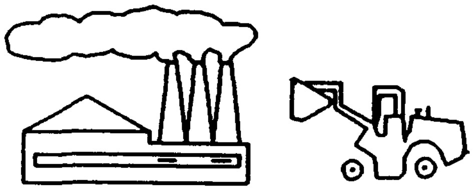
RCRA

Research &
Development

Continuing Operation
Compliance
Readiness

The Difference

INCINERATION



$250 TO $300 PER TON

COMPOSTING

$100 PER TON (TARGET)

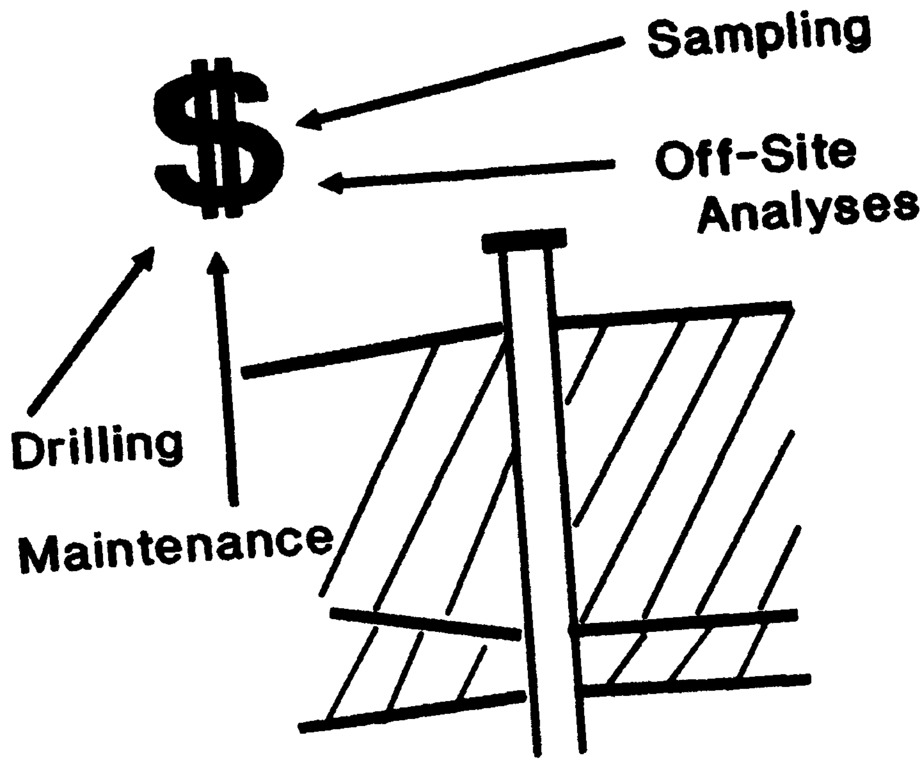
POTENTIAL SAVINGS

$150 MILLION TO $ 1 BILLION

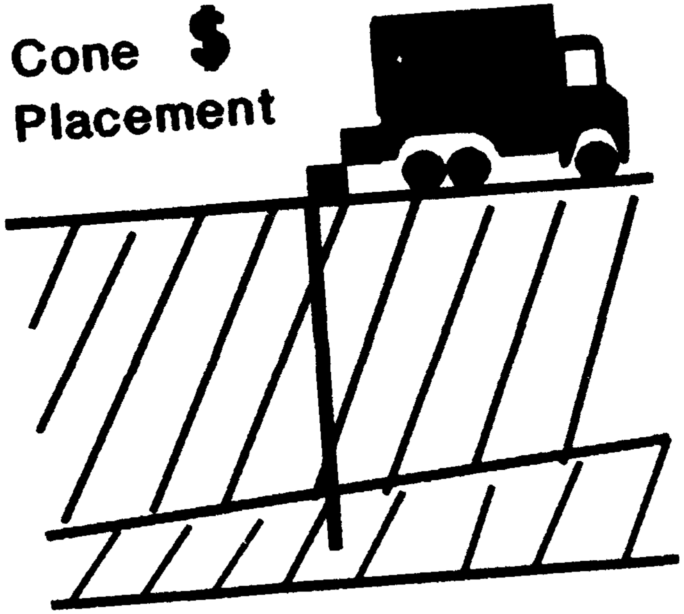
Contaminated Soil Treatment

• Explosives •

The Difference



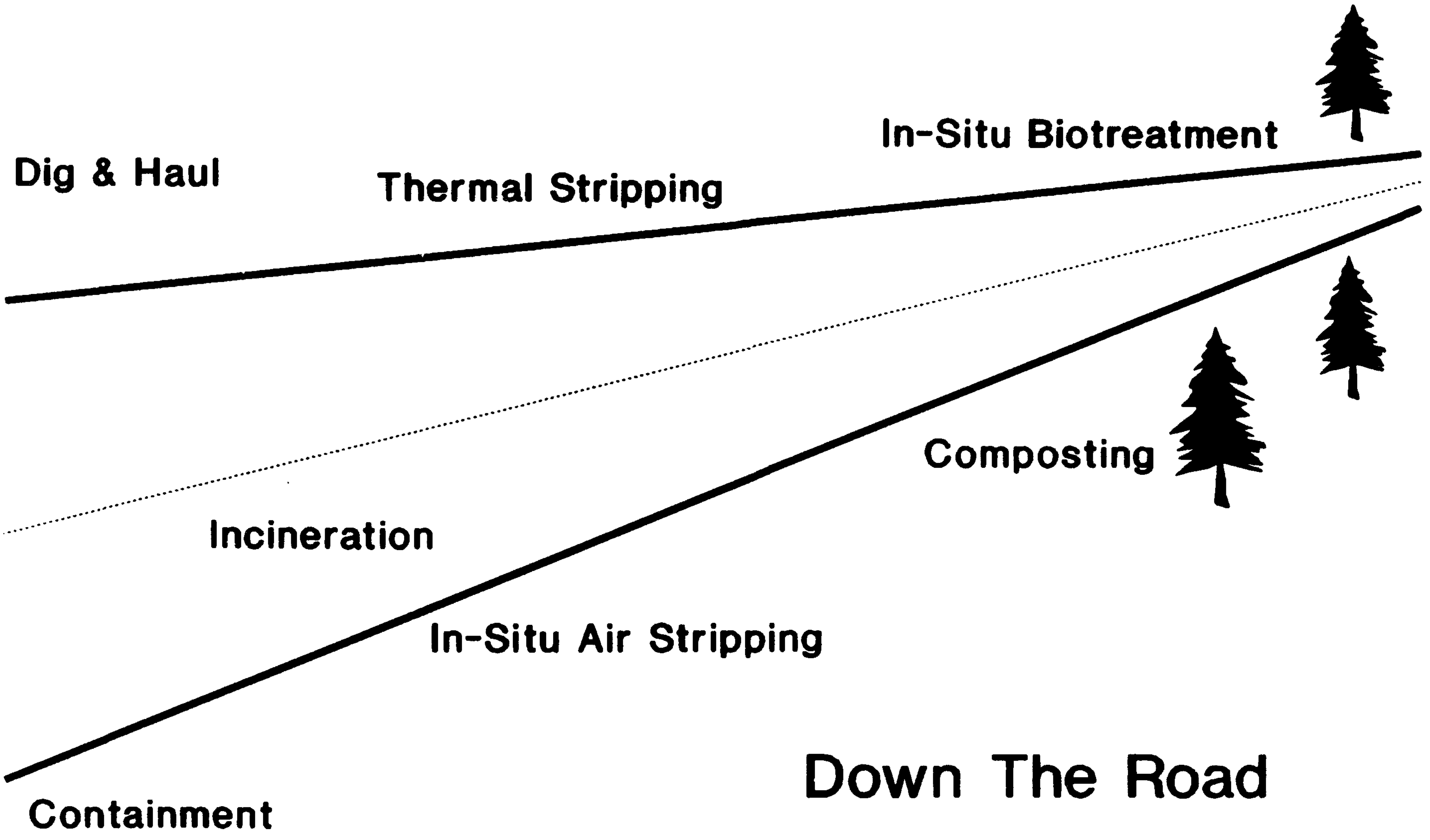
Monitoring Well



Cone Penetrometer Technology

Site Assessment/Monitoring

The Difference



Dig & Haul

Thermal Stripping

In-Situ Biotreatment

Incineration

Composting

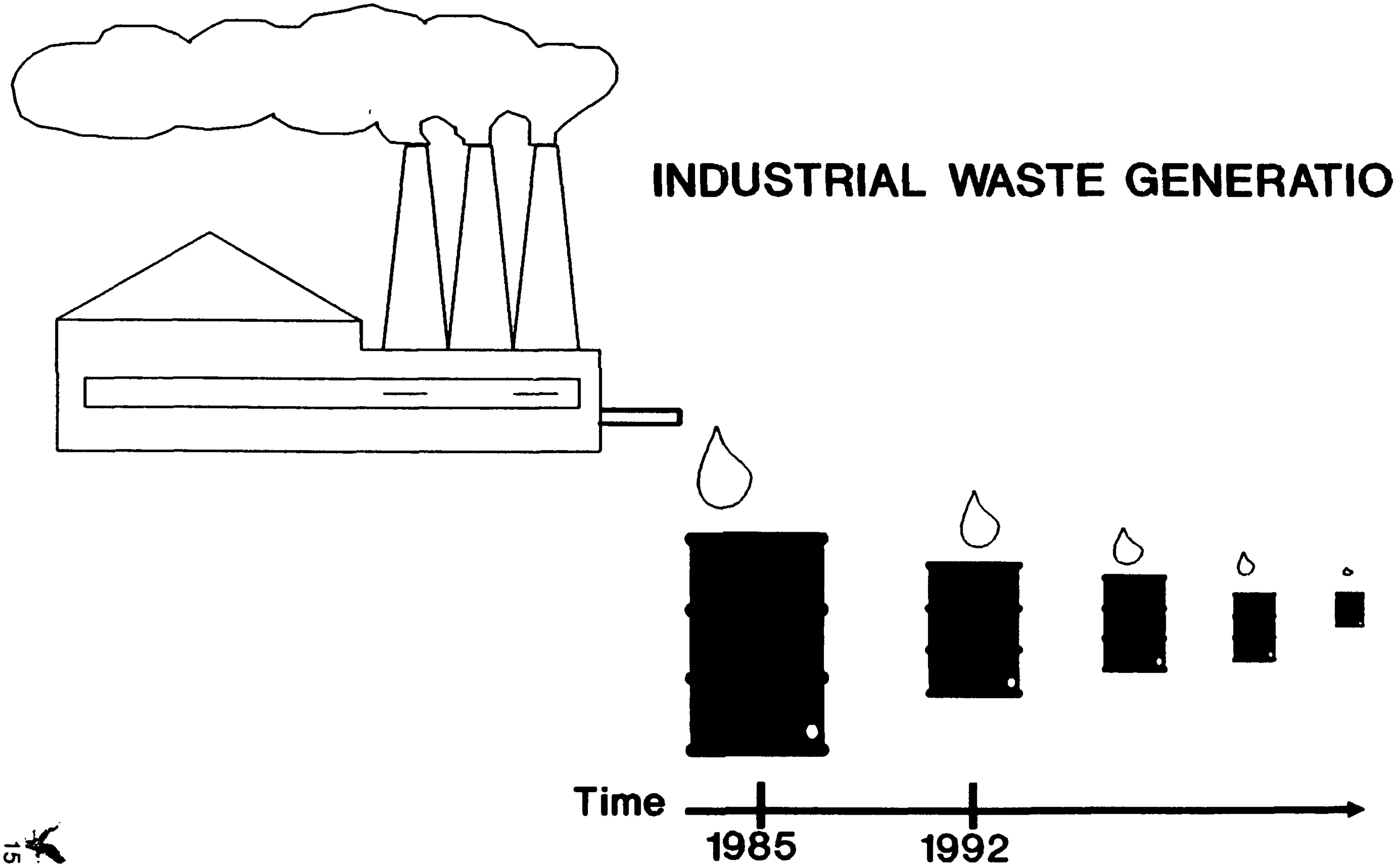
In-Situ Air Stripping

Containment

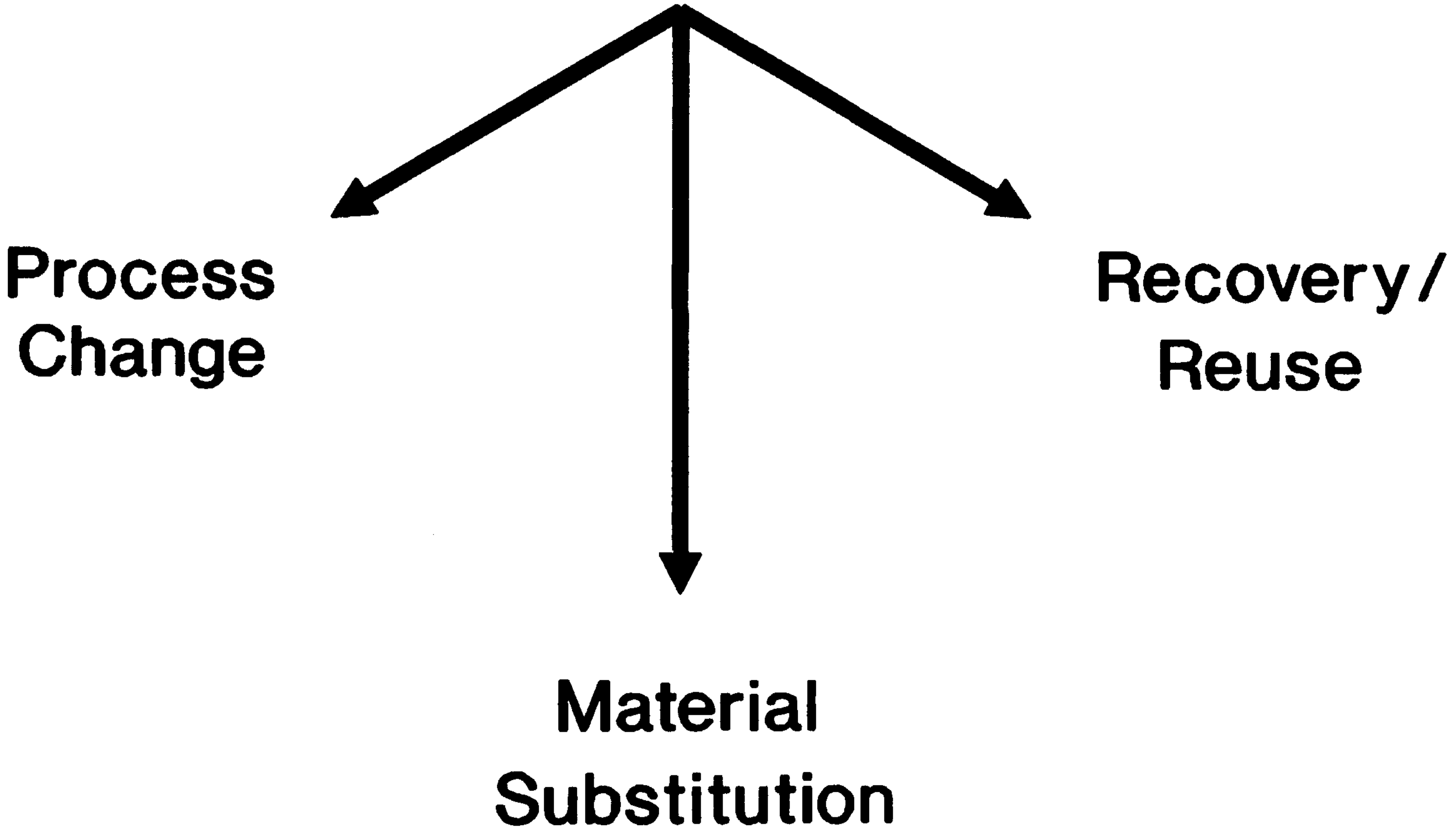
Down The Road

The Difference

INDUSTRIAL WASTE GENERATION



RESEARCH & DEVELOPMENT
IN
HAZARDOUS WASTE MINIMIZATION

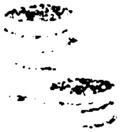
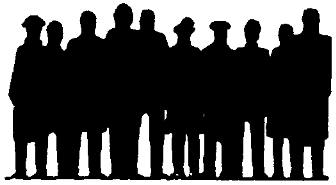


Process
Change

Recovery/
Reuse

Material
Substitution

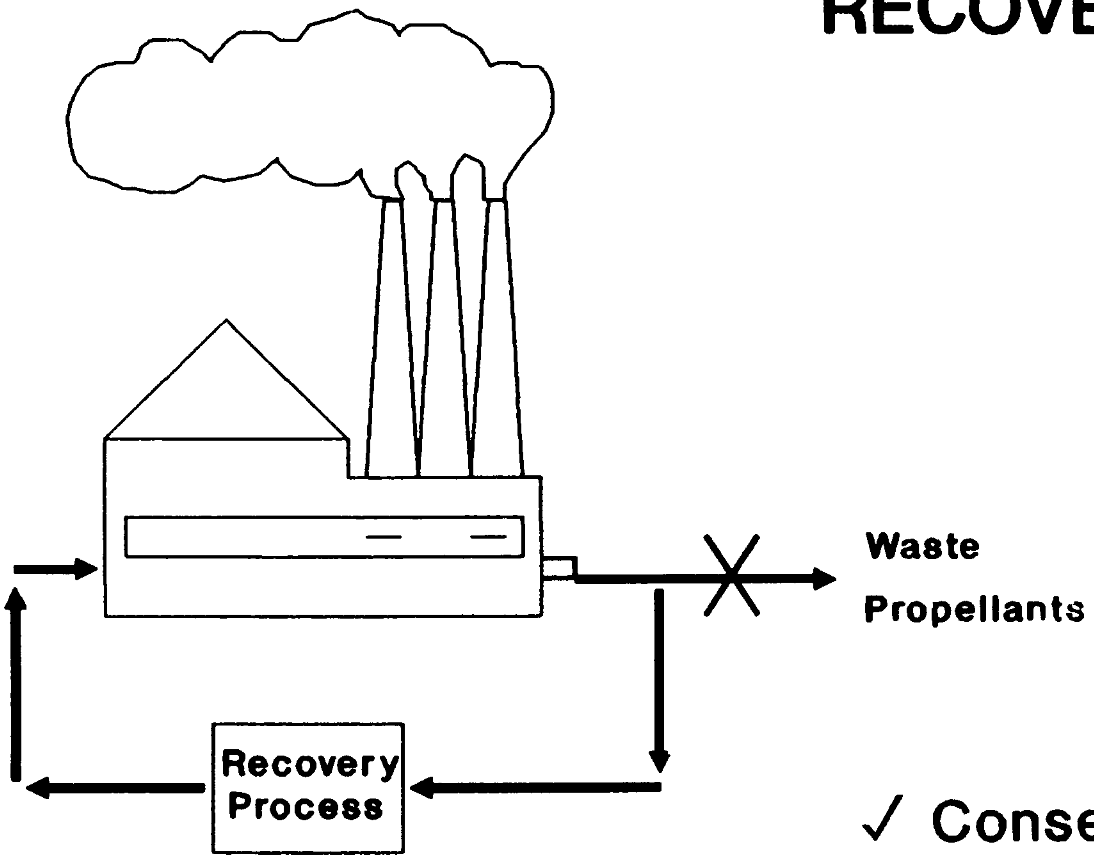
The Difference

	■ Conventional ■ Chemical Stripping	■ New ■ Plastic Media Blasting
Waste Generation	● 	● 
Cost Associated with Waste Disposal	● 	● 
Occupational Hazard Risk	● 	● 

PAINT STRIPPING

The Difference

PROPELLANT RECOVERY/REUSE


Waste Propellants

Recovery Process

- ✓ Conserves Resources
- ✓ Reduces Wastes

FUTURE

~~Cadmium Plating~~	Aluminum Ion Vapor Deposition
~~Chemical Paint Stripping~~	Fluidized Bed Paint Stripping

✓ Reduce or Eliminate Hazardous Waste Generation

✓ Reduce Cost and Liability of Waste Management

✓ Reduce Overall Costs

MAKING THE DIFFERENCE

SUCCESSFUL ACCOMPLISHMENT OF
EMVIRONMENTAL RESEARCH & DEVELOPMENT

More
Aggressive

ENVIRONMENTAL CLEANUP AND
WASTE MANAGEMENT

Less
Costly

More
Effective

IMPROVED ARMY READINESS

With
Public
Support

Title Slide (1). Theme of presentation.

The theme of this presentation reflects the fact that results of the conduct of the Army environmental R&D program "make a difference." Throughout the presentation, comparisons are made between current and future R&D products and baseline environmental management. Technology development as conducted by the Army environmental R&D program "makes a difference" by presenting timely, effective, and cost-efficient solutions to needs of the installation restoration program and the Army industrial complex.

Slide (2). Introduction.

The primary drivers of the Army environmental R&D program include the requirements of the installation restoration program as regulated by SARA and continuing operations of the Army industrial complex primarily regulated by RCRA. The conduct of environmental R&D allows for continued operation of the military base to maintain readiness while complying with local, state, and national environmental regulations.

Slide (3). The Difference: Solvent-Contaminated Soil Treatment.

This slide is indicative of the impact technology development has on the relative cost of environmental management. Baseline in this case are dig and haul operations which currently cost (roughly) $175/ton of soil. In addition, the ever-increasing cost of land disposal will cause these costs to grow with time. Alternatively, technologies have been developed which can reduce these costs. In-situ air stripping which costs approximately $40/ton can be used in some conditions. Where in-situ methods are not practical, low temperature thermal stripping techniques can be used at a cost of approximate $90/ton.

Slide (4). The Difference: Explosive-Contaminated Soil Treatment.

Explosive-contaminated soils present a significant, and often unique, problem to the Army. Current estimates indicate the presence of perhaps one million cubic yards of explosive-contaminated soil on Army property. Currently incineration is employed to treat these soils at a cost of $250 to $300 per ton. Ongoing efforts to develop a more cost-effective technology to treat these soils have resulted in the development of composting techniques which have been shown to be effective. A target cost for composting explosive-contaminated soil is $100 per ton which may allow the Army to realize a substantial cost savings compared to the baseline - incineration.

Slide (5). The Difference: Site Assessment/Monitoring

Site assessment and monitoring activites play an important role in the installation restoration program. A current baseline for monitoring of groundwater and contaminant migration is the use of monitoring wells. The costs associated with the use of these wells include those for installation and maintenance as well as costs associated with sampling and off-site analyses. In addition, redundant placement of monitoring wells is necessary due to uncertainties associated with their location. The use of a recent R&D product employing cone penetrometer technology has the potential to supplement the use of monitoring wells by providing quick information which can be used to intelligently locate monitoring wells as well as providing a means for fast turn-around in-place analyses.

Slide (6). The Difference: Down the Road.

Looking down the road at environmental R&D in support of installation restoration activities, continuing advancements are made to produce more effective and less costly technologies to remediate contaminated sites. Recent developments in biologically-based treatment concepts such as composting, have given rise to promise for future application of in-situ biotreatment techniques for soil and groundwater.

Slide (7). The Difference: Industrial Waste Generation.

One of the goals of environmental R&D is the prevention of pollution which might ultimately result in the need for future remediation. Industrial wastes generated during munition production and handling operations and standard maintenance activities are of great concern. The surest way to reduce the environmental impact of these operations is to minimize the generation of these wastes. The Army's goal for reducing hazardous waste generation is a 50% reduction of those hazardous wastes generated in 1985 by 1992. Environmental R&D actively supports this goal through technology development and implementation.

Slide (8). R&D in Hazardous Waste Minimization.

The role of R&D in HAZMIN generally takes the form of technology development to implement changes in existing processes to reduce waste generation, the substitution of less hazardous materials where feasible, and the recovery and reuse of waste materials.

Slide (9). The Difference: Paint Stripping (Chemical vs. Plastic Media Blasting).

A good example of where R&D has made a difference in industrial operations is paint stripping. The use of plastic media blasting in paint stripping processes has been viewed as a promising alternative to chemical stripping. Demonstrations of the use of plastic media blasting have allowed for a comparison to be made between its use and a baseline paint stripping method employing hazardous chemicals. In these demonstrations, it was shown that less waste was produced (70%) resulting in a reduction of disposal costs. In addition, it was shown that health-based risks were reduced by the use of plastic media blasting.

Slide (10). The Difference: Propellant Recovery/Reuse.

Currently, waste energetic materials such as propellants are either stored, open burned/open detonated where possible, or incinerated. A technology has been developed to recover waste propellants to allow for their reintroduction into the propellant manufacturing process. This development involves the grinding of the waste propellants which allows them to be resolvated and returned to the production line. Not only would implementation of this process result in significant reduction in generated wastes, but provides a method to conserve valuable Army resources.

Slide (11). Future.

Active environmental R&D efforts are being conducted to continue the development and implementation of technologies for hazardous waste reduction or elimination. Examples of technologies which are being developed for implementation in Army operations are the use of aluminum ion vapor deposition and fluidized bed paint stripping processes. Current cadmium plating operations at Army depots generate a large volume of hazardous wastes. The replacement of these operations with aluminum ion vapor deposition has the potential to eliminate this entire waste stream. Some chemical paint stripping operations can potentially be replaced with fluidized bed paint stripping which reduces hazardous waste generation as well as overall costs associated with existing paint stripping methods.

Slide (12). Conclusion: Making the Difference.

In summary, the work being done in environmental R&D is important and can have significant positive impact on accomplishing our long-term Environmental Leadership Goals. The success of the environmental program is essential in maintaining a strong national defense posture by improving Army readiness with the added benefit of increased public support as the public continues to recognize our proactive program.

Demonstration Projects Under the U.S. EPA Superfund Innovative Technology Evaluation Program

John F. Martin
Risk Reduction Engineering Laboratory
United States Environmental Protection Agency
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ABSTRACT

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 provided for federal funding to respond to releases of hazardous substances to air, water or land. The Superfund Innovative Technology Evaluation (SITE) Program resulted from the Superfund Amendments and Reauthorization Act of 1986 (SARA) which added an "Alternative or Innovative Treatment Technology Research and Demonstration Program" to Title III of CERCLA. The SITE Demonstration Program has as its major thrust the documentation of reliable performance and cost information for innovative alternative technologies. With this information new technologies may be more adequately considered for cleanup of Superfund sites. The demonstration projects identify limitations of the technology, the need for pre- or post-treatment of wastes, applicable wastes and waste media, potential operating problems, and the approximate cost of applying the technology. Currently there are 38 active projects in the Demonstration Program. Eight of these projects involve solidification/stabilization, nine concentrate on thermal processes, five are biological processes, and the remaining 16 include physical/chemical separation and treatment techniques. This paper briefly discusses the types of projects that are active in the program and highlights those demonstrations which have been completed.

INTRODUCTION

The Superfund Innovative Technology Evaluation (SITE) Program resulted from the Superfund Amendments and Reauthorization Act of 1986 (SARA) which added an "Alternative or Innovative Treatment Technology Research and Demonstration Program" to Title III of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA). The SITE Program is intended to accelerate the use of new and innovative treatment processes as well as evaluate innovative measurement and monitoring techniques. Within the SITE Program, the Demonstration Program and the Emerging Technology Program are responsible for innovative/alternative waste treatment technology development. (1)(2)

The goal of the SITE program is to ensure, to the extent possible, that innovative/alternative technologies are developed, demonstrated, and made commercially available for the permanent cleanup of Superfund sites. Through the program, the Agency wants to provide accurate and reliable performance data on these technologies for potential users.

An Emerging Technology Program, part of the SITE Program being implemented by the Risk Reduction Engineering Laboratory (RREL) in Cincinnati, provides a framework for encouraging and testing pilot-scale technologies that have been proven at the bench-scale but are not ready for field evaluation. EPA is able to provide funding to developers through a competitive cooperative agreement program to help support pilot-scale equipment development and testing. Cost sharing by the technology developer is an important aspect of this program which is intended to foster the commercialization of additional technologies having application to the cleanup of hazardous waste sites.

During the first year of the Emerging Technology Program, seven projects were initiated. Evaluation of proposals from the second-year solicitation is completed and seven more projects have been added along with one addition to the first year projects. The third round of evaluations is progressing and the third series of awards for emerging technology projects is expected during the summer, 1990.

DEMONSTRATION PROGRAM

Technologies selected for demonstration must have been developed by the private sector and must be either at final stages of field-scale development with hardware available, or fully developed with all equipment constructed and ready to use at a hazardous waste site. Emphasis is placed on innovative/alternative technologies which have been developed to the extent that a demonstration will lead to the application and commercialization of the process. The technology demonstration will provide performance and operating cost data to allow potential users to make decisions on the cost effective applicability of the technology for a specific site.

EPA believes that technology developers, as well as the Agency, will benefit from participation in the SITE demonstration program through a variety of ways.

1. Developers will have an opportunity to operate a process at field-scale on hazardous waste materials at a Superfund site.

2. The demonstration will provide developers with valuable regulatory experience and interface with Federal, State, and local authorities.

3. Participation will greatly increase public awareness of a developer's technology and its capabilities through EPA's technology transfer activities (conferences, meetings, papers, video tapes, etc.).

4. A field demonstration will provide the developer, and potential users, technical and economic information on the applicability of a process for cleanup of hazardous waste sites.

5. EPA provides for monitoring, data analysis, and reporting for each demonstration, yielding an unbiased presentation of the technology's capabilities and performance.

6. EPA has established a financial assistance program that can provide up to fifty percent of the demonstration costs to qualified developers.

The scale of the demonstration projects will be flexible in order to accommodate the wide variety of technologies that are expected to be in the program. The criteria for determining the scale will be based on the priority to provide data that is acceptable from both the QA/QC and the user community perspective.

Technology demonstrations will be conducted at Federal or State Superfund sites (remedial or removal action sites), EPA Test and Evaluation (T&E) facilities, federally owned sites, private sites, or the developer's facility. Generally, Superfund sites are preferable for the demonstration and do not require a permit. However, if necessary, EPA may assist a developer in acquiring permits. Implementation of demonstrations at areas that are not Superfund sites may be delayed because of the need for acquiring permits or exemptions. The Office of Solid Waste and Emergency Response (OSWER) maintains the lead in selecting sites, with the concurrence of the developer, that will be compatible with selected technologies.

In general, the developer is required to operate the technology at the selected site. EPA is responsible for preparing the Demonstration Plan, all sampling and analytical activities, and all reporting. The developer and EPA must agree to the content of the Demonstration Plan which consists of four major sections: an Operations Test Plan, a Sampling and Analysis Plan, a QA/QC Plan, and a Health and Safety Plan.

Products of the Demonstration Program

In general, the final products of each demonstration project will be two EPA reports. A Technology Demonstration Report presents the results of the demonstration system's performance and includes a description of the technology, an overview of the operations test plan, a summary of the sampling and analysis procedures, a discussion of health and safety issues, a presentation of the test results (with associated QA/QC data), and a listing of available cost data. An Applications Analysis Report discusses the applicability of the technology to other waste sites and types, capital and operating costs, regulations which may apply, and additional data from other sources.

While the above reports are the primary vehicles for disseminating demonstration results, the projects will also be discussed at technical conferences, published as technical papers and journal articles, and summarized in bulletins, brochures and handouts. These reports and papers will provide EPA, the States, and the public with valid performance data on new commercial technologies with potential solutions to uncontrolled waste site problems. Endorsements, approvals, and/or certifications of any technology are not a part of the SITE program.

Current Program

There are 38 active projects in the Demonstration Program. Eight of these projects involve solidification/stabilization, nine concentrate on thermal processes, five are biological processes, and the remaining 16 include physical/chemical separation and treatment techniques. During January of each year, requests for proposals are distributed in response to a solicitation for projects advertised in the *Commerce Business Daily* and trade journals. Developer proposals are reviewed by EPA for selection into the SITE Demonstration Program by mid-summer. Twelve new demonstration projects were accepted this year (1989).

COMPLETED DEMONSTRATIONS

Electric Infrared Incineration

The electric infrared incineration unit (originally developed by Shirco Infrared Systems, Inc.) is a mobile thermal processing system using electrically powered silicon carbide rods to desorb organic contaminants and bring them to combustion temperature. Remaining combustibles are incinerated in an afterburner. Full-scale demonstration of the electric furnace was carried out at an oil refinery site near Tampa, Florida, from August 1 to August 4, 1987, and a second demonstration of the system, at pilot-scale, took place at the Rose Township Dump Site in Michigan from November 2 to November 11, 1987. In both tests, at standard operating conditions, PCBs were greatly reduced and most of the metals concentrated in the ash. Data available suggest that the unit can handle solid particles in the range of 5 microns to 2 inches in diameter. (3)(4)(5)

American Combustion Technologies, Inc.

The PYRETRON, an oxygen-air-fuel burner, uses advanced fuel injection and mixing concepts to provide faster ignition and more thorough burning of waste. Operation of the burner is computer controlled to adjust the amount of pure oxygen in a preset manner determined by the operator. The burner can be fitted onto any conventional combustion unit for burning liquids, solids, and sludges. The PYRETRON was demonstrated at the U.S. EPA Combustion Research Facility in Jefferson, Arkansas, from November 16, 1987 to January 29, 1988. Results indicate that oxygen-enhanced operation could successfully destroy wastes such as naphthalene and 1,3,5-trichlorobenzene at twice the feed rate of a conventional kiln. (6)

HAZCON, Inc.

The HAZCON solidification/stabilization technology mixes hazardous waste, cement, water, and an additive called Chloranan, in order to immobilize pollutants by binding them in a concrete-like, leach-resistant mass. This solidification technique, developed by HAZCON, Inc., was demonstrated at a former oil reprocessing plant in Douglassville, Pennsylvania, from October 12 to October 16, 1987. The process can solidify organic-contaminated soil, and the demonstration showed that lead was successfully immobilized. Results from physical testing of the solidified waste were very good with unconfined compressive strength ranging from 1.52 to 10.8 MPa (220 to 1570 psi). Durability test results were also good showing no physical strength changes after twelve wet/dry and freeze/thaw cycles. (7)(8)

Soliditech, Inc.

The solidification/stabilization process developed by Soliditech, Inc. includes the addition of pozzolanic fly ash, kiln dust, or portland cement, along with a proprietary additive, URRICHEM, to a waste material. A batch mixer is used to achieve complete blending of the waste and additive mixture. In the Soliditech process, a multiphase cementation process coats the larger particles with pozzolanic materials, links organic and inorganic components, and seals pore spaces in the solidified waste so that hazardous constituents are chemically and physically immobilized. Demonstration of the Soliditech process was conducted from December 5 to December 9, 1988 at the Imperial Oil /Champion Chemical Superfund Site, an abandoned oil recycling facility in Morganville, New Jersey. Contaminants from the site included PCBs, heavy metals, petroleum hydrocarbons, and low levels of volatile organics. Short term testing of treated soil blocks indicates a high degree of physical stability, and solute extraction and leaching studies show stabilization of all contaminants of concern at this site.

Chemfix Technologies Inc.

The Chemfix process is a patented solidification/stabilization process utilizing soluble silicates and silicate setting agents for immobilizing solid or liquid metallic- and organic-bearing waste streams. The silica reagent forms inorganic polymer chains (insoluble metal silicates) that physically entrap organic colloids within the microstructure of the matrix. The cross linked matrix displays good stability and is a friable product similar to clay. Demonstration of this technology was conducted during March 1989 on waste from four areas of the Portable Equipment Salvage Company site in Clackamas, Oregon (a former metal salvage facility). The process appeared to successfully immobilize metals, (lead and copper), and good physical properties in the treated material were indicated by low permeability and high resistance to weathering cycles.

C.F. Systems Corporation

This process utilizes liquified gases as extracting solvents to remove organics such as hydrocarbons, and oil and grease from wastewater or contaminated sludges and soils. Carbon dioxide is usually used for aqueous solutions while a propane/butane mixture is used with sediment, sludge, and soil. Demonstration of this technology was conducted on PCB-contaminated harbor sediment from New Bedford, Massachusetts, during September 1988. Harbor sediments containing 350 ppm PCB were extracted to 10 ppm after ten passes through the unit. Sediments containing 2,250 ppm PCB were reduced to a 96 ppm level after six passes through the extractor. (9)

International Waste Technologies

This demonstration combined a solidification/stabilization process developed by International Waste Technologies (IWT) coupled with an in-situ soil mixing process developed by Geo-Con. The stabilization process attempts to immobilize organic and inorganic compounds in wet or dry soils by using reagents to polymerize with the soils to produce a cement-like mass. The Geo-

Con/DSM Deep Soil Mixing System delivers and mixes the stabilization chemicals with the soil while a batch mixing plant prepares the chemical feed. The Deep Soil Mixing System employs an auger equipped with cutting and mixing blades to treat soil columns 0.91 meters (36 inches) in diameter. The IWT stabilization demonstration took place at a PCB-contaminated site in Hialeah, Florida, during April 1988. The preliminary results of the SITE demonstration showed that the process produced a dense, solidified mass with good physical properties except for resistance to freeze/thaw cycles. The mixing system achieved a homogeneous soil/reagent blend with minimal difficulties. (10)

Terra Vac, Inc.

This process removes volatile organic compounds (VOCs) from the soil, above the water table, by vacuum extraction. An area of contamination is defined, extraction wells are installed, and then vacuum pumps draw subsurface contaminants from the wells, through a liquid separator, and into an activated carbon filter. The technology works best at sites that are contaminated by chemicals having a Henry's Constant greater than 0.001. The in-situ vacuum extraction demonstration operated at the Groveland Wells Superfund Site in Groveland, Massachusetts, from December 1987 to April 1988. The technology has been used at several sites across the country for recovery of gasoline, carbon tetrachloride, and TCE; and it appears to be applicable in all weather conditions. During the SITE demonstration, 590 kg (1300 pounds) of volatile organics, mainly TCE, were extracted during a 56-day operational period. (11)(12)

Ultrox International, Inc.

The Ultrox process is an ultraviolet (UV)/oxidation treatment using a combination of UV light radiation, ozone, and hydrogen peroxide to oxidize organic compounds in water. The system consists of a reactor module housing the UV lamps, an air compressor/ozone generator, and a hydrogen peroxide feed unit. The entire system is portable for on-site treatment. The Ultrox process was demonstrated in San Jose, California, at a former drum recycling facility. From February 27 to March 10, 1989, approximately 49 cubic meters (13,000 gallons) of contaminated groundwater were treated. The process met discharge standards for the site and no volatile organics were detected in the exhaust gas from the treatment unit. Ozone discharge in the off-gas was less than 0.1 ppm.

Toxic Treatments (USA), Inc.

A portable treatment unit is used for in situ air and steam stripping of volatile organics from soil. Holes are driven into the site by special drills which have been modified to provide injection of steam and air into the soil through the cutting blades. A shroud, placed on the ground surface above the cutting blades, collects the organics and carrier gas (steam and air) for separation by condensation, distillation, and activated carbon columns. During September 1989, the Toxic Treatments (USA), Inc. unit was demonstrated on a site in San Mateo, California, contaminated with chlorinated solvents, plasticizers, adhesives, and paint additives. Monitoring activities and dye studies were carried out by EPA for about a month.

BioTrol, Inc.

Two systems were provided by BioTrol, Inc. for field evaluation. The first, a fixed-film bioreactor, was evaluated while treating contaminated groundwater. The system uses a continuous flow reactor with a submerged, fixed-film biomass support. Microbes in the reactor (usually indigenous bacteria) grow on a plastic support material as heated, conditioned wastewater is pumped through. The second unit, a soils treatment system, consists of a soil washing and classification unit, the fixed film bioreactor, and a slurry bioreactor. The washing unit, utilizing water for scrubbing, classifies the soil material and removes the contaminated fine fraction. Water from the unit is pumped to the bioreactor described above and the fines will be treated in a specially designed slurry bioreactor. The demonstration took place at the MacGillis & Gibbs Superfund site in New Brighton, Minnesota, from July through October 1989. The site is contaminated with pentachlorophenol and polyaromatic hydrocarbons. Approximately 666 cubic meters (176,000 gallons) of groundwater and 31.8 metric tons (35 short tons) of soil were treated during the demonstration period.

UPCOMING DEMONSTRATIONS

Over the next several months, into early 1990, EPA is planning to take a number of technologies to the field for demonstration. In the biological treatment area, the powdered activated carbon treatment system (with wet air oxidation of waste solids) developed by Zimpro/Passavant Inc. is planned for demonstration at the Syncon Resins Superfund site in New Jersey. The next thermal process to be undertaken will be the circulating fluidized bed combustor developed by Ogden Environmental Services. The McColl Superfund site in California is planned to host the field work. Physical/Chemical treatment technologies to be demonstrated include the freeze crystallization unit by Freeze Technologies Corporation (Stringfellow Superfund site in California), a microfiltration system provided by DuPont Corporation and the Oberlin Filter Company (Palmerton Zinc Superfund Site in Pennsylvania), a steam injection/vacuum extraction process developed by Solvent Services, Inc. (Solvent Services Superfund Site in California), and a steam stripping/extraction unit offered by AWD Technologies, Inc. (San Fernando Valley Superfund Site in California).

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Treatment of Organic Contaminated Groundwater By Using Ultraviolet Light and Hydrogen Peroxide

SITE DESCRIPTION

The SAAD is an electronics supply depot consisting of storage, maintenance, and office facilities at 8350 Fruitridge Road, in Sacramento. Present operations at the SAAD include shelter repair, electro-optics equipment repair, metal plating, and treatment of metal plating wastes. Past operations have included night-vision device repairs and automatic data processing.

The SAAD is located in the center of Sacramento County, approximately 7 miles southeast of downtown Sacramento. Encompassing approximately 485 acres (2 square kilometers), SAAD is immediately surrounded on all sides by land zoned as commercial/light industrial property. A map of the site is shown in Figure 1.

SAAD has a topography that is relatively flat with ground surface elevations ranging from 36 to 42 feet above mean sea level. SAAD is situated within the Morrison Creek drainage basin with Morrison Creek being the only surface water located near the depot. Until it was diverted around the southern border of the site by the U.S. Army Corps of Engineers in 1945, Morrison Creek bisected SAAD at the center of the eastern boundary and flowed across the site toward the west. Morrison Creek discharges into the two overflow basins of the Sacramento and American Rivers and eventually empties into the Sacramento River. Mean annual precipitation at the site is approximately 17 inches.

Depth to ground water beneath the site is approximately 78 feet. The ground water gradient is approximately 1.5 feet per thousand feet and the flow direction is to the south-southwest.

Subsurface geologic data from the SAAD indicates a number of small sand channels in the upper 140 feet which are difficult to trace. This upper section has been grouped into two zones, "A" and "B", based on the relative permeabilities of the lithologies encountered. Beneath the "B" zone at a depth of about 140 feet, a silty zone occurs with a thickness varying from 8 to 14 feet. This zone appears to be a relatively continuous confining layer. This zone overlies the "C"

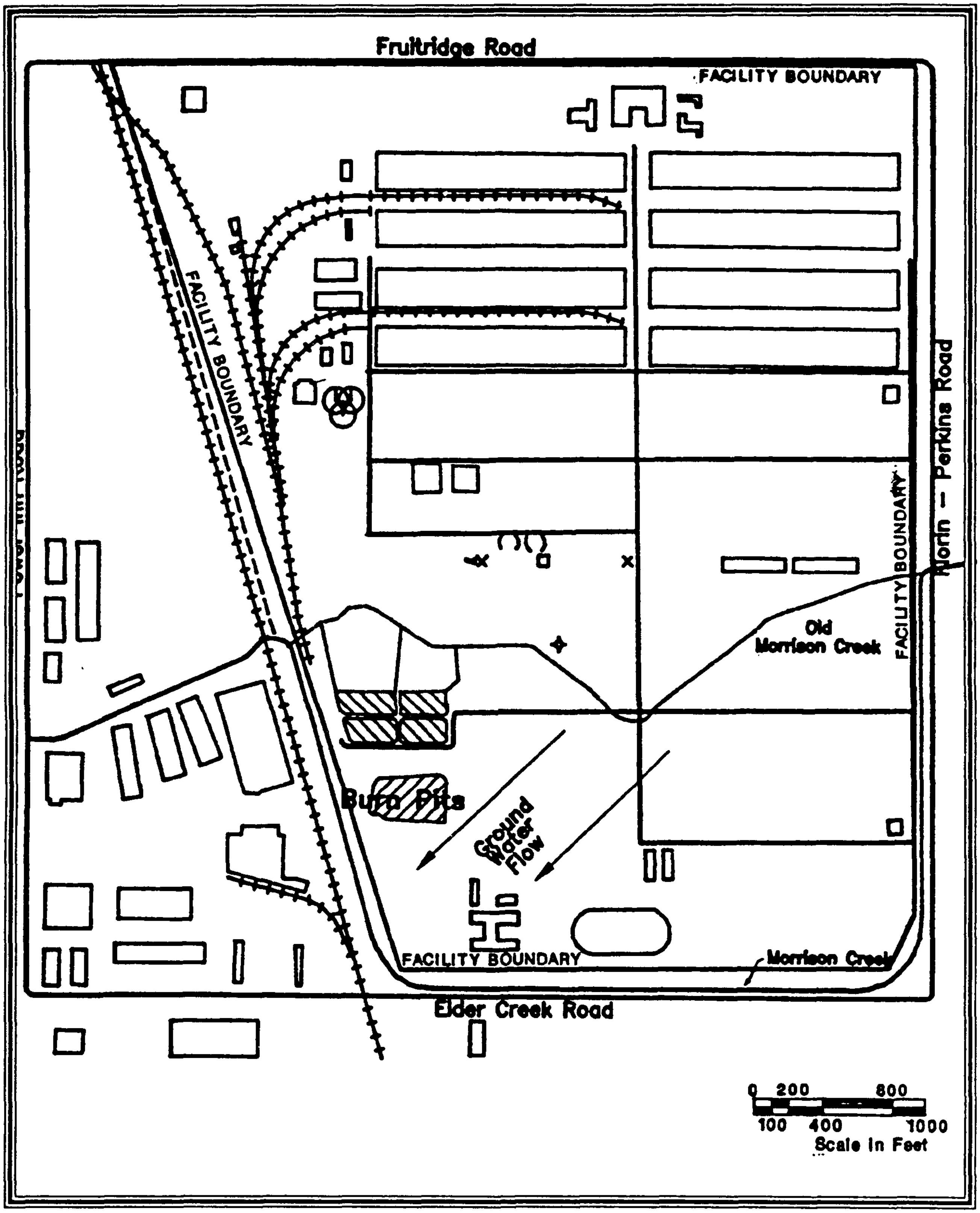

Figure 1
Site Map

zone, which has an approximate thickness of 20 to 25 feet. The "C" zone is underlain by a clayey silt zone approximately 8 to 15 feet thick. This zone overlies the 'D" zone, which is encountered at approximately 200 feet below ground surface.

A review of aerial photographs by the U.S. Environmental Protection Agency (USEPA) showed several areas where past treatment and disposal practices may have created contamination. Ground water samples collected by SAAD from 1981 to 1988 indicated that several chemical compounds were present; primarily trichloroethene, tetrachloroethene, 1,2-dichloroethane, and cis/trans-1,2-dichloroethene. These compounds have been consistently detected at levels above drinking water standards in the "A" and "B" zones. The approximate boundary of the plume is shown in Figure 2. An area known as the burn pits is considered the likely source of the organic compounds found in ground water at the SAAD site.

SAAD's containment, extraction and treatment of contaminated ground water is intended to reduce potential health risks from exposure to ground water contaminants by treating the water to meet Federal and State drinking water standards. A wide range of clean-up options were considered. Some options were eliminated during preliminary screening of alternatives because they did not effectively address contamination, there were potential problems associated with implementing a clean-up method, or costs were excessive compared to other alternatives that achieve the same degree of protection. The alternative selected for use at the SAAD entails extraction of the affected ground water, treatment using ultraviolet radiation/chemical oxidation technology, and reuse of the ground water at a local industrial facility.

The Army is the lead agency in charge of the project at the SAAD. The USEPA and DHS provide support to the Army under a Federal Facilities Agreement negotiated in December 1988. The project is managed by the Technical Review Committee through the Depot, the Corps of Engineers (Sacramento District) and the technical contractor to the Corps, Kleinfelder and Associates.

SUMMARY OF ALTERNATIVES CONSIDERED

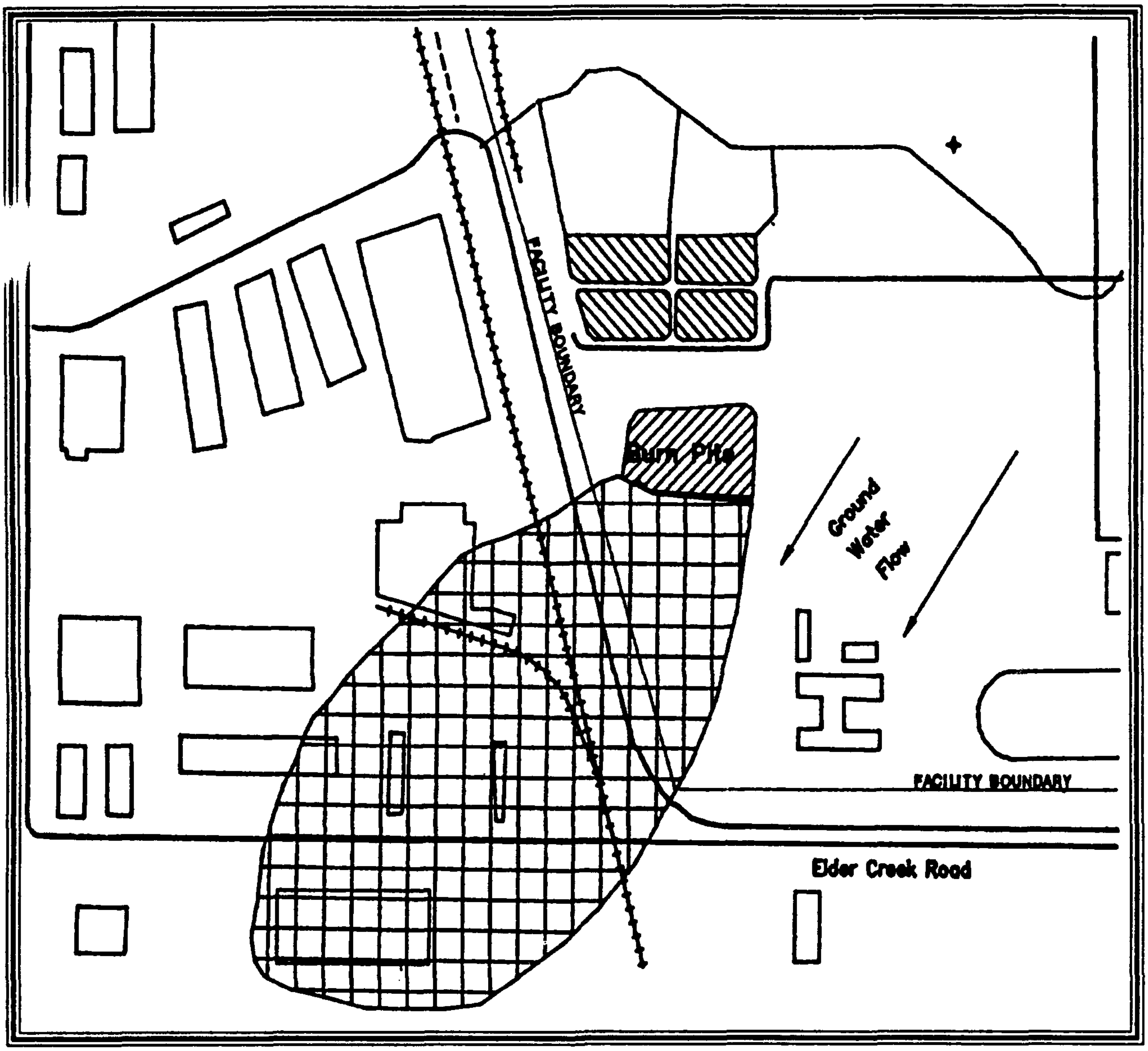

Figure 2
Approximate Plume Boundaries

Fourteen clean-up options for the SAAD site were considered in an Operable Unit Feasibility Study (OUFS). After evaluating options for technical feasibility, implementability, and cost, a detailed analysis was performed on the six best alternatives. Each of the six best alternatives to perform ground water clean-up is briefly described below:

1. No Action - The no-action alternative was used as a baseline to evaluate other potential alternatives. Under the no action alternative, no control or remediation of the affected ground water would occur. However, a limited ground water monitoring program would monitor for the presence of the organic compounds and track their migration from the SAAD site. Immediate implementation of this alternative is possible.

Estimated Construction Cost: $51,000
Estimated Annual Maintenance Costs: $25,000

2. Ground Water Extraction, Treatment by Air Stripping, and Surface Discharge - Under this alternative, wells extract the affected ground water, contamination is removed from the ground water by air stripping, and treated ground water is discharged to Morrison Creek. Compounds removed from the ground water by the air stripper would be transferred to the air without further treatment. Other alternatives using air stripping with air emission control were considered, however, were eliminated during preliminary screening due to excessive costs. This alternative also includes monitoring of ground water, surface water, treatment plant influent, and discharge water over the term of the operation to assess the effectiveness of extraction and treatment, and compliance with discharge requirements. Construction could be completed within approximately 12 months. The quality of ground water in the aquifer would be restored to meet current drinking water standards after 10 to 15 years of operation.

Estimated Construction Cost: $1,170,000
Estimated Annual Maintenance Costs: $242,000

3. Ground Water Extraction, Treatment by Air Stripping, and Industrial Reuse This alternative is similar to Alternative 2 above, except that treated water would be discharged to a local industrial facility for reuse instead of to Morrison Creek. Other construction details and monitoring requirements will be the same. The quality

of ground water in the aquifer would be restored to meet current drinking water standards after 10 to 15 years of operation.

Estimated Construction Cost: $1,345,000
Estimated Annual Maintenance Costs: $207,000

4. Ground Water Extraction, Treatment with Ultraviolet Radiation/Chemical Oxidation, and Surface Discharge - This alternative is similar to Alternative 2 except that ultraviolet UV radiation/chemical oxidation is used for treatment, not air stripping. The organic contamination would be destroyed by the treatment process, without releases to the air or creation of residual wastes. Other construction details and monitoring requirements will be the same. Construction of this alternative could be completed in approximately 12 months. The quality of ground water in the aquifer would be restored to meet current drinking water standards after 10 to 15 years of operation.

Estimated Construction Cost: $1,530,000
Estimated Annual Maintenance Costs: $298,000

5. Ground Water Extraction, Treatment with Ultraviolet Radiation/Chemical Oxidation, and Industrial Reuse - This alternative is similar to Alternative 4 above, except the treated water would be discharged to a local industrial facility, not to surface water. Other construction details and monitoring requirements will be the same. Construction of this alternative could be completed within about 12 months. The quality of ground water in the aquifer would be restored to meet current drinking water standards after 10 to 15 years of operation.

Estimated Construction Cost: $1,764,000
Estimated Annual Maintenance Costs: $264,000

6. Ground Water Extraction and Discharge to the Sacramento Regional Wastewater Treatment Plant - Under this alternative wells would extract ground water, which would then be discharged without treatment to the Sacramento Regional Wastewater Treatment Plant (SRWTP). The organic compounds in the water would be diluted in the sewer system and ultimately released to the air in the treatment plant, and discharged to the Sacramento River. This alternative also includes monitoring of ground water and discharge water to assess the effectiveness of the extraction process, and

compliance with discharge requirements. Construction of the alternative could be completed in about 12 months. The quality of ground water in the aquifer would be restored to meet current drinking water standards after 10 to 15 years of operation.

Estimated Construction Cost: $1,316,000
Estimated Annual Maintenance Costs: $197,000

EVALUATION OF ALTERNATIVES

The six best alternatives were evaluated with respect to nine evaluation criteria, which are summarized below:

1. Short-term effectiveness - Addresses the period of time needed to complete the remedy, and any adverse impact on human health and the environment that may be posed during the construction and implementation period, until the clean-up goals are achieved.

2. Long-term Effectiveness and Permanence - Refers to the ability of a remedy to maintain reliable protection of human health and the environment over time, once cleanup goals have been met.

3. Reduction of Toxicity Mobility and Volume Through Treatment-(TMV) - Refers to the anticipated ability of a remedy to reduce the toxicity, mobility, and volume of the hazardous components present at the site.

4. Implementability - Refers to the technical and administrative feasibility of a remedy, including the availability of materials and services needed to carry out a particular option.

5. Cost - Evaluates the estimated capital and operation and maintenance costs of each alternative.

6. Overall Protection of Human Health and the Environment - Addresses whether or not a remedy provides adequate protection and describes how risks posed through each pathway are eliminated, reduced or controlled through treatment, engineering controls, or institutional controls.

7. Compliance with Applicable or Relevant and Appropriate Requirements {ARARs} - Addresses whether or not a remedy will meet all ARARs of federal and state environmental statues and/or provide grounds for invoking a waiver.

8. State Acceptance - Indicates whether, based on its review of the information, the state concurs with, opposes, or has no comment on the preferred alternative.

9. Community Acceptance - Indicates whether community concerns are addressed by the remedy and whether or not the community has a preference for a remedy. Although public comment is an important part of the final decision, EPA is compelled by law to balance community concerns with all of the previously mentioned criteria.

A summary of the alternatives is presented in Table 1. All the final alternatives considered use ground water extraction to control migration and remove contaminated ground water. The main differences are: 1) the treatment technology, if any, to be used to treat contaminated ground water prior to discharge, and 2) the discharge option to be used.

All of the alternatives considered except Alternative 1 (No Action) provide protection of human health and the environment and meet the current ARARs. However, only alternatives that use UV radiation/chemical oxidation result in permanent destruction of the contaminants, unlike air stripping or discharge to the SRWTP. The potential health risk from operation of a UV radiation/chemical oxidation system is lower than for air stripping because the organic compounds are not released to the air. Therefore, the most desirable alternative is the UV radiation/chemical oxidation for ground water treatment.

Three disposal options for the extracted ground water were evaluated: 1) surface water discharge to Morrison Creek, 2) industrial reuse, and 3) discharge to the SRWTP without treatment. No significant public health or environmental impacts are expected to result from any of the disposal options. Alternatives that entail industrial reuse are preferred because the water would serve beneficial purposes prior to being discharged to Morrison Creek or the sewer. More time may be needed to implement industrial reuse because a long-term agreement with the industrial user would be necessary. Also, there would be some uncertainty relative to acceptance of the water for the 10 to 15 years needed to complete remediation. Negotiating a water reuse agreement could delay implementation of the alternative; however, a delay could be avoided by temporarily discharging the treated ground water to the SRWTP.

Based on the information presented in the OUFS report, Alternative 5 (ground water extraction, treatment with UV radiation/chemical oxidation, and industrial reuse) is the preferred alternative.

In summary, the selected alternative is believed to provide the best balance among alternatives relative to the evaluation criteria used to weigh the potential options. Based on the information available at this time, the Army, the USEPA and the California DHS believe the selected alternative is protective of human health and the environment, attains current ARARs, is cost-effective, and uses permanent solutions and alternative treatment technologies to the maximum extent practicable.

TABLE 1
SUMMARY OF DETAILED ANALYSIS OF GROUND WATER OUFS ALTERNATIVES

Assessment Criteria	Alternative No. 1 - No Action	Alternative No. 2 - Containment by Pumping, Air Stripping, Surface Discharge	Alternative No. 3 - Containment by Pumping, Air Stripping, Industrial Reuse
Description	No mitigating measures. Continued ground water monitoring.	Install extraction well system; Pump and treat using air stripping; Discharge to Morrison Creek; Ground water and performance monitoring.	Install extraction well system; Pump and treat using air stripping; Discharge to local industrial facility; Ground water and performance monitoring.
Short-Term Effectiveness	No significant risk from monitoring.	Low risk during construction.	Low risk during construction.
Long-Term Effectiveness and Permanence	Long-term health risks remain from ingestion of contaminated water from offsite production wells	No significant risk to public or environment would remain, once cleanup goals are attained.	No significant risk to public or environment would remain, once cleanup goals are attained.
Reduction in Toxicity, Mobility, and Volume	No treatment used.	The organic compounds are transferred to the air, but not destroyed unless vapor-phase carbon is used.	The organic compounds are transferred to the air, but not destroyed unless vapor-phase carbon is used.
Implementability	No technical impediments to implementation. Regulatory concurrence not probable.	Technologies used are readily available. About 12 months needed for construction.	Technologies used are readily available. About 12 months needed for construction. Negotiation with industrial user could delay implementation unless interim discharge to SRWTP is used.
Compliance with ARARs	Does not comply with ARARs.	Complies with ARARs, but does not meet statutory preference for treatment.	Complies with ARARs, but does not meet statutory preference for treatment.
Overall Protection of Human Health and the Environment	Does not provide protection. No mitigation of primary exposure pathway.	No significant health risk during construction and operation, except for air emission. No significant risk remains once cleanup goals are attained.	No significant health risk during construction and operation, except for air emission. No significant risk remains once cleanup goals are attained.
Cost	Capital $ 51,000 Annual $ 25,000 Present Worth $288,000 Economic Life 30 years	Capital $1,170,000 Annual $ 242,000 Present Worth $3,449,000 Economic Life 30 years	Capital $1,345,000 Annual $ 207,000 Present Worth $3,299,000 Economic Life 30 years

TABLE 1
SUMMARY OF DETAILED ANALYSIS OF GROUND WATER OUFS ALTERNATIVES
(CONTINUED)

Assessment Criteria	Alternative No. 4 - Containment by Pumping, UV Chemical Oxidation, Surface Discharge	Alternative No. 5 - Containment by Pumping, UV Chemical Oxidation, Industrial Reuse	Alternative No. 6 - Containment by Pumping, SRWTP Discharge
Description	Install extraction well system. Pump and treat using UV oxidation technology. Discharge to Morrison Creek. Ground water and performance monitoring.	Install extraction well system Pump and treat using UV chemical oxidation technology. Discharge to local industrial facility. Ground water and performance monitoring.	Install extraction well system. Pump and discharge untreated water to sewer routed to SRWTP. Ground water and discharge monitoring.
Short-Term Effectiveness	Low risk during construction.	Low risk during construction	Low risk during construction.
Long-Term Effectiveness and Permanence	No significant risk to public or environment would remain.	No significant risk to public or environment would remain, once cleanup goals are attained.	No significant risk to public or environment would remain, once cleanup goals are attained.
Reduction in Toxicity, Mobility, and Volume	Technology destroys volatile organic compounds without formation of residual by-products.	Technology destroys volatile organic compounds without formation of residual by-products.	Compounds are either removed during pure oxygen activated sludge process or levels reduced by dilution. No destruction of organics achieved.
Implementability	Only two vendors offer technology used, but they both have operating systems at other sites. About 12 months needed for construction.	Only two vendors offer technology used but they both have operating systems at other sites. About 12 months needed for construction. Negotiation with industrial user could delay implementation unless interim discharge to SRWTP used.	Easily implemented within 6 to 12 months. SRWTP has agreed to accept water.
Compliance with ARARs	Complies with ARARs.	Complies with ARARs.	Complies with ARARs, but does not meet statutory preference for treatment.
Overall Protection of Human Health and the Environment	No significant health risk during construction and operation. No significant risk remains once cleanup goals are attained.	No significant health risk during construction and operation. No significant risk remains once cleanup goals are attained.	No significant health risk during construction and operation. No significant risk remains once cleanup goals are attained.
Cost	Capital $1,530,000 Annual $ 298,000 Present Worth $4,341,000 Economic Life 30 years	Capital $1,764,000 Annual $ 264,000 Present Worth $4,250,000 Economic Life 30 years	Capital $1,316,000 Annual $ 197,000 Present Worth $3,177,000 Economic Life 30 years

BIOLOGICAL TREATMENT OF DIESEL CONTAMINATED SOIL FROM UST LEAK USING LAND FARMING TECHNIQUES.

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ABSTRACT

In pursuance of federal and state regulations concerning Underground Storage Tanks (UST's), Anniston Army Depot (ANAD) is initiating leak testing of UST's located on the installation. In support of this effort, a study in remediation of diesel contaminated soil using aerobic and facultative anaerobic bacteria is in progress. Approximately 7000 cubic yards of diesel contaminated soil was excavated from an UST leak site. The soil was spread over four separate plots ranging in size from 0.4 to 1.6 acres. The soil was then tilled to a thickness of eighteen inches, and treated with solutions of bacteria, emulsifier, and fertilizer. A second bacterial treatment was applied three weeks after the initial treatment. The soil is tilled, aerated and watered twice per week using conventional farm equipment. Soil sampling is conducted once per week, and soil hydrocarbon concentrations are determined using soxhlet extraction with Infrared analysis in monitoring the progress of the degradation. When representative samples are determined to be less than 100 ppm, the degradation will be considered complete. The study is presently in its fifth week, and the degradation is expected to be completed within eight to ten weeks. Initial results show the degradation to be proceeding as expected.

INTRODUCTION

Present methods for dealing with land-based spills of oil or petroleum containing material have generally relied on the removal of the contaminated soil to a secure landfill. This type of approach is impractical and costly when it occurs in areas that are remote from such a landfill. Site remediation through the use of biological treatment is a method which has come to the fore front within the past ten years. Through the use of subsurface microbes clean-up of spills and spill residues can become a safe, low cost alternative to the transport of contaminated soil.

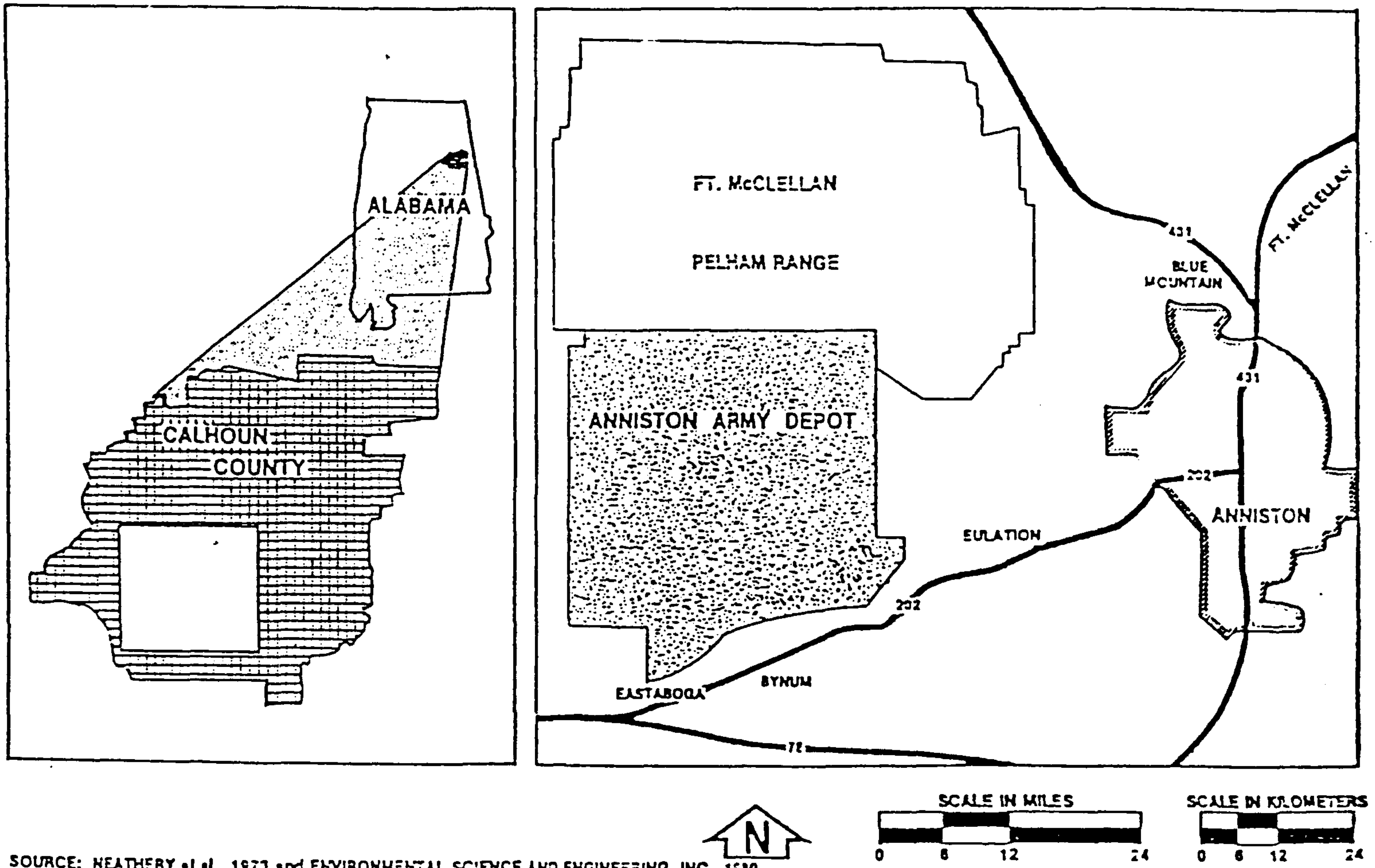
The advantages to biological treatment can be numerous. Several major advantages are associated with the implementation of biological waste treatment. Because of the characteristics of specific microbes, under ideal environmental conditions, numerous organic compounds can be completely metabolized yielding totally innocuous compounds. The ability to culture specially selected and adapted microorganisms for this type of process is significant. The availability and cost of obtaining these microbes can significantly reduce the expenditures of any site remediation program.

Biological treatment when used in land farming techniques presented this organization with a means by which all treatment could be done "in house." Equipment requirements for land farming are similar to most type agricultural applications so the need to obtain outside help was minimal. Application of bacteria, nutrients, PH control, moisture control and tilling methods to surface soils are all readily accessible items.

BACKGROUND

Anniston Army Depot (ANAD) is located in northeastern Alabama in the foothills of the Appalachian mountain chain. The Depot is approximately 10 miles from the town of Anniston and encompasses 15,214 acres. ANAD is in Calhoun County and is within a 2-hour drive of Birmingham, Alabama, and Atlanta, Georgia (Figure 1). The basic functions of the Depot are to operate a supply depot for receipt, storage and shipment of General Services Administration and Defense Logistics Agency items; to maintain and operate an ammunition depot for small arms, explosives, guided missiles, and other components; to operate a maintenance depot for the overhaul, repair, modification and conversion of combat vehicles, weapons, artillery and other components; and to support tenant units.

During a pretest procedure of an inactive facility designed to incinerate obsolete ammunition, ANAD personnel filled an



SOURCE: HEATHERY et al., 1973 and ENVIRONMENTAL SCIENCE AND ENGINEERING, INC., 1980

FIGURE 1: LOCATION MAP OF ANNISTON ARMY DEPOT, ANNISTON, ALABAMA

ANNISTON ARMY DEPOT

underground storage tank (UST) with 500 gallons of Number 2 diesel fuel, only to discover four days later that the tank was empty. Approximately 7000 cubic yards of soil were contaminated from the diesel fuel release which occurred on August 29, 1988. Regulatory officials were immediately notified, and the tank and surrounding soil were excavated. The UST was located in the northwest quadrant of ANAD, at building 393. The zone of contaminated soil was not found to have intercepted the water table.

A geological survey of the UST leak site was conducted by the U.S. Army Environmental Hygiene Agency (AEHA) during the period between September 12-30, 1988. The lateral and vertical extent of soil contamination were determined through soil sampling from 31 borehole locations as shown in Figures 2 and 3. Figure 2 also shows the maximum concentrations of total petroleum hydrocarbons (TPH) found at each borehole location within the zone of contamination. The depth of soil contamination did not exceed 25 feet in any location sampled. Maximum TPH concentrations within the contamination plume ranged from 136 to 4310 ppm.

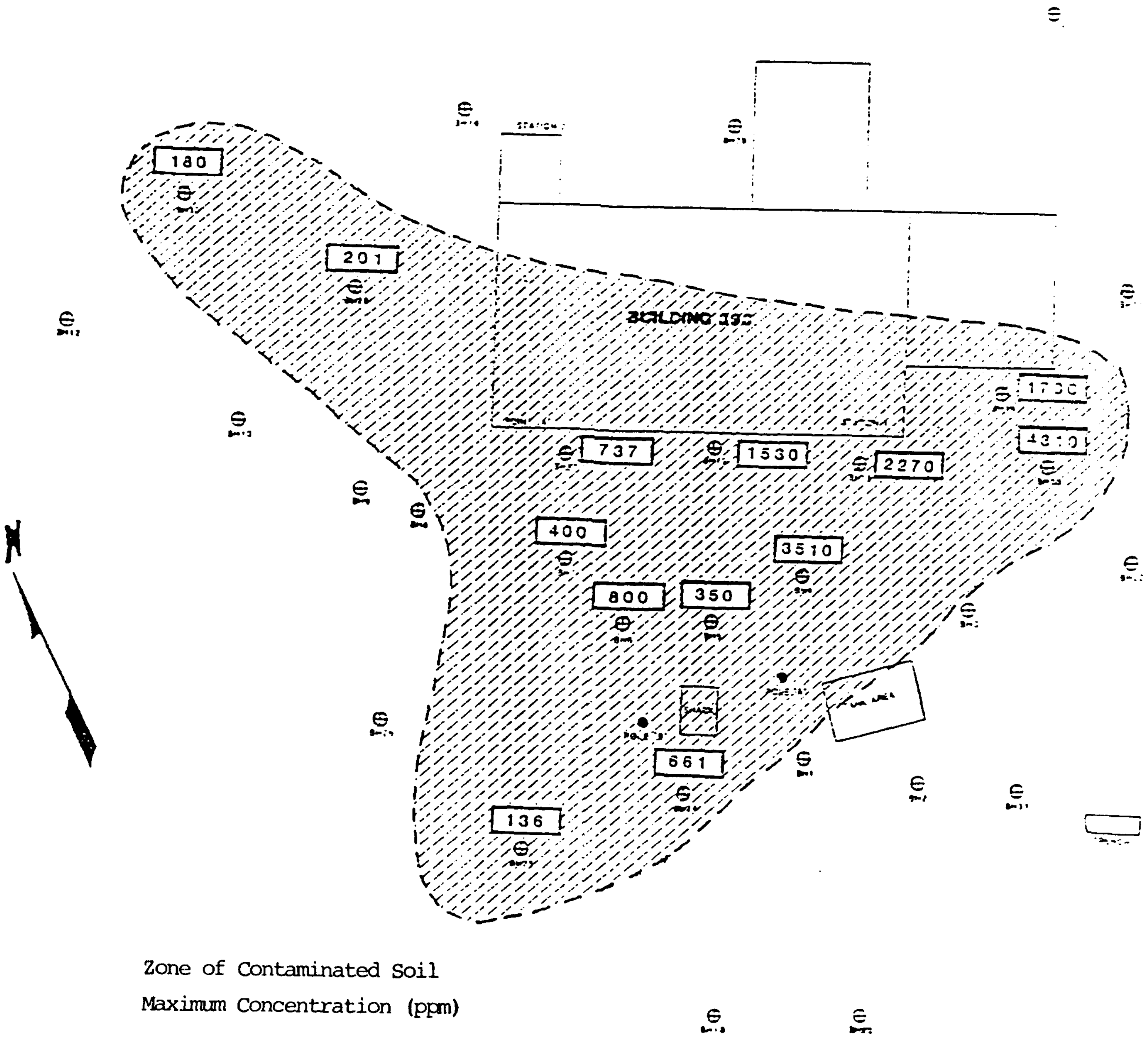
The soils encountered in all of the borings consisted primarily of clay. At most of the borehole locations, the lithology consisted of a brown clay loam or brown silty clay for the upper 2-4 feet, followed by a red clay extending to the bottom of the borehole. It was determined through ground water sampling that the zone of contaminated soil did not intercept the water table. The depth of soil contamination did not exceed 25 feet in any of the boreholes. In the zone of contamination, the borings indicated that the depth to water was greater than 36 feet.

Excavation of the contaminated soil was conducted during the period from June through July of 1989. The entire contamination plume shown in Figure 2 was excavated to a depth of 25 feet and spread over four separate plots to a thickness of eighteen inches. Photographs of the excavation area, the land farm plots, and the biological treatment process are presented in Figures 4, 5, and 6. Biological treatment of the contaminated soil using land farming techniques was conducted for a ten week period from August through October of 1989. In accordance with the Alabama Department of Environmental Management (ADEM) regulations, when representative TPH concentrations were determined to be less than 100 ppm, no further remedial action was required.

METHODS

Upon completion of the excavation, soil samples were taken from the excavation area for verification of removal of all contaminated soil. ADEM approval was then obtained to

Figure 2. Lateral Extent Of Contaminated Soils



Zone of Contaminated Soil

Maximum Concentration (ppm)

Figure 3. Cross Sectional View of Contaminated Soils

Location of Cross Section Shown on Figure 3

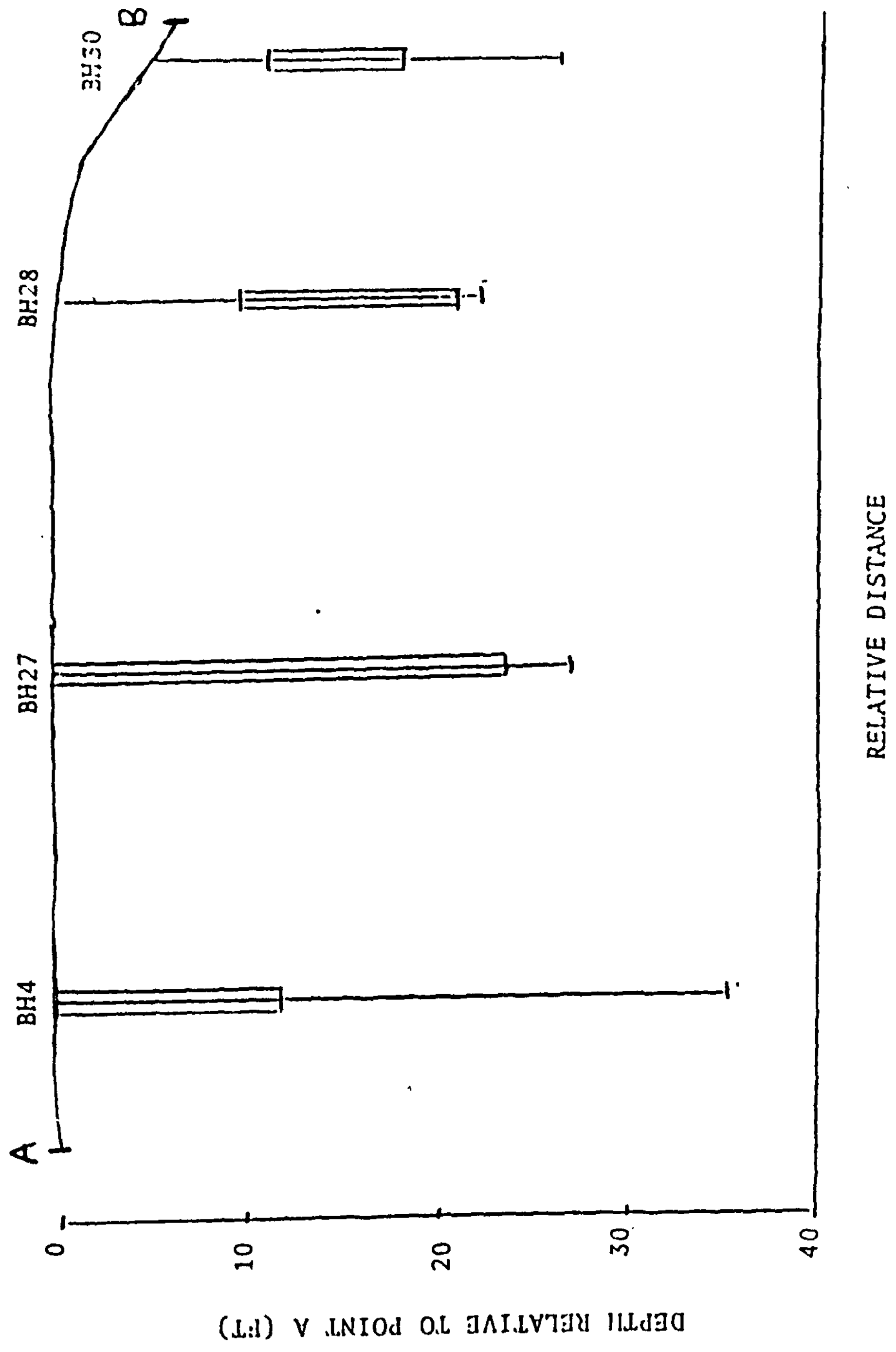


Figure 4

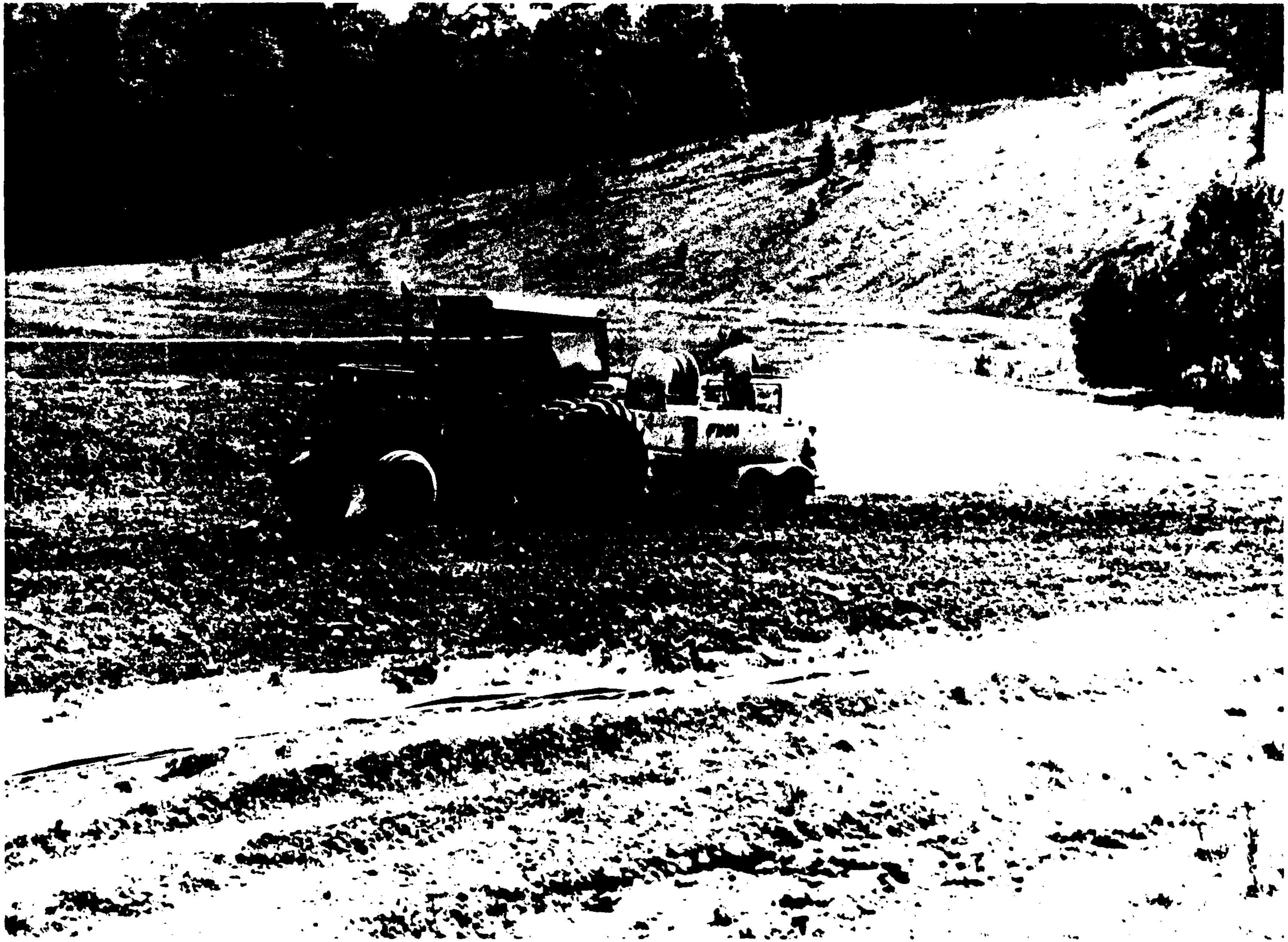


Figure 5

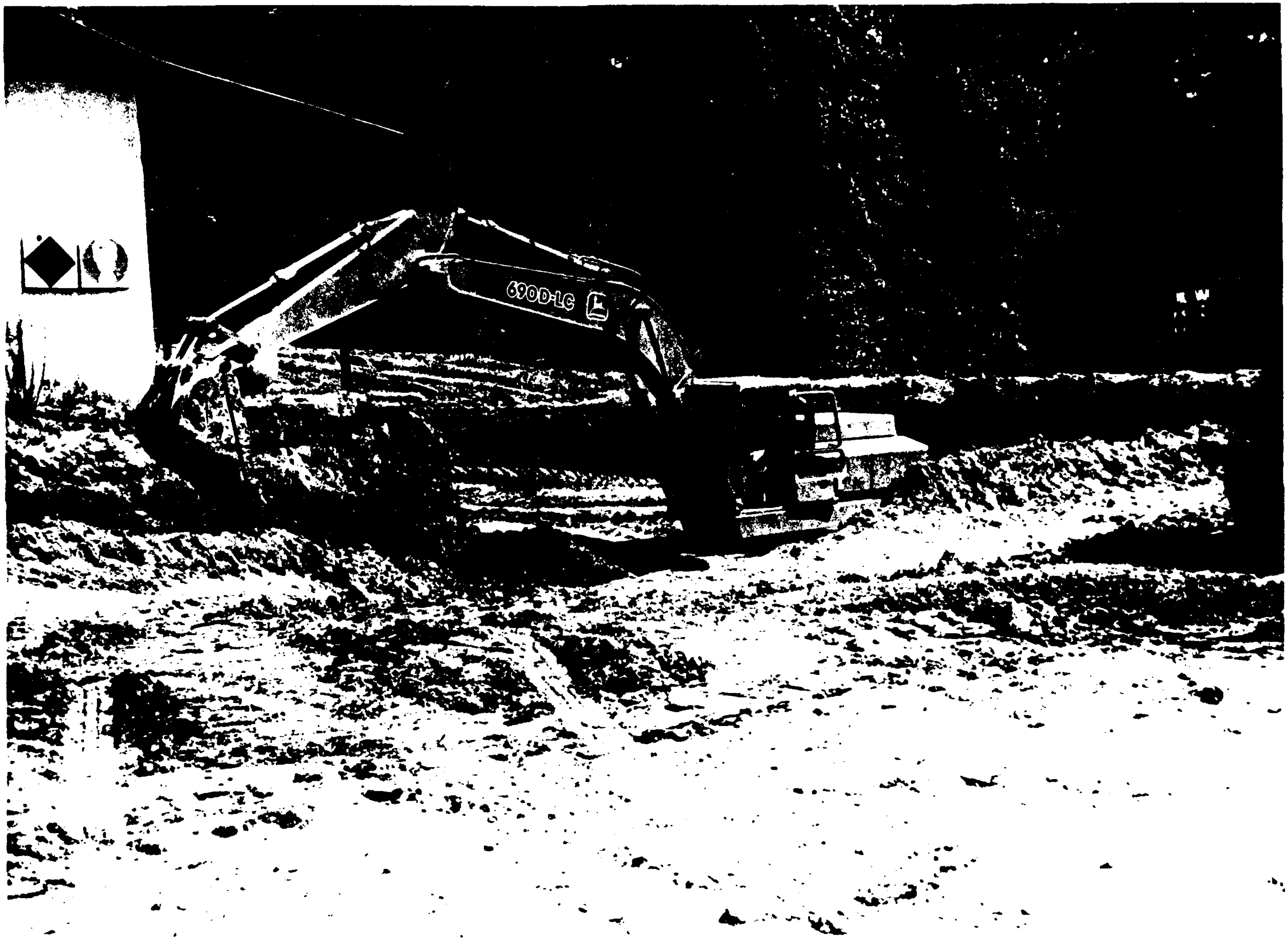


Figure 6

backfill the excavated area with fresh dirt. Contaminated soil removed from the excavated area was spread over four separate plots for landfarming. The landfarm plots ranged in size from 0.4 to 1.4 acres and were bermed to prevent run-off. The landfarm areas were lined with ten mil plastic before spreading the contaminated soil to prevent leachate seepage into uncontaminated soil. The contaminated soil was then spread to a thickness of approximately eighteen inches over each of the landfarm areas.

Biological degradation of the hydrocarbons within the contaminated soil was accomplished using an aerobic and facultative anaerobic bacteria capable of degradation of hydrocarbons. Treatment of the contaminated soils consisted of application of solutions of bacteria, emulsifier, and fertilizer in amounts of 33 pounds of bacteria per 1000 cubic yards of soil, 25 pounds of emulsifier per 1000 cubic yards of soil, and sufficient fertilizer to yield a minimum of 15 mg/l NH-N and PO-P. A second such treatment was applied three weeks after the initial treatment. Soil pH was maintained between 7 and 8, and soil moisture content from 30-40 percent. The soil was tilled, aerated, and watered a minimum of twice per week over the ten week degradation period using conventional farm equipment.

Soil sampling of the contaminated soil was conducted once per week. Depth composite soil samples were collected from four locations within each of the four land farm plots. These sampling locations were labeled FM (middle of front quadrant of plot), M1 (middle of second quadrant of plot), M2 (middle of third quadrant of plot) and RM (middle of rear quadrant of plot), as referenced in Table I. Soil hydrocarbon concentrations were determined using soxhlet extraction with infrared analysis in monitoring the progress of the degradation. In accordance with ADEM regulations, remediation was considered complete when soil TPH concentrations were found to be less than 100 ppm.

RESULTS

The results of soil TPH concentration monitoring are presented in Table I and in Figures 7 through 11. Table I contains weekly soil TPH concentration data from each of the four soil sampling locations within each land farm plot and the average of the four locations for each plot. Figures 7 through 11 present graphical representations of average soil TPH degradation over time for each of the four plots. Daily average ambient temperature and rainfall data recorded during the project time frame are presented in Table II.
Overall, the results show that the combined effects of biological degradation and TPH volatilization through elevated summertime ambient temperatures were effective in

TABLE I. SOIL BIOREMEDIATION DATA

DATE	DAY	TOTAL PETROLEUM HYDROCARBON CONCENTRATIONS (ppm)																			
		Land Farm Plot 1					Land Farm Plot 2					Land Farm Plot 3					Land Farm Plot 4				
		FM	M1	M2	RM	AV	FM	M1	M2	RM	AV	FM	M1	M2	RM	AV	FM	M1	M2	RM	AV
7/27	0	740	1850	--	348	979	905	1657	--	4040	2201	44	191	--	20	85	--	--	--	--	1088
8/7	11	176	496	--	458	377	20	208	--	87	105	20	198	--	86	101	20	20	--	543	194
		First Biological Treatment																			
8/14	18	335	255	342	181	278	42	805	499	431	444	186	416	398	220	305	386	155	213	146	225
8/21	25	389	451	688	1224	688	455	1035	489	350	582	422	578	96	74	293	557	20	389	239	301
8/28	32	358	662	598	93	428	84	67	512	1482	536	365	27	69	191	163	71	295	196	20	318
9/5	40	367	1125	1204	154	713	42	136	103	410	173	212	20	56	249	134	118	20	40	20	50
		Second Biological Treatment																			
9/11	46	373	248	535	*3763	385	60	162	706	515	361	20	101	199	134	114	109	73	39	20	60
9/18	53	425	601	645	985	664	872	528	328	378	527	32	25	309	153	130	*438	108	45	94	82
9/26	61	216	201	279	283	245	54	417	36	*4137	169	41	124	20	20	51	--	--	--	--	--
10/3	68	221	768	453	47	372	20	277	512	772	395	20	20	--	--	20	20	--	--	--	20

FM = Soil Sample - Middle of Front Quadrant of Land Farm Plot.
M1 = Soil Sample - Middle of Second Quadrant of Land Farm Plot.
M2 = Soil Sample - Middle of Third Quadrant of Land Farm Plot.
RM = Soil Sample - Middle of Rear Quadrant of Land Farm Plot.
AV = Average TPH Concentration for entire Plot.
* Pocket of high contamination - value not considered in average.
-- Soil Sample Not Taken.

TABLE II. AMBIENT TEMPERATURE AND RAINFALL DATA DURING PROJECT

JULY			AUGUST			SEPTEMBER			OCTOBER		
DATE	TEMP (°F)	RAIN (in)	DATE	TEMP (°F)	RAIN (in)	DATE	TEMP (°F)	RAIN (in)	DATE	TEMP (°F)	RAIN (in)
9/1	70	0.2	8/1	82	---	9/1	83	0.1	10/1	73	1.3
9/2	77	0.9	8/2	80	0.4	9/2	78	---	10/2	71	0.0
9/3	74	0.1	8/3	80	---	9/3	80	---	10/3	70	---
9/4	73	0.6	8/4	82	0.0	9/4	77	---	10/4	65	---
9/5	80	0.6	8/5	84	---	9/5	76	---	10/5	65	---
9/6	76	0.3	8/6	87	---	9/6	74	---	10/6	68	---
9/7	82	---	8/7	73	---	9/7	79	---	10/7	63	---
9/8	83	---	8/8	71	---	9/8	81	---	10/8	59	---
9/9	83	---	8/9	71	---	9/9	81	---	10/9	55	---
9/10	82	---	8/10	71	---	9/10	79	1.0	10/10	58	---
9/11	80	0.2	8/11	75	---	9/11	80	---	10/11	65	---
9/12	82	1.5	8/12	75	---	9/12	76	---	10/12	68	---
9/13	81	---	8/13	77	---	9/13	81	---	10/13	69	---
9/14	82	---	8/14	76	2.2	9/14	81	---	10/14	68	---
9/15	82	---	8/15	78	---	9/15	75	0.6	10/15	72	---
9/16	78	---	8/16	79	0.6	9/16	71	---	10/16	71	0.3
9/17	68	---	8/17	78	0.1	9/17	71	---	10/17	69	0.2
9/18	81	---	8/18	73	---	9/18	68	---	10/18	47	0.4
9/19	81	2.5	8/19	79	---	9/19	70	---	10/19	45	---
9/20	81	---	8/20	83	---	9/20	71	---	10/20	42	---
9/21	80	0.1	8/21	83	---	9/21	75	0.2	10/21	50	---
9/22	82	0.6	8/22	85	---	9/22	76	0.7	10/22	57	---
9/23	83	---	8/23	85	---	9/23	59	---	10/23	61	---
9/24	83	---	8/24	84	---	9/24	56	0.1	10/24	70	---
9/25	83	---	8/25	83	---	9/25	57	1.1			
9/26	73	0.2	8/26	82	1.7	9/26	66	---			
9/27	81	---	8/27	81	---	9/27	67	---			
9/28	62	---	8/28	84	---	9/28	68	0.1			
9/29	84	---	8/29	85	---	9/29	63	0.4			
9/30	84	0.5	8/30	72	0.7	9/30	70	0.2			
9/31	82	0.1	8/31	81	---						

TEMP - 24-hr Average Ambient Temperature (oF)
RAIN - Total 24-hr Rainfall (inches)
--- - No Rainfall Recorded

FIGURE 7. TPH CONCENTRATION VS TIME

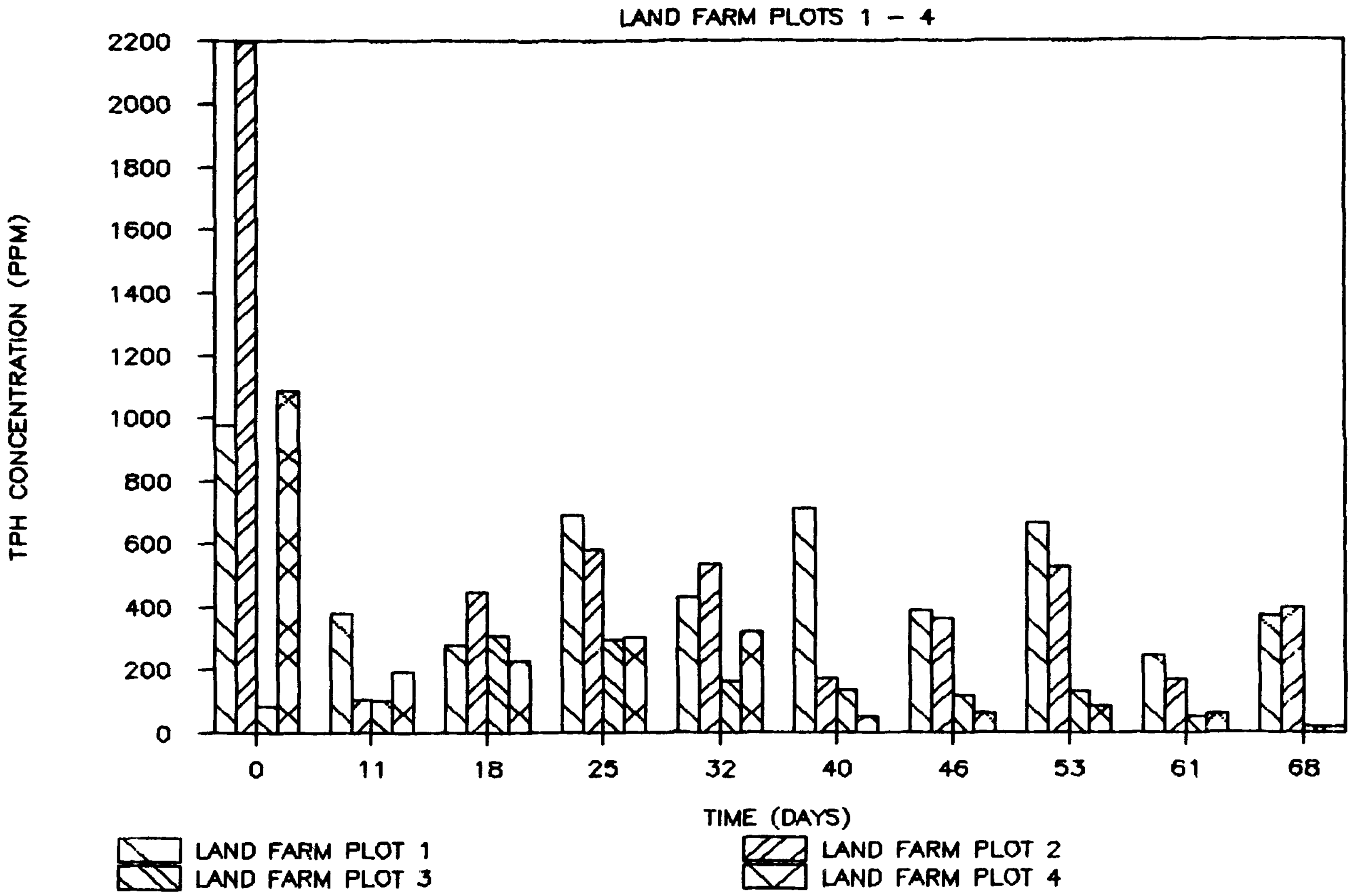


FIGURE 8. TPH CONCENTRATION VS TIME

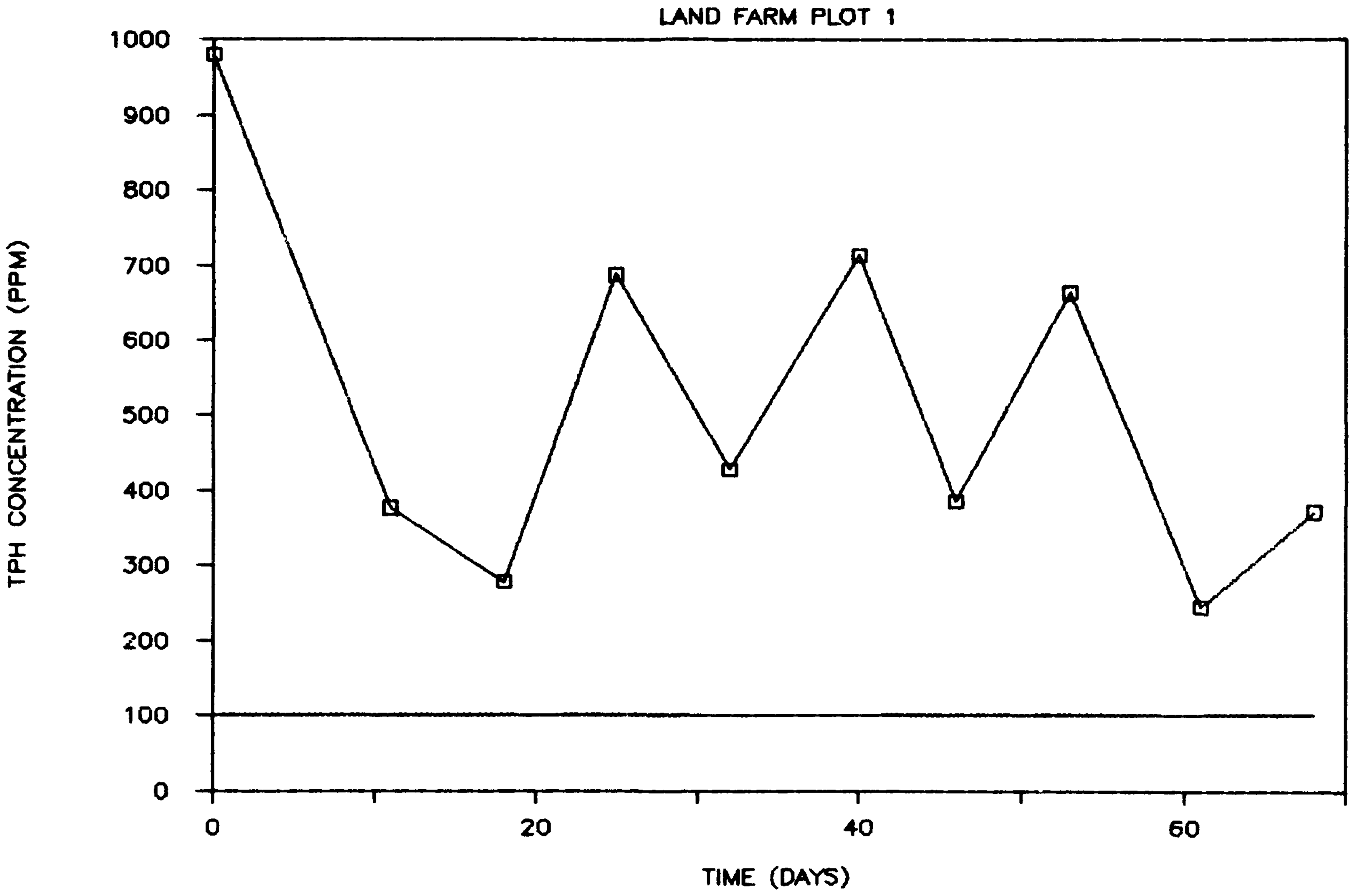
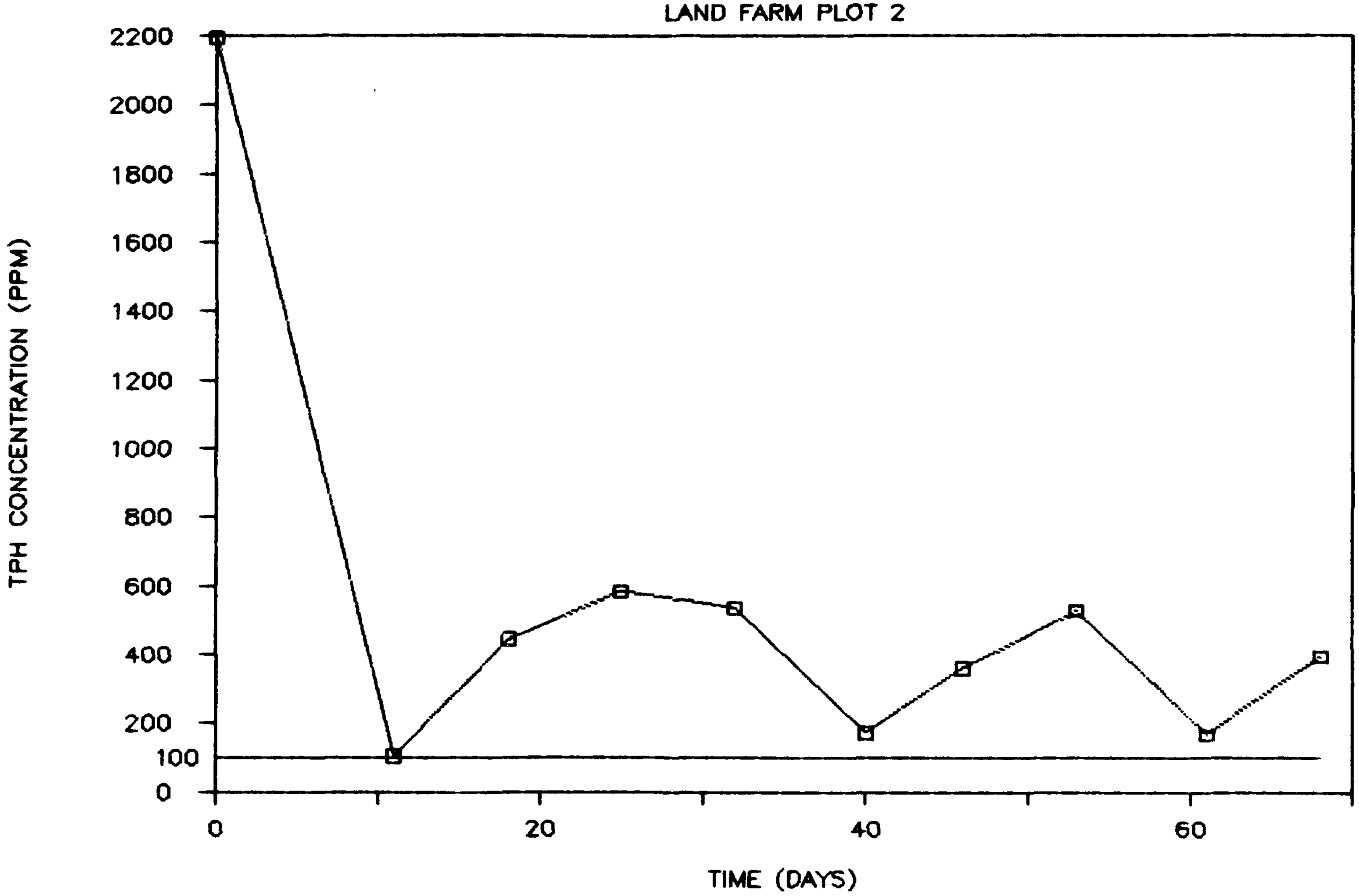
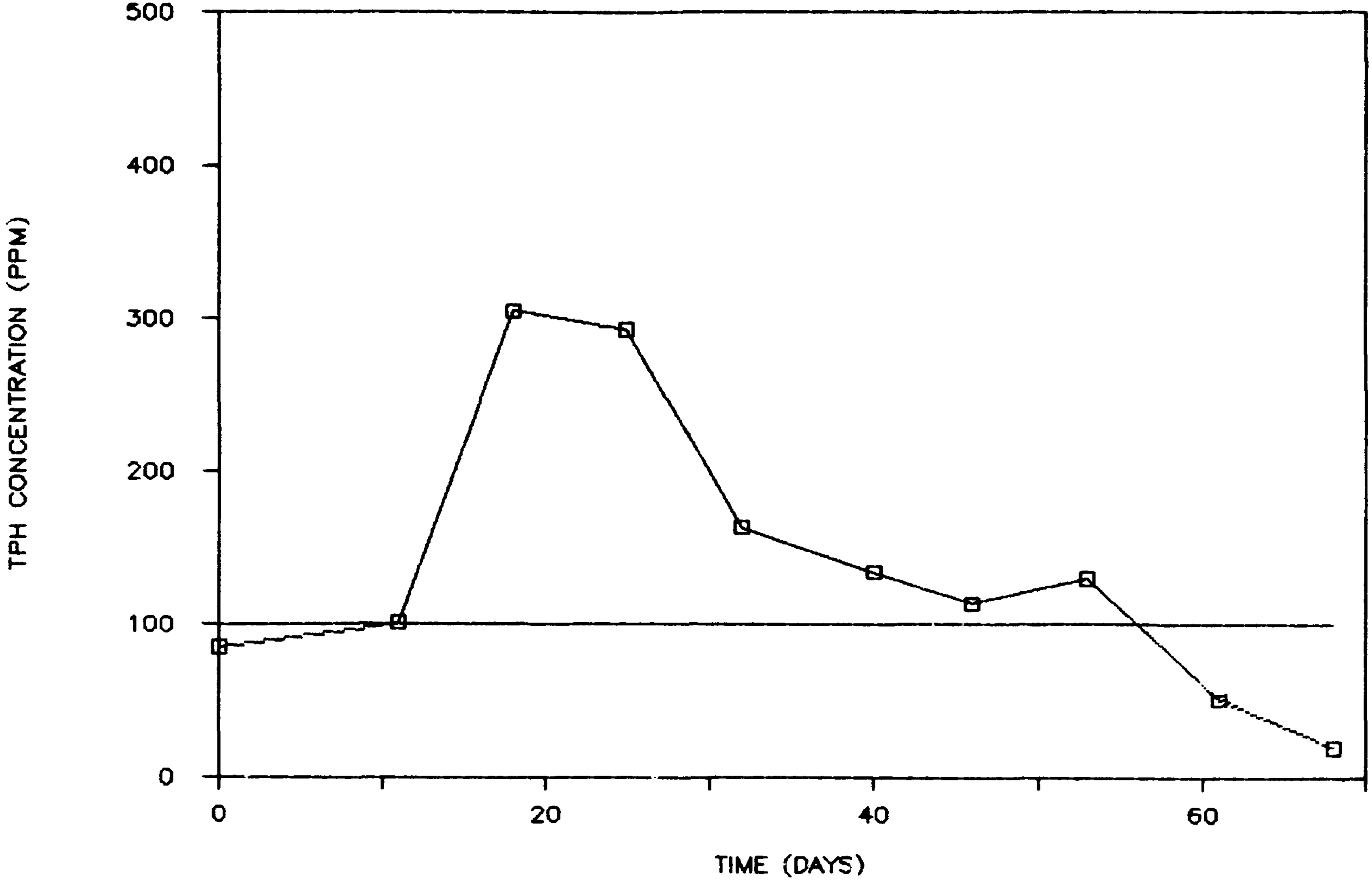


FIGURE 9. TPH CONCENTRATION VS TIME



LAND FARM PLOT 2

FIGURE 10. TPH CONCENTRATION VS TIME



LAND FARM PLOT 3

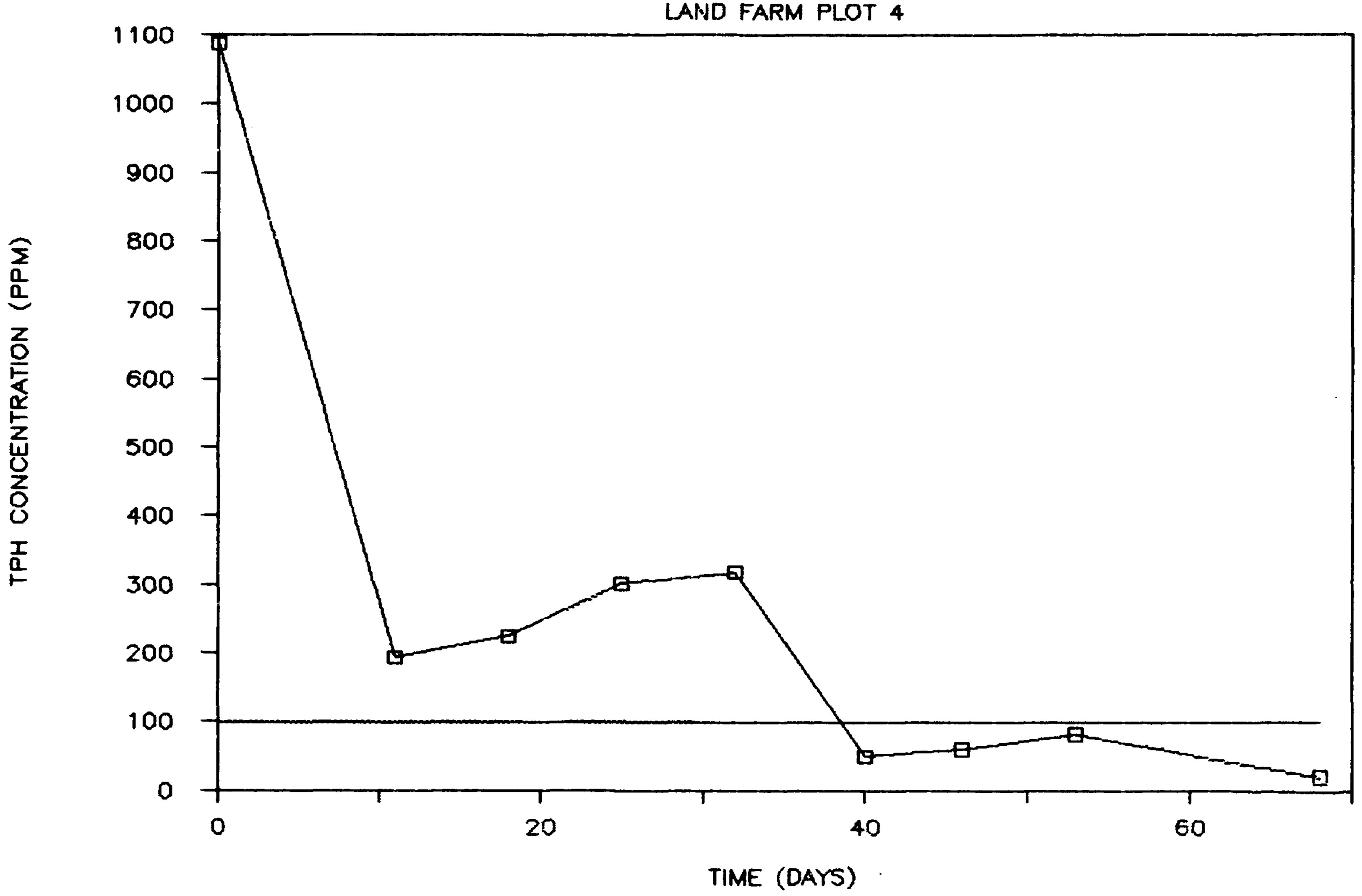


FIGURE 11. TPH CONCENTRATION VS TIME

LAND FARM PLOT 4

degradation of the TPH concentrations within the soil. Remediation of land farm plots 3 and 4 was considered complete after the October 3 soil sampling, and TPH concentrations in land farm plots 1 and 2 have been significantly reduced.

The TPH concentration data are sometimes erratic due to soil sampling in pockets of high contamination, redistribution of TPH concentrations within the soil resulting from biweekly tilling operations, and initial inconsistencies in soil sampling techniques. However, the general trends of all four plots show decreasing soil TPH concentrations. TPH concentrations of land farm plots 3 and 4 fell below 100 ppm after 61 and 40 days, respec [illegible] Landfarming of plots 1 and 2 is presently continuing [illegible] to higher initial TPH concentrations.

Data collected on and after August 21 (day 25) are considered more accurate and reflective of true soil TPH concentrations due to standardization of sampling techniques during and after this sampling period. Data collected during the August 21 sampling show that plots 1 and 2 contained TPH concentrations of approximately 600 ppm, and plots 3 and 4 contained TPH concentrations of approximately 300 ppm. TPH data collected during the period from August 21 (day 25) to October 3 (day 68) show that remediation of plots 3 and 4 from 300 ppm down to less than 100 ppm TPH was accomplished in 43 days. Plots 1 and 2 TPH data beginning August 21 show that TPH concentrations were reduced from approximately 600 ppm to between 300 and 400 ppm during the same 43 days.

A cost comparison of the Army's cost for remediation compared with a cost estimate received from an environmental contractor is presented in Table III. The data shows that the remediation was accomplished with a total cost to the Army of $104,133. The contractor cost estimate for the same job was $1,050,000. The cost savings to Army for use of in-house resources was therefore just under 1 million dollars.

CONCLUSIONS

When looking at the data taken from this biological treatment, it is very difficult to identify exactly how much of the contaminant was degraded by the bacteria. Although it can be seen that there has been significant decrease in the amount of TPH within the soil, a certain portion of this decrease can be attributed to the use of land farming in itself. Volatilization of the contaminant because of soil being exposed to weathering was certainly a major factor in the decrease of the contaminant.

Factors that may have had a significant impact in decreasing levels were not always constant. As an example, although the soil moisture content was to be kept at a constant level throughout the process, this was not always possible. Since the locations of the plots were too distant from any water source, provisions were made to bring in a water truck to wet the soil during the week. Due to the dryness of the soil and extreme heat during this time frame, it became almost impossible to keep the soil moisture at a level needed for optimum growth of bacteria. During the latter part of the treatment, we could see the effects that a greater rainfall was having on increasing the degradation of contaminant.

What should be noted when undertaking an operation such as this is the significant cost savings of use of in-house resources compared with contractor cost estimates. Prices quoted for complete cost of clean-up start to finish were in excess of 1 million. Total cost to this installation amounted to only $16,136, using "in-house" assets. Total cost to the Army of $104,133, although greater than depot costs, also reflects a significant savings.

Overall, it can be concluded, that land farming with biological treatment is an effective means of remediation for diesel contaminated soils. This technique is also economically attractive when compared with alternatives such as removal of contaminated soil off site for disposal in a hazardous waste landfill, or in situ treatment or land farming performed by a contractor.

TABLE III. REMEDIATION COST COMPARSION

ARMY COST ESTIMATES ASSOCIATED WITH PROJECT:

			Extened	Total
Equipment (Depot Owned)	Hours Used	Rate		
3 Scrapper (Pan)	1000	$18.95	$18,950	
2 Bulldozer	1000	13.70	13,700	
1 Grader	160	8.85	1,416	
1 Rubber Tire Roller	80	10.45	836	
1 Tractor w/disker	120	6.65	798	
1 Tractor w/Spreader	30	6.65	200	
1 Tractor w/Hydroseeder	30	6.65	200	
1 Water Truck	40	4.20	168	
SUBTOTAL				$36,268
Labor	Hours	Wage Rate		
Laborers (DEL)	1505	$15.00	$22,575	
Management Personnel	320	17.00	5,440	
SUBTOTAL				$28,015
Geohydrologic Survey *				$23,000
Lab Support	# Samples	Cost per Sample		
COE Lab, Atlanta	148	$75		$11,100
Equipment (Rental)				
1 Tracked Excavator				$3,000
Materials				
Hydrobac (Bacteria)			$6,000	
Polybac-E (Emulsifier)			800	
Sample Containers			800	
Liquid Fertilizer			376	
Lime			60	
SUBTOTAL				$8,036
Administrative Costs				$1,000
				$110,419

* - This service provided by AEHA at no expense to Depot.

TABLE III. REMEDIATION COST COMPARSION (con't)

CONTRACTOR COST ESTIMATE:

Costs are determined by total soil to be removed and treated. Polybac Corporation quoted price is $150 per Cubic Yard .

7,000 cubic yards x $150 per cubic yard = $1,050,000
=========

This price would include Geohydrologic Survey needed to determine extent of contamination.

SUMMARY:

		Savings
Contractor Remediation	$1,050,000	
Remediation Cost Incurred By Army	$110,419	$939,581
Depot Actual *	$23,136	$1,026,864

* - These numbers represent extraordinary expenses not usually incurred in day to day operations (materials, COE lab support, and rental equipment).

USING A THREE-DIMENSIONAL SOLUTE TRANSPORT MODEL TO EVALUATE REMEDIAL ACTIONS FOR GROUNDWATER CONTAMINATION AT PICATINNY ARSENAL

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As part of an effort to clean up ground water contaminated with trichloroethylene (TCE) at the Picatinny Arsenal, a three-dimensional solute transport model was developed. The model was used to design a cost-effective pumping plan for interim remedial action at the site.

The Picatinny Arsenal is located in Morris County, New Jersey, approximately four miles northeast of Dover. The installation, officially known as the U.S. Army Armament Research, Development and Engineering Center, performs research on munitions and weapons. Recent investigations have found concentrations of TCE and other volatile organic solvents in ground water. The metal plating shop in building 24 has been identified as a possible source of contamination. TCE and other solvents were used in degreasing operations at this metal shop.

Three-dimensional models of ground water flow and solute transport were developed and applied to the TCE plume in the shallow aquifers around building 24. These models were used to design remedial action pumping plans to prevent contamination from reaching Green Pond Brook and to clean up the contaminated ground water. Ground water will be pumped from collector wells and piped to a treatment plant, probably an air stripper, where TCE and other volatile organic contaminants will be removed.

The U.S. Geological Survey MODFLOW model was used to simulate the ground water flow at the site. The ground water flow system at the site was represented as a three layer model. The first layer was the water table aquifer in the permeable glacial sediments near the land surface. The second layer was the confined glacial aquifer. The third layer was the fractured limestone and dolomite underlying the glacial sediments. The model was calibrated to the existing observation well data.

A new program was written to translate the output of the MODFLOW model to a format suitable for input to the three dimensional, random-walk solute transport model (RAND3D). This program (PREMOD3D) computes three dimensional velocity vectors and sink (wells, gaining streams) locations for input to RAND3D.

RAND3D is a three dimensional solute transport model based on the random walk algorithm. Several significant improvements were made to the model for this study. It allows the user to simulate the movement of contamination including the effects of advection, dispersion, retardation, and decay. The progress of the plume is graphically displayed on the computer screen during the simulation at a scale selected by the user.

Six different pumping schemes for remedial action were then simulated using the three dimensional solute transport model, RAND3D. The model was used to evaluate the effectiveness of the pumping collection wells in the top layer of the glacial sediments on preventing TCE from reaching a stream.

ADVANCED DESIGNS AND IMPROVED OPERATING PROCEDURES FOR THE EGLIN AIR FORCE BASE DEPLETED URANIUM FIRING FACILITY

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SUMMARY

Armor-penetrating projectiles fabricated from depleted uranium (DU) are routinely test fired at Eglin Air Force Base (AFB) as part of the ammunition surveillance program. The catchment facility for the projectiles consists of a large sand butt in a reinforced concrete building that contains all spent DU rounds and DU-contaminated byproducts. The sand is screened periodically to remove DU projectiles and other oversized materials. Complete sand replacement is required after three firing/sifting cycles to reduce the quantity of fine material in the butt. The current system is effective, but disposal of the uranium-contaminated sand is very costly.

This paper describes equally effective but less costly systems that can be generally grouped as (1) alternate catchment media and catchment design, (2) sand/DU separation, and (3) improved operations using the current facility. A detailed economic model was developed to compare systems involving sand/DU separation, sand reuse, and changes in operating procedures.

Water and ice were considered as potential alternates for sand but were rejected for use at Eglin AFB. Polymeric materials were considered but rejected because many are flammable and generate toxic fumes if burned. Alternate catchment designs, coupled with water or ice for stopping the DU penetrators, were ultimately rejected as too costly. However, alternate designs and catchment media would probably be very competitive for a new-start facility.

The U.S. Air Force has funded three sand/DU separation studies since 1982. Physical separation methods clearly cannot meet regulatory requirements for unrestricted disposal. It is possible, but prohibitively expensive, to meet regulatory requirements for unrestricted disposal using an acid-leaching process.

The least expensive and most flexible alternative involves drying, sizing, and reusing the bulk of the sand. The discounted capital and operating cost for the next 20 years is estimated to be $5 million for reuse, compared with $18 million for the status quo. The Oak Ridge National Laboratory, which is now designing a prototype system to dry, size, and reuse the sand, plans to demonstrate the technology at Eglin AFB in 1990.

BACKGROUND

The 30 mm GAU-8 armor piercing incendiary round, containing a 300-g depleted uranium (DU) penetrator, is test fired at an Eglin AFB site into a catchment

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[a] U.S. Air Force Engineering Systems Center, Tyndall Air Force Base, Florida

[b] Oak Ridge National Laboratory is operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400

containing 400 yd^3 of sand. The sand is contained in a reinforced concrete structure that is nominally 20 ft tall, 22 ft wide, and 45 ft deep.

The catchment must be maintained to provide adequate safety and environmental protection. Large fragments (>½ in.) are removed after firing 17,000 rounds to prevent ricochets. Currently, the sand in the butt is replaced every 70,000 rounds because the fines produced by DU firing tend to plug the air-filtration system. The sand removed from the butt is a low-level radioactive waste.

The present system is safe and protects against environmental damage, but it is very expensive. A 1986 to 1987 effort to package, ship, and bury sand from three butt-replacement operations cost $3,000,000 and would cost over $4,000,000 in 1990.[1] The disposal cost for low-level waste has increased from \$31.50/ft^3 in 1987 to an estimated \$60/ft^3 in 1990.[2] The disposal charge for the southeast compact is expected to double again in the next three years as the new above-ground repository is built and brought on line.[2]

In 1987, the Air Force Engineering Services Center funded the Oak Ridge National Laboratory (ORNL) to develop an equally safe and less costly system for test-firing DU ammunition. The project consists of four phases:

1. criteria development, catchment evaluation, and sand/DU separation technology survey,
2. bench-scale sand/DU separation tests,
3. systems evaluation, and
4. demonstration testing.

To date, tasks 1, 2, and 3 have been completed. ORNL is now defining the program for demonstration testing based on the results of the first three tasks.

CRITERIA FOR THE EGLIN AFB DU TEST FACILITY

Operational Criteria

A sand/DU separation or treatment system would be operated intermittently, twice a year at most and possibly less than once per year. The principal operational considerations are these:

1. the treatment system must be operated by personnel now available at the test site to avoid excessive costs,
2. the system must withstand long inactive periods and be easily maintainable,
3. the DU test facility exists, and any new waste-treatment method requiring major changes of the existing facility would be at a distinct economic disadvantage relative to ones that may be applied with slight facility modification.

Regulatory Criteria

Alternative DU catchment systems must meet Eglin AFB operational needs and ensure compliance with health, safety, and environmental regulations and directives. The Nuclear Regulatory Commission site license limits total DU at the test site to 80,000 kg.[3] In practice, this limitation does not affect operations at the test site. Compliance with a variety of industrial hygiene and health physics requirements is achieved through personal protective equipment and radiation-monitoring devices.

Environmental Protection Agency regulations limit the activity of solid waste and wastewater discharged to the environment to 35 pCi/g and 40 pCi/mL, respectively.[4] With DU, 35 pCi/g sand corresponds to ~40 ppm DU (on a mass basis).[4] Separation processes that provide "clean" sand at an activity >35 pCi/g yield no economic benefit because the "clean" product remains a low-level radioactive waste.

The 40 pCi/mL limit for wastewater also affects the selection of separations options. Though past operations at the test site have frequently involved contacting water with DU-contaminated sand and have not generated any water with activity >40 pCi/mL, test results show this event to be within the realm of possibility. Limestone in the sand in the presence of fully oxidized uranium (both of which are not improbable events) and mildly acidic water can easily dissolve enough DU to surpass the 40 pCi/mL limit.[5]

Although these considerations proved to be quite important in the final selection of the system, the early phases of the project examined a wide range of options, including alternative catchment materials in lieu of sand and a broad range of potential separation devices. These evaluations are described in the following section.

DU CATCHMENT ALTERNATIVES

The following criteria were deemed appropriate for consideration of alternative catchment media for the Eglin AFB gun-test facility:

1. easy and complete DU recovery;
2. improved catchment operation (i.e., the cost and time involved in separating DU from sand, as required by the current system, should not be replaced by a different but roughly equivalent effort);
3. safe operation (e.g., no flammable or toxic media can be considered);
4. robust design (i.e., it is believed that systems requiring complex or high-speed mechanical devices would be inappropriate for a gun-test facility because of the requirement for specialized personnel).

Consideration of a range of options revealed that only two types of alternative catchment media hold any chance of satisfying the required criteria, namely, water or density-enhanced water solutions and ice of various physical forms. Other options considered but rejected include plastic foams, such as polystyrene foam particles, which are attractive for a number of reasons but cannot be used because of flammability.

Water Catchments. The chief advantage of water as a stopping medium is that it allows for complete and easy DU recovery. Moreover, one can envision a relatively simple system requiring no specialized operations; only simple supporting equipment, such as transfer pumps and valves, would be required. The chief disadvantages of using water result from its inherent properties as a liquid.

1. There is an uncertainty in the response of either a closed (no free surface) or open (with a major free surface) water pool to a rapid sequence of nearly collinear bullets. The concern is that the size and rate of collapse of the vapor wakes would be such that a rapid bullet sequence would require excessive stopping length.
2. In contrast to a solid as a stopping medium, significant pressures generated by bullet impacts would be transmitted to the catchment walls. Either steel or prestressed concrete containers designed for sharp, repetitive internal pressure loadings would be required.
3. The water medium is most naturally suited to a vertical gun test orientation for both containment and vapor-cavity collapse. However, a vertical orientation would require a new test building, an extensive vertical working distance either above or below ground, and a vertical gun mount.

The stopping power of a catchment medium for high-velocity bullets depends primarily on its density and strength. On both counts, water is poorer than sand. However, density enhancement by the massive addition of a heavy salt appears to be a feasible method for obtaining a significant increase in density. A number of highly soluble heavy salts exist that are relatively inexpensive and can be obtained in bulk. The use of calcium bromide or calcium iodide could result in a two- or threefold density increase over plain water.

The principal problem in using water as a stopping medium is its behavior following a rapid sequence of nearly collinear bullets. A horizontal catchment with a free surface is probably not feasible because of the formation of persistent vapor wakes. As a result, excessive stopping lengths are required for a multiple firing test. Increasing pool depth tends to reduce vapor "cratering," but excessive water depths (>100m) would be required.[4]

A perfectly closed catchment would collapse voids (because of water compressibility or reflected pressure waves) in less time than the duration between successive bullets. The required stopping length for a bullet sequence would therefore not differ from the requirement for an individual bullet (i.e., from 5 to 10 m).[4] However, some detailed design issues need to be resolved to determine cost and feasibility.

Ice Catchments. The potential advantage of ice as a catchment is the possibility of combining the beneficial features of sand and water. Ice pieces of several possible physical forms may, like sand, bear a load under impact, thus shielding the walls of the target building from the force of the bullet impact. However, like water, DU may be easily separated by simply melting the ice. Adaptation of the existing catchment building to ice would require some extensive modification, including

1. structural reinforcement of the roof to support the weight of the ice maker and provisions for maintaining the ice maker;
2. a new front wall, including a guard shield, to protect the ice maker from stray bullets;
3. a water sealant for the building interior;
4. a drain equipped with a sieve for collecting the DU penetrators; and
5. possible extension of the building resulting from the diminished stopping power of ice relative to sand.

In addition to these building modifications, a supporting water-storage and handling system, including a water pool of ~16,000-ft^3 capacity for water storage, a pump/filter unit for emptying the catchment following a test firing, and feed pumps from the storage pool and to the refrigeration unit, would all be needed.[4]

An ice catchment was not recommended because it requires significant modifications to the test butt and an extensive refrigeration system maintenance program. However, ice catchments may be very suitable for a new-start facility. Ice offers a facile procedure for complete DU recovery, fits better to a horizontal firing orientation than water, and may require a less sturdy building because of the load-adsorbing properties of solid ice.

Thus, the conclusions regarding ice catchments are similar to those presented for use of water. The resulting ease of complete recovery of the hazardous material makes both of these concepts worth considering. However, both would require either extensive modification of current facilities or a completely new system.

SAND/DU SEPARATIONS TESTS

Numerous DU/sand separation methods were tested under prior subcontract to the Air Force, under subcontract to ORNL, and at ORNL facilities in an attempt to reduce the activity to 35 pCi/g. Following is a brief review of the equipment tested and results.

Dry Magnetic Separation. No separation was achieved using standard devices using wet or dry feed that rely on ferromagnetism. Tests at ORNL using a paramagnetic separator gave varying results. Occasionally, extremely good separations were achieved, but results generally were erratic. In no case did the achieved separation suffice to allow unrestricted disposal of the clean product stream.[6]

Electrostatic Separation. Modest separations were achieved for relatively large particles (-10/+20 mesh). In this fraction, ~96% of the DU in the feed was captured in the waste product stream, consisting of 43% of the feed. Separations for smaller-sized fractions were poorer. Fine dust formation was a troublesome product in all except the coarsest sizes (i.e., >20 mesh).[7]

Jigging. Three separate jigging tests were performed. An internal Air Force study reported that a feed activity level of 1000 pCi/g was reduced to 50 pCi/g by recycling the clean product through a standard mineral jig multiple times.[8] However, no mass flows are reported to enable separation efficiency to be evaluated. Jigging tests by Keane indicated a fair degree of separation per pass: a feed containing 1.67% DU produced a clean product stream containing 0.49% DU and consisting of 66.1% of the feed.[7] Keane repeated these tests six years later under subcontract to ORNL with essentially similar results.[9] While separations reported by Keane may be considered satisfactory for many applications, they are far from meeting criteria for unrestricted disposal.

Shaking Table. This wet separation technique is only applicable to top-sized limited (>10 mesh) material. It could be used to separate DU fragments from sand and pebbles but is not applicable to the bulk of the sand.[7]

Static and Moving Belt Separations. These wet separators use either an inclined sluice or moving belt on which the slurry moves downward, counter to the motion of the belt. A modest separation was achieved using the -20 mesh size fraction. A clean product of 0.16% DU was obtained from a feed containing 0.29% DU.[7]

Rotating Spiral Concentrator. This device consists of a disc with a peripheral rim with an axis of rotation inclined from the vertical. The disc has a hole in the center and a spiral riffle that decreases in curvature from edge to center. Heavy materials migrate to the center hole and collect as concentrate. Performance generally improves if the coarse sizes are removed.

Tests indicate that significant DU concentration is achievable (0.71% DU feed concentrated to 62.7% DU), but a 0.45% DU tails stream accounted for 99.6% of the feed.[7] In addition, the large amounts of water required for operation must be stored for analysis and possibly treated before disposal.

Fluidized Bed Tests. Elutriating bed tests using a feed at 26,300 pCi/g activity level yielded a clean product stream in the 2000 pCi/g range that represented ~50% of the feed mass.[5] Optimization of test conditions would be likely to improve this result significantly.

Chemical Leaching Tests. Measures necessary to cleanse contaminated sand down to 35 pCi/g without wholesale dissolution of the sand itself are described by Elliott.[10] In summary, strong oxidants (including three nitric acid washes with intermediate clean water washes and one intermediate drying step) are required to achieve a clean product at <35 pCi/g activity. Acid leaching was included in the economic analysis.

Screening Separations Tests. Several screening tests were performed in conjunction with sand sampling and size distributions surveys. These showed that from 50 to 75% of the DU is contained in the +10 mesh size fraction (which accounts for ~12% of the total sample).

An additional DU concentration was found associated with the fines (i.e., -60 mesh). About 18% of the DU fed to a screen separator may be captured in the -60 mesh fraction, which should be removed in any case because of the operational difficulties fines cause. Thus, separations by screening could result in up to 90% DU removal in the coarse (+10 mesh) and fine (-60 mesh) size fraction.

Bench-scale tests performed by Keane defined the conditions required for proper screen operations, as well as allowable mass flows as a function of screen opening size.[9] These tests showed that moisture levels >2% caused poor screen performance. Because the general moisture level of the feed sand would be at that level or higher due to environmental conditions and the need for dust control, screening operations to separate the -60 mesh fraction would require drying the feed to <2% moisture.

EVALUATION OF DU/SAND SEPARATION METHODS

A necessarily subjective summary of the various DU/sand separation methods is shown in Table 1. Each separator is evaluated on a scale of 1 to 5 in each of the five performance categories shown. Note that no physical separation method can reduce the activity level to 35 pCi/g. Although chemical leaching

Table 1. Evaluation of DU/sand separations methods

Separator device	Evaluation categories					
Water medium separators	Test evaluation	Ruggedness simplicity	x Cost commercial availability	x Safety	x Separation efficiency[a]	= Overall performance factor
Fluidized bed	b	4	2	3	3	72
Hydroclone		4	2	3	3	72
Jig	b, c	4	5	3	2	120
Spiral	c	4	3	3	3	108
Shaking table	c	4	5	3	2	120
High gradient magnetic		2	1	2	2	8
Open gradient magnetic		3	2	3	1	18
Chemical leaching	c	1	1	1	5	5
Dry separators						
High gradient magnetic		1	1	2	2	4
Open gradient magnetic	b, c	4	3	3	1	36
Electrostatic	c	3	3	2	2	36
Dry classifier		4	3	2	3	72
Sifting through screens	b	4	5	4	3	240

[a] No single device provides sufficient separation for derating sand, except chemical leaching

[b] Evaluated in phase II of current study

[c] Evaluated in earlier Air Force contract studies

has a very low overall performance rating, it is the only separation technique enabling unrestricted disposal.

SYSTEMS EVALUATION FOR EGLIN AFB

The key to reducing disposal costs is reducing waste volume. Systems for minimizing the amount of low-level waste considered in this study include

1. alternate catchment designs or catchment media that limit the production of low-level waste to the DU penetrators,
2. sand/DU separation to reduce the activity of the sand to <35 pCi/g,
3. sand processing and reuse to limit the amount of low-level waste, and
4. operational changes to limit the amount of sand that must be replaced periodically.

Alternate catchment media is potentially cost effective for a new-start facility but was not considered because it is clearly not a cost-effective replacement for the existing facility. Therefore, the following systems were compared to the current operation:

1. sand/DU separation via acid leaching,
2. sand reuse by means of size screening to remove fragments and DU fines, and
3. minor changes to the test butt to limit the amount of sand that becomes contaminated with DU (similar to the test butt used by the GAU-8 manufacturer).

Flow sheets for the status quo and three alternative systems are given in Figs. 1 to 4. Detailed economic models were developed for the status quo and each of

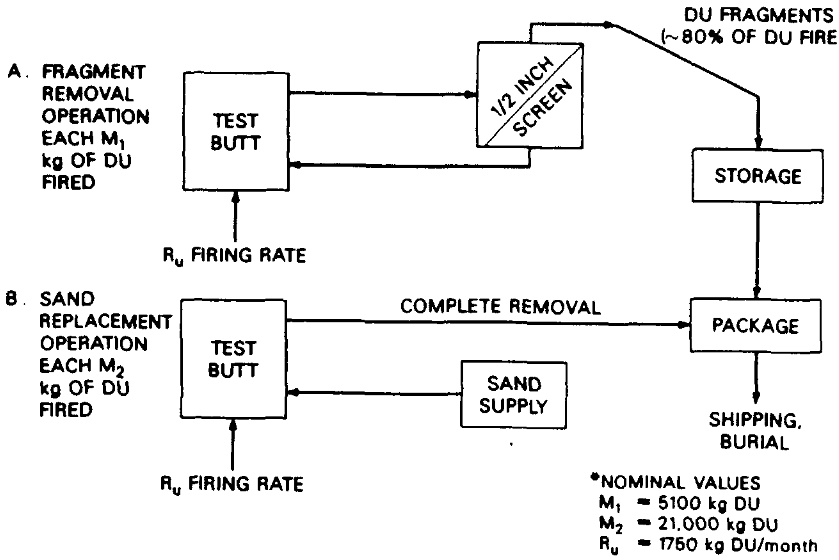


Fig. 1. Flow sheet for status quo catchment maintenance system.

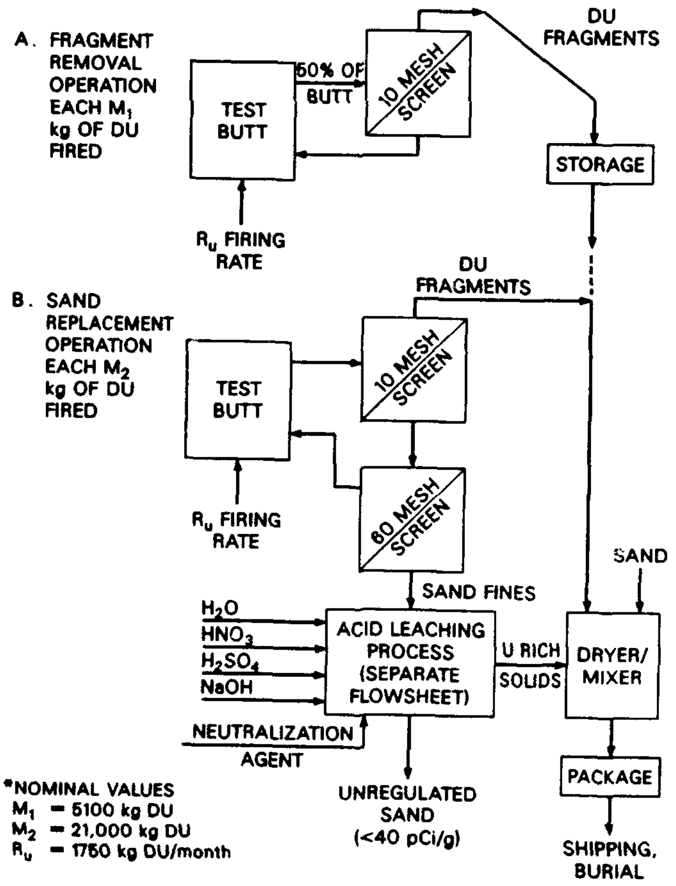
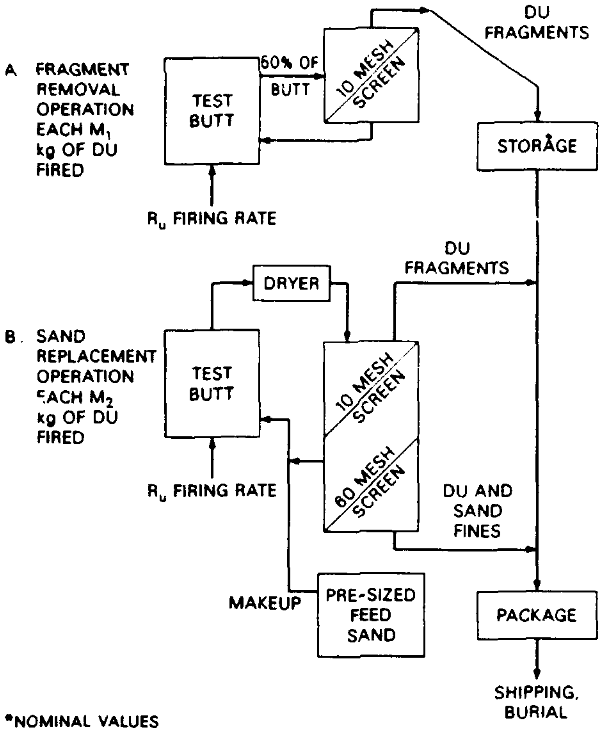
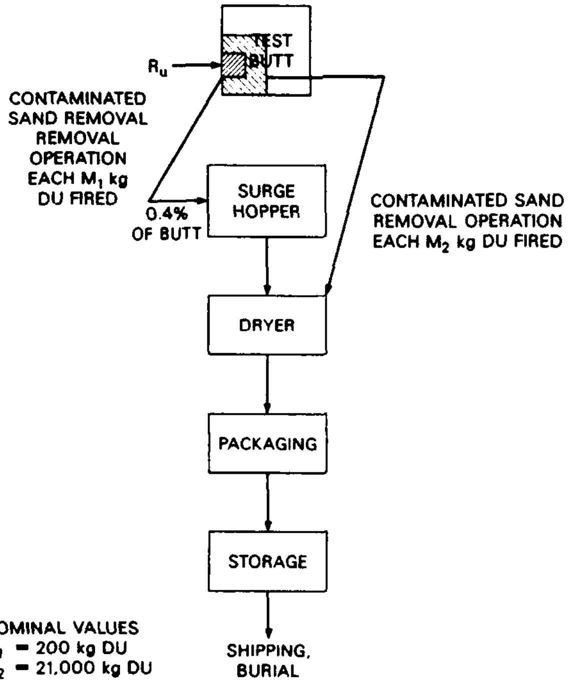


Fig. 2. Flow sheet for acid leaching system.



*NOMINAL VALUES
M_1 = 5100 kg DU
M_2 = 21,000 kg DU
R_u = 1750 kg DU/month

Fig. 3. Flow sheet for sand recycle system.



*NOMINAL VALUES
M_1 = 200 kg DU
M_2 = 21,000 kg DU
R_u = 1750 kg DU/month

Fig. 4. Flow sheet for modified catchment system.

these systems. Noneconomic aspects of each alternative were quantified using a rating factor matrix.

Economic Comparison of Systems

The life-cycle cost of each alternative was compared using guidelines provided in Air Force Regulation 178-1 and OMB Circular A-94.[11, 12] Several of the assumptions used in the economic analysis are listed in Table 2. Detailed flow sheets, operational data, and cost data for each alternative are included in the economic evaluation report by Wichner and Bradshaw.[13]

The life-cycle cost for each system (based on the historical work load of 17,000 rounds/year) is shown in Fig. 5(a).[13] The Eglin AFB DU firing mission is expected to expand to ~70,000 rounds/year; similar data for the higher firing rate are given in Fig. 5(b).[14] The accuracy of the data is estimated to be ±30%.

Table 2. Partial list of data used in economic analysis

GAU-8 firing rate (1979-88, rounds/year)	17,000
GAU-8 firing rate (projected, rounds/year)	70,000
Sand in test butt (yd^3)	400
Rounds fired between fragment removal operations	17,000
Rounds fired between fines removal operations	53,000
Low-level waste disposal charge (1989, \$/ft^3)	38
Low-level waste disposal charge (1990, \$/ft^3)	60
Low-level waste disposal charge (post-1992, \$/ft^3)	100
Low-level waste charge real escalation rate (%)	10
Low-level waste packaging (status quo, \$/ft^3)	33
Low-level waste packaging (alternative systems, \$/ft^3)	23
Low-level waste transportation (\$/ft^3)	4.1
Contract labor rate (\$/h)	47
Discount rate (%)	10

Technology-dependent cost data

	Status quo	Acid leaching	Screening reuse	Modified test butt
Capital (1989, \$K)	0	5600	600	420
Decommissioning (1989, \$K)	500	1500	500	500
Operating and maintenance	[a]	[a]	[a]	[a]

[a] Basis for O & M costs is technology-dependent. Detailed data provided in Ref. 13.

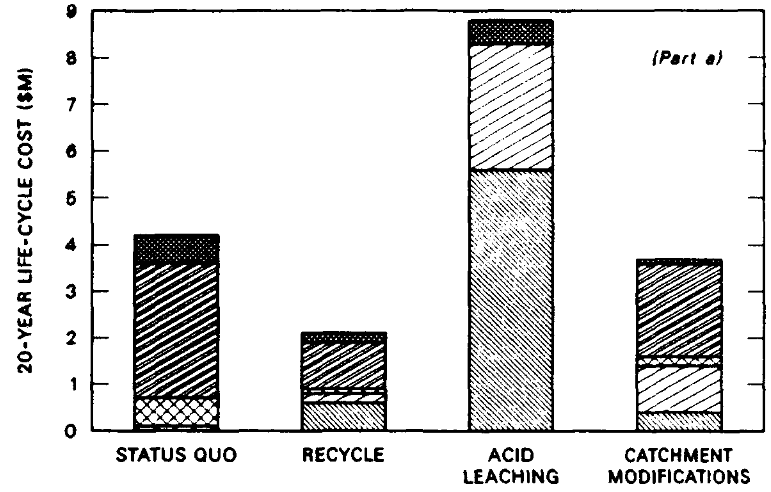


Fig. 5a. Life-cycle cost at historical firing rate (17,000 rounds/year).

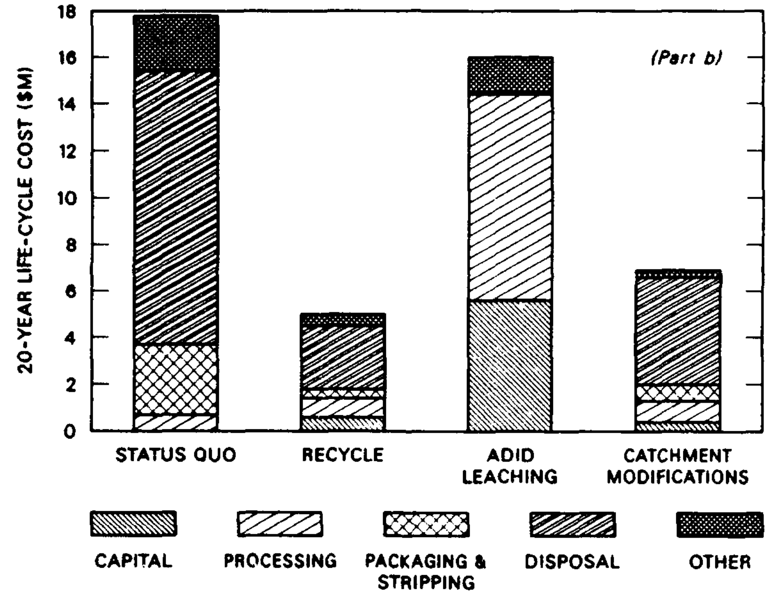


Fig. 5b. Life-cycle cost at projected firing rate (70,000 rounds/year).

The cost categories are defined as

1. capital equipment, facilities, and startup;
2. labor for on-site sand processing operations plus radiation monitoring, supervision, equipment startup and shutdown, and maintenance;
3. labor and transportation for packaging and shipping low-level waste;
4. disposal charges for low-level waste; and
5. other costs, including operating and safety plans, system shutdown after a 20-year operating period, and replacement sand.

Reusing the sand is the clearly the least costly alternative. Reuse remains the least costly alternative over the entire range of credible values for low-level waste disposal cost, DU firing rate, and sand fines production rate (resulting from DU firing).[13] The cost of the capital equipment for drying, sizing, and reusing the sand will be recovered in the first sand-replacement cycle.

Noneconomic Comparison of Systems

Noneconomic factors, such as technical feasibility, health, safety, environmental risks, and complexity are each as important (if not more important) than economic considerations. Table 3 is a rating factor matrix similar to that used to compare separation methods. A geometric sum is used rather than an algebraic sum because each rating area is vital to overall system acceptability (i.e., advantages in one area do not compensate for weaknesses in others).

Table 3. Noneconomic comparison of sand/DU treatment systems

System	Technical feasibility	HSE[a]	Complexity	Overall performance rating
Status quo	5	5	4	100
Acid leaching	4	1	1	4
Screening reuse	4	5	5	100
Modified test butt	5	3	4	60

[a] Health, safety, and environmental

Technical feasibility. The status quo and modified test butt systems are now in use and hence clearly feasible. The reuse alternative involves drying and screening; both operations are well-established commercial technologies that have not previously been used for DU-contaminated sand. Acid leaching has been successfully tested at the bench scale, and similar processes are used by DOE contractors to recover weapons-grade uranium from a variety of slag materials. Leaching is technically feasible.

Health, safety, and environmental risk. The risks for the status quo and reuse systems are comparatively low because both (1) involve infrequent operator interaction with radioactive material, (2) avoid the use of water and hence lessen the probability of soil or water contamination, and (3) use simple and reliable processing schemes. The modified butt alternative is proven and simple, but operators must frequently handle and work in the immediate vicinity of low-level radioactive materials. Acid leaching is designed to dissolve the DU in highly corrosive solvents and therefore involves significantly more risk than the others.

Complexity. Sand/DU processing operations are intermittent and conducted by general laborers. The status quo and modified butt alternative requires off-site contractor support for a sand-replacement operation. Equipment mobilization is expensive, and an off-site contractor adds to the administrative complexity. The reuse system is relatively simple and eliminates the need for off-site contractor support to process and package the DU-contaminated sand. The acid leaching process is very complex, involving at least 16 chemical processing steps.

SAND DRYING, SCREENING, AND RECYCLE SYSTEM

ORNL is recommending that the Air Force dry, screen, and recycle the intermediate-sized uranium-contaminated sand. Fig. 6 is a flow sheet for such a process. Successful implementation of a drying/sizing system will save the Air Force several million dollars over the next 20 years. The $600,000 capital cost will be recovered during the demonstration test because the volume of low-level waste generated during the sand replacement operation will be reduced by ~90%.

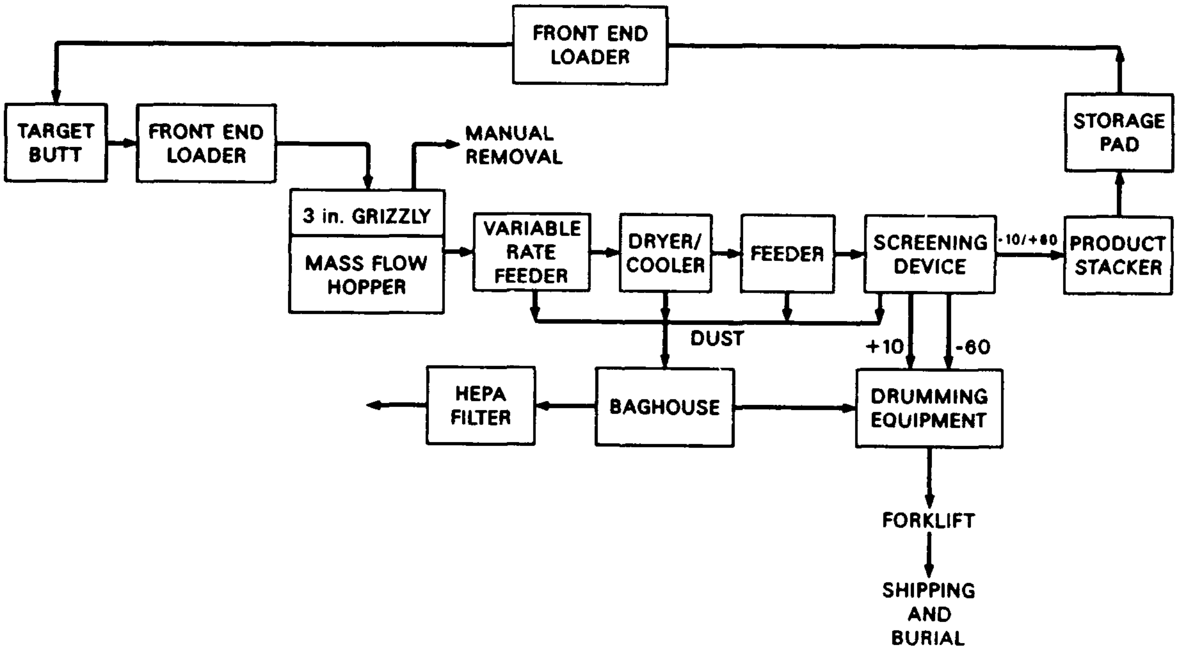


Fig. 6. Flow sheet for drying, screening, and recycle process.

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LOW TEMPERATURE THERMAL TREATMENT (LT^3) OF SOILS CONTAMINATED WITH AVIATION FUEL AND CHLORINATED SOLVENTS

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ABSTRACT

Successful pilot study of Low Temperature Thermal Treatment (LT^3) (Patent No. 4,738,206) of soils contaminated with volatile organic compounds led to a full scale demonstration to evaluate the use of this technology at DOD installations. The LT^3 process developed by Weston Services, Inc. under contract with the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) was used in a test of remediating soils contaminated with aviation fuel (JP4) and trichloroethylene (TCE). Tinker Air Force Base, Oklahoma was selected as the demonstration site. An abandoned landfill area had high concentrations of contamination in a clay soil which was determined to be ideal for this test. The LT^3 process performed better than expected and achieved cleanup levels at lower temperatures, higher processing rates and shorter residence times than previously thought possible. This directly translates into cost savings for future remediation sites. Test results indicitive of the performance and potential application of this technology will be presented.

INTRODUCTION

Thermal processes for decontaminating hazardous waste laden soils have focused on incineration. Raising the soil to temperatures at which the contaminants present undergo decomposition is an effective means of cleaning the soil. Effective that is in terms of contaminant removal, not cost. In raising the soil to the elevated temperature, energy is expended needlessly, causing increased operating costs. In addition, contact heating between the combustion gases and the contaminated soils produces a large volume of contaminant laden vapor which must be processed through pollution abatement equipment. The larger the volume of this vapor phase, the larger (and costlier) the down stream equipment.

To decrease energy requirements and simultaneously reduce downstream pollution abatement equipment and operations costs, a low temperature thermal treatment system has been developed. The rationale for this system centers around those drawbacks to incineration listed above. First, by heating the contaminated soil only enough to volatilize the organic contaminants, energy is saved. Second, using indirect heating of the soil, downstream pollution abatement equipment cost is reduced, both in capital and operating costs.

Development of the LT^3 process began in August, 1985 with the operation of a pilot scale thermal processor.[1] Use was made of an indirect heat exchanger which operated by contacting the soils with heated augers which both transported and heated the soil. Volatile contaminants were released from the soil and processed through an afterburner. The pilot system schematic is shown in Figure 1. The success of this pilot scale system prompted the performance of an economic evaluation[2] and bench scale tests[3] that resulted in a full scale LT^3 system.

The bench scale system was operated to determine if results from the pilot scale could be effectively reproduced on a smaller scale, thereby providing a low cost means to pre-screen potential soils and contaminants. The bench scale system was also used to determine the effects of temperature and residence times on different soils. Of particular note during this study was the processing of soils containing semi-volatile contaminants from diesel fuel and JP4. Results indicated the potential for bench scale data to be used in scale up. This would greatly simplify pre-screening of soils by reducing the costs of sampling as well as the amount of soil required. A central laboratory was established at Weston to perform pre-screening tests rather than constructing a pilot unit at each site.

On April 19, 1988 U.S. Patent Number 4,738,206 was issued for a Low Temperature Thermal Treatment Process for removing volatile and semi-volatile organic contaminants from soil.[4] A full scale LT^3 system was designed and constructed by Roy F. Weston, Inc. under this patent based on the results of the pilot and bench scale systems. Initially, the full scale system was used to treat petroleum contaminated soils at a site in Illinois. The first test of this equipment in the remediation of hazardous wastes was performed at Tinker Air Force Base, Oklahoma. The results of the test program at Tinker will be described.

PROCESS DESCRIPTION

The full scale low temperature thermal treatment system used two, thermal processors operated in series. The first processor is mounted on top the second. Four intermeshed screws in the first processor convey the soil through a jacketed trough where it falls by gravity into the second processor. The second is identical to the first except the direction of travel of material is reversed. In this way, soil enters the unit on one side and exits the unit on the opposite side thereby reducing the space requirements

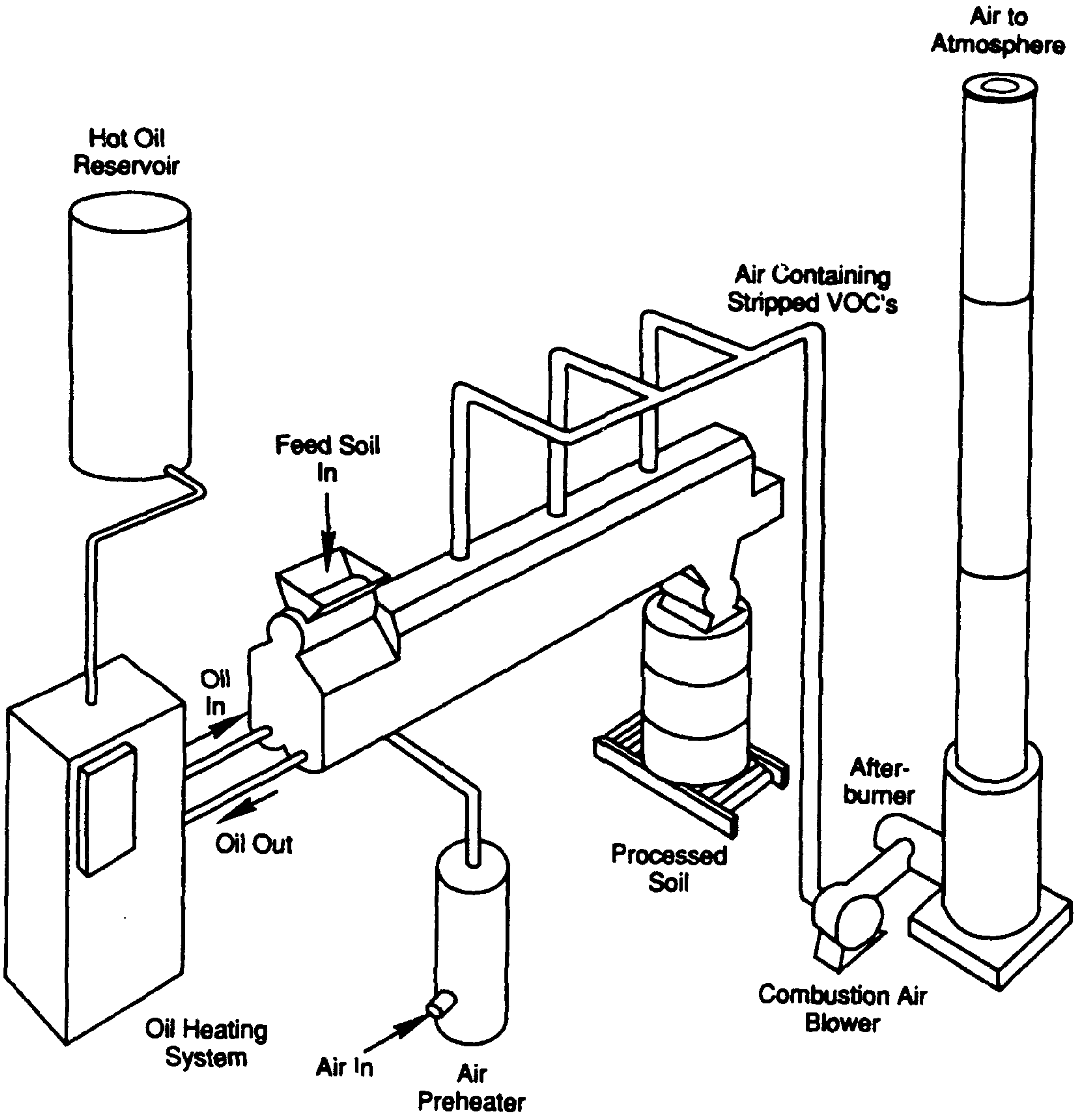

Figure 1: Schematic Diagram of the Pilot Scale LT^3 System

necessary for operations as well as reducing the flow of contaminated soil outside of the processors.

A 7.6 million KJ/hr hot oil system provides a heat transfer fluid, Dowtherm HT, to the hollow screws and jackets of the thermal processors. Temperature controls allow the oil to be maintained at temperatures up to 343°C. A portion of the combustion gases from the oil heater are passed through the thermal processor at about 375°C. This is done for two reasons. First, waste heat recovered from this stream maintains the volatile stream exiting the thermal processor at a temperature high enough to avoid condensation of the contaminants on the walls of the exhaust ductwork. Second, the exhaust acts as an inert atmosphere to maintain the gases in the thermal processor below their lower explosive limit.

The vapor stream from the thermal processor consists of the contaminants being removed, water vapor from the soil and exhaust gases from the hot oil heater. This stream exits at approximately 150 °C (maximum) and flows through a fabric filter, condenser, afterburner and caustic scrubber system. The fabric filter removes particulate carried over from the processor. The vapor stream then passes through an air cooled condenser which reduces the temperature to approximately 52°C. Water and organics condensed reduce the load on the afterburner. The afterburner is a 3.7 million KJ/hr gas fired, vertical, fume incinerator operating at 982 °C. The afterburner is operated at a minimum 3% excess oxygen and the exhaust is continuously monitored for O_2, CO and total hydrocarbons. The 982 °C exhaust from the afterburner is quenched to approximately 82 °C. It then passes through a packed bed absorber where acid gases produced in the afterburner are neutralized with a caustic solution.

A liquid stream is produced by the condenser which is water rich but does contain some hydrocarbons. The aqueous phase is separated from the organic phase in an oil-water separator. The aqueous phase is processed through a water treatment system consisting of fabric filters followed by granular activated carbon. This water is then used as makeup water for the scrubber and for dust control on processed soil. The organic phase from the separator is either drummed for off site disposal or injected into the afterburner.

A block diagram of the system is shown in Figure 2 and a schematic layout of the system is shown in Figure 3. The system described here is mobile and can be transported on 5 trailers. Utilities required for operation are propane or natural gas, electricity and process water.

discharges from the system include the scrubber stack exhaust, the processed soil, the granular activated carbon and filter cake, and, if not injected into the afterburner,

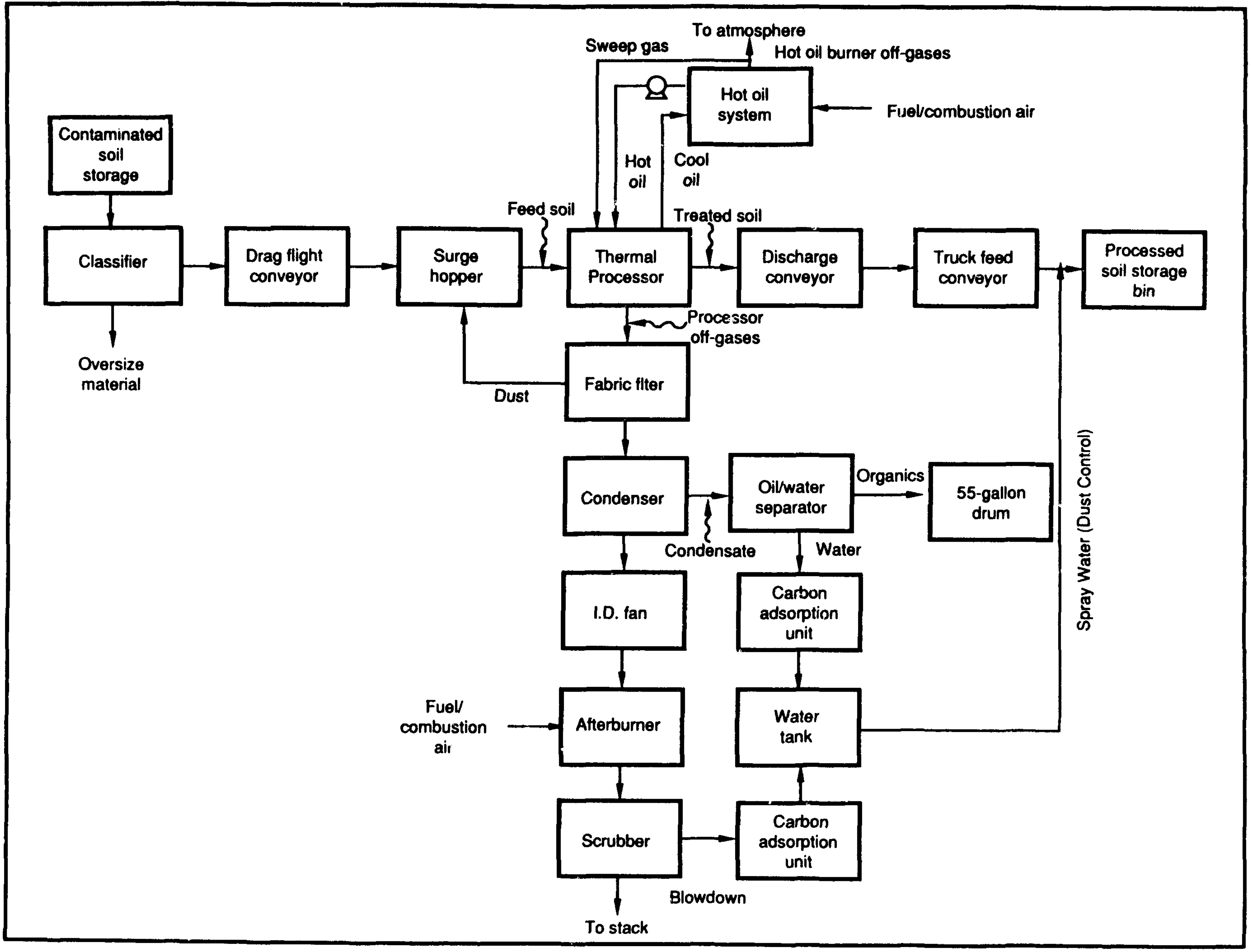

Figure 2: Block Diagram of the Full Scale LT^3 System Used at Tinker Air Force Base, Oklahoma

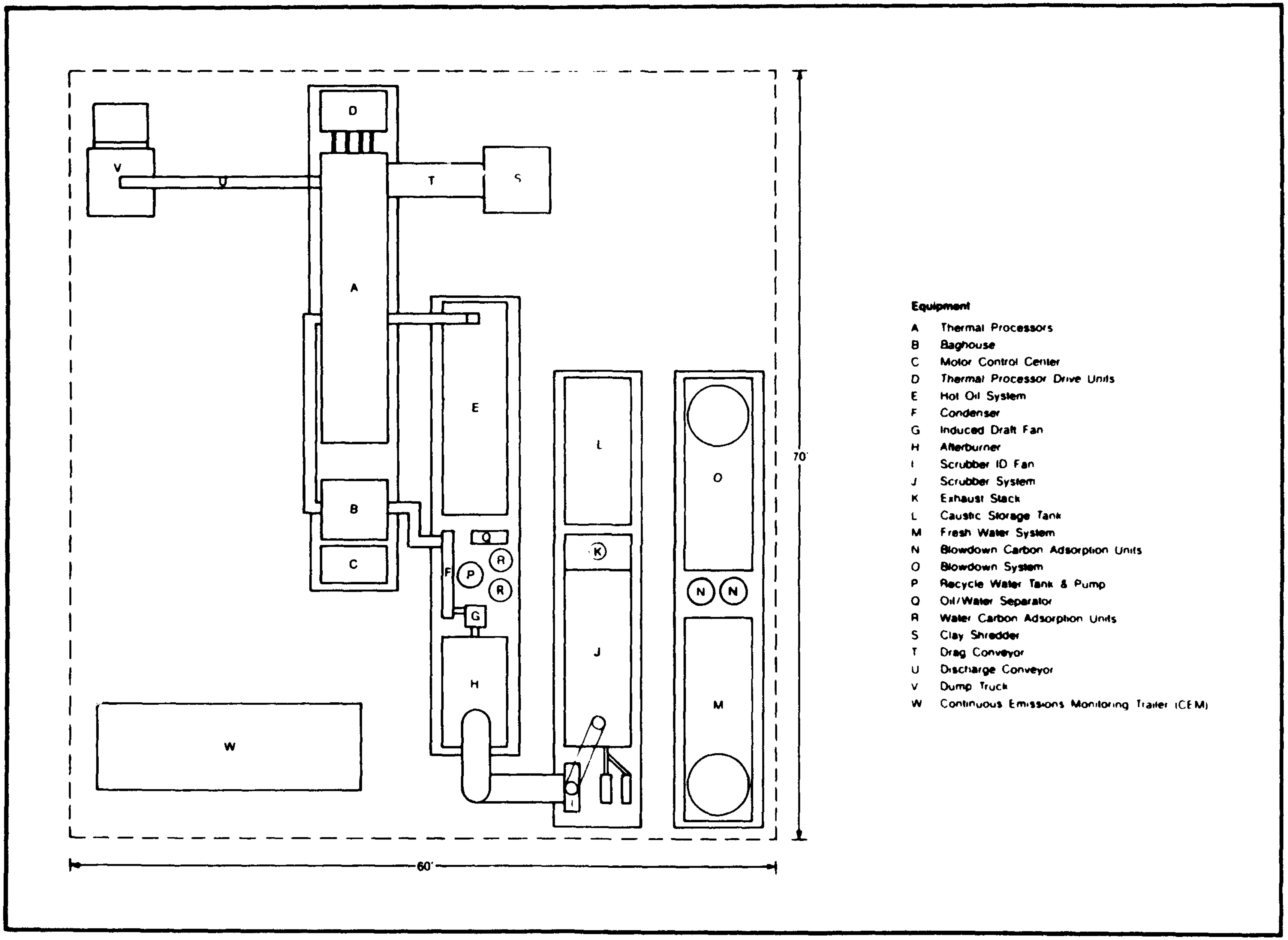

Figure 3: Schematic Diagram Showing Equipment Layout of the Full Scale LT^3 System Used at Tinker Air Force Base, Oklahoma

the organic phase from the oil-water separator. The maximum utility load for the unit is as follows:

Liquid Propane	2.27 m^3/day
Process Water	40.88 m^3/day
Electricity	600 amp/460 V (3 phase)

Operation requires 8 personnel for continuous operations including a site manager and an instrumentation technician.

SITE DESCRIPTION

To test the capabilities of the full scale LT^3 system a site contaminated with compounds of specific Army concern was desired. Objectives in site selection were to find a location which had a clay soil matrix contaminated with JP4. JP4 was selected as the contaminant of choice as spills of this fuel on Army bases may require remediation and diesel fuel contaminated soil had already been tested in this unit.[5]

Coordination with the U.S. Air Force resulted in Tinker Air Force Base, Oklahoma being selected as the test site. Remedial investigations on this active Air Force support base turned up an abandoned sludge dump in one of the bases landfill areas. Survey and analysis of the area estimated 600 m^3 of sludge contaminated clay soil. Analysis of soil and water from this site indicated JP4 and trichloroethylene in high concentrations along with other potential contaminants in lesser concentrations, probably constituents of diesel, kerosene and other solvents. The land fill was no longer in use and outside of everyday operational traffic. The Air Force personnel at Tinker Air Force Base as well as the state and federal regulators were in favor of the test. The mixed wastes which included TCE, a listed hazardous waste, provided an opportune site for demonstration of the LT^3 technology on a full scale. The site layout is shown in Figure 4.

Due to the presence of listed hazardous wastes, a permit was required for the test. An application for a Research, Development and Demonstration (RD&D) permit was filed in accordance with the requirements of RCRA. An approved RD&D permit was issued by Region VI, EPA 120 days after application. This permit authorized the conduct of the test plan for the LT^3 process.

TEST PLAN AND RESULTS

The test plan for the full scale LT^3 system was designed to meet the following objectives:

- determination of effectiveness of the full scale LT^3 system at removing JP4 and chlorinated solvents from soil.

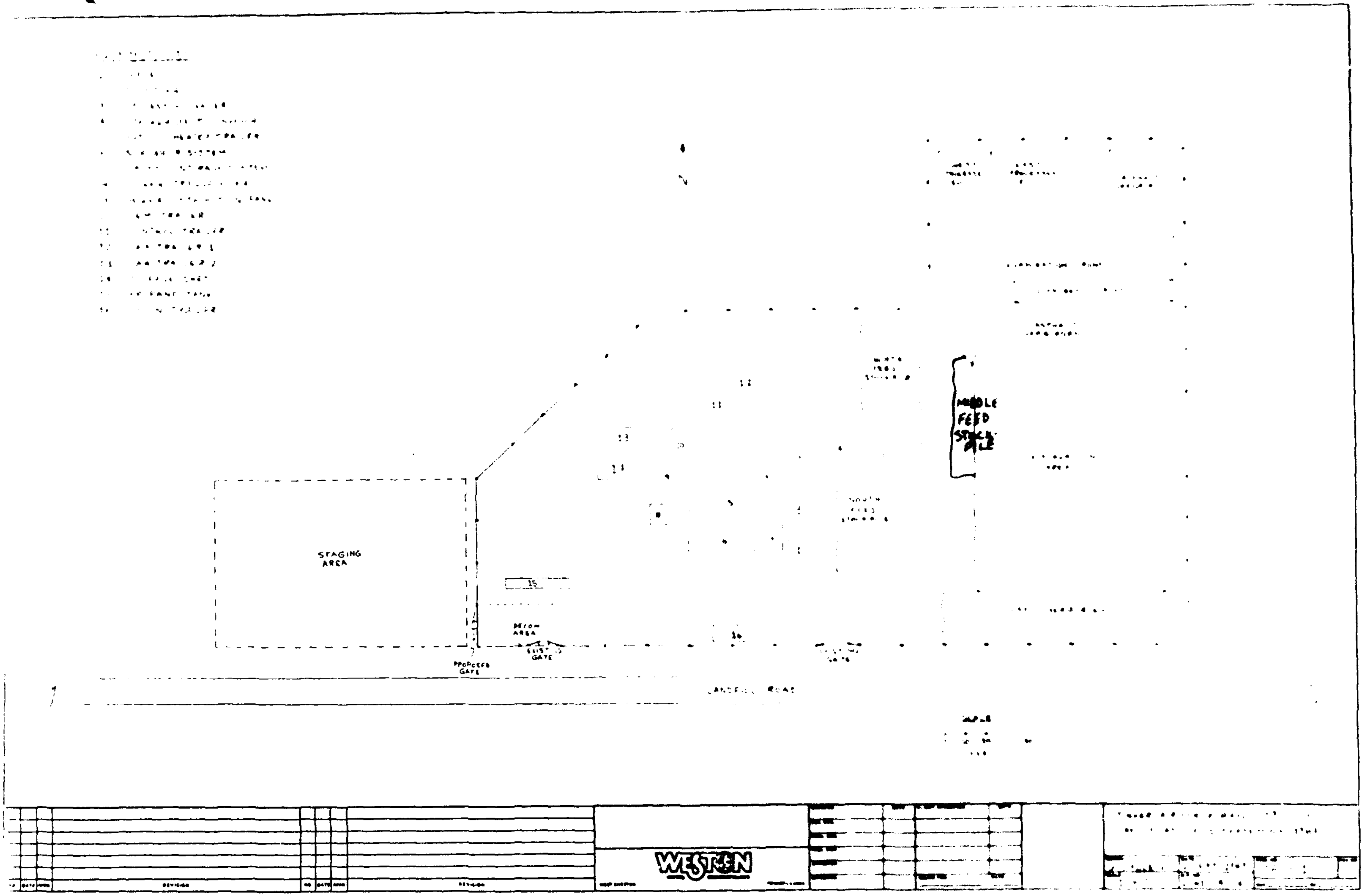

Figure 4: Site Layout for the Demonstration of the LT^3 System at Tinker Air Force Base, Oklahoma

- determination of impact of system parameters on effectiveness
- evaluation of the use of a stripping agent to enhance contaminant removal.
- determination of optimum operating conditions.
- determination of stack emissions.

Goal cleanup levels (GCL) were established for the test based on previous requirements or established standards. These goals were accepted by the EPA regional office in the RD&D permit. Table 1 lists the GCL for contaminants found above the detection level in soils processed.

Table 1: Partial List of Goal Cleanup Levels

Contaminant	GCL (ppb)
Trichloroethylene (TCE)	70
1,2-Dichlorobenzene	125
1,4-Dichlorobenzene	10,800
Toluene	330
Total Xylenes	150

The first test run was conducted at the high end of the hot oil temperature to be tested, 315 °C. This run established that the process is capable of remediating soils contaminated with JP4 and TCE. Results are presented in Table 2. Following this run, the system was operated at a reduced hot oil temperature (204 °C) in an attempt to establish a lower operating limit for hot oil temperature from which an optimum would be determined. The results of this run are presented in Table 3. Comparison of the results shown in table 2 and 3 indicate no significant difference between the two operating conditions in terms of contaminant removal.

At this point, an attempt was made to reduce the residence time to establish a maximum processing rate. The temperature was also reduced to 150 °C to determine the lower effective operating temperature. The results of this test are not conclusive as the test was aborted due to mechanical failure caused by overloading the processors.

Table 2: Results of First Test Run

Contaminant	Feed Soil Concentration (ug/kg)	Processed Soil Concentration (ug/kg)	GCL (ppb)
TCE	37,250	5.4	70
1,2-Dichlorobenzene	35,000	BDL	125
1,3-Dichlorobenzene	3,500	ND	NS
1,4-Dichlorobenzene	8,700	ND	10,800
Toluene	8,700	ND	330
Napthalene	4,300	BDL	NS
Total Xylene	5,900	ND	150

ND - not detected
BDL - below detection limit
NS - not specified

Table 3: Results of Second Test Run

Contaminant	Feed Soil Concentration (ug/kg)	Processed Soil Concentration (ug/kg)	GCL (ppb)
TCE	111,000	5	70
1,2-Dichlorobenzene	15,000	BDL	125
1,3-Dichlorobenzene	BDL	BDL	NS
1,4-Dichlorobenzene	ND	ND	10,800
Toluene	8,300	ND	330
Napthalene	5,000	BDL	NS
Total Xylene	11,400	ND	150

ND - not detected
BDL - below detection limit
NS - not specified

Testing at higher production rates (less residence time) and lower temperatures resulted in mechanical failure of the process equipment. The system was overloaded. The maximum soil processing rate achieved was 60% above the design rate at 11,364 kg/hr. Although this rate was not demonstrated for a sustained period, a sustained rate of 9091 kg/hr was established. A final test was conducted at a higher production rate but at a previously tested intermediate temperature (204 °C) to confirm the data of the 3 previous tests. The results are presented in Table 4.

At this time in the test program, analysis of the soil indicated the presence of Arachlor 1260, a polychlorinated Biphenyl (PCB). The system was never intended to process wastes of this nature nor were they expected. This discovery halted all operations and investigation eventually led to the cancellation of the remainder of the test. A complete description of the events following the PCB discovery and the actions taken will be reported at a later time.

Table 4: Results of Fourth Test Run

Contaminant	Feed Soil Concentration (ug/kg)	Processed Soil Concentration (ug/kg)	GCL (ppb)
TCE	10,575	23.4	70
1,2-Dichlorobenzene	53,000	BDL	125
1,3-Dichlorobenzene	BDL	ND	NS
1,4-Dichlorobenzene	14,750	BDL	10,800
Tolune	BDL	BDL	330
Napthalene	BDL	BDL	NS
Total Xylene	ND	ND	150

ND - not detected
BDL - below detection limit
NS - not specified

CONCLUSIONS

Although the test plan was cancelled prior to completion, the results of the test at Tinker Air Force Base are positive. Three of the five objectives of the test were met. It was determined that low temperature thermal treatment technology is effective at removing JP4 and TCE from soil. Optimum operating conditions for the full scale system were established as the mechanical limits of the processing equipment. At the levels of contamination in the soils tested, the range of operating conditions had no discernible effect on removal efficiency.

Two objectives were not met in the test plan due to the premature cancellation of the test. First, the use of stripping agents to improve contaminant removal was not investigated. The results of tests performed showed removal of contamination to near or below detectable limits in all cases. The use of a stripping agent would not have improved this result at a detectable level. The second objective, determination of emissions, was not met as stack testing was not performed for the test runs made. Stack sampling was to be conducted only at the optimum operating conditions. As the PCB discovery halted testing during the determination of the optimum conditions, no stack sampling was performed. This is not felt to be a significant impediment to fielding the LT^3 technology. The afterburner and scrubber system are standard unit operations used in similar treatment systems for contaminant laden streams. Although no field data was collected on this system, its standard configuration is expected to meet or exceed the required discharge criteria.

The LT^3 full scale system tested was capable of remediation of soils contaminated with volatile and semi-volatile compounds. Processing rates obtained indicated a cost for remediation between $90 and $100 per metric ton of soil fed to the system. The unit was determined capable of processing at a rate of 9090 kg/hr. Removal of the contaminants present was consistantly below the criteria established for cleanup.

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THE ARMY'S HAZARDOUS WASTE MINIMIZATION PROGRAM AND ITS NEED FOR INCREASED RESEARCH AND DEVELOPMENT

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ABSTRACT

The Army's entire hazardous waste minimization (HAZMIN) program has undergone significant change during the past few years. From starting as a policy to eliminate used solvents the HAZMIN program has grown into the development of new technologies such as paint stripping by plastic media blasting and metal plating by ion vapor deposition. The Army's HAZMIN program is still in its infancy though with the majority of the funding and attention still on used solvent elimination. The research and development (R&D) community needs to aid this program by broadening the horizons of their research into more of the less dominant and visible hazardous waste streams and develop technologies that will help reduce or eliminate these costly and potentially dangerous wastes. The Army's HAZMIN goal is to reduce hazardous waste generation by 50% by the end of 1992 using the amount generated in 1985 as the baseline. While a large amount of effort and money is being spent on HAZMIN activities the amount of hazardous waste generated annually is actually increasing. Therefore, to achieve the Army's goal, significant new advances in HAZMIN technology will be required of the R&D community. As an incentive to HAZMIN in general and the development of new technologies there will be a waste reduction incentive awards program started in fiscal year 1990 This program will be used to provide monetary incentives for good HAZMIN ideas. As envisioned this awards program will identify both installation and individual achievements in hazardous waste reduction.

Introduction

The United States Army operates hundreds of installations and facilities around the world. Within the continental U.S. alone, the Army operates about 1500 such installations and facilities. Within its national defense and readiness mission, the Army currently generates about 100,000 metric tons of hazardous waste annually. Although this amount represents less than one percent of the hazardous waste generated within the U.S. each year, it nevertheless presents serious challenges to the Army for proper storage, treatment, disposal, and minimization.

In response to the national emphasis on environmental protection and recognizing the potential significant cost savings, the Army has developed a broad based, comprehensive hazardous material/hazardous waste (HM/HW) management program during the 1980's. Although initially instituted in response to increased Congressional, media and regulatory pressure, the Army program is now also a productivity improvement initiative.

Background

With the passage of the Resource Conservation and Recovery Act (RCRA) in 1976, the U.S., for the first time, mandated the "cradle to grave" management of hazardous wastes. In 1980, the U.S. Environmental Protection Agency (EPA) issued the first regulations under this law. These regulations established rigid standards for hazardous waste generators and hazardous waste treatment, storage and disposal facilities (TSDF's). However, Congress was frustrated with the lack of national progress and in 1984 passed the Hazardous and Solid Waste Amendments to RCRA. This law established strict timetables for permitting HW TSDF's and schedules to ban HW from land disposal. In addition, this law required generators of HW to certify that they had in place a HW minimization program to reduce the volume and/or toxicity of the HW generated. However, no specific reduction criteria were established.

Army Hazardous Waste Minimization Program

The generation of HW by the Army results in both short and long term liability in terms of costs, environmental damage, and mission performance. Reducing the volume and/or toxicity of HW in the Army presents significant challenges for all levels of management because of factors such as, the diversity of HW generating activities, the number of hazardous waste generators, the organizational structure, the size and location of the installations, and the potential liabilities associated with waste management.

The emphasis of the Army hazardous waste minimization (HAZMIN) program will be on source reduction methods such as materials substitution. Where this approach is not feasible or economically practicable, the Army will promote recycling, on-site treatment and other alternatives such as materials recovery, process change, the use of minimum packaging, increased use of returnable or reusable containers, segregation of wastes, reuse, and off-site treatment to reduce the quantity or toxicity of HW.

The Army HAZMIN program has seen tremendous change and growth in only the past five years. In 1984, the Army instituted a Used Solvent Elimination

(USE) program. This program required installations to develop procedures to eliminate the disposal of recyclable solvents.

In 1985, the Department of Defense (DOD) Joint Logistics Commanders issued a policy that each service develop a hazardous waste minimization program and required that information on new and existing technologies be exchanged between the services and DOD.

In 1987, the Army established a formal HAZMIN policy and goal to reduce HW generation 50% by the end of 1992 when compared to a 1985 baseline year. Also, the Army established a "corporate-level" HAZMIN Workgroup to develop HAZMIN policy to meet the Army's goals and to coordinate the involvement of all Army elements. Since then, the Workgroup has met every few months to maintain the momentum. The Army HAZMIN policy requires that all MACOMs develop and maintain programs that; emphasize source reduction and recycling, consider reducing the toxicity of hazardous wastes, require routine audits of generating activities, require an economic evaluation of HAZMIN alternatives, and emphasize command support.

In 1987, the DOD issued policy enabling the services to utilize the Defense Environmental Restoration Account (DERA) for "seed" money for HAZMIN projects and initiatives. The DERA fund was established by Congress in 1984 as a special DOD appropriation for cleaning up old hazardous waste sites within the U.S. Since then, the Army has spent about $4-8 million annually from this appropriation to fund HAZMIN projects. But, this funding level is still much less than necessary and installations find it difficult to institute HAZMIN objectives because of the limited funding. The majority of HAZMIN projects that are easy for installations to start are recycling projects. But, the installations get little or no credit for this type of HAZMIN since EPA continues to consider recycling as a HW treatment operation.

Other draw backs to the implementation of HAZMIN initiatives have been that the installations never had to consider the cost of their own HW disposal because they did not have to use their own funds for this effort. Therefore, they never realized the total cost of generating this waste. Beginning in fiscal year 1990 the cost of hazardous waste disposal will be decentralized so that installations will have to budget for their own funds to dispose of the wastes they have been producing. Also, there has been no outward show of appreciation for HAZMIN ideas. But, also in fiscal year 1990 there will begin an annual HW reduction awards program to provide cash awards to installations and individuals as an incentive to develop and implement HAZMIN ideas.

Continuing Issues/Problems

The Army is required to comply with both the substantive and procedural aspects of Federal, State, and local environmental laws and regulations. Maintaining comprehensive and up-to-date knowledge of all the potentially applicable regulations in all the many jurisdictions which legally regulate Army HM/HW management activities and ensure compliance with them is a formidable task. This is especially true when historically the installation environmental office has been a deeply buried, under staffed, and under funded organization responsible for the entire installation management of 14 major environmental programs. These aspects of installation environmental management are very slowly changing. But, even with all the time and energy spent on HM/HW management from the Department of the Army (DA) to the installation level there remain problems that have to be dealt with. These problems include ensuring that all personnel that manage HW receive proper training, the changing of attitudes toward HM/HW management from one of an extra duty to one of this is the cost of doing business, and finding new less hazardous ways of doing the job and meeting the mission.

Technology transfer is another continuing problem. New systems and chemicals are being developed and are now usable but the people who can put them into full scale use do not know about them. The organizations developing new technologies must also begin to consider how this information will be distributed and aid in the preparation of technology transfer packages. Groups who provide guidance on environmental and engineering requirements need to be given the information on new technologies so that they can transfer this material during the normal course of their work. Some of these groups are the Army Toxic and Hazardous Materials Agency, Corps of Engineers, Engineering and Housing Support Center, Army Materiel Command, Deputy Chief of Staff for Production.

On-going HAZMIN Developments

The Army has many HM/HW initiatives underway that will aid the installation in complying with environmental regulations and reducing the amount of wastes generated. Among these initiatives are systems to help the installation track HM onto and through the installation and HW disposal, a HAZMIN awards program to stimulate HW minimization ideas, the development of an integrated HM/HW management plan for the Army, and a HW source reduction study dealing with the Army material acquisition life cycle process.

The Corps of Engineers Construction Engineering Research Laboratory (CERL) is a fundamental player in the development of these initiatives. CERL has developed and is now fielding a bar code tracking system for the management of incoming HM and the tracking of the disbursement of these materials. Along with the bar code system a personal computer (PC) operated database has been developed to aid installation environmental coordinators in monitoring the movement of HM/HW across their installations and to compile data on quantities, location, disposition, and costs of these items. CERL has also developed a PC program to provide an economic analysis of HW minimization options to allow installations to not only make good engineering decisions but economically sound ones.

The Assistant Secretary of the Army for Research, Development, and Acquisition (ASARDA) is conducting a major study into the opportunities for reducing HW at the source throughout the Army material acquisition life cycle. This study is divided into three phases dealing with incorporating environmental considerations into the weapon systems development process, identification and quantification of HM used in the Army, and development and demonstration of HAZMIN approaches, technologies, and solutions. This study when completed (1990) will provide a most comprehensive review and identification of the Army's use and generation of HM/HW.

As can be seen there are many different initiatives currently underway to provide direction, guidance, and aid to installations in the area of HM/HW management. Therefore, the need to provide coordinated DA management was recognized. To this end, a DA integrated HM/HW management plan is being developed. This plan will identify the current state of HM/HW operations in the Army, define the impacts of these operations, recommend actions to minimize the impacts and propose goals for program implementation. The plan will breakdown all the aspects of Army HM/HW operations into discrete elements such as systems acquisition, material procurement, material distribution, material use, waste containment, and final waste disposal and provide recommendations to minimize the impacts of HM/HW on each element.

Increased Researched and Development Needs

The Army HM managers are required to control HM to minimize hazards to public health and the environment. The managers will accomplish this by developing and procuring material in such a way as to minimize the environmental hazards, limit the use of HM to the maximum extent practicable, employ procedures that provide the greatest safety during storage, use, and disposal, develop safe, environmentally sound methods to store and ultimately dispose of HM, and provide appropriate training to persons who manage, use, store, and dispose of HM.

The managers of HM continue to need help. While minimizing the hazards of the use of HM is possible it would be a far better situation if the materials were non-hazardous and did not require intense managing. Therefore, more research into commercially available alternative materials is needed. But this is not enough. The Army's HM/HWs move through the use-generation system in such a manner that almost no one oversees the entire life cycle or looks at HAZMIN alternatives on a true life-cycle basis. The HM are procured centrally on a lowest cost per unit (gallon, pound, etc.) basis. While this is good for the procurement personnel it may not be good for the Army overall if there is a cost for disposing this material. Research and development is needed in the formulation of chemicals (solvents, degreasing agents, painting compounds, etc.) to be used for military applications that have an overall life-cycle cost that is minimized. Many non-hazardous chemicals are produced commercially but these are formulated primarily for private sector industrial applications and do not in many cases come up to military specifications.

The objective of the Army's HW managers is to protect human health and the environment and to conserve valuable material and energy resources. Material resources will be reused, recycled, and reprocessed whenever possible. The Army HW program will ensure that wastes are managed; to reduce the need for corrective actions, to minimize the volume or toxicity of waste prior to disposal using economically practicable methods that emphasize source reduction, recycling, and reuse. To aid these managers additional R&D is needed in the extension of the life of baths and solutions. Plating and neutralization baths and rinse solutions have historically been changed on a basis of time in use rather than ability to do the job. This concept has changed to one of checking the solutions for strength which has added life to many systems and reduced the quantity of HW generated. In some cases the solution is still usable but the time required to accomplish the task has increased past that deemed efficient by the users. The development needed here is one of finding ways to add strength back to diminished solutions (additives or in line filtering systems, etc).

The largest source of HW (approximately 80%) in the Army is the generation of red/pink water which comes from the manufacture and load, assemble, and pack (LAP) of explosives. To decrease this waste extensive work will be required to either develop new explosives of equivalent potential or to develop efficient recycling systems that can return these explosives to the manufacturing or LAP process. An innovation in this one area alone could attain the Army's 50% reduction goal. Efforts are presently underway at the U.S. Army Toxic and Hazardous Materials Agency on this waste stream but additional work, especially in the explosive formulation will be required if a significant reduction of this waste is to occur.

Summary

The Army is moving ahead in the area of hazardous waste minimization but presently available techniques and technologies are not enough. The research and development community will have to be a vital and progressive player in providing the technologies to fill the gaps between commercial R&D and military unique requirements. They will also have to increase their efforts in the distribution of these technologies so that new ideas are not only developed but implemented.

DESCOM HAZMIN PLAN

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DESCOM has targeted six major waste streams into a concentrated effort to approach zero waste generation. Each waste stream is assigned to one depot to identify and recommend the necessary technologies. These depots are designated CTX (Center for Technical Excellence) for the waste stream. Technologies approved by the CG for command wide implementation will then be quantified. Each initiative will then be implemented across the command in one procurement action.

USATHAMA has major initiatives in fluidized bed furnace technology to reduce solvent and paint stripping wastes. Ion vapor deposition to reduce cadmium plating wastes, and several other areas directly affecting DESCOM's targeted waste streams. Completed USATHAMA projects in plastic media blasting and other areas provide data for evaluation by CTX depots. The existing working relationship between USATHAMA and DESCOM is a prime resource for this program.

Dramatically increasing costs of disposal and cleanup make even modest reductions in the hazardous waste output of an industrial activity cost effective. In addition, if depots are not kept within increasingly stringent EPA regulations, substantial fines will be incurred. Costly cleanup of hazardous waste spills is avoided if substitutes for existing processes are implemented.

Environmental concerns are prevalent in the press, Congress, and in public opinion. The only possible defense against criticism for inaction is an in-house effort to voluntarily reduce hazardous waste. DESCOM has an aggressive command program for implementation of identified technologies.

Worker concerns for short term and long term safety in the workplace also provide powerful incentive for this type of proactive approach. Personal safety also provides the workers at the depots a vested interest in cooperating with this effort if they are convinced that it has high level support.

Concentrating the effort for multiple installations at one depot is the most cost effective utilization of limited resources and provides the additional benefit of increased technology transfer within the AMC industrial complex.

USATHAMA R&D SUPPORTING HAZARDOUS WASTE MINIMIZATION AND VOC CONTROL AT ARMY DEPOTS

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ABSTRACT

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) and PEI Associates, Inc. (PEI) recently conducted inspections of eight Army depots to identify research needs related to hazardous waste minimization and the control of volatile organic compounds (VOCs). The depots visited were Anniston, Corpus Christi, Letterkenny, Red River, Sacramento, Sharpe, Tobyhanna, and Tooele. The focus of the information collected was on methods of paint application and removal, degreasing operations, and wastes generated from electroplating operations. This information was used by USATHAMA to define several research projects that PEI is conducting with the assistance of the depots under the Pollution Abatement and Environmental Control Technology (PAECT) contract. These projects will address specific waste minimization problems at selected facilities. All Army depots are actively investigating and implementing waste minimization programs, but they are constrained in part by lack of resources and the need for improved technical information. The research being conducted by USATHAMA will benefit waste minimization efforts and VOC control at all depots. This paper summarizes the findings resulting from the depot visits.

A total of 69 potential waste minimization and VOC reduction/control projects were identified at the eight depots. USATHAMA and PEI have chosen the following demonstration projects: 1) evaluation of paint-application systems to increase transfer efficiency and to reduce VOC emissions and hazardous paint sludge at Sacramento; 2) extension of the lives of alkaline paint-stripping baths by filtration to reduce the amount of these stripping solutions disposed of as hazardous wastes at Letterkenny; and 3) installation and evaluation of an electrodialysis unit at Corpus Christi to lengthen the useful life of a chromium-stripping tank on a magnesium parts line. In addition to these projects, two related projects are being conducted: 1) installation, demonstration, and evaluation of an aluminum ion vapor deposition system at Anniston as a potential replacement for cadmium electroplating, and 2) installation, demonstration, and evaluation of a fluidized-bed parts cleaning system at Red River to reduce hazardous waste from degreasing and paint-stripping operations.

INTRODUCTION

U.S. Army depots are involved in repairing and refurbishing Army vehicles and equipment. Operations include metal pretreatment and metal finishing, such as paint application, paint stripping by abrasive blast media, chemical paint stripping, chemical cleaning, degreasing, and electroplating. These operations generate large amounts of hazardous waste and air pollutants. Also, wastewater from some of these operations must be treated in a wastewater treatment facility. This not only entails treatment costs, but also costs for transportation and disposal of the resulting sludge.

Hazardous waste minimization (HAZMIN) offers a viable method for making progress in solving problems created by hazardous waste generation. Preventing the generation of waste at the source reduces the amount of waste that must be tracked, treated, handled, manifested, and/or disposed of. This approach also reduces the long-term liability and frequently results in significant cost savings. In addition, waste minimization reduces worker risk because it decreases the handling of hazardous waste and results in the use of nontoxic or less toxic chemicals.

The Army has established a goal of 50 percent reduction of hazardous waste by 1992 (relative to 1985 baseline figures). A depot's work load, however, varies with the demand for particular items and with the types of material processed, and the generation of hazardous waste varies with the work load. Thus, an increase or decrease in hazardous waste generation from one year to the next does not necessarily mean the depot is performing better or worse than it did the year before.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is conducting research and development projects concerning hazardous waste minimization at Army depots. Recent projects have included demonstration testing of plastic media blasting at Letterkenny Army Depot and the use of alternative paint strippers at Sacramento Army Depot. PEI Associates, Inc., is currently under contract to USATHAMA to assist in the completion of HAZMIN projects at Army depots.

Under this contract, USATHAMA and PEI personnel participated in meetings and facility tours at eight Army depots between April and July 1989. The eight depots were Anniston (Alabama), Corpus Christi (Texas), Letterkenny (Pennsylvania), Red River (Texas), Sacramento (California), Sharpe (California), Tobyhanna (Pennsylvania), and Tooele (Utah). The purpose of these visits was to acquire comparable information on waste minimization and sources of VOC emissions at the depots. Information was collected both on potential tasks that PEI will conduct in the near future and potential research projects that USATHAMA may select for long-term effort. Trip reports were prepared that contain comprehensive information on maintenance operations at each depot and recommendations for HAZMIN efforts. These trip reports were collected in a single document, which could be used by the depots to increase technical information transfer and coordination among the depots. A total of 69 potential waste minimization projects were identified that range widely in technical effort and scope of work. Based on the current scope of work, interest of depot personnel, the applicability of the projects at several depots, and the potential for hazardous waste or VOC reduction, USATHAMA and PEI selected three projects for completion within a year. Each project will be implemented on an operating production line at one of the depots.

This paper presents some of the findings from the depot visits and describes the three projects currently being implemented. Two related task orders under the same contract that involve waste minimization at Army depots also are discussed briefly.

PAINT APPLICATION

Paint application is a major source of VOC emissions and hazardous waste generation at Army depots. Each problem is addressed separately.

VOC Emissions

Under the current project, PEI and USATHAMA are considering control and reduction of VOC emissions as well as hazardous waste minimization. Depots are undertaking action to reduce VOC emissions where required by State regulations. These regulations are highly dependent on the State in which the depot is located. The four depots located in California and Pennsylvania (Sacramento, Sharpe, Letterkenny, and Tobyhanna) are under the most regulatory pressure to reduce VOC emissions. In some locations, such as the Anniston depot in Alabama, the limits set on VOC emissions are high; depots in such areas are currently under no time-critical regulatory pressure to reduce VOC emissions. Corpus Christi is exempt from many VOC regulations because the depot processes aircraft. Depots in Pennsylvania, for example, are restricted to a total of 50 tons per year of VOC emissions from surface-finishing operations, whereas Anniston has a limit of 100 tons per year per source (e.g., per paint booth). Even in States without stringent VOC regulations, however, State agencies frequently expect the depots to make a reasonable attempt to reduce VOC emissions and to complete a health and safety evaluation before the State issues a permit for a new VOC source.

California uses three methods of regulating VOC emissions from surface-finishing operations: total VOC emissions from surface-finishing operations, transfer efficiencies, and the VOC content of the paint. The VOC content of paint in California is limited to 340 g/L (2.8 lb/gal); enamels contain more than 340 g/L and are not used. The depots also must achieve a 65 percent transfer efficiency in their paint operations, regardless of VOC content of the paint or total VOC emissions. More stringent regulations are being considered to increase the required transfer efficiency to 85 percent and the maximum VOC content to 280 g/L (2.3 lb/gal). Other States often follow California's lead in promulgating new regulations, and other depots may be required to meet more stringent regulations in the future.

Stack controls for VOCs are generally expensive options for reducing VOCs that are released to the atmosphere. The exhaust air from a VOC-generating operation such as painting contains relatively low concentrations of VOCs, so incineration technologies would require a large amount of supplementary fuel. In addition, sources of VOC emissions are usually spread throughout a depot rather than concentrated in one location because of the historical development of the depot and because many separate buildings have full complements of surface pretreatment and finishing operations. A VOC control technology such as an incinerator, a carbon adsorber, or some other control device would be required for each source, or sufficient ducting and fans would be required to vent all sources or groups of sources to one control device. Implementation and operation of these technologies would thus be very expensive.

VOC Source Reduction — Because of the expense of applying a VOC control technology, depots are focusing on reducing VOC emissions at the source by switching to low-VOC, high-solids paints and improving paint-application transfer efficiencies. For example, several depots have switched to single-component chemical-agent-resistant coatings (CARCs), which contain a lower VOC content than do dual-component CARCs. High-solids paints, however, are reported to be more abrasive and to wear out spray gun parts more quickly.

Depots are also focusing on alternative paint-application technologies such as the high-volume, low-pressure systems to attain better transfer efficiencies. Some of these paint systems, however, reportedly do not achieve the transfer efficiency claimed by the vendor. Also, for some guns, the operators must paint slower to achieve a good coat quality, and in some cases they are unable to paint the camouflage pattern.

Under the current contract with USATHAMA, PEI will investigate selected paint-application systems to evaluate their effectiveness in reducing VOC emissions. PEI will install paint-application systems and/or different spray guns on an actual painting production line at one of the depots and measure the following variables, among others, to assess the effectiveness of the paint-application system:

° Paint usage rate.
° Amount of paint on parts (to calculate transfer efficiency).
° Speed of paint application to achieve good coat quality.

- Ability to paint camouflage pattern.

The information developed from this project will allow depot personnel to compare available techniques for reducing VOC emissions and will provide an objective basis for choosing specific paint-application systems. These data will be available by October 1990.

One problem with reducing VOC emissions is that the painting line is, by necessity, production-oriented. The painters see their job as painting, not as reducing VOC emissions. Therefore, the focus is often on painting a part as quickly as possible. This is done by increasing nozzle pressure, using a wider nozzle angle, and paying less attention to overspray, all of which result in lower transfer efficiencies and higher VOC emissions. Operator training will increase awareness of the importance of achieving improved transfer efficiencies.

Generation of Hazardous Waste

In addition to VOC emissions, painting operations create large quantities of hazardous waste. Waste results from excess paint, cleaning solvents, and the capture of paint particulates to prevent their release into the atmosphere. Paint wastes are hazardous because the organic solvents used as carriers may be toxic or flammable. In addition, some paints still contain heavy metals such as lead and chromium; however, most of these paints are gradually being phased out.

HAZMIN for Dry Filters — The two major types of control currently in use are dry filters and water-wash paint booths. All depots use dry filters on at least some paint booths to capture paint particulates. These filters are changed when sufficient paint has accumulated and flow becomes restricted. Methods of waste minimization include the following:

- Recharacterization.
- Segregation.
- Replacing paints with hazardous characteristics.
- Improving transfer efficiencies.
- Development of alternative methods for capturing the paint particulates.

Some depots dispose of dry filters as hazardous waste, whereas other depots have shown that their filters are nonhazardous. All depots disposing of the filters as hazardous waste should conduct characterization studies to determine if the filters actually are nonhazardous. If the filters are allowed to dry thoroughly, carrier solvents will not be present, and the filters will not be hazardous because of flammability. Paints containing heavy metals, however, may cause the filters to be hazardous. For example, one depot still uses yellow safety paint, which contains chromium. The depot segregates the filters used to trap this paint from other filters that are disposed of as nonhazardous wastes. This method prevents the disposal of the filters as hazardous waste because of the hazardous characteristics of a small portion of the paint. The use of paints with nonhazardous characteristics would also render the filters nonhazardous.

Improving transfer efficiencies is another effective method of waste minimization for dry filters. The study PEI and USATHAMA are conducting to reduce VOC emissions from painting operations also will reduce the amount of dry filters requiring disposal. High-volume, low-pressure and other paint-application systems (e.g., electrostatic, air-assisted airless, and airless) improve transfer efficiencies by reducing overspray. This overspray contains VOCs, which are emitted to the atmosphere, and paint particulates, which are captured by dry filters. Reducing the overspray will reduce the amount of paint particulates collected by the filters, and thereby extend filter life and reduce the amount of filters that must be disposed of.

Tobyhanna is experimenting with the use of Styrofoam filters as an alternate method of capturing paint particulates. Paint that is caught on these filters can reportedly be knocked off or scraped off so that only the paint and not the entire filter must be disposed of. Experiments at Tobyhanna have shown that the filters do not trap the paint particulates sufficiently well to justify replacing other dry filters; however, Styrofoam may be used in conjunction with other filters to reduce the amount of particulates captured by the other dry filters, and thereby extend their useful lives and reduce waste volume.

HAZMIN for Water-wash Paint Booths — The second major type of control of paint particulates resulting from overspray is the use of water-wash paint booths. In a water-wash paint booth, the back of the booth contains a wall of falling water that passes over an air vent. As the overspray is drawn through the wall of water, paint particles are washed into a trough at the base of the wall. Sludge accumulates in the trough, and the booth is periodically shut down to remove the sludge. This paint sludge is a major hazardous waste problem at several depots. Waste minimization opportunities include methods of separating sludge from the water and methods of separating water from the sludge. All methods listed for the dry filters are also applicable. As with the dry filters, improving the transfer efficiency of paint application (a current USATHAMA/PEI project) will reduce the amount of overspray and therefore the amount of sludge that accumulates in the trough.

A few depots are exploring the use of cyclone separators (hydrocyclones) combined with detackifying agents to remove sludge from the water and to minimize sludge volume. Detackifying agents assist in coagulating and precipitating or floating paint particles to allow them to be easily separated from the water. Figure 1 shows a schematic of a water-wash paint booth that has been fitted with a hydrocyclone system. Water from the water-wash trough contaminated with paint solids is pumped to the cyclone separator. Centrifugal action throws the more dense paint particles to the side, where they fall into a 55-gallon drum. Water reduced in solids content exits the top of the hydrocyclone.

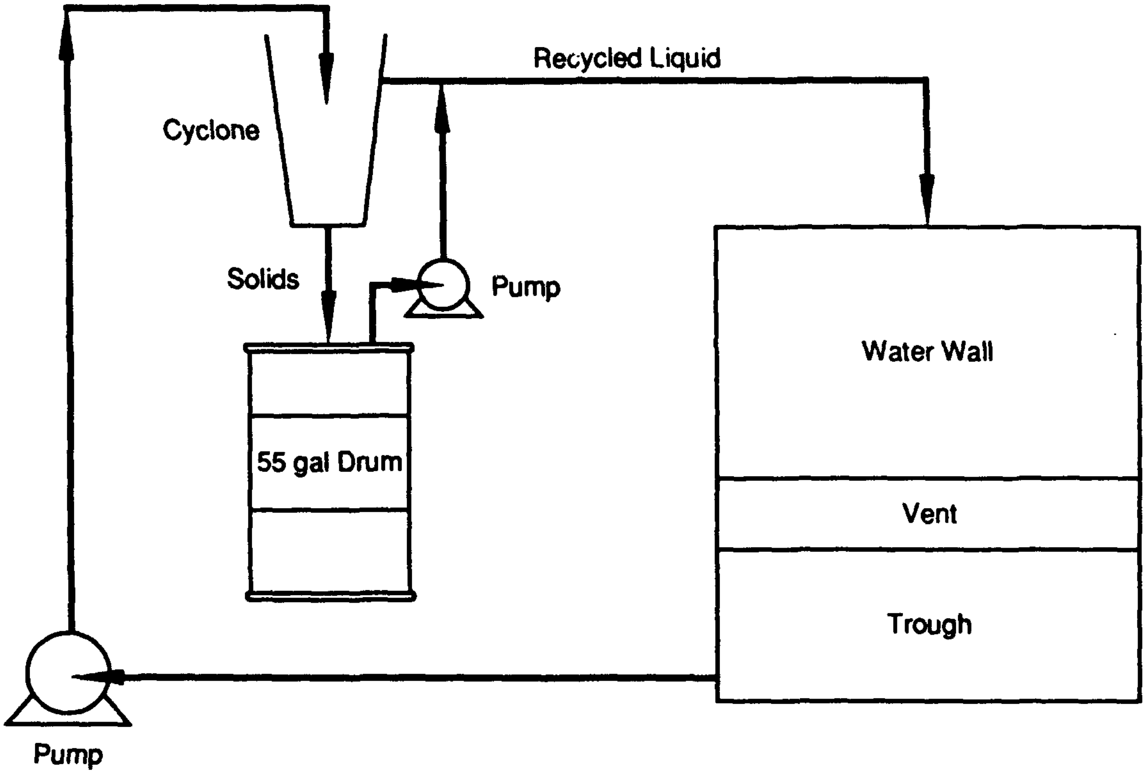

Figure 1. Water-wash booth with cyclone separator.

The solids continue to settle, and a pump can be placed at the top of the drum to remove excess liquid. All water is recycled back to the booth, which reduces the amount of wastewater sent to the wastewater treatment plant.

Anniston has purchased several cyclone separators, but has had considerable difficulty with the viscous CARC paint plugging the cyclones. Corpus Christi is also considering purchasing some of these units, and personnel believe they may have found an effective detackifying agent, which they plan to use to solve the plugging problem. An opportunity exists for the transfer of technical information between depots. The key to the success of this method appears to be identifying both the physical system for sludge removal and the chemical compounds that must be added to the water to ease sludge removal and to reduce sludge volume. One depot uses skimmers to remove sludge from the top of the water. These automatic methods of removing sludge from water-wall booth water result in lower labor costs because shoveling out the sludge on a periodic basis is a labor-intensive process. Downtime is also reduced because the booths do not need to be shut down to remove the sludge.

Finally, once the paint sludge has been generated, the volume can be reduced through dewatering processes. One depot reported that it had successfully processed some paint sludge through a filter press, but it does not have the funds to purchase a filter press dedicated to this purpose. The liquid from the filter press probably would require additional treatment or it could potentially be recycled.

PAINT REMOVAL

A wide variety of chemical and mechanical paint-stripping methods are used at the depots. The choice of a paint stripping method varies among the depots and depends in part on the items processed. Chemical and mechanical paint removal are discussed separately.

Chemical Paint Removal

The major chemicals used in paint stripping are methylene chloride and alkaline formulations. Phenolic strippers were previously used, but they have been replaced with methylene chloride because of health and safety concerns. Methylene chloride is now a target for replacement because it is a suspected carcinogen. Corpus Christi still uses ortho-dichlorobenzene in some paint-stripping operations. Parts to be stripped of paint are usually dipped in a tank containing the process solution. Corpus Christi, which processes aircraft, has often used a method in which methylene chloride is brushed or sprayed onto an aircraft part, and the paint is then scraped and washed off. This method typically generates large amounts of VOC emissions, hazardous waste, and wastewater. New booths have recently been constructed to reduce VOC emissions.

After paint-stripping solutions have stopped working or when laboratory tests indicate decreased chemical activity, they are generally drummed and disposed of as hazardous waste. The liquid is sometimes pumped from the top of a tank, and the sludge is place in drums for disposal; the liquid can then be pumped back into the tank for continued use. One depot changes its tanks during regularly scheduled production shutdowns every 6 months regardless of the condition of the stripping solution. This mode of operation is currently being reevaluated to determine if the solutions could be used for longer periods.

<u>HAZMIN for Chemical Paint Strippers</u> — The following methods for reducing hazardous waste from chemical paint strippers are currently being investigated by USATHAMA and several depots: the use of nonhazardous paint strippers, using strippers with longer useful lives, increasing the useful life of a given stripper, and decreasing the sludge volume that is disposed of as a hazardous waste. A study sponsored by USATHAMA is currently being conducted at Sacramento to identify a suitable replacement for the methylene-chloride-based paint stripper. The initial phase of this study involved screening numerous stripping agents to assess their effectiveness. One of these strippers was selected for full-scale implementation on the metal cleaning production line. The stripper was performing well, but it ceased working after 6 months. The useful life of this stripper was judged to be too short, and a new stripper is now being tested on the production line. Red River is also conducting studies on nonhazardous alternate chemical strippers.

Although several alternative strippers and other chemical cleaning agents are touted as being nonhazardous, these chemicals may nevertheless dissolve a sufficient amount of metal from cadmium- and chromium-plated parts to create a characteristically hazardous solution (i.e., EP Toxic for metals). In addition, some concern has been raised about the actual environmental benefits of some of these strippers. Alternative strippers result in hazardous waste reduction only if they can be treated in the wastewater treatment plant rather than being disposed of as hazardous waste, if they have longer bath lives than currently used chemicals, or if they can be more readily recovered and recycled. Alternative chemical strippers containing hazardous compounds should also be less volatile than chemicals such as methylene chloride and thus reduce VOC emissions. A large part of the driving force toward substitution of current strippers such as methylene chloride involves their volatility and the resulting worker exposure.

Much of the hazardous waste generated from paint stripping is the sludge from these operations. A filter press could be used to minimize the sludge volume; the liquid phase would require further treatment or could potentially be reused. Paint-stripping solutions become weakened over time, and must be disposed of as hazardous waste. The lives of paint strippers can be extended by appropriate maintenance procedures (e.g., making the specified chemical additions to the tanks based on laboratory analysis and vendor recommendations), if these are not already followed as standard operating procedures.

One of the HAZMIN projects that USATHAMA and PEI are pursuing is the exploration of filtration of solids as a means of extending the lives of paint-stripping solutions. Leaving solids in the process tank after the paint is removed from a part may result in a continuing chemical reaction between the stripper and the solids, which reduces chemical activity and depletes the stripping agent. Filtering the solids out of the solution may result in longer bath lives, fewer tank change-outs, and less hazardous waste. Because methylene-chloride-based strippers are being phased out as a result of health and safety concerns, this project will focus on filtration of alkaline paint strippers containing sodium or potassium hydroxide, sodium gluconate (a rust remover), and various wetting agents. The project will be implemented on a process tank at Letterkenny that is currently being used on the production line so the data collected will be representative of actual operations.

During this project, the reduction in hazardous waste that can be achieved by filtration will be quantified. Process variables of the system will be determined, such as the filter pore size that results in the greatest life extension without creating an excessive pressure drop for the pumps, the filter media that can withstand the corrosive environment, and the pumps that can effectively handle the sludge. Factors that may affect the life of the process bath (solids content, particle-size distribution, concentration of contaminants, and the concentration of active ingredients) will be investigated. Baseline data will be collected to determine the contamination profile over time of the stripping agent as currently used. A filtration unit will be purchased and installed, and comparable data will be collected to determine the effect of filtration on the characteristics of the process bath. These data will be useful to all depots interested in evaluating techniques for minimizing hazardous waste from paint-stripping operations.

Abrasive Paint Stripping

Abrasive blasting is also used to strip paint at Army depots. The operation can occur in a walk-in booth, a hand cabinet, or an automatic blast booth. The operation creates blast media that falls to the booth floor and a fine dust that is suspended in the air and removed from the booth via a circulation system. The material that falls to the floor of the booth, which is potentially reusable, can be collected in floor vents and transported to a recirculation system consisting of cyclone separators, screen filters, and fabric filters. When this technique is used, the fine dust is collected in 55-gallon drums or roll-off containers, and the coarser media particles are recycled to the booth.

Spent media are usually disposed of as hazardous wastes because they contain heavy metals, especially cadmium, chromium, and lead. Chromium and lead are components of paint pigments, and cadmium and chromium are used to electroplate parts. Many paints containing chromium and lead are being phased out; however, equipment processed at depots is often 10 or more years old and has been painted with older paints that are no longer in use. Thus, even if all paints were changed today, it would take many years for all field equipment to be painted with nonhazardous paints. Similarly, as long as cadmium and chromium are used in electroplating, the chance exists that these metals will contaminate the spent blast media enough to render the media hazardous.

The numerous types of abrasive blast media used include walnut shells, steel shot, aluminum oxide, peridot, glass beads, and plastic beads. A few depots still use some sand as a blasting medium, but it is being phased out because of health concerns such as silicosis and the hazard of explosion. The specific type of medium used depends in part on the items processed at the depots. For example, depots that process heavily corroded steel parts use hard abrasive media such as aluminum oxide or steel shot. Depots that process aluminum items use the softer media such as walnut shells or plastic beads. Some depots still use handsanding on some items.

HAZMIN for Abrasive Paint Stripping — Several waste minimization opportunities exist for abrasive media blasting, including the following:

- Implementing or improving recycling of the blast media.
- Switching to more appropriate media with longer usable lives.
- Alternative blast methods.
- Optimization of blast parameters.
- Removing paint only when necessary.

Some depots do not use cyclone separators or other equipment for recycling media, whereas personnel at some other depots do not believe that their current system is achieving efficient recycling. Implementing or improving the recycling of media could reduce waste significantly. Many of the blasting booths are very old, and the most efficient method of implementing a recycling program may be to purchase and install new booths with recycling capabilities; however, the capital costs would be high. Recycling blast media creates more dust because the particles are finer than those in virgin blast material. Finally, recycling media concentrates metals as the number of recycle loops increases. Media that are not recycled may not have metal concentrations sufficiently high to render them hazardous; recycling the media and concentrating the metals may cause the spent media to be a hazardous waste.

Another waste minimization opportunity involves changing the blast operations to use media that are more applicable to the parts the depot processes, and that may be more recyclable and have longer lives. Sharpe uses garnet in its current blasting operations to remove paint and heavy rust from old steel parts; they are considering changing their operations to use steel shot, which will not degrade as quickly. Tobyhanna personnel are evaluating the feasibility of replacing aluminum oxide blast material with a medium called zirconia alumina, which is reported to have a longer life than aluminum oxide and to generate less waste. Zirconia alumina puts less wear on parts, recycles more, but it also costs approximately three times more than aluminum oxide and its effect on corrosion resistance is unknown.

Plastic media blasting has been used widely by the Air Force to replace methylene chloride in stripping paint from aircraft. Compared with chemical stripping, blasting with plastic media is quicker, generates less hazardous waste, and prevents VOC emissions. Compared with some other abrasive media, plastic media particles do not damage sensitive substrates, they may be more recyclable, and they may generate less hazardous waste. Blasting with plastic media is also much faster than handsanding. Plastic media blasting is currently being used or implemented at Letterkenny, Sacramento, and Corpus Christi. Aluminum electronics shelters are processed at Letterkenny and Sacramento, and aluminum aircraft skins are processed at Corpus Christi. Corpus Christi will use plastic media blasting to replace up to 70 percent of its methylene chloride operations; however, some methylene chloride will still be used because abrasive blasting cannot reach all areas of some parts.

Blasting and recycling equipment often must be designed for a particular type of media. For example, cyclones must be sized for particles of a particular density and abrasiveness. Some depots have tried a blast medium such as plastic using equipment designed for another material, which may not give a true measure of the medium's performance. Cooperation among depots would help in this case, as a depot interested in the effectiveness of a certain medium on particular items could send these items to a depot that has a facility that already uses the medium. USATHAMA conducted a demonstration test of plastic media blasting at Letterkenny. The testing included optimizing the choice of plastic media (hardness and sieve size) and blast conditions, and involved an analysis of damage to substrates, waste generation compared with that of walnut shells, economics, rust removal, and materials suitable for use with plastic media. The complete results can be found in "Demonstration Testing of Plastic Media Blasting at Letterkenny Army Depot," USATHAMA, December, 1988.

An operational change that can reduce hazardous waste and VOC emissions from both paint application and paint removal is to strip paint only when necessary and to paint only those areas of a part that need painting. Some depots will automatically strip an entire vehicle, or some customers will insist that the entire vehicle be stripped. Other depots, however, selectively strip areas of a part by handsanding or abrasive blasting and then paint either those areas or the entire item. Some types of abrasive media, such as plastic, may also be able to strip only one layer at a time, so that the top coat could be removed while the primer is left as a base for a new coat of paint. Although the Army is converting all paint to the CARC system, guidelines specify that a part should not be stripped and repainted solely to provide a CARC surface.

DEGREASING AND CLEANING SOLVENTS

In addition to paint stripping, depots also use various chemicals in metal degreasing and cleaning operations. These chemicals are sources of both VOC emissions and hazardous waste. All depots except one have replaced trichloroethylene with 1,1,1-trichloroethane as a solvent in vapor degreasers. Trichloroethylene has been replaced because it is a suspected carcinogen and because it contributes to ozone formation, whereas 1,1,1-trichloroethane has been exempt under most VOC regulations because it does not contribute to ozone formation.

Several depots have experimented with recycling 1,1,1-trichloroethane, but these efforts have been plagued with a variety of problems, including acidification of the product and equipment failure. Tooele has an effective solvent-recycling program in which 1,1,1-trichloroethane, stoddard solvent, and lacquer and polyurethane thinners are distilled and the product is reused. The recycled solvent is not added back into the paint because of concerns regarding paint quality, but personnel at Tooele hope to overcome this limitation. The recycled paint thinner is currently used for wash-down.

An alternate technique for reducing both paint stripping and degreasing waste involves fluidized-bed parts cleaning. In the fluidized bed, grease and paint are burned off the parts and gaseous emissions are processed in an afterburner. The fluidized medium is aluminum oxide, which provides for efficient heat transfer. USATHAMA and PEI will conduct a demonstration test of the fluidized-bed method of degreasing and paint removal at Red River. The testing will include processing a wide variety of parts available at the depot from ongoing production. Testing will be conducted to determine the advantages and disadvantages of the technique. Of particular importance will be tests designed to determine what effect the heat of the fluidized bed has on the various parts. Parts will be subjected to mechanical property tests before and after processing in the fluidized bed to determine if any effect or damage occurs. Atmospheric emissions testing will be conducted to quantify releases to the atmosphere. This technology's effectiveness in degreasing and paint removal on parts typically processed at depots will be evaluated in a report.

Numerous other chemicals are used for such cleaning purposes as pickling and removing rust. For example, phosphoric acid is frequently used to remove rust. Two depots evaluated the use of a product to replace phosphoric acid baths. The vendor claimed that the product was nonhazardous and would generate less hazardous waste than the phosphoric acid rust removers. When personnel at Tobyhanna evaluated this product, they concluded that it was not a promising alternative for phosphoric acid because some soluble metals in the product create a hazardous waste, a large amount of agitation is required, the product acted slowly on the part, and the product costs about six times more than the phosphoric acid solution. Tooele also tested this product on a variety of parts and concluded that the product performed about as well as phosphoric acid, but that it was much more expensive. Tooele also tested the product for long-term rust inhibition, but, again, the product fared no better than phosphoric acid.

ELECTROPLATING AND SURFACE FINISHING

Electroplating operations at Army depots consist primarily of cadmium and chromium electroplating; however, other metals are plated on a smaller scale, including brass, copper, gold, nickel, silver, tin, and zinc. Other metal-finishing operations include chromate conversion coating (also known as alodining) and metal electrostripping.

Electroplating and other metal-finishing operations generate several types of hazardous waste. A direct source of waste is the dumping of spent solutions. Also, drag-out from the process tanks contaminates the rinse water, which then must be treated before it is discharged to the local sewer or water body. In the wastewater treatment plant, the water is generally treated with lime to precipitate metals as metal hydroxides; one depot uses a sulfide precipitation process. In either case, the sludge is a listed waste (F006) and is generally EP Toxic for cadmium and/or chromium if these metals are used in the metal-finishing operations. The wastewater treatment sludge probably represents the largest volume of waste generated from electroplating operations. The electroplating solutions are rarely replaced and do not generate much hazardous waste. Other process solutions, such as chromic-acid stripping or chromate conversion coatings, are changed more frequently and generate more hazardous waste than do electroplating solutions.

The literature contains a multitude of waste minimization options for metal-finishing operations, and several methods are currently used by the depots. Waste minimization methods can be targeted at the process tank itself, at the wastewater from the rinse tanks, or at the sludge generated by the wastewater treatment plant. These methods include the following:

- Lengthening the lives of the process tanks.
- *Replacing solutions with less hazardous solutions.*
- Using alternative processes.
- Reducing drag-out.
- Recovering metals from the wastewater.
- Segregating sludge

- Recharacterizing the waste sludge.
- Redesigning the treatment plant or changing operations.
- Recovering metals from the wastewater treatment plant sludge.
- Reducing sludge volume.
- Following proper operating practices

HAZMIN for Process Solutions

Beginning at the source of the problem, waste minimization methods can be targeted at the process tank itself. Several depots have eliminated cyanide-based cadmium electroplating by using other types of process baths, such as a sulfuric-acid-based solution. This method results in improved worker health and safety as well. In some cases, zinc can be used to replace cadmium. One depot is considering replacing decorative chromium electroplating with nickel followed by buffing, which is reported to give the same quality of appearance.

Another method targeted at the metal-finishing process tank is to lengthen the life of the process solution, which decreases the amount of dumping that occurs. Some tanks (e.g., electroplating baths) are not changed very frequently because the part to be plated has been thoroughly cleaned and does not introduce many contaminants. Contaminants generally consist of metals that dissolve from the parts that were treated, the copper bus bars, upstream process drag-in, the tank liner, catalysts, anodes (lead, tin, antimony), and metallic ions in the water supply. The hexavalent chromium needed for operations in chromic acid tanks is reduced to trivalent chromium, which creates product quality problems. Other process tanks, such as those used for chromate conversion coatings and chromium stripping operations, become contaminated more rapidly.

The contaminants from chromic acid tanks are trivalent chromium and other metals. Removing the metal contaminants and oxidizing trivalent to hexavalent chromium can extend the useful life of the bath. Under the current contract with USATHAMA, PEI will evaluate the effectiveness of an electrodialysis unit to remove metal contaminants and to oxidize the trivalent chromium to hexavalent chromium.

Electrodialysis for Chromic Acid Solutions — Figure 2 presents a diagram of an electrodialysis cell, in which a voltage is applied to drive selected ions through a semipermeable membrane. For rejuvenation of the process bath, positive metal ions are driven away from the anode (which contains a positive charge) and through the membrane (which is permeable to positive ions). The trivalent chromium is oxidized at the anode and does not pass through the membrane.

The solution surrounding the anode is called the anolyte, and the solution surrounding the cathode is called the catholyte. In a standard electrodialysis

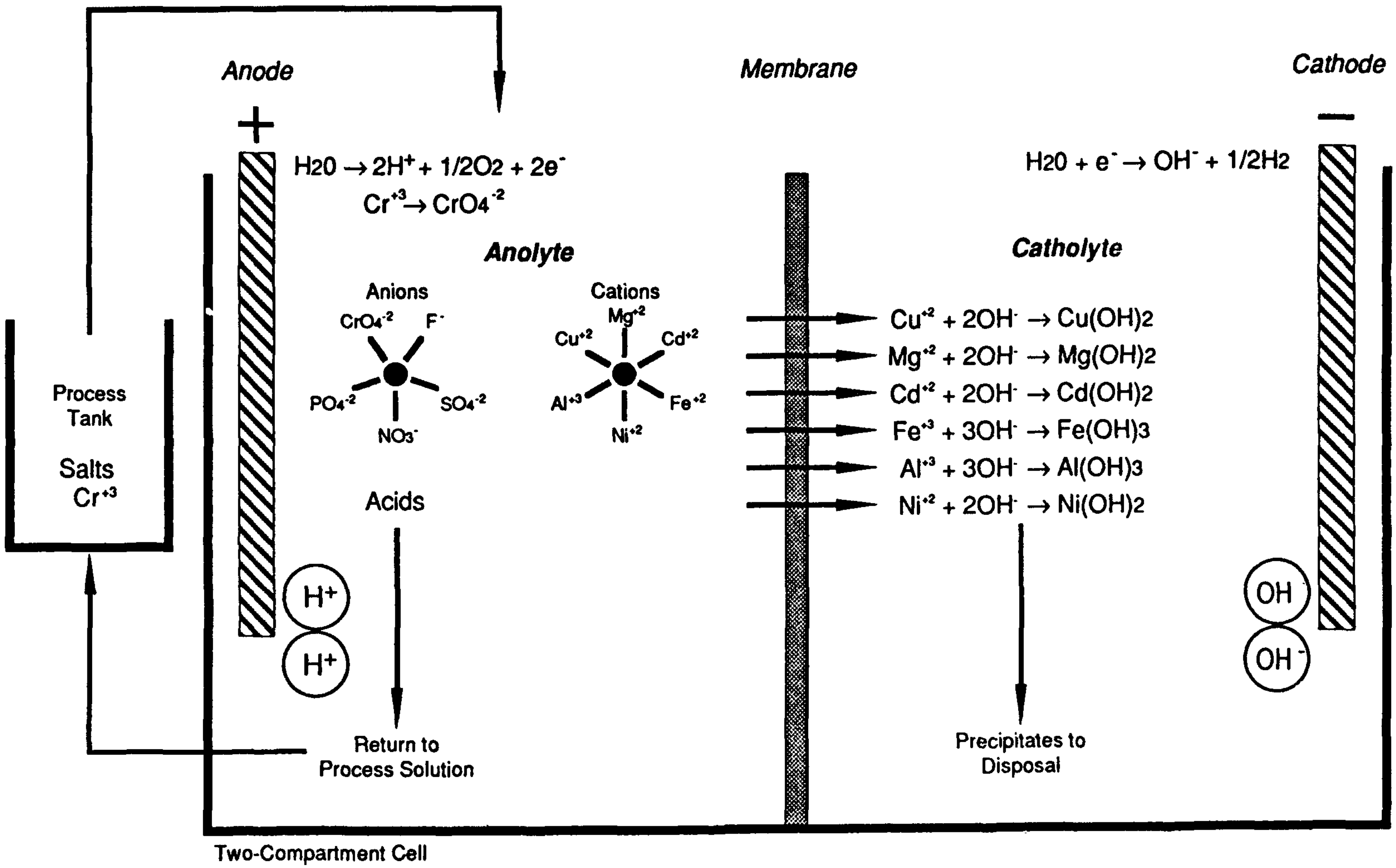

Figure 2. Purification of process tank by electrodialysis.

unit, the catholyte is acidic, and the metal ions are reduced and deposited on the cathode. After a period of time, the metal on the cathode builds up to a point where a high voltage is necessary to maintain a constant amperage and there is a possibility of burning out the cathode. At this time, the cathode must be removed and the metal deposits brushed off.

An electrodialytic cell patented in 1985 (the Ionsep process) uses a caustic rather than an acidic catholyte. As the contaminant metal ions pass through the semipermeable membrane, they react with hydroxide ions and precipitate. The hydroxide ions are continuously formed at the cathode. Hydrogen ions are formed at the anode, and trivalent chromium is oxidized to hexavalent chromium; this produces a solution of chromic acid that can be returned to the chromic acid process bath. The process tank can thus be continuously rejuvenated, which extends the life of the solution.

The USATHAMA/PEI project will be implemented on a process tank currently in use on the production line at Corpus Christi. The electrodialysis unit will be purchased and installed on a chromic acid strip tank that strips chromium from magnesium parts. The tank is emptied every two weeks, and 165 gallons of concentrated chromic acid is disposed of as hazardous waste. This project will reduce the hazardous waste generated from this operation and reduce chromic acid usage. The system can later be expanded at the depot's discretion to include recovery of chromium from the rinse water. A report will be prepared to transfer the information collected to other depots, nearly all of which use chromium process baths to some degree. The extent of waste reduction achieved will be quantified so that other depots can evaluate the potential of this technology to achieve HAZMIN goals.

Aluminum Ion Vapor Deposition — Another method of waste minimization that is targeted at the process itself involves replacement of some electroplating operations with entirely different processes. For example, a possible replacement for some cadmium plating operations is a relatively new technique — aluminum ion vapor deposition (AIVD). In the AIVD process, clean dry parts to be coated are placed in an evacuated chamber with aluminum and an inert gas. A high electrical potential is applied between the part being coated and the aluminum. The aluminum is vaporized and drawn to the part, resulting in a very uniform, adhesive coating. The coating thickness can be controlled by varying the electrical potential and the application time. Aluminum, unlike cadmium, is not a toxic metal, and the AIVD process reportedly produces no sludges, wastewaters, or any type of hazardous waste. Although derivations of the AIVD process have existed for several years, the potential of the AIVD system to reduce hazardous waste generation has only recently been recognized.

USATHAMA and PEI will purchase a full-scale AIVD unit for installation and evaluation at Anniston. Support equipment will also be purchased, including loading racks, chemical cleaning tanks, a blasting cabinet, and a chromate conversion tank. A 6-month demonstration test will be conducted to determine the applicability of this technology for reducing hazardous waste. A variety of parts will be subjected to demonstration testing and then tested for adhesion, coating thickness, and corrosion resistance. In addition, fasteners will undergo torque tension tests to determine the effect of the AIVD process on the fasteners. This project will also entail gaining the acceptance of users to replace cadmium electroplating with aluminum ion vapor deposition.

Reducing Volume and Contamination of Wastewater

Additional waste minimization projects can be aimed at reducing the amount of chromium and water sent to the wastewater treatment plant. The amount of chromium sent to the plant can be reduced by reducing drag-out and by recovering metals from the wastewater. Simple methods of reducing drag-out include using drainage boards between the process tank and rinse-water tank. Allowing the part to drain on this board and returning the drippings to the process tank will reduce drag-out. A spray rinse can also be used before the tank rinse to spray the part and return most of the drag-out to the process tank. The extra water from the spray rinse can be used to replace water lost through evaporation. One problem at some of the depots is that the parts are irregular in shape and contain many holes that trap the liquid process solution.

Countercurrent triple rinses are an effective method of reducing the wastewater sent to the wastewater treatment plant. In some cases, the most concentrated rinse can be returned to the plating tank, perhaps with the aid of a technology to concentrate the solution, e.g., evaporation. Closed-loop recycling, however, causes a buildup of contaminants, so deionized water and technologies for removal of metal ions often must be used. A primary obstacle to implementation of triple rinses at depots is lack of available space for the extra equipment. Simple operational changes such as running the rinse water only when parts are actually being processed rather than continuously can also significantly reduce wastewater flow. Conductivity meters can be installed in rinse water tanks so that the rinse water only runs when necessary, i.e., when a certain level of contamination is detected.

Many metals can be efficiently recovered from the electroplating wastewater and returned to the process tank by methods such as ion exchange, evaporation, reverse osmosis, and electrodialysis. Corpus Christi is pursuing a project on its chromium electroplating line that uses ion exchange and electrodialysis in a closed-loop process that returns chromium to the plating tank in a useful form and recycles all water to the rinse tanks. The closed-loop system is shown in Figure 3. In this system, two ion exchangers remove the cations and anions from the water and the clean water is recycled to the rinse tank. The cation resin is regenerated with sodium hydroxide and the anion resin is regenerated with sulfuric acid. The resulting regenerant solutions can be

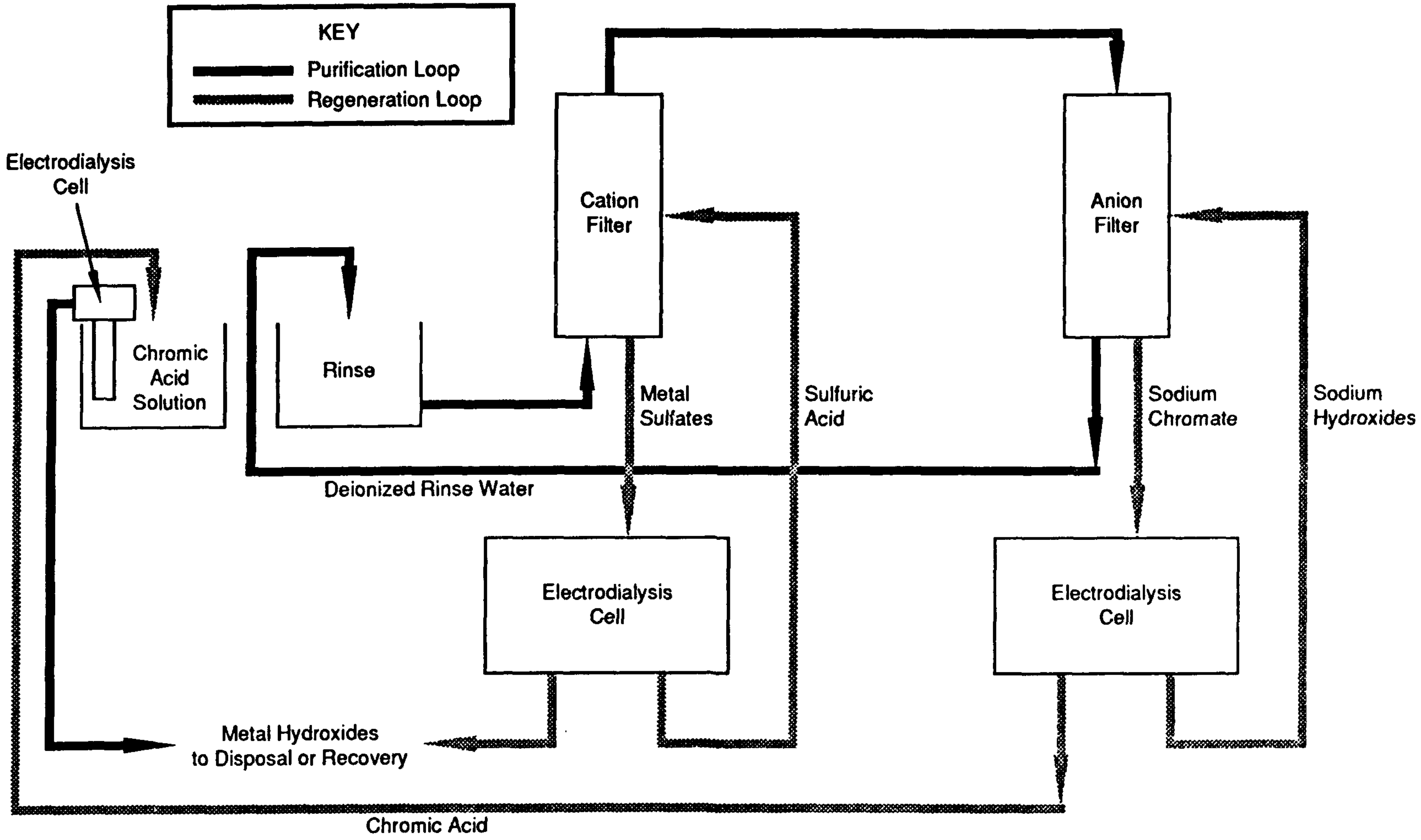

Figure 3. Closed-loop system for recovery of chromium.

processed in separate electrodialysis units. The Ionsep units discussed previously are reportedly capable of separating the salt solutions into sodium hydroxide and sulfuric acid so that these reagents can be reused in the regeneration process. The unit also removes metal contaminants and oxidizes trivalent chromium to hexavalent chromium so that it can be reused in the process tank. The two separate projects to be pursued by Corpus Christi and USATHAMA/PEI will provide information on the versatility of the electrodialysis unit from Ionsep. One project is targeted toward extending the life of a chromic acid stripping bath on a magnesium line; the other project will target extending the life of a chromium electroplating tank and preventing chromium from being sent to the wastewater treatment plant.

Reducing Sludge Volume

Finally, waste minimization efforts can be directed to the treatment of the wastewater once it reaches the wastewater treatment plant. Generally, metals in the wastewater are precipitated with lime, which generates a sludge containing metal hydroxides. Several depots generate large quantities of sludge disposed of as hazardous waste. Methods for minimizing this waste include segregating nonhazardous from hazardous sludge, recharacterization of the waste, redesigning the treatment plant or changing operations, recovering metals from the wastewater treatment plant sludge, and reducing the sludge volume after it is generated.

Some depots send all wastewaters to the same treatment plant, so all the sludge is commingled. In this case, the entire volume of sludge must be disposed of as a hazardous waste. Segregation of nonhazardous and hazardous sludge can significantly reduce the amount of hazardous waste. One depot is beginning to separate a phosphate sludge generated from phosphating operations and its cadmium/cyanide sludge. The phosphate sludge can then be disposed of as nonhazardous. Personnel at the depot estimate this will result in up to a 50 percent reduction in the amount of sludge disposed of as a hazardous waste.

In some cases, the metals concentrations in the sludge may not be large enough to be EP Toxic for any of the hazardous metals present. At one depot, the effluent from the wastewater treatment plant was sent to the sewage treatment plant, and the sludge generated at the sewage treatment plant was then disposed of as a hazardous waste because earlier tests had shown the sludge to be hazardous. Closer investigation by depot personnel revealed that the wastewater treatment plant was not operating correctly during the earlier tests, and was not achieving sufficient metals removal. The depot has reanalyzed the situation and is moving toward recharacterizing the sewage sludge and disposing of it as a nonhazardous waste. Other cases also may call for recharacterization and possible delisting of the sludge if it is not EP Toxic.

Some recent research has been conducted on recovering metals from the sludge; however, the metals concentrations in depot sludges are often very low, and metal recovery may not be cost-effective. Efforts should be directed at preventing the formation of a significant amount of sludge by waste minimization targeted at the process tank or the contaminated wastewater before it enters the treatment plant and mixes with other wastewaters.

Finally, after the sludge has been formed, waste minimization can be directed at reducing the volume of the sludge through dewatering. Some depots have only recently installed dewatering facilities. A filter press achieves the most effective volume reduction but it requires manpower for maintenance. Some depots have also experienced problems with rupturing of the cells.

CONCLUSIONS

Although U.S. Army Depots are beginning to make significant progress toward waste minimization, significant obstacles still remain, including lack of sufficient technical information transfer and available resources. USATHAMA and PEI visited eight Army depots to identify research needs relative to HAZMIN. Comprehensive trip reports were prepared and compiled into a single document that can be used by the depots for increased coordination and communication among depots. Three projects were selected for implementation in addition to two other HAZMIN projects currently being pursued by USATHAMA and PEI.

1) Evaluation of paint-application systems. This project will assess the transfer efficiency of several paint-application systems or spray guns. Higher transfer efficiencies result in less overspray and fewer VOC emissions and airborne paint particulates. With less overspray, dry filters will not be used up as quickly and water-wall paint booths will not generate as much sludge; thus, less hazardous waste must be disposed of.

2) Evaluation of filtration to extend the lives of paint-stripping solutions at Letterkenny. This project will use a filtration system to remove solids from a paint-stripping tank. A lower amount of solids will prevent a continuing chemical reaction between the stripper and the solids, and thus extend the life of the process solution.

3) Evaluation of electrodialysis to extend the life of a chromic acid tank at Corpus Christi. An electrodialysis unit will be installed on a chromic acid tank. The unit will remove metal contaminants and oxidize trivalent to hexavalent chromium; this will rejuvenate the solution, extend its life, increase product quality, and result in less hazardous waste generation. The system can be expanded later to include recovery

of chromium from the rinse water. Corpus Christi is also pursuing a similar project involving the recovery of chromium from electroplating rinse water.

4) Demonstration of aluminum ion vapor deposition as a replacement for cadmium electroplating. A full-scale ion vapor deposition unit will be installed at Anniston to demonstrate its ability to replace cadmium. Adhesion, coating thickness, and corrosion resistance will be monitored.

5) Demonstration of a fluidized-bed parts cleaner. A full-scale fluidized-bed parts cleaner will be installed at Red River to evaluate its ability to reduce hazardous waste from chemical stripping and degreasing operations.

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A 75 L, continuous flow, immobilized cell bioprocess system was developed specifically for volatiles degradation.and was tested at a chemical production site having extensive halocarbon contaminated ground water. The ground water contains a variety of one- and two-carbon chlorinated compounds. EDC is present in far greater concentration than any of the other organics, and was routinely observed at concentrations in excess of 1,800 mg/L.A detailed discussion of the reactor design has bben presented elsewhere (Friday and Portier, 1989) and is summarized as follows: the current system consists of three functionally distinct subsystems The first is a raw effluent conditioning system which removes foreign materials via a 100-μ filter, dilutes recovered ground water to the degree required to achieve biologically acceptable toxicant concentrations, adds nutrients, and adjust/maintains media pH and temperature. Biological conversion occurs in the second subsystem (reactor vessel) which is partitioned into two distinct volumes. In the first, air is sparged into the feed waters to mix and aerate the influent water. Admixed air is then separated from the water before it enters the second reaction stage. In the second section, the water moves in plug flow through a bed packed with porous biocarrier on which the selected chlorinated aliphatic-degrading organisms are immobilized throughout the support. Modular column units have been fabricated which can be mechanically coupled to provide a desired packed bed volume and control the extent of the bioconversion. Design considerations have included gas sparging/gas distribution, maintenance of carrier integrity, gas/liquid separation, and materials of construction. The reactor is instrumented to allow pH, temperature, and dissolved oxygen levels to be continuously monitored and controlled. In addition, a gas scrubbing unit is attached to remove organic vapors from process off-gases prior to release into the environment. A third subsystem provides final clarification of the decontaminated water.

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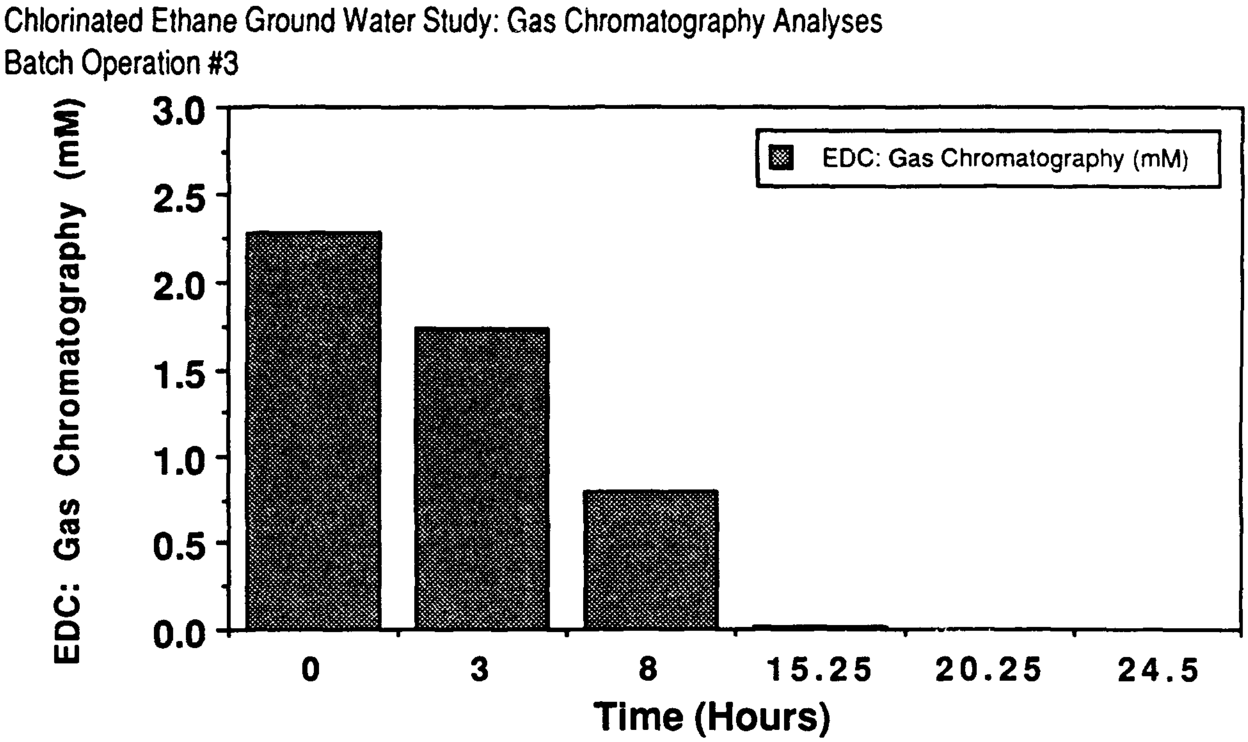

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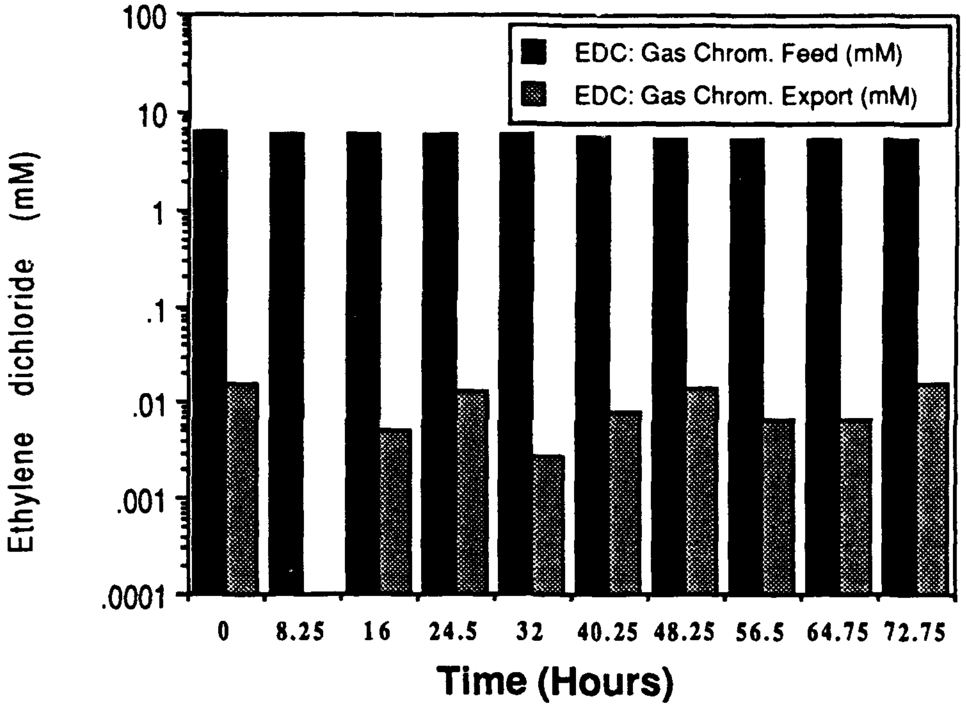

Figure 2. Reactor influent and effluent ethylene dichloride (EDC) concentrations in continuous flow operation.(adapted from Friday and Portier, 1989)

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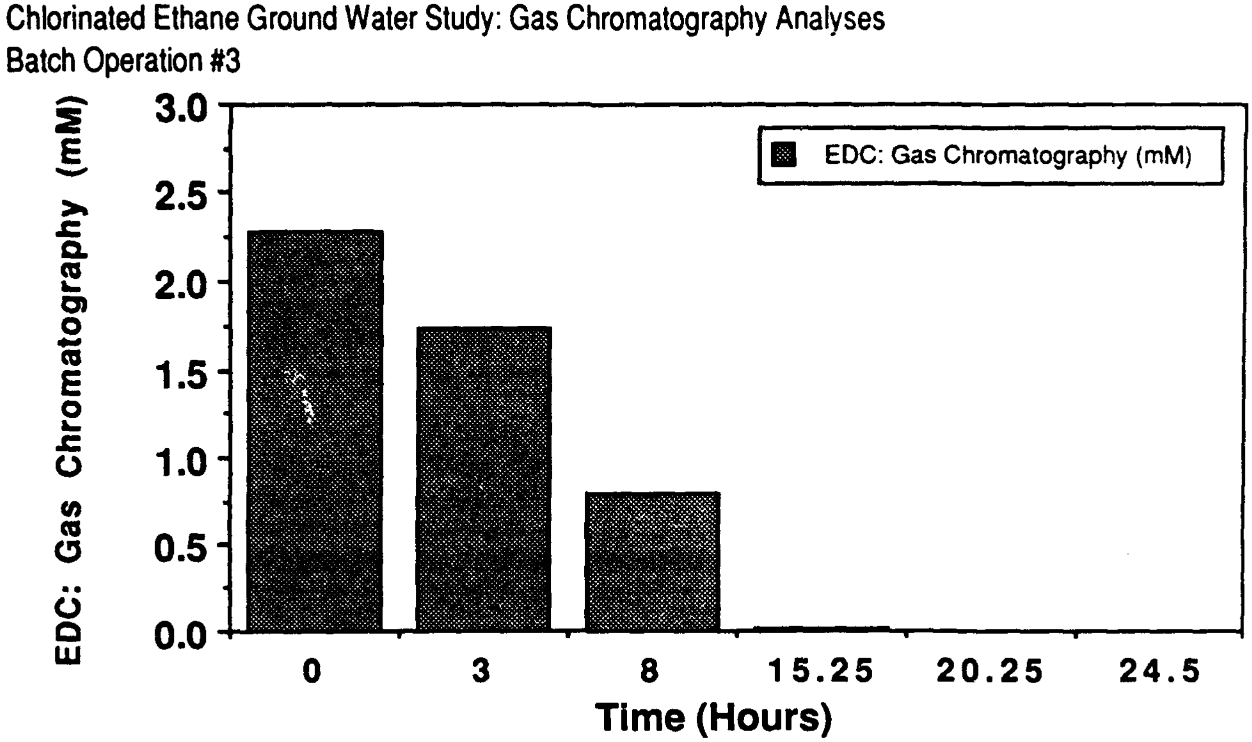
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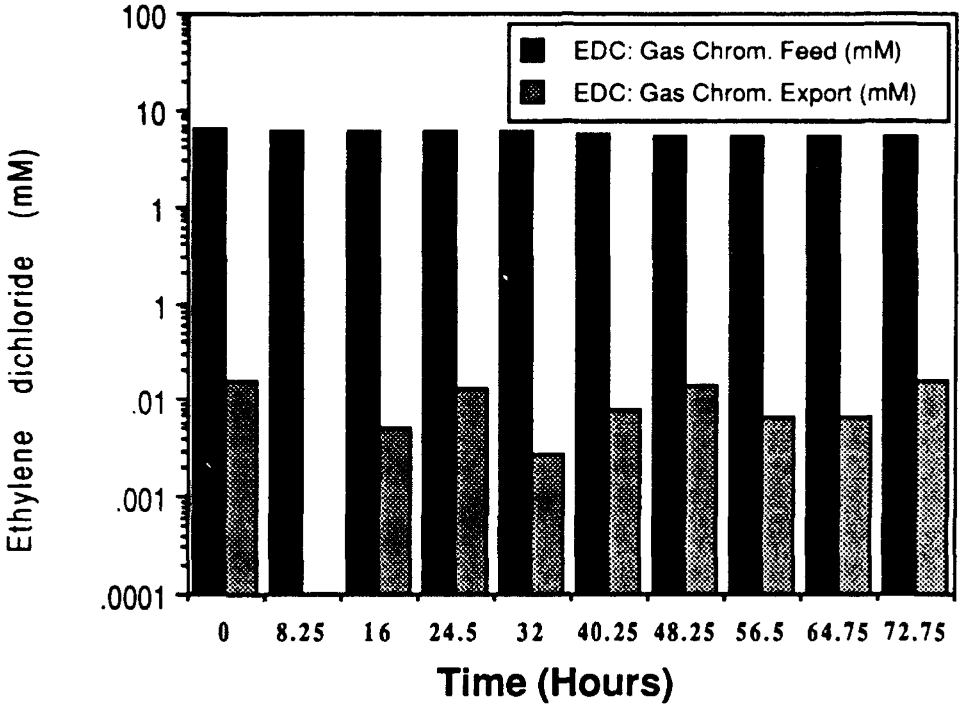

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Removal and Fixation of Lead from a Contaminated Water Using an Integrated Microbial Consortium

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ABSTRACT

The objective of this research was to investigate the lead sequestering potential of a mixed microbial ecosystem emerging in a synthetic pond system containing simple, natural enrichments. This project examined the dynamics of lead transport and stabilization in the ecosystem and the chemical speciation of the lead.

Synthetic ponds were prepared in a controlled environment chamber and enriched with grass silage. Populations of microbial species arising spontaneously in the pond, were developed for metal tolerance and re-inoculated into a lead-infused water column. Natural ecosystem dynamics resulted in a typical 2-phase system: (1) a bacterial bloom, in which the lead was mobilized from the soil bed into the water column, and (2) a cyanobacteria phase, during which the lead became stabilized in the floating biomass at the pond surface. The microbes annealed tightly to the grass silage producing a lead-laden biomass floating on the pond surface. This structure permitted lead recovery by simple pond raking. Eight lead spikes of 100 mg/L, added to the system, were rapidly removed from the water column and held in the surface biomass. This system demonstrates important potential for low-cost metal recovery and water purification; it compares favorably with several conventional methods of water decontamination.

KEYWORDS

Lead; water; bacteria; cyanobacteria; silage; metal tolerance.

INTRODUCTION

The potential of various microbes to concentrate elevated levels of heavy metals has long been observed in the natural environment (Trollope and Evans, 1976; Stokes et al, 1975). Metal tolerant species, apparently generated in polluted environments, may display an increased capacity for metal sorption and thus provide important biological material for both water purification and metal recovery.

The efficiency and cost-effectiveness of both applications is directly dependent on the rate of metal uptake and holding capacity of the microbes. Although the potential use of various microbial species, including some resistant strains, for metal decontamination of wastewater has recently been demonstrated by Lester and Sterrit (1985), increased rate of metal uptake and retention will be important to the development of such systems. The research reported here investigated lead sorption by a mixed microbial system, explored the advantages of using a complete and integrated ecosystem for metal uptake, and examined some of the possible mechanisms for lead transfer through the system with eventual binding of lead in the microbial biomass.

In order to attain the objectives of this research, strategies were applied to (1) stimulate enhanced production of biomass and consequent lead recovery by simple enrichments of the microbial environment, (2) increase the tolerance and uptake capacity for lead by the component microbial species through mutagenesis and adaptation, (3) investigate the metal holding capacity of the enriched microbial ecosystem by applying a series of lead spikes over a 30-day period. Although this approach is not entirely unique, biotechnological research has generally considered single strains as functional units for metal uptake and, thus, have focused on strain development for specific processes. This research defines the entire microbial ecosystem, acting in concert, as the functional unit and attempts to optimize processes and relationships as the role of each becomes apparent.

The microbial ecosystem employed here arose spontaneously after pond enrichment with grass silage and followed a predictable microbial succession as the organic acids present in the silage served as chemotaxins for a variety of microbes. Initially, a bacterial bloom occurred in the water column, followed by a succession to dominance by blue-green algae (cyanobacteria) in 3-4 days. The algae population concentrated at the surface and became firmly attached to the floating silage in a gelatinous mat. This mat was maintained in suspension as a result of buoyancy imparted by entrained gas as generated during biological activity. As bacteria populations decreased in the water column, heavy bacterial associations with the floating algae were observed. This surface biomass, composed of silage, bacteria and cyanobacteria, remained stable as the climax community for more than 30 days. Ecosystem processes and microbial relationships resulted in the mobilization of metal in the soil bed and water column with ultimate deposition in sulfide rich sulfate reducing zones of the surface biomass. Since the processes involved are complex, no attempt has been made to define all the mechanisms of lead transport through the pond or the chemical systems involved in stabilizing the metal in the floating mat. However, the following system factors have been determined to be significant in defining metal uptake efficiency: (1) movement of the metal from the soil through the water column to the surface, (2) holding capacity of the biomass for the lead, (3) chemical speciation of lead, and (4) rate of uptake in a total, functioning ecosystem as compared with the metal removal capacity by the component cyanobacteria.

MATERIALS AND METHODS

Ecosystem Design

Figure 1 illustrates the simulated ponds used in these experiments. Clear plastic tanks (15 cm x 12 cm x 11 cm) were layered with 3000 g of sandy-loam soil. The soil was taken from compost and estuary environments in order to insure inoculation with a wide variety of soil microbes, including anaerobes which might be expected to function well in water-logged soil. Three liters of brackish water were added (medium contained in mg/L: $CaCl_2$, 70, $MgSO_4 \cdot 7H_2O$, 55, NaCl, 350, KCl, 29, K_2HPO_4, 0.5). Initial pH was adjusted to 7.5 and generally rose to 9.5 in 7-10 days. Silaged grass clippings (0.9 g/tank dry wt) were added to the surface of the water column together with 10 ml of log phase cyanobacteria culture of either wild type Anabaena sp (NB-19) or metal-resistant strain (NB-19-Pb). All ecosystems were maintained at 30° C in a controlled environment chamber. Illumination was provided on a day/night cycle by 3 incandescent 60-watt bulbs and 2 fluorescent 34-watt tubes placed 25 cm from the pond surface.

Silage Preparation and Application

Fresh-cut grass clippings were packed in 1-liter jars, excluding air pockets, and allowed to process anaerobically for 20 days at room temperature (McDonald, 1981). Finished silage was used to enrich the water column in order to stimulate the microbial bloom.

Sampling and Analyses

Water column was sampled at a depth of 2 cm, surface biomass was completely harvested by carefully raking it from the pond and the soil samples were selected as random cores at a depth of 2 cm below the soil surface. All biomass and soil samples were acid hydrolyzed (Standard Methods of Water and Wastewater, 1985) and analyzed for metal content with a Varian 700 atomic absorption unit. For specific experiments, designed to indicate bacterial involvement in metal transport, 5 mL of water column were taken at a depth of 1 cm and passed through a Millipore filter (0.45 μm) Filtered and unfiltered water samples were analyzed for lead content.

Development of Metal-Tolerant Strains

Cultures (100-mL) of NB-19 were grown to log phase in Allen/Arnon medium with 30 ppm lead and irradiated with long-wave uv to induce mutagenesis (exposure: 10-mL culture of 10μg/mL NB-19 irradiated for 5 min at a distance of 56 cm). Irradiated strains were cultured in a step-wise exposure (7 ppm/wk) with increasing concentrations of Pb until the desired tolerance was reached. Bacterial metal resistances were developed specifically for this ecosystem by using a mixed population selected from the water column after silage enrichment. Bacteria were cultured to log phase in medium simulating the chemical conditions of the pond water column. Medium was made by washing 20 g/L silage and 500 g tank soil with brackish water and fortifying with 4.8 g/L glucose. Strains were adapted to elevated lead resistances by step-wise culture in lead solution increasing by 100 ppm/wk. No ultraviolet exposure was used with the bacteria, as the desired tolerance level was reached by the adaptation procedures. Since the objective was to develop a functional ecosystem in the presence of lead, no attempt was made to isolate or identify single bacterial strains. Lead uptake capacity by tolerant strains was measured by sampling the culture medium during a 3-week period and the harvested biomass at the end of the experiment. All bacterial and algal cultures were grown in a controlled environmental chamber (4 incandescent 50-watt bulbs at 33 cm, 30° C, with continuous shaking at 150 rpm. Algal cultures were sparged with 3% CO_2 for 3 h/d at a rate of 150 mL/min).

Analyses for Anaerobic Zones

The presence of anaerobic zones was investigated by 2 methods: (1) oxygen and redox micro-probe analyses of the floating biomass, measured at various depths in the microbial mat and (2) the presence of viable anaerobes, including sulfur-reducing species, in the mat.

General anaerobic bacteria were cultured on plates of agar medium simulating the chemical conditions of the water column as described above. Sulfur-reducing bacteria were grown on agar plates of selective medium (Bacto sulfate API produced by Difco Laboratories). Mat samples were prepared for bacterial analyses by vortexing 1 g of the mat in the culture medium and spreading 0.05 mL volumes on the agar surfaces. Agar plates were incubated in anaerobic jars for 3-5 days at 30° C. Since the process of extracting bacteria from the mat was not done under anaerobic conditions, resulting colonies indicated the presence of (1) spore-forming anaerobes, (2) species of strict anaerobes which are able to withstand short exposure to oxygen, or (3) facultative bacteria. Sulfur-reducing species were indicated by black colonies resulting from the precipitation of ferrous sulfide.

Experimental Design

Metal-tolerant microbes, originally selected from the system and developed for lead resistance, were inoculated into the water column together with the silage enrichment and the lead nitrate. The bacteria and cyanobacteria were allowed to progress through their natural successional stages to the stable climax community of a silage-microbe biomass floating at the water surface. Metal concentrations were monitored daily in the water column and the soil bed. The biomass, developing at the surface, was generally not disturbed until the final harvest at the end of the experiment. In specific experiments, designed to monitor the metal flow within the system, a series of 10 identical tanks were set up and the surface microbes were harvested from 1 tank daily during the various successional stages. Metal analyses of the biomass were correlated with those of the water column. These experiments provided data on the migration of the metals during the formation of the silage-microbe mat at the water surface.

All experiments were performed in triplicate and data presented are means of 3 trials with three samples at each data point. In specific figures, showing typical ecosystem dynamics, results are presented as one representative trial.

Lead Application

Lead was added to the water column using atomic absorption standard solutions of lead nitrate (Fisher Co.). The lead usually precipitated with the anions in the water column depositing on the soil bed. No adjustments were made in pH (initially set at 7.5) or ion concentrations in order to prevent this precipitation, since it did not interfere with subsequent transport of metal to the mat.

In the lead spiking experiments, designed to determine the holding capacity of the microbial biomass, 300 mg/tank (rate of 100 mg/L) were added during the 30-day test period.

RESULTS AND DISCUSSION

Strain Development for Metal Tolerance

Irradiation and adaptation procedures, described above, produced elevated lead tolerances in both cyanobacteria and bacteria (Table 1). The metal-tolerant strains, grown in lead-infused medium, and the wild types, cultured without lead, showed identical patterns of succession in the simulated ponds. No bacterial growth or algal biomass production occurred when unadapted bacteria (wild types) were inoculated with the lead-infused water.

Lead Speciation and Transport

Initial deposition of lead as a solid into the soil was not surprising in view of the high levels of chloride in the water column (Table 2). Figure 2 gives a predominance area diagram based on the composition of the water column, using solubility products compiled from Sillen and Martell (1964, 1971). Based on the observed range of pH conditions during these studies, the predominant solid phase was concluded to be the basic lead chloride, $Pb_2Cl(OH)_3$. The computations in Table 2, based on known chloride hydroxide and sulfate equilibria indicated that equilibrium concentrations of lead in the systems should have been consistently less that approximately 2 mg/L. While this discrepancy is difficult to rationalize, there were strong indications that both transport of lead from the soil and mobilization of lead in the water column were dependent on the bacterial component of the system. The most rapid period of lead uptake by the surface mat corresponded to >6 log decrease in the bacterial population in the water column. In addition, substantial water column lead levels were associated with materials retained by a 0.45 µm filter, which were probably bacterial cells. It can be postulated that the bacteria functioned in 2 ways to moderate lead behavior in these systems. First they take the lead up from solution by an undefined sorption mechanism and secondly, they excrete an extracellular chelating agent enabling the lead to remain in solution well in excess of predicted solubility limits. Such a cheating agent might well be elaborated by a metal tolerant mutant as a chemical functioning to detoxify the lead by complexation. The subsequent role played by this postulated sorption/chelation phenomenon of in the transport to and deposition of lead in the mat may simply be an artifact of the system by which the bacteria protect themselves from lead toxicity. It is, however, a most fortuitous phenomenon.

Ecological Succession and Pattern of Lead Transport

Figure 3 shows the results produced from a series of 10 identical tanks inoculated with resistant microbes and 300 mg/tank of lead. The floating biomass from one tank was harvested daily and analyzed for lead content. The quantities of lead in the biomass, correlated with the lead remaining in the water column, suggested a pattern of transport from the water to the surface mat.

The first 4 days of culture could be characterized as the bacterial phase. During this period a bacterial bloom of 10^{+7} to 10^{+9} cells/mL occurred in the water column and a heavy, brown bacterial film built up on the pond surface around the silage. Generally during this period (days 1-4), the lead lost from the water column was located in the soil bed, with little uptake occurring at the surface. As the algal phase initiated, with green filaments attaching to the floating silage, lead began to accumulate in the surface biomass, indicating the predominant role of algae in sequestering lead. However, the involvement of bacteria in the process appeared to be substantial. Any interference with the bacterial phase (i.e. omitting the inoculation of metal-tolerant bacteria) prevented the establishment of the surface mat and resulted in almost total deposition of the lead in the soil. In addition, analysis of filtered and non-filtered samples of the water column showed that approximately 20-40% of the water column lead was attached to particles >0.45 µm in diameter. Presumably, motile strains of lead-laden bacteria moved from the water column to establish stable communities with the silage/algae at the surface. It is also notable that the rapid accumulation of lead in the mat corresponded to a rapid decrease in the water column bacterial levels, further reinforcing a linkage between bacterial behavior and lead transport in this system.

In Figure 1 a theoretical diagram of the floating biomass is presented. It is believed that the heterogeneous array of micro-environments in the silage-microbe mat provided conditions appropriate for lead precipitation (i.e. anaerobic zones containing sulfate-reducing bacteria yielding sulfide and leading to the formation of PbS). That portion of the lead deposited as a lead sulfide in the extra-cellular regions is effectively rendered non-toxic. Thus, the total ecosystem structure becomes the protective mechanism for the microbes. This method of detoxification likely accounts for the fact that the accumulated levels of lead in the biomass during the spiking experiment (Figure 4) actually surpassed the metal-tolerance limits of the microbes indicated in Table 1.

Microbial sulfate reduction with subsequent metal-sulfide precipitation has been identified in the southeastern soils (Bachenheimer and Bennett, 1961) and has recently been linked to plasmid activity in Mycobacterium scrofulaceum, isolated from brackish water (Erardi et al., 1987). However, reducing conditions occurring at the pond surface is a rather unique aspect of the silage/microbe system described in this paper, as such environments generally occur primarily in the soil-water interface at pond bottom. The phenomenon of metal precipitation at the top of the water column has important implications for metal recovery. Since the system maintains its own buoyancy by trapped gases, the metal-laden biomass can be harvested without energy-intensive mechanical flotation or centrifugation. It can simply be raked from the pond surface.

Some evidence has been developed regarding the chemical environment of the mat which is strongly supportive of the proposition that sulfide is a major controlling factor in the behavior of lead in this system. Microprobe analyses of the mat indicated that there was a significant difference between DO levels and oxidation-reduction potentials between the top and bottom of the silage/microbe mat (mat top: DO = 3.4 mg/L, E_c = -40 mv; mat bottom: DO = 0, E_c = -200 mv). Recognizing that the actual oxidation-reduction potential values will usually be substantially more negative than those measured and that there will likely be micro environments within the mat characterized by more reducing conditions than other areas, it is probable that significant regions at the bottom of the mat will be able to sustain sulfate reduction. In addition, samples of mature mat were acidified and examined both by smell and by use of lead acetate paper. The unmistakable odor of hydrogen sulfide and the resulting sulfide-positive response with the lead acetate paper indicates that sulfide was generated in the mat by sulfate reduction and is probably playing a major role in immobilization and accumulation of lead in the mat.

Holding Capacity of the Silage-Microbe Mat

Figure 4 shows the results of a spiking experiment maintained for 30 days. After the stable climax ecosystem was established (day 6), lead uptake was twice as rapid with additional spikes. At the end of the experiment lead was not removed as effectively from the water column, although the biomass appeared to have been healthy and functional. Lead remaining in the water column on day 30 may be a result of the sloughing off of lead-laden microbes from the undersurface of the mat. The peak at day 10 does not represent a spike, but rather dropping of lead into the water column from the mat, followed by rapid resorption.

The holding capacity of this system surpassed that of NB-19-Pb in unialgal culture. In addition, the stable concentration of bacteria in the water column throughout the experiment suggested the ability of the microbes to be self-sustaining in an ecosystem which was continually stressed by lead infusions.

The phenomenon of metal precipitation at the top of the water column has important implications for metal recovery and represents an additional advantage of the mixed microbial system over single-microbe methods. Since the silage/microbe ecosystem maintains its own buoyancy by trapped gases, the metal-laden biomass can be harvested from the top without energy-intensive mechanical flotation or centrifugation. It can simply be raked from the pond surface.

Comparison of a Mixed Microbial Ecosystem with Unialgal Metal-Uptake Systems

Table 3 shows that the mixed microbial ecosystem was substantially more efficient in removing lead from contaminated water than either NB-19 or NB-19-Pb cultured alone. However, this efficiency seemed to be related to the rapid rate of biomass production, rather than the concentration capacity of the microbes. While lead uptake per mg biomass was lowest in the ecosystem method, the rate of water column purification was 3 times higher. Although the single cultures of NB-19 and NB-19-Pb were grown under ideal conditions, the rate of biomass production and lead uptake by these cultures was significantly lower than the ecosystem method.

The mechanisms of lead sorption are particularly obscure in a complex ecosystem and may be quite different from those involved in single microbe cultures. The simple factor of the buoyancy of the grass silage was significant in that the microbes were stabilized at the surface, rather than at the pond bottom or in the water column. In the surface mat the microbes established a level of stratified organization, which was effectively stabilized in a matrix of bacterial slime. This bacterial-algal association (Figure 1) may have provided a micro-environment favorable to the mobilization and subsequent depositing of lead.

CONCLUSIONS

The mixed microbial ecosystem, enriched with silaged grass and inoculated with metal-tolerant strains, shows good potential for three important applications: water purification, pond soil bed decontamination and low-cost metal recovery. In this system a number of problems generally associated with metal removal from water and soil were solved in rather simple ways.

From a practical standpoint, this process offers substantial advantages over both conventional methods such as lime precipitation and less common techniques such as ion exchange. In contrast to these methods, the microbial system can be designed to display high selectivity for one or more specific metals and has been demonstrated to function efficiently over a wide range of metal concentrations. In addition, the selectivity of this system offers the potential for recovery of metals in relatively pure form from complex mixtures by use of such options as sequential treatment of a complex mixture by a series of metal-specific ecosystems. Harvesting of metal-laden surface mats would be significantly easier than settling and subsequent dewatering of sludges.

Operationally, the microbial systems would be very much less demanding in terms of complex engineered systems and consumption of chemicals for precipitation or regeneration of resins and thus less costly with respect to both capital and operating costs. While there are inadequate data available at present to perform a detailed economic analysis of these microbial systems, there is strong evidence that they will be fully competitive with physical and chemical methods of metal removal and recovery.

It is projected that in biotechnical applications, the most economical methods may be those which employ the normal ecosystems or most closely imitate the natural processes. It is important to consider that the system described here is driven by microbial processes which evolved not as single cell cultures but rather as a consortium of microbial species functioning as an elaborate and elegantly cooperative unit.

ACKNOWLEDGEMENT

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Table 1. Tolerance Levels of Metal-Adapted Strains.

Microbes	Pb Tolerance (ppm) Initial	Pb Tolerance (ppm) Final
Anabaena sp.		
NB-19	30	NA
NB-19-Pb[a]	30	400
Bacteria, mixed[b]	100	900

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[a] NB-19-Pb is the metal-tolerant Anabaena strain inoculated into tanks involving elevated concentration of Pb.

[b] Mixed bacteria were selected from the water column 2 cm below the floating mat. They were adapted to metal tolerance as a heterogenous population and used as inocula for all mat experiments involving Pb concentrations above 100 ppm.

Table 2. Composition of Solution Based on Inorganic Equilibria.

Initial Composition	mM
Ca^{+2}	0.63
Mg^{+2}	0.22
Na^{+1}	5.98
K^{+1}	0.39
Cl^-	7.63
SO_4^{-2}	0.22
HPO_4	0.003

Controlling Solid = $Pb_2Cl(OH)_3$ (Figure 2)

$pK_{so} = 33.6$

Soluble Species	Log B	Concentration, M pH = 7	Concentration, M pH = 10
Pb^{+2}	---	5.6×10^{-6}	*
$PbCl^+$	1.32	1.7×10^{-8}	*
$PbCl_2$ (aq)	1.69	2.1×10^{-10}	*
$PbCl_3^-$	1.88	*	*
$PbOH^+$	6.46	1.6×10^{-10}	5.1×10^{-8}
$Pb(OH)_2$ (aq)	10.45	1.6×10^{-9}	5.0×10^{-8}
$Pb(OH)_3^-$	13.79	*	1.1×10^{-8}
$PbSO_4$ (aq)	2.77	8.3×10^{-7}	*
$Pb(SO_4)_2^-$	3.62	1.5×10^{-9}	*
Total Soluble Pb	---	$8.1\ 10^{-6}$	$1.1\ 10^{-7}$

* Concentrations $<10^{-10}$ M

B values compiled from Sillen and Martell (1964, 1971).

Table 3. Comparison of a Mixed Microbial Ecosystem with Unialgal Metal-Uptake System.

Microbial system	Final biomass	Initial Pb, ppm mg/l	Pb uptake mg/l/d[a]	Concentration capacity mg Pb/mg biomass
NB-19	90 ±1	30	0.92 ±0.05	0.27
NB-19-Pb	80 ±8	300	8.18 ±0.05	2.25
Mixed[b]	3,340 ±437	800	23.00 ±6.00	0.15

(a) Number of culture day used for the uptake/day calculation was the total culture time up to the first sign of biomass deterioration. (b) Mixed microbial biomass floating on pond surface (Figure 1).

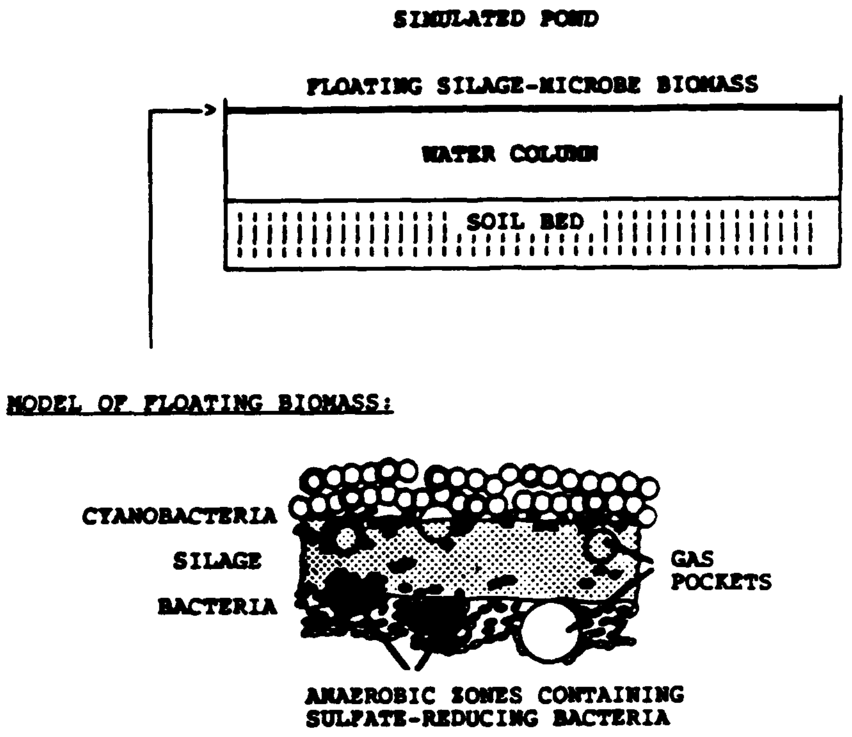

Figure 1. Model of the Silage-Microbe Ecosystem.

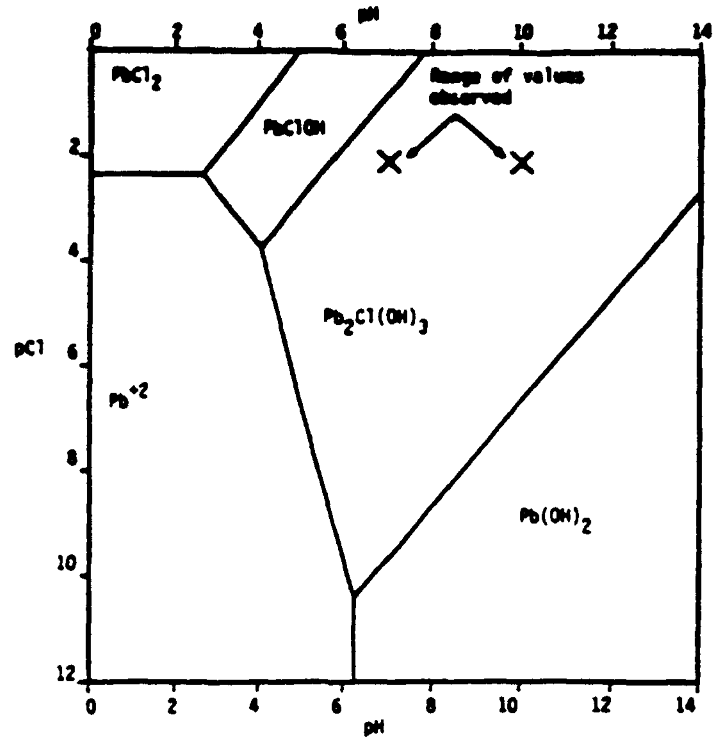

Figure 2. A Predominance Area Diagram of Lead Species in the Water Column.

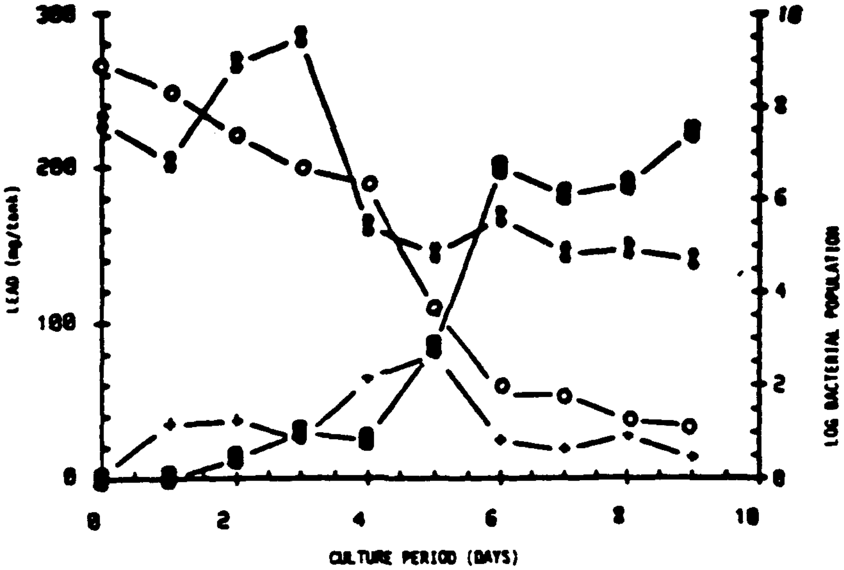

Figure 3. Lead Flow Through the Soil, Water Column and Surface Biomass During Culture. A series of 10 tanks were harvested daily and analyzed for lead concentration, together with the water column and soil bed. Lead concentrations: * - in water column, 0 - in surface mat of microbes, + - in soil, # - bacterial population in water column. Lead nitrate was added to the water column (3-liter) at a rate of 100 mg/l.

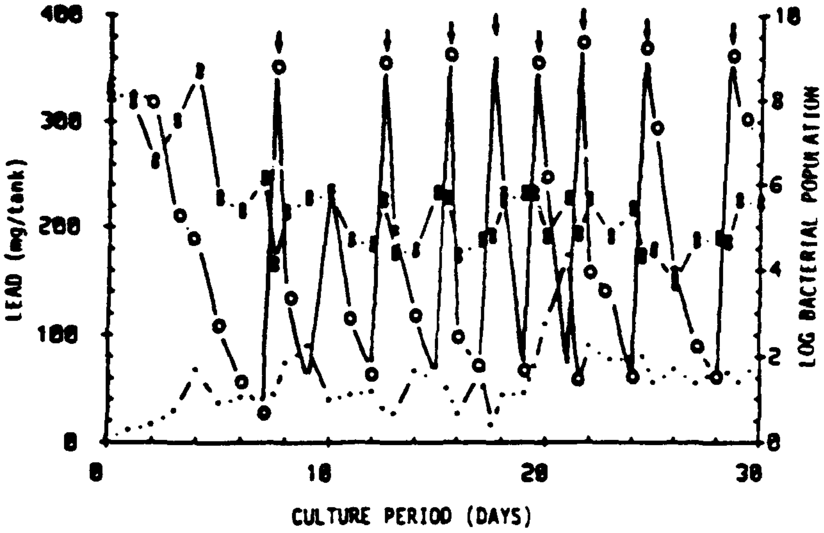

Figure 4. Holding Capacity of the Silage-Microbe Ecosystem with Continuous Spiking of Lead. Lead nitrate (300 mg/tank) was added initially to 3-liter tank water column. After maturation of the microbial surface mat, lead spikes were added with a pipet solution under the algal phase mat (days 7-28). Lead was monitored in the soil and water column, leaving the mat undistrubed until the end of the experiment. Lead concentrations: * - in water column, . - in soil: # - log bacteral population in water column, arrow ↓ lead spiked.

MICROBIAL CULTURING FOR EXPLOSIVES DEGRADATION

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Los Alamos National Laboratory

Remediation of explosives contaminated soil and disposal of explosives are two important applications in which biological degradation of explosives may provide a safe and cost effective approach. Initial studies at Los Alamos have obtained microbial cultures that are promising. These cultures were obtained from a site at Los Alamos National Laboratory that has been contaminated for approximately 30 years with a mixture of 2,4,6-trinitrotoluene and other conventional explosives. Experiments with these cultures have shown them to be capable of either converting the ring carbons of 2,4,6-trinitrotoluene to carbon dioxide or under using 2,4,6-trinitrotoluene as a sole source of carbon for growth; both of these studies are done in liquid culture with completely defined media, including pure crystalline TNT or (U-ring^{14}C) 2,4,6-toluene. These cultures are being further adapted to growth with TNT as the sole source of carbon. The cultures are mixtures of several soil microbes.

Environmental Reclamation

GOAL: NEW SOLUTIONS TO OLD PROBLEMS

COST EFFECTIVE BIODEGRATION of EXPLOSIVES and ORGANICS

Problem: Contaminated Soil, Process Waste, Aging Weapons, TNT, RDX, NHX, Nitroglycerin, Nitrocellulose, Toluene

Solution: Complete Microbial Degradation

SELECTIVE CHELATORS for TOXIC and RADIOACTIVE METALS

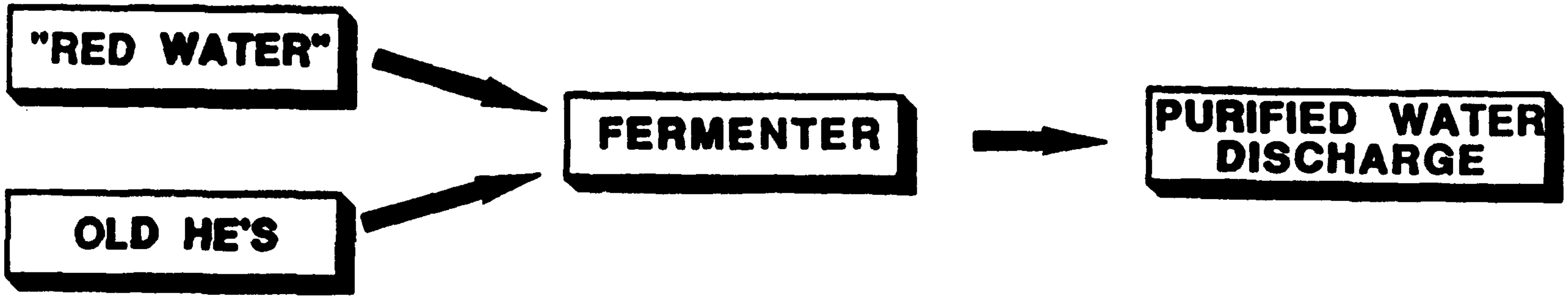
Problem: Contaminated Soil, Ground Water, Manufacturing Equipment, Process Waste

Solution: Metal Specific Biological and Synthetic Chelators

INC DIVISION

EXAMPLE APPLICATIONS

HIGH EXPLOSIVE CONTROL-TECHNOLOGY



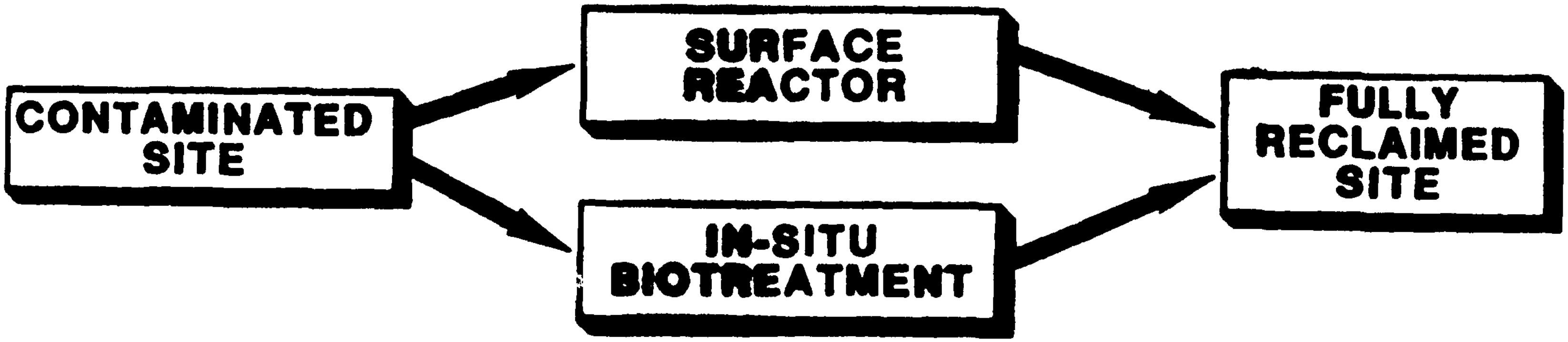
"RED WATER"

OLD HE'S

FERMENTER

PURIFIED WATER DISCHARGE

HIGH EXPLOSIVE REMEDIATION



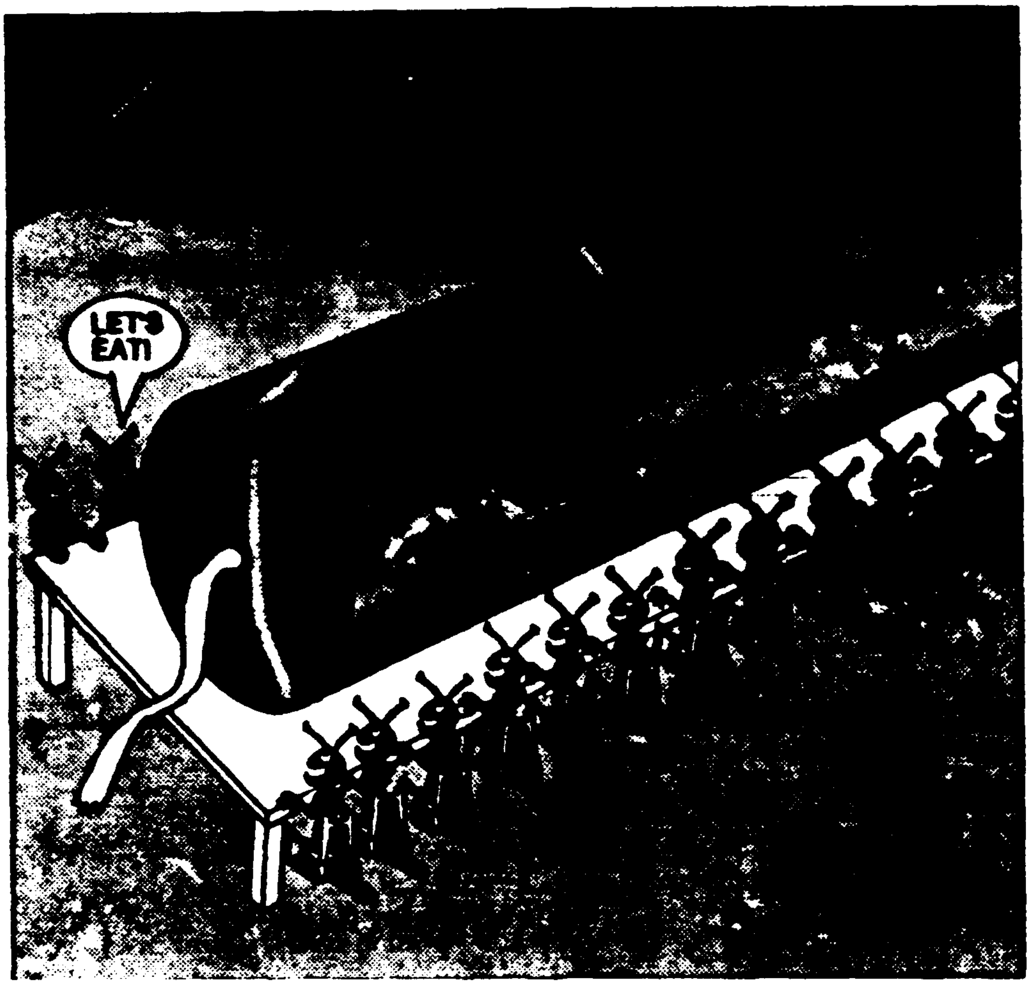
CONTAMINATED SITE

SURFACE REACTOR

IN-SITU BIOTREATMENT

FULLY RECLAIMED SITE

INC DIVISION, Los Alamos



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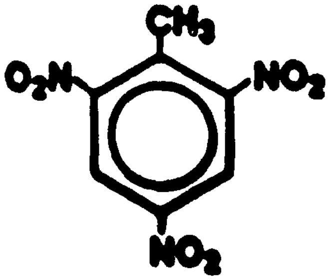
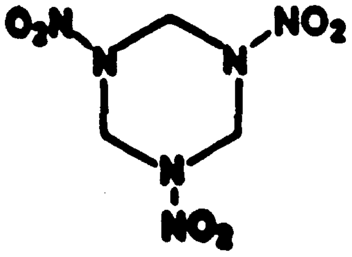


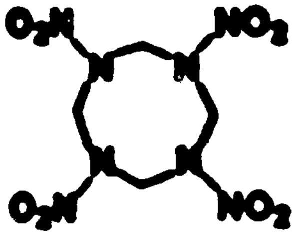
2,4,6-Trinitrotoluene

TNT



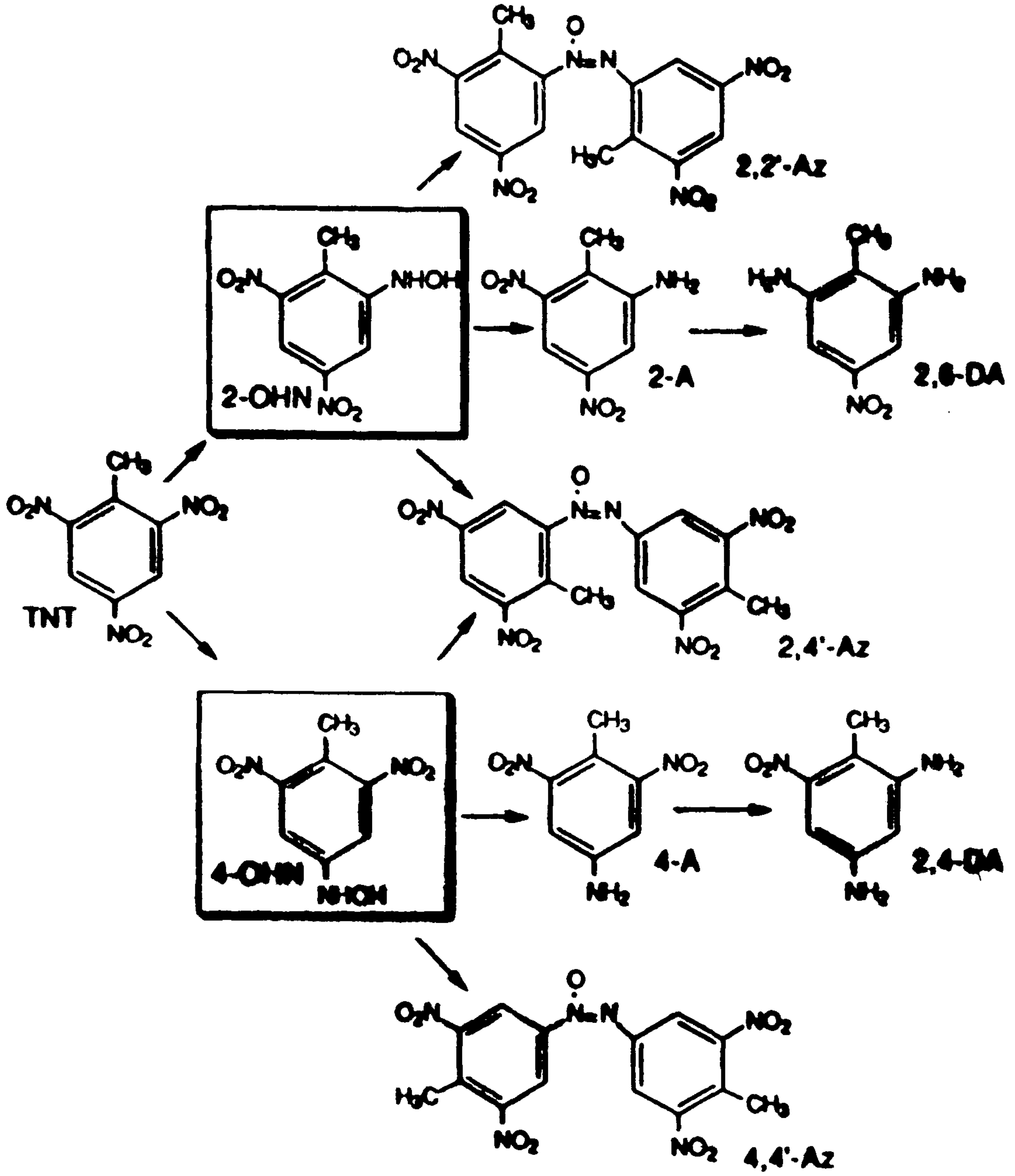
Hexahydro-1,3,5-Trinitro-1,3,5-Triazine

RDX



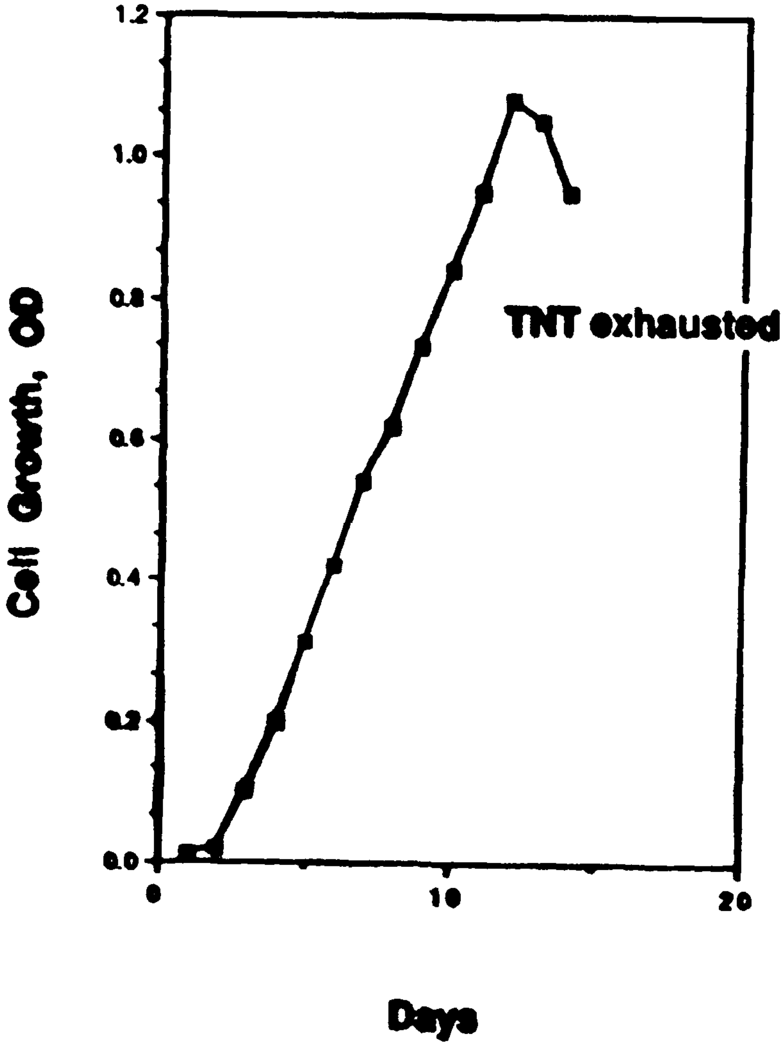
Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetraazocine

HMX



Reductive biotransformation scheme for TNT based on products isolated from compost (Kaplan and Kaplan, 1982). The hydroxylamino intermediates (boxed) were not isolated. Examples of the nomenclature used above are: 4-amino-2,6-dinitrotoluene, 4-A; 2,4-diamino-6nitrotoluene, 2,4-DA; 2,2',6,6'tetranitro-4,4'-azoxytoluene, 4,4;-Az; and 4-hydroxylamino-2,6-dinitrotoluene, 4-OHN.

Microbial Degradation of TNT



Growth with TNT as the Sole Source of Carbon

INC DIVISION, LosAlamos

HAZARDOUS WASTE MINIMIZATION PROGRAM
PAINT SLUDGE WEIGHT REDUCTION

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ABSTRACT

Tooele Army Depot (TEAD), UT produces approximately 28,000 gallons of paint sludge each year. This waste is generated from the activities of maintenance and refurbishing of military vehicles and equipment. Disposal of this waste through contractors costs TEAD over $1,000,000 per year. The Ammunition Equipment Directorate, TEAD, conducted a feasibility study for minimizing the amount of paint sludge to be disposed of through contractors, thus reducing disposal costs. A series of tests was conducted in 1988 to determine if paint sludge could be reduced in volume and weight by incineration. The results of the feasibility tests showed that (1) a military standard deactivation furnace reduced the paint sludge weight by 90 percent, (2) the residual dry ash, which contains heavy metals, can be disposed of in a hazardous waste landfill, (3) the furnace was capable of incinerating 11 pounds per minute of paint sludge, equivalent to approximately one drum per hour, and (4) in a preliminary economic analysis, it was estimated that annual savings of about $1,000,000 could be achieved. A pilot scale process has been designed and fabricated. The pilot process is expected to increase the throughput and decrease the labor required to process paint sludge.

ACKNOWLEDGMENT

This study was sponsored by Commander, U. S. Army Depot System Command, ATTN: AMSDS-T, Chambersburg, PA 17201-4170, coordinated through the Environment Management Office at TEAD.

INTRODUCTION

Tooele Army Depot (TEAD) produces approximately 28,000 gallons of paint sludges of various constituents each year. These wastes are being generated from depot activities such as maintenance, modification, and refurbishing of military vehicles and equipment. Disposal of these wastes through commercial contractors costs the depot over one million dollars per year (see Appendix). U.S. Army Depot System Command (DESCOM) through the Environment Management Office at TEAD, has tasked and funded the Ammunition Equipment Directorate to conduct a feasibility study for minimizing the amount of paint sludges that are to be disposed of through contractors, thus reducing the costs of disposal.

This report discusses the test procedures employed, the process equipment used, and the results of the feasibility study. Also, discussed briefly is the plan for a pilot study, equipment to be used, operational procedures, and the anticipated results. Finally, a preliminary economic analysis and a recommendation for further action are presented.

PAINT SLUDGE

The paint sludges considered are polyurethane paints and contain mixtures of polyurethane, epoxy-polyamides, paint thinner, chromium, lead, organic and inorganic pigments, titanium oxide, zinc oxides, various organic solvents, additives, water, dirt, and other impurities. Chemical and physical characteristics including the rheology, sedimentation, and hardening of paint sludge mixtures require specially designed pumps, macerator, and feed injector for processing in an incinerator. Enamel paints are used in small amounts and are not considered in this study.

FEASIBILITY STUDY

A simplified feasibility study was conducted to determine if the paint sludges can be reduced in volume and weight by incineration in a standard military furnace at AED's test facility.

Description of Test Equipment

Furnace

The APE 1236 Deactivation Furnace was considered to be appropriate for incineration tests. The APE 1236 Deactivation Furnace is a standard military kiln furnace, unlined, equipped with internal spiral flights, to accomplish the destruction of a large variety of obsolete and unservicable explosive munitions in ammunition demilitarization activities. The furnace consists of feed and discharge conveyers, a four section cast-steel retort, a fuel-oil burner, a combustion air blower, an exhaust stack, and control panels as seen in figure 1. Addition of an air pollution control system (Kit APE 1236-E010) for control of particulate and visible emissions permits the furnace to be operated within appropriate air pollution guidelines.

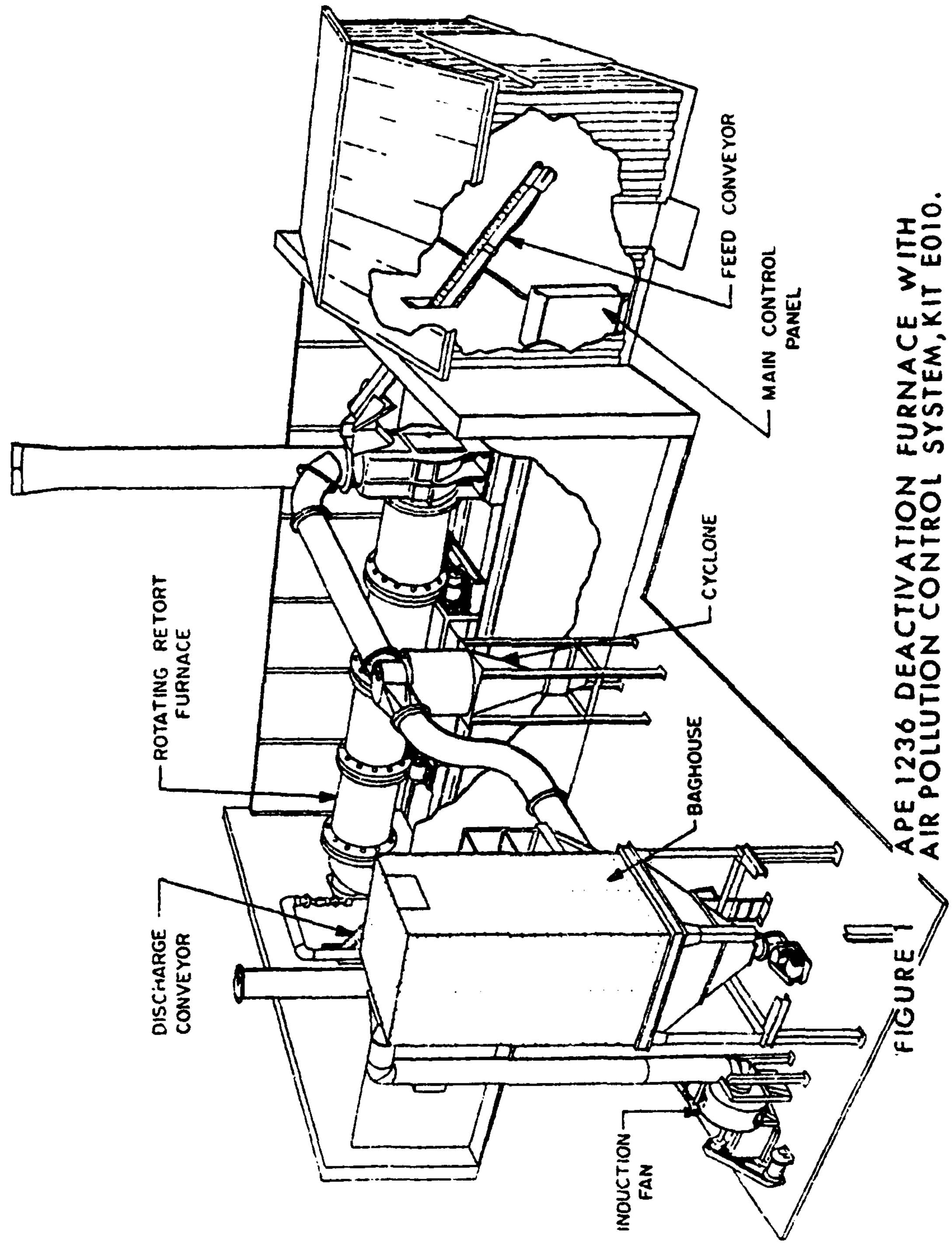


FIGURE 1 APE 1236 DEACTIVATION FURNACE WITH AIR POLLUTION CONTROL SYSTEM, KIT E010.

Figure 1.

The furnace burner uses number 2 fuel oil, at rates of 6 GPH at low-fire to 23 GPH at high-fire. The temperature in the furnace is maintained by the Temperature Controller and recorded on the Chart Recorder, both located in the Main Control Panel. Static pressure (draft) in normal operation, measured at the base of the vertical exhaust stack, is maintained from -0.09 to -0.50 inches of water. The deactivation furnace is operated within steel and concrete barricades which provide protection for the furnace operating personnel. The overall dimensions of the furnace system are 29'5" in length, 4'5" in width, 8'5" in height (less stack), and 49,040 pounds in weight.

Air Pollution Control System

The Air Pollution Control System (APCS) consists of an afterburner, a cyclone, a baghouse, an induction fan, a high temperature quencher, a low temperature gas cooler, and a wet scrubber system.

An afterburner, which is an integral part of the APE 1236 Deactivation Furnace system, was used throughout the feasibility study to enhance combustion efficiency. The afterburner has an operation temperature range of 1200oF to 2000oF, to provide a minimum residence time of 2.5 seconds. The overall dimensions of the afterburner are 30' in length, 5' in diameter, with a 3" refractory lined interior and steel construction.

The high temperature quencher is a large cylindrical cyclone constructed from mild steel and equipped with 8 water nozzles capable of spraying 1-5 GPM of water to facilitate the cooling of the hot gas from the afterburner. It is capable of lowering the gas temperature from 1800oF to 1000oF in a normal operation. The overall dimension of the unit is 22' in height and 4' in diameter.

The low temperature gas cooler is constructed from mild steel. This gas cooler is capable of cooling the gases from 1000oF to 250oF and is capable of cooling approximately 4700 SCFM volume of hot gases. This unit is a forced air cooling type.

The dry cyclone is capable of processing approximately 4700 SCFM volume of cooled gases, removing the combustion particulate greater than 30 microns in size, lessening the loading burden of the wet scrubber system. The overall dimensions of the unit are 34" in diameter, 17'1" in height (with frame) and 1,500 pounds in weight.

The baghouse contains 100 filter bags fitted over wire retainers and clamped to collars attached to the tube sheet. The overall dimensions of the baghouse are 72" in length, 72" in width, 20'6" in height and 3,950 pounds in weight.

Wet Scrubber System

The wet scrubber system consists of a venturi scrubber, a packed bed scrubber, classifiers, a draft fan/stack, and pumps and tanks.

Venturi scrubber is constructed from fiberglass reinforced resin. The venturi scrubber will remove the rest of the particulates, less than 30 microns in diameter, from the gas stream. The concurrent process liquid will have a flow rate of 80 GPM. The pressure drop in the Venturi is at 25 to 45 inches of water.

Packed bed scrubber is constructed from fiberglass reinforced resin. The packed bed scrubber will absorb and remove all toxic and corrosive gases from the gas stream. It is designed to achieve the removal efficiency of 99.9 percent by using an appropriate process liquid for the absorption medium. The countercurrent process liquid has a flow rate of 120 GPM, and a pressure drop of 15-25 inches of water.

The particulates laden process liquid from the venturi and packed bed scrubbers is partitioned through the banks of hydrocyclones classifier where the suspended particulates are removed from the liquid. The particulate free liquid is recycled back to the scrubbers.

The draft fan and the exhaust stack are constructed from corrosion resistant materials. The draft fan has an 80 HP motor and is capable of delivering 60 inches of water at negative pressure. The exhaust stack is 30 feet tall, equipped with gas monitoring ports.

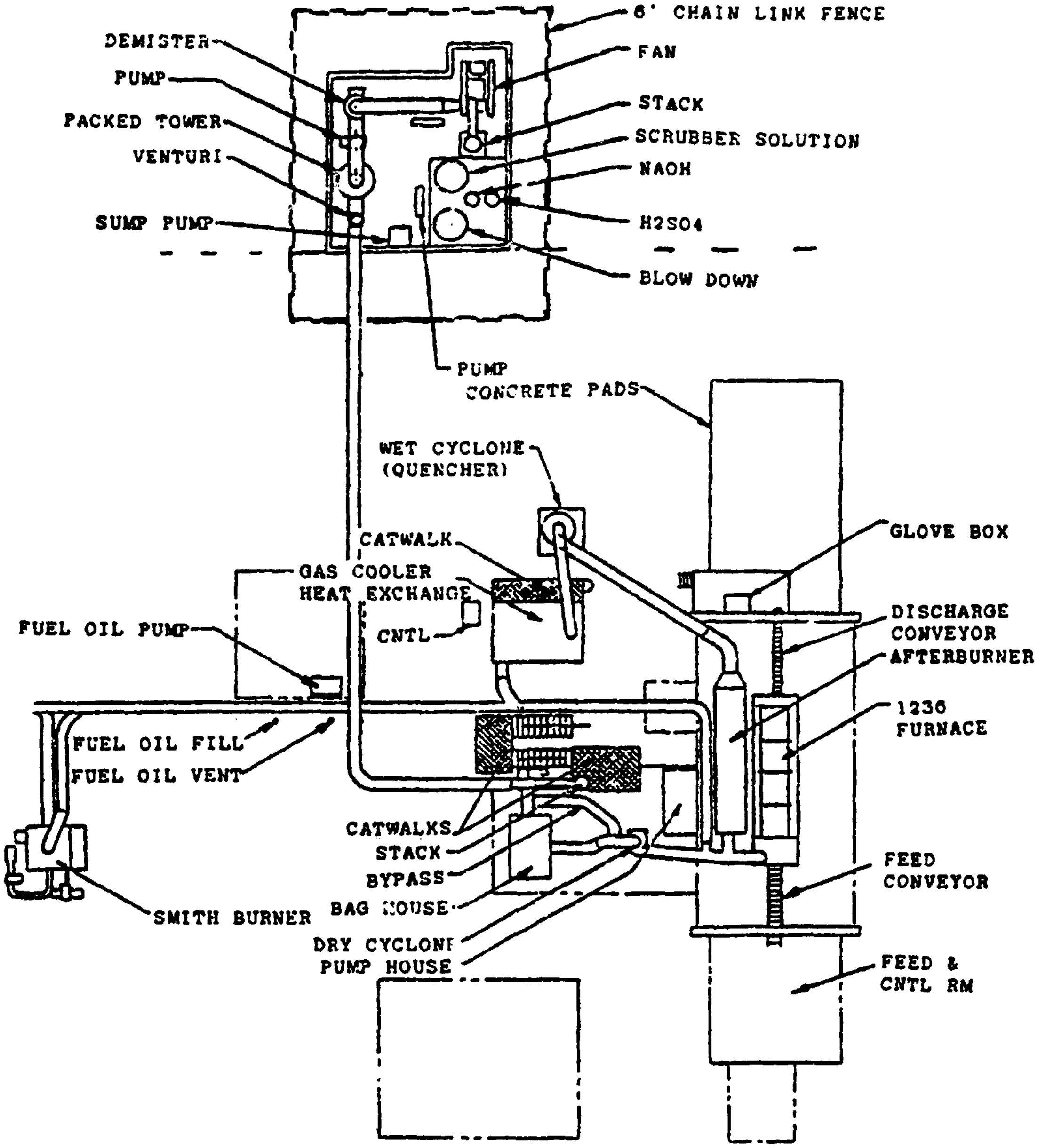
The incineration system layout overview is shown in figure 2.

Test Procedure

Two test procedures, the bagging method and the canister method were tested.

Bagging Method

Sample Preparation. Two large ammo boxes containing about 100 pounds of paint sludge, were obtained from a drum stored at the paint shop for each incineration test. Figure 3 shows the storage drum containing polyurethane paint sludge. The sludges were manually stirred, thoroughly, to produce a homogeneous mixture. Approximately three pounds of sludge were poured into a zip-lock plastic bag, using a stainless steel funnel, as seen in figures 4 and 5. The plastic bag containing the paint sludge was then placed in a paper sack and reweighed. The paper sacks were needed to prevent premature melting of the plastic bags in the feed chute. Figure 6 shows the bagged samples ready for incineration.



Incineration system at AED

Figure 2.

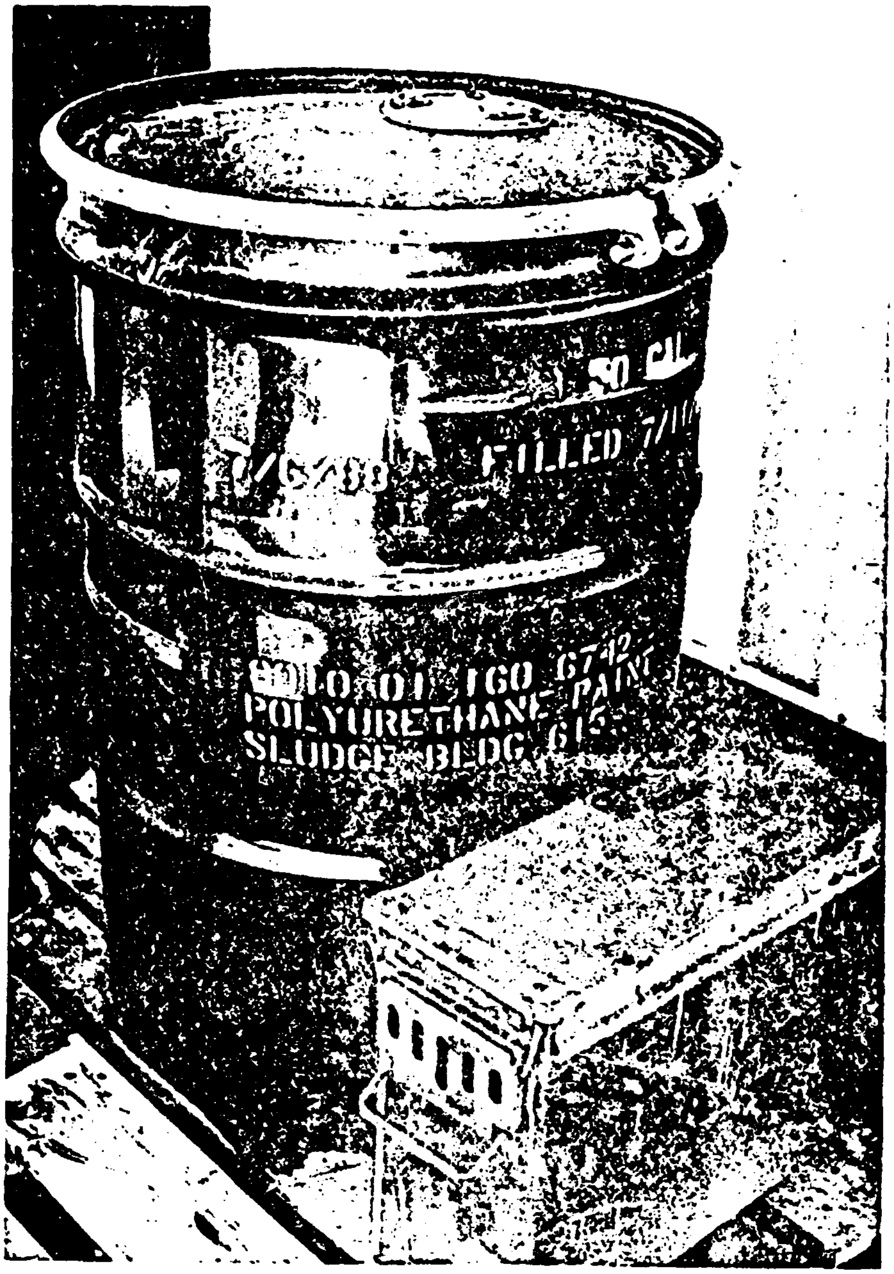


Figure 3

Paint sludge storage drum (Paint Shop)

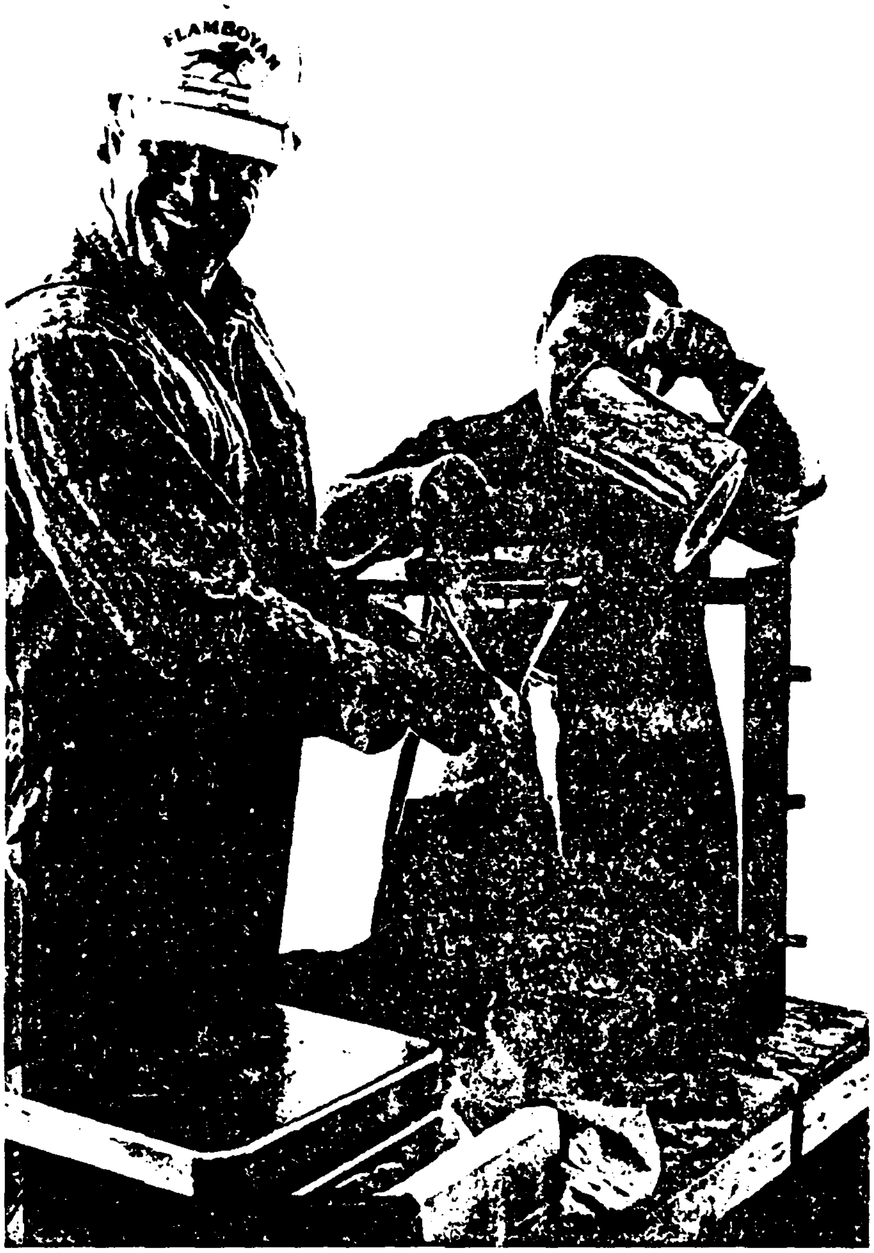


Figure 4

Bagging of paint sludge

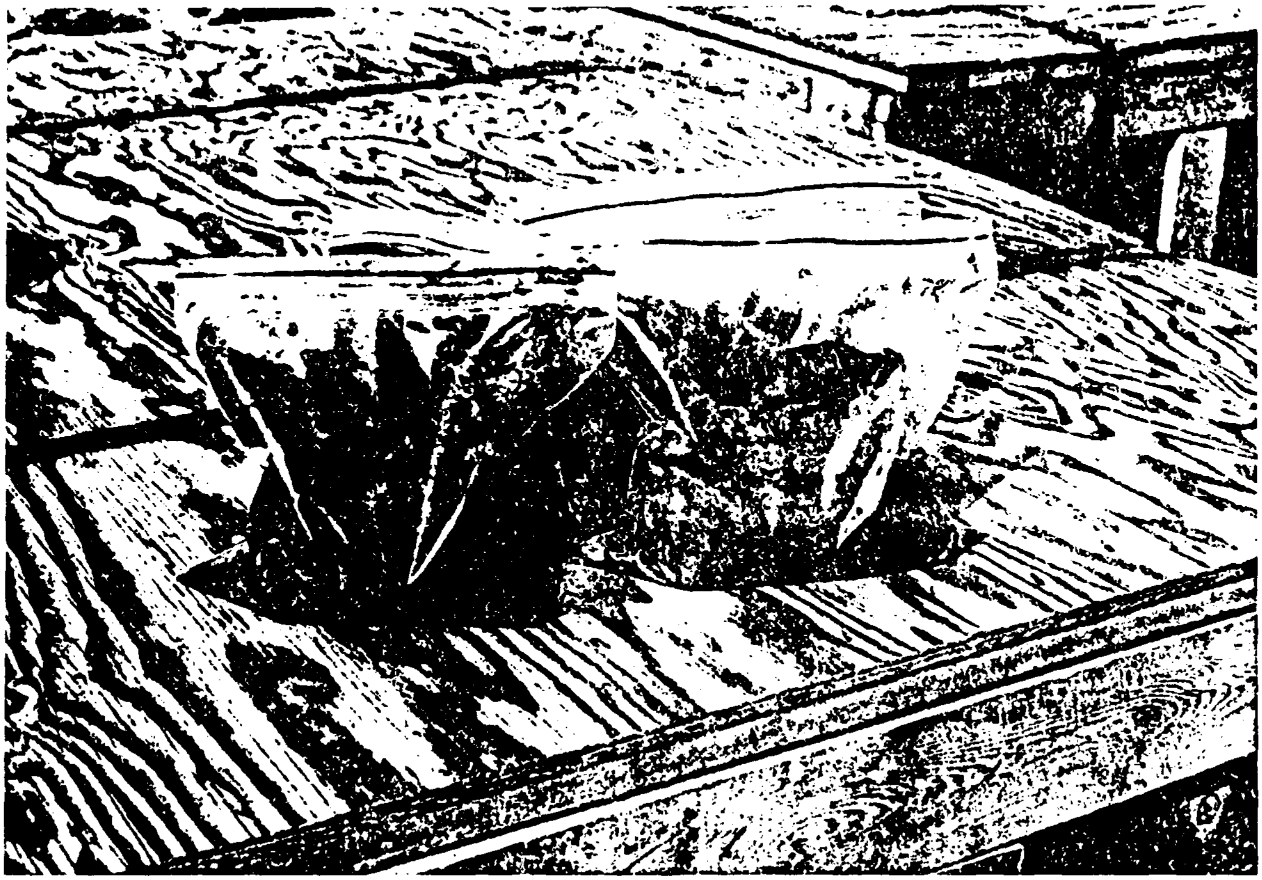


Figure 5

Paint sludge in plastic bags

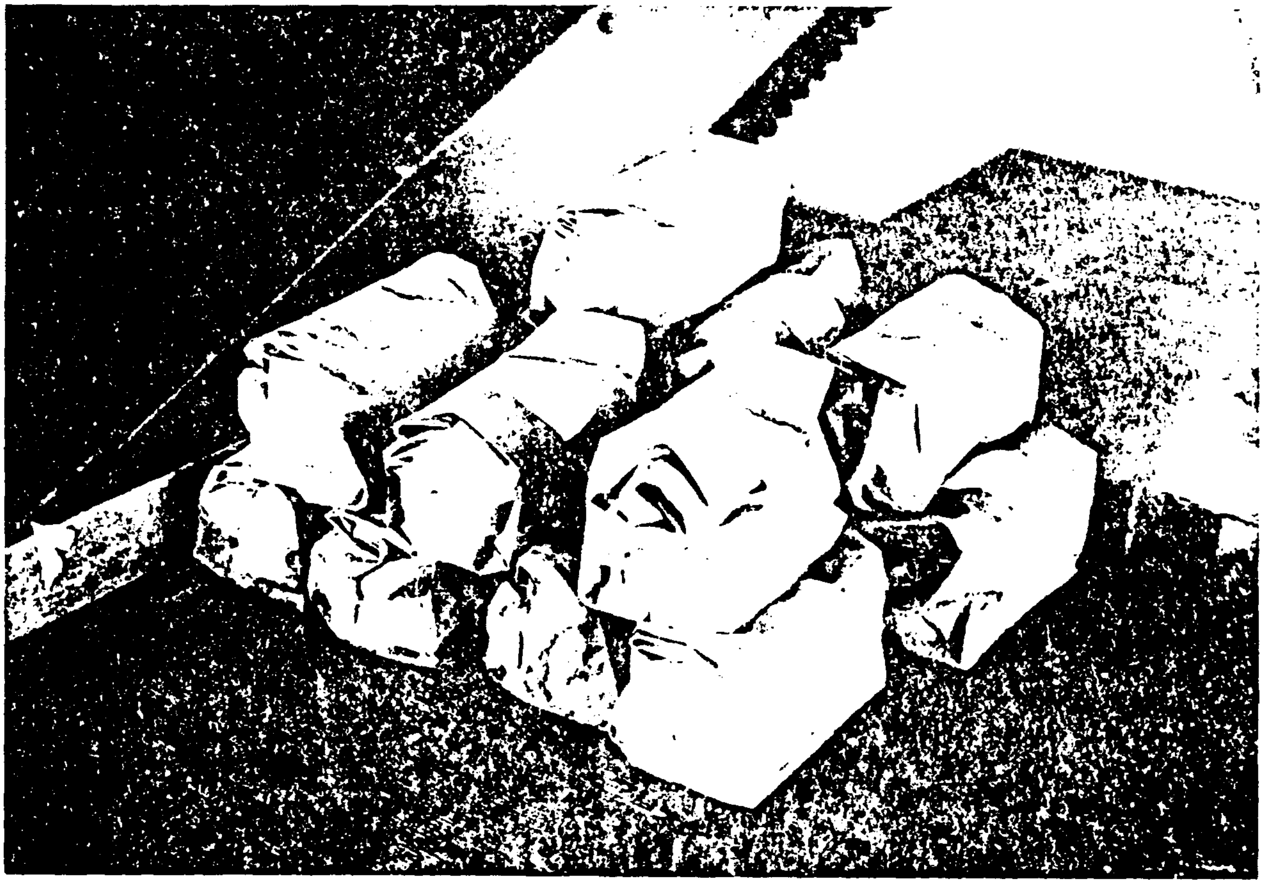


Figure 6

Bagged paint sludge ready for incineration test

Furnace Conditions. The APE 1236 Deactivation Furnace was preheated to 1300oF at the burner end, and 450oF at the stack end. Thermal equilibrium was reached in one hour. To maximize the combustion time, the rotation rate of the furnace was set at 0.33 RPM which provided a combustion residence time of 28 minutes.

Feeding and Feed Rate. The feed rate was controlled by placing an appropriate number of bags containing the paint sludge on the feed conveyer each minute. The maximum feed rate was determined by observing fugitive emissions, caused by over feeding, from the furnace and the draft fan housing.

Canister Method

Sample Preparation. Thirty steel canisters were fabricated from 4-inch mild steel tubing. The bottom end was sealed by welding on a circular steel disk. The top end was machined such that a paint can lid would fit flush. A photograph of a machined canister is shown in figure 7. Figure 8 shows the canisters filled with paint sludge for incineration. The paint sludge was prepared as discussed in the bagging method sample preparation section.

Using a stainless steel funnel, the canisters were each filled with 2.7 pounds of paint sludge and sealed with paint can lids by lightly tapping the lids into the canisters. When a canister containing paint sludge was fed into the furnace, high temperature caused expansion and the lid would pop open, spilling the paint sludge inside of the furnace where burning could take place.

When paper sacks and plastic bags are burned, additional smoke and pieces of charred paper are created. Rotary kilns and furnaces, such as the APE 1236, are not efficient at burning paper products. By replacing bags and sacks with metal canisters, problems were eliminated, more draft was made available for the combustion of the paint sludge and thus the feed rate was increased.

Furnace Conditions. The same as described in the previous section.

Feeding and Feed Rate. The same as described in the previous section.

Results

Feed Rate

A maximum of 11 pounds per minute burning rate was achieved during the feasibility incineration tests.

The burning of the paper and plastic bags in the furnace resulted in large volumes of smoke and burning debris which caused fugitive emissions escaping from the feed chute area of the furnace. The fugitive emissions limited the feed rate to three pounds per minute. For the bagging method, by replacing paper sacks and plastic bags with steel canisters, the paint sludge feed rate was increased to 11 pounds per minute with no fugitive emissions. It is anticipated that the final feed rate may exceed this value because the furnace did not reach its draft limited burning capacity, which would have been indicated by fugitive emissions during the feasibility tests. The results of the feasibility study are given in Table 1.

TABLE 1

PAINT SLUDGE INCINERATION

DATE SEPTEMBER	RUN NUMBER	MATERIAL PAINT SLUDGE	DRAFT RANGE INCHES	STACK TEMPERATURE RANGE F.	BURNER TEMPERATURE RANGE F.	BURNING RATE LBS./MIN
	2	WET	0.18 0.20	440 490	1250 1510	2/2
30	1	WET	0.20 0.24	435 475	1290 1460	1
	2	WET	0.20 0.24	440 490	1270 1500	1
OCT. 3		WET	0.17 0.22	440 490	1300 1520	3
11		WET	0.09 0.14	400 640	1200 1400	3
12		WET	0.10 0.17	360 640	1160 1400	3
17		WET	0.13 0.20	400 450	1160 1380	3
18		WET	0.15 0.20	400 540	1200 1400	6
19	1	WET	0.15 0.20	380 420	1200 1400	6
	2	WET	0.15 0.20	400 860	1100 1380	6
	3	RESIDUE	0.15 0.20	380 420	1150 1400	2
20	1	RESIDUE	0.15 0.20	380 420	1160 1400	2
JAN.10		CAN/WET	0.25 0.30	380 420	1000	10.8

Table 1

Burning rate, paint sludge Incineration

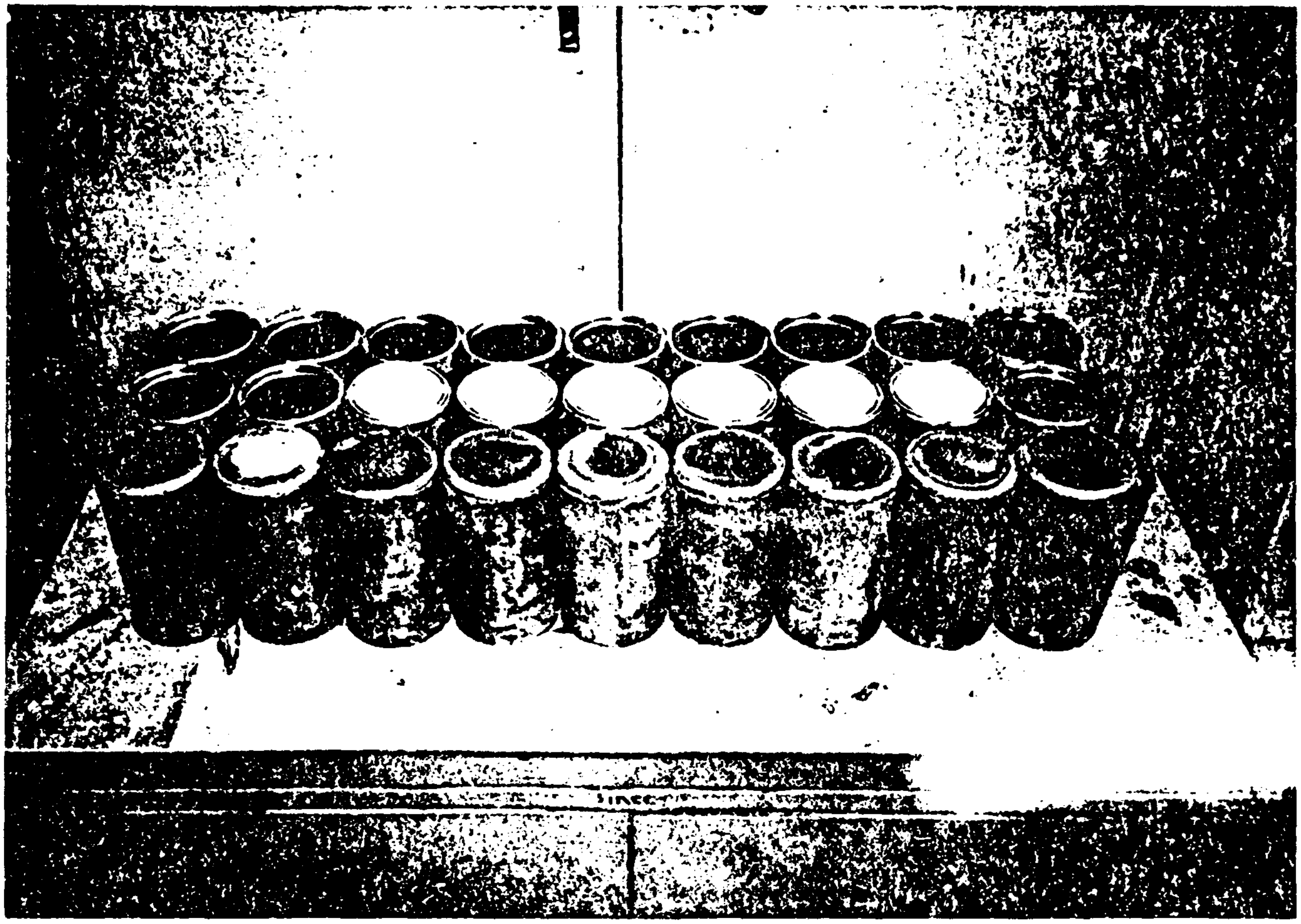


Figure 7

Canisters

Figure 8

Canisters filled with paint sludge

Weight Reduction

The single most significant fact of this study to date is the weight reductions that have been demonstrated during these initial tests. The test results showed that the weight of paint sludge fed can be reduced by 83 percent to 96 percent. This large variation in reduction rates may have resulted from the fact that the sample sludges were taken from non-uniform, non-homogeneous storage drums on different days. Also, accumulation of ash in the retort, cyclone, or other parts of the duct system may account for some of the variations. The results indicate that approximately 90 percent of the paint sludge consists of combustible organic compounds, such as plasticizers, hardeners, organic pigments and a mixture of organic solvents, that an ecologically safe destruction of these compounds using a standard military furnace such as APE 1236 Deactivation Furnace is entirely possible, and that the ash or residue of the paint sludge is noncombustible inorganic matter, such as oxides of metals and inorganic pigments. The test results are give in Table 2.

Ash Residue

The noncombustible ash discharged from the furnace is light green in color and is made up of fine granule solids. It has no odor and is light in weight. This dry residue would be considered a landfillable hazardous waste due to its heavy metal content. Chemical analyses will be performed on the ash to determine the specific constituents and their concentrations. Some of the residue ash collected is shown in figure 9.

ECONOMIC ANALYSIS

Approximately 39,000 gallons of various paint sludges and related solvent items will be produced at TEAD and disposed of through commercial contractors in 1989. The most costly item for disposal is polyurethane paint sludge, due to the large quantity that is generated (28,000 gallons). This economic analysis will be limited to a discussion of the disposal cost of polyurethane paint sludge to illustrate the savings that can be realized by in-house processing. The average density of polyurethane paint sludge is 13.85 pounds per gallon, and the disposal cost to TEAD is \$3.07/lb, as reported by Environmental Management Office (see Appendix).

The following calculations demonstrate the costs and savings. This computation does not include the expenditures for storage, transportation, maintenance, administrative, and overhead costs.

Cost for Paint Sludge Disposal Through Contractor

28,215 Gal x 13.85 lbs/gal = 390,778 lbs.

At \$3.07/lb, disposal cost to TEAD is

390,778 lbs x \$3.07/lb = \$1,199,688

TABLE 2

PAINT SLUDGE INCINERATION

DATE SEPTEMBER	RUN NUMBER	MATERIAL PAINT SLUDGE	DRAFT RANGE INCHES		STACK TEMPERATURE RANGE F.		BURNER TEMPERATURE RANGE F.		INITIAL WEIGHT LBS.	RESIDUE WEIGHT LBS.	PERCENT REDUCTION %
	2	WET	0.18	0.20	440	490	1250	1510	29.30	1.00	96.59
30	1	WET	0.20	0.24	435	475	1290	1460	30.45	1.30	95.73
	2	WET	0.20	0.24	440	490	1270	1500	30.40	2.25	92.60
OCT. 3		WET	0.17	0.22	440	490	1300	1520	32.95	2.80	91.50
11		WET	0.09	0.14	400	640	1200	1400	59.55	9.10	84.72
12		WET	0.10	0.17	360	640	1160	1400	60.50	6.90	88.60
17		WET	0.13	0.20	400	450	1160	1380	62.00	8.10	86.94
18		WET	0.15	0.20	400	540	1200	1400	65.60	8.60	86.89
19	1	WET	0.15	0.20	380	420	1200	1400	62.10	10.00	83.90
	2	WET	0.15	0.20	400	860	1100	1380	59.95	6.20	89.66
	3	RESIDUE	0.15	0.20	380	420	1150	1400	24.35	18.50	24.02
20	1	RESIDUE	0.15	0.20	380	420	1160	1400	24.30	7.30	69.96
JAN 10		CAN/WET	0.25	0.30	380	420	1000		78.30		

Table 2

Weight reduction, paint sludge incineration

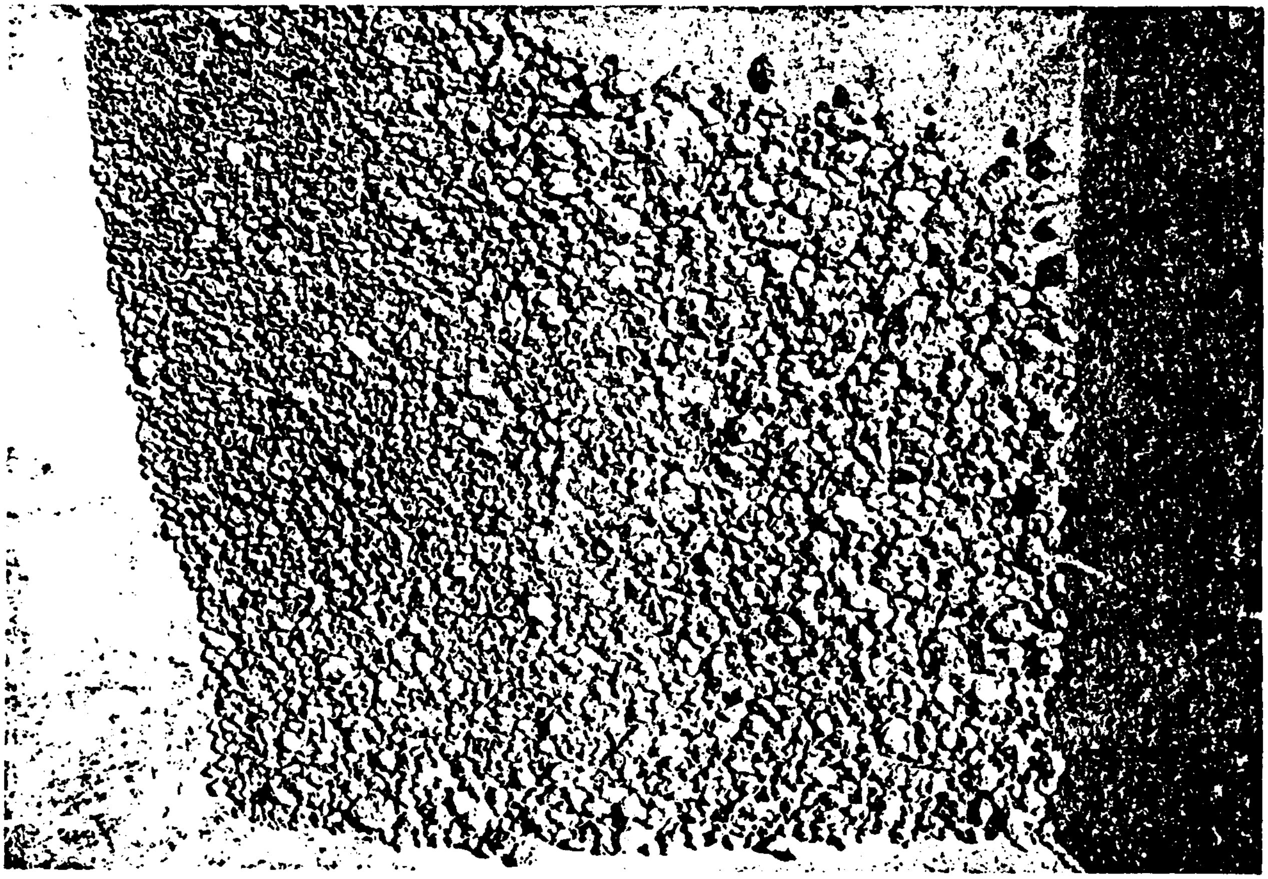


Figure 9

Residue ash, paint sludge incineration

Cost of In-House Weight Reduction Process

If TEAD decides to use the weight reduction process on paint sludge in-house, the cost of the process can be calculated. Again the hidden expenditures are not considered for this simplified computation. Should the pilot study prove that approximately 15 pounds of the sludge can be processed per minute (11 pounds per minute feed rate is already established in the preliminary tests), then the total hours required for processing 390,778 pounds of polyurethane paint sludge is 434 hours.

390,778 lbs x (min/15lbs) x (hr/60 min) = 434 hrs

Labor cost for two operators at \$19.21/hr rate is \$16,674.

434 hrs x \$19.21/hr x 2 = \$16,674

Diesel fuel cost to operate the furnace, including the afterburner at the consumption rate of 55 gals/hr and at a cost of \$0.94/gal is \$22,438.

55 gal/hr x 434 hrs x \$0.94/gal = \$22,438

Cost of electrical power at \$0.07/kwhr is \$3,646.

120 kw x 434 hrs x \$0.07/kwhr = \$3,646

Total operating costs at \$16,674 (labor) + \$22,438 (fuel) + \$3,646 (electricity) = \$42 748.

Increasing the operating cost by 30 percent to cover preparation for operators and equipment:

30% x \$43,758 = \$12,827

Total cost for in-house weight reduction operation is \$55,585.

\$12,827 + \$42,758 = \$55,585

Cost of Ash Disposal Through Contractor

During these tests, many samples of paint sludge were incinerated, with detailed data kept on the initial sample weights and the final residue weights, see Table 2). When the data was averaged, the final residue was found to be 10.29% of the initial weight of the paint sludge. Ten percent will be used for calculations. Cost of ash disposal through contractor is \$119,970.

The amount of final residue after incineration is

10% x 390,778 lbs = 39,078 lbs

The cost of disposal of this residue at \$3.07/lb is

39,078 lbs x \$3.07/lb = \$119,970

Economic Return To Government

$119,970 + $55,585 = $175,555

Therefore the savings to TEAD is

$1,199,688 - $175,555 = $1,024,133

Economic return to government per year is $1,024,133. Although this savings excludes maintenance and capitalization of the furnace as well as storage, administration and overhead costs, the savings is significant enough to warrant continued efforts in developing and testing the pilot plan equipment at AED's furnace test site.

CONCLUSIONS

The results of the feasibility study substantiated the project concept. The Army's standard furnace, the APE 1236 Deactivation Furnace, equipped with the necessary pollution control system is adequate for the reduction in weight of paint sludges by incineration.

During the feasibility tests, a feed rate of 11 pounds per minute was achieved. Approximately one drum of paint sludge can be processed through the furnace each hour. However, it is anticipated that the feed rate may be increased to 15 pounds or greater per minute when the proposed pilot equipment is tested. This projection is based on the fact that the sludge will be continuously metered, which facilitates improved steady state combustion, elimination of fluctuations of the combustion zone in the furnace, and efficient utilization of the draft.

Substantial paint sludge weight reduction was achieved during the feasibility tests. An average of about 90 percent of the paint sludge was burned off, leaving 10 percent incombustible fine granule solids as incineration ash. The residue, which consists of inorganic pigments, inert filler materials and some heavy metals, can be disposed of as hazardous waste for landfill operations through commercial contractors.

Cost effectiveness of the process has been addressed in a very preliminary economic analysis which excludes capitalization, overhead, and maintenance costs. This analysis concludes that a significant savings (about one million dollars) can be realized by Tooele Army Depot each year at current paint sludge production rates.

It is recommended that the pilot scale study be implemented so that the full scale process can be developed and the economics can be verified. The pollution emission measurements which may affect the operating constraints and determine the permitability of the process should also be considered.

PILOT STUDY

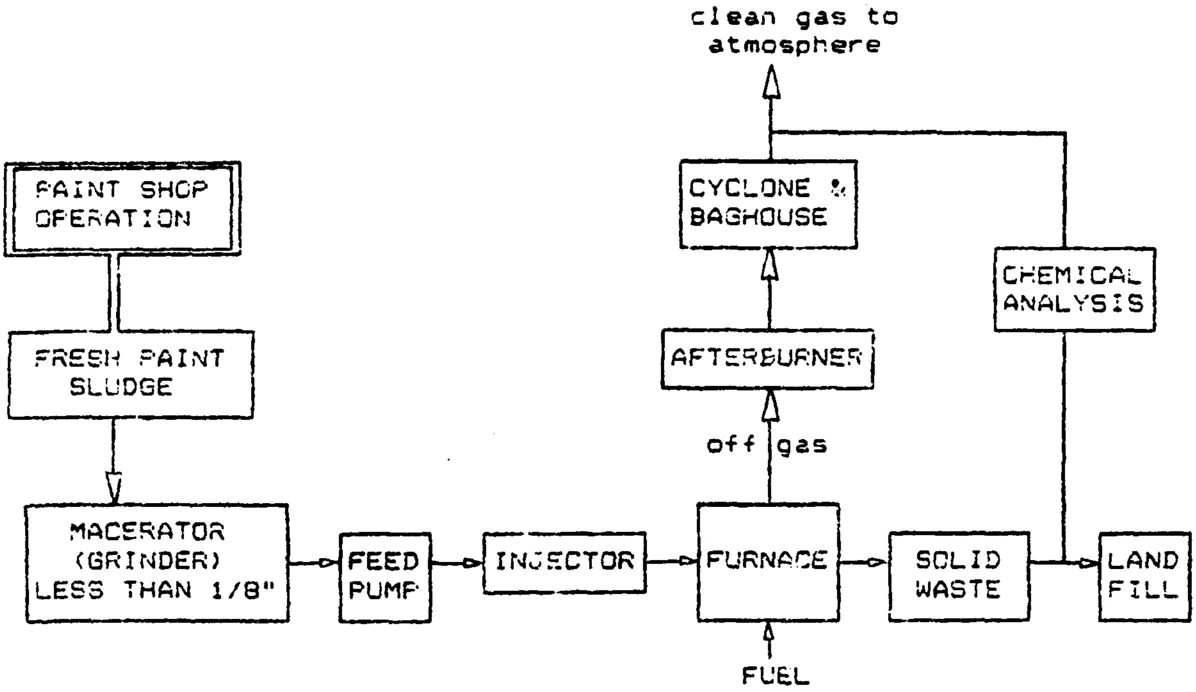
The feasibility study was conducted as a batch process to simplify the work involved. The study was conducted to prove that a standard, existing military furnace, such as the APE 1236 Deactivation Furnace, can be used to reduce the amount of paint sludges for disposal, a significant reduction in weight and volume of the paint sludges can be achieved within the environmental constraints, and that the process developed is cost effective and would produce a considerable savings to the government.

The results of the feasibility study showed that all three objectives can be achieved. It was found that the APE 1236 Deactivation Furnace can be used without modifications in its configuration or in its normal operational procedures. Approximately 90 percent weight reduction was achieved with a preliminary testing procedure. A very preliminary economic analysis indicated that about one million dollars, excluding capitalization, maintenance, etc., would be saved by the Tooele Army Depot each year at current production levels by processing paint sludge. Based on these results, a pilot study has been formulated to demonstrate that paint sludge can be fed continuously into the furnace. The pilot plant is a feed system only and no furnace modifications are required. It is desired to define the necessary equipment, controls, and procedures which would be used to design production mode equipment. The final production mode process equipment will consist of a portable unit that can be assembled and dismantled on demand. This unit will be designed to process all of the paint sludges produced at the TEAD facilities. A schematic flow chart for the pilot study is given in figure 10.

Basic Equipment, Layout, and Test Procedure

There are five major components in the process equipment used in the pilot study. Some of the equipment is rented and some purchased for this project. A brief description of equipment and operations is given in this section. A process equipment layout is shown in figure 11.

Paint sludge, received in 55 gallon drums from the Paint Shops will be stirred to produce a homogeneous mixture and then pumped into a macerator unit using the transfer pump. Lumpy solids in the paint sludge will be broken and mixed to a homogeneous slurry containing particles smaller than 1/8-inch in diameter. The paint sludge will be continuously pumped through a feed metering pump loop and then back to the macerator unit. This continuous pumping of the paint sludge is necessary to keep the sludge in a homogeneous suspension. The consistency of the paint sludge requires a special metering pump which would accommodate the unique physical characteristics of the material. The pump is constructed with a stainless steel stator, lined with Viton, and a special alloy rotor, which pushes the material along the length of the tubular cylinder pump body. Industries handling peanut butter and other similar materials, use this type of pump.



FLOW CHART

Figure 10

Process concept flow chart of pilot study

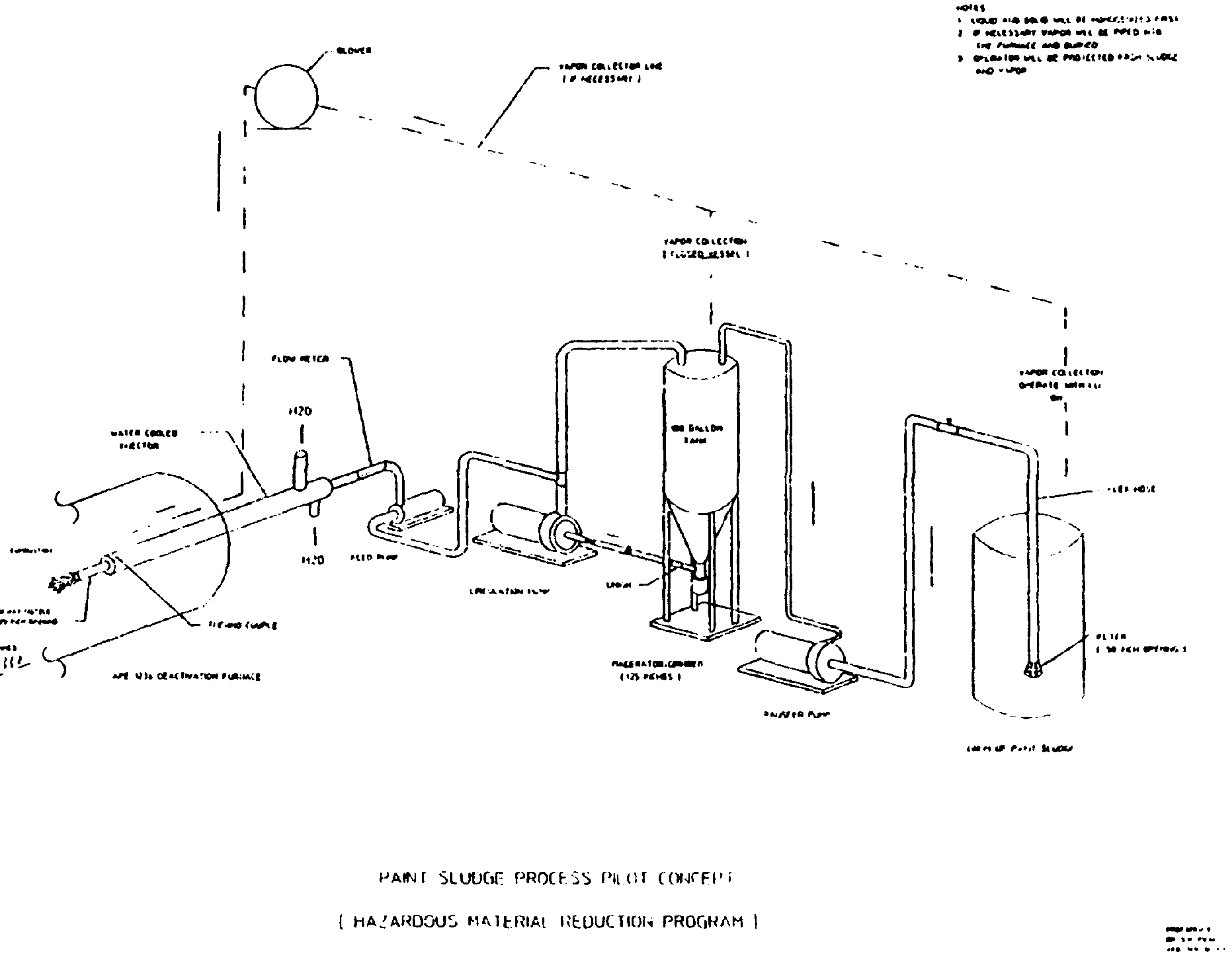


Figure 11
Schematic diagram of process equipment layout

a water cooled, double walled paint sludge injector was constructed from stainless steel. It is water cooled to eliminate, or minimize, the premature evaporation of highly volatile organic solvent from the sludge in the injector. Experience indicates that this type of sludge/slurry has a tendency for hardening, sedimentation, and plugging the injector line and nozzle, requiring frequent system disassembly for cleaning. A schematic diagram of the feed injector is shown in figure 12.

All test personnel will be educated and thus protected from unnecessary exposure to harmful chemical compounds and fumes by strictly adhering to the prescribed industrial safety standards and procedures, including personal protective equipment. Solvent vapor will be collected and vented through an appropriate ventilation system, if necessary.

Anticipated Results

The pilot study process and the process equipment were carefully designed and selected to achieve optimum results. Special attention was given to the unique chemical and physical characteristics of the paint sludges while designing the pilot process system.

The bagging of the paint sludge is a labor intensive operation. In the pilot system, the sludge will be pumped from the drums into the macerator unit. After homogenization the paint sludge will be circulated through pipe lines, which eliminates the manual work that is associated with the bagging operation. A special feed pump has been purchased for this project. The paint sludge feed stock will be metered into the furnace at a relatively low pressure, producing a small granular residue after the burning is completed. The feed rate can be adjusted while conducting the incinerator tests.

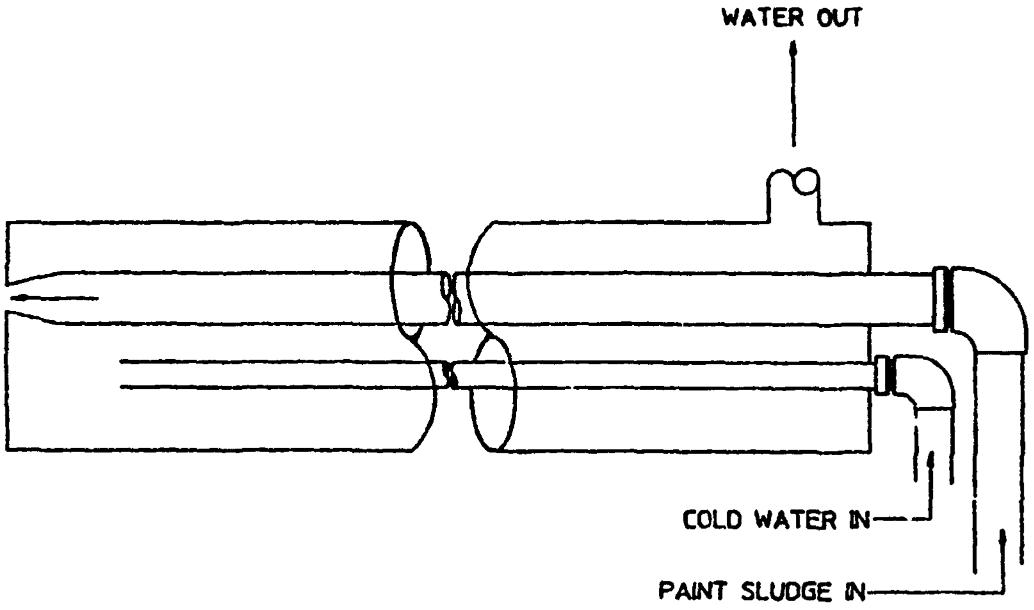
With this new system, it is anticipated that the feed rate may be increased by 50 percent to 15 pounds or more per minute. The new system will deliver a smoother and steady flow of the paint sludges and eliminate surges and fugitive emissions. The incineration parameters obtained in the pilot plant can be used to design the production system.

Quantitative Measurements

Throughout the testing done during the pilot study, all parameters, stream flows, stack emissions, etc., will be monitored. This data will enable a more accurate analysis of the economics and feasibility of the final process.

Pollution Monitoring

A sufficient quality and quantity of data will be gathered to assess the environmental impact of paint sludge incineration, and to determine if a permit for the process can be obtained. It would be advantageous for trial burn testing for this process to be included with the testing for the furnace upgrade which is scheduled for September 1989.



WATER COOLED INJECTOR

Figure 12

SUMMARY

Tooele Army Depot produces approximately 28,000 gallons of paint sludge each year. This waste is generated from the activities of maintenance and refurbishing of military vehicles and equipment. Disposal of this waste through contractors costs the depot over one million dollars per year. The Ammunition Equipment Directorate (AED) has conducted a feasibility study for minimizing the amount of paint sludge to be disposed of through contractors, thus reducing disposal costs.

A simplified feasibility study was conducted in 1988 to determine if paint sludge could be reduced in volume and weight by incineration in the APE 1236 deactivation furnace at the AED test facility. The following results demonstrated that substantial weight reduction could be achieved. The standard APE 1236 furnace reduced the paint sludge weight by about 90 percent. The residual dry ash, which contains heavy metals, can be disposed of in a hazardous waste landfill.

A feed rate of 11 pounds per minute was used, equivalent to approximately one drum per hour. It is estimated that at this rate the furnace could process all of the paint sludges generated at TEAD by operating one day per week.

In a preliminary economic analysis, excluding capitalization, maintenance, and administrative costs, it was estimated that annual savings of about one million dollars could be achieved.

A pilot scale process has been designed and partially fabricated. In this study the throughput rates and percent weight reduction will be determined. The pilot process is expected to increase the throughput and decrease the labor required to process paint sludge. Funding for the pilot study is being pursued.

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APPENDIX

This table lists the estimated CY 1989 costs for disposal of the major waste streams at Tooele Army Depot. These figures are based on 1987 or 1988 waste rates and 1989 disposal costs.

CY 1989
(Estimated)

Waste Description	Unit Cost	Estimated Annual Amount	Estimated Annual Cost	Waste Hazard Codes MSCIRBD
Accelegold (Alocvne)	$1.86/gal	5400 gal*	$10,044	M C R
Blast Grits	0.14/lb	337760 lbs	47,287	M B
Carbon Removing Compound	2.07/gal	3355 gal	6,945	S
Enamel Paint Sludge	1.36/gal	1100 gal	1,496	S I B
Gasoline	1.41/gal	1540 gal	2,171	M I B
Lacquer Thinner	3.47/gal	1650 gal	5,726	MS I BD
Paint Dust Waste	2.07/gal	1045 gal	2,163	M
Paint Stripper	2.27/gal	1595 gal	3,621	S
Paper Paint Filters	2.07/gal	6545 gal	13,548	M B
Phosphoric Acid	1.86/gal	8784 gal	16,338	M C
Photographic Developer	2.16/gal	60 gal	130	M
Plating Solution	1.86/gal	1600 gal	2,976	C
Polyurethane Paint Sludge	3.07/gal	28215 gal	1.2 mil.	MS RB
Polyurethane Paint Thinner	3.47/gal	8965 gal	31,109	S I BD
Smut-Go	1.56/gal	3080 gal	4,805	M
Sodium Hydroxide	1.36/gal	52062 gal	70,805	M C
Sulfuric Acid Electrolyte	1.86/gal	1980 gal	3,683	M C
1,1,1-Trichloroethane	2.07/gal	6875 gal	14,231	MS D

* This amount is high for 1988 because of the cyanide concerns earlier this year.

CODES:

M - Heavy metal concentrations (e.g. lead, arsenic, mercury, chromium)

S - Hazardous waste listed solvents (e.g. methylene chloride, xylenes)

C - Corrosive hazardous wastes (i.e. high or low pH values)

I - Ignitable hazardous wastes

R - Reactive hazardous wastes (i.e. materials containing cyanides or sulfides or materials which readily combust or explode in air, water, or when exposed to an ignition source)

B - Materials which have the potential to be reduced in volume or provide heat energy when they are incinerated

D - Wastes which have the potential to be distilled are recovered

SOLVENT RECYCLING WITH ONSITE DISTILLATION--A CASE HISTORY

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INTRODUCTION

The Department of Defense (DoD) has initiated a used solvent elimination (USE) program to eliminate the disposal of recyclable solvents as wastes (Reference 1). The Army has adopted this program and applied it to any Army activity which generates more than 400 gallons per year of any used organic solvent (defined as organic fluids used for cleaning, thinning, calibration or similar purposes). Army Materiel Command (AMC) installations were required to fully implement the USE program by 1 October 1986.

Several technologies are available to recycle solvents so that they can be reused for their original purposes. One promising technology which has broad application for solvent recovery is distillation (Reference 2). Distillation operations can be implemented in several options: installation-owned recycling systems, contractor-owned recycling systems, and sale-to-recycler (including manufacturer take-back). The selection of the best option should be initiated with an economic analysis, and then compared the advantages and disadvantages between management and logistics requirements, including the recovered solvent quality control.

Tooele Army Depot serves as an excellent case history for solvent recycling. As part of their mission of rebuilding military vehicles and equipment, Tooele Army Depot generates approximately 7,800 gal/yr of waste 1,1,1-trichloroethane, 13,600 gal/yr of waste Stoddard solvent, and 7,100 gal/yr of polyurethane thinner. After conducting an economic analysis between disposal without recovery and recovery with onsite distillation, Tooele Army Depot had selected and installed three (3) batch distillation units onsite to recover these used solvents.

SOLVENT PHYSICAL AND CHEMICAL PROPERTIES

1,1,1-Trichloroethane (TCA) is used for vapor degreasing, and is an excellent solvent for cleaning plastics, polymers, and resins. It has been found increasing use in metal cleaning due to the OSHA limitations posed on trichloroethylene (TCE) and perchloroethylene (PERC). However, it has the tendency to hydrolyze and to form acid byproducts when boiled in the presence of water. It also reacts with aluminum, zinc, and magnesium.

Polyurethane paint thinner contains oxygenated compounds (such as methyl ethyl ketone and alcohol), toluene, and xylene. The thinner is used to thin paints, to prepare the painting surface and to clean the painting equipment such as paint spray guns.

Stoddard solvent is also commonly called PD 680 Type I or Type II. The two types are distinguished by their ignitablity, i.e., Type I has a flash point of 100 °F whereas Type II has a flash point of 140 °F. The low evaporation rates and high flash points make the Stoddard solvent a widely used solvent for cold cleaning for removing oils, greases and dirt from metals.

TABLE 1 tabulates the physical, chemical and health related properties of these three solvents.

DISTILLATION UNIT DESCRIPTIONS

One Progressive Recovery, Inc., (Columbia, Illinois), Model SC-100 unit, and two Model-50 units are used at Tooele Army Depot for solvent distillation. The general information of these two models are tabulated in TABLE 2.

The distillation unit incorporates a thermal heating rod in a hot-oil jacketed system. The heating rod is immersed in the thermal heat transfer oil. The heat transfer surface consists of the side walls as well as the base of the vessel.

The distillation of solvent is based on the principal of convective heat transfer from the thermal fluid to the solvent product. The greater the thermal input and transfer surface provided, the greater the clean solvent output rate. The unit is constructed of stainless steel for long service life and purity of product.

The control panel is housed in a NEMA 12 enclosure. All switches, push buttons and pilot lights are industrial grade, U.L. listed. Intrinsically safe barrier relays, with their associated blue wire "safe strip", are used in the control scheme. These provide for all aspects of the Class I, Division, Group D explosion-proof area as well as safety in the control circuitry.

The batch distillation cycle is controlled by a temperature setpoint. Once a certain temperature is reached, the operation of the batch is stopped.

DISTILLATION CURVE

Initial start-up and derivation of distillation curve for each solvent is very important for the success of the operation. These are accomplished by examining the physical and chemical characteristics of the solvent requiring distillation and choosing an operating temperature based on the solvent's boiling

TABLE 1. PHYSICAL, CHEMICAL AND HEALTH PROPERTIES OF SOLVENTS

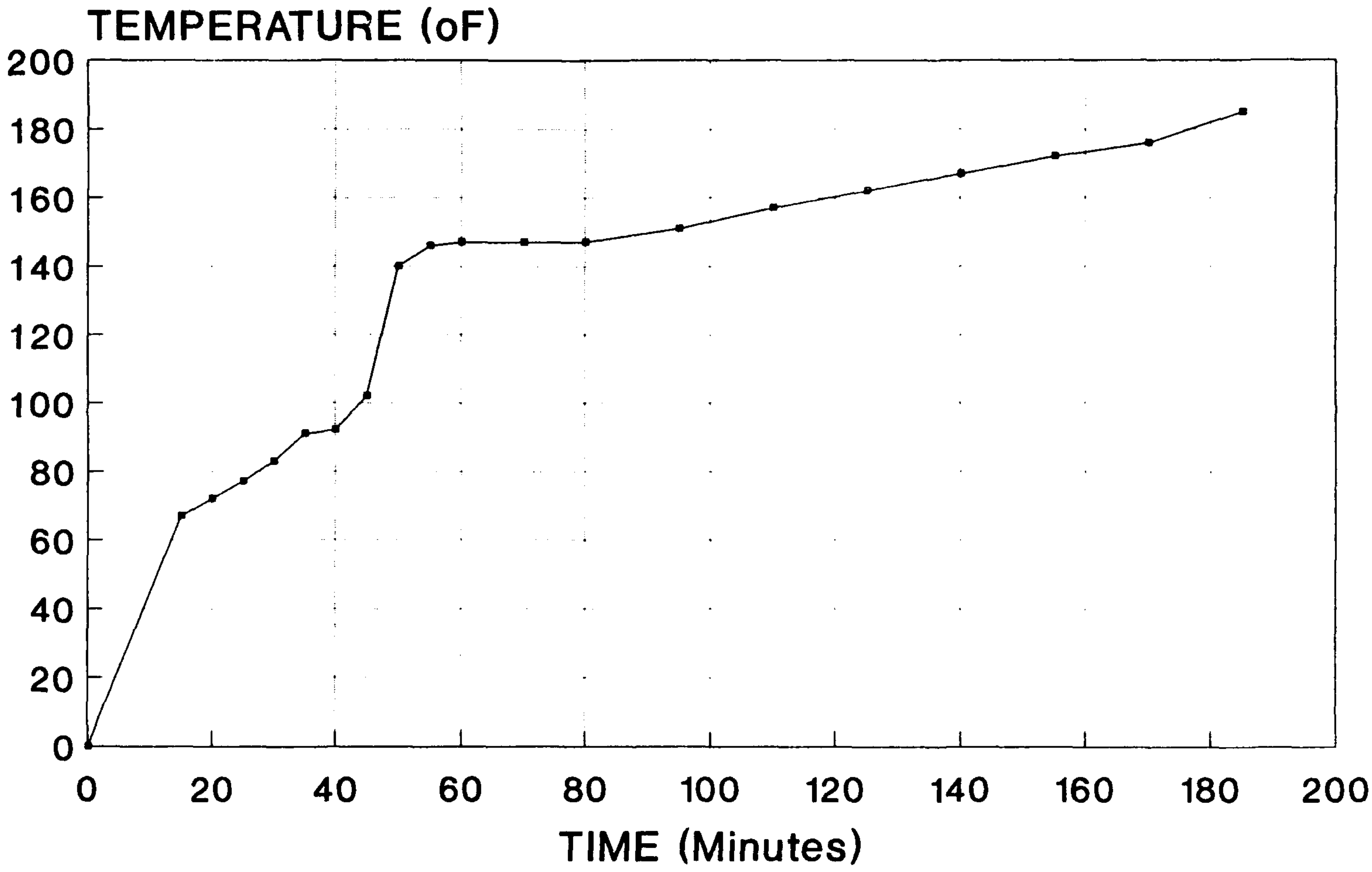
Physical, Chemical & Health Properties		TCA	Polyurethane Paint Thinner	PD 680 (Type I)
Specific Gravity		1.300-1.324	0.85	0.776
Density (lb/gal)		10.8-11.0	7.1	6.5
Boiling Point (°F)		167	179	300-400
Flash Point (°F)		None	42	105
Vapor Pressure (mmHg)		100	35.1	<11
Vapor Density (air=1)		4.5	3.4	<1
Evaporation Rate (Ethyl ether=1)		2.6	16.8	--
Water Solubility		Insoluble	5%	Insoluble
Explosive Limits,	LEL	7.5%	1.7%	1.1%
	UEL	16%	--	6%
OSHA PEL		TWA 350 ppm	--	TWA 500 ppm
ACGIH TLV		TWA 100 ppm	TWA 100 ppm	TWA 350 ppm
NOISH REL,	TWA	--	--	350 mg/m^3
	Ceiling	350ppm/15M	--	1800 mg/m^3/15M

TABLE 2. SOLVENT DISTILLATION UNIT DESCRIPTIONS

MODEL	CAPACITY (Gal)	DISTILLATION (Gph)	HEATING (Btu)	COOLING WATER (Gph)	POWER (Kw)
SC-50*	35	5.0	25,000	30	7.5
SC-100*	35	7.5	30,000	36	9.0

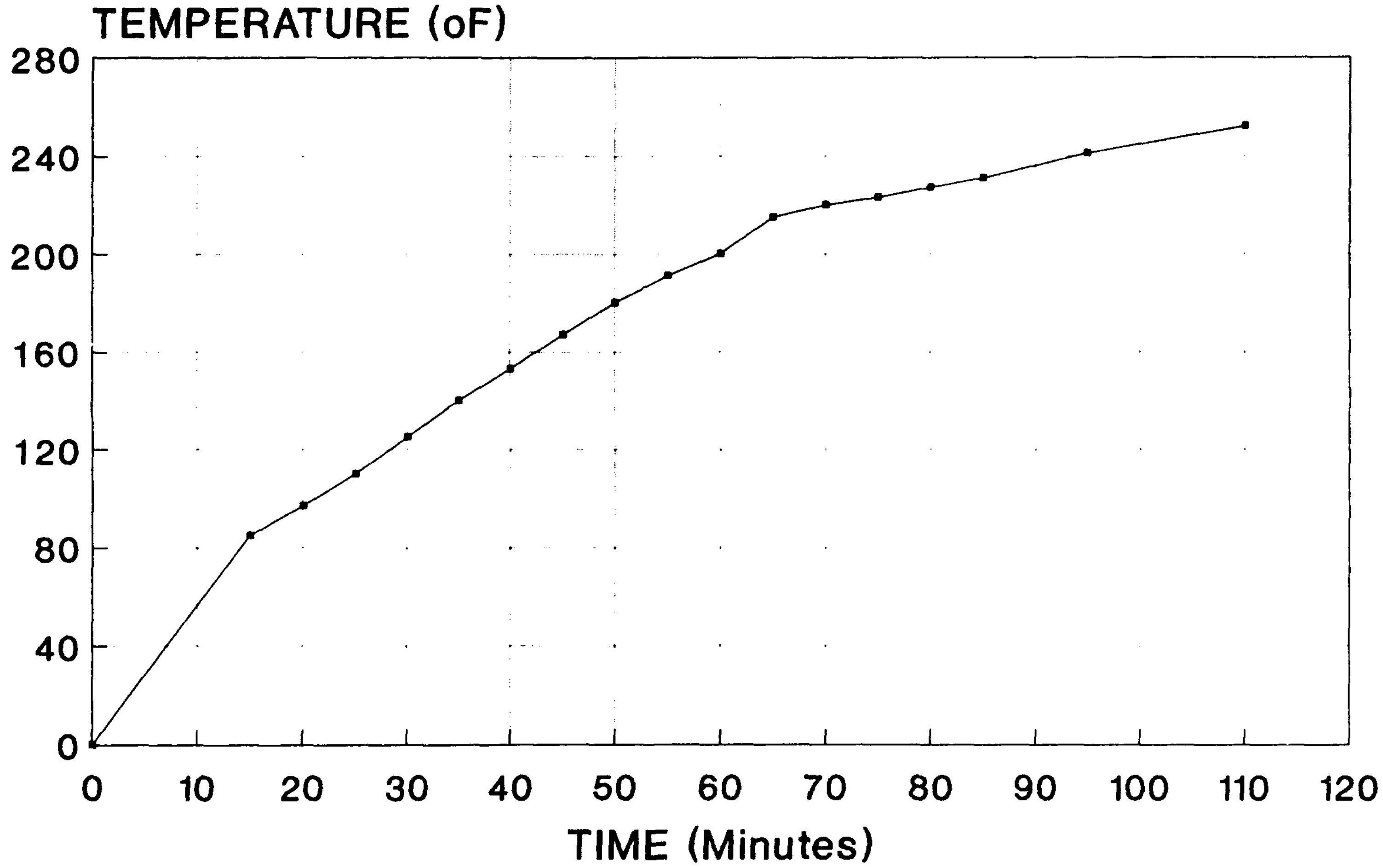
* NOTE: List price for SC-50 is $11,300, for SC-100 is $13,900. Vacuum system is approximately $6,000 additional for each unit.

FIGURE 1.
DISTILLATION CURVE-1,1,1-TRICHLOROETHANE



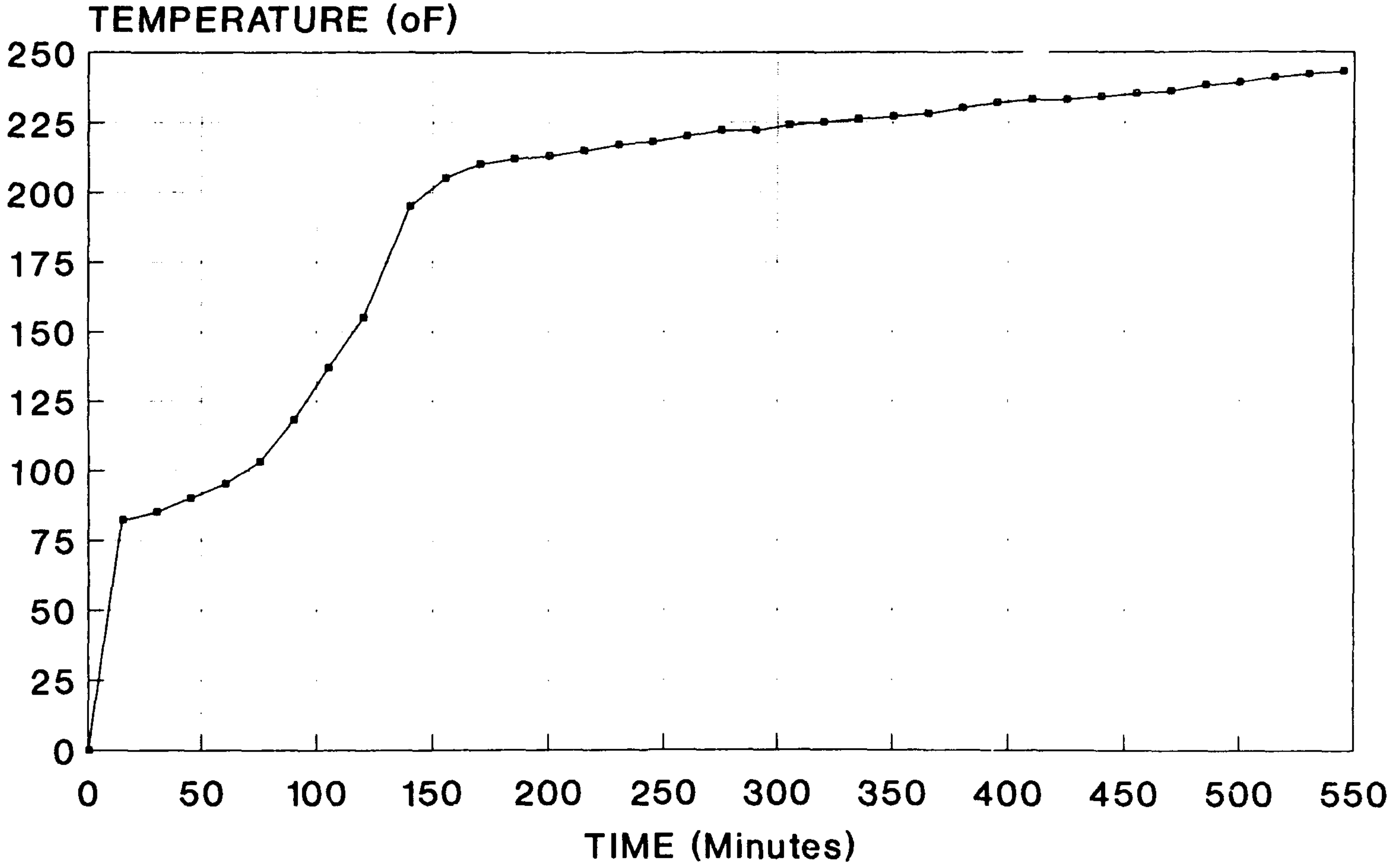
NOTE: Recovery Efficiency = 78%

FIGURE 2.
DISTILLATION CURVE--STODDARD TYPE I



NOTE: Recovery Efficiency = 85%

FIGURE 3.
DISTILLATION CURVE-POLYURETHANE THINNER



NOTE: Recovery Efficiency = 46%

point. Since most solvents are actually multi-component mixtures, the optimum boiling point falls within a certain range. If this range is not met, the recycled solvent quality can suffer due to an imbalance in the recycled components.

At Tooele Army Depot, the Oil Operating Temperature was set at 60 °F above the anticipated boiling point of the solvent, and the Oil High Temperature Limit was set to about 15 °F above the Oil Operating Temperature. For example, the TCA has a boiling point of 167 °F, the Oil Operating Temperature was set at 227 °F, and the Oil High Temperature Limit was set at 242 °F.

After the distillation unit is started for 15 minutes, note and record the temperature on the thermometer each five (5) minutes. Continue the above procedure until steady distillation is established (i.e., when temperature remains constant). Then the temperature reading should be taken at 15 minutes intervals until the output rate drops off to almost zero. At this point the vapor thermometer will be reading its highest.

A Distillation Curve will be drawn with the data recorded above, as shown in FIGURES 1, 2, and 3 for TCA, Stoddard solvent, and polyurethane paint thinner, respectively. The "cut" temperatures are temperatures at which solvents can be separated, and they will show on the graph as a "plateau". Throughout several trial-and-error batch cycles, the optimum temperature settings can be obtained.

RECOVERED SOLVENT QUALITY CONTROL

There is often a concern that the distillation will alter or fail to recover some of the inhibitors and thus the recovered solvent will not perform satisfactory. Therefore, the recovered solvent quality should be tested and provided with additional additives or inhibitors if needed.

A. 1,1,1-Trichloroethane (TCA):

Most chlorinated solvent are not pure chemicals, but are formulated as mixtures of compounds. Proprietary inhibitors are added to commercial solvents to improve their properties or extend their service life. These inhibitors are classified as antioxidants, metal stabilizers, and acid acceptors. One major criterion for determining the quality of recovered chlorinated solvents is the inhibitor level.

Only the unsaturated chlorinated solvents, such as trichloroethylene and perchloroethylene, are prone to auto-oxidation. TCA is essential stable to auto-oxidation, however, it is prone to degradation in the presence of aluminum or aluminum chloride. To prevent these actions, metal stabilizers are added to TCA. These stabilizers will react with metals by complexing or reacting with aluminum chloride or by terminating free radicals through hydrogen donation.

Chlorinated solvents will break down to form small amounts of hydrochloric acid. This hydrochloric acid will cause problems in operation, including contributing to solvent degradation and corrosion of parts and the degreaser system. Therefore, acid acceptors are added to the solvent to neutralize molecules of hydrochloric acid. These acid acceptors are generally amines or epoxides. The composition of the TCA used at Tooele Army Depot are tabulated in TABLE 3.

The aluminum stabilizer is usually recovered during the distillation as demonstrated by Joshi (Reference 3); however, the acid acceptor is partially consumed during the cleaning operation of the solvent. A study by Army Construction Engineering Research Laboratory (USA CERL) indicates that acid acceptance value, which reflects the amount of inhibitor added to inhibit the formation of acid in solvent, is the best criterion to verify the quality of recovered TCA (Reference 4).

After a series of tests at Tooele Army Depot, the recovered TCA requires either the addition of butylene oxide or the mixing of new product to bring the acid acceptor up to the required level (Reference 5):

1. Mix With Butylene Oxide: One-half (1/2) liter of butylene oxide is required in every 55-gallon drum of recycled TCA; or

2. Mix With New Product: The mixture amounts of new product and recovered solvent are shown in TABLE 4.

The recovered TCA sometimes contains up to one-half (1/2) gallons of water in every 55 gallons of solvent recovered. The water probably came from the moisture condensation in the degreaser tank or from the steam cleaning of parts before degreasing operation. Water can be easily separated from the TCA by settling and decanting.

B. Stoddard Solvent:

Stoddard solvent is a very commonly used cold-cleaning solvent. The recover and reuse of this type of solvent is also widely practiced, especially by the contractor-provided solvent recycle services.

The quality of recovered Stoddard solvent at Tooele Army Depot is acceptable according to the specifications except the foul odor. The foul odor appears to be due to sulfur compounds, particularly low molecular weight thiols (mercaptans).

The new Stoddard solvent contains very little sulfur, so these compounds appear to result either from reaction with sulfur picked up during use, perhaps from cutting oil or other sulfur containing materials, or commingling with sulfur containing wastes.

TABLE 3. COMPOSITION OF 1,1,1-TRICHLOROETHANE USED AT TOOELE ARMY DEPOT

INGREDIENT	FORMULA	% BY WEIGHT	FUNCTION
1,1,1-Trichloroethane	CH_3CCl_3	90-95	Solvent
Diethylene ether (1,4-Dioxane)	$C_4H_8O_2$	2.5	Aluminum stabilizer
Butylene oxide	C_4H_8O	2.5-7.5	Acid acceptor

TABLE 4. MIXTURE AMOUNTS OF 1,1,1-TRICHLOROETHANE IN 55-GALLON DRUM

Acid Acceptance As % of NaOH	0 To 0.03 (9.5 to 10 ml)	0.03 To 0.08 (9 to 9.5 ml)	0.08 To 0.10 (8.5 to 9 ml)
New Solvent required	41 Gal	27.5 Gal	14 Gal
Recycled Solvent req'd	14 Gal	27.5 Gal	41 Gal
Total	55 Gal	55 Gal	55 Gal

The used Stoddard solvent (before distillation) contains large quantities of sulfur compounds, nearly all with low volatility, and has little odor. The first one-fourth distillation fraction of the solvent has little objectionable odor despite considerable sulfur content. This indicates that thiols are not produced until a higher temperature is reached, probably from reduction of di- or polysulfides or from cracking of monosulfides. The last one-fourth fraction also contains very little thiol indicating previous completion of formation and removal by distillation of the very volatile thiols.

Extraction of the foulest smelling distillate, the third one-fourth fraction, with 8% sodium hydroxide solution removed most of the objectionable odor, leaving the residue subjectively no worse than new solvent, though it still contained much sulfur.

Reaction with 5% sodium hypochlorite (household bleach) removed most sulfur compounds as well as the odor, resulting in a product much milder in odor than new solvent. A study conducted by Army Construction Engineering Research Laboratory during the evaluation of recovered Stoddard solvent indicated that sodium hypochlorite would serve as a bleaching agent to rejuvenate the absorbance level of spent solvent (Reference 6). For visible absorbance was rated as the best criteria among the seven (7) methods evaluated for predicting the need to change solvent, i.e. to discard used solvent.

Treatment of bleached product with 50% sodium hydroxide produced no noticeable improvement in the odor, and increased slightly both the number and inexplicable, the amount of sulfur containing impurities detectable by GC-FPD. Shaking used solvent (before distillation) with household bleach greatly reduced the sour odor, but much sulfur remained and an emulsion formed which broke quite slowly, particularly if insufficient bleach was used.

The generation of objectionable odor in recovered solvent could be prevented or reduced by exclusion of sulfur from the solvent or by prevention of their interaction. The former would require that sulfur containing materials not be used with the Stoddard solvent, or that solvent contaminated with sulfur be segregated from sulfur-free used solvent. The latter might be accomplished by vacuum distillation, or injection of steam into the solvent to form an azeotropic mixture, in order to reduce the required still temperature. However, these methods could be expensive.

Most of the sulfur compounds present in the distillate can be removed by agitation with 5% sodium hypochlorite solution. If commercial HTH or STB is used it should be dissolved (about 10%), rather than in slurry form, to preclude fire or explosion hazard and to minimize emulsification. Extraction with about 10% sodium hydroxide will also reduce the odor of the distilled solvent by removing the thiols.

C. POLYURETHANE THINNER:

The compositions of the new and distilled polyurethane are listed in TABLE 5. The "cut" temperature during the distillation was approximately 225 °F according to FIGURE 3.

The new polyurethane thinner is a mixture of 2-butanone (MEK), toluene, xylene, n-butyl, and both normal and isomeric hexyl acetates, naphtha, and a trace of amyl acetate. The recycled polyurethane thinner had in addition several alco methoxyethyl acetate, and small amount of α-pinene (from turpentine). Many trace compounds were also seen. MEK (wh has a boiling point of only 176 °F.) and hexyl acetate (which has boiling point of 337 °F.) of the new polyurethane were relatively depleted in the recycled material, while most of the additional components boil from 200-250 °F., though some boil higher. The added alcohols make the greatest effective difference by increasing the polarity and the hydrogen bonding capacity of the solvent.

Due to the difference of compositions between the new and the distilled polyurethane thinners, the recycled polyurethane thinner is not acceptable for paint thinning, but can be used for painting surface preparation (wipe-down) and painting equipment cleaning.

The recycled polyurethane thinner at Tooele Army Depot is estimated to be 4,000 gal/yr. The painting surface preparation requires approximately 1,000 to 2,000 gal/yr, while the painting equipment cleaning requires approximately 1,000 gal/yr. Therefore, there is approximately 1,000 to 2,000 gal/yr of "excess" recycled polyurethane thinner which can not be used for paint thinning.

The majority of used polyurethane thinner (approximately 8,000 gal/yr - 1,000 gal/yr = 7,000 gal/yr = 35 gal/day) came from waste paint, i.e. prepared but not used paint. If a small batch of paint is prepared each time, the quantity of waste paint could be reduced.

If the waste paint reduction rate is one-third, i.e., reducing 12 gal/day, than the used polyurethane thinner would be approximately 5,600 gal/yr and the recycled thinner would be approximately 2,800 gal/yr. This quantity of recycled thinner would be just enough for painting surface preparation and painting equipment cleaning. That is, no "excess" recycled thinner is to be worried about.

Three recommendations have been made for the management of the used polyurethane thinner:

1. Strictly control the batch size of paint prepared each time in order to reduce the quantity of waste paint.

TABLE 5. COMPOSITION OF NEW AND DISTILLED POLYURETHANE THINNER

COMPOSITION	BOILING POINT (°F)	NEW PRODUCT (%)	DISTILLED (%)
Hexyl Acetate	337	47.6	7.2
2-Butanone (MEK)	176	20.4	8.3
Toluene	231	10.6	18.1
1-Butyl Acetate	257	11.5	19.3
m-Xylene	282	4.5	5.0
Naphtha	86-140	2.7	<0.3
o-Xylene	291	1.6	2.5
p-Xylene	281	0.6	2.2
Pentyl Acetate	299	0.5	<0.3
Methoxyethyl acetate	--	--	16.0
Isobutyl Alcohol	225	--	6.8
n-Butyl Alcohol	244	--	2.9
a-Pinene	316	--	2.0
Ethoxyethyl acetate	293	--	1.5
Alkanes	97-258	--	1.3
4-Methyl-2-Pentanone	240	--	1.2
1-Methoxy-2-Propanol	248	--	1.1
2-Heptanone	305	--	1.0
Others	--	--	3.0

2. Consult paint manufacturer and use recycled polyurethane thinner on a trial scale, or sell the "excess" recycled thinner to other users.

3. Distill the used polyurethane thinner in several steps based on the main ingredients' boiling points so that the recycled thinner would be closer to the new thinner composition. If necessary, a vacuum system may be added to reduce the required distilling temperature.

Tooele Army Depot is currently evaluating all these three recommendations.

OPERATION AND MAINTENANCE

A full time operator is retained by Tooele Army Depot to operate and maintain the solvent recycling system. The frequencies of still units cleaning are depending on the type of solvents recovered. For example, the unit for 1,1,1-trichloroethane should be cleaned after every 100 gallons of used solvent recovery; the unit for Stoddard solvent usually does not required much of cleaning; the unit for polyurethane thinner has to be cleaned every three days of operation and usually required pre-soaking of vessel bottom paint residuals for couple hours with heated lacquer thinner.

During the cleaning, the operator has to wear half-face respirator with organic vapor cartridge filter, eye protection and rubber gloves. The residuals have to be scraped off from the tank bottom to a bucket and then transferred to a 55-gallon hazardous waste drum for disposal.

ECONOMIC ANALYSIS

The economic analysis for the used solvent disposal without recovery and the recovery with the three distill units at Tooele Army Depot are shown in APPENDIX.

The quantities of solvents and the costs are based on the actual operational data available at the time of this study. Because there is no contractor-provided recycling services for 1,1,1-trichloroethane and polyurethane thinner at Tooele Army Depot area, the economic analysis does not include this option.

The capital investment for the centralized distillation system at Tooele Army Depot is approximately $112,800. The gross annual savings for onsite distillation is approximately $18,540. Based on a 10% discount factor, the pay back period of the capital investment is approximately 3 years and 1 month for three distill units alone, and approximately 9 years and 1 months including the building.

SUMMARY AND CONCLUSION

Based on the one year operation experience at Tooele Army Depot, the recycling of used 1,1,1-trichloroethane and Stoddard solvent with onsite distillation is a viable and economic alternative; the recycling of used polyurethane thinner, however, requires more studies.

Three recommendations have been made for the management of the used polyurethane thinner: 1. Reduce the quantity of waste paint by strictly control the batch size of paint prepared each time; 2. Trial use of the recovered thinner, or sell the "excess" recycled thinner; 3. Adjust the distillation procedures to improve the recycled solvent quality so that it could be reused for its original purpose. Tooele Army Depot is currently evaluating these three recommendations.

ACKNOWLEDGEMENTS

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APPENDIX

ECONOMIC ANALYSIS FOR USED SOLVENT RECYCLING SYSTEM AT TOOELE ARMY DEPOT

1. OPTION A--Used Solvent Disposal Without Recycling:

	TCA	STODDARD	THINNER	
a. Virgin solvent needed, gal/yr	23,760	16,000	10,460	
b. Cost of virgin solvent, $/gal	7.49	0.89	5.12	
c. Total cost of virgin solvent, $/yr	177,960	14,240	53,560	
d. % solvent spent, %	67	15	32	
e. Quantity of used solvent, gal/yr	7,840	13,600	7,110	
f. Cost of used solvent disposal, $/gal	3.25	3.44	2.27	
g. Total cost of used solvent disposal, $/yr	25,480	46,780	16,147	
h. Annual costs for each solvent, $	203,440	61,020	69,700	
i. TOTAL COSTS, $				$334,160

2. OPTION B--Centralized Installation-Owned Distillation:

	TCA	STODDARD	THINNER	
a. Virgin solvent required (w/recycle), gal/yr	20,000	6,500	8,000	
b. % of solvent spent, %	67	15	32	
c. Quantity of solvent for distillation, gal/yr	6,600	5,530	5,440	
d. Still efficiency, %	78	86	46	
e. Quantity of solvent reclaimed, gal/yr	5,150	4,750	2,500	
f. Still bottom volume, gal/yr	1,210(L*)/240(S*)	780	2,940	
g. Still bottom disposal cost, $/gal	3.25(L)/30.91(S)	3.44	21.80	
h. Still bottom disposal cost, $/yr	3,930(L)/7,420(S)	2,680	64,090	
i. Total still bottom disposal costs, $/yr				$78,120
j. Unit cost of virgin solvent, $/gal	7.49	0.89	5.12	
k. Cost of each virgin solvent, $/yr	149,800	5,790	40,960	
l. Total cost of virgin solvents, $/yr				$196,550
m. Total cost of 3 stills (including installation), $				$49,000
n. Operating costs excluding manpower, $/yr				$5,000
o. Manpower requirements, $/yr				$36,000
p. Building (20 year life), $				$80,000

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* NOTE-- L: liquid; S: solid/sludge

Cost Summary -

(a) Capital Costs, $

3 stills (incl installation)	$49,000
Building	$80,000
Salvage value of building after 10 years (present worth)	($16,200)
Total capital investment	$112,800

(b) O & M Costs, $/yr

Virgin Solvent cost	$196,500
Still bottom disposal	$78,120
Operating cost	$5,000
Manpower	$36,000
Total O&M costs, $/yr	$315,620

3. COST COMPARISON BETWEEN OPTION A AND OPTION B--

a. Gross annual savings with OPTION B compared with OPTION A (not including capital investment):

$334,160 - $315,620 = $18,540

b. Payback period: Approximately 3 years, 1 month for equipment costs only; and
Approximately 9 years, 1 month for equipment and building costs.

Year	Annual Savings	10% Discount Factor	Accumulative Savings
1	$18,540	0.954	$17,690
2	18,540	0.867	33,760
3	18,540	0.788	48,370
4	18,540	0.717	61,660
5	18,540	0.651	73,730
6	18,540	0.592	84,710
7	18,540	0.538	94,680
8	18,540	0.489	103,750
9	18,540	0.445	112,000
10	18,540	0.405	119,510

USE OF ALTERNATIVE CHEMICAL PAINT STRIPPERS TO REDUCE TTO DISCHARGES AND MINIMIZE HAZARDOUS WASTE

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INTRODUCTION

Background

In 1984 the U.S. Environmental Protection Agency (U. S. EPA) placed a limit of 2.13 mg/l on the allowable concentration of Total Toxic Organics (TTO) which can be discharged from metal finishing operations. U.S. Army installation personnel operating these facilities find it difficult to comply with this regulation when using the popular cold chemical paint strippers currently available. The cold stripper formulations are usually based on methylene chloride and phenol. Both of these compounds contribute to TTO. Besides contributing to the TTO problem, methylene chloride is a suspected carcinogen, and methylene chloride wastes are among the solvent wastes under evaluation by U. S. EPA for potential ban from landfill disposal.

Objective

The objective of this study was to identify and evaluate commercially available paint strippers and laboratory developed strippers. Successful strippers are operationally effective and environmentally acceptable replacements for strippers based on methylene chloride. The goal is to alleviate TTO compliance problems and minimize environmental and health risks and disposal liabilities.

Approach

To test operational success, alternative stripper formulations were first evaluated in the laboratory. Materials meeting the criteria established for success in the laboratory tests were subsequently evaluated on a pilot scale. The environmental, health, and safety aspects of the selected strippers were also evaluated to ensure that the candidates are acceptable replacements. The final step in this process is a full-scale field test.

EVALUATION CRITERIA FOR AN ACCEPTABLE PAINT STRIPPER

Criteria for a successful paint stripper were developed in collaboration with Sacramento Army Depot (SAAD). The following criteria were selected:

1. Acceptable stripping speed (SAAD upper limit of 2 hours)
2. Effective for a broad spectrum of coatings
3. Not rapidly evaporated or depleted and easily replenished when it does become depleted
4. No TTO contributing chemicals
5. Environmentally acceptable
6. Safe to use
7. Relatively easy to dispose
8. Commercially available
9. Easy to procure

In addition, more specific criteria for environmental, health, and safety acceptability of an alternate paint stripper were selected in cooperation with SAAD. These criteria are listed in Table 1.

SELECTION OF COATINGS AND STRIPPERS FOR TESTING

Based on a knowledge of coatings chemistry, coatings for stripper testing were selected based on common occurrence in the military inventory and, in some cases, because they represented the hard-to-strip end of the spectrum. Three coating systems were selected. All were tested on aluminum substrate and one on steel. Table 2 lists the coating systems by specification, resin type, and substrate material.

Candidate replacement strippers were solicited from industry and were previewed for probable success before inclusion in the test program. Laboratory developed formulas were formulated based on a working knowledge of paint stripper raw materials gathered during the course of this evaluation. (Organic strippers may contain any or all the following materials: (1) primary solvents, (2) cosolvents, (3) activators, (4) retarders, and (5) surfactants.)

MS-111, which conforms to Mil-R-46116, is a stripper which contains methylene chloride, phenol, and formic acid. It was included in this study as a control against which alternatives would be measured. None of the strippers evaluated in FY 89 contain methylene chloride or phenol both of which are TTO contributors. Common solvents in the other alternative strippers include 2-(2-butoxyethoxy) ethanol, n-methyl-2-pyrrolidone, monoethanolamine, aromatic hydrocarbon solvents, and tetrahydrothiophene 1-1 dioxide.

Table 1. Environmental, Health, and Safety Hazard Criteria for Paint Strippers

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I. Degree of Hazard

1. Concentration of hazardous components in stripper
2. Safety
   - a. Corrosivity
   - b. Reactivity
   - c. Ignitability
3. Toxicity and Environmental Fate
   - a. Human toxicity (TWA--OSHA, TLV, carcinogenicity, mutagenicity, teratogenicity, irritation, other toxicity
   - b. Environmental toxicity and fate
     - (1) Toxicity
       - (a) Acute
       - (b) Chronic
     - (2) Accumulative environmental fate
       - (a) Environmental transport
       - (b) Bioaccumulation
       - (c) Persistence

II. Use Factors

1. Volume of stripper used per year
2. Use conditions (e.g., elevated temperature)
3. Health regulations
4. Discharge restrictions

III. Disposal considerations

1. Regulations
2. Effects on sewage treatment plants
3. Costs

Table 2. Coating Systems Selected for Study

	Specification for:			
Designation	Primer	Topcoat	Coating Type	Substrate Material
A	TT-P-1757	TT-E-489	Zinc-chromate/ Alkyd	Aluminum
B	MIL-P-24441, Formula 150	MIL-P-24441, Formula 152	Epoxy Polyamide/ Epoxy Polyamide	Aluminum
C	MIL-P-53030	MIL-P-53039	Water Thinned Epoxy/ CARC Urethane	Aluminum
D	MIL-P-24441, Formula 150	MIL-P-24441, Formula 152	Epoxy Polyamide/ Epoxy Polyamide	Steel

PROCEDURES AND METHODS

Stripper Performance

Steel and aluminum stock panels were cut into 2 by 3 inch coupons with a 0.25 inch hole drilled on center and 0.5 inch from one end. Cleaned panels were coated on one side at the manufacturer's recommended dry film thickness using conventional air atomization equipment. Dried test panels were aged for 30 days at 105 degrees F in a drying cabinet.

The laboratory evaluation of stripping performance was based on a laboratory-scale mockup of a typical stripping process. Steps in the test were immersion in stripper, caustic dip for acidic strippers, water rinse, and steam cleaning. Nineteen (19) alternate stripper formulations were evaluated in FY89 and an additional eleven (11) were analyzed in FY88. These strippers were evaluated under controlled conditions with the four coating/substrate combinations on uniform coupons which were described previously. Manufacturer's recommendations for optimal operational conditions were followed. Stripping parameters are listed in Table 3. Strippers were evaluated for percentage of coating removed for each paint system at specific time intervals. The percentage of coating removed was determined by overlaying the coupon with a clear mylar grid subdivided into 20 equal areas. Percentages were determined to the nearest 5 percent.

Table 3. Stripping Parameters

Stripper	Stripping Temperature	Stripper Concentration	Hot Caustic Dips
FY 89			
Ardrox 2302	71 C (160 F)	Neat	No
Ardrox 5300-W	82 C (180 F)	Neat	No
Brulin Non-Chlorinated	82 C (180 F)	Neat	No
Chemical Solvents SP-MNP	82 C (180 F)	Neat	No
Eldorado HT-2230	82 C (180 F)	Neat	No
EZE 570-81	71 C (160 F)	Neat	No
Grow Group Non-Meth 161	Ambient	Neat	No
Intex Chemical 8798	82 C (180 F)	Neat	No
McGean-Rohco Cee Bee A-477	82 C (180 F)	Neat	No
Omega R-824	71 C (160 F)	Neat	No
Paint Tech. Center (CERL) #12	85 C (185 F)	Neat	No
Paint Tech. Center (CERL) #13	88 C (190 F)	Neat	Yes
Paint Tech. Center (CERL) #14	77 C (170 F)	Neat	No
Patclin 106 Q	82 C (180 F)	Neat	No
Patclin 125	82 C (180 F)	Neat	No
Pavco Decoater 3400	82 C (180 F)	Neat	No
Pentone Penstrip R-3936	82 C (180 F)	Neat	No
Turco 5555-B	71 C (160 F)	Neat	No
Turco 5668	82 C (180 F)	Neat	No
FY 88			
Enthone S-26	Ambient	Neat, 20%, 10%, 5%	Yes
Envirosolv	Ambient	Neat	Yes
Fine Organic 606	82 C (180 F)	Neat	No
Grow NonMeth 120	49 C (120 F)	Neat	No
Grow NonMeth 140	49 C (120 F)	Neat	No
Key Chemical 570	79 C (175 F)	Neat	No
MS-111	Ambient	Neat	Yes
Oakite ALM	82 C (180 F)	Neat	No
Patclin 103B	82 C (180 F)	25%	No
Patclin 104C	82 C (180 F)	50%	No
Pavco Decoater 3321	82 C (180 F)	Neat	No
SafeStrip-66	54 C (130 F)	Neat	No

Alternative strippers which performed adequately in the laboratory tests were evaluated in a pilot test at SAAD using depot parts rather than test coupons. Stripping temperatures and dilution ratios with water were the same as in the laboratory tests. Parts were placed in a 15-gallon dipping basket and lowered into the stripper in a 25-gallon stainless steel tank. After stripping, the parts were rinsed in water in a 55-gallon drum and finally were cleaned with a steam/hot water lance.

Alternative strippers performing successfully in the pilot scale evaluation were considered for full scale production use at SAAD. Full scale evaluation was performed during normal production operations at SAAD in a 1500 gallon tank. Qualitative results as well as periodic quantitative coupon analysis were reported by SAAD personnel. Quantitative coupon analysis was conducted employing prepared specimens identical to those used in laboratory evaluations except that they measured 3 by 9 inches.

Environmental, Health, and Safety Evaluation

After criteria for evaluation of environmental, health, and safety acceptability were selected, a process was needed to assign numerical ratings to permit a quantitative comparison of the hazards associated with each stripper. We developed a procedure which consists of a matrix for each stripper in which each criterion was scored for each component of the stripper. If data were available from the manufacturer's Material Safety Data Sheet for a characteristic of the stripper mixture, a total stripper score for that characteristic could be directly assigned. In most cases, however, a total weighted average score for each criterion for the total stripper mixture was calculated by summing the result of the score for each component times the percent of that component in the stripper. A total score for each stripper was determined by summing characteristic scores. In addition, in order to evaluate the potential impact of a particularly hazardous component, a worst case hazard score was calculated for each stripper by summing the highest score for a component in each hazard category.

Several existing scoring procedures for individual criteria were used (Table 4). If a score were reported in the literature for a criterion for a stripper component, that score was used. In other cases, the same procedure was used to assign a score. If data for assigning a score were lacking, the values were calculated if possible. There were no existing scoring procedures for corrosivity, so we developed our own scale similar to those for other criteria which were found in the literature.

Table 4. Rating Schemes Applied in Environmental and Safety Evaluation of Paint Strippers

Rating Scheme	Criteria Rated	Scale*	Reference
Sax Toxicity Ratings	Toxicity	0 - 3	1
National Academy of Sciences Hazard Ratings	Fire Hazard, Aquatic Toxicity, Water-borne Human Toxicity	0 - 4	2
National Fire Protection Association Hazard Classifications	Flammability, Reactivity	0 - 4	2
CERCLA Toxicity Ratings	Toxicity	0 - 3	3
Ontario Ministry of the Environment Rating Scales	Bioaccumulation, Toxicity	0 - 3	4
Developed for this study	Corrosivity	0 - 3	5

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* In all cases, 0 equals no or minimal effect and the highest score equals the highest level of effect.

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RESULTS

Stripper Performance

The results of the FY89 laboratory stripping tests are shown in Table 5. Table 6 shows the results of laboratory evaluations conducted in FY88 which have been reported previously and are included here for comparison purposes. The strippers are listed in order of descending stripping power.

Table 5. Results of Laboratory Paint Stripping Tests (FY89)

Stripper	0.5 hr	1.0 hr	1.5 hr	2.0 hr	3.0 hr
MS-111	ABCD*				
PTC #13	ABCD				
Turco 5668	-	AD	ABCD		
McGean-Rohco A-477	A	A	ABD	ABCD	
Patclin 106Q w/seal	AD	AD	ACD	ACD B=20%	
Intex 8798	A	ACD	ACD	ACD B=85%	ABCD
Ardrox 2300	AC	AC	AC	ACD B=30%	
Patclin 125	D	AD	AD	ACD B=65%	
Ardrox 5300-W	A	A	AD	ACD B=50%	
Eldorado HT-2230	A	A	A	ACD	
PTC #12	A	A	AD	ABD	
EZE 570-81	AD	AD	AD	AD C=30%	

Table 5, Continued

Omega R-824	A	A	AD	AD B=90% C=80%
Pentone R-3936	A	A	AD	AD C=5%
Pavco Decoater 3400	A	A	A	ACD
Chemical SP-MNP	A	A	A	A D=90%
PTC #14	A	A	A	A D=15%
Turco 5555-B	A	A	A	A
Grow Non-Meth 161	-	-	A	A
Brulin Non-Chlorinated	-	-	-	-

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*A: zinc-chromate/alkyd (aluminum); B: epoxy polyamide/epoxy polyamide (aluminum); C: epoxy/polyurethane CARC (aluminum); D: epoxy polyamide/epoxy polyamide (steel)

Table 6. Results of Laboratory Paint Stripping Tests (FY88)

Stripper	0.5 hr	1.0 hr	1.5 hr	2.0 hr	3.0 hr
MS-111	ABCD*	-	-	-	-
Fine Organic 606	ABCD	-	-	-	
Patclin 104C 50%	ABC	ABCD	-	-	-
Enthone S-26 neat	AC	AC	AC	ABCD	-
Enthone S-26 20%	A	AD	AD	ABCD	-
Enthone S-26 10%	A	AC	ACD	ABCD B=95%	-
Patclin 103B 25%	AD	AD	AD	ACD B=65%	ACD B=80%
Oakite ALM	A	A	A	ABD C=35%	ABCD
Enthone S-26 5%	-	-	-	AD B=40% C=80%	-
SafeStrip-66	A	A	AD	AD B=10% C=15%	AD B=65% C=20%
Key Chemical 570	A	A	A	A	A
Pavco Decoater 3321	A	A	A	A	A
Nonmeth 120	A	A	A	A	-
Nonmeth 140	A	A	A	A	-
Envirosolv L	-	-	-	A A=50%	-

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*A: zinc-chromate/alkyd (aluminum); B: epoxy polyamide/epoxy polyamide (aluminum); C: epoxy/polyurethane CARC (aluminum); D: epoxy polyamide/epoxy polyamide (steel)

Of the strippers evaluated in FY89 three performed at the level of the control stripper MS-111, within the established two hour time constraint. This brings to seven the total number of strippers which have been successful in laboratory evaluation. Enthone S-26 for reasons previously reported was not considered to be a successful laboratory candidate.[1] The remaining candidates except for USACERL formulated PTC #13 were evaluated in pilot scale tests at SAAD. PTC #13 is not commercially available and insufficient health and safety data were available at the time pilot scale tests were performed; therefore, it was not included in those tests. Table 7 lists the strippers evaluated in the pilot scale tests at SAAD.

Table 7. Pilot Scale Test Candidates

Strippers:
McGean-Rohco Cee Bee A-477
Fine Organics FO 606
Oakite ALM
Patclin 103B
Patclin 104C
Turco 5668

All the strippers evaluated in pilot scale tests at SAAD except for Patclin 103B performed at a level consistent with laboratory test results. The steam cleaning operator reported eye irritation from Patclin 104C. The addition of a hot caustic dip eliminated this problem, but the line operators still complained of the odor. Life cycle costs for this stripper were estimated to be higher than for the other alternative strippers because of its higher evaporation rate and the need for a hot caustic or hot water rinse. Further consideration of Patclin 104-C was withdrawn. The remaining four strippers were considered to be candidates for full-scale production tests.

Environmental, Health, and Safety Evaluations

The results of the ratings of the most promising candidate strippers compared to MS-111 for environmental, health, and safety criteria are listed in Table 8. The strippers were scored based on both the concentrated product and the mixture in use, taking into account the dilution of some of the strippers with water. The higher the total score, the greater the risks. The total weighted average scores show that any of the seven candidate strippers are less hazardous than MS-111. Based on

Table 8. Paint Stripper Hazard Summary

		MS-111	Oakite ALM	Pat. 103	Pat. 104
	HUMAN		1.5*	0.6	1.0
TOXICITY	TOXICITY	2.2	2.3**	2.2	1.9
	ACUTE		0.5	0.2	0.6
	ENVIRONMENTAL	1.1	0.8	0.9	1.1
	CHRONIC		1.4	0.6	0.9
	ENVIRONMENTAL	2.1	2.1	2.3	1.8
ENVIRONMENTAL FATE	BIOACCUM-		0	0.1	0.1
	ULATION	0.1	0	0.2	0.2
	PERSISTENCE		0.2	0.1	0.2
		2.5	0.4	0.3	0.5
	ENVIRONMENTAL		1.3	0.6	1.0
	TRANSPORT	2.9	2.0	2.1	1.9
SAFETY	CORROSIVITY		1.1	0.4	0.8
	OF STRIPPER	3.0	1.7	1.6	1.7
	REACTIVITY		0.6	0.4	0.6
	OF STRIPPER	1.2	0.8	1.5	1.2
	IGNITABILITY		1.1	0.5	0.6
	OF STRIPPER	1.2	1.6	1.8	1.2
TOTALS (WITH H_2O)		no water	7.7	3.5	5.7
TOTALS (W/O H_2O)		16.3	11.7	12.9	10.8

* = 1st number calculated w/ water ** = 2nd number calculated w/o water

Table 8, Continued.

			F.O. 606	C.B. A-477	Turco 5668	PTC
TOXICITY		HUMAN TOXICITY	2.1	2.6	2.0	2.2
		ACUTE ENVIRONMENTAL	0.6	0.8	0.6	1.0
		CHRONIC ENVIRONMENTAL	1.9	2.0	1.6	2.4
ENVIRONMENTAL		BIOACCUM-ULATION	0	0	0	0
	FATE	PERSISTENCE	0.7	0.5	0.2	0
		ENVIRONMENTAL TRANSPORT	1.8	1.6	1.4	1.7
		CORROSIVITY OF STRIPPER	2.7	2.8	2.4	1.4
SAFETY		REACTIVITY OF STRIPPER	0.2	0.5	0.4	1.6
		IGNITABILITY OF STRIPPER	1.1	1.4	1.0	1.6
TOTALS (WITH H_2O)			no water	no water	no water	no water
TOTALS (W/O H_2O)			11.1	12.2	9.8	11.9

* = 1st number calculated w/ water ** = 2nd number calculated w/o water

composition in the stripper tank, the strippers which do not contain water have less favorable environmental hazard ratings than the other candidate strippers, primarily because they are not diluted with water. Scores based on components other than water are relatively comparable for the candidate strippers and in all instances less hazardous than MS-111. Table 9 lists the order of relative hazard for the alternative strippers based on weighted average and worst case scores. Turco 5668 appears to be slightly preferable from an environmental and safety hazard point of view. Hazardous waste concerns and environmental regulations restricting discharges are also much more favorable for the candidate strippers compared to MS-111 (Table 10).

Table 9. Total Stripper Hazard Scores from Worst to Best

Weighted Average (without water)		Worst Case	
MS-111	16.3	MS-111, ALM	22.0
Patclin 103	12.9		
Cee Bee A-477	12.2	Patclin 103, 104	19.5
PTC	11.9		
ALM	11.7	PTC	17.0
Patclin 104	11.5		
FO 606	11.1	Cee Bee, Turco, FO 606	16.0
Turco 5668	9.8		

Table 10. Regulatory Restrictions

	MS-111	Oakite ALM	Pat. 103	Pat. 104
HAZARDOUS WASTE CONCERNS	4	2	1	4
WASTEWATER EFFLUENT CONCERNS	4	2	1	1
DISCHARGE RESTRICTIONS	TSCA,RCRA CERCLA CWA	TSCA,FIFRA RCRA CWA	TSCA,CWA	TSCA
HEALTH & SAFETY REGULATIONS	3 TWA VAL 500 PPM 5 PPM 5 PPM	3 TWA VAL 3 PPM .2 PPM 3 PPM	1 TWA VAL 3 PPM	Not Established
ADDITIONAL HEALTH & SAFETY CONCERNS				

MS - 111	All the compounds are a hazardous waste and wastewater effluent concern. They appear in several lists of hazardous compounds that are either now or will soon be stringently regulated. Also some of them are carcinogens, mutagens and teratogens.
OAKITE ALM	Few of the compounds are on hazardous waste and wastewater concern lists. There are no definite carcinogens but equivocal data that one may be. Three components are mutagens and teratogens.
PATCLIN 103B	Few of the compounds are on hazardous waste and wastewater concern lists. There are no carcinogens, but a mutagen and teratogen and two possible teratogens.
PATCLIN 104C	Four of the compounds are on hazardous waste lists and wastewater concerns. There is one suspect carcinogen and mutagen, some possible teratogens.

Table 10, Continued

	F.O. 606	C.B. A-477	TURCO 5668	PTC
HAZARDOUS WASTE CONCERNS	1	0	2	2
WASTEWATER EFFLUENT CONCERNS	2	0	2	2
DISCHARGE RESTRICTIONS	TSCA,RCRA	TSCA	TSCA,CERCLA CWA	TSCA,RCRA CERCLA,CWA
HEALTH & SAFETY REGULATIONS	1 TWA 3 PPM 3 PPM	2 TWA 3 PPM	1 TWA 3 PPM	1 TWA 5 PPM
ADDITIONAL HEALTH & SAFETY CONCERNS				

F.O. 606	One component is on hazardous waste and wastewater concern lists. There are one possible carcinogen, two mutagens and a teratogen.
C.B A-477	The components are not listed as definite hazardous waste or wastewater concerns. There are one suspect carcinogen and two mutagens, one teratogen.
TURCO 5668	Two components are considered hazardous waste and wastewater concerns. Three are mutagens, one a confirmed teratogen and another a possible teratogen.
PTC	Two components appear on hazardous waste and wastewater lists. There are two mutagens and one teratogen, three possible teratogens.

FIELD TESTS

Oakite ALM was evaluated in FY89 at SAAD in a full-scale field test. Results were somewhat disappointing. Depletion of the active components either through evaporation or absorption in the tank led to an early decline in stripping power as shown by excessive stripping time both for production parts and for uniform test coupons. Because of the nature of the production operations at SAAD the evaporation rate was above an acceptable level. The manufacturer analyzed the depleted stripper and provided a replenishment solution. The replenishment proved to be of marginal help. The full-scale evaluation of Oakite ALM was discontinued after approximately 9 months at SAAD.

Besides the stripper performance evaluation, environmental monitoring was performed during the field test with Oakite ALM. Samples of stripper from the tank, rinse water, and steam sump liquid were collected periodically for chemical analyses. Results of the analyses revealed the presence of a complex mixture of aromatic hydrocarbon compounds besides the compounds reported by the manufacturer as components of the stripper. These compounds increase the hazard and decrease the environmental acceptability of the stripper compared to the estimates based on the composition listed by the manufacturer. Of the 14 positively identified additional compounds, 13 are on the TTO list. Ten of the compounds are listed hazardous wastes and 12 are priority pollutants. One is on the California Proposition 65 list of candidate chemical carcinogens and two others are possible carcinogens. Four of the compounds are mutagens and four are teratogens.

No other full-scale production tests have been conducted. However, FO 606 will be evaluated at SAAD and Turco 5668 will be used at Red River Army Depot (RRAD) in FY90.

CONCLUSIONS AND RECOMMENDATIONS

Seven candidate strippers demonstrated performance in laboratory tests consistent with the goals of the study and six of these strippers were evaluated on a pilot scale. Four of the pilot-scale candidates tested at SAAD have been recommended for full-scale production use on an experimental basis. Oakite ALM was evaluated in full-scale production at SAAD and did not meet their minimum requirements nor did it perform at a level consistent with laboratory and pilot-scale tests. In addition, chemical analyses of ALM stripper and rinse water samples revealed the presence of a complex mixture of aromatic hydrocarbon compounds which were not listed by the manufacturer and pose considerable health and environmental risk. During FY90, Fine Organics FO-606 and Turco 5668 will be used at SAAD and RRAD, respectively. McGean-Rohco Cee Bee A-477 also is recommended for full scale use on a trial basis.

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ROTATING BIOLOGICAL CONTACTOR
AND AIRCRAFT PAINT STRIPPING WASTES

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ABSTRACT

The Naval Civil Engineering Laboratory has completed a pilot scale leveled demonstration of treating toxic organic laden wastewaters from Navy aircraft paint stripping facilities. The Navy operates 41 shore-based aircraft paint stripping facilities that in the past generated over 200 million gallons of highly contaminated and toxic wastewaters annually. A laboratory scale Rotating Biological Contactor (RBC) system tested earlier indicated that this technology was well-suited for treating the Navy's Aircraft Paint Stripping Wastewaters(APSW). The laboratory studies established that the phenolic paint stripping wastewaters were treatable by the RBC at phenol removal efficiencies and methylene chloride removal efficiencies greater than 95 percent (mean influent 280 milligrams per liter (mg/l) and 370 mg/l respectively). Therefore a pilot unit RBC was fabricated and field tested at the Pensacola Naval Aviation Depot (NAD). The test goal was to assess the performance of the RBC system under field conditions. The pilot RBC system was operated over a wide range of hydraulic and organic loadings during the seven month test period. The pilot plant performance was assessed by monitoring the reactor influent and effluent concentrations in terms of COD, phenol, methylene chloride, chromium, and 1,1,1-trichloroethane. Influent dissolved oxygen and pH were monitored. The microbiological populations associated with the various steady states were studied to gain further understanding of the RBC process. The RBC performance was not adversely affected under the variable field test conditions at average influent Chemical Oxygen Demand (COD) concentrations of 5000-6000 mg/l. The optimal operating parameters for both hydraulic and organic loadings based on the treatment performance for the presently discharged wastewater occurred at 0.12 gallons per day per square foot (gpd/sf) and 5.39 lb COD/day/1000 sf. Incoming wastes ranged from 0.12 to 0.54 gpd/sf. The RBC was able to handle the process shock loadings from organics that periodically occurred from the industrial discharges. The treatment unit also restored itself to normal treatment performance levels after the shock conditions were removed. The occurrence of chromium in paint stripping wastewaters did not pose a threat to regulatory compliance.

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ROTATING BIOLOGICAL CONTACTORS AND AIRCRAFT PAINT STRIPPING WASTES

The Naval Civil Engineering Laboratory has completed a pilot scale leveled demonstration of treating toxic organic laden wastewaters. The various research and developmental test phases concentrated on one specific type of industrial waste discharge, that issuing from Navy aircraft paint stripping facilities. The Navy operates 41 shore-based aircraft paint stripping facilities that in the past generated over 200 million gallons of highly contaminated and toxic wastewaters annually. These facilities are located at Naval Aviation Depots (NADs) and Naval Air Stations (NASs).

Consequently there exists a need to treat or otherwise neutralize these wastewaters. The Naval Civil Engineering Laboratory conducted a developmental test and evaluation (DT&E) of a rotating biological contactor (RBC). A laboratory scale RBC system tested earlier indicated that this technology was well-suited for treating the Navy's Aircraft Paint Stripping Wastewaters(APSW). Therefore, in this DT&E phase, a pilot unit was fabricated and tested in a Navy field environment. The site selected for the DT&E tests was the Pensacola Naval Aviation Depot (NAD) at Pensacola Naval Air Station, Pensacola, Florida.

The test goal was to assess the performance of the RBC system under field conditions and to meet the following four test criteria:

a) Discharge Regulations Compliance,
b) Organic and Hydraulic Loading Rates,
c) Upset Restart Time, and
d) Maximum Toxics Tolerance.

During the field test, these test parameters were studied over a wide range of conditions. In addition, other key operating conditions were investigated, such as the optimum influent feed compositions necessary for attaining the best levels of treatment. The RBC was operated over a period of 7 months during which time the performance of the system in removing Chemical Oxygen Demand (COD), methylene chloride, and 1,1,1-trichloroethane from the paint stripping wastewater was evaluated. The RBC performance was not adversely affected even under the variable field conditions of wastewater characteristics.

BACKGROUND

A total of 63 aircraft paint stripping facilities are operated by the Navy, 41 of which are shore operations and 22 are aboard ships. Six of the 41 shore operations are found at Naval Aviation Depots (NADs), while the remaining 35 facilities are located at Air Intermediate Maintenance Departments (AIMDs) inside the Naval Air Stations (NASs). The overall scheme of Navy Aircraft Paint Stripping operations is shown in Figure 1.

The six NADs are the major generators of APSW. The APSW contains significant concentrations and variety of hazardous chemicals including methylene chloride, phenols, 1,1,1-trichloroethane, ortho-dichlorobenzene, chromates, detergents etc. Untreated APSW is contributes to the violation of discharge limits at some installations and is impacting Navy owned treatment works (NOTWs) performance at others.

At the NADs, paint coatings from aircraft and ground support equipment are stripped to bare metal (or composite surfaces) as a part of the rework procedure. The aircraft paint stripping wastewater (APSW) is generated during the coating removal and washdown procedures. Although there are efforts at adopting wastewater-free paint removal options, it is unlikely such procedures could be ready for full implementation in the next few years. Even then, it is anticipated that the chemical stripping will not be completely displaced and will remain a significant portion of the Navy's paint stripping operations.

The Navy's practice for disposing APSW at the NADs has been that of discharge into the base industrial sewers (Figure 2). The exception here is the Alameda NAD which has chrome removal facilities right outside the strip cells or hangars. The APSW, after combining with other industrial wastewaters, are treated at Navy industrial waste treatment facilities. The effluents from here are either discharged to the Navy-Owned Treatment Works (NOTWs) at NADs Cherry Point, Jacksonville, and Pensacola, or to the Publicly Owned Treatment Works (POTWs) at NADs Alameda, North Island, and Norfolk. The NOTWs and the POTWs are essentially similar facilities commonly known as sanitary wastewater treatment plants which use biological processes to removal pollutants.

These Navy industrial wastewater treatment facilities are generally designed for the removal of inorganic pollutants with provisions for oil/water separation. The oil/water separators usually are quiescent type separators which allow the oil to float to the top and overflow to collection tanks. Sometimes, automated skimmers are employed to skim off the oil. Succintly, Navy industrial wastewater treatment facilities are actually plating shop wastewater treatment facilities. The treatment cesses designed to remove cyanide and heavy metals including avalent chromium, and to neutralize the waste stream. Typically, these facilities do not have effective treatment provisions for the removal of toxic organic pollutants in the APSW.

The NADs Alameda, North Island, and Norfolk have to comply with the EPA's metal finishing industry pretreatment standards, while NADs Cherry Point, Jacksonville, and Pensacola have to comply with the limits as specified in their respective National Pollution Discharge Elimination System (NPDES) permits. The APSW, without proper treatment, is impacting the ability of these Naval installations to meet their wastewater discharge limits.

The most critical problem faced by the Navy installations, relates to wastewater discharge regulations. With the recent passage of the Clean Water Act Amendment (1987), EPA is now requiring toxicity monitoring requirements for NPDES permits. This will have a direct impact on Navy installations that generate APSW since the latter is a source of toxic organics in the Navy's wastewater. Navy installations that discharge to municipal sewers will also be impacted. They will feel a ripple down effect as POTWs pass on down more stringent requirements reflecting their requirements.

In the past few years, as a result of regulatory pressure and lack of viable options for treating the phenols in the APSW, many of the NADs have switched to using phenol-free strippers. North Island and Pensacola NADs are two examples here. These phenol-free strippers formulations typically have very high concentrations of methylene chloride. The NADs have all also found out that the non-phenolic strippers are not very efficient. Commonly, two or three applications of these strippers would be needed to do the same job. This has resulted in increased stripper usage, labor costs and downtime of the aircraft. Additionally, there is also prolonged exposure of Navy personnel to methylene chloride's health hazards. The latter is a widely studied and known carcinogen. The author has learned recently that both North Island and Pensacola NADs are planning a return to the use of phenolic strippers.

DRY PAINT STRIPPING

The plastic media blasting (PMB) process has been investigated by various Navy organizations as a substitute for the chemical paint stripping process. It is expected that the PMB process cannot completely replace all chemical paint stripping due to the PMB's inherent process limitations. Most of the NADs have procured portable PMB equipment to be used in glove-boxes and walk-in blast booths for stripping aircraft parts and components. The use of PMB on airframes has not been approved by the proper authorities at NAVAIR. Many problems still need to be overcome before PMB can be approved for full implementation. There are equipment system problems and there are problems relating to process application. If equipment operators are not fully trained, highly skilled, or capable of maintaining concentration during work, expensive aircraft components could very easily be damaged.

INITIAL RESEARCH EFFORTS

NCEL was tasked by the Naval Facilities Engineering Command (NAVFAC) in FY84 to investigate the problem of Navy APSW disposal. A report which described the Navy's problem in handling this waste stream was prepared. This same report also assessed the state of technology and recommended a research and development plan.

In 1985, the APSW of NADs was characterized and laboratory studies were initiated. Laboratory treatability studies were conducted on four promising treatment options. Two of these were chemical and the remaining two were biological.

Treatability study results showed that the chemical oxidation option using hydrogen peroxide was feasible technically but not economically. The use of chlorine dioxide was found also to be excessively expensive. Of the two biological treatment options studied, the RBC process was determined to be more suited for the treatment of APSW. This was due mainly to its simplicity and inexpensive operations and maintenances when compared to the activated sludge process. Although the initial RBC study setup was crude and only simulated APSW was used in the experiments, results has shown its promise in removing phenols from the APSW.

In 1987, a laboratory scale RBC system was fabricated and studied. Both simulated and actual APSW were used. Again, the results were encouraging. The RBC process demonstrated tolerance of shock loads. It accepted COD and phenol concentrations of up to 8,000 mg/l and 2,000 mg/l respectively. In terms of overall organic loading, the system was taking 10 lb. COD/day/1,000 sq.ft. The laboratory RBC unit could easily treat 1,000 mg/l of phenol. In summary, the laboratory RBC unit was able to achieve a mean removal efficiency of 95 percent for both phenol and COD, and over 97 percent for methylene chloride. As a result of these studies, a field scale RBC system was fabricated for test and evaluation at a selected Navy site. This latter test is the subject of this report.

RBC THEORY

The principle involved in the biological treatment of wastewater is that of using microorganisms to breakdown pollutants in the wastewater. To sustain life and to grow, the microorganisms consume the pollutants or other available organic compounds in the wastewater along with dissolved oxygen. The microorganisms actually grow on the surface of the polyethylene media disks. This surface growth is kept wet by the constant rotation of the disks. It is there they consume the organics and imbibe dissolved oxygen from the liquid film that wets the surface growth. As the media disks rotate, the liquid film is alternately replenished with a fresh source of organics. Generally, in domestic wastewater treatment, the diverse variety of constituents in the wastewater can provide all that is needed by the microorganisms for growth. However this is not necessarily the case for industrial wastewaters. Nutrients are added to make up the required minimum nutrient needs for sustaining the growth process.

The RBC system is started by using a mixed population or culture of microorganisms from a domestic wastewater treatment plant. For this project, activated sludge and sewage from the primary clarifier at the Navy's sewage treatment plant at Pensacola was used to start the microbial growth on the RBC disks. It takes a few days from the introduction of sludge and sewage, before growth of microorganisms will start to occur.

The wastewater to be treated, in this case APSW, was then gradually added to the influent in increasing proportions so as to acclimate the microorganisms. To maintain a healthy growth of microorganisms on the disks, a certain disk rotational speed is used to produce sufficient shear so as to slough off excess microorganisms into the tank. These are carried off with the effluent from the RBC reactor. A settling tank is typically used to remove these biosolids from the effluent downstream. It is necessary to settle and remove these biosolids (cell tissue) otherwise if not removed would contribute to the organic level in the final effluent. As the organics are removed, the wastewater becomes pollutant clean.

Field Scale RBC Pilot System Description.

The field scale RBC pilot system was made up of three components They were the

a) Flow Equalization Subsystem.
b) RBC Reactor.
c) Monitoring Laboratory.

The flow equalization subsystem. Although the RBC process can operate and accommodate conditions beyond the typical ranges for biological system, variations in the feed can reduce its performance. This subsystem was designed for coping with large flow variations. There was also added a nutrient feed provision to enhance the growth of the microorganisms in the RBC reactor.

The RBC reactor. The RBC reactor is a specially fabricated rectangular steel tank which is partitioned into three compartments connected by strategically placed circular ports. The three compartments or three RBC stages are therefore operated in series. The circular media, or disks are affixed to a common axle which is driven by a electric motor. The disks are rotated. Approximately 40 % of the rotating surface area is submerged in the wastewater. There are four disks in each stage. Two more disks were added to each stage in later tests. They were all constructed of high density polyethylene.

The monitoring laboratory. A free standing 8' by 10' portable building was procured to serve as a field monitoring laboratory for the RBC system. This laboratory provided sheltered space for conducting monitoring tests, storage for analytical chemicals, wastewater samples and other supplies, and houses other activities of field personnel during the testing and evaluation of the RBC.

RBC System Installation

The field scale RBC pilot system was physically installed within a bermed area immediately outside of the hangar which houses the aircraft paint stripping operations at Pensacola (Figure 3). Our selection indicated that the test unit was to function as a pretreatment device.

Two 8'x10' portable aluminum buildings were procured and were anchored to the ground by base personnel. The RBC reactor and part of the flow equalization subsystem were placed inside one of the buildings. The second building housed the monitoring laboratory. Some of the storage drums used for flow equalization were left standing outside in between the two buildings. Base personnel connected electricity to both buildings, the laboratory in addition had a water line connected to it.

The APSW used for testing was withdrawn from an in-ground pit (sand trap) which is located between the hangar and the portable buildings. The wastewaters generated within the the paint strip cells is first collected in a deep sump inside the hangar and then pumped to the in-ground pit before being discharged into the industrial sewer.

FIELD TEST METHODOLOGY

The procedures used in this field test followed that typically practiced in evaluating biological treatment process. The field RBC system first had to be "started up" and become an established biological system. This was achieved by using an acclimation procedure to promote the satisfactory growth of microorganisms on the disks. Once the RBC system was established then several sets of conditions or steady-state phases were conducted.

The RBC system was operated over a wide range of hydraulic and organic loading conditions to test and evaluate the RBC process. The RBC process performance was assessed by monitoring the reactor influent and effluent concentrations in terms of COD, phenol, methylene chloride, chromium, and 1,1,1-trichloroethane. Influent dissolved oxygen and pH were monitored for process control purpose. The microbiological populations associated with the various steady states were studied to gain further understanding of the RBC process in this application. This was accomplished by performing microbiological studies on samples of microorganisms collected from the RBC disks.

The various project phases were:

I. Acclimation Phase.

II. RBC basic unit (Configuration A): 28 sq.ft. media surface area per stage, diluted APSW as influent feed,

(a) Steady State Phase I (Flow rate = 45 gpd)
(b) Steady State Phase II (Flow rate = 30 gpd)
(c) Steady State Phase III (Flow rate = 10 gpd)

III. RBC modified unit (Configuration B): 42 sq.ft. media surface area per stage, concentrated APSW as influent feed,

(d) Steady State Phase IV (Flow rate = 10 gpd)

(e) Steady State Phase V (Flow rate = 25 gpd)
(f) Steady State Phase VI (Flow rate = 40 gpd)

During each of these phases, paint stripping wastewater was collected and diluted or concentrated before feeding to maintain an approximate COD level of 5000 mg/l. Nutrient were added appropriately. With influent feed introduced at various rates, a wide range of loading conditions were tested. The acclimation phase was used to establish the microorganisms on the media and to adapt the mixed microbial culture to the paint stripping wastewater. Data on COD, methylene chloride, 1,1,1-trichloroethane for the influent and stagewise effluent of the RBC were collected during each phase of the project.

To facilitate process monitoring, test kits (Hach Kits, EPA approved) were used for analyzing COD, phenol and chromium. These analytical tests were done in the field laboratory. The use of test kits allowed quick turn around and gave the field crew greater control over the RBC process. Standard laboratory tests were also performed every now and then to double check the data obtained from the test kits. The use of test kits required minimum skill. This feature was consistent with the objective of providing a treatment option that was simple and easy to operate.

RESULTS OF FIELD TRIALS

The field scale RBC study aimed at testing the RBC system for its pretreatment potential under field conditons. The earlier studies conducted in the laboratory tested the RBC on a smaller scale and on phenolic stripping wastewater(synthetic and actual). By the time transition to the field occurred the activity due to regulatory pressures had switched to non-phenolic strippers. These contained appreciable amounts of methylene chloride. The laboratory studies established that the phenolic paint stripping wastewater is treatable using RBC at phenol removal efficiencies and methylene chloride removal efficiencies greater than 95 per cent (mean influent phenol:280 mg/l and mean influent methylene chloride:370 mg/l). Both the laboratory and field studies indicated that the occurrence of chromium in paint stripping wastewaters did not adversely affect the RBC performance and also did not pose a threat to regulatory compliance.

The RBC system potential to remove organics from the paint stripping wastewaters was evaluated on a basis of COD, methylene chloride and 1-1-1 trichloroethane. The RBC performance was studied over a seven month period. The RBC was subjected to a wide range of organic loadings during the study. The RBC performed well in removing organics under these varied loadings over long periods of time. The wastewater treated during the field study differed from the wastewater collected earlier and tested in the laboratory. Namely the activity had substituted non-phenolic strippers from that previously used. Secondly, extensive water reduction practices had been employed resulting in higher proportions of detergents in the wastewater. The increased concentrations of detergents resulted in severely depleted oxygen levels in the wastewater. (This was also borne out by noting large concentrations of foam in the test pit.) Consequently the field trials had to be altered. During the field study the stage 1 compartment of the RBC was supplied with diffused air to compensate for this depletion.

The steady state phases I-VI test data indicated that the nutrients additions (of glucose and sewage components) could be withheld from the influent by the end of the acclimation period. It became apparent that the paint stripping wastewaters could be treated biologically by itself at average influent COD concentrations of 5000-6000 mg/l. The optimal operating parameters for both hydraulic and organic loadings based on the treatment performance for the presently discharged wastewater occurred at 0.12 gpd/sf and 5.39 COD/day/1000 sf. Incoming wastes ranged from 0.12 to 0.54 gpd/sf. The RBC performed very well during the process shock loadings that occurred during the test runs. The treatment unit also restored itself to normal treatment performance levels after the shock conditions were removed.

The field studies conducted on the actual *non-phenolic* wastewaters revealed the potential of the RBC in meeting the pretreatment standards prescribed by the metal finishing regulations for Total Toxic Organics (TTO) for all of the steady states except VI which was run at the highest hydraulic conditions.

Also the treatment performance for the RBC met a significant limitation imposed by the regulators on Pensacola. The paint strip cells at Pensacola are required to comply with the hazardous waste regulation (40 CFR 261.3). This requirement specifies a limit of 25 ppm on discharges of paint stripping wastewaters from Building 3557. Thus the usage of this treatment scheme would eliminate contract hauling of wastes from the building.

CONCLUSIONS

The RBC system has proven itself to be a reliable and cost effective method of treating aircraft paint stripping wastewaters. It has characteristics of simplicity of operation and due to the low generation of biomass produced for the wastes treated structural stability is ensured. The RBC experiments conducted in the laboratory and in the field provide evidence of high degrees of removal of the most common toxic organics present in high concentrations in aircraft paint stripping wastewaters i.e. methylene chloride, phenol and 1,1,1-trichloroethane.

In comparison with other biological treatment units the RBC demonstrates 50 % lower operations and maintenance costs when compared to activated sludge. Also the RBC has more contact time and aeration capability, more and effective and controlled biomass sloughing when compared to a trickling filter.

The RBC may have application in treating wastewaters generated at Naval facilities due to industrial operations other than those tested under this program. It has the flexibility of being used as a pretreatment device or alternatively as a tertiary treatment unit at a NOTW. The simplicity of its operation, its process flexibility in adapting to organic shocks and its low costs make the RBC a suitable alternative for Navy requirements.

Stratification of Particulate and VOC Pollutants In Horizontal Flow Paint Spray Booths

By

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Introduction

The U.S. Environmental Protection Agency (EPA), in a joint program with the U.S. Air Force, has been conducting a research and development test program on emissions from paint spray booths. The goal of the program is to develop emissions control concepts that will permit efficient and economical control of pollutants from these sources. One approach is to reduce the volume of gases from the painting operation that must be processed in a control system. This could result in a corresponding reduction of control system capital and operating costs. This test program on an aircraft parts paint spray booth was designed to characterize the pollutant discharges both within and exiting a typical back-draw spray booth for which emissions control and flow reduction strategies are being developed.

The testing program from which the results of this paper are based represents two distinct efforts. The first was to assess the internal booth environment to define the industrial hygiene conditions within the booth, and the second was to define the emissions parameters which might govern the operating capability and limitations of a control concept. This paper presents the results of particulate and volatile organic compound (VOC) pollutant concentrations and flow studies of a horizontal flow spray booth. The results of the program indicate that flow management schemes in this type of booth might be devised which take advantage of the natural flow pattern and physical/chemical properties of the generated pollutants. This paper presents these findings and their implications for devising economical and efficient booth control strategies.

Site and Test Description

The objectives of the experiments were to determine how and where pollutants passed through and from the booth and the areas of highest concentration. The sampling scheme devised allowed development of a three dimensional representation of the concentration profile in the booth during painting. Thus, it was possible to observe how concentrations varied along the length of the booth and at different heights in the booth.

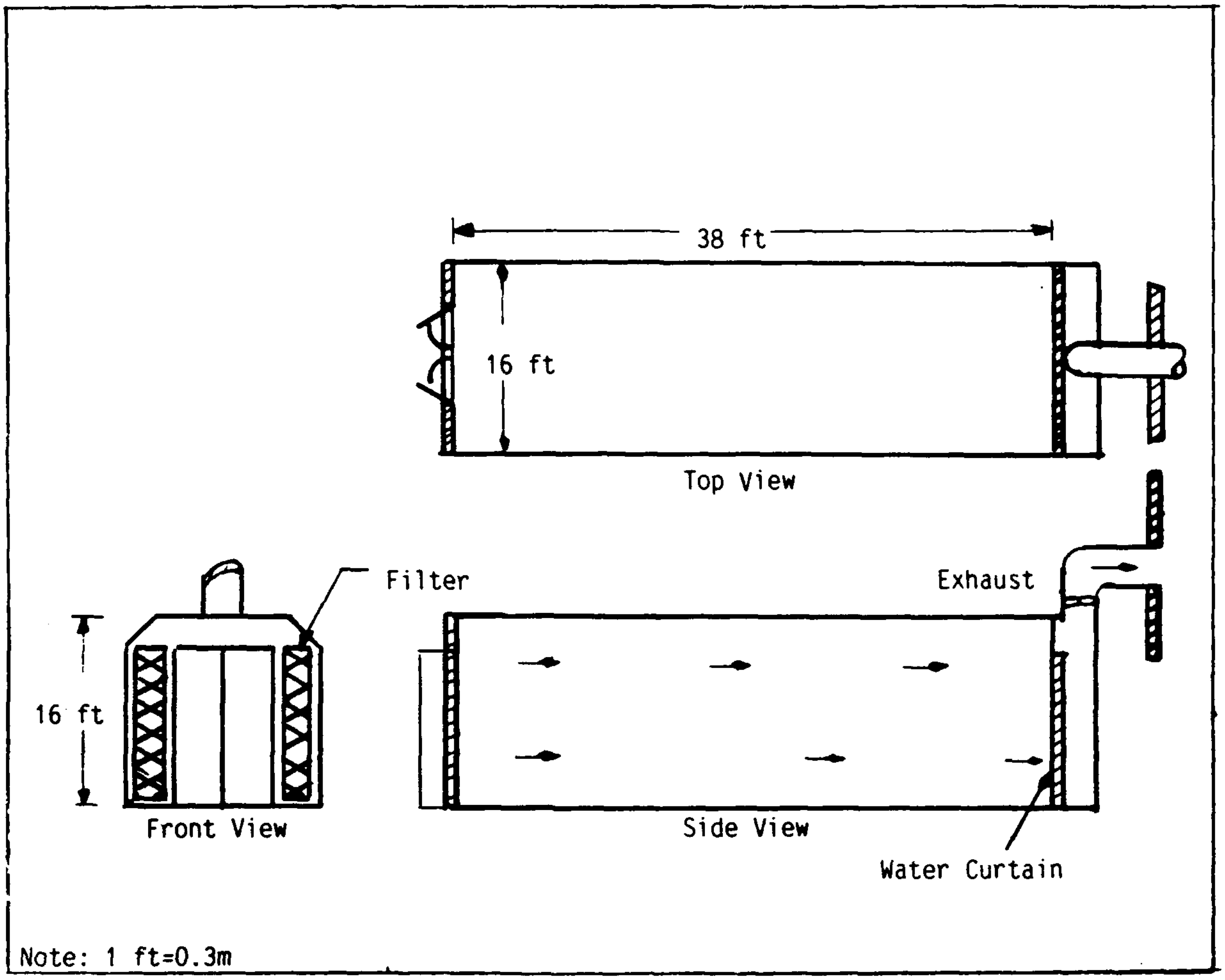

Figure 1. Spray Booth Diagram

The test site was a horizontal-flow back-draw spray booth with air flowing from the front to the rear of the booth exiting through a particulate removal water curtain. Figure 1 describes the general configuration and dimensions of the booth. The measured flow rate through the booth ranged between 11,000 and 11,500 SCFM (5.2 and 5.4 m^3/s).

The booth was instrumented with National Institute of Occupational Safety and Health (NIOSH) personal samplers positioned to form an approximate three dimensional grid matrix scheme inside the paint booth. The sampling instruments were positioned in the booth to define the average particulate concentrations experienced by each respective grid section during the test episode. Figure 2 illustrates the top and side views of the instrument locations in the booth. A total of 21 grid points were located in the booth. Three tests were performed to determine particulate concentration profiles in the booth using the NIOSH 500 sampling protocol and NIOSH personal sampling instruments. In addition, measurements were taken in the duct and at the painters' breathing zone to define duct and breathing zone particulate concentrations relative to the general booth interior. Particulate concentrations in the duct were determined using EPA Method 5 emissions sampling procedures.

Two tests were performed to define average VOC concentrations within the booth. The same grid scheme and sampling locations were used as described for the particulate tests. These experiments were conducted in accordance with the NIOSH 1300 procedure and using personal sampling instruments. Duct VOC measurements were taken using EPA Method 25 and Bay Area Air Quality Management District (BAAQMD) Method ST-7. Each painting episode and sample collection experiment lasted approximately 40 minutes.

Items painted during the experiments were general aircraft ground equipment of various sizes and shapes ranging up to approximately 8 ft (2.4 m) in height. They were selected to represent a range of items typically painted in a spray booth.

Results

Particulate:

The results of the particulate experiments indicate that the average paint particle concentration measurements tend to stratify at approximately the vertical height at which it was generated. To show this phenomenon, the concentration values at each respective height and length along the width of the booth were plotted logarithmically for each test. This permitted a determination of the relative average concentration along the length of the booth for any horizontal plane defined by the grid sections in that plane. Figures 3, 4, and 5, developed from each test, respectively, are an average of those values. They represent the average concentration along the length of the booth

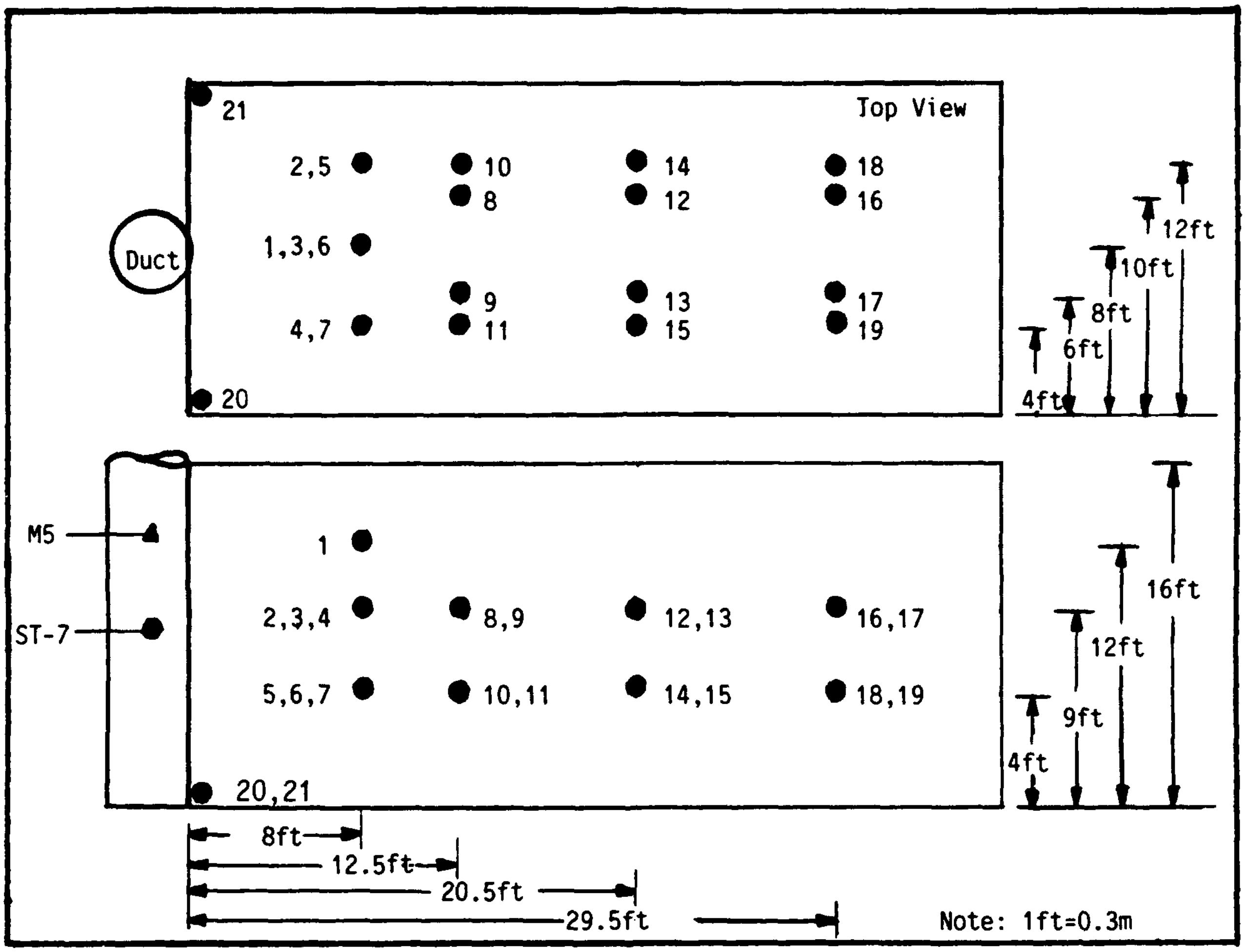

Figure 2. Booth Sampling Locations.

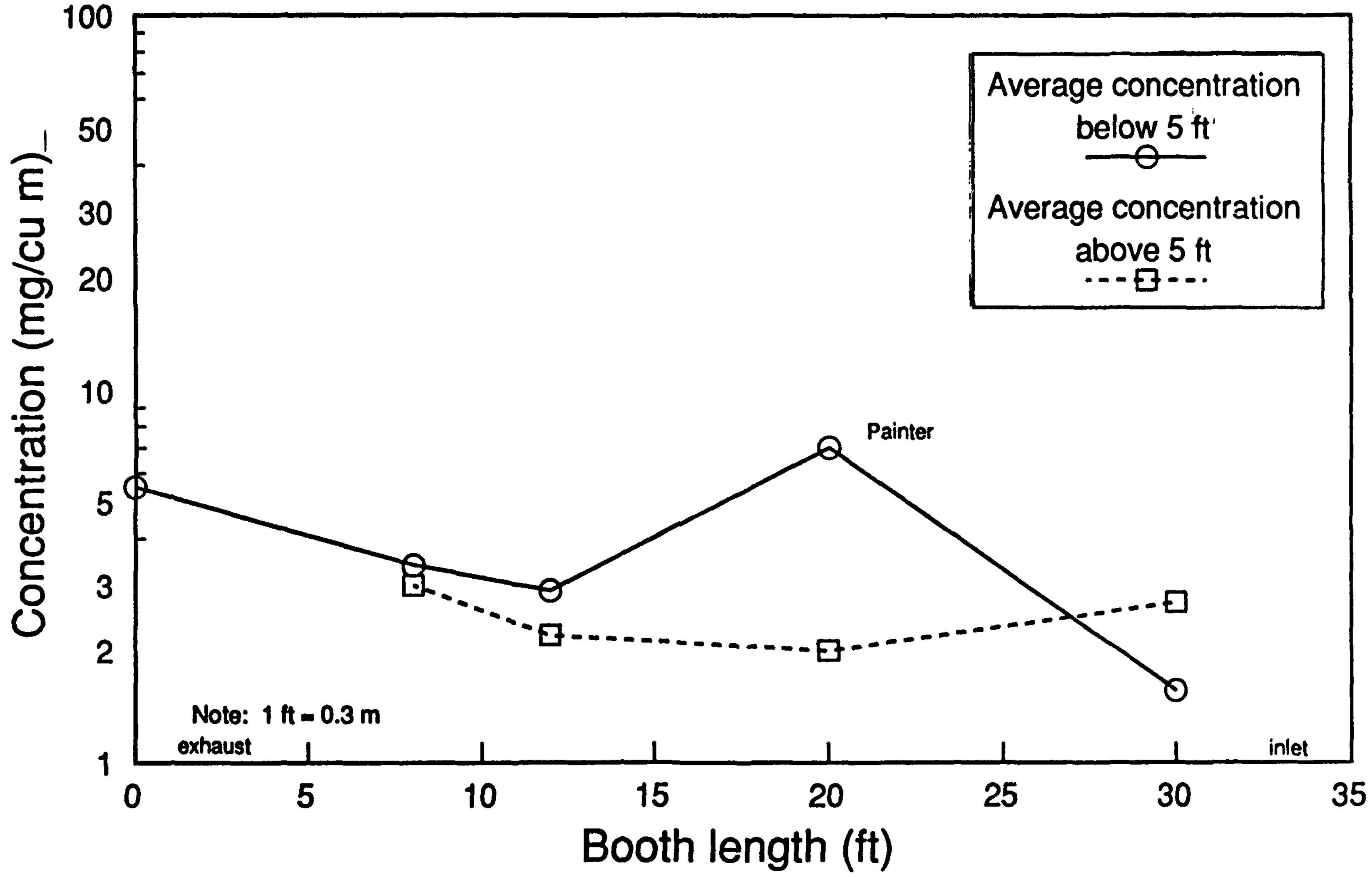

Figure 3. Average particulate concentration along length of test booth, particulate test 1.

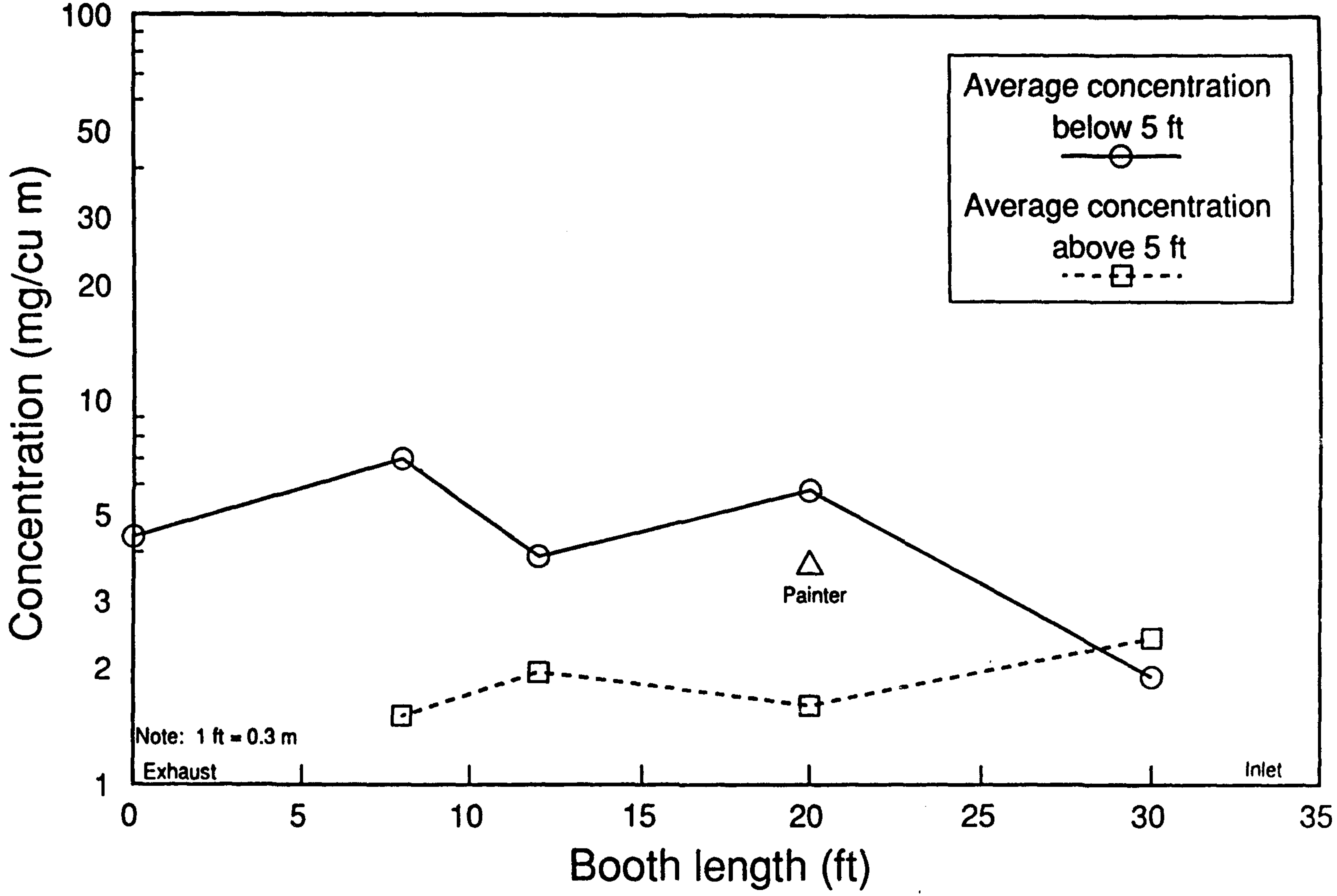

Figure 4. Average particulate concentration along length of test booth, particulate test 2.

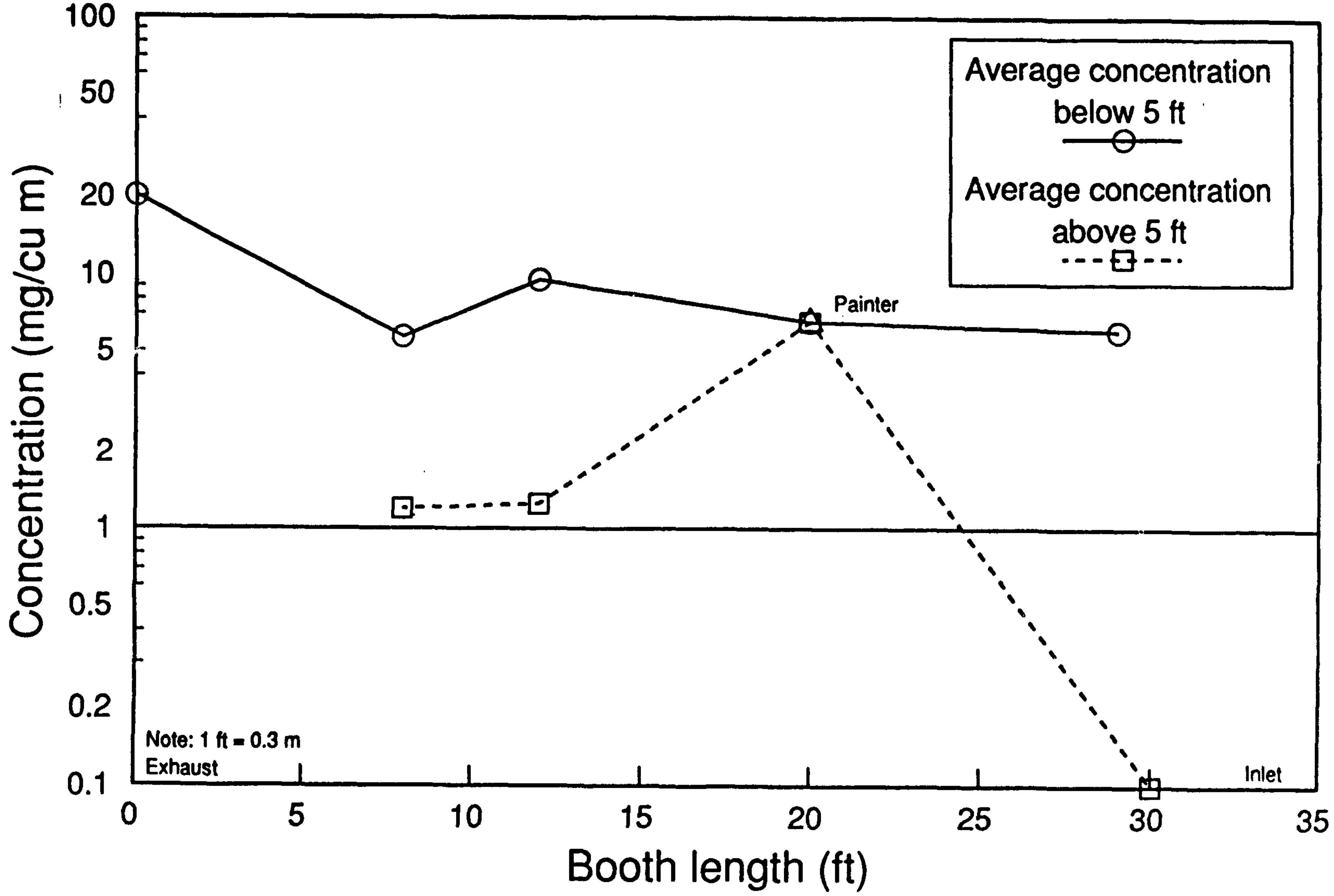

Figure 5. Average particulate concentration along length of test booth, particulate test 3.

for height ranges of 0-5 and 6-12 ft (0-1.5 and 1.8-3.7 m).

As indicated in Figures 3, 4, and 5, two distinct concentration regions are indicated. The concentration profile indicated that the particulate loadings in the lower portion of the booth were from 40 to 95 percent greater than those observed in the upper region of the booth.

Volatiles (VOC):
The volatile organic compound (VOC) test utilized the same sampling instrumentation and locations described for the particulate experiments. The VOC results indicated a more distinct separation of the concentration ranges than those defined for particulates. The VOC concentration profiles clearly tend to decrease in the upper levels of the booth and correspondingly increase in the lower level of the booth as the downstream distance from the painting zone increases. Figures 6 and 7 present the results of those experiments. In Figure 6, VOC test 1, the average concentration in the upper portion of the booth was measured at 8 ug/l or 3 percent of the average concentration, 271 ug/l, measured in the lower portion of the booth. Similarly, in Figure 7, the concentration in the upper portion of the booth was observed to be 22 ug/l, or 20 percent of the lower booth concentration, 108 ug/l.

Conclusions

The finding that the average concentration at the higher levels of the booth is typically lower and tends to decrease as the distance from the painting zone increases can be considered important in the design of horizontal flow spray booths. The painting zone was located between 10 and 25 ft (3.0 and 7.6 m) from the discharge end of the booth. The results indicate that the particulate matter does not rise from the general level of paint application which would have resulted in equalization of concentration at all levels of the booth downstream from the painting zone. Little vertical mixing of the pollutants was apparent. More importantly the results indicate that the greatest mass of particulate matter or paint overspray falls to and concentrates at the lower level of the booth as it proceeds to the exhaust exit of the booth. As confirmed by the results, it would be expected intuitively that the particulate matter would fall since it is heavier than air. Conventional booth design, however, seems to assume that the pollutant establishes an equilibrium in the booth which would result in approximately the same concentration at all downstream levels of the booth.

Similarly and equally important is the dispersion of VOCs in the booth. Similar to the particulate trend, the VOC concentration tended to increase as it approached the lower booth exhaust area. However, the degree of concentration is indicated to be even greater with as much as 80 percent of the generated VOC exhausting from the lower portion of the booth.

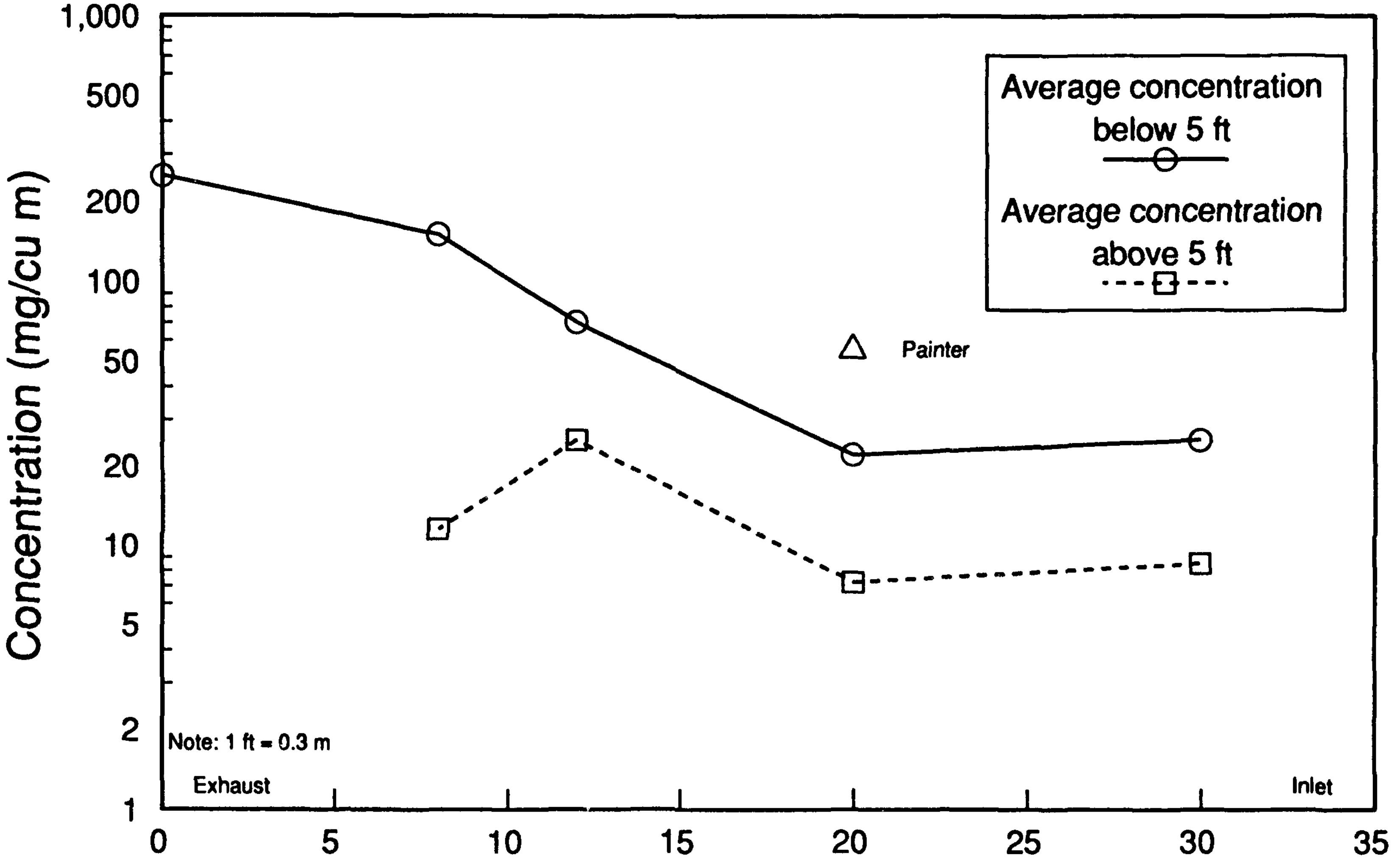

Figure 6. Average VOC concentration along length of test booth: VOC test 1.

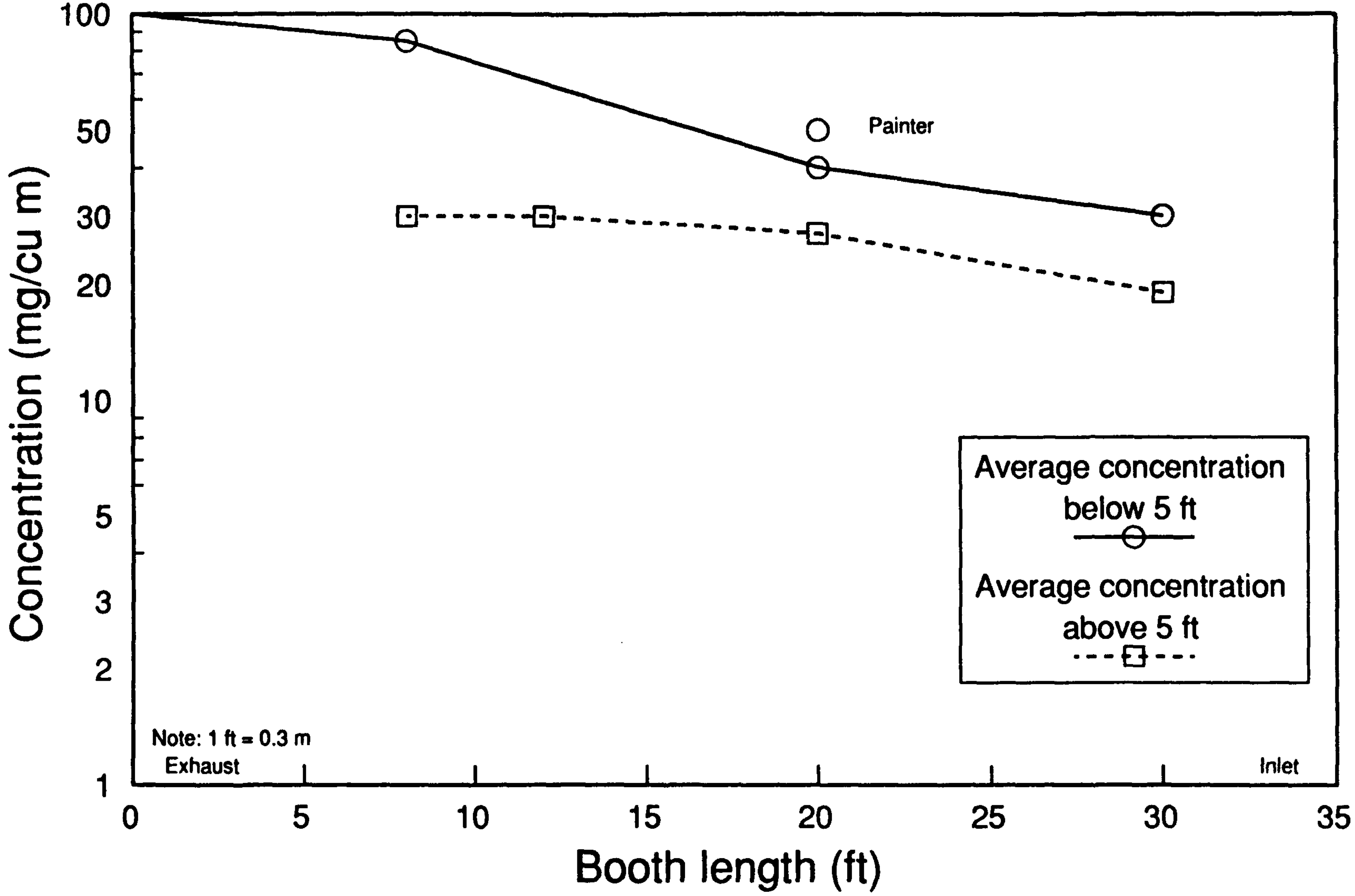

Figure 7. Average VOC concentration along length of test booth: VOC test 2.

These findings indicate a possible approach to enhance the effort to reduce the cost of controlling pollution from paint spray booths. First, since the particulate tends to fall as it progresses from the point of generation, by increasing the distance from the primary painting area to the booth exhaust exit, a significant portion of the particulate could be expected to fall at the lower levels of the booth. A similar scenario can also be envisioned for VOCs, but with greater efficiency. The results indicate that the partitioning of the booth into two zones might be an approach to reduce the volume of pollutant laden discharge that requires pollution control. One discharge, the lean stream from the upper region of the booth, might be directed to the atmosphere via only a particulate control system. The second stream, the pollutant rich discharge which contains the greatest volume of volatile pollutants, can be directed to a VOC control system. This would result in a significant reduction of the volume of exhaust that must be directed to a pollution control system. Partitioning the booth exhaust into two exhaust streams will not alter the operating characteristics of the booth. The booth can be operated within all of the safety and operating code requirements which govern flow volumes and velocities within spray booths. Assuming that the flow in the booth is approximately laminar, it is estimated that a minimum of 50 percent reduction of exhaust flow to the control system can be achieved by partitioning, yet permitting the capture of up to 80 percent of the booth exhaust pollutants. If feasible this scenario could result in a reduction in capital and operating cost for the control system since the total volume of gas that would require processing could be reduced compared to an unpartitioned booth.

At present the research results suggest only a possible concept for reducing the capital and operating cost for spray booth emissions control. It does indicate, however, that a significant portion of the process pollutants can be collected from a relatively small volume of the total booth air flow.

The Council for Health and Environmental Safety of Soils (CHESS):

A Coalition to Standardize Approaches to Soil Contamination Problems

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INTRODUCTION

Soil contamination has become recognized as a significant environmental and public health concern over the past decade. The range of contaminants in soil is now known to be very broad, including petroleum, heavy metals, dioxins, pesticides, organic solvents and others. The presence of such contaminants in soil is affecting the use of land throughout the United States, including types of development and insurance policies. The costs associated with clean-up activities have escalated enormously, often to the point of having a major impact on business and residential development. Along with these increased costs of clean-up is the emerging concern that soil contamination may present significant health concerns as a result of groundwater contamination, soil ingestion, crop contamination, and localized air pollution.

Recent surveys have indicated important differences at the state and federal level concerning how to deal with soil contamination. Widespread inconsistencies between and within states have lead to confusion in the private sector concerning what to expect from regulatory agencies and what the scientific/technical basis is for their actions.

On November 9th and 10th, 1987, the International Society for Regulatory Toxicology and Pharmacology convened a meeting at the University of Massachusetts, Amherst, MA, to assess the need to create an Expert Committee or Council to develop a consensus risk assessment methodology with respect to soil contamination. The attendees of the meeting included representatives from the federal and state public health and environmental agencies, the private sector and Society representatives. More specifically, these representatives were from the University of Massachusetts, United States Environmental Protection Agency (USEPA), Agency for Toxic Substances and Disease Registry (ATSDR), New Hampshire Department of Public Health (NHDPH), the Association of State and Territorial Health Officers (ASHTO) - Environmental Subcommittee, New Jersey Department of Environmental Protection (NJDEP), Electric Power Research Institute (EPRI), American Petroleum Institute (API), McLaren-Chemrisk, Inc., and the Society 's Vice President, Secretary, and Legal Council.

The attendees at the meeting agreed that there was a crucial and immediate need for a consensus risk assessment methodology for assessing soil contamination as well as consensus approaches to analyses and remediation. Furthermore, they concluded that the Society should play a significant leadership role in this area by creating a Council comprised of recognized experts in the area of soil contamination and relevant disciplines to develop a consensus methodology which would then be made available to federal and state agencies, the private sector and the scientific community.

Thus, on November 24, 1987, the International Society for Regulatory Toxicology and Pharmacology created the Council for Health and Environmental Safety of Soils - CHESS. The Council's goal would be to provide leadership in soil contamination issues by:

- Providing consensus guidelines on analytical techniques, risk assessment methodologies, and remediation of contaminated soils.
- Conducting scientific evaluations and analyses and providing recommendations.
- Providing technical information transfer.
- Providing education and training functions.
- Enhancing dialogue amongst affected groups.

ORGANIZATION

The Society's first action was to appoint as Council Chairman, Edward J. Calabrese, Ph.D., University of Massachusetts, Amherst, MA, and as Managing Director, Paul T. Kostecki, Ph.D., University of Massachusetts, Amherst, MA. It is the responsibility of the Chairman to oversee the overall conduct of CHESS, provide continuity between the Governing Board, Council and Expert Committees, and insure that the Governing Board's directives are implemented. The Managing Director is responsible for day-to-day activities and working with the Expert Committees in coordinating technical as well as administrative information.

The Council for Health and Environmental Safety of Soils (CHESS) oversees the actions of the Expert Committees and is directed by a

Governing Board through the Chairman and Managing Director. The Governing Board is appointed by the International Society of Regulatory Toxicology and Pharmacology. The organizational relationship of the Society, Governing Board, Council and Expert Committees is shown in Figure 1.

Governing Board

To insure that the goals and objectives of CHESS are met, the Society in conjunction with the Chairman, established an overall Governing Board of 17 members (Figure 2). CHESS policy is set by the Governing Board which provides oversight and guidance to all aspects of Council activities, including approval of operational procedures, and assurances that procedures as followed. Governing Board members were selected from relevant federal, state, and private sector organizations. The Governing Board meets three to four times a year to review and modify, if necessary, operational procedures.

In addition, the Governing Board assures all Committees are balanced and unbiased, that the Council's activities are mission oriented, that scientific reviews are done properly and that adequate funds are available.

Council

The Governing Board selected Council members by voting from a list of nominees developed by the Governing Board and the Chairman. The Governing Board determined that Council membership should reflect the areas of interest: analysis, environmental fate, public health, remediation, and decision theory as well as balancing federal, state and private sector perspectives (Figure 3). Technical supervision is provided by the Council which provides oversight and guidance to the expert committees, reviews committee reports and serves as a quality assurance component during product development. The Council meets several times a year, or as often as necessary, depending on funding, in the conduct of their duties.

Expert Committees

Four Expert Committees have been created, they are: Analysis/Environmental Fate; Environmental Health; Remediation; User Application. The Expert Committees are charged with development of CHESS products by working with the Chairman and Managing Director. It is the function of the first three Expert Committees (Analysis/Environmental Fate; Environmental Health; Remediation) to provide necessary technical expertise and insure scientific soundness of all CHESS products and recommendations. The User Applications Committee insures that CHESS products are relevant and useful to the user communities. The Expert Committees are charged with the development of CHESS products by working with the Chairman and Managing Director.

OPERATION

CHESS products will be developed by initial identification and review by the Expert Committees of information presently available in each area. This may include federal and state reports and in-house documents as well as private sector material. This information will be identified through literature searches and through the knowledge each Council and Committee member will bring to his/her Committee.

Each Committee will then thoroughly review the information and:

- Recommend an existing document (methodology).
- Modify and/or consolidate existing documents.
- Develop an entirely new document.

Since a great deal of frag[illegible]k has been done in a number of areas, it is anticipated that the second course of action will be the most common. Since CHESS' goal is to develop peer-reviewed, consensus procedures, acceptance of a given procedure is as important as its technical merit. This may necessitate working with sections of existing documents that meet both criteria.

Expert Committees will meet as often as necessary depending on funding to insure successful completion of the tasks. Committee responsibilities, in relation to the anticipated reports, are outlined in Figure 4.

Upon completion of the products by the Committees, the methodology will be subjected to a rigorous peer-review process. The Council Chairman will oversee the review process which will be coordinated by the Managing Director.

PRODUCT

The ultimate product of CHESS will be comprehensive decision-making methodology which will be applicable to all types of soil contamination sites including those related to Superfund sites, leaking underground storage tanks, surface spills, mining operations, and many others. The methodology will incorporate a decision-making framework for site-specific considerations from initial analyses to final corrective action. The methodology will include concern for sensitive environmental receptors such as groundwater, public health risks, land use options, as well as other factors.

The CHESS product will be designed to be readily adopted for use by multiple organizations with particular emphasis on state agencies which are responsible for site evaluation, contamination determination, environmental and public health risk evaluation, and remediation and clean-up.

Development of the decision-making methodology will most likely generate independent reports in a number of areas:

Site Evaluation Procedures

This report will describe the necessary steps for a proper site evaluation for contaminated soils. Ideally, the approach should be applicable to a wide range of environmental and contaminant situations as well as levels of effort (i.e., screening, in-depth evaluation). In the decision-tree type of format a first step screening may lead directly to a risk assessment or even a clean-up action or to a more intensive site evaluation, depending on the circumstances. The site evaluation will contain at a minimum such site characteristics as: historical use, hydrogeologic profiles, sociodemographic information, land use practices, soil and climatic information.

Screening and Analytical Techniques

This report will describe appropriate applications of various field screening (olfaction, portable organic vapor analyzers, portable GC/MS, etc.) and laboratory analytical techniques. It would identify and discuss the strengths and weaknesses of each methodology and recommend ways to standardize their application.

Sampling Procedures

This report will describe how sample collection would be performed in order to insure the collection of representative and useful information. The report would cover the best soil sampling methodologies for a particular contaminant or groups of contaminants, their transport and storage, as well as developing sampling patterns to insure statistical strength and the determination of contaminant extent.

Contaminant Identification

This report will describe the procedures necessary to identify unknown soil contamination, the approximate age of that contamination as well as the degradation products.

Environmental Sensitivity Criteria

This report will establish environmental sensitivity criteria which would consist of: prioritizing site characteristics from product no. 1, e.g., hydrogeologic, climate, soil parameters, biotic factors such as vegetation and wildlife presence; synthesis of bioconcentration and environmental fate information; identification of current and future land use practices (residential, agricultural, recreational, commercial, industrial, etc.); incorporation of sociodemographic parameters.

Risk Assessment

This report will provide a standardized risk assessment methodology for soil contamination. It will identify and recommend and/or direct users to: databases for hazard assessment values for various contaminants, indicating compound selection methodologies for streamlining the procedure; exposure values (environmental fate data-field or modeling); a methodology for the synthesis of this information into a decision-tree format.

Health and Environmental Assessment - Remedial Options

This report will identify the types of remedial options available for the clean-up of contaminated soils as well as their relative effectiveness and costs. The report will consider the occupational and community health risks associated with each option. This information will be an important factor in the risk management process.

The reports as well as the final product may be produced in several formats including:

- Hard copy
- Interactive Software
- Video Workbooks

REVIEW

The organizational structure of CHESS is designed to permit peer-review of relevant documents at two sequential levels. The first level of review for technical committee reports will be by the Council. A second level of review which will incorporate not only scientific evaluation but also relevance to federal and state agencies will be conducted by the Governing Board. In addition, both the Governing Board and Council will have at their disposal the option to obtain external review from independent experts.

SUPPORT

Funding for CHESS has been sought from a broad base of organizations including state departments of public health and environmental protection, federal agencies, [illegible]ations and the private sector. CHESS contributions are made directly to the Society which provides the University of Massachusetts with a grant to support the Chairman and Managing Director's activities.

As of the beginning of this year CHESS has received support from a number of groups including: federal - Agency for Toxic Substances and Disease Registry, USEPA/Office of Health and Environmental Assessment, USEPA/Office of Underground Storage Tanks; private - Chevron, Eastman Kodak, Electric Power Research Institute, Ford Motor Co., Gillette, Goodyear, Hercules, Hoechst Celanese, Morton-Thiokol, Public Service Gas and Electric, Texaco, and Union Carbide.

TECHNICAL INFORMATION EXCHANGE

Following successful completion of the CHESS products the Council will conduct a comprehensive program of technical information transfer to federal, state, and private sectors as well as other organizations for which the product is intended.

Information transfer activities will include a combination of the following:

- Journal articles through the Society's journal, Regulatory Toxicology and Pharmacology.
- Presentations and special sessions at major conferences such as the Annual Petroleum Contaminated Soils Conference at the University of Massachusetts, Amherst, MA.
- Regional workshops devoted to bringing the CHESS concept and products to targeted groups.
- A book comprised of the CHESS products published and distributed by a major publishing firm.

FIGURE 1. Organizational Chart

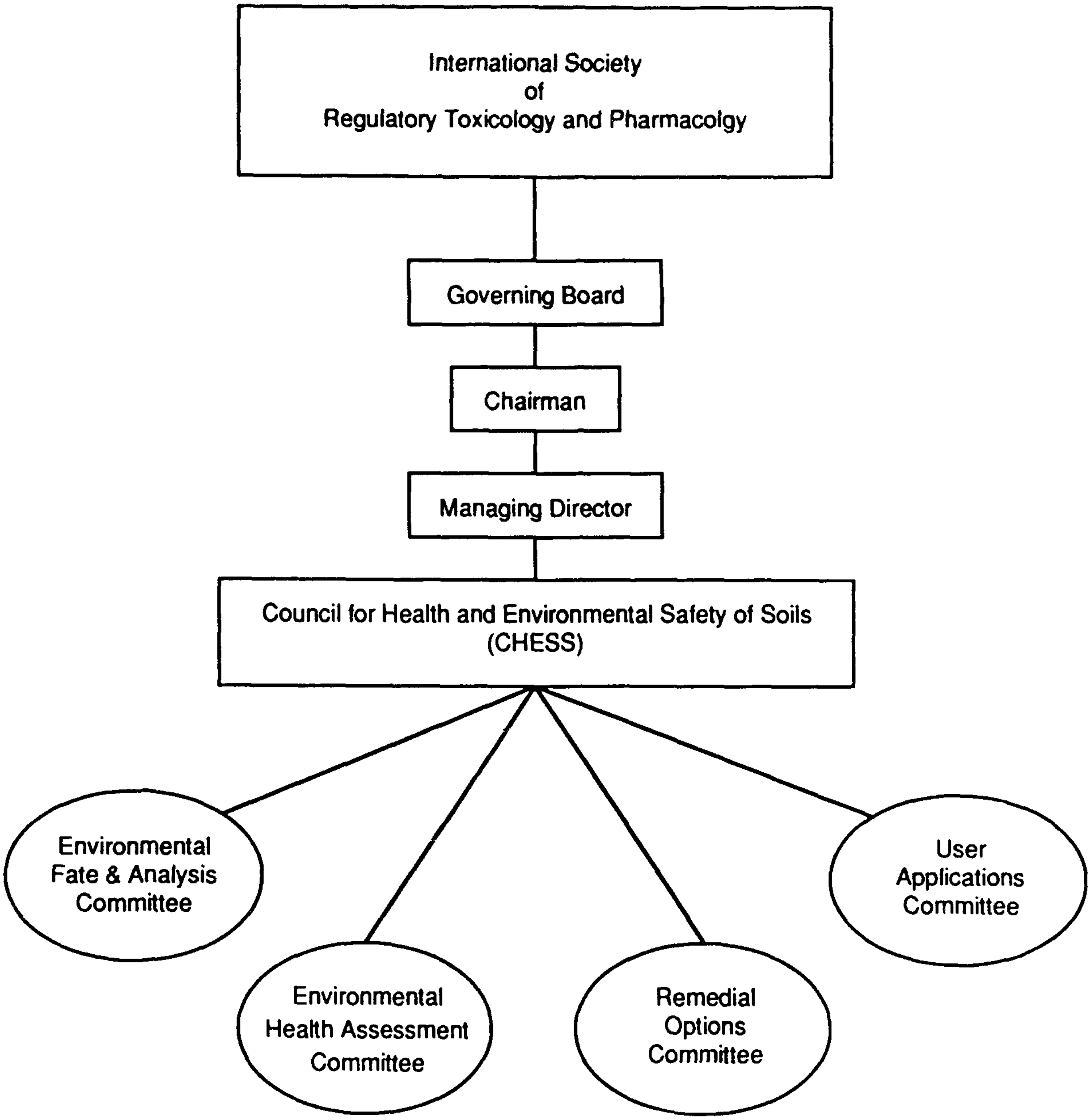


Figure 1: CHESS Organization

FIGURE 2. Governing Board - CHESS

MEMBER	AFFILIATION
Dr. Edward J. Calabrese	University of Massachusetts Environmental Health/Sciences School of Public Health Amherst, MA 01003
Dr. Jelleff Carr	International Society of Regulatory Toxicology and Pharmacology 6546 Belleview Drive Columbia, MD 21046
Dr. John Doull	University of Kansas Medical Center Department of Pharm. Toxic. & Therapeutics Kansas City, KS 66103
Dr. Robert Drew	American Petroleum Institute Health & Environmental Science Department 1220 L Street Washington, DC 20005
Dr. William Farland	U.S. EPA Office of Health & Env. Assessment 401 M Street, SW Washington, DC 20460
Dr. John Frawley	International Society of Regulatory Toxicology & Pharmacology Hercules, Inc. Hercules Plaza 1313 Market Plaza Wilmington, DE 19894
Dr. Peter Galbraith	Connecticut Department of Health Services Bureau of Health Promotion Washington Street Hartford, CT 06106

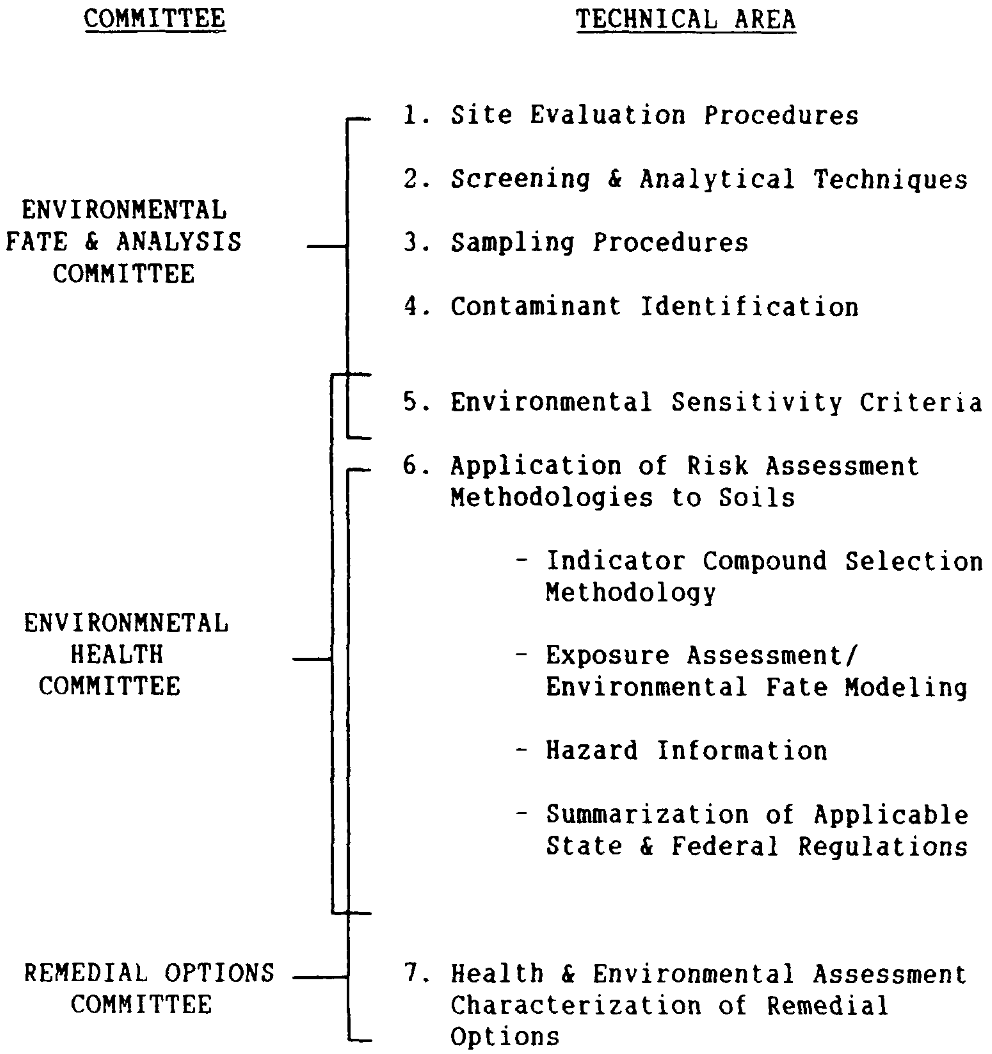
FIGURE 2. Governing Board - CHESS (Continued)

MEMBER	AFFILIATION
Dr. Barry Johnson	Agency of Toxic Substances & Disease Registry 1600 Clifton Road, NE Atlanta, GA 30333
Dr. Donald R. Lesh	Global Tomorrow Coalition 1325 G Street, NW Washington, DC 20005-3104
Dr. Antony G. Marcil	World Environment Center 419 Park Avenue, South Suite 1403 New York, NY 10016
Dr. Gordon Newell	Electric Power Research Institute 3412 Hillview Avenue Palo Alto, CA 94303
James Solyst	National Governor's Association National Resources Policy Studies 444 North Capital Street Washington, DC 20001
Dr. Robert Tucker	Department of Environmental Protection Office of Science and Research Trenton, NJ 08625
Thomas P. Grumbly	Clean Sites, Inc. 1199 North Fairfax Street Alexandria, VA 22314
Thomas P. Looby	Association of State and Territorial Health Officers Colorado Department of Health 4210 East 11th Avenue Denver, CO 80220

FIGURE 3. Council for Health and Environmental Safety of Soil

MEMBER	AFFILIATION
Dr. James Dragun	The Dragun Corporation 3240 Coolidge Berkley, MI 48072
Dr. Allan Hathewar	University of Missouri School of Engineering RFD 4, Box 66 Rolla, MO 65401
Dr. Dorothy Keech	Chevron Oil Field Research Co. P.O. Box 446 3282 Beach Blvd. La Habra, CA 90631
Dr. Renate Kimbrough	U.S. EPA, A-101 401 M Street, SW Washington, DC 20460
Dr. Robert Menzer	MEES Program Room 0313 Symons Hall University of Maryland College Park, MD 20742
Dr. Warner North	Decision Focus 4984 El Camino Real Los Altos, CA 94022
Dr. Dennis Paustenbach	ChemRisk 980 Atlantic Avenue Suite 100 Alameda, CA 94501
Dr. Brian Strohm	New Hampshire Public Health Service Department of Health & Welfare Division of Public Services Hazen Drive Concord, NH 03301

FIGURE 4. CHESS Technical Review Areas and Committee Responsibilities.



COMMITTEE

TECHNICAL AREA

ENVIRONMENTAL FATE & ANALYSIS COMMITTEE

ENVIRONMNETAL HEALTH COMMITTEE

REMEDIAL OPTIONS COMMITTEE

1. Site Evaluation Procedures
2. Screening & Analytical Techniques
3. Sampling Procedures
4. Contaminant Identification
5. Environmental Sensitivity Criteria
6. Application of Risk Assessment Methodologies to Soils
   - Indicator Compound Selection Methodology
   - Exposure Assessment/ Environmental Fate Modeling
   - Hazard Information
   - Summarization of Applicable State & Federal Regulations
7. Health & Environmental Assessment Characterization of Remedial Options

TOXICOLOGICAL AND CHEMICAL CHARACTERIZATION OF COMPOSTED EXPLOSIVES PROCESSING WASTE[1]

W.H. Griest, C.-h. Ho, A.J. Stewart, R.L. Tyndall, E. Tan and M.R. Guerin
Oak Ridge National Laboratory

Mesophilic and thermophilic composts of explosives-contaminated sediments from the Weston experiment at the Louisiana Army Ammunition Plant are being characterized chemically and toxicologically as part of a study of the ability of composting to produce a safe, decontaminated material for disposal. The two composts have been leached using the EPA Toxicity Characteristic Leaching Procedure and the Synthetic Precipitation Leach Test. Both sets of leachates have been characterized for high explosive compounds by HPLC, a metals screen by ICP, and EPA Target Compound List (TCL) semivolatile organic compounds and PCBs/pesticides by EPA Contract Laboratory Program procedures. The latter leachates also have been tested for acute and chronic toxicity to Ceriodaphnia and fathead minnow larvae, and for microbial mutagenicity with Ames test strains TA-98 and TA-100.

Consistent with the greater degradation of explosive compounds in the thermophilic compost, the concentrations of leached explosives compounds and TNT metabolites are lower in the thermophilic compost leachates. Except for sub-ug/L concentrations of a few pesticides, no EPA TCL species were detected. Leached metals were not present in concentrations high enough to be of concern. Toxicity of the Synthetic Precipitation Leach Test leachates was low, and the thermophilic leachate was about one-half as toxic as the mesophilic compost leachate. Bacterial mutagenicity was barely detected in the filtered (<0.22 um) leachate is being determined. The toxicity test results are consistent with the greater degradation of explosive compounds by the thermophilic compost, but the toxicity cannot yet be attributed to explosives or their biotransformation products. The toxicity of the explosives compounds and available metabolites is being determined to aid in understanding the toxicity of the leachates. Work is now focusing upon organic solvent extracts of the composts. The toxicity testing and chemical analysis will include the whole extract and chemical fractions, some of which will include explosives and expected biotransformation products. Organically-bound explosives biotransformation products also will be sought, and their potential for long-term releases will be examined in hydrolysis experiments. Future studies will include a control compost that lacks explosives to allow us to determine any toxicity contributed by the explosives, their transformation products, or natural compounds present in compost mixtures. Periodic samples from active composts will also be studied to assess changes in toxicity and transformation products with time.

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[1] Research sponsored by the U.S. Army Biomedical Research and Development Laboratory (Dr. Wayne Mitchell, COR), Interagency Agreement 1016-B123-A1, under U.S. Department of Energy Contract DE-ACO5-84OR21400 with Martin Marietta Energy Systems, Inc.

Plant Uptake from TNT Contaminated Soils

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Introduction

In 1988 the U.S Navy requested the U.S. Army Engineer Waterways Experiment Station (WES) to evaluate the potential for Trinitrotoluene (TNT), Royal Demolition Explosive (RDX) and their degradation products to contaminate food webs at an installation in northwestern U.S.A. There was a concern that TNT and RDX might be taken up by plants and subsequently might be contaminating wildlife grazing on site.

The site was a former ordnance disposal area comprising 5.7 hectares which was used for burning and detonating ordnance from about 1946 until 1963. Previous data indicated that the site was highly contaminated with TNT, RDX and degradation products.

The WES has developed bioassessment procedures to quantify contaminants from a substrate into food webs associated with a site. Procedures use either plants and/or soil invertebrates as indicators of potential contaminant migration (Francingues et. al. 1985). When target wildlife receptors suspected of being exposed to contaminants are soil invertebrate feeders, an earthworm bioassessment is conducted. The earthworm bioassessment gives an accurate indication of the potential for contaminants to migrate from soil into soil invertebrates. If bioaccumulation is observed in earthworms exposed to the contamination for 28 days, then there is reason for concern that the contamination of food webs associated with soil invertebrates could occur and management strategies can then be formulated for the site to minimize food web transfer. If bioaccumulation is not observed, then there is little concern that food webs are being contaminated.

When target wildlife receptors suspected of exposure to contamination are plant grazers, then a plant bioassessment is conducted. Plant bioassessments can evaluate one or more plant species to determine if contaminants are being taken up into plants and to determine the potential for animals grazing on the plants to become contaminated. Since the major concern of the Navy was for plant grazers such as the black tailed deer, a plant bioassessment was performed. Various plant species naturally colonizing the site were grown in contaminated soil from the site to determine differential uptake of TNT and RDX among the selected plant species. In addition, soil amendments were evaluated during the plant bioassessment to improve plant growth on contaminated soil and reduce uptake of contaminants by the plants.

Methods and Materials

Based on prior information, three locations on the site, (D1, D2, D3) presumed to be contaminated with TNT and RDX, were selected for sampling. Three, 208 litre (55 gal) drums of soil were collected from each location, sealed, and transported by refrigerated truck to the WES for a plant bioassessment. Chemical analysis of the soils indicated that a wide range of

TNT concentrations were present and that all RDX concentrations were below detection limits (Table 1).

Table 1. TNT Soil Concentrations

Location	Soil Concentration (mg/kg)
D1	3030
D2	3.39
D3	30.7

Soil from each location was sieved through a 2.5 cm. screen to remove rocks and metal fragments and placed in an experimental unit consisting of a 30.5x15.2 cm or 15.2x15.2 cm plexiglass cylinder covered at one end with unbleached cotton muslin. Each cylinder was then slipped into an opaque PVC cylinder to eliminate light and minimize any photodegradation of soil TNT.

Plants selected for evaluation were species or cultivars appropriate to the biogeographical location of the site (Table 2) and included local species that could naturally colonize the sites.

Table 2. Plant Materials

Species	Common Name	Source	Rate*
Hypericum calcinum	St John's Wort	Classic Ground Covers/ The Flower Center	1 plant
Cytisus scoparius	Scotch Broom	Newell Wholesale Nursery/ The Flower Center	1 plant
Pseudotsuga meniesii	Douglas Fir	"	1 plant
Thuga placata	Western Red Cedar	"	1 plant
Alnus rubra	Red Alder	"	1 plant
Festuca elatior	Tall Fescue (Alta)	Davenport Seed	0.454 g seeds
Dactylis glomerata	Orchard Grass (Potomac)	"	0.228 g seeds
Medicago sativa	Alfalfa (Moisture Tolerant)	"	48 seeds

* rate per experimental unit

Preliminary screening tests and field observations had indicated that plants did not grow well in the D1 soil that contained 3030 mg/kg TNT. Therefore, the D1 material was fertilized or amended with either horse manure or straw at the rates shown in Table 3.

Table 3. Soil Amendments

Soil	Amendment and Rate
D1	Fertilizer (15-5-10) 336 kg/ha
	Horse Manure 143.5 mt/ha
	Horse Manure 286.9 mt/ha
	Straw 15.0 mt/ha
D2	Fertilizer (15-5-10) 336 kg/ha
D3	Fertilizer (15-5-10) 336 kg/ha
	Horse Manure 143.5 mt/ha

Manure and straw were evaluated as amendments to complex the TNT/RDX and enhance plant establishment and growth. Each test cylinder was then planted with the species to be evaluated. A commercially available potting soil was used as a reference to assess environmental conditions for plant growth. Each species/treatment was replicated six times. Plants, once established, were allowed to grow 45 days before harvest.

Harvested above ground biomass for grasses and alfalfa, and newly grown leaves on the other species were washed in three rinses of reverse osmosis purified water, blotted dry, weighed, freeze dried, and reweighed. The freeze dried plant material was sealed in amber glass jars and shipped overnight to an analytical laboratory for analysis of TNT and RDX.

Results

Analysis of soil samples from the three sites, D1-D3, showed a wide range of TNT concentrations from a low of 3.39 to a high of 3,030 mg/kg (Table 1). Concentrations of RDX were very low at all locations, and most samples were below detection limits.

Vegetative establishment was successful on the D2 and D3 soils without soil amendments other than fertilizer . Establishment of plant materials on the D1 soil, containing the highest TNT soil concentration, was generally unsuccessful with the exception of St John's Wort, Western Red Cedar, and Tall Fescue (Table 4).

Table 4. Summary of New Biomass by Substrate and Reference Material (g dry weight)

Species	Substrate							
	D1				D2	D3		Ref
	*DM	MN	ST	UA	UA	MN	UA	UA
St John's Wort	1.59	1.48	1.05	1.72	2.33	8.86	4.81	1.01
Scotch Broom	0	0	0	0.46	30.56	9.65	4.24	15.95
Douglas Fir	0	0	0	0.05	1.80	3.91	1.97	1.05
Western Red Cedar	0.72	0.61	0	0	2.79	3.37	3.03	0.44
Red Alder	0	0.04	0	0	13.46	14.60	5.00	26.08
Tall Fescue	0.03	0.02	0.01	0	16.33	13.74	7.74	27.77
Orchard Grass	0.07	0	0	0	16.13	12.15	2.12	23.70
Alfalfa	0	0	0	0	9.27	11.06	1.81	68.06

* DM=Manure-286.9 mt/ha, plus 15-5-10 fertilizer 336 kg/ha
MN=Manure- 143.5 mt/ha, plus 15-5-10 fertilizer 336 kg/ha
St=Straw- 15 mt/ha , plus 15-5-10 fertilizer 336 kg/ha
UA=Unamended, 15-5-10 fertilizer 336 kg/ha

Soil amendments of horse manure, up to 286.9 mt/ha, and straw were not sufficient to increase the growth of the remaining test plant species on a soil with a TNT concentration of 3030 ug/g.

In a smaller pot experiment, Tall Fescue was grown in 15 soil mixtures of D1 and D2 to give a soil TNT concentration range of 3, 37, 71, 138, 205, 272, 340, 407, 474, 541, 609, 676, 1,349, 2,021, and 3,030 mg/kg with and without horse manure at a rate of 143.5 mt/ha. Multiple linear regression analysis was used to develop an equation relating TNT soil content to biomass production and to quantify soil TNT levels that significantly inhibited plant growth or resulted in death. Results of the regression showed that biomass production was significantly correlated to soil TNT concentration and to the manure soil amendment (Figure 1 and Table 5). A significant decrease in biomass occurred on unamended soil at a TNT concentration of 65 mg/kg and continued to decline rapidly as TNT concentrations increased. Biomass on manure amended soil was significantly reduced at a TNT concentration of 960 mg/kg.

Table 5. Relationship of Plant Biomass vs. Soil TNT Concentration

Complete Equation:

$$\mathrm{Ln(Biomass)} = 6.88231 - 0.010283 * [\mathrm{Ln(TNT)}]^3 + 0.36310 * [\mathrm{Ln(TNT)} * \mathrm{Manure}]$$

$\Pr > F = 0.0001$, $R^2 = 0.75$

Units: Biomass, kg/ha
Soil TNT, mg/kg
Manure, 1 for manure amendment, 0 for no amendment

The TNT contents of plant tissues are presently being determined.

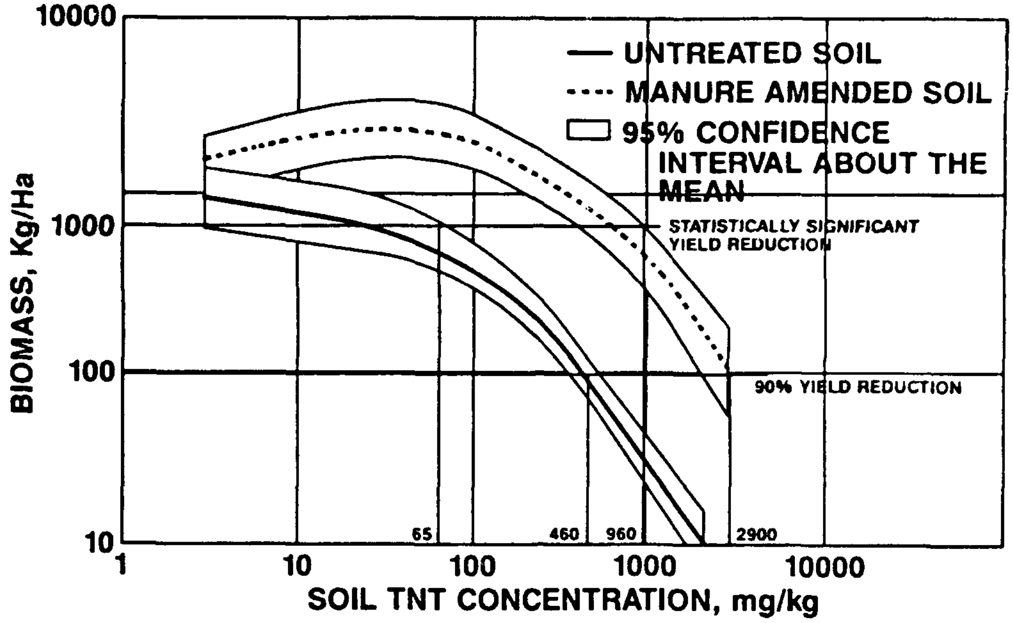

Figure 1. Biomass vs. Soil TNT Concentration of Tall Fescue Grown on Unamended and Manure Amended Soils

Conclusions

Significant concentrations of TNT may prevent colonization by many plant species. Addition of organic soil amendments can significantly increase soil TNT concentration tolerance of some plants, such as Tall Fescue, by over an order of magnitude. Good growth of Tall Fescue was possible on soil contaminated with up to 960 mg/kg when horse manure was incorporated at a rate of 143.5 mt/ha, while growth began to decline significantly at a concentration of only 65 mg/kg when no manure amendment was applied.

Plant tissue concentrations of TNT should allow evaluation of differential uptake of TNT by plant species. Plants that do not appear to take up TNT will be incorporated into management strategies that will minimize TNT mobility into food webs on site.

Acknowledgement

This research was sponsored by Ms. Leslie A. Karr, Naval Civil Engineering Laboratory, U.S. Department of the Navy, Port Hueneme, CA.

References

Francingues, N. R., Palermo, M. R., Lee, C. R., and Peddicord, R. K. 1985. "Management Strategy for Disposal of Dredged Material: Test Protocols and Contaminant Control Measures,: Miscellaneous Paper D-85-1, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

EVALUATION OF SURFACE RUNOFF CONTAMINATION FROM TNT AND RDX CONTAMINATED SOIL*

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U. S. Army Engineer Waterways Experiment Station
Vicksburg, MS 39180, 601-634-3585

Introduction

In 1988 the U.S. Navy requested the U.S. Army Engineer Waterways Experiment Station (WES) to conduct surface runoff and biotechnical erosion control and stabilization tests on Trinitrotoluene (TNT) and Royal Demolition Explosive (RDX) contaminated soil from a site in the northwestern USA. The site was a former ordnance disposal area comprising 14 acres which was used for burning and detonating ordnance from about 1946 until 1963. Previous data indicated that the site was severely contaminated with TNT, RDX and degradation products.

The WES has developed the WES Rainfall Simulator, Lysimeter System to directly quantify surface runoff water quality from contaminated material and to compare erosion control and stabilization techniques. Soil is brought to the WES and placed in soil lysimeters. Rainfall events are applied to the soil, using a rainfall simulator, prior to treatment and again after treatment with soil amendments and/or vegetative establishment. Different vegetative covers and soil amendments can then be directly compared to untreated soil to quantify surface runoff water quality control.

Extensive field verification studies have been conducted with the WES Rainfall Simulator, Lysimeter System to develop vegetative biomass versus surface runoff suspended solid relationships (Westerdahl and Skogerboe, 1982; Lee and Skogerboe, 1984). These studies showed that suspended solids were highly correlated to vegetative biomass and vegetation species (R-sq. > 0.90). Additional field verification studies were conducted on contaminated dredged material to evaluate, quantify and predict heavy metal, polychlorinated biphenyl (PCB), and polyaromatic hydrocarbon (PAH) concentrations in surface runoff from upland dredged disposal sites prior to dredging (Skogerboe et al, 1987). The WES Rainfall Simulator, Lysimeter System was proven to be an effective tool for predicting surface runoff rates, soil loss, and contaminant concentrations including heavy metals, PCB, and PAH (Skogerboe et al, 1988). The system has become part of the U.S. Army Corps of Engineers standard testing protocol for evaluation and management of dredged material (Francingues et al., 1985).

Methods and Materials

Based on prior information, three locations were selected on the site for sampling because they were contaminated with TNT and RDX. Nine, 208 liter (55 gal.) drums of soil were collected from each location, sealed, loaded into a refrigerated truck, and transported to the WES for surface runoff water quality tests. The soil from each location was placed in a soil lysimeter, 4.57 m x 1.22 m x 0.15 m deep, and prepared for surface runoff water quality testing. The surface runoff tests were divided into three parts:

1. Initial evaluation of unvegetated, unamended soil
2. Evaluation of vegetated soil
3. Evaluation of amended and vegetated soil

All simulated storm events were conducted using reverse osmosis purified water at a rate of 5.3 cm/hr until 30 minutes of surface runoff had occurred. Surface runoff samples were collected and analyzed for suspended solids, pH, TNT, RDX, and several TNT degradation products.

Surface runoff water quality tests were first conducted on unvegetated, unamended soil from each of the three locations: D1, D2, and D3. The soil in the lysimeters was then seeded with Festuca elatior (Tall Fescue) 'Alkar' and grown until maximum biomass was achieved. Based on the results of several plant growth tests, the D1 soil was amended with 11 mt/ha, straw

(5 tons/acre), and the D3 soil was amended with 143 mt/ha, horse manure (64 tons/acre). The amendments were incorporated throughout the entire 15 cm (6 in) depth of the soil using a shovel, and Tall fescue was reseeded. Surface runoff water quality tests were conducted as before.

All statistical analysis of data was conducted using SAS analysis of variance and multiple linear regression at a = 0.05 level of significance

Results

Analysis of soil samples from the three site locations showed a wide range of TNT concentrations from low to very high (Table 1).

Table 1. TNT Soil Concentrations

Location	Soil Concentration (mg/kg)
D1	3030
D2	3.39
D3	30.7

Concentrations of RDX were low at all locations, and most samples were below detection limits. Vegetative establishment without soil amendments was successful on the D2 and D3 soils but unsuccessful on the D1 soil probably due to the high TNT soil concentration (Table 2).

Table 2. Biomass Yields on TNT Contaminated Soils

Location	Biomass (kg/ha)
D1	14
D2	2100
D3	3500

Results of the surface runoff water quality tests on bare soil showed significant concentrations of total and filtered TNT in the runoff water from the D1 and D3 soils (Table 3). Filtered TNT sample concentrations were significantly less than the total concentrations, however filtered sample concentrations did account for a substantial portion of the total. Additional rainfall simulation tests on the D3 soil showed that suspended solids, total TNT, and filtered TNT concentrations in surface runoff were significantly reduced by the establishment of Tall fescue (Table 4). Suspended solids concentrations from unamended, vegetated soils were not significantly different between soils from the three locations with similar biomasses but were significantly reduced as biomass increased. Insufficient biomass, however, was produced on the D1 soil to significantly reduce suspended solids and TNT concentrations. Runoff samples from the vegetated D2 soil were not analyzed for TNT because concentrations from the unvegetated soil were very close to the detection limits.

Table 3. Surface Runoff TNT Concentrations (mg/l) from Unamended, Unvegetated Soil

Location	Total Concentration	Filtered Concentration
D1	3.0	0.92
D2	0.00039	0.00056
D3	0.33	0.071

Table 4. Surface Runoff Suspended Solids and TNT Concentrations from the D3 Soil (mg/l)

	Suspended Solids	Total TNT	Filtered TNT
Unvegetated	1500	0.33	0.071
Vegetated	20	0.011	0.0074

Surface runoff tests were completed on the amended soils, however, TNT analysis of runoff samples were not completed at the time this paper was prepared. Some vegetation was established on the D1 soil (140 kg/ha) and suspended solids were significantly reduced by an order of magnitude.

Conclusions

Significant concentrations of TNT in both total and filtered samples may be eroded from TNT contaminated soils particularly when the soil is unvegetated. Vegetation did significantly reduce suspended solids, total TNT, and filtered TNT in surface runoff, however, organic soil amendments were required for vegetative establishment on the soil containing 3030 mg/kg TNT. Even with the soil amendments, the vegetative cover on the D1 soil was poor but sufficient to significantly reduce the suspended solids concentrations in surface runoff. Although chemical analysis has not been completed on runoff samples from soils amended with organic material, it is anticipated that TNT concentrations in surface runoff will be further reduced by the amendments.

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INTERACTIONS OF 2,4,6-TRINITROTOLUENE (TNT) WITH SOILS[1]

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ABSTRACT

Adsorption and desorption studies of 2,4,6-trinitrotoluene (TNT) were conducted using uncontaminated soils collected from 13 Army Ammunition Plants. Steady-state adsorption and desorption of TNT were achieved within 2 h. Batch TNT adsorption isotherms were best described by the Langmuir adsorption model, an indication that monolayer adsorption occurs; i.e., as more sites in the soil are filled, the rate of adsorption declines. The adsorption coefficient (K_d) obtained by averaging all soils was 4.0. TNT adsorption coefficients were most highly correlated with extractable iron, cation exchange capacity, and clay content. Almost all of the adsorbed TNT was desorbed after three sequential desorption cycles. Therefore, soil sorption will not effectively prevent mobility of TNT through the soil unless adsorption increases over extended periods of time, or more strongly adsorbing decomposition products are formed. Evidence for increased adsorption of TNT from amended soils over time was observed in soils used in a related TNT plant uptake study. Results of soil analyses in the related study demonstrated irreversible adsorption of TNT through time, and showed losses of TNT from the soil by some other mechanism, possibly volatilization. The implication of irreversible adsorption is under estimation of TNT concentrations in soils taken from the field. Loss of TNT from soils over time raises interesting possibilities for remediation of TNT-contaminated soils. Redox potential and pH exerted no measurable effects on adsorption and desorption. Two degradation products of TNT, 4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene, were detected during the 24 h degradation study period under both oxidized and reduced conditions. Microbial degradation was greater in reduced than in oxidized soils, but differences were not significant.

INTRODUCTION

Only a few mechanisms potentially affecting the environmental fate of 2,4,6-trinitrotoluene (TNT) have been studied; i. e., photodecomposition, in which 1,3,5-trinitrobenzene was identified as the principal product forming in natural waters (Burlinson, 1980), and microbial transformation, in which the predominant changes were reduction of nitro groups to amino groups, and coupling of rings to produce azoxy compounds (Kaplan and Kaplan, 1982). No cleavage of the TNT ring structure by microorganisms has been reported in the literature. Although ground water contamination has been detected (Spalding and Fulton, 1988), a review of the literature revealed no information concerning sorption of TNT in soil or in reduced sediments, such as those in waste disposal lagoons.

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MATERIAL AND METHODS

Batch adsorption and sequential desorption studies were conducted with uncontaminated surface soils collected from 13 Army Ammunition Plants (AAP). Test soils were amended with ^{14}C-labeled TNT. Results of adsorption studies were correlated with soil properties. Effects of pH and redox potential on adsorption, desorption, and transformation were examined by conducting batch tests on soils preincubated under controlled conditions. Detailed methods are reported by Pennington (1988).

RESULTS AND DISCUSSION

Adsorption and desorption kinetics were determined using two soils selected on the basis of organic carbon (OC) content: Joliet AAP soil which is relatively high in OC (3.6 %), and Louisiana AAP soil which is relatively low (0.37%). TNT reached adsorption steady state in Joliet AAP within 1.0 h, i.e., no significant difference in solution concentration between 1.0 and 10.0 h. Similar results were found in soil from the Louisiana AAP except that steady state conditions were reached within 0.5 h. A slight decrease in solution concentration was noted after 10 h at highest treatment concentrations in both soils. In view of subsequent results in transformation studies, this decrease may be attributable to gradual formation and adsorption of transformation products.

Desorption steady state in Joliet AAP soil was reached within 1.5 h and in Louisiana AAP soil within 2 h. Thus, desorption occurs almost as rapidly as adsorption. From 2 to 10 h, no significant change in the concentration of TNT in the solutions was observed. When steady state desorption was reached, Joliet AAP soil still retained an average of 12.5 percent of the adsorbed TNT; Louisiana AAP soil retained an average of 6.25 percent.

Adsorption data were fit to the Langmuir Isotherm Model, the Freundlich Isotherm Model, and a linear model to relate solid and aqueous phase contaminant concentrations in soils (Weber, 1972). Examination of R-square values across models for each soil indicated that the adsorption data best fit the Langmuir Isotherm Model for every soil (Table 1). The fact that the data fit the Langmuir Model indicates that adsorption of TNT reached a maximum as adsorption sites in the soil were filled. Average adsorption coefficent (soil to solution ratio, or K_d) for all soils was 4.0.

Results of a correlation analysis (Steel and Torrie, 1980) of adsorption K_d values with soil properties are shown in Table 2. Adsorption was most closely correlated with extractable iron, CEC, and percent clay.

Statistical comparison of slopes for adsorption and desorption isotherms within each soil type (difference between two independent regressions, Steel and Torrie, 1980) showed no significant differences at the 0.05 level of probability. This result is an indication of absence of hysteresis, i.e., adsorption and desorption occurred to the same extent. The mean percentage adsorbed was 13.9; the mean percentage desorbed after three sequential desorption cycles was 88.3. The average percentage retained by the AAP soils was 12. Lack of hysteresis suggests that continued desorption, or leaching, may remove more, and perhaps all, of the TNT from the AAP soils.

R-square values and adsorption coefficients for tests under controlled conditions of pH and redox potential are shown in Table 3. Examination of R-square values for the linear, Freundlich, and Langmuir models indicated little difference between models for all combinations of pH and redox potential. Results of a statistical comparison of K_d values between combinations of test conditions for both adsorption and desorption indicated no significant differences. Therefore, pH and redox potential exerted no effect on adsorption of TNT by the tested soils.

Results of gas liquid chromatographic analysis of TNT and its transformation products indicated that degradation of TNT occurred during the 24 h test. Lack of homogeneity in variances after several transformations of the data precluded the use of parametric analysis and made quantitative comparisons difficult. However, several trends in the data were observed. Under both oxidized and reduced conditions, the transformation products 4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene were detected. Biotic reduction exceeded abiotic reduction of TNT under both oxidized and reduced conditions. Microbial transformation appeared to be greater, or perhaps faster, under reduced than under oxidized conditions.

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Table 1. R-square values for regression of isotherm models and adsorption coefficient (K_d)

Soil	Langmuir	Freundlich	Linear	K_d
Cornhuskers	1.0	0.96	0.93	[illegible]
Crane	0.99	0.94	0.92	3.[illegible]
Holston A	1.0	0.96	0.94	[illegible]
Holston B	0.99	0.94	0.99	3.[illegible]
Iowa	1.0	0.96	0.93	[illegible]
Joliet	1.0	0.97	0.93	[illegible].8
Kansas	0.99	0.97	0.94	5.[illegible]
Lonestar	0.99	0.90	0.89	2.[illegible]
Longhorn	0.99	0.94	0.92	3.[illegible]
Louisiana	0.98	0.89	0.88	2.[illegible]
Newport	0.98	0.88	0.87	2.3
Radford	0.99	0.93	0.90	3.[illegible]
Savanna	0.97	0.89	0.88	2.5
Volunteer	0.99	0.95	0.93	4.05

Table 2. Correlation values (R) for adsorption K_d values with soil properties.

Parameter	R	Parameter	R
Fe	0.89	% silt	0.17
CEC	0.87	pH	0.17
% Clay	0.70	Mn	0.041
% OC	0.40	EC	-0.40
Ca	0.35	% sand	-0.55
Al	0.18		

Table 3. R-square values for regression of isotherm models and adsorption coefficients (K_d) for adsorption of TNT by Joliet AAP soil under selected conditions of pH and redox potential.

Eh	pH	Langmuir	Freundlich	Linear	K_d
-150	5.0	0.75	0.84	0.90	7.1
+450	5.0	0.94	0.91	0.92	5.7
-150	6.5	0.86	0.90	0.90	9.5
+450	6.5	0.98	0.98	0.99	5.5
-150	8.0	0.91	0.95	0.94	7.3
+450	8.0	0.97	0.98	0.98	5.6

TECHNOLOGY EVALUATION FOR TREATMENT/ABATEMENT OF TNT RED WATER

by

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ABSTRACT

Red water is the wastewater resulting from the purification of trinitrotoluene (TNT), which, because of its reactivity, is listed as a K047 waste by the Resource Conservation Recovery Act (RCRA). A lack of suitable treatment/disposal options for the generated red water affects both plants that produce peace-time quantities of TNT and those that would be mobilized during military conflicts. Extensive efforts have already been expended on the evaluation of technologies for the treatment of red water. A portion of these efforts culminated in a 1980 report issued by Chemical Systems Laboratory (CSL), in which 10 technologies were evaluated based on their technical merit for the treatment of red water. The evaluation concluded that three technologies were technically feasible, but that two of these involved a change in the TNT purification process, which would present unwanted ramifications regarding handling and usage in the TNT specifications. Based on these conclusions, the U.S. Army pursued the one recommended treatment technology for implementation at the Radford Army Ammunition Plant (RAAP). Because of various developments, the U.S. Army, through the United States Army Toxic and Hazardous Materials Agency (USATHAMA), elected to perform an updated technology evaluation to reevaluate the technologies evaluated in 1980 and to determine whether or not processes developed since 1980 might be feasible for the treatment of red water. This paper presents the evaluation procedures and findings of the evaluation of 31 technologies for red water treatment. The technologies fell into five categories: biological, chemical/physical, thermal, purification modifications, and mixed/other treatment processes. The 31 technologies were initially evaluated against a set of preliminary evaluation criteria that reduced the number to 16. These 16 technologies were then subjected to a secondary set of evaluation criteria to identify and prioritize the technologies with the greatest potential for red water treatment. From this paper evaluation of the technologies, an existing

industrial technology already permitted for K062 wastewater, wet air oxidation, supercritical water oxidation, and the Sonoco Sulfite Recovery Process emerged as the technologies with the greatest potential for red water treatment.

INTRODUCTION

The U.S. Army is considering starting up one or more of its currently mothballed trinitrotoluene (TNT) production plants and the Radford Army Ammunition Plant (RAAP) in Virginia is the leading candidate. Before production can be resumed, a technology must be developed for treating or disposing of the process wastewater (commonly called red water). When TNT production plants were previously operated, red water was either sold to paper mills as a source of sulfate/sulfite or was incinerated in onsite kilns. Paper milling technology has changed, however, and paper mills are no longer interested in purchasing red water. Also, the onsite kilns did not provide sufficiently complete destruction of red water organic compounds to satisfy current environmental standards. Because of its reactivity, red water is listed as K047 hazardous waste.

The TNT is manufactured by the three-stage nitration of toluene which involves the use of mixtures of nitric and sulfuric acids (see Figure 1). The sulfuric acid does not have a direct role in the reactions, but it serves to tie up the water generated by nitration. In benzene ring substitutions, the methyl group is an ortho and para director and the nitro group is a meta director. Consequently, the symmetrical TNT or 2,4,6-TNT or alpha TNT is the predominant isomer formed.

Alpha TNT is the preferred isomer, and the other TNT isomers must be removed. This is accomplished by treatment with a 15 percent aqueous solution of sodium sulfite, commonly referred to as sellite. Sellite preferentially reacts with a nitro group meta to the toluene to produce a dinitrotoluene sulfonate that is water-soluble (see Figure 2). Alpha TNT reacts with sellite only to a limited extent. Therefore, red water will contain sodium dinitrotoluene sulfonates and sodium nitrite formed by TNT purification, unreacted sodium sulfite, and sodium sulfate and nitrate formed from the neutralization of sulfuric and nitric acids. The RAAP red water is about 15 percent by weight dissolved solids. Of these, about 45 percent are inorganic sodium salts and about 55 percent are organic sodium salts, primarily dinitrobenzene sulfonates. Nonionized organic compounds are present only in trace amounts.

The dinitrobenzene sulfonates are strong acids with strengths comparable to hydrochloric and nitric acids. The Handbook of Chemistry and Physics (1980) cites 0.2 as the ionization constant of benzene sulfonic acid. Fieser and Fieser (1950) say that benzene sulfonic acid is as strong an acid as hydrochloric acid. By analogy with benzoic acid and toluic acid, toluene sulfonic acid should be as strong or stronger than benzene sulfonic acid. Moreover, nitro groups on the benzene ring enhance the acidity of organic acids; benzoic acid and phenol are examples. Therefore, attempts to convert

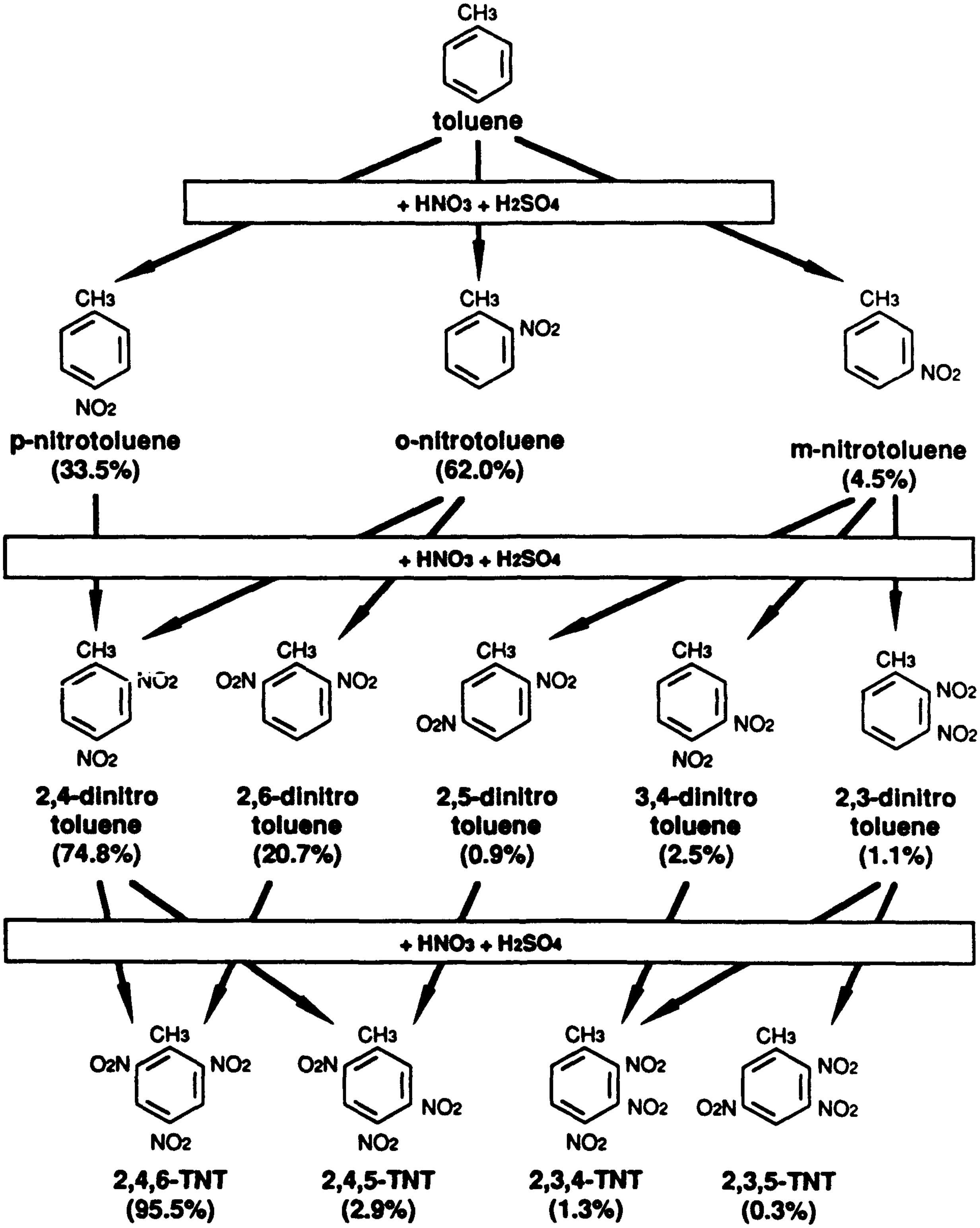


Figure 1. TNT process chemistry - three stage nitration of toluene with nitric and sulfuric acids.

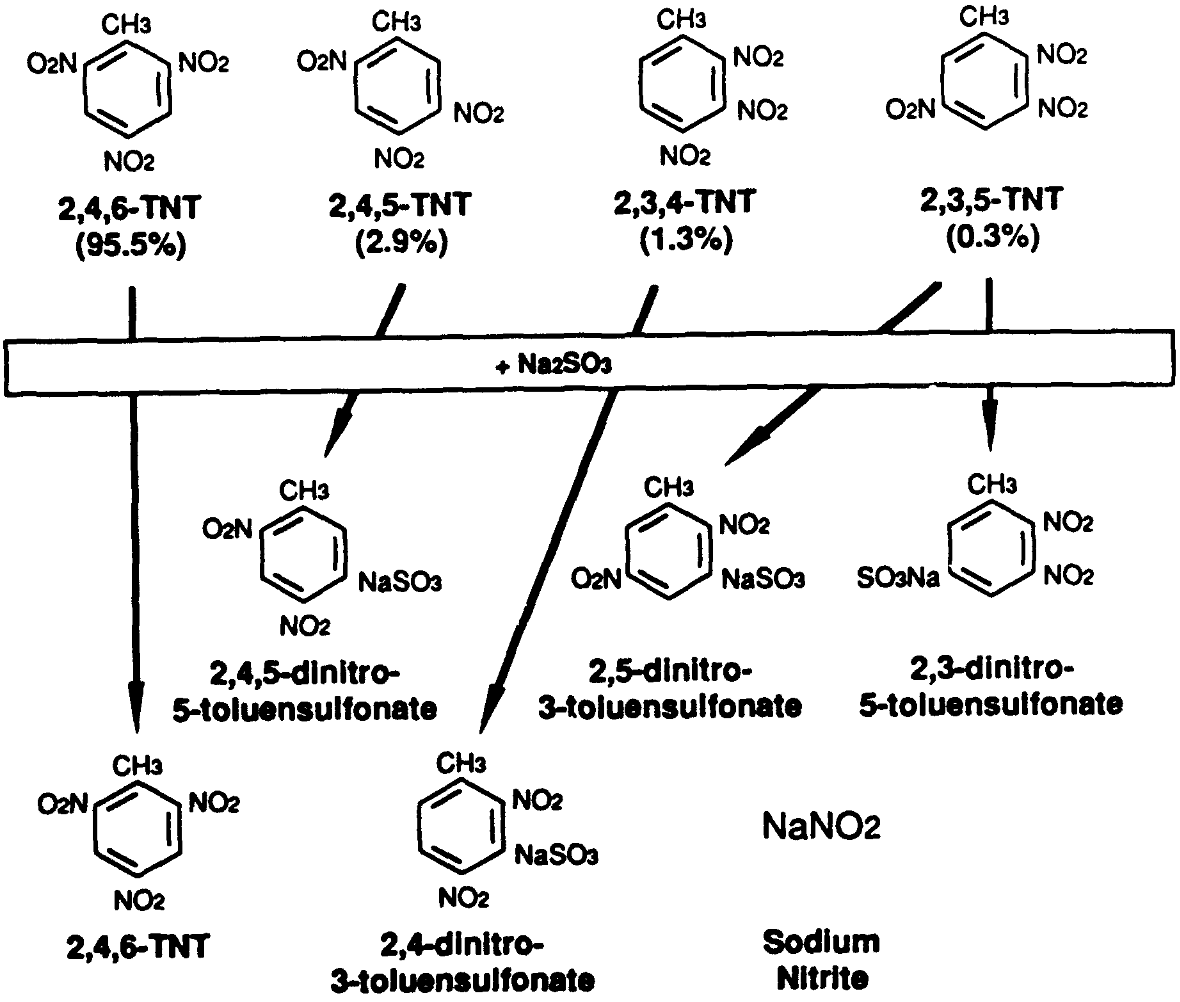


Figure 2. TNT purification with sodium sulfite.

dinitrotoluene sulfonate anions to a nonionized acid and then to separate red water into organic (neutral) and inorganic (ionized) fractions, followed by separate treatment of each fraction, are likely to produce sulfur dioxide emissions from the acidification of sulfites and nitrogen oxides from the acidification of nitrites. This renders red water treatment more difficult.

A wastewater stream, commonly called pink water, is generated by such TNT handling operations as loading artillery shells. Pink water is primarily an aqueous TNT solution with a TNT concentration of about 100 ppm. Pink water contains few or no ionic compounds. It has been wrongly assumed that pink water and red water are similar and that red water is merely more concentrated. Based on this assumption, the erroneous conclusion has been drawn that a technology that has been used to treat pink water can readily be adapted to treat red water.

PRELIMINARY EVALUATION OF TECHNOLOGIES

Of the 31 technologies that received preliminary screening, 10 had been evaluated in the 1980 Chemical Systems Laboratory (CSL) report, 7 were proposed by USATHAMA, and 14 were proposed by others on the basis of technical advances made since 1980. Table 1 identifies all the technologies introduced in the preliminary evaluation.

Preliminary evaluation criteria were as follows:

- The technology could not require any changes in the TNT production process.
- If the technology was evaluated in the 1980 CSL Report and not recommended for further evaluation, significant technical advances must have occurred since 1980.
- The manufacturers or developers of the technology should be willing to assist in the necessary R&D work to adapt the technology for red water treatment.
- The treated product must be suitable for recycle, discharge, or disposal or be amenable to further treatment to render it suitable.
- At the preliminary assessment stages, the technology must have received the benefit of any uncertainty and would receive secondary level evaluation.

A decision tree was used to prescreen the technologies. The decision tree analysis is traced for the Sonoco Sulfite Recovery Process which survived the preliminary evaluation and for stabilization/solidification which was eliminated. The decision tree for the Sonoco Sulfite Recovery Process (see Figure 3) was as follows:

TABLE 1. TECHNOLOGIES SELECTED FOR PRELIMINARY SCREENING

Technologies Evaluated in 1980 CSL Report

Listed in order of most to least favorable per the 1980 CSL report.

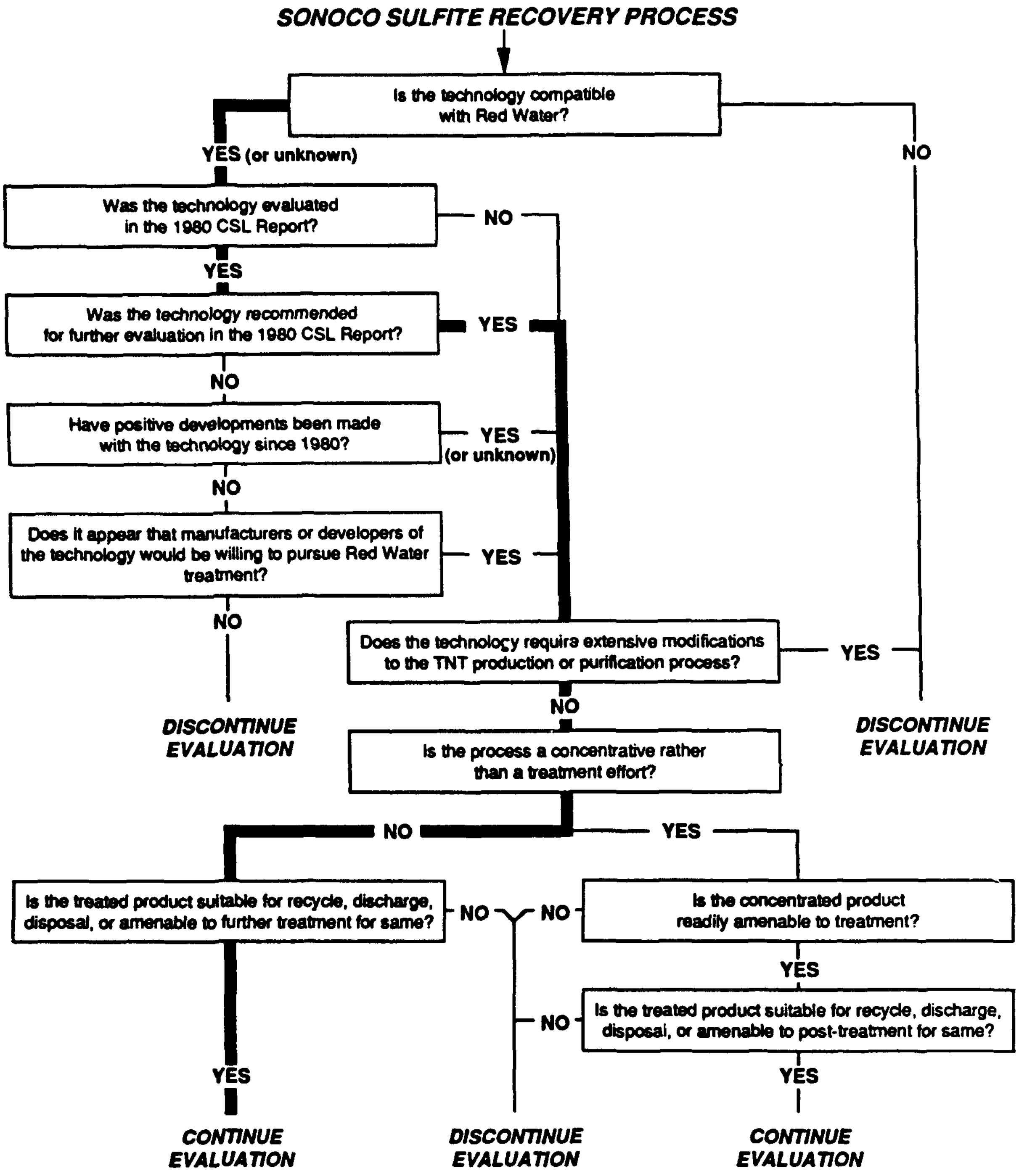
Sonoco Sellite Recovery Process
Magnesium Sulfite Purification
Nitric Acid Purification
Fluidized Bed Reduction
Concentration followed by Incineration and Landfill
Tampella Recovery Process
Ammonium Sulfite Purification
SCA Billerud Recovery
Reverse Osmosis
Acidification

Additional Processes Proposed by USATHAMA

Argonne National Laboratory Process
Biodegradation by White Rot Fungus in a Packed-Bed Reactor
Biodegradation by British Royal Ordinance
Hybrid Thermal Treatment System (HTTS)
Slagging Rotary Kiln
Submerged Combustion
Supercritical Water Oxidation

Additional Technologies

Biodegradation by White Rot Fungus in a Rotating Biological Contactor
Carbon Adsorption
Catalyzed Wet Oxidation
Composting
Freeze Technology
Ion Exchange
Land Treatment
Licensing Existing Industrial Technology - DuPont, Air Products and Chemicals
Liquid-Phase Oxidation -(Ozone or Peroxide with Ultrasound or U.V.)
Plasma Arc
Solidification/Stabilization
Surfactant Technology
Thermal Separation
Wet-Air Oxidation



Identify how concentrative effort might be suitable as a pre-treatment step.

Identify polishing treatment to allow for recycle, discharge, or disposal of dilute stream effluent.

Figure 3. Prescreening decision tree for Sonoco sulfite recovery process.

- Is the technology compatible with red water? Yes. Pilot-scale studies have indicated that the Sonoco Sulfite Recovery Process is compatible with red water; however, more thorough testing with red water is needed.

- Was the technology evaluated in the 1980 CSL Report? Yes.

- Was the technology recommended for further evaluation in the 1980 CSL Report? Yes. Of the 10 processes studied, the Sonoco Sulfite Recovery Process was judged to be the best suited for adaptation to red water treatment.

- Have positive developments been made with the technology since 1980? Yes. Since the construction at RAAP has been stopped, most developments have involved paper evaluations only; however, the evaluations have been positive.

- Does it appear that manufacturers or developers of the technology would be willing to pursue red water treatment? Yes. The Sonoco Corporation is willing to help in sorting out the adaptation of the process to red water treatment.

- Does the technology require extensive modifications to the TNT production or purification process? No. The recovered sulfite could be recycled to the purification process, however. Whether the ash produced in the multiple hearth furnace will contribute impurities to the sellite in high enough concentrations to affect the TNT purification step is currently not known.

- Is the process a concentrative effort rather than a treatment effort? No. The red water is converted into sellite.

- Is the treated product suitable for recycle, discharge, or disposal, or is it amenable to further treatment to render it suitable? Yes. The product (sellite) may be suitable for recycling into the TNT purification process; however, it is not known whether impurities in the sellite will affect this process.

- The Sonoco Sulfite Recovery Process survived the go/no go decision tree and was recommended for further evaluation.

It should be noted that the Sonoco process has some uncertainties that will require additional development work to resolve; however, for purposes of the preliminary examination, it was assumed that these unknowns are resolvable. The decision tree for stabilization/solidification (see Figure 4) was as follows:

- Is the technology compatible with red water? Unknown. Stabilization/solidification techniques have been tested successfully on synthetic military waste sludges and simulated pink water. The

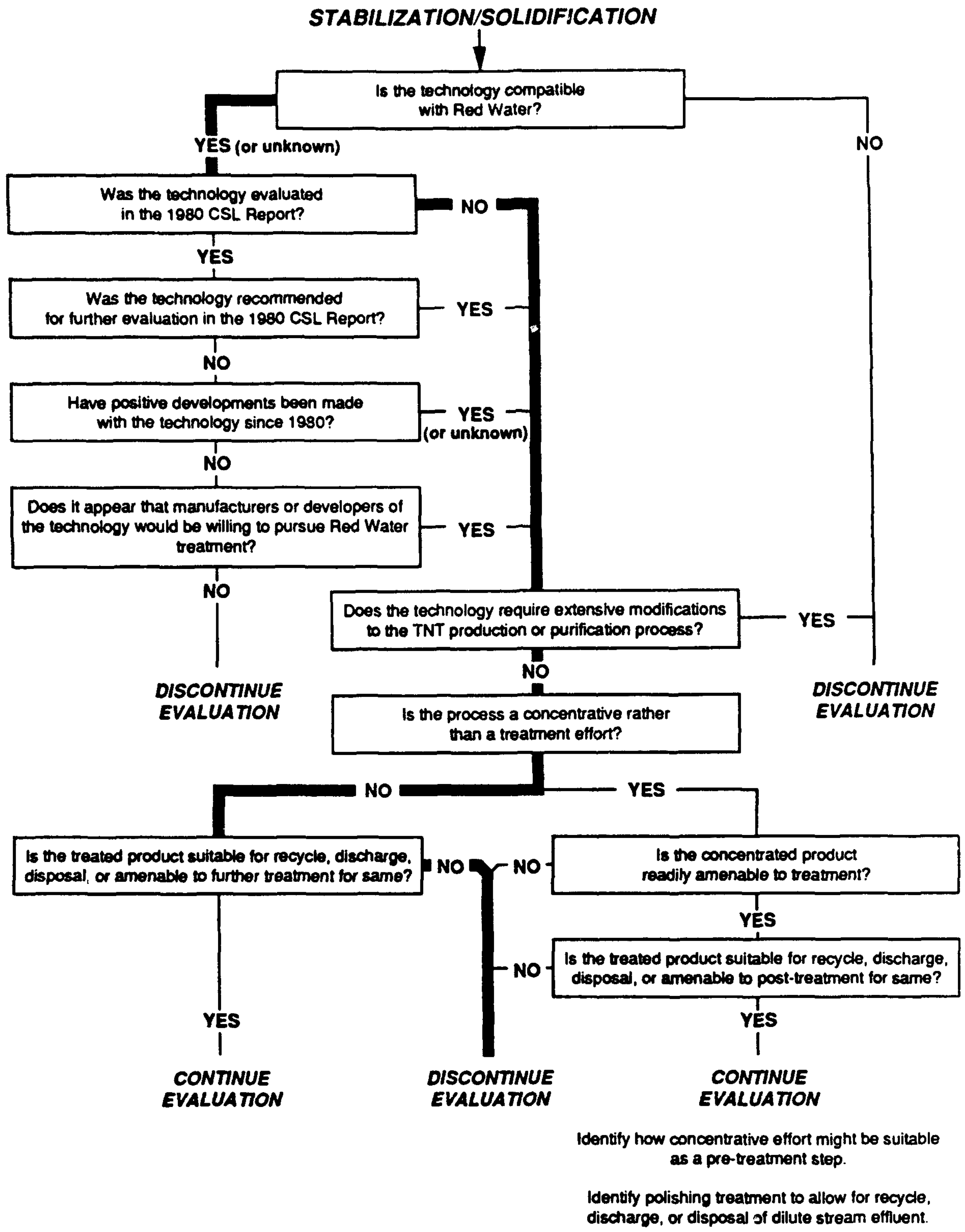


Figure 4. Prescreening decision tree for stabilization/solidification.

technology, however, has not been shown to render nonreactive the synthetic sludges containing nitrobodies such as nitrocellulose. Stabilization/solidification has not been tested on red water or a comparable simulation.

- Was the technology evaluated in the 1980 CSL Report? No.
- Does the technology require extensive modifications to the TNT production or purification process? No. The red water would be treated after it has left these processes.
- Is the process a concentrative rather than a treatment effort? No.
- Is the treated product suitable for recycle, discharge, or disposal or amenable to further treatment to render it suitable? No. Stabilization/solidification techniques have not been shown to render red water nonreactive, which is a requirement for land disposal.

Stabilization/solidification was not recommended for further evaluation.

Sixteen of the 31 technologies survived the preliminary evaluation (Table 2) and were recommended for secondary evaluation. Circulating-bed combustion, a proprietary thermal treatment marketed by Ogden Environmental Services, was discovered after the preliminary evaluation and was added to the list. No additional information was obtainable on biodegradation by the British Royal Ordinance Technology, so this technology was dropped. Biodegradation by white rot fungus on a packed-bed reactor was found to have advantages over biodegradation by white rot fungus on a rotating biological contactor, so only the packed bed option was evaluated. Consequently, a total of 15 technologies received secondary evaluation.

SECONDARY EVALUATION OF TECHNOLOGIES

The objective of the secondary evaluation was to obtain a relevant and comparative ranking of the 15 technologies to identify the technologies that possessed the greatest potential as candidates for detailed evaluation and possibly pilot-plant testing. PEI and USATHAMA derived a weighted scale in which the factors and their weights were as follows:

- Theoretical potential - 10 points
- Current application and status of technology - 20 points
- Environmental impact - 50 points
- Time and cost to develop the technology to the implementation stage - 10 points

TABLE 2. TECHNOLOGY STATUS FOLLOWING PRELIMINARY EVALUATION

Status following preliminary evaluation		
Passed	Failed	Technology
		Biological Treatment Processes
X		Biodegradation by British Royal Ordinance
X		Biodegradation by White Rot Fungus in a Rotating Biological Contactor
X		Biodegradation by White Rot Fungus in a Packed-Bed Reactor
	X	Composting
	X	Land Treatment
		Chemical/Physical Treatment Processes
X		Catalyzed Wet Oxidation
X		Liquid-Phase Oxidation (Ozone or Peroxide with Ultrasound or UV)
X		Surfactant Technology
X		Wet-Air Oxidation
	X	Acidification
	X	Carbon Adsorption
	X	Freeze Technology
	X	Ion Exchange
	X	Reverse Osmosis
	X	Solidification/Stabilization
		Thermal Treatment Processes
X		Hybrid Thermal Treatment System (HTTS)
X		Plasma Arc
X		Slagging Rotary Kiln
X		Submerged Combustion
X		Supercritical Water Oxidation
X		Thermal Separation
	X	Fluidized-Bed Reduction
	X	Incineration by CIL
	X	SCA Billerud Recovery
	X	Tampella Recovery Process
		Processes for Elimination of Red Water Production
	X	Ammonium Sulfite Purification
	X	Magnesium Sulfite Purification
	X	Nitric Acid Purification
		Mixed/Other Treatment Processes
X		Argonne National Laboratory Process
X		Licensing Existing Industrial Technology - DuPont, Air Products and Chemicals
X		Sonoco Sulfite Recovery Process

- Complexity of process and system operation, flexibility of operating parameters - 20 points

Maximum available 110 points

Points were deducted for theoretical potential if there were major questions that could render the technology unworkable. For example, liquid-phase oxidation received 6 of 10; the deduction was made because the organic matter was oxidized to unidentified organic compounds rather than carbon dioxide and water. The unidentified organic compounds might require either expensive or a yet-to-be-developed treatment technology.

The ideal (and unrealized) status of a treatment technology would be for the entire process to have been demonstrated with RAAP red water with no remaining major technical obstacles. The further the technology was removed from this ideal status, the more probable that a major R&D effort will be required to adapt the technology to RAAP red water. The scale recognizes gradation from RAAP red water to red water from another army ammunition plant to a waste stream similar to red water. The scale also recognizes that a technology used for treating a solid may require adaptation to treat a liquid such as red water. These adaptations will require time and money. The less well defined the technology is, the greater the probability of encountering serious obstacles.

Environmental impact is a major concern and accounts for 50 of the 110 points. Awards are 10 points each for air, water, and recyclability, and 20 for solid waste. Red water is almost entirely sodium salts, which are leachable if landfilled. These solids would be products of treating a K047 waste and would be hazardous by definition unless specifically delisted. Solid wastes account for 20 points because they are expected to create a greater problem. The Sonoco Sulfite Recovery Process is the only technology that received a recycling credit.

Environmental emission awards are reduced when it seems probable that the treatment process will generate a stream requiring additional treatment. Awards are also reduced when the technology is not well enough defined to estimate what emissions will occur and what additional emission controls will be required. Wastewater discharge awards were reduced when incomplete destruction of red water organic compounds left behind uncharacterized and potentially toxic organic compounds.

An acceptable process for treating red water is a necessary condition for the startup of a TNT plant. Therefore, the time and cost required to implement a technology are pertinent factors weighted at 5 points each. (Capital cost and annual operation and maintenance costs are important considerations, but these will be addressed in a third stage of evaluation.) Some of the technologies are still in the preliminary stage of development, and estimates regarding cost and development time can only be very rough.

The ideal process would take place in a single stage at ambient temperature and pressure and generate no corrosive, ablative, or toxic products, waste, or emissions. It would operate in an automated mode with minimal operator attention and could handle wide variations in feed rate, feed composition, and operating parameters. It would be easy to start up and shut down. Sufficient units would be in commercial service so that thousands of hours of operating experience would be available to assist in development of the process for red water treatment. Such a nonexistent technology would receive the full 20 points.

Process complexity has a possible 5 points. Deductions are made for multiple processing steps and operation at high temperatures, high pressure, in a corrosive environment, and where solids circulate at high velocities (ablation). Any combination of these conditions tends to increase the frequency of breakdowns. More attention to materials of construction and control of operating parameters becomes mandatory.

The difficulty-of-operation factor is worth 5 points. A complex operation will require full operator attention, and an error or inattention is likely to result in a process upset or system breakdown.

Red water varies in both composition and rate of generation. A process that can handle fluctuations and surges is more reliable. This factor is worth 5 points.

The evaluator's judgment of the technology is worth 5 points. Factors considered include a higher allowance for a technology that is in commercial service and for a technology that is well enough defined to permit better estimates of the preceding factors.

Table 3 presents a breakdown of the technologyies and the subjectively assigned scores for each evaluation constraint.

RESULTS AND DISCUSSION

As shown in Table 3, the four technologies that received the highest rating are as follows:

- Licensing of existing industrial technology (the process at DuPont's Deepwater, New Jersey, facility) - 95
- Wet-air oxidation - 76
- Supercritical water oxidation - 75
- Sonoco Sulfite Recovery Process - 72

Questions have been raised concerning the potential rapid decomposition of red water and red water solids. Reports indicate that red water is less stable when heated or acidified. Therefore, it would be prudent to perform differential thermal analysis (DTA) and thermogravimetric analysis (TGA) on

TABLE 3. COMPARATIVE EVALUATIONS

Technology	Theoretical potential of technology (10)	Current application of technology (20)	Environmental impact, air (10) wastewater (10), solid waste (20) recyclability (10), total (50)				Time and cost to develop implementation stage (5 each 10 total)		Complexity of process (CP), complexity of operation (CO), process flexibility (PF), evaluator's judgement (EJ) (5 each, 20 total)				Total (110)
			Air (10)	Waste-water (10)	Solid waste (20)	Recy-clability (10)	Time (5)	Cost (5)	CP (5)	CO (5)	PF (5)	EJ (5)	
White rot fungus on packed bed reactor	7	6	7	3	6	0	3	3	4	3	5	4	51
Catalyzed wet oxidation	5	5	4	0	5	0	2	1	2	1	1	1	27
Liquid phase oxidation	6	4	3	0	18	0	2	1	3	4	5	0	47
Solids precipitation with surfactants	7	7	5	0	0	0	2	2	1	1	1	1	27
Wet air oxidation	10	12	10	4	18	0	4	3	2	3	5	5	76
Hybrid thermal treatment system	10	6	7	7	14	0	2	2	1	1	1	0	51
Plasma arc	10	4	9	9	18	0	3	2	1	1	3	1	61
Slagging rotary kiln	10	6	8	8	16	0	3	3	1	1	1	0	57
Submerged combustion	10	4	7	7	14	0	3	3	1	1	1	1	52
Supercritical water oxidation	10	12	10	8	18	0	3	2	1	4	3	4	75
Thermal separation	8	2	4	9	10	0	2	1	1	1	1	0	39
Circulating bed combustion	10	6	7	10	18	0	3	1	2	2	2	3	64
Argonne National Laboratory process	7	5	9	2	18	0	2	1	1	1	1	0	47
Licensing existing industrial technology	10	18	10	10	20	0	5	5	4	4	4	5	95
Sonoco Sulfite Recovery	10	14	8	6	14	8	3	1	2	2	2	2	72

red water and red water solids before heating or acidifying pilot-plant scale quantities.

In differential thermal analysis, the heat absorbed or emitted by a chemical system is monitored by measuring the temperature difference between that system and an inert system, such as glass beads, as the temperatures are increased at a constant rate. Differential thermal analysis would reveal a strongly exothermic reaction indicative of rapid decomposition.

In thermogravimetric analysis, the mass of sample is recorded continuously as the temperature is increased linearly from ambient to as high as 1200°C. A significant weight loss would also reveal a rapid decomposition or explosion.

Licensing an existing technology provides the most completely developed technology of the four highest rated technologies. Red water would be sent to DuPont's Deepwater, New Jersey, wastewater treatment plant. The facility already has a permit to accept K047 wastes (red water), and it would be acceptable to the New Jersey Department of Environmental Protection to send RAAP red water to Deepwater. This proprietary technology has the best-defined costs of the 15 technologies evaluated. It uses bacterial oxidation combined with other proprietary treatments. Total capital investment would be either $350,000 for the purchase of five railway tank cars or zero if the tank cars were leased. Quoted operating costs are 32 cents per gallon for treatment and 16 cents per gallon for rail freight from Radford to Deepwater.

Wet-air oxidation involves oxidation with air or oxygen at 175° to 327°C (347° to 621°F) and 2,069 to 20,690 kilopascals (300 to 3000 psi). In 1956, M. Seidman of Zimpro Corporation (now Zimpro Passavant) carried out laboratory scale (150 to 325 ml) investigations of red water oxidation with red water obtained from the Joliet Arsenal in Illinois and the Volunteer Ordinance Works in Tennessee. Wet-air oxidation reduced the chemical oxidation demand (COD) by 96 to 97 percent. No red color remained, but the residual oxidizable material was not identified.

Red water is classified as RCRA hazardous because of its reactivity. If the residual oxidizable material has been rendered sufficiently nonreactive to be delisted as a hazardous waste and is sufficiently nontoxic to be treatable in a standard wastewater treatment plant, wet air oxidation is a viable technology because of its comparatively low capital and annual costs ($2.5 million and $990,000, respectively). If the process effluent requires additional treatment, capital and annual costs will be higher.

Supercritical water oxidation is similar to wet-air oxidation except that oxidation takes place above the critical temperature and pressure of water [374.14°C (705.5°F) and 22.09 megapascals (3205 psi)]. Supercritical water oxidation has not been attempted with red water but greater than 99.9 percent destruction of several RCRA hazardous wastes has been achieved. By analogy with wet-air oxidation, red water should be oxidizable.

The higher degree of oxidation may eliminate or lessen the requirement for treatment of the effluent. The increased operating temperature and pressure would probably increase equipment costs. This may be partially offset, however, by obtaining a faster reaction that would reduce the required size of the equipment.

If the combination of the higher operating temperature of supercritical water oxidation and red water stability presents a potential problem, having a wet-air oxidation unit and a supercritical water oxidation unit in series might be advantageous. Some of the higher costs of using two reactors may be offset by each reactor being significantly smaller than the reactor in a single unit system.

Enough development work has been performed on the Sonoco Sulfite Recovery Process (Sonoco Process) to demonstrate its technical feasibility. Higher operating costs are offset to a degree in that sodium sulfite solution (sellite) is produced for use in the TNT production plant. Further development work is necessary for effective designing and sizing of the process equipment. Sellite is recycled and the buildup of impurities may generate a waste stream requiring further treatment. In 1984, the estimated capital cost of the Sonoco Process facility at RAAP was $28 million, which is relatively high.

As in conventional paper pulp black-liquor processing, sulfites, sulfonates, and sulfates are reduced to sulfide. In the paper plant, organic matter (lignin) from wood is the reducing agent. Because red water lacks the dissolved organic matter to serve as a reducing agent, petroleum coke is added. Hydrated alumina ($Al_2O_3 \cdot mH_2O$) is also added, which ties up sodium as solid sodium aluminate ($NaAlO_2$), and avoids the problem of dealing with sodium sulfide slag. Hydrogen sulfide (H_2S) is oxidized to sulfur dioxide (SO_2). The SO_2 is absorbed in sodium aluminate solution and yields sodium sulfite (Na_2SO_3), which is recycled to the TNT production plant, and hydrated alumina, which is recycled to the red water treatment process.

The third-stage evaluation should have sufficient laboratory and pilot-plant testing so that surviving technologies can be evaluated with respect to sizing process equipment, defining process effluents and required effluent treatments, and defining the process well enough to permit budgetary estimates of capital and annual costs.

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DEVELOPMENT OF A PROCESS FOR TREATING RED WATER BY ORGANIC/INORGANIC SEPARATION AND BIODEGRADATION[*]

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ABSTRACT

The final stage of TNT production involves the purification of TNT by selective conversion of the unsymmetrical isomers into water-soluble sulfonates by reaction of the crude TNT with an aqueous sodium sulfite (sellite) solution. This treatment generates an intense, red-colored waste stream commonly referred to as "red water," which has been listed as a hazardous waste by the EPA. Its composition is primarily soluble organic sulfonates and the sodium salts of sulfate, sulfite, nitrate, and nitrite. TNT is no longer produced in the United States because of environmental concerns associated with this red water waste stream.

Argonne National Laboratory (ANL) is developing a process for treating red water. This process couples the separation of the organic and inorganic constituents of red water and treatment of the organics by biodegradation to nonhazardous products. Sludge formation in the biotreatment step is greatly reduced by removal of the inorganics and is further minimized by conversion of the sodium-containing organics to their respective acidic forms during the organic/inorganic separation. The level of separation in the process will be such that the inorganic residues can qualify as nonhazardous byproducts. Initial efforts have been directed at performing proof-of-concept investigations of process steps that can achieve these goals. Candidate processes being examined for separating the organic constituents from actual red water samples are (1) flocculation, (2) foam fractionation, and (3) aqueous biphasic solvent extraction. Each of these methods has shown promise in generating a salt-free organic product and an organic-free salt fraction. The biotreatment work has centered on cleavage of the aromatic moiety as a first step in detoxifying the organic constituents of red water. Microbial cultures and enzymes have been obtained for the biotreatment, and limited experiments have been performed with red water having a reduced salt content to demonstrate viability.

[*] Work supported by the U. S. Army, Material Command.

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INTRODUCTION

The final step in the production of TNT (2,4,6-trinitrotoluene) involves the purification of TNT by selective conversion of the unsymmetrical isomers into water-soluble sulfonates by reaction of the crude TNT with an aqueous sodium sulfite (sellite) solution. This treatment generates an intense, red-colored waste stream commonly referred to as "red water," which has been listed as a hazardous waste by the EPA. Its composition is primarily soluble organic sulfonates and the sodium salts of sulfate, sulfite, nitrate, and nitrite. TNT is no longer produced in the United States due in large part to the lack of an economical and environmentally acceptable waste disposal process for the red water.

In the past, the red water was disposed of by direct discharge into waterways and sewer systems. More recently, the red water was disposed of by incineration, biological treatment, or through consignment to nearby paper mills for its sodium and sulfite content [PAL]. Incineration is not currently a viable option because of high energy requirements, the high cost associated with the abatement of NO_X and SO_X emissions, and the problems associated with disposal of the ash residue, which contains leachable salts and unburned red water components [HELBERT]. Initial efforts at biological treatment of waste-water containing TNT were unsuccessful. Microbial transformation resulted in an effluent that was actually more toxic to fish and presented problems for sludge disposal.

The Sonoco Sulfite Recovery Process (SRP) was chosen a few years ago as the waste treatment technology for demonstration at the Radford Army Ammunition Plant (AAP). The Radford SRP was designed to recover sulfur from red water as a sellite product for recycle in TNT purification. At the same time, the Radford SRP was expected to oxidize the red water organics into water, nitrogen, and carbon dioxide with only trace amounts of nitrobody entrained in the effluent gases [PAL]. TNT production and the Radford SRP were designed to operate as a closed loop with no discharge of solid or liquid wastes. After completion of pilot-plant studies, construction of a full scale facility was begun at Radford. However, this construction was recently halted because of mounting capital costs. Consequently, other red water treatment alternatives are needed.

Staff members at Argonne National Laboratory are developing a new process for treating red water. This process couples the separation of the organic and inorganic constituents of red water by a continuous, high-throughput process, and treatment of the organics by biodegradation. The level of separation will be sufficient to qualify the inorganic residue as a nonhazardous (delistable) byproduct. To minimize sludge formation in the biotreatment step, all inorganic constituents are removed from the organic feed stream, and the sodium salts of organic red water compounds are converted to their respective acidic forms.

CHARACTERIZATION OF RED WATER SAMPLES

The development work described here was carried out using actual red water samples obtained from CIL, Inc. (Canadian Industries Limited Inc., McMasterville, Quebec), which uses a continuous process for the manufacture of TNT. The red water from CIL is expected to be representative of what would be produced by continuous production lines in the U. S. The organic and inorganic composition of red water from continuous TNT processing has been reported by Eckenrode et al., [ECKENRODE] and is listed in Table I. Total solids were reported at approximately 30 wt.%. The details of the analytical procedures were not reported.

Table I. Typical Composition of Red Water[a,b]

Chemical	Weight %
Sodium sulfite/sulfate	8 - 12
Sodium nitrite	3 - 4
Sodium nitrate	0.3 - 0.5
Dissolved 2,4-dinitrotoluene	0.03
Dissolved 2,4,6-trinitrotoluene	0.1
2,4,6-TNT-sulfite complex	3 - 7
Sulfonate of 2,4,5-trinitrotoluene	6 - 8
Sulfonate of 2,3,4-trinitrotoluene	2 - 4
Sulfonate of 2,3,6-trinitrotoluene	0.4 - 0.8
Sulfonate of 2,3,5-trinitrotoluene	0.05
Sodium nitroformate	0.2
2,4,6-trinitrobenzoic acid, sodium salt	0.1 - 0.5
[c]White compound, sodium salt	0.1 - 0.5
3,4-dinitrobenzoic acid, sodium salt	0.03
2,3-dinitrobenzoic acid, sodium salt	0.03
Trinitrobenzene-sulfite complex	0.3 - 0.5
Trinitrobenzaldehyde-disulfite addition compound	0.2 - 0.4
Trinitrobenzyl alcohol	0.2 - 0.5

[a] Adapted from [ECKENRODE]

[b] Determined for red water from the continuous process.

[c] *2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene* or 1,9-dicarboxy-2,4,6,8-tetranitrophenazin-N-oxide.

The as-received material from CIL had a density of 1.2039 g ml^{-1}(22°C) and a pH of 8.5. Upon refrigeration, solids identified as thenardite (Na_2SO_4) and mirabilite or Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) precipitated from solution. However, no suspended solids were present in the as-received red water that was stored at room temperature.

A solvent extraction method was used to separate the organic constituents from the red water prior to ion chromatographic analysis for sulfate, sulfite, nitrate, and nitrite. The quaternary amine extractant, trioctyl(methyl)ammonium chloride (Aliquat 336, as a 0.2M solution in toluene), was assumed to exchange chloride on a one-to-one basis with the organic sulfonates and carboxylates. Studies with synthetic solutions indicated that Aliquat 336 did not extract the inorganic salts at high pH. The concentration of the organics was calculated from a chloride analysis of the pale-yellow aqueous phase obtained after multiple extractions. The organic acid concentrations were also confirmed by titration with concentrated nitric acid. Results are given in Table II and are compared with data reported by others. Chromatographic results for the inorganic salts are also reported in Table II. The weight percent of total solids present was determined after air drying at room temperature to a constant weight. While the percentages for the organics and the solids agree with the literature values, the inorganic salt percentages are significantly lower than the literature values. The reason for this discrepancy is not known at this time. The difference between the weight percent of total solids and the combination of organic and inorganic salts is about 13 weight percent. This is probably due to water of hydration, which would be associated with the solids, and also to the presence of nonvolatile, nonionic organics.

Table II. Composition of Red Water Sample from Continuous Lines at CIL

	Weight%		
	Literature Values		
Component	Eckenrode[a]	Pal[b]	Experimental[c] Results
Organics[d]	9 - 14	17.3	16[e]
$NaNO_3$	0.3 - 0.5	1.7	<0.03
$NaNO_2$	3 - 4	3.5	<0.03
Na_2SO_4	8 - 12	0.6	3
Na_2SO_3	f	2.3	0.08
Solids	30 - 32	g	32[h]

[a] From [ECKENRODE]

[b] From [PAL]

[c] Based on ion chromatographic analysis of aqueous phase after repeated extraction with Aliquat 336.

[d] Sodium salts of sulfonic and carboxylic acids.

[e] Based on titration and on ion chromatographic results assuming a one-to-one exchange with chloride and an average formula weight of 284 g/mol for the organic sodium salts.

[f] Combined with result for sodium sulfate.

[g] Not given.

[h] Determined by air drying two portions of red water.

ORGANIC/INORGANIC SEPARATION

The majority of the organic compounds in red water are sulfonate salts and as such are extremely hygroscopic and therefore insoluble in nonpolar organic solvents. Separation by conventional solvent extraction requires a very powerful extractant in order to favorably partition the organics into an organic diluent. A quaternary amine (Aliquat 336) was used successfully to separate the acidic organics from red water and is useful as an analytical approach; however, the organic phase complex is so stable that stripping the loaded organic phase would be extremely difficult.

Desulfonation of the organics would vastly reduce their aqueous-phase solubility and permit their physical separation from the red water. Possible reaction routes for the desulfonation of aromatic compounds include: (1) thermal [ASKAROV, CERFONTAIN, GILBERT], (2) photochemical [El'TSOV-A, El'TSOV-B], (3) reductive [FUCHS], and (4) biological [SOEDER, STAVSKAYA]. Although desulfonation can be practical in some applications, it is not considered a viable option for red water treatment. Deactivation of the benzene ring by the nitro groups makes the sulfur-carbon bond highly resistant to cleavage.

Three processes for organic/inorganic separation appeared to offer enough potential to warrant laboratory investigation: (1) foam fractionation, (2) flocculation, and (3) biphasic solvent extraction. These three methods and initial results are discussed below.

Foam Fractionation

Foam fractionation is one of several adsorptive bubble techniques for selectively separating solutes from a solution or particulates from a suspension. These separation processes take advantage of the tendency of either hydrophobic or surface active substances to preferentially concentrate at the air/water interface. In foam fractionation, rising gas bubbles are used to carry the substance to the liquid surface where a collectable foam is produced. Red water produces a stable foam at a pH less than five. Under these conditions, the organic constituents appear to concentrate in the foam, and under the limited set of conditions tested thus far, concentration factors of the organic components in the range of 10-30% (i.e., an enrichment ratio of 1.1 to 1.3) have been realized in a single stage. A 1 to 10 dilution of the red water with distilled water still produced a stable foam; however, at 1:100 dilution, a stable foam is not obtained by sparging the fractionation column with air.

Even in the absence of a stable foam, the adsorptive bubble technique can be used to enrich the adsorbed species with the use of a tall, narrow foam column. In this configuration it is possible to get internal reflux and multistage operation in a single column [RUBIN]. Unfortunately, the scale up difficulties associated with the use of tall foam columns have prevented the use of this technique where high throughput (i.e., thousands of gallons per day) in a single column is required [RUBIN]. Application to red water processing would thus require the use of many, lower-capacity columns.

Flocculation

Coagulation and flocculation are commonly used methods for industrial wastewater treatment. Inorganic polymers such as the hydroxocomplexes of Fe^{3+} or Al^{3+} and organic polymers such as polyacrylamide or polyethylenimine are very effective at bringing about the destabilization of colloidal particles, thus leading to their aggregation with subsequent removal by sedimentation or filtration. Treatment with organic flocculants in conjunction with microfiltration has been shown to be an effective means for removing oily contaminants from wastewaters [BHAVE]. In addition, organic polymers can be used in removing noncolloidal materials such as heavy metal ions found in electroplating waste streams [CHAUFER]. Complexation-flocculation or complexation-ultrafiltration processes may also be applicable to the removal of organic constituents found in red water. Such processes rely on preferential interaction between the negatively charged nitroaromatic sulfonates and a basic polymer such as polyethylenimine having a mixture of primary, secondary, and tertiary amine groups. Membrane filtration can then be used to separate the organic fraction from the low molecular weight inorganic salts. If the sulfonate-polymer interaction is reversible (e. g., through adjustment of pH), the recovery and recycle of the polymer become a possibility.

As a separation technique for red water treatment, flocculation involves polymer interactions between particles ranging in size from single anions to colloidal particulates. As the size of these particle-polymer units grow, this material becomes easily filtered from solution. With the formation of a "sweep floc," rapid bridging between particles takes place and colloidal particles can be enmeshed in these precipitates, allowing small amounts of flocculant to remove anionic species from solution in large excess of the stoichiometric amounts.

Initial experiments have shown that high molecular weight flocculants can be used to selectively precipitate the nitroaromatic sulfonates from red water. Two different types of flocculants were studied - a high molecular weight (>4 x 10^6 daltons) cationic polymer (Magnafloc 1596C-SP) and a neutral poly(ethylenimine) having an average molecular weight of 10,000 daltons. With red water samples diluted 1:50 with deionized water, the cationic flocculant, at a dose level of 250 ppm, produced an easily filtered precipitate, which resulted in a 50% reduction in color at 400 nm. Under similar conditions, the poly(ethylenimine) was much less effective. However, at 200 ppm, the neutral polymer was capable of producing a clear yellow supernatant when used in conjunction with hydrous iron colloid at a total iron concentration of 5 mM.

These results suggest that in the absence of any particulate material, red water treatment by flocculation may not offer the best possibility of separation. However, it could be effective as a polishing step in conjunction with microfiltration for producing a delistable inorganic stream.

Biphasic Solvent Extraction

Aqueous biphase systems were originally developed by Albertsson in the mid-50s for the separation of microbial cells, cell organelles, and viruses [ALBERTSSON]. Biphasic separation involves solute partitioning between two immiscible aqueous phases--a polymer-rich layer and an inorganic salt layer. Biphase formation may also be achieved in the absence of any dissolved salts by using a combination of water soluble polymers. These combinations typically involve a straight chain polymer such as polyethylene glycol (PEG) and a highly branched polymer such as Dextran. In recent years, interest in biphasic systems for application in biotechnology [KULA, WALTER], separations of metal ions [ZVAROVA], ultrafine particles [ANANTHAPODMANABHAN], and organics [GULLICKSON] has increased dramatically.

With regard to wastewater treatment, aqueous biphasic systems have similarities with conventional solvent extraction but do not utilize an organic diluent, which itself may become a source of pollution. In addition, the water-soluble polymers that have been used in biphase formation are inexpensive, nontoxic, and biodegradable. They can also be removed from the process effluents for recycle by ultrafiltration or electrodialysis.

Research to date on solvent extraction using aqueous biphasic systems has concentrated on the PEG system. The PEG system is of interest because of the expected high level of sulfate and other anionic salts in red water (8-12% Na_2SO_4/Na_2SO_3, 3-4% $NaNO_3$, 0.3-0.5% $NaNO_2$ [ECKENRODE]). At room temperature, concentrations of approximately 7.5% PEG and 6% Na_2SO_4 by weight easily form an aqueous two-phase system. And, as the phase diagram in Figure 1 indicates, increasing temperature promotes biphase formation at much lower salt and PEG concentrations. Since TNT is in the molten state (temp. > 80°C) when sent to the sellite scrubbers, biphase formation should be easily attained.

Red water introduced into such a system concentrates the organic component in the top (PEG) phase, with a distribution ratio of about 10 for a single stage. Through successive batch contacts of undiluted red water with 7.5% PEG (PEG previously equilibrated with 6% Na_2SO_4), a 1000-fold reduction in color of the red water was achieved by the fourth stage. Based on literature data for the PEG system, the distribution ratios of the inorganic salts should be less than one [ZVAROVA]. If this enrichment factor were maintained and not affected by the changing organic and salt concentrations throughout a process, an extremely effective countercurrent solvent extraction process could be designed. It is highly likely that as the organic material is removed from the residual salt solution, the distribution ratio will remain high or continue to increase, providing a highly organic-free salt stream.

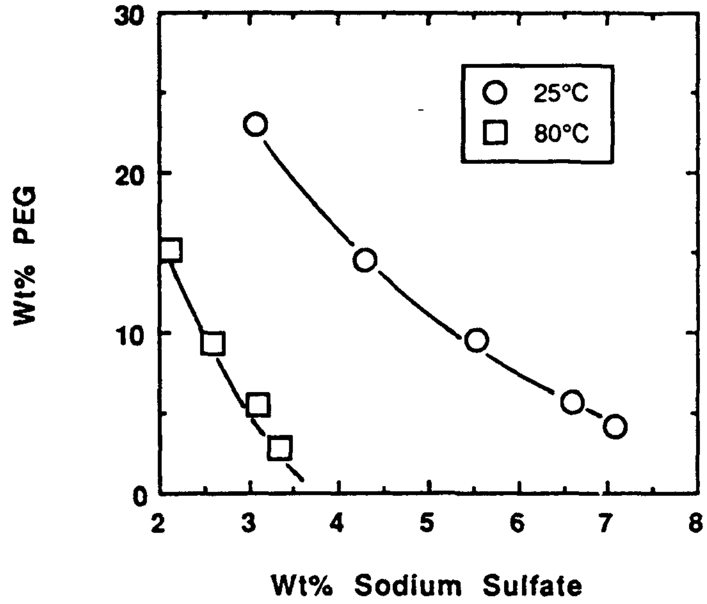

FIGURE 1. Binodial Curves for the PEG / Sulfate System. System Compositions Above the Binodial are Biphasic.

Biphasic solvent extraction is thought to be the technology with the greatest promise for successfully separating the inorganic and organic constituents of red water. This process would be run in a continuous, countercurrent mode using a multistage contactor (e.g. mixer-settler, pulsed column, or centrifugal contactor). The choice of contactor technology would be determined by economics and process requirements. As the red water stream flows countercurrent to the flow of the polymer phase, the organic content of the red water will steadily decrease, providing an organic-free salt solution that exits the process. Conversely, as the polymer phase moves through the extraction section, its organic concentration increases. Before exiting the process, the organic-rich polymer phase would be scrubbed with an aqueous acid solution to convert the sodium salts of the organic sulfonates to their acidic forms. If necessary, an additional scrub section can be added to further reduce the inorganic salt concentration in the polymer phase. Because of the phase behavior of the PEG system (see Figure 1), sulfate or sulfite is required to maintain the biphase. Scrubbing inorganic salts from the PEG phase, therefore, would require the use of a second polymer, such as dextran, that is immiscible with the PEG phase. Ultimately, the degree of salt removal from the red water organics would be dictated by the combination of economics and the capabilities of the biotreatment process.

BIOTREATMENT

The organic constituents of red water include a complex mixture of substituted aromatic compounds (see Table I). For biotreatment to be effective in detoxifying these contaminants, it is believed that cleavage of the aromatic rings would be a necessary first step. Since biological processes have been used successfully for other substituted aromatic compounds, various microbial and enzymatic treatments are being tested. Non-specific ligninases from the white rot fungus *Phanerochaete chrysosporium* and bacterial consortia isolated from the Joliet AAP being tested for their ability to transform the organic constituents of red water into less hazardous products that can be handled by conventional stack cleaning and wastewater treatment equipment.

The *P. chrysosporium* strain (BKM-F-1767) that was used in the biotreatment studies was obtained from T. K. Kirk of the USDA, Forest Products Labs, Madison, WI. This fungus has been shown to cleave a variety of bonds in lignins and different recalcitrant aromatic compounds [KIRK, BUMPUS]. This catalytic activity is believed to be the result of the lignin peroxidase isozyme which is secreted into the culture medium during the ligninolytic phase of fungus growth.

Initial tests indicate that *P. chrysosporium* is capable of growth in the presence of salt-reduced red water. In these experiments, the Na_2SO_4 concentration was lowered by refrigeration of the red water sample. As shown in Table III, the red water actually stimulates fungal growth if it is introduced before the ligninolytic phase. Thus, the red water was not inhibitory to the germination of conidia and growth of mycelium. Red water has a characteristic UV absorbance peak at 345 nm, which is significantly reduced by fungal growth. Preliminary HPLC analysis confirmed an alteration of the red water components. Further work will be required to identify the specific reactants and their degradation products. A combination of HPLC and NMR analysis will be used to demonstrate ring hydrolysis or mineralization of the red water aromatics.

A combination of treatment approaches will be examined in an effort to optimize the biological degradation of red water. For example, UV or ozone pretreatment prior to microbial inoculation is one option. The most promising biotreatment protocol will be used as a basis for the conceptual design of a full-scale facility and will be integrated with the organic/inorganic separation for bench-scale demonstration using actual red water.

Table III. Effect of Red Water on the Growth of *P. chrysosporium*[a]

	Dry Wt of Mycelium, mg		
Red Water Addition	Day 4	Day 7	Day 13
No Red Water Added	36.3	46.5	77.7
Conidial Inoculation (day 1)	36.0	61.1	113.3
Start Ligninolytic Phase (day 4)	36.3	45.8	113.3
End Ligninolytic Phase (day 7)	36.3	46.5	71.5

[a] Cultures were grown following the procedures of Tien and Kirk [TIEN]. The red water concentration in the growth media was at a 1:1000 dilution.

CONCLUSIONS

Laboratory-scale, proof-of-concept experiments have demonstrated that inorganic/organic separation with biotreatment of a salt-free red water has promise. During the next year we plan to further develop this technology to the point that a conceptual design and cost estimate for a full-scale plant integrating both steps can be made. Based on successful development and reasonable economics, future plans are to demonstrate the process at laboratory pilot-scale at ANL. This would be followed by further studies at an appropriate field site before moving to full-scale design and implementation at an army installation.

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ENGINEERING STUDY OF A SEQUENCING BATCH REACTOR FOR DENITRIFICATION OF MUNITION WASTES

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ABSTRACT

Biological denitrification, using a sequencing batch reactor (SBR), is being pilot tested for treatment of nitrate wastes resulting from nitroguanidine production at the Sunflower Army Ammunition Plant (Desoto, Kansas).

Because of the number of variables involved, and the potential cost of a full-scale facility, a mathematical model of the reactor has been developed to help establish design and operating criteria, and also to have a diagnostic tool in the event of reactor upsets.

The model is currently being tested experimentally, at both the bench and pilot scales, prior to setting design criteria for a full-scale facility.

INTRODUCTION

In the relative absence of oxygen, denitrifying microbial consortia utilize nitrate as an oxidizing agent, converting the nitrate first to nitrite and then to nitrogen gas. If the intermediate product, nitrite, accumulates beyond a certain point, it will become toxic to the organisms and the denitrifying process will cease. A carbon source must also be added to the reactor, and in the present case methanol is being used for that purpose.

In order to utilize the denitrifying consortia, a sequencing batch reactor (also known as a fill-and-draw, or fed batch reactor) was chosen. This type of reactor has a number of operational advantages over a conventional tertiary treatment process. SBRs are operated in a cyclical mode by alternately filling, reacting, settling, and drawing down, all in the same vessel (see Figures 1 and 2). As a result, they are capable of much greater flexibility than a conventional design. For example, the fill rate can be adjusted from rapid (approximating a batch reactor) to slow (approximating a flow reactor). Furthermore, the reactor contents can be tested prior to discharge. SBR's have been used successfully in commercial applications treating highly contaminated leachates in vessel sizes as large as 500,000 gallons.

MATHEMATICAL MODEL

Nitrate does not inhibit microbial growth, and its removal rate was therefore characterized by a Monod expression. However nitrite, which is formed as an intermediary product, is inhibitory, and its rate of removal was therefore modelled using an Andrews expression. The carbon source (methanol) was assumed to be in excess.

The current model neglects settling, since it is based entirely on reaction kinetics. Furthermore, it assumes that reaction occurs during all three phases of SBR operation (fill, react, and draw).

The following equations for the reactor are given in dimensionless form. These equations were solved numerically on a VAX 11/780 using a semi-implicit method.

During Fill:

Nitrate Balance

$$\frac{du}{d\tau} = \frac{1}{\delta\sigma_1 + \tau}(u_f - u) - \frac{u}{1 + u}\beta x$$

Nitrite Balance

$$\frac{dv}{d\tau} = \frac{1}{\delta\sigma_1 + \tau}(v_f - v) + \frac{u}{1 + u}\beta x \rho - \frac{v}{w + v + \gamma v^2}\beta x \eta \phi$$

Biomass Balance

$$\frac{dx}{d\tau} = \frac{-1}{\delta\sigma_1 + \tau}x + \frac{u}{1 + u}\beta x + \frac{v}{w + v + \gamma v^2}\beta x \phi - \beta x v \varepsilon$$

During Reaction and Draw:

Nitrate Balance

$$\frac{du}{d\tau} = -\frac{u}{1 + u}\beta x$$

Nitrite Balance

$$\frac{dv}{d\tau} = \frac{u}{1 + u}\beta x \rho - \frac{v}{w + v + \gamma v^2}\beta x \eta \phi$$

Biomass Balance

$$\frac{dx}{d\tau} = \frac{u}{1 + u}\,\beta x + \frac{v}{w + v + \gamma v^2}\,\beta x 0 \;-\; \beta x v \varepsilon$$

Dimensionless Quantities:

$$u = \frac{s}{K}, \quad u_f = \frac{s_f}{K}, \quad x = \frac{b}{Y_1 K}, \quad w = \frac{K'}{K}, \quad \phi = \frac{\mu}{\mu_m}, \quad \eta = \frac{Y_1}{Y_2}$$

$$\rho = \alpha Y_1, \quad \tau = \frac{t\, Q_f\, \sigma_1}{V_R}, \quad \beta = \frac{\mu_m V_R}{Q_f\, \sigma_1}, \quad \gamma = \frac{K}{K_i}, \quad \delta = \frac{V_o}{V_R}$$

$$\sigma_1 = \frac{t_1}{t_3}, \quad \sigma_2 = \frac{t_2 - t_1}{t_3}, \quad \sigma_3 = \frac{t_3 - t_2}{t_3}$$

$$v_f = \frac{p_f}{K}, \quad v = \frac{p}{K}, \quad \varepsilon = \frac{k\, K}{\mu_m}$$

where:

V_R is the maximum fill volume

V_o is the mixed liquor volume at the beginning of a cycle

Q_f is the feedflowrate

b is the biomass concentration in the reactor

s_f and s are the nitrate concentrations in the feed and in the reactor, respectively

p_f and p are the nitrite concentrations in the feed and in the reactor, respectively

Y_1 is the yield coefficient for nitrate

Y_2 is the yield coefficient for nitrite

k is the rate at which cells are killed by the nitrite

α is the stoichiometric ratio of nitrite to nitrate

t_1 is the fill time, $t_2 - t_1$ is the react time, $t_3 - t_2$ is the draw-down time, and t_3 is the total cycle time

μ is the specific growth rate:

$$\mu = \mu_N + \mu_I$$

$$\mu_N = \frac{(\mu_m)s}{K_s + s}$$ (Monod expression for non-inhibitory nitrate)

$$\mu_I = \frac{(\mu)p}{K' + p + (p^2/K_i)}$$ (Andrews expression for inhibitory nitrite)

RESULTS

Figure 3 shows the theoretical survival regions assuming no settling of the biomass, and therefore indicates conservative regions of operability. In Region I, the biomass eventually washes out of the reactor. In Region II, there is a steady-cycle biomass concentration even if there is no settling. In Region III, there may be survival or washout of the biomass, depending on the initial biomass concentration. Therefore, given a nitrate feed concentration (u_f), the required reactor volume (or flow rate) can be determined from the dimensionless hydraulic residence time (β).

Figures 4 and 5 compare the shape of the model-generated curves of nitrate and nitrite removal with batch data from a 1200 gallon pilot reactor. The pilot reactor was fed rapidly once or twice each day, but was not fed at night, with the result that the organisms had to reestablish their metabolic equilibrium the next morning when the reactor was fed again. This meant that the reactor was operating in essentially a discrete batch mode, and the theoretical curves were calculated for a batch mode using a modification of the SBR equations shown above. The comparison between theory and experiment is very good, and indicates the ability of the model to follow the qualitative trends in the data.

Figures 6 to 8 show the consequences of the model predictions. Figure 6 indicates what happens when a steady-cycle is reached after successive rapid (batch) fills. That is, the reactor is fed on a regular basis so that the nitrate concentration is never zero for an extended period. As a result, the organisms do not need to be reacclimated each morning and their performance improves. By contrast with Figure 5, the nitrite concentration does not peak, and in fact declines quickly, once steady operation is reached.

Figures 7 and 8 show what happens in the first cycle if, instead of filling the reactor instantaneously (batch mode), the fill time (σ_1) increases to 10% and 50% of the total cycle time, respectively. Slower filling reduces nitrite levels to virtually zero, and also reduces the peak nitrate levels. This would improve reactor operability, but increase capital cost - slower filling will result in a larger reactor volume for the same throughput.

CONCLUSIONS

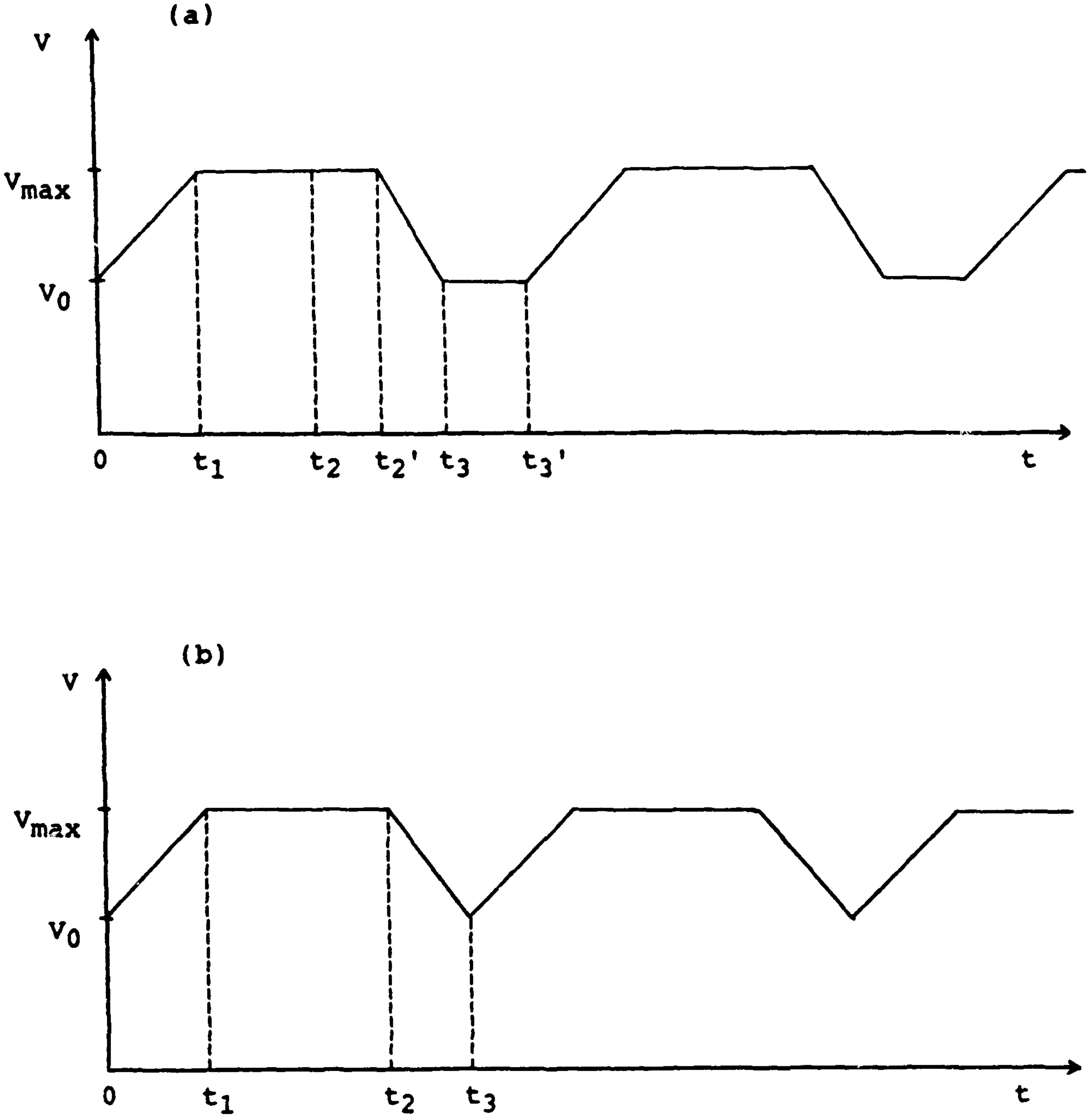
A mathematical model has been developed that can successfully indicate sequencing batch reactor performance in a denitrification process.

The model indicates that steady-cycle operation, at slower fill rates, can maintain low nitrite and nitrate levels in the effluent.

FUTURE WORK

Two important parameters remain to be evaluated before final design of the full-scale unit is completed. These involve temperature effects, and the optimum methanol/nitrate ratio in the feed.

FIGURE 1



Qualitative Representation of the Volume Change During Cycles: (a) generalized case;(b) special case (with no settle or idle phase)

FIGURE 2

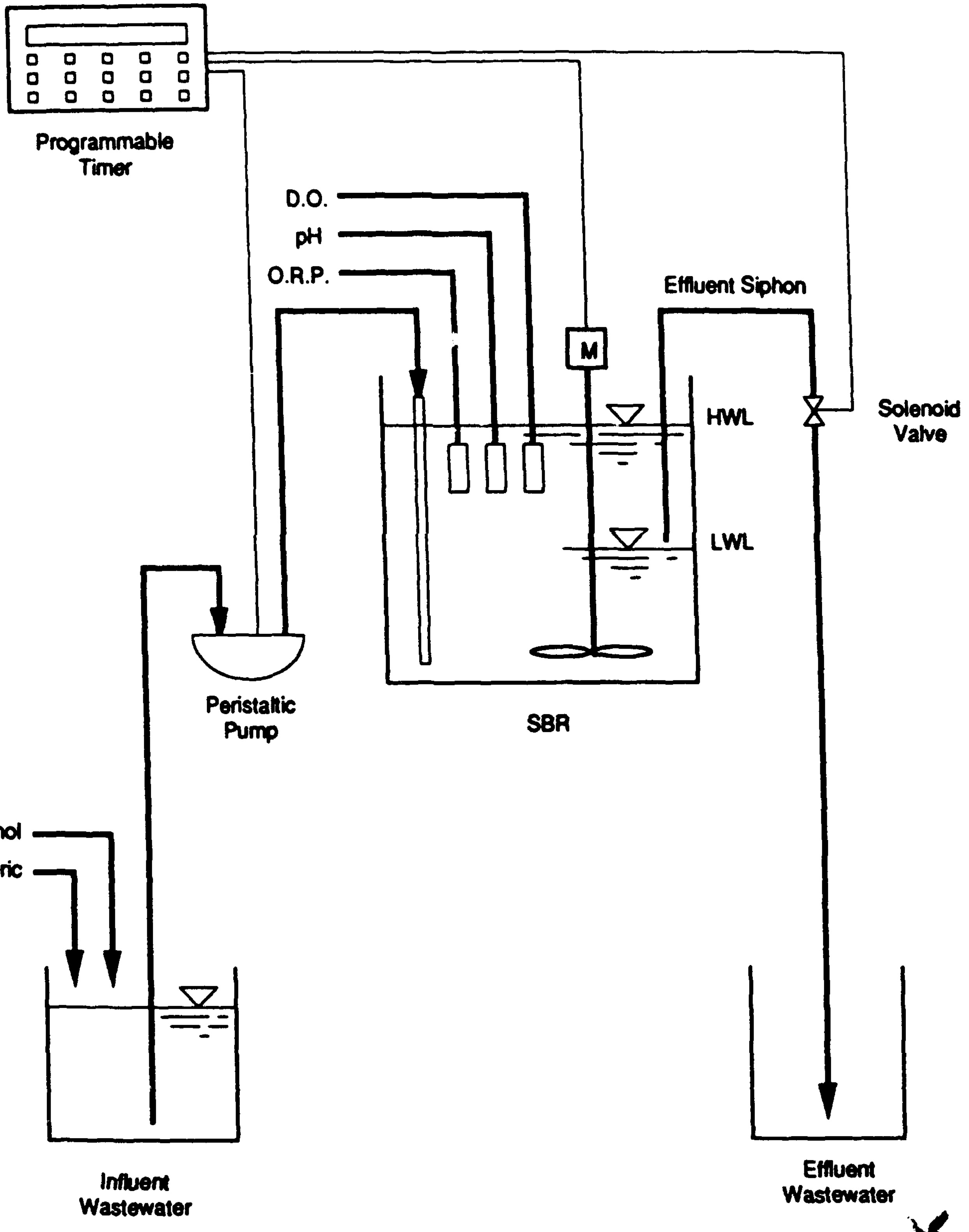

Programmable Timer
D.O.
pH
O.R.P.
Effluent Siphon
M
HWL
LWL
Solenoid Valve
Peristaltic Pump
SBR
Methanol
Phosphoric Acid
Influent Wastewater
Effluent Wastewater

FIGURE 3

operating diagram

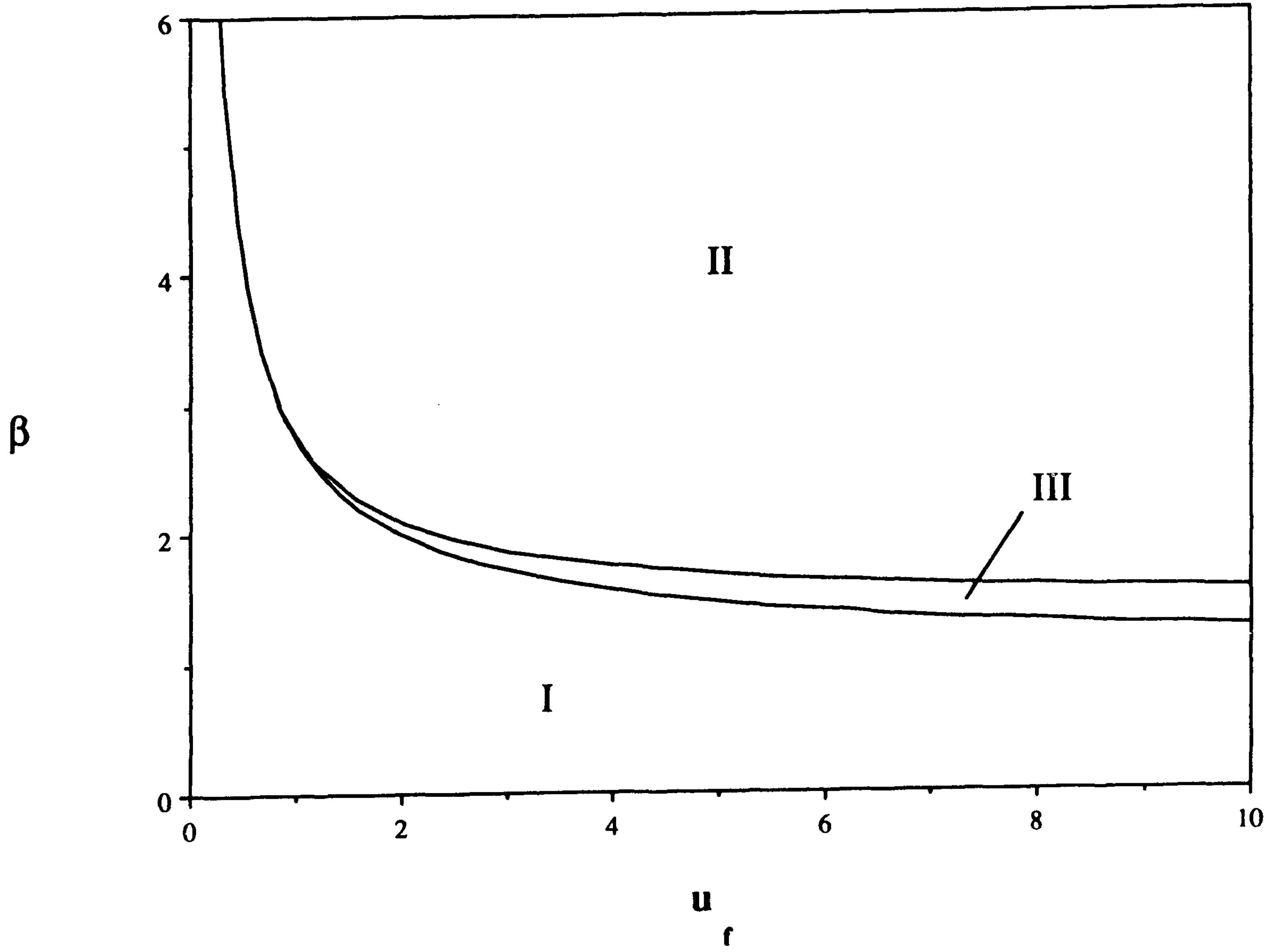
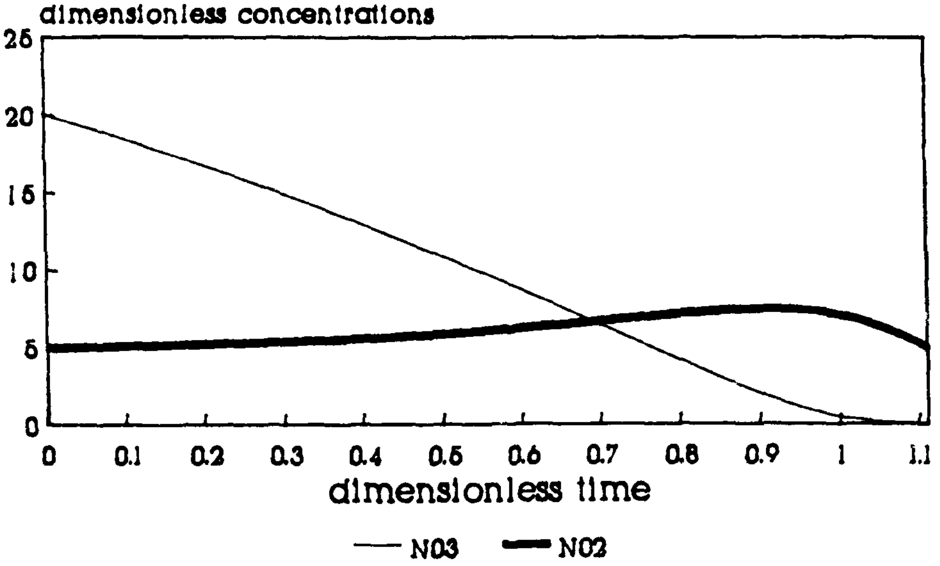


FIGURE 4

SIMULATED BATCH DATA
Ist CYCLE



BATCH DATA FROM KANSAS
DATE OF RUN 08-28-1989

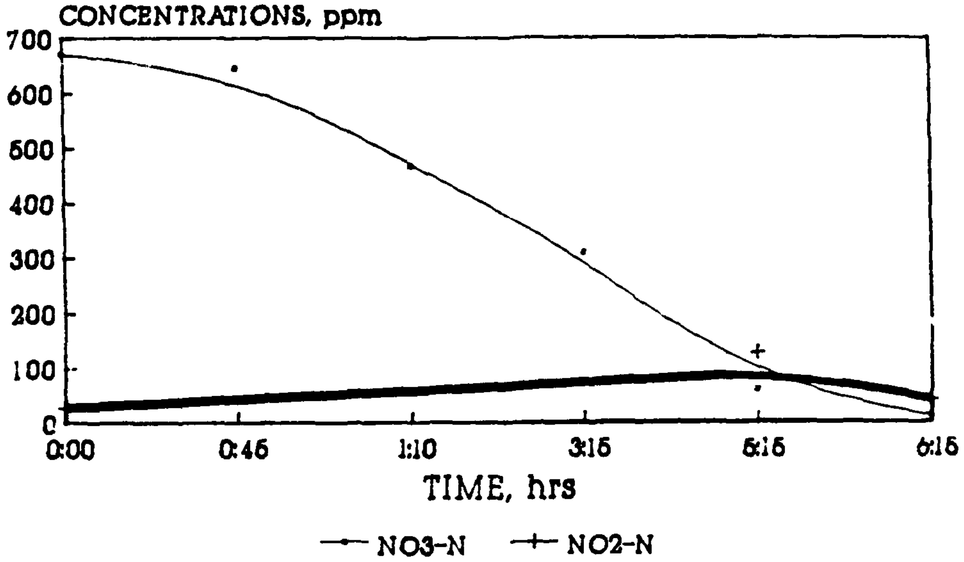
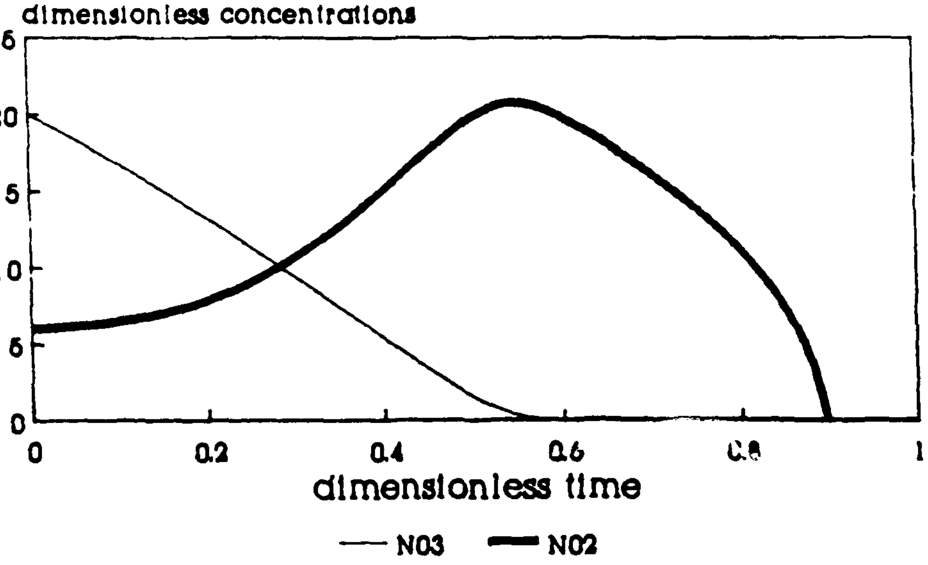
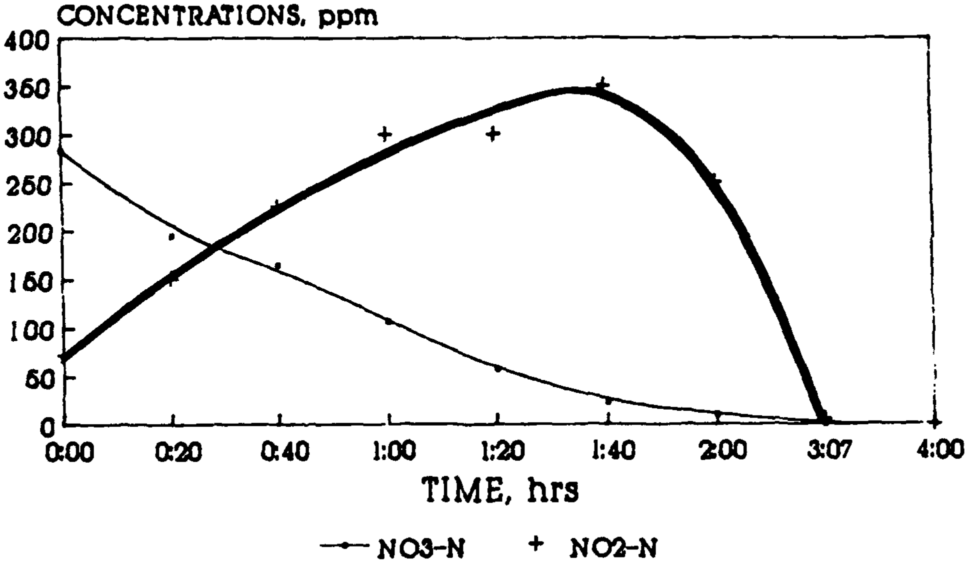


FIGURE 5

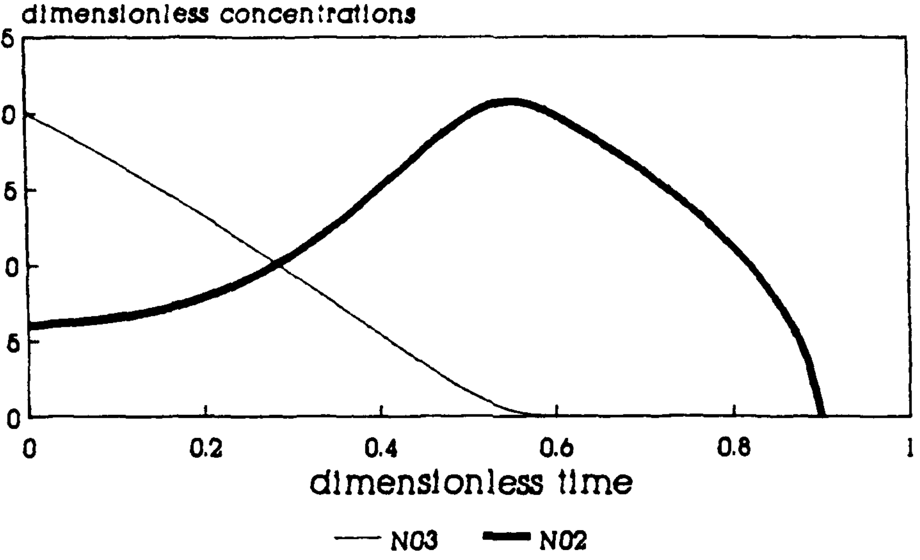


SIMULATED BATCH DATA
Ist CYCLE

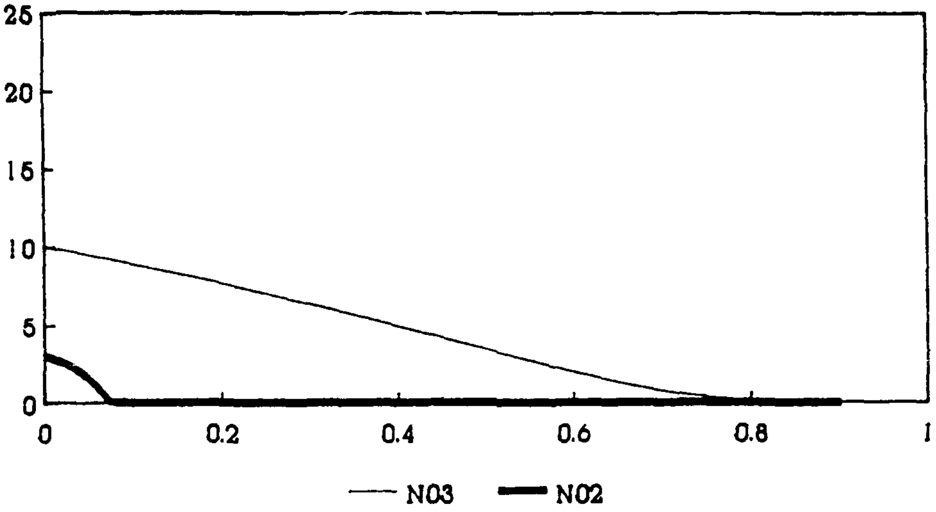


BATCH DATA FROM KANSAS
DATE OF RUN 09-22-89

FIGURE 6



SIMULATED BATCH DATA
1st CYCLE



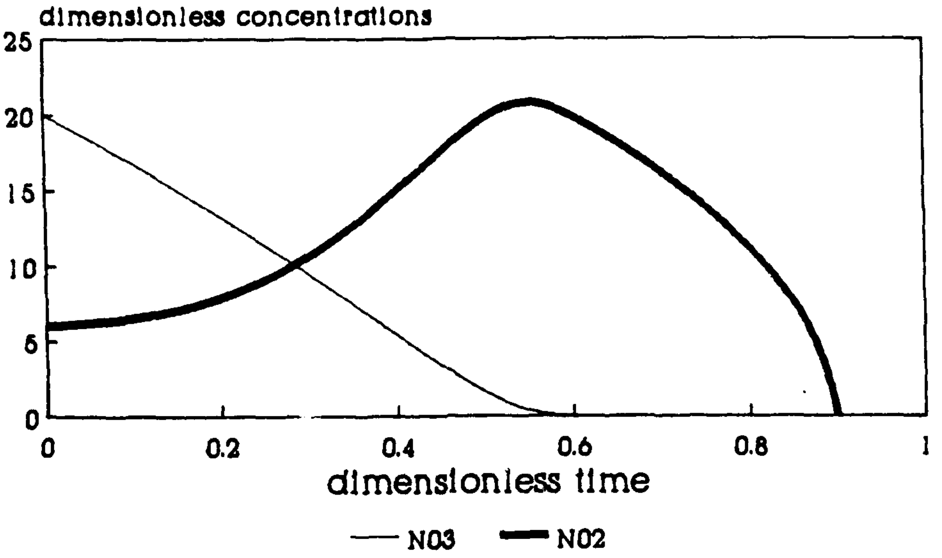
SIMULATED BATCH DATA
STEADY CYCLE (AFTER 21 CYCLES)

delta=0.5 phi=1.61 gamma=2.0 w=0.5
eta=16.28 rho=2.21 eps=0.0

FIGURE 7

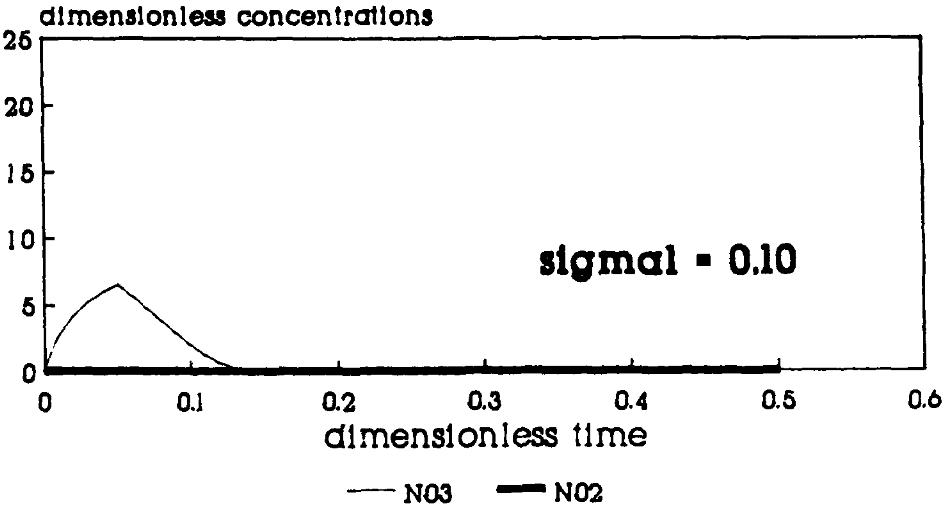
SIMULATED BATCH DATA

Ist CYCLE



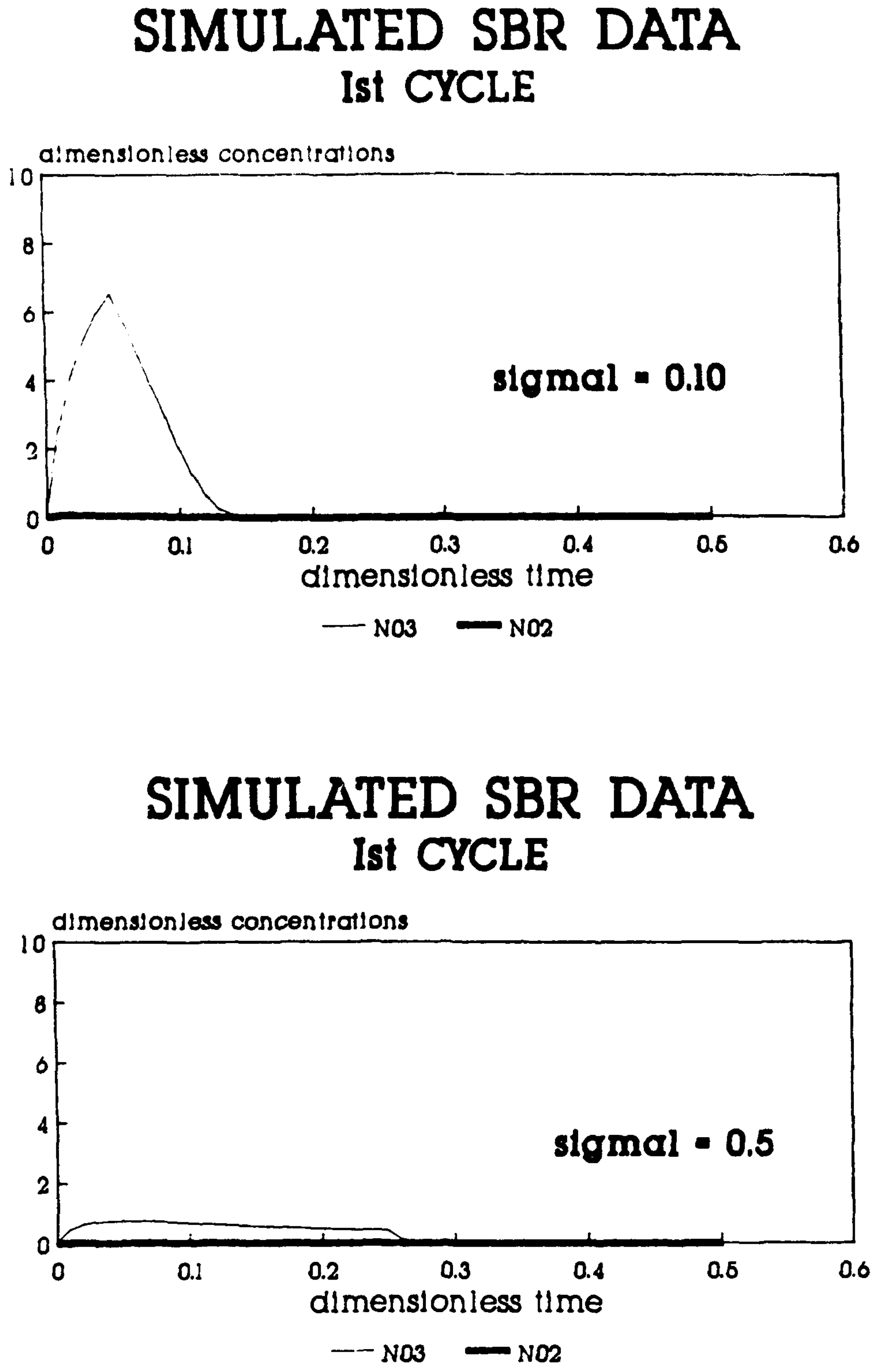
SIMULATED SBR DATA

Ist CYCLE



delta=0.5 phi=1.61 gamma=2.0 w=0.5
eta=16.28 rho=2.21 eps=0.0

FIGURE 8



delta=0.5 phi=1.61 gamma=2.0 w=0.50
eta=16.28 rho=2.21 eps=0.0

ENVIRONMENTAL CONCERNS IN TESTING LIQUID GUN PROPELLANTS

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ABSTRACT

The US Army is investigating the use of liquid propellants for use in large and medium caliber guns. The propellants of greatest interest are LGP 1845 and LGP 1846. These two propellants are made of hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) and water.

As the liquid propellant program progresses the need for testing larger quantities of the propellants has arisen. Increased production for large scale hazard testing, vulnerability testing and testing in the gun have produced a need for development of a environmental assessment of testing and fielding these propellants. Disposal and demilitarization procedures need to be determined.

Small scale biodegradability studies have been completed on the ingredients of these propellants. TEAN was found to be biodegradable under all conditions and HAN would not persist in most soils. Scaling up these studies is in progress. This work and the current disposal techniques will be discussed.

An Environmental Assessment (EA) has been prepared for the vulnerability tests that are currently being conducted. In the course of preparing the EA, items of concern included; partial decomposition, nitrogen oxide release, spills and disposal of unreacted or partially reacted propellant. How each item was addressed and handled will be discussed.

INTRODUCTION

The US Army is currently investigating the use of liquid propellants (LP) in large and medium caliber guns. The propellants are homogeneous and use hydroxylammonium nitrate (HAN) as an oxidizer in conjunction with various amine nitrates as fuels. Such systems have been determined to be the most promising candidates. Propellants LGP 1845 and LGP 1846 have undergone extensive characterization and testing and consist of HAN as the oxidizer, triethanolammonium nitrate (TEAN) as the fuel and water in two proportions as a diluent. Propellant compositions are designed to be stoichiometric so as to only produce N_2, CO_2 and H_2O as combustion products. Therefore, the HAN to TEAN molar ratio in both propellants is 7:1 (HAN:TEAN weight ratio = 3.167). LGP 1845 is, by definition, 11 M in nitrate and LGP 1846 has, by definition, 20 weight % water. This gives propellant compositions listed in Table I. Values in parenthesis are calculated using a predicted density.

Table I. Propellant Compositions

	Density	HAN		TEAN		H_2O	
	g/mL	Wt%	M	Wt%	M	Wt%	M
LGP 1845	1.46998	(62.884)	9.625	(19.850)	1.375	(17.266)	(14.000)
LGP 1846	1.44998	60.806	(9.180)	19.194	(1.312)	20.000	(16.040)

As this program progresses and requires greater amounts of propellant, the effect on the environment of fielding a LP weapon system becomes increasingly important. From the production plant to the actual gun, liquid propellant environmental impacts will differ significantly from conventional propellant environmental impacts. From dealing with production wastes to cleaning up accidental spills, to combustion products, liquid propellant systems require a completely new scenario.

To address these items, one must conform to Army Regulations, the Environmental Protection Agency and all federal, state and local legislation. This paper will attempt to treat these issues and satisfy each independently and collectively.

Small scale laboratory tests for biodegradation have been completed on propellant ingredients. Larger scale methods are being investigated for demilitarization and disposal. As gun testing escalates, production increases, and process development and survivability testing continue, larger and larger quantities of propellant are being shipped, handled and consumed. The impacts of all these advances to the environment require evaluation.

The US Army has set forth policies, responsibilities and procedures for intergrating environmental considerations into Army planning and decision making by implementation of the National Environmental Protection Act.
The Army has established criteria to determine what actions require preparation of Environmental Assessments (EA), Environmental Impact Statements (EIS) and identify applicable categorical exclusions.[1]

BACKGROUND

Characterization

In characterizing these propellants, a number of physical properties have been measured or theoretically estimated. The effect of the molecular structure of TEAN on the propellant physical properties has also been investigated. The purpose of these studies was to produce a model that will predict properties not yet measured including temperature and pressure effects. In general, this attempt has been successful.

Being homogeneous and undergoing no phase transformations under the entire temperature scale of military interest -55° C to 65° C, physical properties of these propellants exhibit unusual character. Vapor pressures of LGP 1845 and LGP 1846 are consistently lower than the partial pressure of the water they contain; the only volatile component. Density increases with decreasing temperature. Viscosity increases with decreasing temperature in accordance with the Vulman-Thamer-fletcher equation for molten salts. Although these property variations must be taken into consideration in gun design, it is expected that the gun will operate properly over the entire temperature range of interest.

Mixtures of HAN, TEAN and water at concentrations near that of the propellants exhibit properties of molten salts. The TEAN appears to be incorporated into a matrix that suppresses its properties. The hydroxyl groups available in TEAN appear to extend the size and coherence of the matrix. Equilibrium and transport properties both give evidence to this. Molecular structure and interactions are an important mechanism in the composition and decomposition of the propellants.[2]

Toxicity

Extensive toxicity testing has been completed, however additional testing is required on these materials. A complete medical research plan has been approved by the Office of the Surgeon General (OTSG). Areas that have been investigated are oral ingestion, aerosol inhalation, dermal and ocular exposure.[3-10]

The following are guidelines established by the completed work on toxicity testing of these items. Testing to date has been performed solely on animals, no humans. LP 1845 and LP 1846 are considered toxic as far as ingestion, dermal contact and inhalation. The principal personal hazards associated with HAN-based liquid propellants are contact of the liquid on the eyes, exposure of the skin to the liquid, and inhalation of aerosol vapor.

The following toxic responses have been shown on exposure to the HAN-based LPs:

OCULAR: Applications of LP 1846 to rabbit eyes elicited responses including conjunctival redness, chemosis, iritis, corneal opacities and neovascularization of the cornea. All lesions were reversible except the neovascularization.

ORAL: The short term toxic response to oral ingestion of LP 1845, 1846 is methemoglobin formation and a reduction in the oxygen carrying capacity. This results in respiratory distress and cyanosis. Long range tests showed signs of splenic congestion and reticuloendothelial hyperplasia. Results such as anemia, anorexia, myloid hyperplasia of the bone marrow and degenerative changes such as B and T cell atrophy in the spleen were seen in the higher dose levels.

DERMAL: Dermal tests resulted in a high incidence of chronic and ulcerative dermatitis. Heinz body formation and red blood cell destruction was seen in the higher dose levels.

INHALATION: Inhalation of aerosol was seen to produce the following effects in high dosage tests; weight loss, spleen and liver enlargement, respiratory irritation and blood dyscrasia. Minimal effects were seen at low dose levels.
As stated previously, propellant vapor is not a problem.

Due to these test results, personnel protection is recommended. No eating, drinking or smoking when working with the propellants. Gloves, glasses or goggles, and protective clothing shall be worn when contact with the propellant is probable. Maximum allowable workplace airborne concentration of HAN is recommended at 3 mg/m^6. Caution: the effects of skin exposure, oral ingestion and aerosol inhalation are additive.

Disposal

Small scale laboratory tests have been completed by USA Natick Research and Development Center to provide proper disposal guidelines, process water treatment and determine the effects of spills on soils. Triethanolamine was mineralized under aerobic and anaerobic conditions. No significant concentrations of intermediates were identified during the biotransformation of this material. HAN was found to be chemically unstable at pH 5.9 and above. Based on these results, Natick recommends biological treatment as a viable route for propellant waste streams.[11]

Conclusions from these tests indicate a need for evaluation of these materials at higher concentrations. Also, TEAN solutions contained small amounts of nitrosamine contamination. With the solution to those two concerns, it appears biological treatment could be a viable option for disposal of these materials.

Production

With the detection of the nitrosamine contamination in TEAN samples, it was undertaken to determine if manufacturing parameters could be controlled to eliminate nitrosamines in the product. TEAN is manufactured by an acid base neutralization of triethanolamine with nitric acid. A study was performed and it was determined that using the following conditions there are no detectable nitrosamines synthesized. The amine should always be added to the acid, never the reverse. The amine should be at least 97% pure, used neat and the temperature should be kept below 4° C.[12]

The liquid propellant program is scaling up. Such increased testing has resulted in a closer watch on the environmental aspects of fielding LPs. The first 155mm regenerative gun was fired June 1988. A vulnerability test program was initiated at Aberdeen Proving Ground in December 1988 and production has expanded since 1987. As the propellant is handled, transported and consumed in larger quantities, the chances of adverse environmental impacts increase.

Vulnerability Testing

The objective of the vulnerability test program was to assess the susceptibility of LP to initiation by ballistic attack. An understanding of the susceptibility to initiation will permit analytical evaluation of the survivability of combat vehicles which employ liquid propellants and will provide a basis for designing more survivable equipment.

This action is intended as a preliminary examination at the vulnerability of the liquid propellant. The objectives of this action are:

a. To provide some initial insight into the vulnerability aspects of liquid propellants and to assess their reactions and the causes of the reactions under varying conditions of ballistic impact.

b. To provide some initial input to assist in the hazard classification process required of all liquid propellants.

c. To provide guidelines and recommendations to ongoing LP container design efforts in the area of survivability requirements.

DISCUSSION

Biodegradation

Propellant ingredients, HAN and TEAN were investigated separately in the Natick biodegradation studies. Also tested were two other amine nitrate fuels, Trimethylammonium nitrate and isopropylammonium nitrate. Test results show that all three fuels were biodegradable. Under aerobic and anaerobic conditions TEAN was mineralized with no evidence of intermediates formation. Intermediates were detected only when the system was perturbed (ie. nutrient reservoir changed). TEAN was mineralized in minimal medium in which it was the only source of carbon and nitrogen under aerobic conditions.

TEAN is readily mineralized in organic poor or organic rich or in flooded soils at concentrations up to 0.5%. Initial rates of decomposition are rapid with a subsequent leveling off of activity and gradual release of carbon dioxide. This was found in both aqueous and soil batch systems investigated.

HAN was reported to be unstable above pH of 5.9. This suggests but does not definitely establish that the nitrate salt of hydroxylamine has a greater instability in soils than that of the free amine as it is reported to be unstable above a pH of 6.8. Hydroxylamine disappears rapidly from soils through a number of chemical reactions as indicated in the literature. Reactions have been shown in organic as well as inorganic soil components. With the potential reactions in soils and the suggested instability above pH of 5.9, it would be expected that under most environmental conditions HAN would not persist. HAN did not demonstrate biodegradability at limited low pH studies.[11]

A paper study is current being conducted to identify technologies available for disposal and demilitarization. Although the easiest method for demilitarization is dilution with water, the problem of disposal still has to be addressed. Based on the previous work, a very preliminary conclusion is that the propellant can easily be treated in a bioreactor. There are instances in combat when this type of disposal will not be available so this and other techniques need to be evaluated.[13]

Toxicity Concerns

The approved medical research plan has six tasks. These six tasks are as follows:

Task 1. - Obtain documentation on previous human exposure to the propellant or its principal components.

Task 2. - Design medical surveillance, emergency treatment and prospective epidemiology protocols for current exposure to propellant or its components.

Task 3. - Conduct additional acute and chronic toxicological assays.

Task 4. - Construct a hypothetical scenario of future use of this material, including the phases of manufacturing, field storage, transport in bulk, distribution at field sites, use in a weapon system and disposal of the material, both in the field and the garrison.

Task 5. - Construct a scenario of human exposure, based on the material use scenario.

Task 6. - Summarize data collected in Tasks 1-5 and determine the necessity for future research.

These six tasks will lead to safety release of the material for full scale engineering development. As the weapon system in developed, a request for a Health Hazard Assessment (HHA) will be issued by the developer. The HHA consists of a risk analysis of the system. It will be used to determine if the hazards of this system can be reduced or eliminated. A final HHA is issued just prior to full scale production.[14]

Vulnerability Test Environmental Assessment

The vulnerability testing that is underway at Aberdeen Proving Ground presented a different environmental concern. As the containers of propellant were attacked by different threats, possibility of environmental impacts varied. A test setup was designed to avoid impacting the environment. The containers of LP were setup in a modified hull of an M113 Armored Personnel Carrier (APC). The APC had a watertight interior to allow containment of any residue LP or wash water. The interior of the APC was stripped as much as possible to allow easy rinsing after shots. All holes were welded shut to maintain a watertight seal, and the APC was tilted and had a closable drain installed at the low point to permit easy draining of residue LP and water. After the LP shots, it was required to wash down the interior of the APC and to save the used water for chemical analysis to evaluate residue LP contained in it, thus the requirement for the APC to be watertight.

The APC described above was placed in a steel barricade at the ballistic range used for this test. The barricade consisted of three walls, a floor and a partial roof. The walls and roof served to stop any debris that may be thrown by the explosion of the warhead. The open side allowed the air blast to dissipate over an unpopulated area. The floor served to contain any leakage of liquid propellant from the APC. Absorbent materials were placed around the APC and the open side of the barricade to contain any accidental spills.

The following is a list of all the environmental concerns and how they were addressed to have no significant impact on the surroundings.

1. Disposal of residual LP and wash water - After the shot was fired and pressure and temperature in the APC return to ambient or one hour lapsed whichever is greater, a sample of the residual LP was taken when available. As was expected, the residual LP consisted primarily of HAN,

TEAN and water. Following this sampling, the interior of the APC was rinsed and drained into polyethylene drums through the low point drain. All residual LP and wash water will be disposed of as recommended by installation procedures upon results of bioassay. The options available are:

a. If nonhazardous waste, disposing in the sanitary sewer in accordance with the material safety data sheets.

b. If hazardous waste, properly containerizing the material, moving it to conforming storage and turning custody over to Aberdeen Proving Ground for disposal via a licensed hazardous waste contractor.

2. Release of NO_x - Partial decomposition or partial reaction of the LP may produce small amount of NO_x. There are no federal, state or local regulations on the amount of NO_x that can be released in the air. Arrangements are made with the county for notification of test dates.

3. Accidental aerosolization of LP - If reaction of the LP were to produce such high pressures that the APC might break welds or come apart, small amounts of LP may be aerosolized and released into the atmosphere. Testing by AEHA has shown that 300 mg/m^3 is non-injurious for short term exposure (15 min or less). Any aerosolization would be instantaneous, not sustained. The potential for exposure was minimal due to the fact that the test fixture sat for 1 hour, and any aerosol produced would have settled in that time.

4. Personnel Protection - All personnel involved in the testing were informed of the precautions necessary in handling these propellants. Toxicity testing is in progress on these materials. At this time the recommendations are: protection against dermal and ocular exposure, oral ingestion and aerosol inhalation. This means wearing gloves and safety glasses. No eating, drinking or smoking was allowed while handling the

propellants was allowed. If the material is allowed to settle for one hour after the shot, potential for exposure is minimized.

Current Programs for Disposal

One of the largest assemblage of propellant is located at the manufacturing plant. Currently LP for this program is being produced at one location. It is being produced in the pilot plant of a large rocket propellant manufacturer. Since this facility routinely handles propellant waste and incineration is the available disposal technique, all wastes from LP 1845 or 1846 or their components are incinerated.

The other largest consumer of LP is the gun firing test ranges. This location does not have a disposal facility . Propellant wastes are contained and disposed of as hazardous waste. No other option is available at this facility.

Wastes from the vulnerability tests were contained and evaluated for disposal in the sewage treatment plant at Aberdeen Proving Ground. The Environmental Management Office at this facility required that a bioassay be done to determine the biodegradability of the effluent before it was introduced to the sewage treatment. Results of the bioassay are discussed below.

A sample of the effluent was taken and neutralized with sufficient NaOH to bring the pH close to 7.0. At this point the toxicity to Daphnia pulex was measured at various effluent concentrations for a 48 hour exposure. Results are in Table II.

Table II. Bioassy Test Results

Concentration (mg/L)	Percent Survival
0.0	95
50.0	60
100.0	20
200.0	0
500.0	0
1000.0	0

Although the toxicity was high, at low concentrations the daphnia did survive exposure to the effluent. The Environmental Management Office approved the disposal in the sanitary treatment plant of the neutralized material at a rate of 1 drum (55 gallon) per day.

PROPOSED ACTIONS

A life cycle EA covering the entire LP will be prepared following the completion of the paper study on disposal and demilitarization techniques. The proponents of the program do not feel that an EIS will be required. At this time the only impact that the propellant would have on the environment would be in the instance of a large spill and we feel that spills can be contained and handled in a manner that would avoid a large environmental impact.

During the design portion of building a LP manufacturing plant, an EIS will be written. This will cover all aspects of environmental impact from ground breaking, start-up and operation. Impacts may be significant due to the actual construction of the facility.

When the paper study of disposal and demilitarization techniques is complete, a second phase will be initiated to evaluate identified techniques on a bench or pilot plant scale. This will begin is October 1989.

CONCLUSIONS

Based on all the studies completed and the ones currently initiated, it appears that at this time there is nothing environmentally evident to preclude fielding a LP system. Also, mechanisms are in place to continue evaluating environmental concerns as they arise and protect the environment during the development and testing of LP.

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AN OVERVIEW OF CHEMICAL AND BIOLOGICAL PROCESSES THAT MAY LEAD TO DEGRADATION OF HAN AND TEAN IN THE ENVIRONMENT

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ABSTRACT

The U.S. Army is developing a liquid propellant which will possibly be used in certain applications as a replacement for conventional munitions. The propellant includes an oxidizer (hydroxylammonium nitrate), a fuel (triethanolammonium nitrate), and water. In anticipation of widespread (both continental U.S. and abroad) use of the propellant, USATHAMA began a research program to identify the procedures which could be implemented for disposing of the propellant in instances such as spills or destruction of waste or off-spec liquid propellant. In this paper the chemistry of the liquid propellant is reviewed and chemical, physical, and biological processes which result in the degradation of the propellant components and similar compounds are described. In addition domestic and foreign regulations which pertain to environmental releases of the propellant and/or its degradation products are discussed. Those processes which may individually or in combination be useful for the safe disposal of the liquid propellants, liquid propellant-contaminated soil, and sediments are also discussed in this paper.

INTRODUCTION

The United States Army is currently investigating the use of liquid propellants (LPs) in large and medium caliber guns. By definition, a propellant contains all the necessary chemical components for combustion, as opposed to, for example, gasoline, which requires the addition of an oxidizer. The liquid propellant currently being investigated contains an oxidizer, hydroxylammonium nitrate (HAN), a fuel, triethanolammonium nitrate (TEAN), and water. Since both fuel and oxidizer are present in the propellant, the mixture is potentially dangerous. However, the liquid propellant formulation has been found, under normal handling conditions, to be quite stable and incapable of vigorous combustion except when detonated in a confined space such as the firing chamber of a gun.

Several liquid propellant formulations are being considered by the U.S. Army as replacements for conventional munitions. The most useful formulations to date are LGP 1845 and 1846, whose compositions are shown in Table 1 (1). These formulations contain stoiciometric quantities of fuel and oxidizer and their complete combustion produces carbon dioxide, nitrogen, and water. The total energy of these propellants increases with decreasing water content. The thermal initiation temperatures of this formulation are reported to vary inversely with nitrate-ion concentration (2).

TABLE 1. PROPELLANT COMPOSITIONS

	Composition		
Propellant	HAN, wt. %	TEAN, wt. %	Water, wt. %
1845	63.23	19.96	16.81
1846	60.79	19.19	20.02

In a study (3) conducted by the U.S. Army Natick Research Center for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), it was determined that the TEAN stock solutions prepared in early studies were contaminated with N-nitrosodiethanolamine (NDELA). NDELA is a known animal carcinogen (4, 5, 6) and poses both an exposure hazard to workers manufacturing the TEAN and gun crews using the propellant. A contaminant study (7), however, concluded that proper manufacturing techniques nearly eliminate the production of

NDELA. Nevertheless, the possible formation of NDELA during potential disposal scenarios and its subsequent environmental fate are not yet fully elucidated and hence NDELA should be considered as a potential hazardous impurity until waste treatment and handling methods are shown to negate this potential hazard.

In conjunction with anticipated widespread use of the HAN-TEAN liquid propellant, not only in the USA but abroad, the U.S. Army is undertaking efforts aimed at preventing environmental pollution at facilities involved in the handling or storage of liquid propellant. In conjunction with the Army's pollution prevention program, procedures for demiliterization and disposal of the propellant will be developed, and the potential environmental impact of these procedures will be assessed.

In this paper potential methods for demilitarizing and disposing of liquid propellant residues are described which, on the basis of engineering, environmental, and cost considerations, appear to be feasible.

Objectives of the Study

The objectives of this study are summarized below:

1) Identify existing Department of Defense (DOD) data pertinent to demilitarization and disposal of the HAN-TEAN propellant.

2) Review existing information regarding the chemical/physical characteristics, destruction, and disposal of the HAN-TEAN propellant and related compounds.

3) Evaluate the technical feasibility, environmental considerations and cost-effectiveness of the potential demilitarization and disposal techniques.

4) Evaluate the environmental impact of selected disposal techniques.

5) Review domestic and foreign environmental regulations to ensure that the selected disposal activities comply with the pertinent environmental statutes.

PHYSICAL CHARACTERISTICS OF LP

One of the most significant structural features present in HAN and TEAN is the hydroxyl group. The presence of this group in a molecule often results in hydrogen bonding which decreases vapor pressure, increases boiling point, and enhances water miscibility (1).

HAN-water mixtures at low HAN concentration are aqueous solution of a 1:1 electrolyte. As concentration increases, the system gradually changes from an aqueous solution to a molten salt that solidifies at temperatures well below the freezing point of either of its components (1).

TEAN-water mixtures are more complex and do not exhibit homogeneity over the broad concentration range observed for HAN. TEAN behaves much like an ordinary ionic salt, forming saturated solutions that are approximately 5 Molar at room temperature. The molecular weight and melting point of TEAN (212 and 80.4°C) are higher than those of HAN (96° and 48°C) (1).

The liquid propellants LGP 1845 and 1846 are homogeneous liquids and do not undergo any phase transitions over the entire temperature range of military interest. The propellant has a freezing point of -100°C and a thermal decomposition point (at ambient pressure) of 125°C. The HAN-TEAN formulation is odorless and the active ingredients, being salts, have no vapor pressure. The density of LGP 1845 is higher than that of LGP 1846 at all temperatures because the salt content of LGP 1845 is higher. The surface tension of LGP 1845 is normally higher than that of 1846, and the values for either propellant are not substantially different from those of water.

At 25°C, the propellant exhibits the following physical properties mentioned below:

Density: 1.430 g/cc
Kinematic viscosity: 4.965 cst
Dynamic viscosity: 7.100 cp
Surface tension: 66.901 dynes/cm
Glass transition: -100°C

Energetics at Loading Density of 0.2000 g/cc:

Flame temperature: 2469 K
Impetus: 898.3 J/g
Pressure: 207.80 MPa

CHEMICAL CHARACTERISTICS OF LP

The liquid propellant can fume off if heated, but does not burn unless pressurized. To avoid the fuming of propellants and its components, they should not be exposed to temperatures greater than 60°C. Almost all vapors from the propellants are water vapors.

The oxidizing or the reducing agent will react with HAN-based propellants. When ignited at elevated pressure (in a confined space such as a gun barrel), the decomposition could progress to a violent reaction. Partial decomposition of liquid propellant (e.g., during fuming) produces toxic NO_x compounds.

HAN-based LP in its pure state looks like water, so any coloration indicates a reaction and this would imply that the propellant should be handled with extreme caution. They are electrically conducting ionic solutions, therefore no static charge can be built up. To avoid chemical reactions, the propellant must not come into contact with acids or bases.

Liquid propellants react with most metals and other common materials; therefore, great care must be taken in selecting the container to store and seal the propellant. It should be stored in thin wall containers that will vent at 15 psi gauge (i.e., 15 psi above atmospheric pressure). This will prevent vigorous reaction initiation at high pressures.

After the injection of the liquid propellants [illegible] high-pressure and high-temperature environment (gun barrel), the propellant vaporizes and reacts giving rise to combustion products in the gas phase. The properties of the combustion products results for LGP 1845 and LPG 1846 were computed by Kounalakis and Faeth (8) and are summarized in Table 2 for pressures of 1 MPa, 10 Mpa, and 100 Mpa. Both reaction mixtures have virtually identical combustion product compositions and have nearly 70% water vapor.

TABLE 2. COMBUSTION PROPERTIES OF HAN-BASE MONOPROPELLANTS (8)[a]

Propellant	LGP 1845[b]			LGP 1846[c]		
Pressure (MPa)	1	10	100	1	10	100
Reactant density (kg m^{-3})	1452	1454	1476	1430	1432	1454
Combustion product properties						
Density (kg m^{-3})	1.30	12.9	129	1.36	13.5	135
Temperature (K)	2133	2152	2163	2027	2039	2045
Composition (% by volume)[d]						
Water vapor	68.8	69.2	69.3	70.6	70.8	70.9
Carbon dioxide	12.7	12.9	13.0	12.2	12.3	12.3
Nitrogen	17.3	17.4	17.4	16.5	16.5	16.6

[a] Adiabatic, constant pressure combustion, with the liquid reactant at 298.15 K.

[b] Reaction composition (% by mass): HAN, 63.2; TEAN, 20; and H_2O, 16.8.

[c] Reaction composition (% by mass): HAN, 60.8; TEAN, 19.2; and H_2O, 20.0.

[d] Major species only. Minor species include: CO, H_2, NO, OH, and O_2.

The synthesis of the TEAN component of the liquid propellant involves the acid-base neutralization of triethanolamine and nitric acid. However, it is believed that during the course of this reaction, a hazardous impurity N-nitrosodiethanolamine (NDELA), an N-Nitrosamine is, formed. N-nitrosamines represent a group of potentially serious pollutants because members of this group of organic compounds are acutely toxic, carcinogenic, mutagenic, or tetrogenic when tested in a variety of animals (9, 10, 11). Through use of improved manufacturing techniques the formation of NDELA has been effectively eliminated and it has been reported (12) that the NDELA decomposes in the HAN/TEAN liquid propellant formulation.

SUMMARY OF CHEMICAL, BIOLOGICAL, AND PHYSICAL REACTIONS WHICH LEAD TO DEGRADATION OF LIQUID PROPELLANTS AND RELATED COMPOUNDS

Liquid propellants are under evaluation for Army applications as a substitute for nitrocellulose in ball powder mixtures. Follow-on programs will most likely require substantial increases in the quantities of these propellants in production. Because of this expected increase in production and usage, a potential for spills and contamination to the environment by liquid propellants can be expected to increase proportionally. Therefore, a proper disposal technology is warranted which should be able to handle any possible scenarios that might dictate the disposal of liquid propellants.

Following are some of the potential scenarios which may require the disposal of liquid propellants:

- Disposal of propellant at the end of its life. At present, BRL is estimating the life expectancy of the propellant to be somewhere around 20 years.
- Disposal of contaminated or ruined (by foul play) propellant which can range from 1 gallon to several thousand gallons.
- In the case of fire during storage or transport of propellant, the disposal of the water used to extinguish the fire.
- Disposal of contaminated soil resulting from propellant spills during use or transportation.
- Disposal of spent propellant containers.

A comprehensive literature review was conducted to identify existing information regarding the disposal techniques of liquid propellants. As expected, it was determined that the literature concerning directly with disposal of liquid propellants was not available. To date, very little work has been done with respect to disposal or degradation of HAN-based propellants because the interest in these compounds is relatively recent. However, a fair amount of work has been done concerning methods of disposing of similar compounds such as triethanolamine, ammonium nitrate, and cutting fluids, and for the one used in cosmetic industries. Therefore, in addition to liquid propellant, the literature search was also concentrated on the disposal techniques that are currently used for disposing of these related compounds and can possibly be applied to propellants. Hence, this section will focus on summarizing the technologies found in the literature that are evaluated for the disposal or degradation of liquid propellants, HAN, TEAN, NDELA/nitrosamine, and other related compounds.

Degradation of Ammonium Nitrate Propellants

Kaplan, et. al. (13) studied the biodegradability of four ammonium nitrate propellants, namely, trimethylammonium nitrate (TMAN), isopropylammonium nitrate (IPAN), triethanolammonium nitrate (TEAN), and hydroxylammonium nitrate (HAN). The results of this study indicated that the first three compounds (TMAN, TEAN, and IPAN) were biodegradable. Under both aerobic and anaerobic conditions, they were decomposed without any significant formation of intermediates. TEAN was decomposed under aerobic conditions in batch and continuous cultures in a variety of media, and under anaerobic conditions in batch systems and denitrification conditions under continuous flow systems. The mixture of microorganisms used for the active systems (batch aqueous, continuous, and soil) was obtained from aerobic and anaerobic sewage sludge and soil.

Results of the Ames test indicated that none of the four ammonium nitrate propellants was mutagenic. These findings suggest that development of a biological approach to treat process waters containing these compounds would be a feasible one.

HAN was found to be chemically unstable above a pH of about 5.9 (13). With a demonstrated instability above pH 5-9 and with numerous potential reactions in soils, it is expected that HAN would not persist under most environmental conditions.

Reports in the literature indicate that hydroxylamine rapidly disappears from soils through a number of chemical reactions with inorganic and organic soil components (14, 15). The HAN was converted to either inorganic forms of nitrogen (i.e., NH_4^+, NO_2^-, NO_3^-), or it was fixed by the organic matter in the soil with a subsequent release of gaseous forms of N. It was postulated that the fixation of the hydroxylamine occurred through the formation of oximes when carbonyl groups in the soil organic matter react with NH_2OH (14):

$$R - C = O + NH_2OH \rightarrow R - C = NOH + H_2O$$

It has also been shown that hydroxylamine undergoes decomposition quite readily. The crystalline solid suffers rapid deterioration at room temperature to yield ammonia, water, nitrogen, and nitrous oxide as principal products (16). Aqueous solutions of hydroxylamine deteriorate when coming in contact with atmospheric oxygen (16). This phenomena of autooxidation should enhance the degradation of HAN under aerobic conditions during biological treatment.

Balandin, et. al (17) reported that cells of Monoraphidium braunii metabolized hydroxylamine, reducing it stoichiometrically to ammonium in darkness. In light, however, the rate of hydroxylamine disappearance was slightly higher than that of the ammonium release to the medium, indicating photoxidiation of hydroxylamine.

USATHAMA has also investigated the potential for composting of explosives and propellant-contaminated sediments (18-22). Field-scale demonstration of static pile composting to decontaminate nitrocellulose (NC) contaminated soils was conducted at Badger Army Ammunition Plant (BAAP) (22). Another field-scale demonstration was conducted at Louisiana Army Ammunition Plant (LAAP) (21) to decontaminate 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-trizine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) contaminated lagoon sediments.

The treatment process involved the mixings of contaminated soils or sediments with straw/horse manure, alfalfa, horse feed, and wood chips to enhance microbial degradation. After 153 days, total explosives at the LAAP facility were reduced by 99% (from 17,872 to 74 ppm) in the thermophilic (55°C) pile. At the BAAP facility, NC concentrations were reduced from 13,086 ppm to 16 ppm after 101 days in a thermophilic pile.

The results of these field demonstrations indicate that composting is a feasible technology and may be suitable for remediating propellant and explosives contaminated soil and sediment.

Degradation of N-Nitroso Compounds

Numerous reports in the literature concern the in vivo and in vitro formation of nitrosamine from the reaction of nitrite with susceptible amines. N-nitrosamines are stable compounds and are difficult to destroy once they are formed. They are stable in neutral and strong alkaline solutions in the absence of light (23). However, when exposed to ultraviolet light, nitrosamines decompose either to aldehydes, nitrogen, and nitrous oxide or quantitatively to amine and nitrous acid depending on the wavelength used. The conditions for the photochemical destruction of nitrosamines in solution in the presence of a HNO_2 scavenger have been described (24, 25).

EVALUATION OF POTENTIAL DISPOSAL TECHNOLOGIES FOR LIQUID PROPELLANTS

On the basis of the literature review, three potential technologies have been identified for the disposal or degradation of HAN-based liquid propellants. The three technologies are thermal destruction, biological treatment, and photolytic degradation. Various thermal destruction process have been developed and applied to degrade waste chemicals. These thermal processes include rotary kiln incineration, liquid injection incineration, and fluidized bed incineration. Available biological treatment processes which may be applicable for the degradation of liquid propellants include composting, aerobic bioreactor, rotating biological contactor, fluidized bed reactor, and trickling filter treatment. Photolytic degradation has been accomplished using closed-loop photolytic reactors as well as solar irradiated ponds and lagoons.

Based on the results of the review of the literature, it is apparent that each of the above technologies may potentially be useful in disposing of off-spec liquid propellant or wastes containing liquid propellant residues. However, the selection of technologies for bench and pilot scale evaluation must be guided by appropriate criteria to ensure that the disposal technology which ultimately is recommended does in fact meet the needs of the [illegible] Army while at the same time complying with the pertinent domestic and foreign environmental regulations.

Six criteria were formulated for use in guiding the process of selecting the degradation technology which is most appropriate for bench scale evaluation. These criteria are: technicial feasibility, cost effectiveness, potential for full-scale implementation, applicability in remote areas, potential for adverse environmental impact, potential for compliance with environmental regulations. Data is not available for each of the technologies which would permit the assessment of the disposal technologies to be based upon rigorous calculations. Rather the three technologies was assigned a score of 0 to 3, depending upon how well the technology complied with each criterion. In the case of the potential for negative environmental impact, negative scores were assigned. As one can see in Table 3 biological degradation would seem to be the most appropriate technology for further study. Some aspects of this technology are described in the following section.

TABLE 3. RESULTS OF APPLYING EVALUATION CRITERIA TO SELECT DISPOSAL TECHNIQUES FOR FURTHER STUDY

Criteria	Thermal	Biological	Photolytic
Technical feasbility	3	3	3
Cost-effectiveness	1	3	1
Potential for full-scale implementation	3	3	2
Applicability in remote areas	1	3	2
Potential for adverse environmental impact (negative score)	-3	-1	-1
Compliance with environmental regulations	1	3	2
Total	6	14	9

BIOLOGICAL TREATMENT

Biological treatment or biodegradation involves the bio-oxidation of organic material using microrganisms. Biological treatment is not a novel technology, and usually relies on the indigenous populations of the site or enrichment with other naturally occurring organisms to accomplish successful treatment. The concepts of biological treatment are often implemented through simple enrichment of appropriate nutrients and by increasing oxygen transfer within the contaminated environment.

Biological treatment is dependent upon a number of environmental factors such as nutrient levels, pH, temperature, dissolved oxygen, and toxicity of waste to be treated. Wastes in any form--solid, aqueous, and gaseous--can be treated biologically. Contaminated sludges and soils can be biologically treated in situ or excavated and treated by solid-phase and slurry-phase bioremediation processes. Enhanced in situ biodegradation is being used for sites having soil and ground water contaminated with readily biodegradable organics such as gasoline and diesel (26, 27). Studies determining the biodegradability of the ammonium nitrate propellants in aqueous and soil systems under a variety of conditions have already been performed (13). It has been shown that both TEAN and HAN are biodegradable.

Following are some of the advantages of biological treatment:

- The technology is cost-effective (in some cases, cost is as little as 10 to 20% of incineration).
- It can easily be done at any location.
- It can degrade recalcitrant compounds.
- Compounds resulting from microbial degradation are relatively innocuous in nature.

The disadvantages of biological treatment are:

- The technology often takes months.
- Nutrient levels, pH, and other operating conditions must be controlled carefully.
- May result in partial degradation.
- Sensitive to high metals and inorganics content.

Several biological treatments have been identified which can potentially be applied in the disposal of liquid propellants. These technologies are:

- Composting
- Aerobic bioreactor
- Trickling filter
- Rotating biological contactor
- Fluidized bed reactor

COMPOSTING

Technology Description

Composting is a biological process used typically for the treatment of wastes with high concentrations of biodegradable organic solids (28). The contaminated wastes are blended with a bulking agent (wood chips, saw dust, etc.) to provide void space for aeration and to support the compost matrix. Waste destruction and conversion are achieved by the use of thermophilic aerobic microorganisms which occur naturally in decaying organic matter. The optimum temperature range for composting is between 35° to 60°C.

The composting process involves four steps (29):

1. Mixing of wastes with a bulking agent to enhance aerobic conditions.
2. Air and indirect heat are introduced to promote thermophilic conditions.
3. Waste stabilization is achieved by a curing step.
4. Separation/screening of the bulking agent from the stabilized waste.

There are three basic types of composting (26): open windrow systems, static windrow systems, and in-vessel (reactor) systems. The open windrow system consists of stacking the compost into elongated piles. Aeration is accomplished by tearing down and rebuilding the piles. The static windrow system also involves long piles of compost. However, the piles are aerated by a forced-air system. Finally, the in-vessel system involves placing the compost into an enclosed reactor. Aeration is accomplished by tumbling, stirring, and forced aeration.

Applicability/Limitation

Many organic chemicals can be treated by composting. The fate of inorganics (cyanides, sulfides, and metals), however, is not yet certain. Compounds that have limited aqueous solubility are not readily metabolized by microorganisms. Wastes must not have excessive moisture because too much moisture will slow processing by absorbing the heat needed for biological growth. Climatological factors are also important since they affect metabolic rates, odor emission, and drying rates.

Technology Status

Composting has been used in the municipal sector for the conditioning of sewage sludge. It has also been used to treat a variety of industrial solid wastes and has been demonstrated at field-scale by USATHAMA for composting explosives and propellant contaminated sediments.

AEROBIC BIOREACTOR

Technology Description

The method involves confining and decontaminating soil in a biological reactor. The reactor consists of a container having the bottom, sides, or walls continuously connected together and a cover suitable for excluding liquids and solids from entering the container. The impermeable sides and bottom would prevent the contaminant from leaking out of the container. At least two treatment courses, each comprising a layer of the contaminated soil, are distributed in the container and subtended by gas distributing system. The thickness of the layer is adjusted to permit a sufficient quantity of oxygen gas to maintain the layer aerobic. The moisture content of the soil is adjusted from 2% to about 90% (optimum is from 40 to 60%) of field saturation, and the nutrient content is adjusted to provide sufficient phosphorus and nitrogen nutrients to ensure that the micoorganisms in the soil are not nutrient limited.

The oxygen in the gas diffuses into the layer of particulate matter where it is utilized by a microorganism to metabolize the organic compound. Volatile metabolisms products, such as carbon dioxide, in the layer of contaminated particulate matter diffuse into the gas containing oxygen and are exhausted from the gas distributing system.

Applicability/Limitation

The process is suitable for biodegrading an organic contaminant, particularly petroleum products or hydrocarbons on soil. The design of the system is fairly simple. It can easily be adopted on site by excavating a pit in the earth and lining the pit with a flexible lining impervious to the organic compound and to water. This technology is suitable for treating only contaminated soil.

Technology Status

The technology has been used at several service stations to degrade hydrocarbon contaminated soil.

TRICKLING FILTER

Technology Description

This technology can be used for handling large quantities of aqueous wastes. The liquid wastes are sprayed over a bed of rocks or synthetic media upon which a slime of organisms is grown (30). The organic material present in the liquid waste is degraded by a population of microorganisms attached to the filter media. Organic material from the liquid is adsorbed onto the biological film or slime layer. In the outer portions of the biological slime layer, the organic material is degraded by aerobic micoorganisms. As the microorganisms are grown, the thickness of the slime layer increases, and the diffused oxygen is consumed before it can penetrate the full depth of the slime layer. Thus, an anaerobic environment is established near the surface of the media.

Applicability/Limitation

This technology is suitable for treating aqueous organic wastes. Trickling filters are efficient in removing alcohols, phenols, phthalates, cyanides and ammonia. It has adequate treatment capacity and can handle large quantities of aqueous waste. The disadvantage of trickling filters is the requirement for very uniform flow rate and a consistent temperature above 0°C. Odors from the filter and flies can be a problem. If the filter must be covered for odor control, forced air ventilation is often necessary.

Technology Status

Conventional technology has been demonstrated to biodegrade leachate from hazardous waste lagoons.

ROTATING BIOLOGICAL CONTRACTORS

Technology Description

Rotating biological contactors aerobically treat aqueous waste streams, especially those containing alcohols, phenols, phthalates, cyanides, and ammonia. The process consists of primary treatment for solids removal followed by the rotating biological contactors where the waste stream comes into contact with the microbial film and the atmosphere. The rate of rotation can be varied to optimize oxygenation of the bacteria and their contact time with the wastes to be degraded. Effluent is then sent to a secondary clarifier.

Applicability/Limitation

Rotating biological contactors are not a sufficient method to remove highly chlorinated organics, aliphatics, amines, and aromatic compounds. Some heavy metals and organic chemicals are harmful to the organisms.

Technology Status

Convention technology.

FLUIDIZED BED REACTOR

Technology Description

The fluidized bed reactor relies on immobilization of microbes on a hydraulically expanded or "fluidized" bed of inert (silica sand) or active (activated carbon) media particles. In this process, the contaminated wastewater and recycled effluent pass upward through the media bed at a velocity sufficient to expand the bed beyond the point at which the frictional drag is equal to the net downward force exerted by gravity. Once at or beyond this point of minimum fluidization, the media particles are individually and hydraulically supported and provide a working interface for the passage and biodegradation of organic contaminated liquids. The fluidized bed reactor provides excellent retention and biomass interface time and this dynamic system reduces the chances of bacterial growth inhibition due to build-up of toxic by-products or inhibitory feed inputs. Apparently this system accumulates a large biomass concentration in the fluidized bed and this allows for the efficient degradation of complex organic compounds at a shorter liquid contact time or hydraulic retention time (HRT) relative to more conventional biological systems.

Applicability/Limitation

The technology is used for fermentation experiments and for aqueous phase to treat organic wastes. The microorganism does not get washed out. The limitation of this technology is that it can be used only for liquid wastes.

Technology Status

The technology is conventional.

ENVIRONMENTAL REGULATIONS

DOMESTIC REGULATIONS

HAN-based liquid propellants exhibit the properties of a characteristically reactive hazardous waste as defined in 40 CFR 261.23(a)(6) under the Resource Conservation and Recovery Act (RCRA). This regulation states that:

> A solid waste exhibits the characteristic of reactivity of... It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

Under normal usage, the propellant is not regulated under RCRA, even though it may exhibit the above properties. Several scenarios may arise, however, when the propellant is no longer usable for its original purpose and must be disposed. It is at this point that the propellant would become a waste that is regulated under RCRA. The remainder of this section deals with the different disposal scenarios.

Noncontaminated Liquid Propellant

Liquid propellant that has exceeded a specified shelf life, is spilled, or is off-specification but is not contaminated with NDELA would have an EPA hazardous waste number of D003 (characteristic of reactivity). Characteristically hazardous wastes, such as the waste propellant, may be treated so that they no longer exhibit the characteristics that made them hazardous. (In the case of HAN-based liquid propellants, demilitarization using either water or NaCl has been suggested (USATHAMA 1989) to render the liquid propellant nonreactive and therefore it would no longer be considered a hazardous waste.) It is important to note, however, that the treatment process is regulated under RCRA and subject to 40 CFR 261 through 40 CFR 280. The treatment facility would be fully regulated under RCRA and therefore require a RCRA Part B permit.

Once a non-DELA propellant waste has been demilitarized to become non-hazardous, under the RCRA regulations, it could be passed to a sewer system and eventually to a wastewater treatment facility. It is suggested, however, that given the public perception of the dangers of propellants, further treatment (e.g., aerobic biological reactor) be utilized for the complete degradation of the HAN and TEAN.

Contaminated Liquid Propellant

Liquid propellant waste or residue that has been identified as a D003 hazardous waste and is further contaminated with NDELA presents another demilitarization and disposal scenario. NDELA-contaminated propellant could also be demilitarized using water or NaCl to make it nonreactive, but it would still be classified as a RCRA hazardous waste under 40 CFR 261.33(f). NDELA is listed as a toxic waste under this section and has been given the EPA Hazardous Waste Number U173. This would require that the liquid propellant waste be further treated to deal with the NDELA (e.g., biodegradation and photolysis). It should again be emphasized that any treatment process for RCRA regulated wastes is regulated under RCRA and requires a RCRA Part B permit.

Treatment standards under RCRA have not been set for NDELA (U173) wastes. Therefore, any effluents or residues generated from the treatment process would still be regarded as a RCRA-regulated hazardous waste, and would need to be landfilled at a hazardous waste facility.

Exclusion

An exclusion under RCRA would apply to the final disposition of the liquid propellants if the facility discharges to a publicly-owned treatment works (POTW) or operates its own wastewater treatment plant permitted under the Clean Water Act. If either of these situations exists and the waste propellant can be discharged to and treated by the treatment plant, then 40 CFR 261.4(a) applies. Under this regulation, the waste propellant and the wastewater treatment facility are excluded from regulations under RCRA. The treatment facility is still required to meet all operating and discharge standards set forth in its operating permit under the Clean Water Act.

It is important to note that the liquid propellant does not become a RCRA-regulated waste until it exceeds a specified shelf life, is spilled, goes off-specification, or becomes contaminated. In the case of the liquid propellant exceeding a specified shelf life, it is permissible to demilitarize the propellant (i.e., make it nonreactive) prior to exceeding the shelf life. This would not be considered treatment of a waste because it would still be a useful product at the time of demilitarization and therefore would not be regulated under RCRA.

FOREIGN REGULATIONS

United Kingdom

HAN-based liquid propellants would be classified as a controlled waste under the Control of Pollution Act of 1974. The Special Waste Regulations (1980) classify a controlled waste as exhibiting any one of the following characteristics:

- Explosive at 21°C
- Harmful to humans
- Medicinal product

The liquid propellant must be disposed of or stored at a licensed facility. The end product of any treatment of a controlled waste must be "environmentally safe." Dr. George Ray (Branch Heat RSD3 - Department of the Environment) stated that while incineration is the standard method of treatment in the U.K., he is very interested in innovative treatment technologies such as the contained biological reactor.

Dr. Ray also stated that the U.S. Army would be Crown Immune from any of the licensing procedures for treatment, storage, and disposal of the liquid propellant because the Army bases are leased from the U.K. government. The U.S. Army would not then be legally bound to comply with the controlled waste legislation, but would still be expected to dispose of the waste in a safe manner.

Federal Republic of Germany

The German Waste Management Act does not use the term "hazardous waste," but rather designates categories of waste that require special administration. These different categories include wastes that because of their nature, quantity, or condition make special demands on disposal operations which are unlike domestic (i.e., household) wastes.

HAN-based liquid-propellant waste would fall under the classification of a "particularly explosible or inflammable" material (Waste Avoidance and Waste Management Act of 1986). These wastes "may be treated, stored, and deposited only in plants or installations licensed for this purpose (waste management facilities)" (Article 4 para 1). The Federal States within W. Germany are each responsible for drawing up waste disposal plans in which special consideration is given to hazardous wastes. Since the legislation has not set any time limits for the completion of the plans, planning has advanced to different stages in the various states and would need to be evaluated for specific geographic regions within W. Germany.

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Title: Decontamination of Explosive Contaminated Structures and Equipment

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As a result of past operations, the U.S. Army has numerous buildings and large quantities of process equipment which is contaminated with explosives. More recently, all detonated ordnance scrap must be treated prior to disposal. Before these materials can be converted to new uses or disposed of, the residual explosives must be removed. Removal of residual explosives is necessary to avoid creating safety and environmental hazards. For example, process equipment may be sold as scrap metal and as scrap it may be cut by a welding torch or disassembled. Should residual explosives by present, detonation of even a small quantity of explosives may result in injury. If the process equipment is to be landfilled, residual explosives may migrate into the soil and ultimately contaminate groundwater. Building structures which have been used for explosives manufacture are usually slated for demolition and disposal of the rubble. Demolition of a building which has residual explosive can be dangerous. Disposal of contaminated rubble may contribute to soil and groundwater contamination.

Probably the most common methods in present use for decontamination are steam cleaning, and decontamination by fire (burn it to the ground) or a flashing furnace. Steam cleaning is in most cases effective but provides only surface decontamination and is not effective on hard to access areas. It is difficult to completely decontaminate concrete with steam. Steam cleaning of complex items such as motors can not assure that interior areas are cleaned. Burning of structures contaminated with explosives has several drawbacks. If other structures are nearby, burning the building may be to risky. Buildings with asbestos should not be burned. Since open burning of a contaminated structure can be viewed as an uncontrolled release of toxic substances, local or state regulators may prohibit intentional building fires. A flashing furnace requires thermal initration of an explosive to initiate any residual reactive materials, and is limited to surface decontamination.

In 1982, USATHAMA began a project aimed at developing new, improved procedures for decontaminating structures and equipment contaminated with explosives. The goal of this on-going project is to develop a method which will be safe, produce little or no waste and will assure a high degree of decontamination. Target compounds for removal are all the major military explosives such as trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-s-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), nitrobenzene (NB), 1,3-dintrobenzene (DNB), 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitorophenylmethylnitramine (TETRYL), smokeless powder (nitrocellulose/nitroglycerin), ammonium picrate (Yellow D). The process to be developed would have to be effective at removing contaminants from metal, wood, painted concrete and bare concrete. An addition goal of the project is to develop a decontamination method which is universally applicable and, thus, can be used on large structures as well as process equipment. The first phase of this project was a review of existing techniques and the consideration of novel techniques.

Phase I of Development Program, Technology Screening

Under contract to USATHAMA, Battelle Columbus Laboratories performed an analysis of existing explosives decontamination techniques and also developed descriptions of novel concepts. Information was gathered from government and private industry manufacturers of explosives. Government facilities were visited to inspect contaminated structures and equipment. In a July 1983 report, Battelle documented the detailed analysis of the following technologies:

Thermal Decomposition Concepts

Flashblast
Microwave Heating
Solvent Soak/Burn
Burn to Ground
Contact Heating
Flaming
Infrared Heating
Hot Plasma
Hot Gases
CO_2 Laser

Abrasive Concepts

Electropolishing
Sandblasting
Ultrasound
Vacu-blast
Acid Etch
Demolition
Cryogenics
Scarifier
Drill and Spall
Hydroblasting

Extractive Removal Concepts

Solvent Circulation
Surfactants
External Steam Generator
Supercritical Fluids
Strippable Coatings
Vapor Phase Solvent Extract
Rad Kleen
Manual Steaming

Chemical Concepts

Radical Initiated Decomp.
Molten Decomp.
Microbial
Ultraviolet and Cat.
Nucleophilic Displacement
Solid State Hydrogenation
Base Initiated Decomp.
Sulfur Based Reduct
Reduction Cleavage
Gamma Rad.
Ozone
Gels
Decomp. with DS2
Sodium Borohydride
Reactive Amines
Chromic Acid
Ascorbate
Foams

Various combinations of methods were also considered. Each technology was evaluated and rated based on destruction efficiency, mass transfer, safety, damage to buildings, penetration depth, applicability to complex surfaces, operating costs, capital costs and waste treatment costs.

Among the thermal decomposition concepts, hot gases received the highest ranking overall and received high scores in all categories. The hot gas process involves exposing contaminated materials to hot gasses in order to vaporize or decompose the contaminants. The hot gasses together with the vaporized explosives and break down products are sent to an afterburner for complete destruction.

The burn to ground method received high scores in most categories but received the lowest possible scores for safety and building damage. The only thermal concept recommend for further development was hot gases.

All of the abrasive concepts received poor scores for waste treatment costs. The abrasive concepts also received low scores for penetration depth. None of the abrasive concepts were considered for further development.

External steam generator (pumping steam into the structure) scored the highest of the extractive removal concepts. However, the low solubility of some explosives in hot water prevents the steam method from being universally applicable. Vapor circulation was the only extraction technology selected for further development.

Three chemical decomposition techniques where selected for further development. The concepts selected were radical initiated decomposition, base initiated decomposition and sulfur based reduction.

From the combination methods evaluated, only a combined chemical/hot gas concept was considered to be worthy of further development.

In all, 56 technologies or combinations of technologies were considered. Six concepts were selected for further investigation. The selected technologies were hot gasses, combination chemical/hot gas, vapor circulation, radical initiated decomposition, base initiated decomposition and sulfur based reduction.

Phase II, Laboratory Tests

In Phase II, the technologies selected from Phase I were developed in more detail. Probably the most important aspect of the development work was the laboratory tests. Test coupons of steel, painted concrete and unpainted concrete were spiked with known quantities of 2,4 DNT, 2,6 DNT, TNT, TETRYL, RDX and HMX. The test coupons were then subjected to the processes under investigation. After appropriate treatment times, the coupons were inspected for residual explosives. Hot gases and the combination of chemical/hot gases yielded the highest degrees of explosives removal. In many cases, the residual explosive levels were below detection limits. Although each of the six processes evaluated in the laboratory phase of testing offered some advantages and disadvantages for particular operations, it was the hot gas process which had a greater range of applications and provided the most complete decontamination.

The laboratory tests did identify some potential problems with the hot gas process. During testing the formation of explosive crystals on the outside surface (originally uncontaminated) of concrete test coupons indicated that the hot gases may cause explosives to migrate through concrete. This raises the concern that during decontamination of a concrete structure the explosives may be driven out of the structure rather than destroyed. It was also noticed that the hot gas process dried out and, thus, weakened concrete.

Pretreatment of concrete with a caustic chemical led to quicker destruction of explosives and allowed hot gas decontamination to proceed at lower temperatures. Quicker destruction of explosives reduces the possibility of migration. Operating at a reduced temperature lessens the drying effects on concrete. Thus, it was concluded that combination of chemical treatment and hot gasses would be the best route to complete decontamination without migration of explosives and with minimal damage to concrete.

The hot gas process, complemented by chemical pretreatment, emerged from the laboratory tests as clearly the most promising technology for wide spread application. The next step was to see how well the process would perform outside the laboratory on a contaminated building.

Phase III Pilot Tests

The Cornhusker Army Ammunition Plant (CAAP) Tests:

Pilot tests of the chemical/hot gas decontamination method were conducted at CAAP in 1987. The tests were conducted for USATHAMA by Arthur D. Little, Inc. The objectives of these first pilot tests were:

1. Determine the effectiveness of hot gas with and without chemical pretreatment.

2. Evaluate the effects of test conditions on the integrity of an actual structure.

3. Provide design criteria for full scale systems.

4. Provide test data for regulatory permitting of the process.

After numerous potential sites were considered, a projectile washout building at Cornhusker AAP was selected as the test site. The building had concrete walls, a concrete floor and a wooden ceiling. Dimensions of the building were 25' long, 25' wide and 11' high. So that two separate tests could be conducted, a dividing wall was constructed in the center of the building. Other modifications to the building included construction of a false ceiling to protect the wooden roof, replacement of the windows and doors with sheet metal and insulation of the outside of the building. Although inspection of the building revealed some TNT contamination, the level of contamination was too low to sufficiently challenge the decontamination method. This problem was resolved by placing TNT contaminated concrete blocks, which were removed from a sump cesspool, inside the test building.

Hot gas was supplied to the building through ductwork by a 3.0 million BTU/hr propane fired burner. Gasses exited the building into a propane fired afterburner. Gasses entering the building, exiting the building and exiting the afterburner were analyzed. In tests where chemical pretreatment was used, a solution of sodium hydroxide and dimethylformamide was employed. Thermocouples were used to monitor temperatures inside the building during treatment. Concrete samples were subjected to mechanical properties tests before and after hot gas treatment.

Conclusions drawn from the Cornhusker pilot tests were:

1. Hot gas decontamination of a building is safe and feasible.

2. Although treatment of surfaces with caustic chemicals did increase explosive removal on the surface of concrete, it had no effect on interior contamination. Further, longer treatment with hot gas alone should be capable of providing complete decontamination.

3. The hot gas decontamination process caused concrete block to loose 5% of its compressive strength and 20 to 30% of its bend (tensile) strength. The effects of this loss in strength would have to be judged on a case by case basis for each building treated. Of course, if the building is not going to be reused, the condition of the concrete after treatment is of no concern.

4. Initial design criteria and cost estimates for decontamination of small and large buildings were developed.

5. Process data, such as composition of effluent gasses from the afterburner, were collected and can be used for applying for regulatory permits for future operations.

The Hawthorne Army Ammuntion Plant (HWAAP) Pilot Tests:

Further pilot tests of the hot gas process (without chemical pretreatment) began in July 1989 at HWAAP. These tests are being conducted for USATHAMA by Weston, Inc. This test series is directed towards the decontamination of process equipment used in explosives operations. The objectives are:

1. Test the process on a variety of materials (vitrified clay, steel, copper, aluminum) with a variety of contaminants (TNT, NC, NG, Ammonium Picrate, RDX, HMX).

2. Test the process on a variety of items including intricate equipment which has areas inaccessible to other treatment processes (pumps, pipes, ship mines, risers, transfer containers, motors).

3. Determine the temperatures and treatment times required to reduce contaminant levels to below detectable limits. Define a process that will render equipment items fit for unrestricted use or disposal.

4. Render large quantities of contaminated equipment fit for unrestricted use or disposal.

A flashing chamber at HWAAP has been modified to accommodate the hot gas process. The same burner and afterburner that was used at Cornhusker AAP are in use at HWAAP. HWAAP has a large store of equipment and munition items which require treatment. Test items have been selected from HWAAP's stores, placed in the modified flashing chamber and treated with hot gas. Test samples also include highly contaminated clay pipe removed from what was once the West Virginia Ordnance Works. Each test had numerous items on a cart which was placed in the chamber. Each item was outfitted with a surface thermo couple.

Test items are sampled for explosives prior to testing. Some items will be spiked with explosives. After testing, the items are sampled for residual explosives with surface wipes and for complicated items, solvent rinses. The detection limit for explosive contamination was about ten micrograms per square meter.

The following is a summary of test run conditions and results:

Test Run Number	Operating Temperature[1] (°F)	Test Duration[1] (Hours)	Heat-Up Rate[2] (°F/hour)	Contaminant Evaluated	Result
T3	500	36	50	Explosives/ Smokeless Powder	A
T2	400	24	50	Explosives/ Smokeless Powder	B
T5	500	24	50	Explosives	A
T8	400	36	50	Explosives	B,C
T13	500	12	50	Explosive/ Smokeless	A
T14	400	12	50	Explosive/ Smokeless	B,C
T15	600	12	50	Explosive/ Spokeless Powder	A
T16	600	6	50	Explosives/ Smokeless Powder	A
T17	600	48	50	Ammonium Picrate	A
T18	500	6	50	Explosives/ Smokeless Powder	A

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[1] During steady-state condition.

2. The heat up rate was achieved at low temperatures but past 400° F the rate reduced considerably. AT 500° F the chamber took almost 24 hours to reach 600° F.

A. Clean (below detectable limits)

B. Some rinsates contaminated

C. Some surfaces contaminated

Conclusions for the Hawthorne Pilot Tests:

1. The hot gas process successfully decontaminated all items tested. TNT, RDX, HMX, DNT, NC, and NG were completely removed for both exterior and interior surfaces.

2. Heating contaminated items to 500° F for 12 hours rendered the items completely decontaminated.

3. Data over 500° F were meaningless because the heat-up time from 500° F to 600° F equaled the 500° F trial times.

Available Documentation:

Final Technical Report: Development of Novel Decontamination and Inerting Techniques for Explosives-Contaminated Facilities, Phase I - Identification and Evaluation of Novel Decontamination Concepts, USATHAMA Report DRXTH-TE-CR-83211, July 1983.

Final Technical Report: Development of Novel Decontamination and Inerting Techniques for Explosive-Contaminated Facilities, Laboratory Evaluation of Concepts, Phase II - Laboratory Evaluation of Novel Explosives Decontamination Concepts, USATHAMA Report AMXTH-TE-TR-85009, March 1985.

Final Report: Design Support for a Hot Gas Decontamination System for Explosives-Contaminated Buildings, Maumee Research and Engineering, April 1986.

SITE CHARACTERIZATION AND PRELIMINARY SYSTEM DESIGN FOR A FIELD DEMONSTRATION OF THE HOT GAS DECONTAMINATION PROCESS FOR CHEMICAL AGENTS[1]

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ABSTRACT

This paper presents the results of a site characterization study and preliminary design of the process equipment in preparation for a field demonstration of the Hot Gas Decontamination Process at Rocky Mountain Arsenal (RMA), Colorado. Building 537 (the HD Thaw Building) was selected as the test location and sampling was conducted December 5-10, 1988. Site characterization objectives included quantifying the concentration and distribution of HD and HD breakdown products in Bldg. 537 and the holding tank pit. Sampling methods included collection of surface wipe, scraped paint, sump liquid, concrete dust, concrete core, and soil core samples. A miniature automatic continuous air monitoring system (MINICAMS) was utilized for air monitoring during sampling to identify probable sources of HD and HD breakdown product vapors and served as a real time monitor. Results of sampling indicate that residual contamination exists in the concrete floor and soil beneath the floor. Ambient air, tanks, and process equipment are also contaminated. Recommendations include utilizing Bldg. 537 for hot gas decontamination demonstrations, and quantifying the extent of the local groundwater table to assess contamination possibilities. Additional site characterization needs are identified. The design study includes a description of the site, system performance goals, heat and mass flow estimates, process equipment components, site modifications, air monitoring requirements, post-sampling requirements, evaluation of steam and water management requirements, waste generation and disposal, failure mode analysis and controls, and operating procedures.

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1.0 INTRODUCTION

The Hot Gas Decontamination Process has been identified as a promising technique for decontaminating facilities such as buildings, storage tanks, process equipment, and sumps that are contaminated with chemical warfare agents. The in-situ process heats the facility using burner exhaust gases. The hot gases volatilize the contaminants which are subsequently destroyed in a downstream afterburner. When the technology is fully developed, the Hot Gas Decontamination Process may provide an acceptable, non-destructive alternative to the Army "5X" regulatory requirement for release of facilities from government control without precautions or restrictions. The "5X" decontamination currently required involves the incineration of agent-contaminated material at 1,000°F for 15 minutes. If the Hot Gas Decontamination Process can be proven safe and effective for the decontamination of structures, it will enable the Army to realize major cost savings in the cleanup of contaminated facilities.

Concept development, laboratory tests, and a pilot test of the hot gas decontamination process(1,2,3) have shown that this treatment successfully reduces or eliminates the chemical warfare agents mustard (HD), Sarin (GB), and VX from building materials. A test structure spiked with HD was successfully decontaminated in a pilot test study. The next step in the development of the Hot Gas Decontamination technology is to conduct a full-scale field demonstration at an existing installation. A subfloor concrete pit and air ventilation duct in Building 537 (the distilled HD Thaw House) at Rocky Mountain Arsenal (RMA), Colorado, has been selected by U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) to be the site of the field demonstration(4).

In preparation for the field demonstration, Battelle Denver Operations performed a pre-demonstration contamination assessment at Building 537 and developed a preliminary design for the hot gas decontamination process equipment to be used in the demonstration.

The objectives of the site characterization task were:

1. To determine the concentration and distribution of HD and HD breakdown products in the structural members and process equipment in the Building 537 pit at RMA.
2. Obtain engineering information to fill data gaps for the design effort of the demonstration system.

This paper presents the results of the pre-test contamination assessment of Building 537. Subsequent sections present background information about Building 537, the methodology of the contamination assessment, results of laboratory analyses, system design conclusions, and recommendations. Detailed reports of these investigations(5,6) were submitted to USATHAMA.

2.0 SITE DESCRIPTION

Building 537 was constructed in 1945 as part of an HD distillation plant, where crude mustard (H) was purified to product HD, a product of suitable stability for munitions filling. Subsequent projects have used the building for demilitarizing bulk HD stocks or HD-filled munitions.

The single-story building, which measures 73 ft x 241 ft x 19 ft high, is divided into three parts: a container unload area in the western end, three central thaw rooms, and a chemical unload and transfer area in the eastern end (Figure 1). The floor and foundation are constructed of poured reinforced concrete, the walls of hollow concrete block, and the roof of concrete with built-up roofing and gravel.

The eastern section contains three original HD unloading booths and one second-generation booth installed in August 1973. In these booths, warmed ton containers from the thaw room were drained of HD by vacuum. The liquid HD was received by two 2,600-gallon steel tanks in the pit, from which it was pumped through pipes to an incinerator in Building 538.

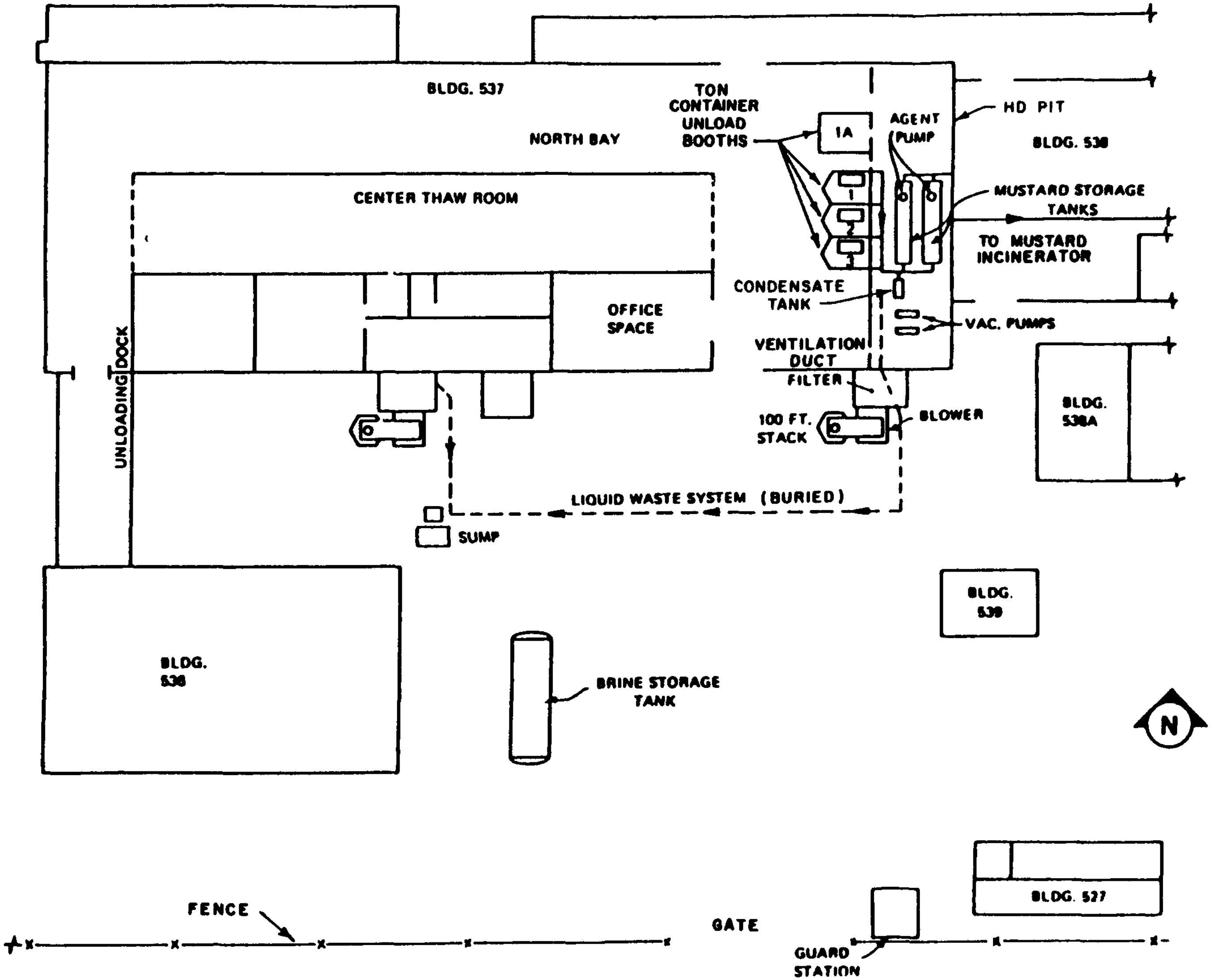

Figure 1. Layout of Building 537 and Nearby Buildings

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Part of the pumping system included a small condensate tank between the pumps and the large holding tanks. This condensate tank is located in the pit just to the south of the holding tanks.

A duct was used to ventilate the unload booths during HD operations. The unload booths were kept under negative pressure by a 36,000 CFM fan. Air was drawn into the duct, passed through a particulate and charcoal filter, and exhausted to the atmosphere through a 100-foot stack.

2.1 CONCRETE PIT

The pit dimensions are 50 ft 7 in x 15 ft 8 in x 9 ft 3 in, with the long axis parallel to the width of Building 537 (Figure 2). A checkered steel plate floor consisting of removable panels (6 ft x 3 ft each) covers the pit. The steel floor is supported by 6-inch steel I-beams.

The floor of the pit is of poured concrete coated with heresite, an anticorrosive phenol formaldehyde resin. As discovered during concrete coring operations of the present study, there were up to three separate "pours" of concrete floor, varying in thickness from 1 inch to 7 inches. The floor slopes to a sump measuring approximately 14 in x 20 in x 20 in deep, which is located in the southwest corner of the pit (Figure 3). In September 1988, the sump contained approximately 10 in of liquid, presumably groundwater, which is believed to be close to the level of the floor of the pit (D.P. Associates, 1987). Only a few inches of water were in the sump when the sampling operation took place in December 1988. The floor appears to be intact, and no cracks were found at the corners of the walls and floors.

All inside walls of the pit are painted with Rustoleum paint. The north wall of the pit is sheet metal, which separates the north access stairway from the pit itself. The eastern wall (between Building 537 and Building 538) appears to be poured concrete 12 in thick below the steel plate floor level, and painted hollow concrete block above this level. Below the Building 538

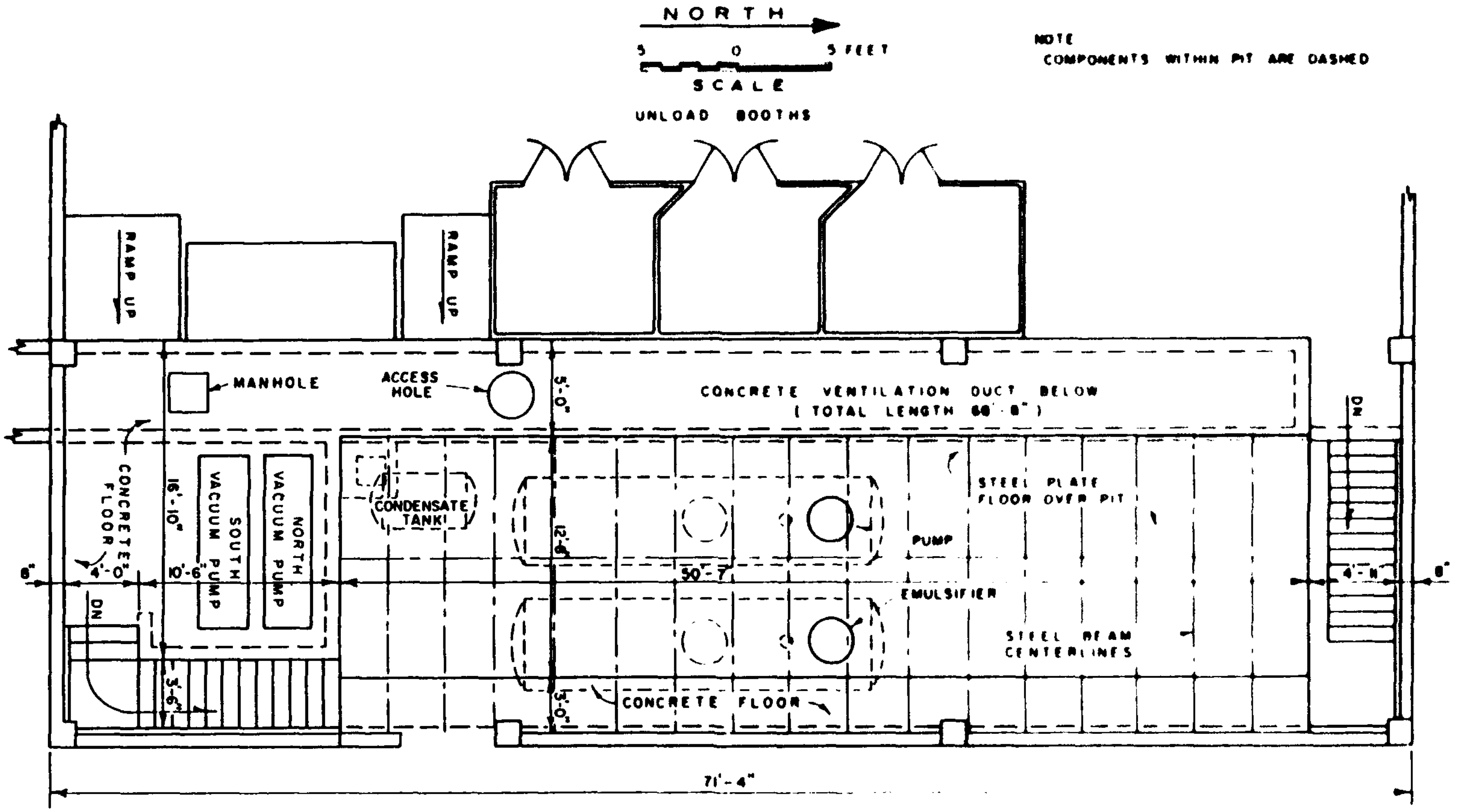

Figure 2. Plan View of Pit and Air Duct, Building 537

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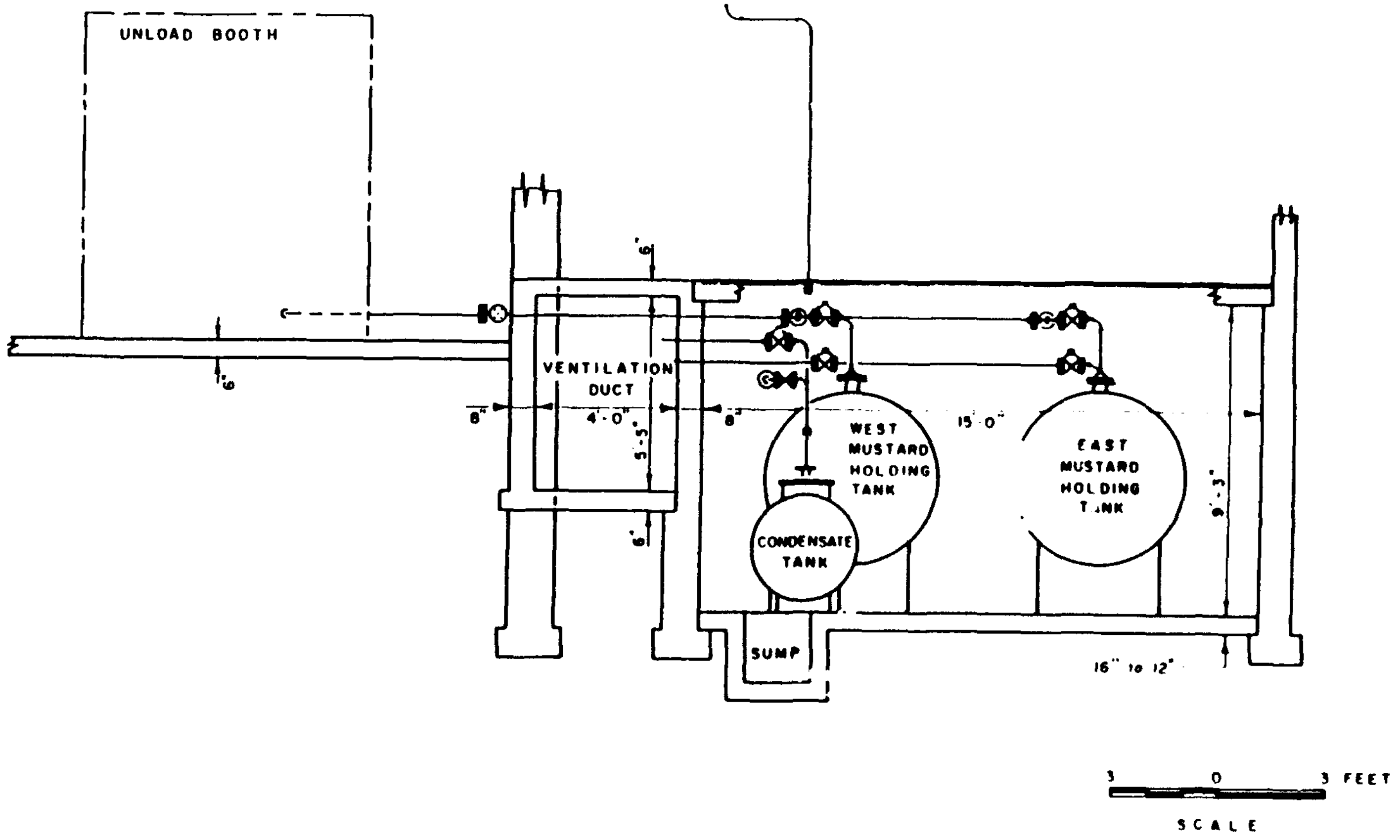

Figure 3. End View Cross Section of Pit and Duct, Building 537

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floor level the concrete wall of the pit is believed to be in contact with soil.

The south wall is poured concrete, 8 in thick. Soil is on the other side of the wall. A concrete stairway in the southeast corner of the pit provides an exit to the south (Figure 4).

The west wall is poured concrete. From the floor elevation of the pit to approximately 2.5 feet above floor level, the wall is 12 in thick, with soil on the other side. The rest of the wall is 6 in thick, and borders the concrete ventilation duct that was used to ventilate the unload booths. Liquids that spilled inside the pit were collected in the sump and were pumped directly into the duct. Wash water and decontamination water from the unload booths were also emptied into the duct, sampled, decontaminated, and then drained to the chemical sewer sump between Buildings 536 and 537.

Process equipment in the pit include two horizontal 2,600-gallon steel tanks, one small condensate tank, and associated piping (Figure 3). The two large tanks rest on wooden pillows atop concrete piers. The tanks are approximately 17 feet in length with a 2.5-foot radius. Numerous flanges are on the top of the tanks and small plugs are on the north ends. The tanks are painted with Rustoleum paint on the outside, and the documents reviewed indicate that they were painted on the inside with Rustoleum paint as well. All flanges are sealed with bolts. A drain valve on the bottom of the north end of each tank drains a small sediment trap. During operations, pumps and emulsifiers were on the top of each tank. At present, one emulsifier on the east tank and one pump on the west tank remain. The flanges on the top of the tanks are accessible from the steel plate floor above the pit.

A small condensate tank (Figure 4) in the southwest corner was part of the vacuum pump system, and was used to keep liquid HD out of the pumps. This tank is still in place, but a pipe that went into the duct is not connected.

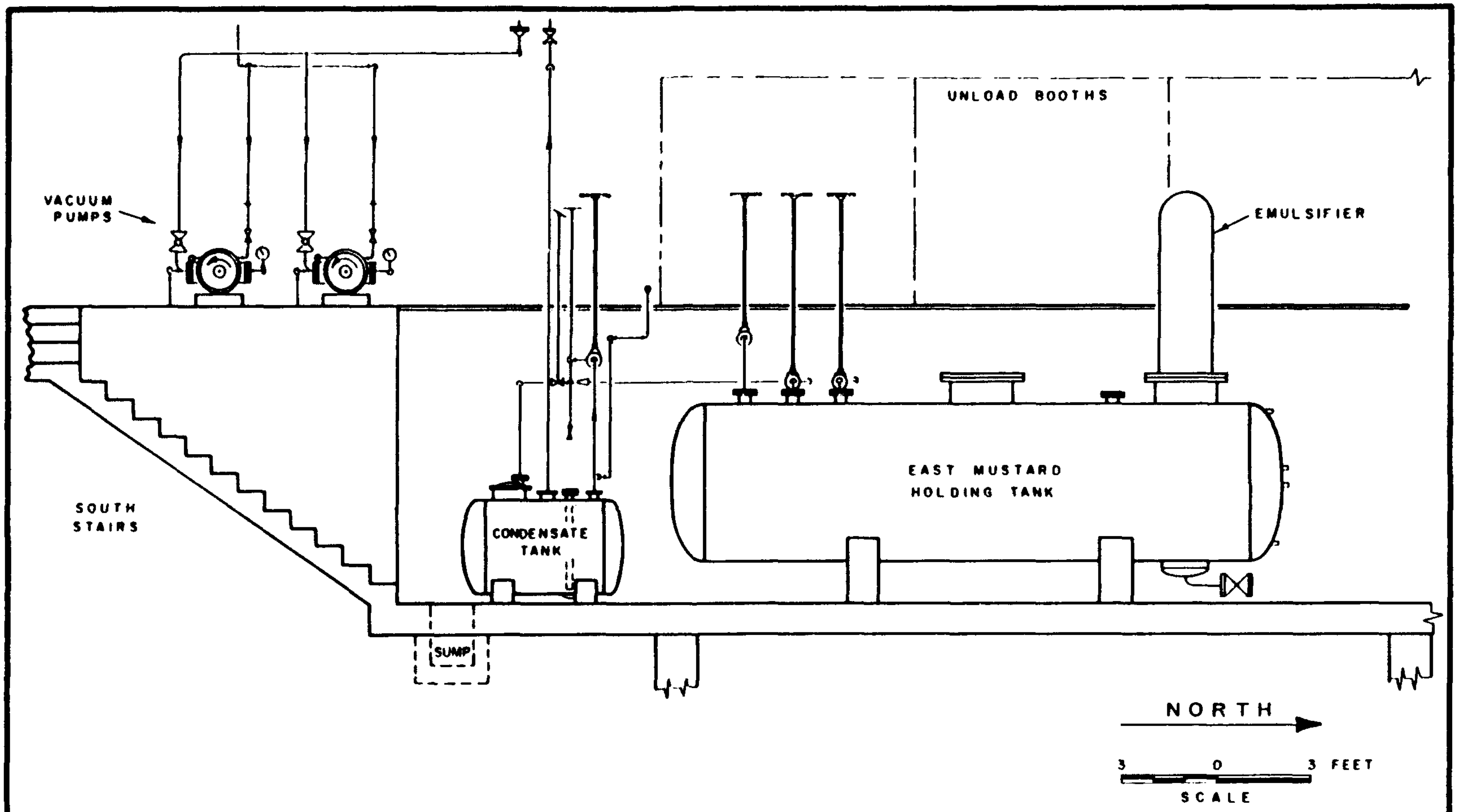

Figure 4. Process Equipment Inside Pit, Building 537

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The tank had been painted, but there is corrosion around the flanges at the top of the tank.

At the completion of the last HD demilitarization project in 1974(7), the facility was decontaminated. The success of the decontamination effort was measured by 8 hour bubbler analyses of ambient air in the building. After the decontamination program was finished, no HD greater than the time weighted average (TWA) of 0.003 mg HD/m^3 was found. (The TWA is defined as the maximum average concentration of chemical agent in air that workers may be exposed to in an 8 hour period over a period of five or more consecutive working days.) This conferred a "3X" decontamination status to the building, which allowed workers to enter without respiratory protection as long as the building was not modified or disturbed. The concrete pit also received 3X status, although entry into the pit was actively discouraged by the RMA safety department. All subsequent air monitoring of Building 537, required by Army regulation on an annual or a quarterly basis, indicated that at no time was the HD concentration above the TWA as derived from a 2-hour bubbler sampling analysis extrapolated to 8 hours.

In June 1987, volatiles released by heating a 3 ft x 3 ft section of the pit floor were analyzed with the very sensitive Trace Atmospheric Gas Analyzer (TAGA). Oxathiane and dithiane, decomposition products of HD, were detected in the unheated air stream both before and after heatup of the floor, but no HD was detected. Periodic monitoring of the facility with liquid or solid sorbent samplers have yielded similar results.

Contamination assessment of the building apparently has been limited to air sampling; no records of analyses of building materials were located and probably such analyses have never been performed.

3.0 SAMPLING METHODOLOGY

The sampling and analysis methods used to characterize the Building 537 HD pit included real-time air monitoring at sub-TWA detection levels, and collection of surface wipe samples, scraped paint, sump liquid, concrete dust, concrete cores, and soil cores.

3.1 AIR MONITORING

Air monitoring was conducted using the MINICAMS instrumentation. The MINICAMS is an automated gas chromatograph with a flame photometric detector sensitive to organo-phosphorus or organo-sulfur compounds. It is capable of detecting HD vapor at approximately 0.1 TWA concentrations (0.0003 mg/m^3) in a sampling and detection cycle time of 380 seconds. The MINICAMS also detects oxathiane, dithiane and thiodiglycol simultaneously with HD and at low concentrations the chromatogram peaks are well-defined with good baseline separation. High concentrations of dithiane produced broad peaks which could overlap the HD detection gate* resulting in false positive readings for HD. However, it was possible during calibration to estimate the dithiane contribution to the signal in the HD gate, and when HD was actually present a shoulder or definite peak could be observed on the tail of the dithiane peak.

The MINICAMS was used for a variety of air sampling activities including the pit survey, air duct survey, ambient air monitoring, closed-space air monitoring of process equipment, monitoring of sampling operations, and confirming adequate decontamination of samples, equipment, and protective clothing. Sampling commenced when portable heaters raised the Building 537 HD

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*The HD detection gate is the range of elution times required for passage of HD through the gas chromatograph column. The gate is determined by calibration with known samples and entered into the instrument control software. It is recorded as two tick marks on the chromatogram baseline that defines the time interval in which the HD peak appears.

pit ambient air temperature to 60°F, the minimum temperature required to volatize HD and breakdown products.

Air sampling at each location was accomplished with a flexible 50 ft heat-traced teflon probe that could be moved to any part of the work area. Radio contact was maintained between the MINICAMS operator, data recorder, and sampling teams during operations.

3.2 SOLID AND LIQUID SAMPLES

Wipe samples were collected using hexane soaked gauze pads which were wiped over the area to be sampled and then placed in sample bottles which contained additional hexane solvent.

Paint samples were scraped from metal surfaces with a stainless steel spatula, collected on a plastic covered plate, and transferred to sample bottles.

Sump liquid was collected using a long handled stainless-steel beaker and poured into sample bottles.

Concrete dust samples were obtained by drilling into the concrete surface with a carbide tipped drill bit, collecting the drilling dust with a spatula, and transferring it to sample bottles.

Concrete cores were obtained with an electric drilling unit that could be anchored to the floor. The drill bits were 2-in OD diamond-tipped coring bits which provided 1 3/4-in OD cores.

Soil cores were obtained with a stainless steel soil recovery probe equipped with a slide hammer and 7/8-in OD removable stainless steel sample tubes. The probe was inserted through the 2-in concrete coreholes to obtain sub-floor soil samples.

Wipe samples, paint samples, liquid, and concrete dust were sealed in amber sample bottles. Concrete and soil cores were placed in 2-in ID teflon tubes, sealed with teflon film and adhesive tape, and overpacked in stainless steel tubes for shipment.

Sample containers were decontaminated with a 50/50 bleach/water solution before being transported to the RMA laboratory for shipping preparation. They were then transported to the Battelle Hazardous Materials Laboratory for analysis.

Sample types and sampling locations in the HD pit are shown in Figure 5.

3.3 LABORATORY METHODS

The laboratory methods used for the extraction of HD from soil and concrete samples were certified prior to the collection of samples at RMA. This was documented in a technical report entitled "Documentation of the Development and Certification of an Analytical Method for Analysis of HD in Soils and Concrete", February 1989, which is included as an Appendix in Reference 5. The laboratory methods for the extraction of the surface wipe, dust, paint, and water samples were performed as screening methods and were not certified using the standard USATHAMA certification process although they were evaluated for estimated detection and quantitation limits. Extracts were analyzed for HD, oxathiane, dithiane, and thiodiglycol using a Hewlett Packard Model 5890A Gas Chromatograph with flame ionization detector, and are shown in Table 1.

Table 1 Estimated Detection Limits for Screening Extraction Methods

	Analyte			
Extraction Method	HD	OXATHIANE	DITHIANE	THIODIGLYCOL
Surface Wipe Sample	0.19 ug	0.19 ug	0.095 ug	1.9 ug
Dust Samples	0.19 ug/g	0.19 ug/g	0.095 ug/g	1.9 ug/g
Paint Samples	0.19 ug/g	0.19 ug/g	0.095 ug/g	1.9 ug/g
Water Sample	0.02 ug/ml	0.02 ug/ml	0.020 ug/ml	0.025 ug/ml

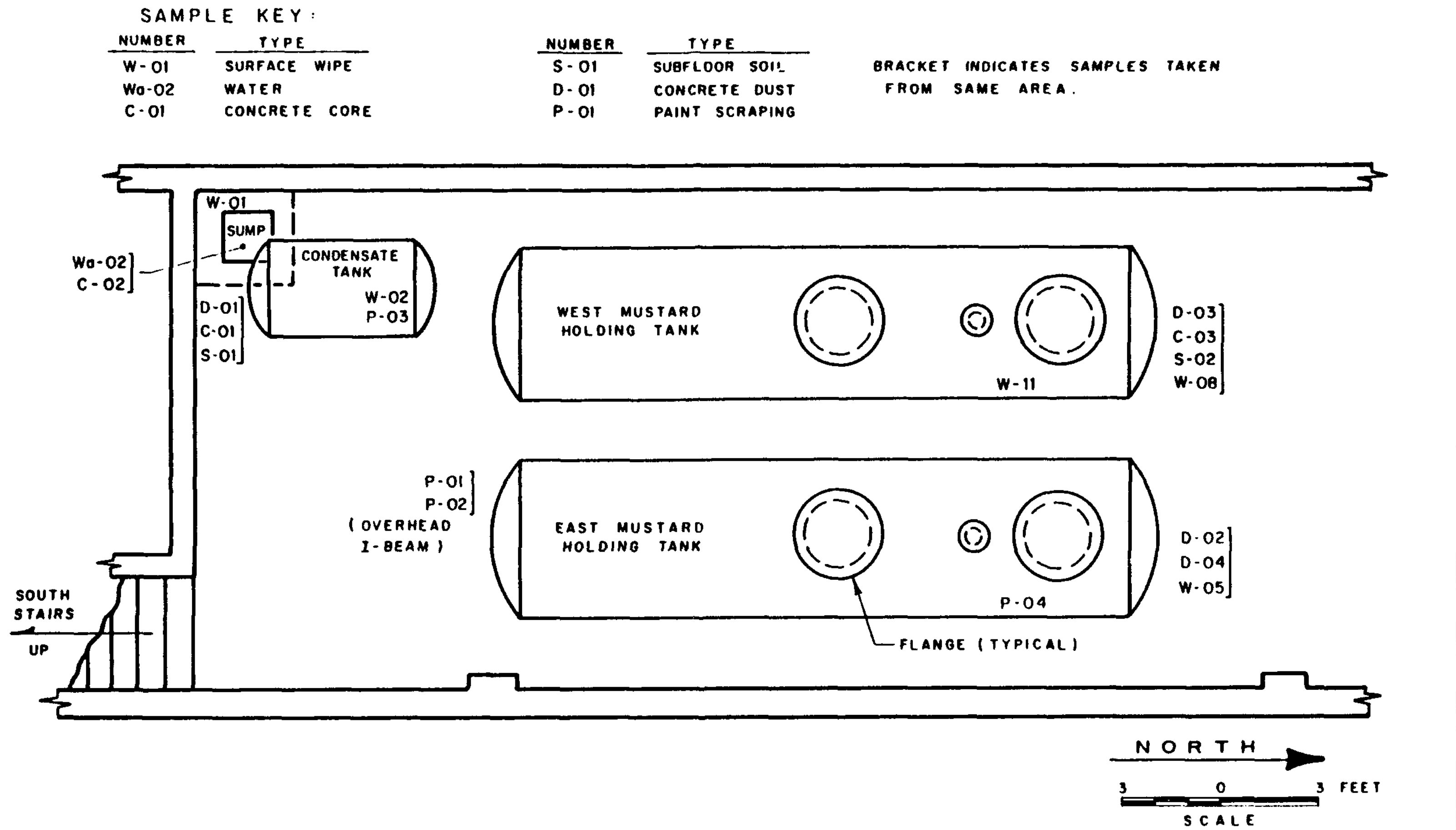

Figure 5. Sample Types, Numbers, and Sampling Locations in Pit

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The solid particulate samples (dust, paint, concrete, and soil) submitted for laboratory analyses were prepared using a chloroform solvent extraction technique. Prior to extraction all samples were mixed and crushed to a finely divided powder so that maximum surface exposure was available to the solvent. Concrete samples were crushed in a diamond crucible, while other solid samples were ground in a mortar. The sample/solvent matrix was mixed using vortex mixing and the final sample extracts filtered to remove any suspended particulate prior to analysis. The extracts contained butyl sulfide as the analytical internal standard for these methods. The water samples were extracted using methylene chloride as the extraction solvent. The surface wipe samples were placed in hexane immediately upon collection. These samples were analyzed as the hexane extract without additional processing. Extracts were analyzed for HD, oxathiane, dithiane, and thiodiglycol using a Hewlett Packard Model 5890A Gas Chromatograph with flame ionization detector. Instrument parameters for the gas chromatograph are shown in **Table 2**.

Table 2 Instrument Parameters for Gas Chromatograph

Capillary Column:	0.32-mm inner diameter x 30-m long
Stationary Phase:	Carbowax 20M, 1.0-um film thickness
Carrier:	Helium
Temperature Program:	50 C (1.0 min) program to 210 C @ 10 C/min
Linear Velocity:	35 cm/sec
Injection Volume:	2-ul splitless
Injector Temperature:	200 C
Detector Temperature:	200 C
Detector Gas Flows:	Air = 130 ml/min Hydrogen = 130 ml/min Oxygen = 15 ml/min

Gas chromatography/mass spectrometer (GC/MS) analyses were conducted on seven of the samples to confirm the presence of the organo-sulfur compounds and an internal standard. The GC conditions used for the GC/MS analyses was matched as closely as possible to the GC conditions used previously. The GC and MS conditions used for these analyses are listed in Table 3.

Table 3 Gas Chromatography and Mass Spectrometer Conditions for Analysis

GC Conditions	
Model	Finnigan MAT 9600
Column	J & W DB-WAX 30M x 0.32mm
Carrier Gas	Matheson He, UHP
Carrier Velocity	35 cm/sec
Injector Temperature	225°C
Interface Temperature	250°C
GC Temp. Program	Initial Temp. 40°C for 3 min Final Temp. 250°C at 15°C/min Final Hold 250°C for 5 min
MS Conditions	
Model	Finnigan MAT 4500
Mode	Electron Impact (EI)
Electron Energy	70 eV
Emission Current	300 uA
Preamp Sensitivity	10^{-7} A/V
EM Gain	~5 x 10^{4}
Mass Range	40-540 amu in 0.8 sec

3.4 HEALTH AND SAFETY PROGRAM

Operations conducted in an environment containing lethal chemical warfare agents are governed by special U.S. Army safety regulations. Prior to sampling, a Site Plan Safety Submission was prepared and consisted of the following documents: a contamination assessment sampling plan, work plans for each sampling process, contamination assessment safety plan, material safety data sheets for suspected contaminants, RMA emergency response plan, a site map of RMA; a detailed site map of Building 537, and results of prior air sampling.

During all sampling efforts the MINICAMS was utilized to monitor ambient air in the pit and main part of Building 537. A localized ventilation system was used at each sample location throughout operations to capture any inadvertent release of HD vapors into the working atmosphere. The system consisted of two ABC M6A1 gas particulate filter units, a six inch diameter flexible duct, and a stainless steel plenum that could be positioned near the sampling operation to collect dust or vapor releases.

Other elements of the Health and Safety Program included: briefings and personnel training, site control, site communications, personnel protective clothing and equipment, decontamination procedures, and site preparation.

Health effects data and worker protection levels are available for HD but not for oxathiane, dithiane, and thiodiglycol. As a precaution, we assumed the same safety requirements for these compounds as for HD.

4.0 RESULTS OF CHEMICAL ANALYSES

MINICAMS air monitoring typically showed HD vapor levels below, or slightly above the TWA. In cases where the TWA appeared to be exceeded, there were large dithiane peaks in the gas chromatograms which overlapped the HD detection gate.

The only high-level vapor detections were recorded for the plastic-bagged emulsifier at 4.70 to 8.53 TWA, and the interior of the three tanks which ranged from 25 to 67 TWA. In all those cases, extremely large dithiane peaks were observed, and it was not possible to determine HD and dithiane peaks independently with the MINICAMS.

Gas chromatography analyses for HD, oxathiane, dithiane, and thiodiglycol were performed in the laboratory on surface wipe samples of the tanks and duct, paint scrapings of support beams and tanks, the sump liquid, concrete dust, and the concrete and soil cores. Results for some of the samples in which HD or breakdown products were detected are shown in Table 4. The complete analytical results are provided in Reference 5.

The GC/MS confirmation analyses showed that HD and HD breakdown products are distributed throughout the RMA Building 537 HD pit. Although the number of samples is limited, the results suggest that HD concentrations in concrete and soil samples increase toward the west and south areas of the pit floor with the highest values in the sediment from the sump. This is consistent with the history of operations conducted in the pit.

It is apparent that the floor of the pit consists of at least two layers of concrete poured at different times. North of the west tank a thin third layer is present, sandwiched between the two thicker layers. This may have resulted from an attempt to seal HD contaminants in a part of the original floor prior to the pouring of the thicker layer that constitutes the existing floor surface.

Probably the most significant result is the confirmation of HD in both concrete and subfloor soil samples, and particularly in the bottom section of the soil core taken east of the sump. Table 5 presents a vertical profile of analytical results for concrete and soil core samples at that location.

5.0 DISCUSSION OF THE CONTAMINATION ASSESSMENT RESULTS

The overall objective of this task was to determine the concentration and distribution of HD and HD breakdown products in the pit in Building 537 at RMA. This objective was realized, and samples taken from concrete floors, process equipment, subfloor soils, sump liquid, and scraped paint were analyzed successfully for HD and breakdown products. The site was not fully characterized, however, because high contamination levels in the tanks, and in the soil below the floor of the pit showed the need for additional sampling and analysis beyond the scope of the present study. HD was found through the entire length of the soil core sample in one location, which showed that the full depth of

Table 4 Results of GC Anlyses of Selected Samples

Sample Description	CONCENTRATIONS IN ug/g HD	Oxathiane	Dithiane	Thiodiglycol
Wipe - North end of west tank (a)	BQL (b)	BQL	3.52	BQL
Paint - Condensate tank	8.71	2.16(c)	6.35(c)	2.23
Concrete Dust - North of east tank	3.79	BQL	0.49	8.16
Concrete Core - North of west tank, bottom of original floor (d)	45	11	30	274
Concrete Core - East of sump, top of original floor. (d)	14	1.4	12	7.5
Soil Core - Bottom of core, 5 in depth.	96(c)	0.13(c)	23(c)	0.56
Core - Compacted sump sediment	2804(c)	BQL	461(c)	BQL

(a) Wipe sample results are in ug.
(b) BQL - Below quantitation limit (HD and Oxathiane = 0.19 ug; Dithiane = 0.095 ug; Thiodiglycol = 1.9 ug)
(c) Confirmed by GC/MS analyses.
(d) HD pit floor has two or more layers indicating multiple concrete floors poured at different times.

Table 5 Results of the Analyses of the Core Samples from East of Sump Area In Pit C-01 and S-01

		Concentration in µg/g			
Sample Description	Sample Depth (in)	HD	OXATHIANE	DITHIANE	THIODIGLYCOL
Top of 2nd concrete floor	1	BCRL	0.56	5.2	10
	2				
Middle 2nd floor	3	BCRL	0.63	3.3	30
	4				
	5				
Bottom of top floor	6	2.8	0.52	1.7	5.9
Top of original floor	7	14	1.4	12	7.5
	8				
	9				
Original floor bottom	10	3.3	0.93	13	11
Top of soil core	11	2.2*	0.90*	20*	0.70
	12				
	13				
	14				
	15				
Bottom of soil core	16	96*	0.13*	23*	0.56

BCRL = Below Certified Reporting Limit = (1.79 µg/g) using USATHAMA QA/QC program (PC version 1 April 1988).

* = Confirmed by mass spectrometry.

HD penetration in the soil below the floor is not known. No concrete cores were taken from the side walls and no soil samples were collected adjacent to the walls, so the lateral distribution of HD in and around the pit walls will require further study. This information will be needed for the engineering design of the hot gas decontamination system to be used for this structure.

The organosulfur vapor contamination levels in all three tanks in the pit were very high, which prevented the collection of wipe samples or liquid samples from the tank interiors. The dithiane peaks for all three tank vapor samples were so large that the HD gate was completely overlapped and it was not possible to determine whether HD was present. For reasons of safety however, it is necessary to assume that HD is present. Before the hot gas decontamination process can be applied in this facility, it will be necessary to open the tanks and determine the quantity and composition of any liquid that may be contained in them. If liquid HD is present, it may be necessary to develop a plan for removal from the tanks prior to hot gas decontamination. The pipes and fittings connected to the tanks also will require thorough checking.

The MINICAMS proved to be very useful for monitoring HD and breakdown product vapors. It was possible to detect HD at about 0.1 TWA in the presence of HD breakdown products. The complete series of HD and breakdown products was reported every 380 seconds in operating conditions that were far from ideal. One problem was the overlap of the dithiane and HD peaks. This could probably be corrected if the MINICAMS were modified to obtain greater separation of these two peaks and this could likely be accomplished by installing a longer column in the MINICAMS and changing the column heating program. Improving the resolution of these two peaks would increase cycle time for the instrument, and this trade-off would need to be evaluated in system design planning. A broader dynamic range for MINICAMS detection of HD and breakdown products is a needed improvement. Whether this could best be accomplished by modifying the existing instrument or software, or by using two or more instruments to cover the required range, will require further evaluation.

Air monitoring performed during the heating cycle of the Hot Gas Decontamination Process will require installation of traps on the sample lines to control water vapor. Water will be generated in the combustion of fuel used to heat the structure, and by vaporization from the structure and surrounding soils. When these vapors are cooled from approximately 750°F within the structure to 300°F in the stack and finally to the ambient temperature of the MINICAMS preconcentrator, condensates will form and potentially interfere with the monitoring instrumentation. Effective trapping and frequent calibration to check sample recovery through the entire sampling and analysis system will be necessary for reliable monitoring. Calibration will be required for the contamination levels and water levels expected during hot gas decontamination operations. Calibration standards will need to contain water in concentrations comparable to those anticipated in the structure during hot gas decontamination, and will need to be injected into the sampling gas stream before the traps.

Another modification that would improve the efficiency of the MINICAMS equipment would be to locate the computer controllers and data recording parts of the instruments in a central monitoring system control station while placing the analysis and gas flow components in protective enclosures as close as possible to the sampling points. This would minimize the length of heat traced sample lines, and also reduce monitoring personnel requirements.

The presence of HD in the concrete floor and subfloor soil places emphasis on the importance of agent vapor containment during hot gas decontamination. The system design will need to include provisions for soil gas venting and monitoring and a secondary containment structure to prevent any release of vapors to the outside atmosphere.

Groundwater levels should be considered also. The sump in the floor of the HD pit contained liquid at levels close to the bottom of the concrete floor, but no water was found in any soil coreholes, which penetrated about six inches into the soil below the floor. In preparation for the hot gas decontamination test, it will be necessary to determine groundwater levels and quality in the vicinity of the structure and to develop a plan for dewatering and water disposal, if necessary.

6.0 SYSTEM DESIGN

6.1 PERFORMANCE GOALS

The hot gas system must heat all parts of the HD pit structure to 300°F and provide total containment of chemical agent. Volatilized organics in the hot gas stream must be captured or destroyed and the overall system design and control equipment must yield adequate data to prove effectiveness and provide a basis for scale-up.

The field demonstration test will be conducted on the HD pit and surrounding soil. Process equipment in the pit will be opened but remain in place for the decontamination test. Piping, process equipment and structures above the pit will be removed to the extent necessary to accommodate decontamination equipment and the secondary agent containment structure. The general concept will be to install a burner to inject heated air into the sealed pit and to evacuate the heated air and contaminant vapors through an afterburner, quench, induced draft fan, and stack.

6.2 SYSTEM COMPONENTS AND FLOW DIAGRAM

The major components of the hot gas system required for Building 537 at RMA are shown in **Table 6**, and their functions are briefly described. Heat and material balances and component sizing are discussed in detail in the system design section of the final report[6].

The process flow diagram is shown in **Figure 6**. The extreme importance of avoiding any release of HD or other contaminants to the environment is addressed in redundancy of burners, carbon filters, and induced draft fans. Also, the secondary containment area shown on the diagram is a shroud installed over the HD pit and as much surrounding structure or soil as is found to be contaminated. During operations, air in the shroud would be maintained at a pressure slightly negative with respect to ambient but slightly positive with respect to the pressure in the pit which would be at least 0.25 inches H_2O below ambient. The purpose of the secondary containment system would be to capture any vapors escaping via the soil surrounding the HD pit and draw them into the pit and contamination destruction system.

6.3 PROCESS EQUIPMENT - SIZING OF MAJOR COMPONENTS

A main burner with a capacity of 4,000,000 BTU per hour was selected based on engineering calculations(6). **Table 7** presents material and heat balances

Table 6

SELECTION OF SYSTEM COMPONENTS

Principal Components of Hot Gas Treatment System

Component	Function
Main Burner	Generation of hot gases within structure; volatilization and degradation of agent.
Afterburner	Air pollution control; destruction of volatilized organics in exhaust gas.
Quench	Cooling of afterburner flue gas prior to induced draft fan.
Barometric Damper	Addition of diluent air; cooling of exhaust stream prior to carbon filters.
Carbon Filters	Backup air pollution control in event of afterburner flame out; capture of volatilized organics in exhaust gas.
Induced Draft (ID) Fans	Maintenance of negative pressure inside structure; control of agent migration.
Stack	Dispersion of treated exhaust gases.
Control System	Provides feedback to actuators to achieve the desired results based on input provided by instrumentation (s.a. thermocouples, pitot tubes, or agent sensors) located throughout the decontamination system. Many of the instruments are for safety, some are to optimize system performance.

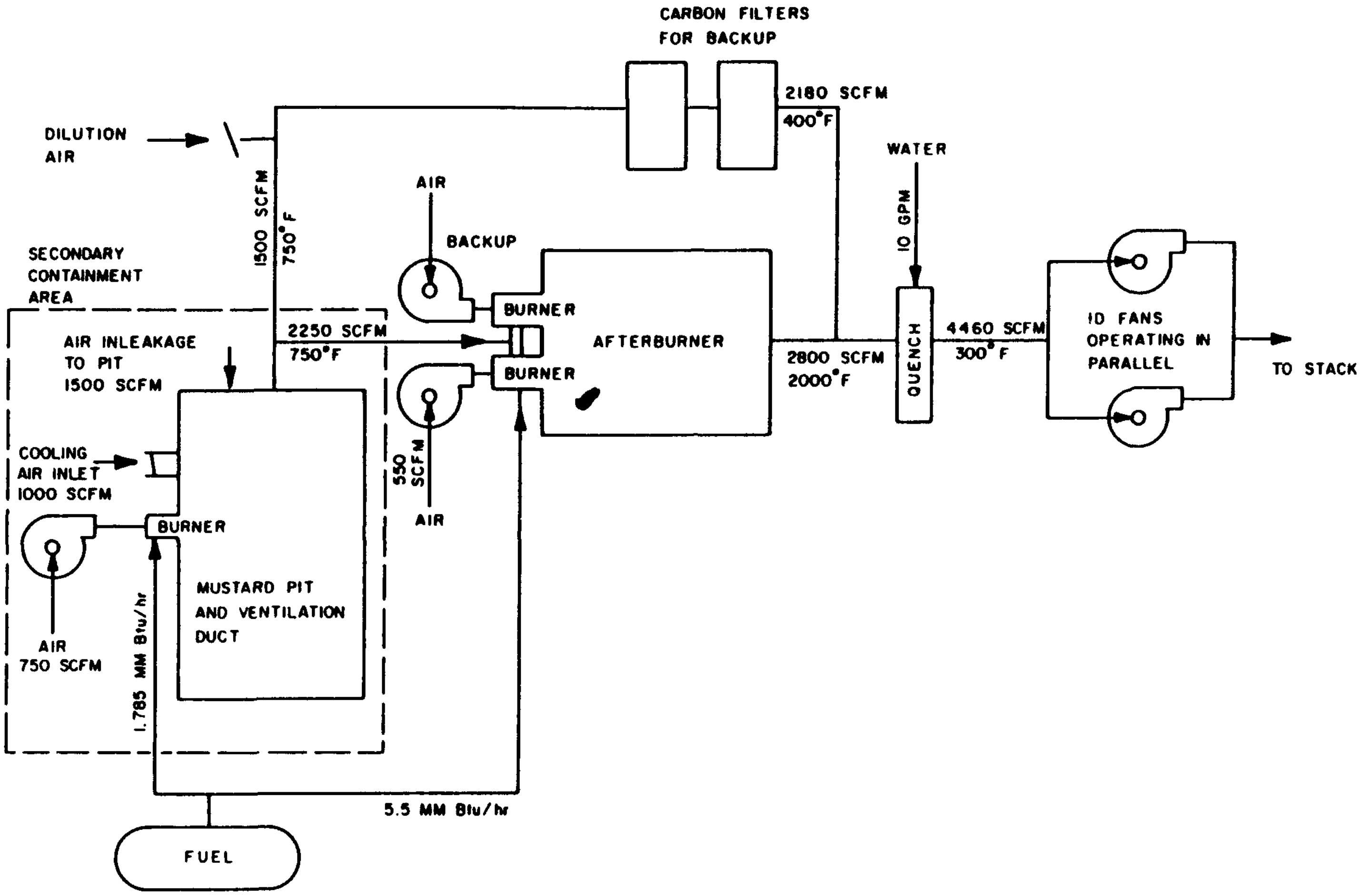

Figure 6. Process Flow Diagram--End of Heating (Including Carbon Filter Backup)

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Table 7. Heat and Material Balances
4,000,000 BTU Main Burner

	Start of Heating	End of Heating
Main Burner (Heater)		
Combustion Air, scfm	750	750
Fuel, BTU/hr	4,000,000	1,785,000
Air Inleakage, scfm	1,500	1,500
Flue Gas, scfm	2,250	2,250
Flue Gas Temperature, F	100	750
Heat Content of Building Air, (100 F base) BTU/hr	0	1,685,000
Heat to Building, BTU/hr	4,000,000	100,000
Afterburner		
Air 0.6 stoichiometric, scfm	750	550
Fuel, BTU/hr	7,500,000	5,500,000
Temperature, F	2,000	2,000
Heat Loss, BTU/hr	500,000	500,000
Afterburner		
Heat Content, BTU/hr	6,940,000	6,500,000
Gas Flow, scfm	3,000	2,800
Quencher Liquid Flow, gpm	10.7	10.0
Quencher Liquid Flow, scfm	1,780	1,660
Stack Gas Flow, scfm	4,780	4,460
Stack Temperature, F	300	300

for a decontamination system driven by a 4,000,000 BTU/hr unit in the pit area. Balances at startup and at the end of heating are provided.

Main Burner. The 4,000,000 BTU/hr heating system includes a 16 osi (ounces per square inch) blower, a fuel and air control valve, a fuel safety train and a propane fired burner.

Afterburner (AFB). The 7,500,000 BTU/hr after burner heating system would include duplicate flame sources. Each flame source would consist of a 16 osi blower, a fuel and air control valve, a fuel safety train and a propane fired burner. The afterburner itself is assumed to be a horizontal, refractory lined cylinder. Its external dimensions would be approximately 5 feet by 17 feet with 4 inches of refractory. The afterburner should be mounted on a semitrailer in order to simplify transportation and set-up/tear-down procedures.

Carbon Filters (CF). The backup air pollution control units will be approximately 4.75 feet in diameter and 3 feet long (external dimensions). The duplicate filters were sized assuming a flowrate of 3,800 acfm, 50 percent filter voidage, and a retention time of 0.3 seconds in each.

Induced Draft (ID) Fans. Each of the ID fans is rated at 8,000 acfm at 300°F and would be driven by a 15 HP motor. One fan of this type will be sufficient to pull the required negative pressure through either the after burner or the carbon filters. A second fan is provided in parallel, for backup purposes.

Butterfly Valve (at concrete duct exhaust). This valve will be adjusted during heatup to ensure adequate heat distribution/air flow in the concrete duct. Its actuator will be controlled at the control panel. If the temperature in the concrete duct is too low (compared to the mustard pit air temperature) this butterfly valve will be opened further.

<u>Butterfly Valve (at cooling air inlet)</u>. This valve is closed during heatup/decontamination, and open during cool down (after decontamination is complete). Its actuator will be controlled by a switch at the control panel.

<u>Quench</u>. The quench allows the addition of water with or/without chemical additives to the AFB flue gas before it enters the ID fan. The quench will be designed to reduce the AFB flue gas to 300°F. It will be built to provide a liquid trap to prevent the release of vapors from the afterburner in the event of a system failure. The liquid seal would force any gases passing out the exhaust system to bubble through the quench liquid.

<u>Barometric Damper (exhaust duct to CF)</u>. This damper allows the addition of 700 scfm of dilution air to the hot gas exhaust prior to the carbon filter backup system. It will be set to maintain a slightly negative pressure in the mustard pit, and will be equipped with an override control operated from the control panel.

6.4 PROCESS CONTROLS

Process monitoring instrumentation is interfaced with a controller that provides feedback to actuators which adjust energy input or air flows to maintain desired temperatures throughout the structure and prevent release of agents. The extreme importance of assuring agent containment is reflected in redundancy of system components as well as control instrumentation. Figure 7 shows the control system with circled letters and lines to the point being monitored. The letters are defined as follows: AA - Agent Sensor/Alarm, P - Pressure, T - Temperature, and UV - Ultraviolet Flame detector.

The first control loop is for the main burner which provides the heat to decontaminate the structure. The burner is equipped with standard safety equipment. The UV flame detector provides information to the burner control that a flame is present and to continue fuel flow to the burner. If a flame is not present then fuel flow to the burner is stopped. The thermocouple

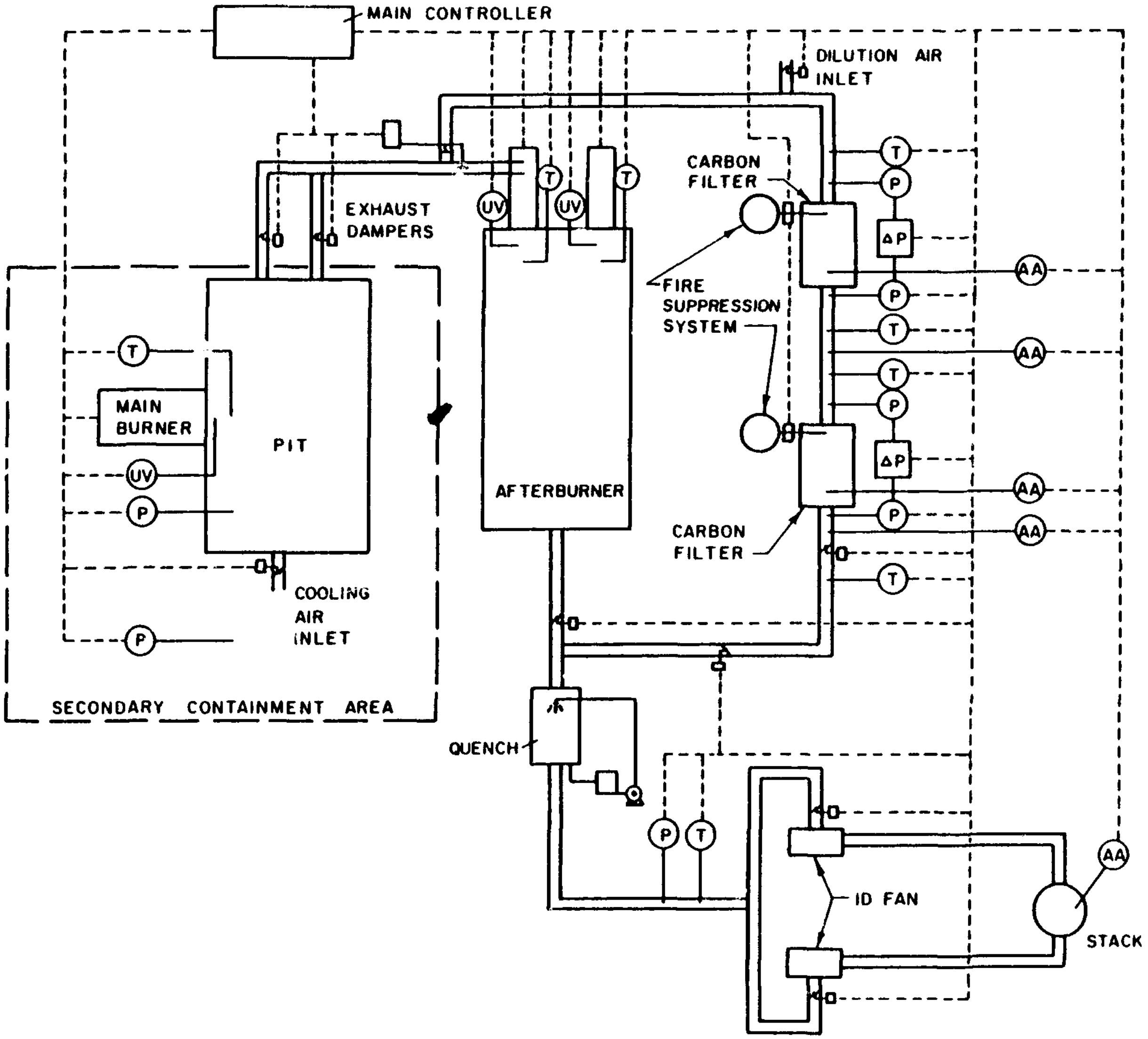

Figure 7. Process Control Instrumentation

monitors the temperature of the area being decontaminated and provides input to the controller which adjusts fuel flow to maintain the structure temperature between set points.

The pressure in the area being decontaminated is monitored and maintained negative with respect to ambient to prevent the release of gases from the area being decontaminated. If the pressure rises above a value of -0.1 inches of water the main burner is shut down. The controller also prevents the burner from being started unless the induced draft fans are running to provide negative pressure. The control loop also requires the afterburner to be in operation before the main burner can be started.

The pressure above the area being decontaminated, within the secondary containment structure will also be monitored. The pressure in this structure will be less than ambient and greater than the area being decontaminated. This maintains a flow of air from low to high contamination zones. The cooling air inlet can be opened in the event the blower fails to maintain air flow of at least six air exchanges per hour within the secondary containment structure. It can also be used to maintain the negative pressure in this structure during decontamination. If necessary, a small damper could also be installed on the secondary containment enclosure to help regulate the pressure differential here.

The other main control loop is for the afterburner burners. It has the same UV and temperature controls as the main burner. It also has an auto-ignition option that relights the burner in the event of a flame-out if conditions are correct for a relight to occur. The afterburner controller provides information to the main burner. In the event of an afterburner shutdown or failure, the main burner will shut down and cannot be started until the afterburner is operating.

The afterburner is equipped with two flame sources which are both full size burners. The primary burner supplies the energy required to maintain the afterburner temperature during normal operation. The secondary or back-up burner is on pilot and will be called upon by the controller in the event that the main burner does not respond to provide the necessary energy. The afterburner is designed to provide approximately 15 minutes of thermal inertia to maintain destruction efficiency for burner reignition attempts and to allow time for switching over to the carbon filters.

Control inputs that can shut down both the afterburner burners and the main burner and also cause the dampers to the carbon filter to open and the afterburner to close, are a loss of negative pressure at the induced draft fans, high temperature at the inlet of the induced draft fans, and chemical agent being detected in the stack. The ducting to the carbon filter is closed during normal operation of the burners. When a condition results in the burners being shut down, the ducting to the afterburner is closed at the same time the ducting to the carbon filter is opened. The induced draft fans are then switched to provide suction for the carbon filters.

The carbon filters,to be used only after an afterburner or quench failure, are sized to handle the anticipated load of vapors individually. The second carbon filter in series is a back-up filter in the event the first carbon filter becomes saturated or organics break through. The carbon filters are monitored for break-through approximately two-thirds through each filter and after each filter. In the event of break-through of both carbon filters the system is backed up with a liquid quench system that uses a solution which can capture the agent being decontaminated. The quench uses a pump to provide scrubbing of the gases. Also, the quench is configured such that a liquid trap that can be flooded to block vapor releases from the afterburner. This adds an additional margin of safety in the event of major problems.

The carbon filters are equipped with a prefilter to reduce the risk of particulates plugging the carbon filters. The main burner would be shut down whenever the carbon filters were in use which reduces the gas velocity through the area being decontaminated. This reduced velocity would reduce the amount of particulate that would be picked up and carried to the carbon filters. Thermocouples and pressure sensors are located before and after each of the carbon filters. The thermocouple before the filter indicates whether the gas stream to the filter exceeds the threshold temperature of the carbon. A fire in the carbon filters would be indicated by a sudden increase in temperature of the thermocouple placed downstream from the filters. This event would result in a fire suppression system functioning. The pressure drop across each filter is monitored to detect plugging.

The induced draft fans are operated in parallel. They are sized to be able to handle the load requirements individually, but will both be operating so that one will pick up the load from the other in the event of an induced fan failure. The induced draft fans are equipped so that they can be valved off for repair during the decontamination operation. The valves/dampers also allow the fans to be used for the afterburner or carbon filters.

The dilution air inlet damper (upstream of the carbon filters) is barometrically operated such that it provides the needed cooling air to reduce the exhaust temperature to 400°F. The damper is also equipped with an actuated override such that it can be controlled by the operator in the control room. The damper that controls the exhaust from the ducting running along the west wall will be operated from the control room by the operator based on the temperatures being monitored in the area being decontaminated. Other exhaust ducts with dampers may be needed to control hot gases to decontaminate other areas of the pit, such as under the pit floor where there are indications of air spaces. Provisions for providing ventilation for heating will need to be added as required by site characterization. Air purges of tanks and pipes will be added to provide movement of gases out of the trapped areas. This can be accomplished through a positive air system or by directed in leakage. Sparge air needs to be controlled to prevent cooling of the item or area receiving the air.

Temperatures will be monitored at approximately 45 locations throughout the structure and the decontamination process equipment. Air flows will be monitored at five locations. Air pressure will be monitored in the HD pit, the secondary containment structure, the ambient exterior zone, across the carbon filters, and in the duct between the quench and ID fans.

Instrument displays, controls, and data recording equipment will be trailer mounted outside Building 537.

6.5 SYSTEM INSTALLATION AT BUILDING 537, RMA

Figure 8 shows the hot gas decontamination system installed in Building 537 at RMA. The dimensions of the secondary containment structure will be determined following additional site characterization sampling to determine the extent of contamination (if any) in the soil surrounding the HD pit. The additional site characterization will also provide information on possible requirements for groundwater management, soil-gas venting into the secondary containment area, and disposal of tank contents.

In the installation plan for the system, an effort was made to have as much of the operating equipment as possible outside Building 537 for ease of access and to minimize site modifications. A number of modifications will be required, however, and these are listed in Table 8.

6.6 AIR MONITORING

The operation of the Hot Gas Decontamination System at RMA will require monitoring and performance tests to demonstrate that the system will not adversely impact local air quality, and to ensure that releases of chemical agents do not occur.

Emissions monitoring can be grouped into three technical area, including ambient impacts, stack emissions, and system performance.

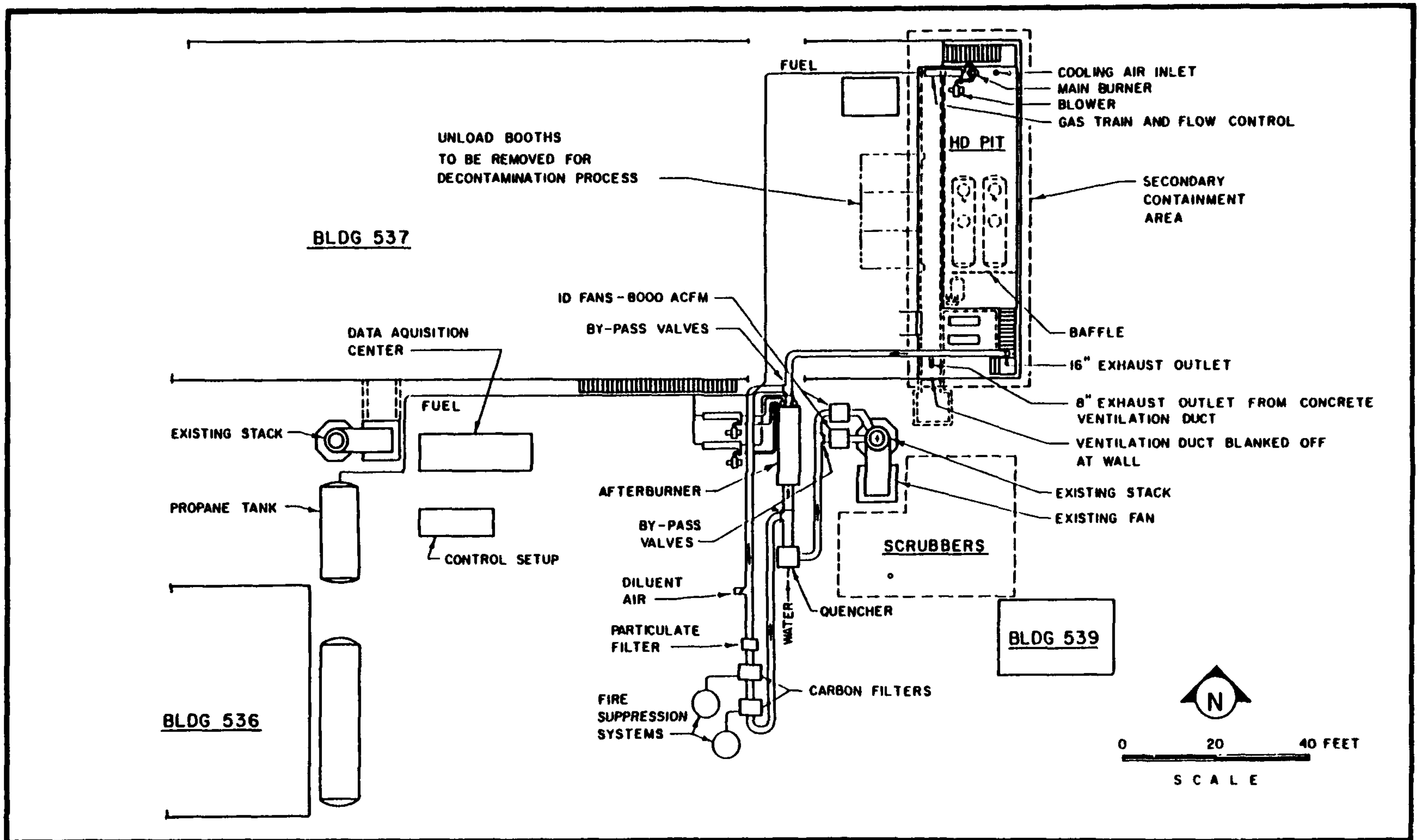

Figure 8. Hot Gas Decontamination System Installed in Building 537 at Rocky Mountain Arsenal

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TABLE 8. SITE MODIFICATIONS AND INSTALLATION OF THE HOT GAS DECONTAMINATION SYSTEM IN BUILDING 537, RMA

1. Remove unload booths.
2. Clear pipes and process equipment above HD pit.
3. Cut and plug pipes passing through HD pit and ventilation duct.
4. Remove sheet metal north wall of HD pit.
5. Open all piping, valves, and tanks in the HD pit.
6. Make openings for installation of air ducts, dewatering equipment and vents for steam and soil gas.
7. Install sparge air piping to the process vessels as required.
8. Modify ventilation duct for proper air flow. Install baffles for air flow control in the HD pit.
9. Modify stack to be used for test.
10. Install system components and instrumentation.
11. Seal HD pit and ventilation duct.
12. Insulate top of HD pit cover.
13. Install secondary containment structure.

Ambient Impacts

The impact of the source on ambient air levels will be determined by a mobile ambient monitoring station. If existing baseline data is not available this should be established prior to operation startup. The station can be a self contained facility with instruments for monitoring SO_2, TSP, NO_2, CO, total hydrocarbons, and the HD compounds.

A source of meteorological data should be available on site or with the mobile station. Monitoring system design, calibration procedures and operations should be as prescribed in the standard EPA methods. (EPA-600/4-77-027). Monitoring should be continuous for the duration of the test. Ambient monitoring for HD compounds would be with bubbler or sorbent tube samplers.

Stack Emissions Monitoring

Stack monitoring will include both a continuous monitor for opacity (as an indication of particulate emissions) and a performance test for emissions releases. The performance test should include an EPA Method 5 sampling train to determine the particulate emission rate. This sampling system can be modified to include an adsorbent sampler for determination of organic breakthrough species (HD and breakdown products). The train is referred to as a Modified Method 5 (MM5) system and furthermore, this sampling system can include a determination of HCl emissions by chemical measurement of the condensed vapor in a basic solution.

For this performance test a total of 3 MM5 trains with a HCl sampling impinger added to the train will be conducted in the stack. Standard EPA Methods 1 through 4 will be used in preparation of the sampling. For this approach it is recommended that two 4 inch threaded and capped sampling ports be installed on the new rectangular duct leading to the stack in accordance with specifications in EPA Method 1A.

Sampling will be conducted for 3 periods during operation of the Hot Gas Decontamination System. Analysis will be made for the following:

- Total particulates from filter and probe
- Volatile organics from the sorbent cartridge
- HCl from collected condensate and basic impinger solution.

Each test will also include an integrated bag sample of effluent gas which will be analyzed for CO_2, O_2, CO, and total hydrocarbons.

System Performance Monitoring

CO_2 and CO will be monitored in the exhaust effluent from the afterburner prior to gas quench. This system will require the installation of a high temperature corrosion resistant, rake type probe in the duct with subsequent gas cooling and condensate collection. The cooled gas products can be continuously measured with a non-dispersed infrared (NDIR) instrument. The results will indicate the quality of combustion and also allow determination of total system exhaust gas dilution.

Chemical Agent Monitoring

Continuous, near-real time monitoring will be conducted for HD and the HD breakdown products oxathiane, dithiane, and thiodiglycol. This will be accomplished with the MINICAMS which has been used successfully to monitor HD at about 0.0003 mg/m^3 and the HD breakdown products in their joint presence. The response time for this degree of sensitivity and with adequate control of interferences should be less than 10 minutes.

HD compounds will be monitored with the MINICAMS at sampling points in the secondary containment structure, the HD pit, the air ventilation duct, and the stack as a minimum. Stainless steel sampling probes will be used with heat traced teflon sample lines. Moisture trapping will be required due to the high concentrations of water in the decontamination gas stream. Requirements for trapping, calibration and control of interferences are discussed in greater detail in References 5 and 6 (Appendix D).

6.7 TEST OPERATIONS

Decontamination

After installation and check-out of all equipment, the hot gas decontamination test will be conducted in three stages: start-up, operation, and shutdown. Monitoring equipment is started and background levels are determined before any process equipment is operated.

The induced draft fans are the first items of equipment started. This provides the negative pressure to the system. The next items to start are the quench followed by the afterburner. The afterburner must be at a minimum temperature of 1900°F before the main burner can be started. This is part of the control interlock system. The main burner will be started at a temperature set point of 400°F. The set point temperature is measured in the hot gas stream entering the HD pit. The set point is increased at a maximum rate of 50°F per hour to 750°F. The set point increase rate is reduced if the monitoring systems indicate excessive steam or contamination vapor generation.

The operation of the hot gas decontamination system is automatic after it has been started and the temperature of the burner gas stream has been set at 750°F. The process controllers maintain temperature and monitor system conditions. The temperature of the various locations of the building are monitored for heat-up rates. The flow of hot gases through different sections may be changed by adjusting the dampers in the exhaust ducts. The decontamination operation is complete when all locations monitored reach a temperature equal to or greater than 300°F for a period of at least one hour, and the air monitoring system no longer detects contaminants.

At this point, the building is considered decontaminated and the cool-down period started.

In the event of a problem or system upset during decontamination, the controllers are programmed to switch over to the activated carbon filter back-up system. While the back-up system is being used, all burners are off. The system can be restarted after repairs or corrections have been made.

The manual override control on the barometric damper is used to adjust the temperature to the carbon filter in case it is not providing the required amounts of dilution air. Care must be taken to maintain the negative pressure on the area being decontaminated.

After decontamination, the main burner is shut off followed by the afterburner. The induced draft fans remain on to pull cooling air into the area that has been decontaminated. After the main burner is off, the cooling air inlet damper can be opened. This allows additional cooling air into the are for cooling. The cool-down period is completed when the surface temperatures of the area decontaminated have reached a safe temperature of about 110°F. The quench is shut down only when the temperature into the quench has reached 400°F or below, in order to protect the ID fans during cool-down.

The equipment can be dismantled after the cool-down period has been completed and the area has been verified decontaminated. The equipment is decontaminated unless the backup carbon filter system was used. The ducting to carbon filter system could be contaminated in the event of its use during operation. The ducting should be checked for contamination in the event of its use during a decontamination operation. The activated carbon should also be considered contaminated if the backup system was used. The rest of the process equipment is self-decontaminating.

Post-test sampling is conducted to verify decontamination. The procedures are the same as those used in site characterization[5] and samples collected include concrete cores, soil cores, wipes from interior and exterior surfaces of process equipment, and water if present in soil coreholes. The insulation on the pit cover, and the un-heated portions of the secondary containment structure will be checked for chemical agent contamination.

6.8 WASTE GENERATION AND DISPOSAL

The process has been designed to minimize the amount of waste generated. However, plans for disposal of the following materials would have to be completed prior to the field test:

a. Tanks, piping, etc. in the pit. This equipment will be decontaminated at the end of the test. It could, therefore, safely be cut up, removed and disposed of in an acceptable manner.

b. Insulation on pit cover. This should be tested at the conclusion of the field study to determine whether it has been contaminated with mustard. Since the pit area will be kept at negative pressure for the duration of the test, it is not expected to become contaminated. If detectable levels of agent are found, the insulation might be combined with other agent contaminated waste at RMA.

c. Carbon filter and associated duct. If the backup air pollution control loop is required during the test, all used carbon filters will need to be disposed of in an environmentally acceptable manner. The duct upstream of the carbon filter should be checked for contamination; it may also require either acceptable disposal or decontamination (for reuse). This particular length of duct could not be assumed to be uncontaminated since the temperature of the incoming gas stream may not be hot enough over a sufficient period of time. The remainder of the process duct work is either located after an air pollution control device or is maintained at a high temperature for sufficient time to be considered decontaminated (to a 5x level) and reusable.

d. Water generated from dewatering efforts. In the event that dewatering of the soil under the pit is required--and the results of pre-test sampling indicate this water to be contaminated, arrangements will have to be made for the safe disposal of this contaminated water. The simplest method of disposal may be to pump this water into the pit (or concrete duct) for evaporation and decontamination of vapors in the hot gas system during the decontamination process.

An alternative to be considered for waste disposal is fabrication of a metal enclosure to be used to decontaminate wastes such as insulation and structural materials. The metal enclosure would be fitted with ducts to receive burner gases and discharge exhaust gases to the afterburner. In short, it would function as a field portable oven for hot gas decontamination of waste materials generated in the building decontamination process. A unit of this type might also be suitable for decontamination of other contaminated materials such as, process equipment, laboratory hardware, or environmental samples.

6.9 FAILURE ANALYSIS

A detailed analysis was conducted to identify possible failure modes, causes, effects, and preventive or corrective actions that could be taken. This was considered particularly important in view of the requirements for assured containment. In Reference 6 there is a detailed analysis of 18 failure modes involving the main burner, afterburner, quench, induced draft fans, carbon filters, carbon filter fire suppression system, central control system, and secondary containment system. All failure modes evaluated are controllable with a combination of standard safety equipment, detection and alarm systems, safety interlocks, alternative agent containment or destruction components, and redundancy.

7.0 CONCLUSIONS

1. The HD pit in Building 537 at RMA contains residual contamination of HD and HD breakdown products in the concrete floor and in the soil below the floor. HD is also present in painted surfaces of process tanks, and it is assumed to be present in residues within process tanks.

2. The HD breakdown products oxathiane and dithiane are present in air, tanks, and process equipment in the HD pit. HD was not detected in the pit atmosphere, except during some sampling operations in which concrete was drilled.

3. The MINICAMS, as modified for this sub-task, is an effective agent air monitoring instrument capable of detecting HD at levels of about 0.1 TWA in the presence of HD breakdown products. The instrument also detects oxathiane, dithiane, and thiodiglycol, and probably could be calibrated to detect any of the volatile organosulfur compounds associated with HD.

   Modifications to the MINICAMS which would make it more suitable for monitoring hot gas decontamination operations include:

   - Lengthening the column and changing the column temperature cycle to obtain greater separation of dithiane and HD peaks
   - Adding software to use the multipoint calibration curves for calculation of HD and breakdown product concentrations

    - Increasing the dynamic range of the system for HD and breakdown products

    - Developing trapping and calibration procedures to ensure reliable performance in H_2O rich atmospheres.

4. The HD pit in Building 537 at RMA is a suitable structure for a demonstration test of the Hot Gas Decontamination Process. It contains known HD contamination in structural materials and process equipment, is relatively simple in design, and should be suitable for installation of the equipment required for hot gas decontamination, agent containment, and air monitoring.

5. Additional site characterization will be required to determine the extent of contamination in sub-floor and surrounding soils, in tanks and piping, and in the groundwater.

6. A hot gas decontamination system design for this site is feasible using available process equipment, controls, and monitoring instrumentation.

7. The HD breakdown products oxathiane, dithiane, thiodiglycol, and possibly several related compounds were present with HD in the HD pit in Building 537 at RMA. It is reasonable to expect these compounds to be present in HD contaminated structures at other military installations. The health effects data for these compounds is not adequate to determine the appropriate worker protection levels.

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IR/HAZMIN NOTEBOOK

- OBJECTIVES OF THE PROJECT
- PROCESS OF OBTAINING INFORMATION FOR AND PREPARING THE NOTEBOOK
- RESULTS
- UPDATE OF THE NOTEBOOK

During this presentation, I will discuss the purposes for the IR/HAZMIN Notebook, the procedure used to prepare the notebook, information about its contents, and the current activities that will lead to an updated edition. The first edition of the notebook was published in the Spring of 1988. Recently, we have begun the process of preparing an updated edition so that the technologies described in the notebook will be as current as possible.

IR/HAZMIN NOTEBOOK PROJECT OBJECTIVES

- PROVIDE A REFERENCE OF INSTALLATION RESTORATION AND HAZARDOUS WASTE CONTROL TECHNOLOGIES
- SERVE AS A MECHANISM FOR TECHNOLOGY TRANSFER AMONG THE SERVICES

The purpose of the notebook is to provide a convenient reference of current installation restoration and hazardous waste control technologies to Dept. of Defense and industrial operations, training and readiness, environmental, and management staffs. It is not designed to provide enough detail to enable the reader to utilize the technology, but rather to inform the reader that particular technologies are available for use, the applicability of the technologies, and points of contact for additional information.

PROCEDURE FOR PREPARING THE NOTEBOOK

FACE TO FACE INTERVIEWS

- PREPARATION OF TECHNICAL NOTES
- TECHNICAL AND EDITORIAL REVIEW
- PRINTING AND DISTRIBUTION

Most of the information that goes into the notebook was obtained through face-to-face interviews with personnel of the three services who have been involved in the development of the technologies. In addition, relevant reports were reviewed for detailed information. Then, a summary of each technology was prepared in the form of a technical note. Once the technical notes were prepared, they were reviewed for accuracy by the USATHAMA staff and by the person who originally supplied the information during the interview. Finally, the notebook was published and distributed.

INTERVIEWS

ARMY

- TOXIC AND HAZARDOUS MATERIALS AGENCY
- CONSTRUCTION ENGINEERING RESEARCH LABORATORY
- WATERWAYS EXPERIMENT STATION
- BIOMEDICAL RESEARCH & DEVELOPMENT LABORATORY

AIR FORCE

- ENGINEERING AND SERVICES CENTER

NAVY

- ENERGY AND ENVIRONMENTAL SUPPORT ACTIVITY
- CIVIL ENGINEERING LABORATORY

All of the services were involved in the interview process. This is a list of the facilities at which interviews were conducted. Prior to the interviews, representatives at each facility were contacted to inform them of the project. A questionaire was sent to the service representatives to describe the nature of the information required for the notebook. The questionaire was filled out by the interviewer. Relevant reports were requested to supply supporting documentation for the information obtained during the interview

TECHNOLOGY CATEGORIES

INSTALLATION RESTORATION

- GROUNDWATER
- SOIL
- STRUCTURES

HAZARDOUS WASTE CONTROL

- RECOVERY & REUSE OF ENERGETICS
- MUNITION WASTE STREAMS
- METAL FINISHING WASTES
- OTHER LIQUIDS, SOLIDS, & GASES
- MANAGEMENT STRATEGIES

ANALYTICAL METHODS & INSTRUMENTATION DEVELOPMENT

HEALTH CRITERIA & ENVIRONMENTAL FATE

Technologies in the notebook represented four general categories as shown on this slide. None of the facilities visited supplied information about technologies in all of the categories. Some facilities were involved with technologies in only one category.

TECHNICAL NOTES

SUMMARIES OF TECHNOLOGIES WITH ENOUGH DETAIL TO EXPLAIN CAPABILITIES AND LIMITATIONS TO THE READER AND PROVIDE A POINT OF CONTACT FOR ADDITIONAL TECHNICAL INFORMATION

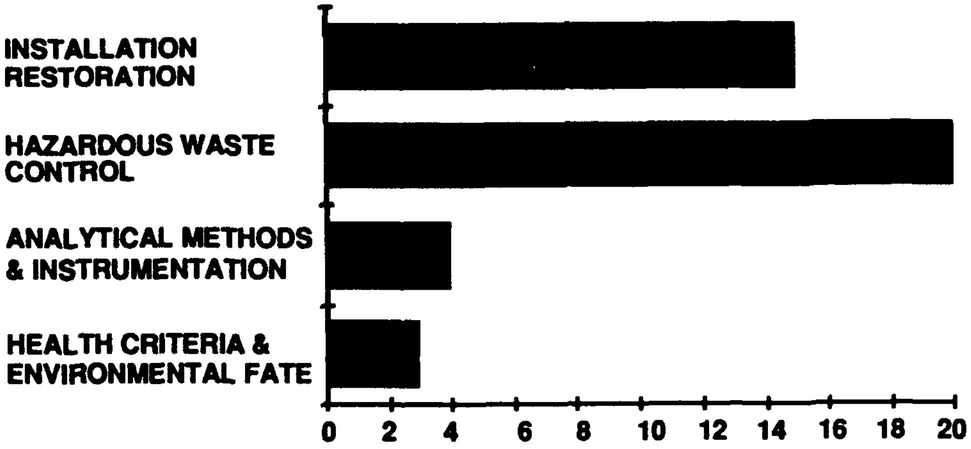
The technology notes ranged in length between one and six pages, including photographs and diagrams. The notes do not contain enough information to implement any of the technologies, but rather provide a brief overview of the applicability, advantages, limitations, and costs of the technologies. If the reader wants additional information, points of contact are given.

TECHNICAL NOTES

PURPOSE
APPLICABILITY
DESCRIPTION
ADVANTAGES & LIMITATIONS
COSTS
AVAILABILITY
STATUS OF DEVELOPMENT
REFERENCES
PHOTOGRAPHS & DRAWINGS
POINTS OF CONTACT

Each technology note contains information about the topics shown on this slide. Cost information must be documented to be included. Only technologies that are past the concept and initial laboratory development stage are included. The determination of the status of development of the various technologies is often quite subjective. Not all of the technologies conform to predetermined levels of development. For example, many of the management technologies were never investigated in a laboratory. The term "pilot plant stage" often was not appropriate, especially for the analytical methods and the environmental fate categories.

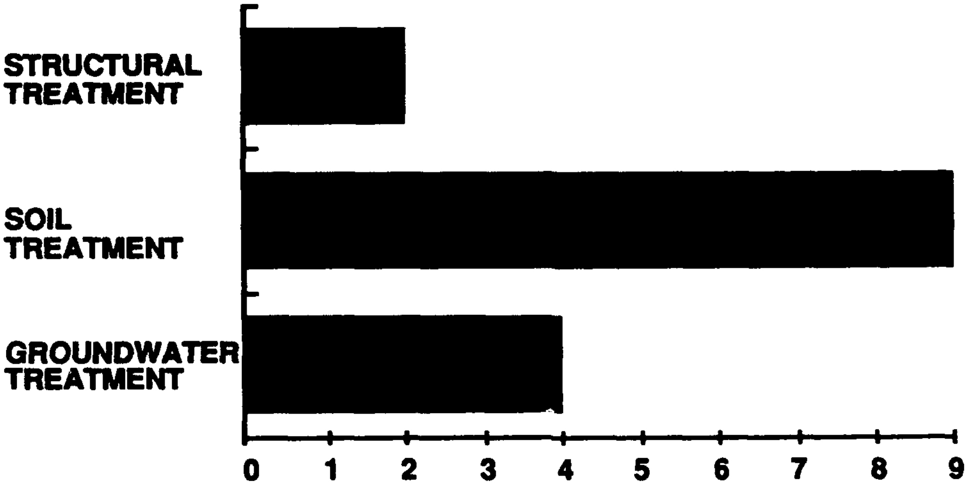
RESULTS



DISTRIBUTION OF TECHNOLOGIES IN THE NOTEBOOK

This slide shows the distribution of the technologies in the notebook according to category. The hazardous waste control category contained the highest frequency of technologies with 20 technical notes. The second most frequent technologies were in the installation restoration category with 15 technical notes. The category for analytical methods and instrumentation included such technologies as the Cone Penetrometer and an Asbestos Microscope. The environmental fate category consisted of water quality criteria for RDX, Nitrocellulose, and Nitroglycerin.

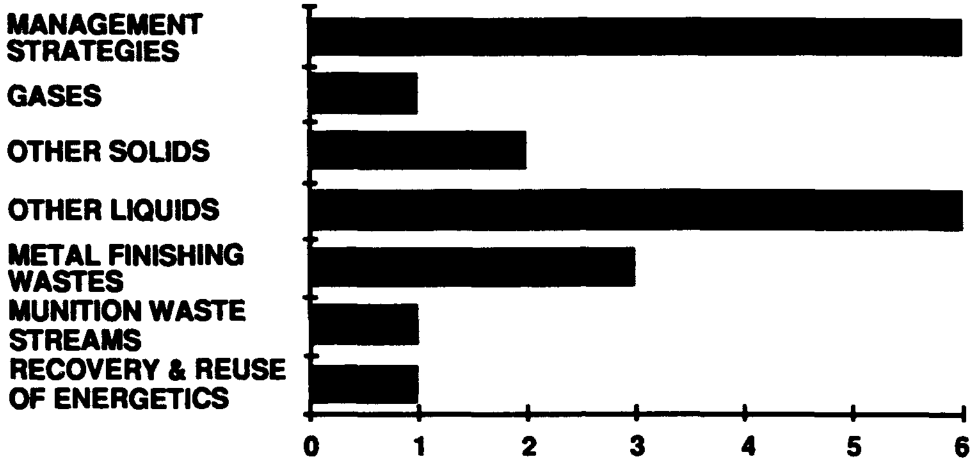
RESULTS



DISTRIBUTION OF TECHNOLOGIES: INSTALLATION RESTORATION

This category includes such technologies as Counter Current Air Stripping, Aerobic Biodegradation of TCE, Incineration of Explosives Contaminated Soils, RF Thermal Soil Decontamination, Composting, and Building Decontamination. Within the installation restoration category, soil treatment technologies had the highest frequency with 9 technical notes. Some of the soil treatment technologies were applicable to the treatment of groundwater as well; for example, In Situ Biodegradation of Fuel Contaminated Soil and Groundwater.

RESULTS



DISTRIBUTION OF TECHNOLOGIES: HAZARDOUS WASTE CONTROL

The hazardous waste control technology category contains notes about such technologies as Use of Explosives as Supplemental Fuels, Hard Chrome Plating, Xanthate Treatment of Heavy Metal Wastes, Tactical Vehicle Maintenance, Plastic Media Blasting, Disposal of Fuel Cell Foam, PCB Transformer Waste Management Program, Used Oil and Solvent Recycling Management Program, and Asbestos Management Program Videotapes.

TECHNICAL & EDITORIAL REVIEW

- TECHNICAL REVIEW BY INTERVIEWEES
- TECHNICAL & EDITORIAL REVIEW BY USATHAMA STAFF
- EDITORIAL REVIEW BY PROJECT STAFF

The technical notes were subjected to a three-level review. First, the notes were reviewed by the person who supplied the information in the interview. Then, the USATHAMA staff and an internal NIPER report review panel reviewed the notebook for technical accuracy and understandability.

PRODUCT

INSTALLATION RESTORATION AND HAZARDOUS WASTE CONTROL TECHNOLOGIES

1988 EDITION

REPORT NO. AMXTH-TE-CR-88010

JANUARY 1988

AVAILABLE FROM USATHAMA

The notebook was published with the title Installation Restoration and Hazardous Waste Control Technologies. Anyone interested can obtain a copy by contacting Carolyn Graham at USATHAMA.

PRINTING & DISTRIBUTION

- LOOSE-LEAF BOUND
- 300 COPIES PRINTED
- DISTRIBUTION - ARMY, NAVY, AIR FORCE, DEPARTMENT OF DEFENSE, AND ENVIRONMENTAL PROTECTION AGENCY
- SUPPLEMENTAL PRINTING AT USATHAMA

The notebook was published in a loose-leaf format. The original printing consisted of 300 copies distributed to various organizations within the Department of Defense and the Environmental Protection Agency. Additional copies were printed at USATHAMA in a bound format.

UPDATE OF THE IR/HAZMIN NOTEBOOK

ADDITIONAL FACILITIES

- NAVAL OCEAN SYSTEMS COMMAND
- DAVID TAYLOR RESEARCH CENTER
- EPA ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
- EPA RISK REDUCTION ENGINEERING LABORATORY

To keep the information in the notebook current, USATHAMA initiated a project to update the notebook. In addition to the facilities visited during the preparation of the first edition, personnel at four other facilities will be interviewed to obtain information for the second edition of the notebook. Most of the interviews for the update have been conducted. Those that remain include the Naval installations in California and the EPA lab in Cincinnati. The planned issue date for the updated notebook is the Summer of 1990.

ACKNOWLEDGMENTS

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U.S. ARMY
TOXIC AND HAZARDOUS MATERIALS
AGENCY
CAROLYN GRAHAM,
PROJECT OFFICER

THE ASSISTANCE AND COOPERATION OF ALL PERSONS INTERVIEWED HAS BEEN APPRECIATED

The project is directed and funded by USATHAMA through a cooperative agreement with the Department of Energy. All those involved in the interview process have been very helpful and cooperative. Without their assistance, this project would not have been possible.

USE OF ACTIVATED CARBON FOR TREATMENT OF EXPLOSIVES CONTAMINATED GROUNDWATER[1]

William L. Lowe, Walter J. Wujcik, Kiliyur N. Panneerselvam, and Peter J. Marks (Roy F. Weston, Inc., West Chester, Pennsylvania 19380); and Wayne Sisk (USATHAMA)

ABSTRACT

Manufacturing activities at Army Ammunition Plants (AAPs) result in the production of organic wastewaters that contain both explosive residues and other organic chemicals. As a result of past waste handling practices at such plants, explosive residues may leach through the soil and contaminate groundwater.

The primary objective of this study was to evaluate the use of granular activated carbon (GAC) to treat groundwater contaminated with explosives. An additional goal was to examine the potential discharge of the explosives 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) from a packed column air stripper used to remove volatile organic compounds from groundwater. Laboratory GAC isotherm studies were conducted to select the two best performing carbon types for further testing using continuous flow pilot columns. Pilot scale continuous flow GAC column tests were conducted at Badger Army Ammunition Plant in Baraboo, Wisconsin, using the two carbons (Hydrodarco 4000 and Filtrasorb 300) selected during the laboratory isotherm studies. A conventional packed column air stripper was used to remove volatile organics from the groundwater prior to treatment by the pilot scale GAC columns. A laboratory method was developed to permit lower detection levels for 2,4-DNT and 2,6-DNT.

The study concluded that concurrent removal of 2,4-DNT and 2,6-DNT from groundwater using continuous flow GAC is feasible. It was also concluded that there is little potential for airborne emissions of 2,4-DNT or 2,6-DNT in the exhaust of an air stripper used to remove volatile compounds.

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[1] Support for this project was provided by USATHAMA under Contract DAAA15-88-D-0010, Task 3.

INTRODUCTION

The United States Army operates explosives manufacturing plants to produce various forms of explosives used in military ordnance. Manufacturing activities at such plants result in the production of organic wastewaters that contain both explosive residues and other organic chemicals. Past waste handling practices at explosives manufacturing plants commonly included the use of unlined lagoons or pits for containing process wastewaters. As a result of these past practices, some explosive residues may leach through the soil and contaminate groundwater. Therefore, the treatment of contaminated groundwater may be required.

Groundwater in the area of the Propellant Burning Grounds at Badger Army Ammunition Plant (BAAP) in Baraboo, Wisconsin has been found to be contaminated with explosives compounds, including dinitrotoluene isomers, volatile organic compounds (VOCs), and related degradation products [1]. A barrier well network to intercept the advancing contaminant plume with associated treatment using air stripping and/or granular activated carbon (GAC) has been proposed.

Much of the currently available literature involves the use of granular activated carbon (GAC) for the treatment of explosives-contaminated wastewater or pink water rather than treatment of groundwater with similar contaminants [2,3,4,5]. Application of this technology to explosives-contaminated groundwater treatment, where both influent concentrations and effluent limitations may be substantially lower, has not been widely reported.

Hinshaw et al.[4] present a multiphase study providing quantitative data on the ability of activated carbon to remove the nitrobodies 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from pink water. The study included preliminary activated carbon screening, isotherm tests of activated carbon, preliminary column tests of selected activated carbons, four in-series column tests, and an economic analysis of activated carbon. Isotherm tests on five different carbons were conducted to select the best performing carbon for further testing using continuous flow columns. Pilot-scale column tests were subsequently performed with four columns in series using one of the five carbons for the treatment of actual ammunition plant pink water. Effluent criteria (40 ug/L TNT, 30 ug/L RDX, 30 ug/L HMX, and 0.7 ug/L 2,4 DNT) were generally met for RDX, HMX, and 2,4-DNT, but not for TNT. The TNT performance limitation was determined to be a physicochemical phenomenon. This phenomenon did not appear during the isotherm tests and points to the importance of performing actual column tests with the wastewaters to be treated.

The effect of pH on the ability of activated carbon to remove nitroaromatic compounds from a munitions-manufacturing waste has also been evaluated. Experiments reveal that activated carbon should have a greater reserve capacity for TNT and other nitroaromatics if wastes applied to it are acidic [3].

The primary objective of this pilot study was to evaluate the use of GAC to treat groundwater contaminated with the explosives 2,4-DNT and 2,6 dinitrotoluene (2,6-DNT). The study included preliminary batch (isotherm) testing followed by column testing using a continuous flow pilot plant. The secondary objective of this test program was to examine the potential for discharge of explosive components from the air stripper.

MATERIALS AND METHODS

All tests performed during this project employed groundwater from well PBN82-02C at BAAP as the test water. Contaminant concentrations in this groundwater varied during the test period. Table 1 presents the anticipated contaminants.

Isotherm Laboratory Tests

Isotherm tests were performed for five different GAC types to evaluate the feasibility of GAC treatment and to select GAC types for further pilot testing. Selection of carbons for isotherm testing was based upon such factors as physical (carbon) characteristics, previous literature [1,4], present use in pink water treatment, current use at BAAP, and manufacturer's recommendations. The carbons tested included Calgon Filtrasorb 200, 300, and 400, and Hydrodarco 3000 and 4000. Table 2 summarizes the test matrix that was followed in conducting the isotherm tests.

Groundwater samples were aerated for 1 hour and 15 minutes to strip off volatiles present in the groundwater. The pHs of the groundwater samples before aeration were in the range of 7.0 to 7.5. After aeration, the pH of the groundwater samples had increased to range from 8.3 to 8.7. Sulfuric acid (H_2SO_4) was added to the aerated groundwater samples to lower the pH to required levels prior to contacting the groundwater with carbon.

Carbons to be tested were pulverized prior to use to ensure that equilibrium conditions would be obtained at a faster rate. Pulverizing carbon has no significant effect on adsorption capacity, but it does increase the rate of adsorption so that laboratory time is not extensive [6]. Preweighted portions of pulverized carbon were added to groundwater aliquots, with carbon dosages ranging from 10 to 5,000 mg/L.

Temperature and pH readings of the solution were taken at the beginning of the agitation period. Samples were placed in 2000-mL Erlenmeyer flasks and covered to minimize liquid and vapor losses during agitation. A shaker assembly was used to agitate the samples for a period of 20 hours.

Following agitation, each sample was vacuum filtered through Whatman No. 5 filter paper into a clean filter flask. The filtered solution was then

Table 1

Groundwater Contaminants
Monitor Well PBN-82-02C
BAAP

2,4-dinitrotoluene (2,4-DNT)
2,6-dinitrotoluene (2,6-DNT)
Carbon tetrachloride
Chloroform
Trichloroethylene
1,1,1-trichloroethane
NO_3
SO_4

Table 2

Isotherm Test Matrix

20-Hour Isotherm Test	Number of Variables
Isotherm tests to select best-performing GAC	5 GACs 1 temperature 1 solution 7 GAC dosages[a] 1 pH[b]
Isotherm tests to determine effect of pH	1 GAC 1 temperature 1 solution 1 pH[c] 5 GAC dosages[d]

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[a] Six varying GAC dosages (10, 200, 500, 1,000, 2,500, and 5,000 mg/L) plus one control (no GAC).
[b] pH studied was 7.0.
[c] pH studied was 4.0.
[d] Five varying GAC dosages (10, 200, 500, 2,500, and 5,000 mg/L).

poured into a labeled sample bottle. The pH was measured in all the filtrate samples and in the control sample. The filtrate and control samples were analyzed for 2,4-DNT and 2,6-DNT.

Air Stripper Pilot Scale Test Program

An air stripper was used to remove solvents from the groundwater prior to its entering the GAC pilot plant. The primary function of the air stripper in this project was to minimize any effects of these solvents on the evaluation of activated carbon adsorption of explosives. The potential for discharge of explosives into the air stream was examined by emissions testing of the exhaust stack. A diagram of the air stripper, showing exhaust gas sampling locations, is presented in Figure 1. The exhaust gas ductwork was configured so as to permit the air stripper to be installed, operated, and tested entirely indoors. The exhaust was routed out of the building through an existing exhaust roof vent. As shown in Figure 1, the ductwork on the final vertical leg prior to sampling was expanded from 4 inches in diameter to 8 inches in diameter. The expansion was necessary to accommodate the selected air sampling methodology. Sampling points were located approximately 6 feet above (downstream from) the expansion point in order to eliminate any effects of flow disturbances caused by the expansion. Samples from the exhaust stack were analyzed for explosives components (2,4-DNT and 2,6-DNT). The adequacy with which the air stripper removed volatiles was verified by comparing GAC pilot-plant influent levels to those in the untreated groundwater.

Samples for explosives analysis were collected from the air stripper exhaust duct using an EPA Modified Method 5 (MM5) sampling train. The train was further modified by the inclusion of an additional XAD-2 resin trap (a total of two) to assure complete collection of target explosives. Sampling was conducted along the horizontal axis of the 8-inch inner diameter duct. The number of sample points and the sampling duration were determined onsite, with a 4-hour sample time anticipated at four traverse points. Sampling was isokinetic (90 to 110 percent).

Volumetric flow rate was determined by EPA Methods 1 and 2 as part of the MM5 train. Moisture content was determined using the EPA MM5 sample train used for collection of explosives. Triplicate test repetitions were performed for each emission parameter.

Activated Carbon Pilot Scale Test

The continuous flow column testing was conducted using the two types of carbons selected from the batch (isotherm) testing. A schematic of the pilot plant, including the air stripper, is shown in Figure 2. A total of four test runs was originally planned. Two continuous flow column tests were actually performed, each using two carbon column tests.

For each test, the total groundwater flow was split between the two test trains (A and B) at different proportions depending on the desired

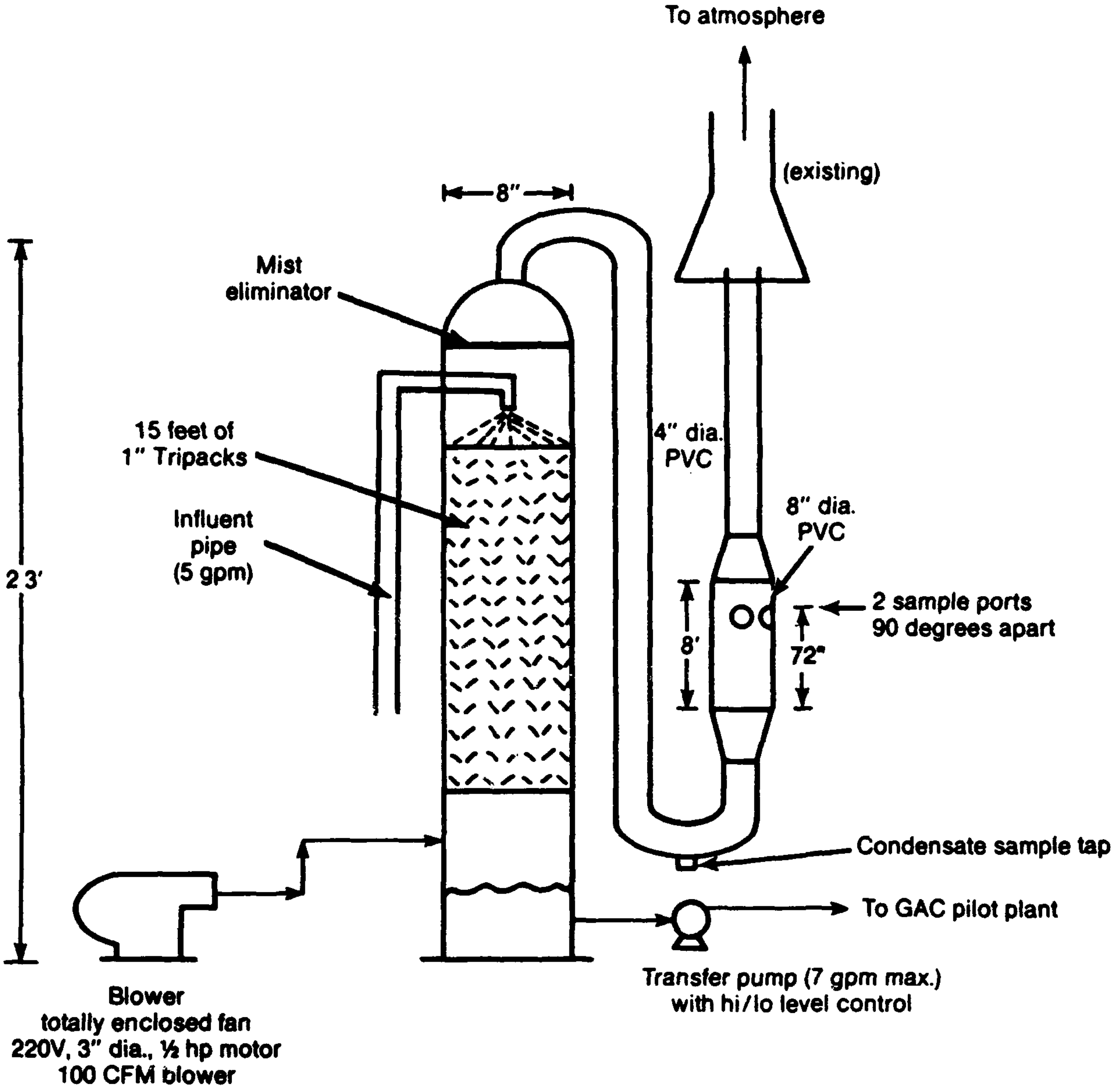

Figure 1. Schematic of air stripper system employed at BAAP.

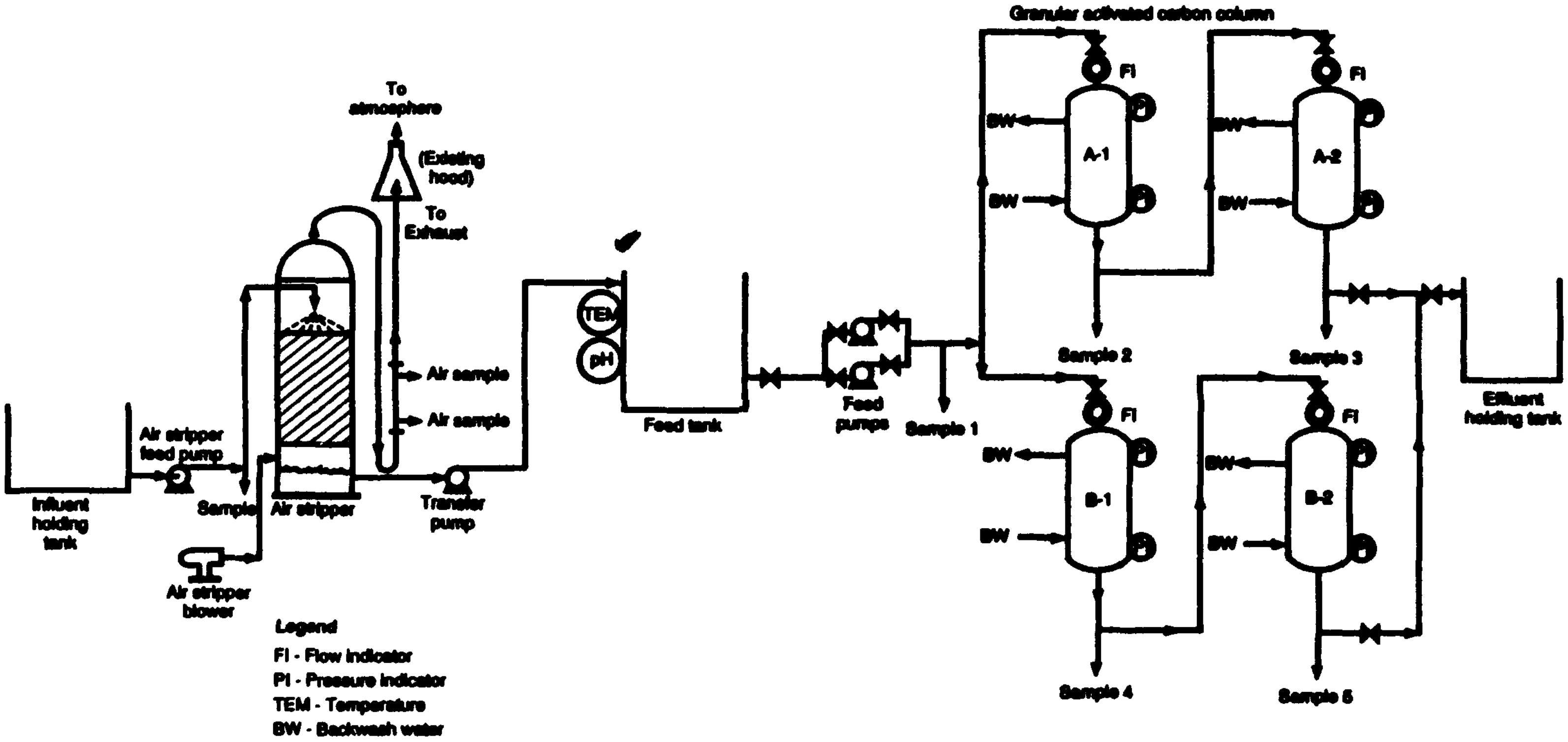

Figure 2. Pilot treatment unit configuration.

hydraulic loading rates. The two columns in Train A and Train B contained carbon types designated as A and B, respectively.

All the tests were conducted inside the test building located at BAAP. The test area was maintained at a minimum temperature of 50°F. The hydraulic surface loading rates that were employed during the pilot tests were 3, 5, and 7 gpm/ft^2. These values are within the range of hydraulic surface loading rates that are normally used in full-scale operation of GAC systems.

Adsorption and breakthrough characteristics were studied in the first column of each parallel pair. The function of the second column was to maintain effluent (discharge) quality within acceptable limits while allowing contaminant leakage up to influent levels (total exhaustion of capacity) of the first column.

Effluent samples from the first column of each train were taken at regular time intervals. Feed samples were collected at different times during each test run but less frequently than effluent samples. Samples were also taken at the outlet of the second column to ensure that the effluent from the pilot plant did not exceed the effluent discharge guidelines.

Flow measurements as indicated by the flow meters at the inlet to each column were recorded at regular time intervals during each test run. Influent and effluent (first column as well as second column) were monitored for pH and temperature at regular time intervals. Inlet pressure and outlet pressure at each column were monitored by means of pressure gauges mounted on the column.

Analytical Methods

A mobile field laboratory was used to provide rapid turnaround of the large number of samples generated during pilot testing. Samples were analyzed in the field laboratory for dinitrotoluenes by liquid/liquid extraction and electron capture gas chromatography. Detection limits were determined by instrument sensitivity as 0.1 ug/L.

In order to verify treatability at very low contaminant influent and effluent concentrations, WESTON's Analytics Division obtained certification from USATHAMA for a low level DNT analytical method employing liquid/liquid extraction and electron capture detector GC analysis. The detection limits established in this certification effort were 0.46 ug/L for 2,4-DNT and 0.017 ug/L for 2,6-DNT. Following certification, this method was used for explosives analyses at WESTON's laboratory.

Samples were analyzed by U.S. EPA Method 8010 for carbon tetrachloride, chloroform, trichloroethylene, and 1,1,1-trichloroethane. Detection levels of 1 ppb were obtained with Method 8010.

EXPERIMENTAL RESULTS AND DISCUSSION

Isotherm Testing

The Freundlich adsorption equation was used in presenting the carbon isotherm test results. Isotherms were developed for 2,4-DNT and 2,6-DNT by plotting the adsorption data on logarithmic coordinates as carbon loading (q_e) versus the equilibrium concentration (C_e) of compound remaining in the groundwater sample. These plots are shown in Figures 3 through 6. Data that resulted in an equilibrium concentration less than the detection level are shown in the figures with an arrow pointing to the upper left-hand quadrant of the graph.

For a given C_e, the greater the q_e value, the better that GAC is in adsorbing a particular compound out of solution [7]. Thus, for the isotherms presented in Figures 3 through 6, the best performing GAC is identified by the line closest to the top of the isotherm graph. The empirical constants of the Freundlich equation for the five test carbon isotherms are presented in Table 3.

2,4-DNT isotherms for all five GACs are presented in Figure 3. At lower carbon dosages (higher q_e), Hydrodarco 4000 was found to be the best performing GAC as indicated by greater values of q_e in comparison with the other carbon types. Although Filtrasorb 400 appeared to exhibit a comparably high adsorption capacity, an elevated detection limit resulting from sample interference in the Filtrasorb 400 sample prevented determination of the actual capacity. Filtrasorb 200 and Filtrasorb 300 were found to exhibit lower adsorption capacities than Hydrodarco 4000. Hydrodarco 3000 gave the lowest adsorption capacity.

An interesting feature of the 2,4-DNT isotherms (Figure 3) is that for two carbons (Filtrasorb 400 and Hydrodarco 4000), at intermediate levels of q_e, the equilibrium concentration of 2,4-DNT increased as the carbon dosage increased (or as q_e decreased). This suggests that desorption of 2,4-DNT may be taking place at carbon dosage levels in the range of 200 to 500 mg/L. Since 2,4-DNT and 2,6-DNT were measured in the same solution and 2,6-DNT isotherms for all the five carbons, presented in Figure 4, did not indicate the presence of this phenomenon, the possibility of experimental error was ruled out. Competitive adsorption, due to the presence of other compounds in groundwater, may be a factor in causing this phenomenon.

For Filtrasorb 200 and Hydrodarco 3000, the phenomenon (i.e., an increase in equilibrium concentration with an increase in the carbon dosage) was not found to be significant. For Filtrasorb 300, the equilibrium concentration decreased as the carbon dosage was increased within the entire range of 10 to 5,000 mg/L.

Figure 4 presents 2,6-DNT isotherms for all five GACs used in this experimental program. It is seen that for all five GACs the equilibrium concentration (C_e) increased with an increase in the adsorption capacity (q_e)

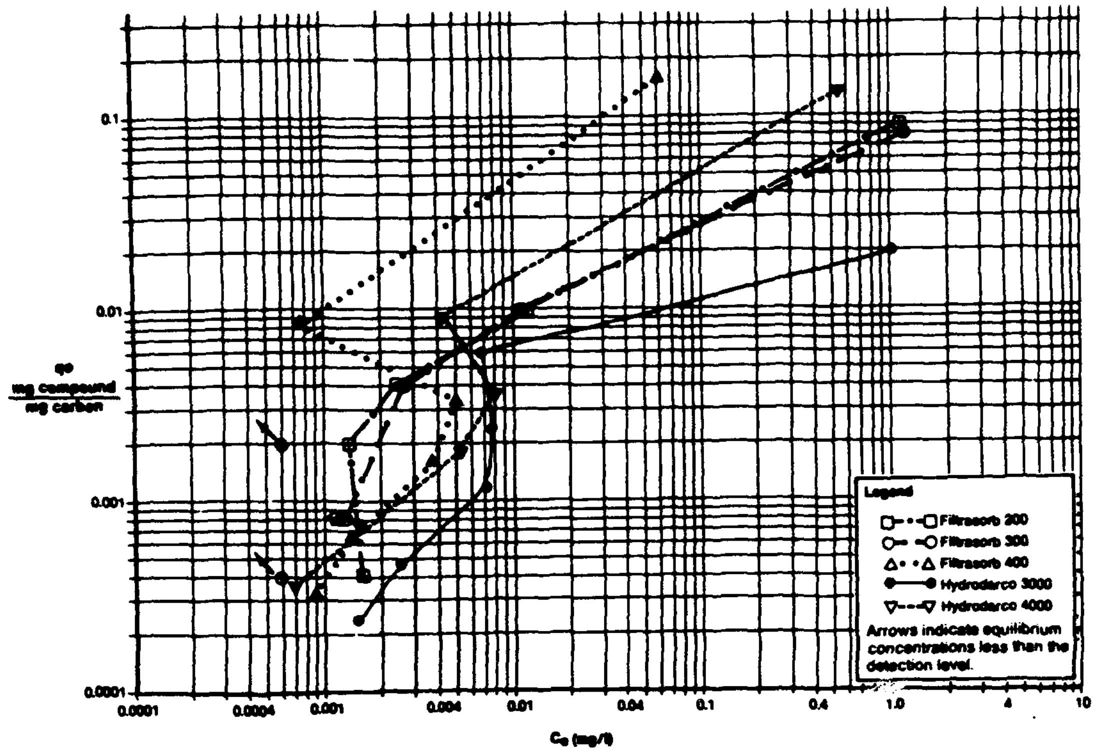

Figure 3. 2,4-DNT isotherms for five GACs using groundwater from monitor well PBN82-O2C at BAAP.

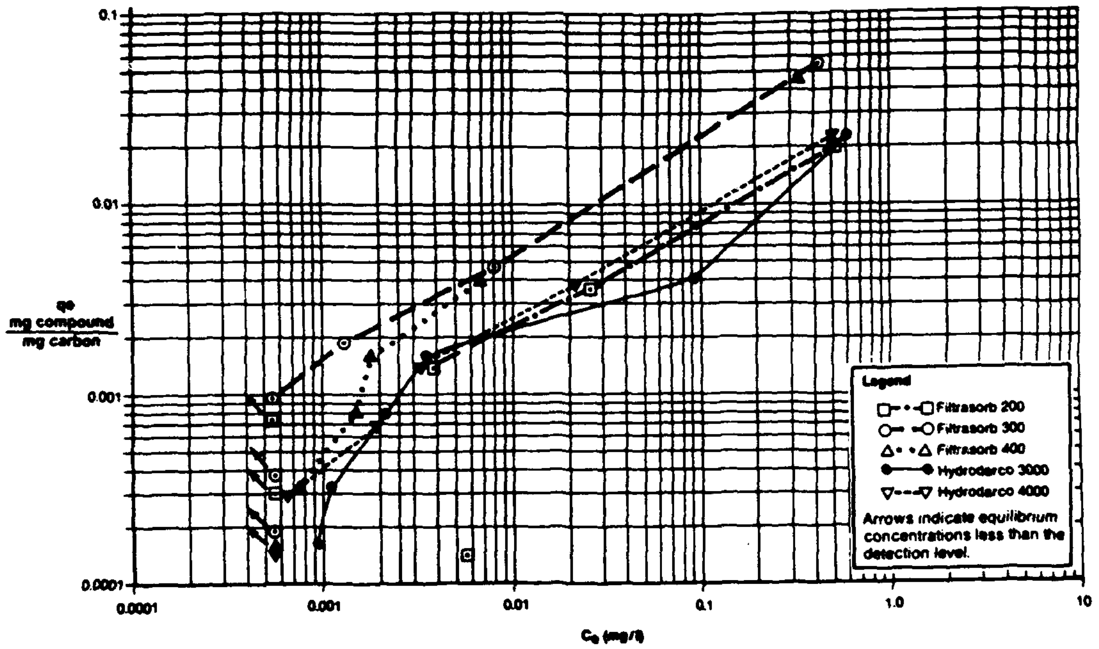

Figure 4. 2,6-DNT isotherms for five GACs using groundwater from monitor well PBN82-O2C at BAAP.

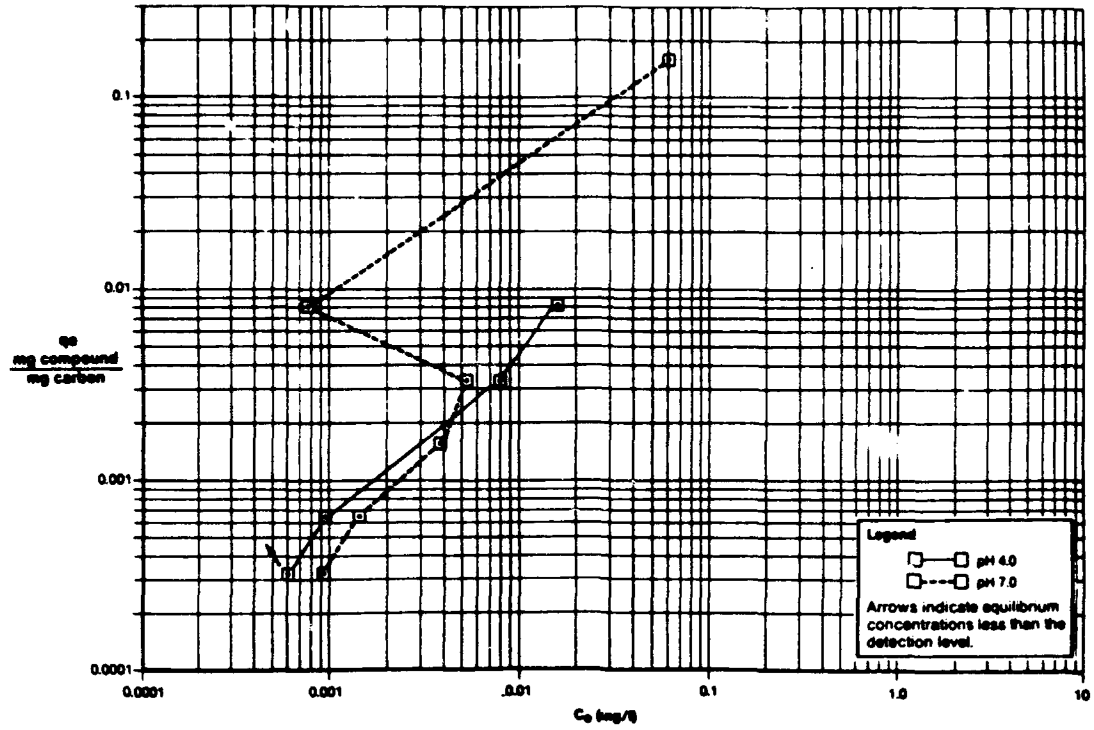

Figure 5. Filtrasorb 400 isotherms showing effects of varying pH on 2,4 DNT removal using groundwater from monitor well PBN82-O2C at BAAP.

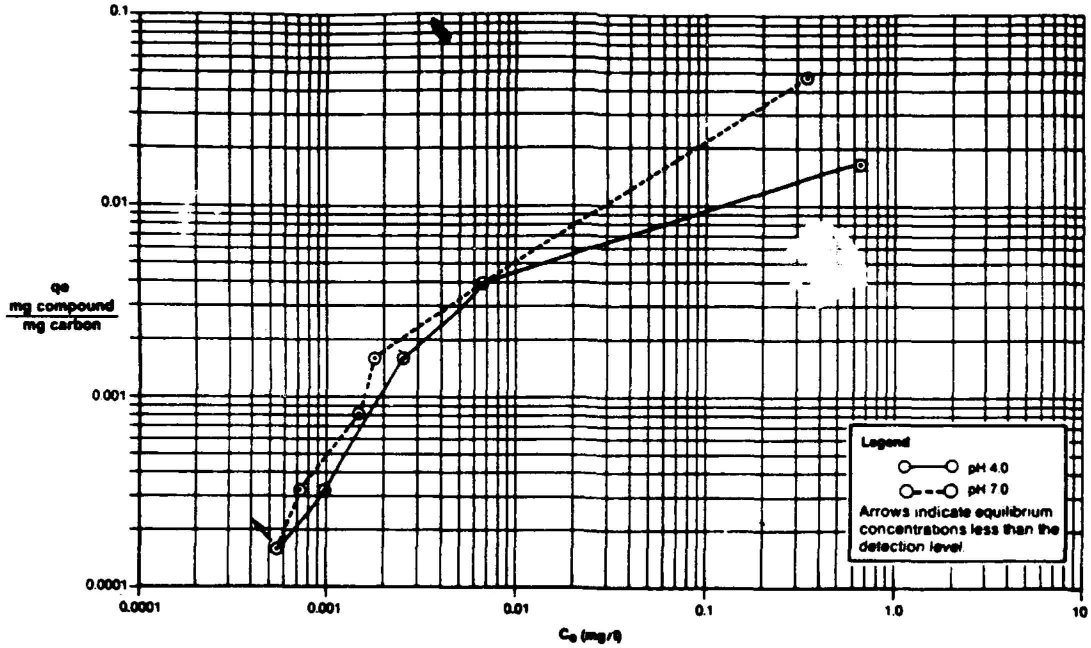

Figure 6. Filtrasorb 400 isotherms showing effects of varying pH on 2,6-DNT removal using groundwater from monitor well PBN82-O2C at BAAP.

Table 3

Empirical Constants of Freundlish Adsorption Equation for Five GACs Using Groundwater from Monitor Well PBN82-02C[a]

Activated Carbon Type	2,4-DNT Isotherms		2,6-DNT Isotherms	
	K[b]	1/n[c] (slope)	K	1/n (slope)
Filtrasorb 200	0.085	0.077	0.03	0.022
Filtrasorb 300	0.075	0.067	0.09	0.086
Filtrasorb 400	(0.9)[d]	(2.72)	0.09	0.086
Hydrodarco 3000	0.02	0.014	0.03	0.029
Hydrodarco 4000	0.2	0.263	0.035	0.024

[a] $q_e = X/M = KC^{1/n}$

[b] Intercept of the isotherm plot at C = 1.

[c] Slope of the line within the concentration range of 0.01 - 1.0 mg/L.

[d] By extrapolation from the maximum equilibrium concentration of 0.06 mg/L (obtained at the lowest carbon dosage of 10 mg/L) to a concentration of 1.0 mg/L.

(i.e., with a decrease in the carbon dosage) over the entire carbon dosage range of 10 to 5,000 mg/L employed in the experimental program.

Filtrasorb 300 gave the highest value for adsorption capacity (q_e), followed by Hydrodarco 4000. Due to an elevated detection limit caused by sample interference, the exact value for Filtrasorb 400 at a carbon dosage of 10 mg/L could not be determined.

The effect of pH on adsorption of 2,4-DNT and 2,6-DNT is shown in Figures 5 and 6 respectively. These results indicate that for both 2,4-DNT and 2,6-DNT at low levels of carbon dosage better performance (higher q_e) was achieved as pH increased from 4.0 to 7.0. This result was unexpected based on past literature [5]. However, the 2,4-DNT and 2,6-DNT isotherms for Filtrasorb 400 indicate that at higher carbon dosage levels, shifts in q_e due to pH variation (from 7.0 to 4.0) were quite small.

On the basis of adsorption capacities for 2,4-DNT and 2,6-DNT, Filtrasorb 300 and Hydrodarco 4000 were judged to be the best performing GACs for removing both contaminants from groundwater at BAAP. The maximum saturation capacities (theoretical maximum loading) for Filtrasorb 300 and Hydrodarco 4000 were estimated by extrapolating the isotherms to $(q_e)C_o$. The carbon loading thus obtained corresponds by definition to a condition when all the carbon is in equilibrium with the influent concentration (C_o). In a carbon column treatment system, this equates to operating a GAC system until the concentration of a particular compound at the column effluent equals the influent concentration. The equilibrium q_e values at different influent concentrations of 2,4-DNT and 2,6-DNT for the five GACs are presented in Table 4.

Therefore, as a result of this isotherm testing program, Filtrasorb 300 and Hydrodarco 4000 were selected for further testing, using continuous flow GAC columns at BAAP.

Air Stripper Test Program

The explosives emissions evaluation during this study consisted of three separate tests during which exhaust gases from the stripper were sampled and analyzed. All three air stripper tests were conducted during the second GAC test run. Stack gases were near saturation at approximately 72 percent relative humidity for all three runs. Explosives emission data from all three test runs are presented in Table 5.

Table 5 indicates that explosives were detected in the exhaust of the stripper. The feed rate to the stripper was approximately 4 gpm of explosives-contaminated water for each time period for each test; therefore, over a 4-hour period approximately 960 gallons of water were processed through the stripper. The contaminated groundwater influent contained 0.18 mg/L of both 2,4-DNT and 2,6-DNT for emissions tests one and two and 0.34 mg/L of 2,4-DNT and 0.19 mg/L of 2,6-DNT for test three. These concentrations equate to 3.62×10^{-4} lb/hr for 2,4-DNT and 2,6-DNT for tests one and two, 6.84×10^{-4} lb/hr for 2,4-DNT test three, and 3.82×10^{-4} lb/hr for 2,6-DNT test three. Comparing input concentrations to

Table 4

Maximum Saturation Capacities (q_e) for Five GACs

Carbon Type	Nitrobody	Influent Concentration C_o (mg/L)[a]	Saturation Capacity (q_e) (mg/mg)
Filtrasorb 300	2,4-DNT	2	0.1
		10	0.21
	2,6-DNT	1	0.09
		4	0.21
Hydrodarco 4000	2,4-DNT	2	0.28
		10	0.62
	2,6-DNT	1	0.03
		4	0.07
Filtrasorb 200	2,4-DNT	2	0.10
		10	0.22
	2,6-DNT	1	0.03
		4	0.06
Filtrasorb 400	2,4-DNT	2	--[b]
		10	--[b]
	2,6-DNT	1	0.09
		4	0.21
Hydrodarco 3000	2,4-DNT	2	0.02
		10	0.03
	2,6-DNT	1	0.03
		4	0.12

[a] Influent concentrations correspond to those anticipated from previous work (10 mg/L for 2,4-DNT and 4 mg/L for 2,6-DNT) and to those actually found in the groundwater sample used for isotherm tests reported here (2 mg/L for 2,4-DNT and 1 mg/L for 2,6-DNT).

[b] Due to an elevated detection limit caused by sample inter ference, the exact value for the data point corresponding to this carbon dosage could not be determined.

Table 5

Summary of Explosives Test Data and Test Results from Air Stripper Stack Testing at BAAP

Test Data	Air Stripper Stack			
Test Location	1	2	3	
Test Date	3/13/89	3/13/89	3/14/89	Series
Test Time Period	0902-1310	1352-1758	0807-1342	Average
Air Stripper Feed Rate (gpm)	4	4	4	
EXPLOSIVES EMISSIONS				
2,4-Dinitrotoluene				
Concentration, lbs/dscf	7.26E-11	9.61E-11	1.26E-10	9.23E-11
Concentration, ug/m^3	1.16	1.54	2.02	1.57
Concentration, ppm/v	1.23E-04	1.63E-04	2.14E-04	1.67E-04
Mass rate, lbs/hr	5.47E-07	7.36E-07	9.59E-07	7.48E-07
2,6-Dinitrotoluene				
Concentration, lbs/dscf	1.97E-10	2.90E-10	2.11E-10	2.32E-10
Concentration, ug/m^3	3.15	4.64	3.38	3.72
Concentration, ppm/v	3.34E-04	4.92E-04	3.58E-04	3.95E-04
Mass rate, lbs/hr	1.48E-06	2.22E-06	1.60E-06	1.77E-06

Note: Standard conditions = 68 degrees F (20 degrees C) and 29.2 inches Mg (760 mm Hg).

output air emissions, on the average 99.8 percent of 2,4-DNT and 99.5 percent of 2,6-DNT remained in the liquid phase and did not exit through the stripper air exhaust.

The exhaust gas ductwork configuration, necessitated by site conditions, shown in Figure 1, required the use of a U-shaped connection between the descending and ascending exhaust gas ductwork. Although this low point was located downstream from the demister, the possibility existed for accumulation of moisture at this point. A sample tap was installed at this point to permit sampling and analysis of any collected moisture.

It was found that the "U" connector at the base of the stack did accumulate contaminated condensate through the course of each test. This water was analyzed and found to contain almost identical levels of explosives as the feed water. These results are presented in Table 6. Therefore, it can be assumed that this condensate is a result of mist carryover through the air stripper mist eliminator and that this water should be returned to the feed tank for reprocessing.

Samples from the GAC influent tank indicated that the GAC influent contained very low concentrations of volatiles, as compared to the raw groundwater. Therefore, the air stripper was effective for its intended purpose of removing volatiles and minimizing their potential impact on the GAC test program.

It should be noted, however, that samples taken from the GAC influent tank represent a composite of the accumulated volume therein. In addition, very low levels of volatile organic compounds concentration in the feed to the air stripper made it difficult to quantify the air stripper efficiency in removing the volatile organic compounds.

Activated Carbon Test Program

In run one the groundwater flow rates for columns A1 and B1 were 0.5 gallon per minute (gpm) each. Columns A1 and A2 contained Calgon Filtrasorb 300 carbon while columns B1 and B2 contained Hydrodarco 4000 carbon. Run one started with the influent water being fed to the air stripper at approximately 1 gpm. The air stripper effluent groundwater was sent to the GAC column feed tank (see Figure 2). The system was operated under these conditions for 12 hours to establish a 2-foot working volume in the feed tank before beginning to feed groundwater through the GAC columns. The system was then operated under these conditions for approximately 35 hours. During this time the GAC feed tank water level began dropping at a rate of approximately 0.5 inch per hour because the air stripper feed rate could not be maintained above 1 gpm.

The problem was thought to be the large pressure drop created by the nozzle in the air stripper. Since a new nozzle with a smaller pressure drop could not be implemented without shutting down the system, a decision

Table 6

Field Laboratory Results for 2,4-DNT and 2,6-DNT for Air Stripper Influent and Condensate Collected in the Air Stripper U-Joint During Stack Testing at BAAP

	Concentration in mg/L	
Sample I.D.	2,4-DNT	2,6-DNT
Test One		
Air Stripper Influent	0.15	0.17
U-Joint Condensate	0.16	0.15
Test Two		
Air Stripper Influent	0.14	0.20
U-Joint Condensate	0.17	0.17
Test Three		
Air Stripper Influent	0.19	0.18
U-Joint Condensate	0.27	0.19

was made between WESTON and USATHAMA to bypass the air stripper in order to increase the GAC feed tank level as needed for the remainder of run one. This bypassing of the air stripper was performed as needed throughout the duration of run one in order to maintain an adequate supply of water in the GAC feed tanks.

The need to periodically bypass the air stripper would result in the presence of volatile components in the feed to the GAC unit. The actual concentrations of volatiles in the GAC feed would depend upon the relative proportions of air-stripped and raw groundwater in the GAC feed tank at any particular time.

Samples were collected every 2 hours from the primary (A1 and B1) columns' effluent. These samples were analyzed for 2,4-DNT and 2,6-DNT. Influent to the GAC system was also collected and analyzed for 2,4-DNT and 2,6-DNT.

Test run one continued for 16 days with primary column 2,4-DNT and 2,6-DNT effluent concentrations reaching approximately one-tenth the influent concentrations. At this point, the decision was made between WESTON and USATHAMA to terminate run one and proceed with subsequent tests.

The second test run examined one of the selected carbon types at two additional flow rates. Both sets of columns contained Hydrodarco 4000 carbon, which appeared to be the better performing carbon based on run one results. For the duration of this test, the influent groundwater stream was split to maintain 0.3 gpm and 0.7 gpm through columns A1 and B1, respectively.

Prior to beginning run two, the air stripper nozzle was removed for replacement as recommended by the manufacturer. However, the original nozzle was found to be clogged with PVC shavings from the piping. The nozzle was cleaned and reinstalled and for run two the air stripper feed rate was controlled at 4 gpm to maintain the 2-foot water level in the GAC feed tank. The system was operated under these conditions for 16 days. During this time, the influent groundwater concentrations decreased, thereby increasing run length required for effluent concentrations to meet influent concentrations. A decision was made between WESTON and USATHAMA to end the test at this point.

Four graphical presentations are provided for each test run, two for 2,4-DNT and two for 2,6-DNT. The first plot for each contaminant shows the primary columns' effluent concentrations as a function of elapsed time, while the second plot shows the primary columns' effluent as well as the column's influent concentration as a function of elapsed time. These graphic illustrations are presented in Figures 7 through 14.

These data clearly show that the use of new granular activated carbon in continuous flow columns produced very low effluent explosives concentrations, generally in the low part per billion (ppb) range during the early

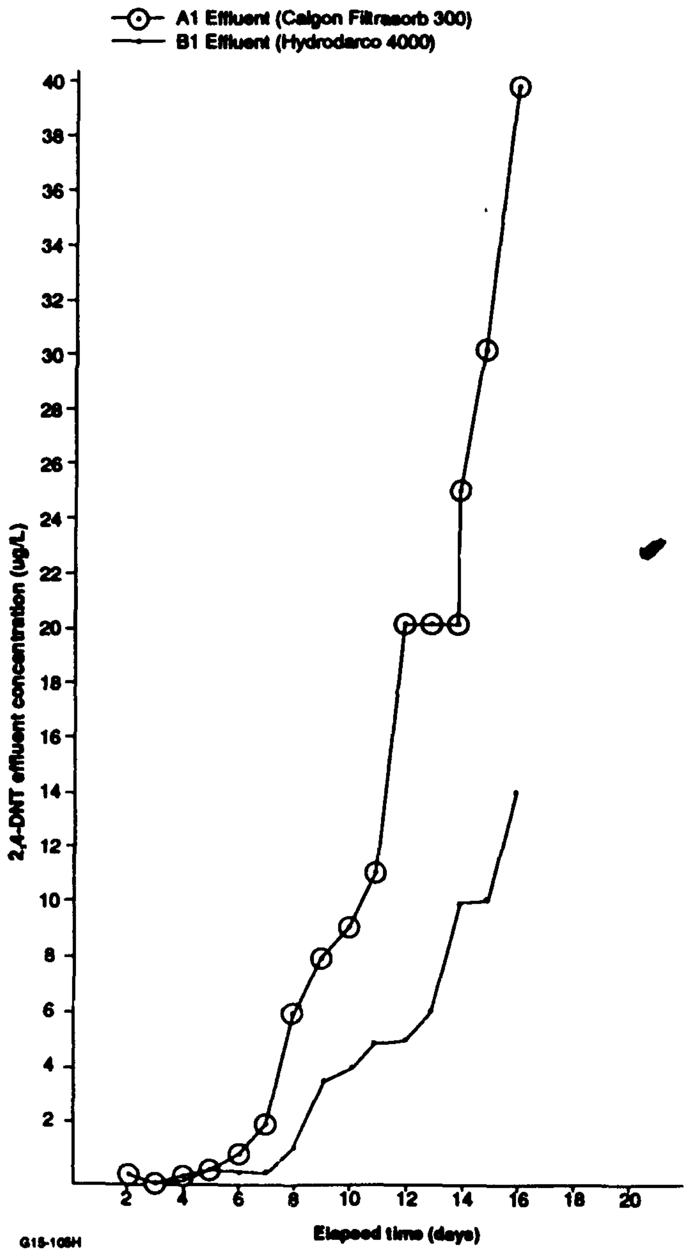

Figure 7. 2,4-DNT concentration, using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

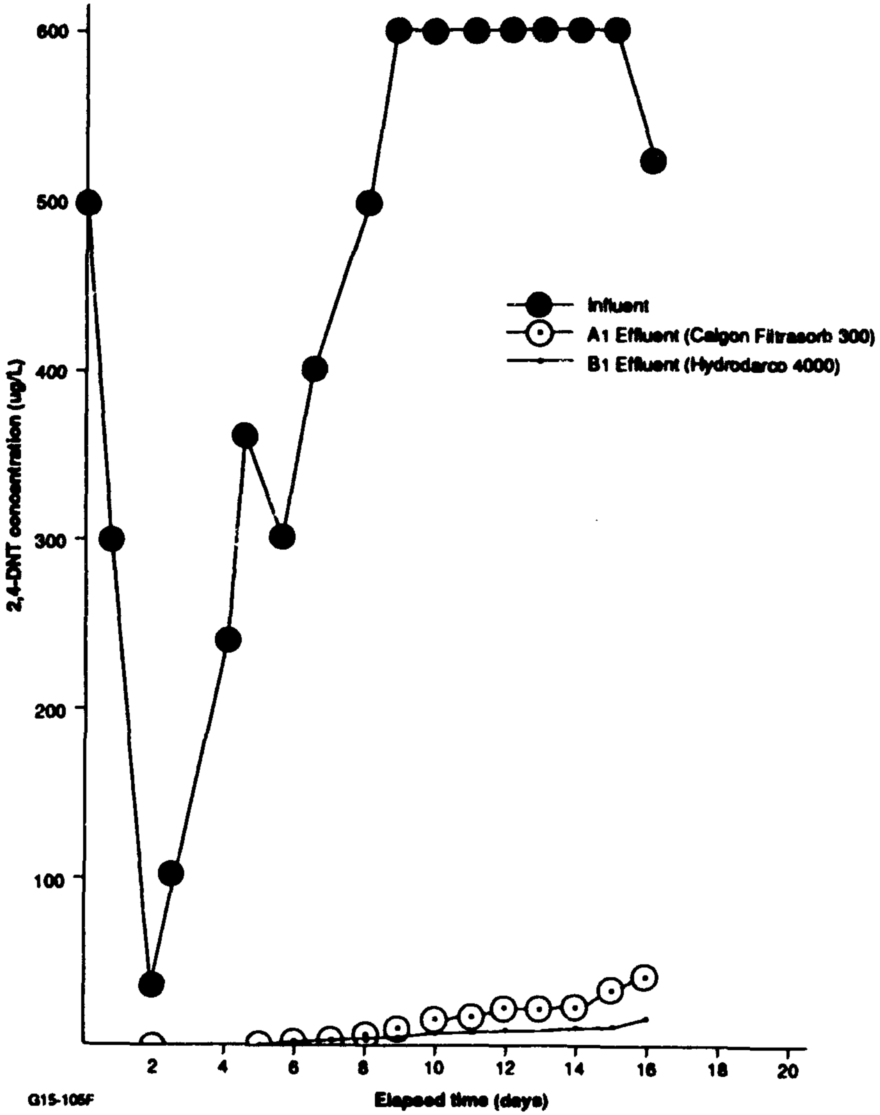

Figure 8. 2,4-DNT concentration using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

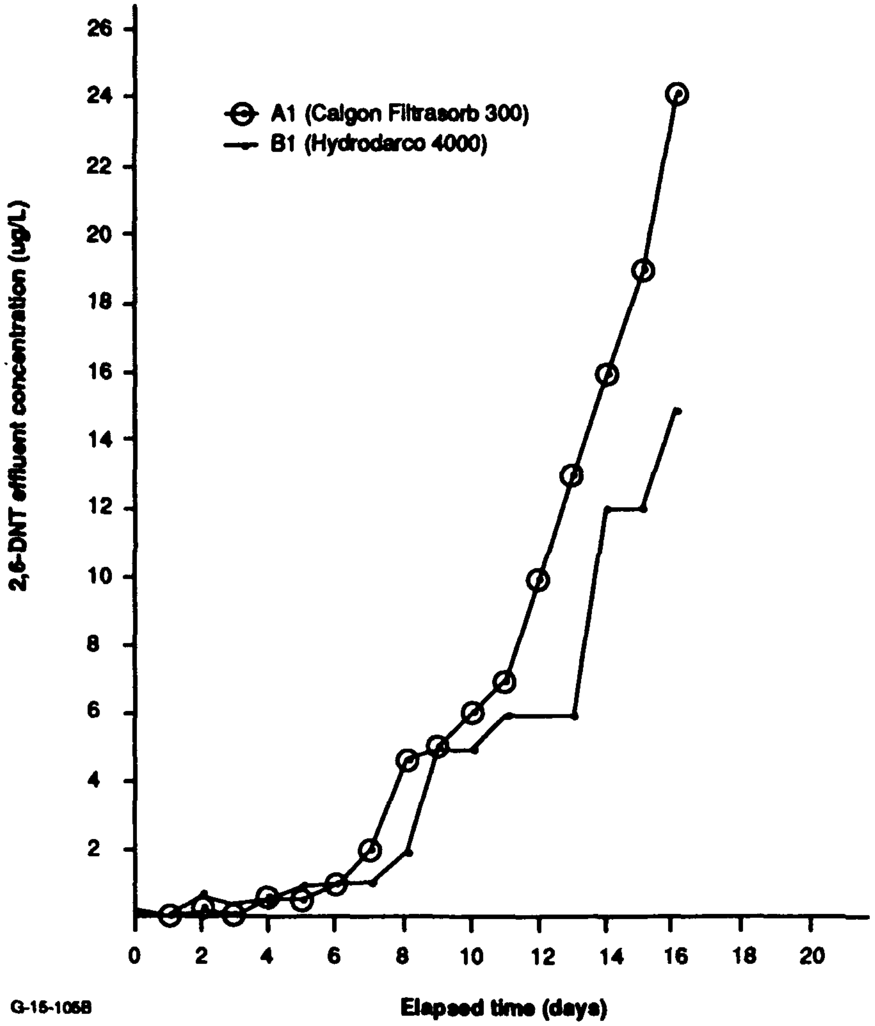

Figure 9. 2,6-DNT concentration using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

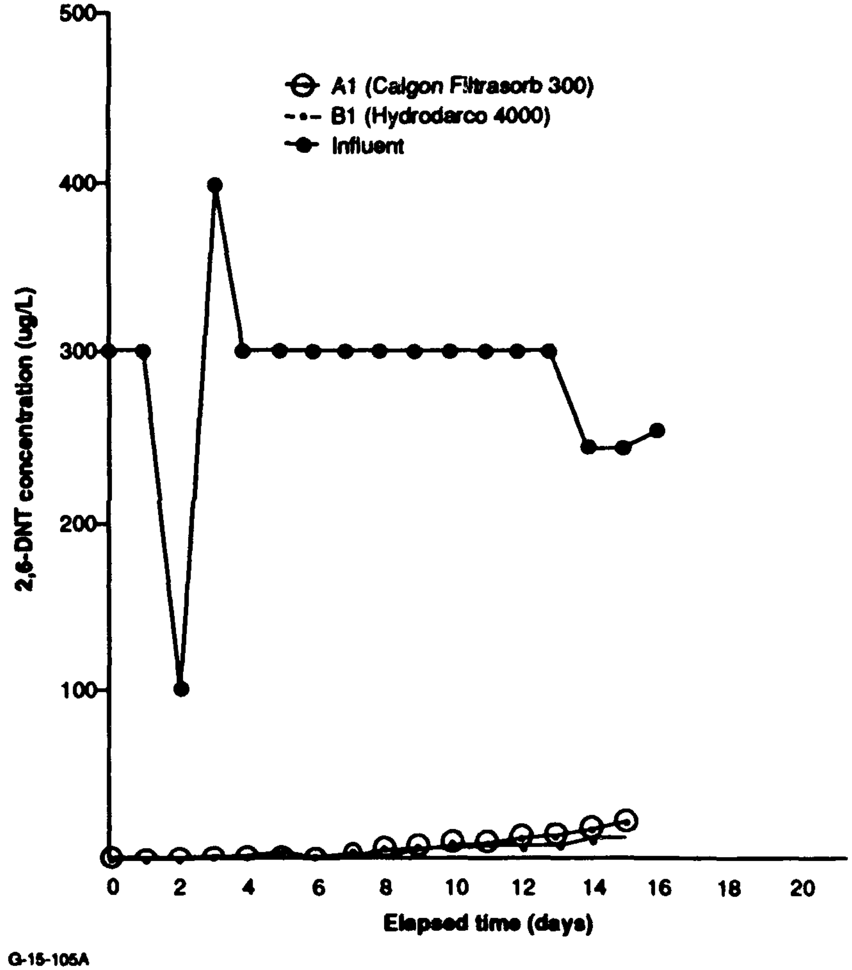

Figure 10. 2,6-DNT concentration using early morning data (0600-0800) from field laboratory results for run one (starting 15 February 1989) at BAAP.

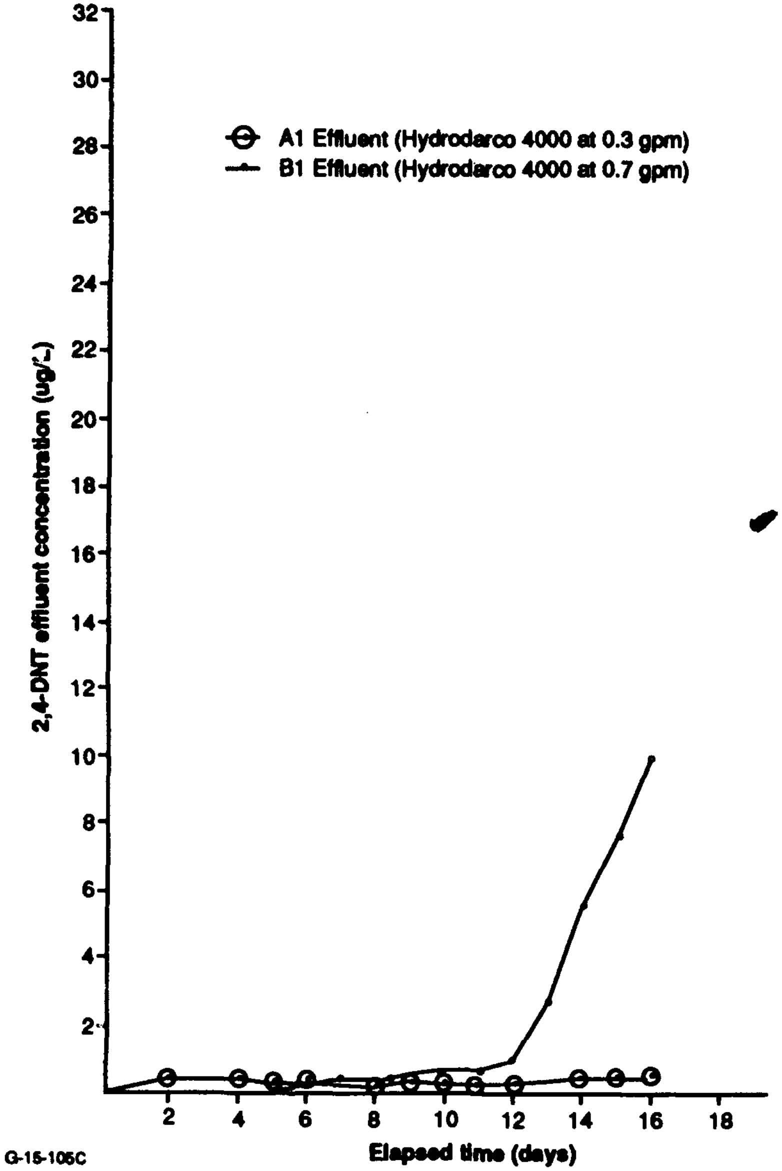

Figure 11. 2,4-DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.

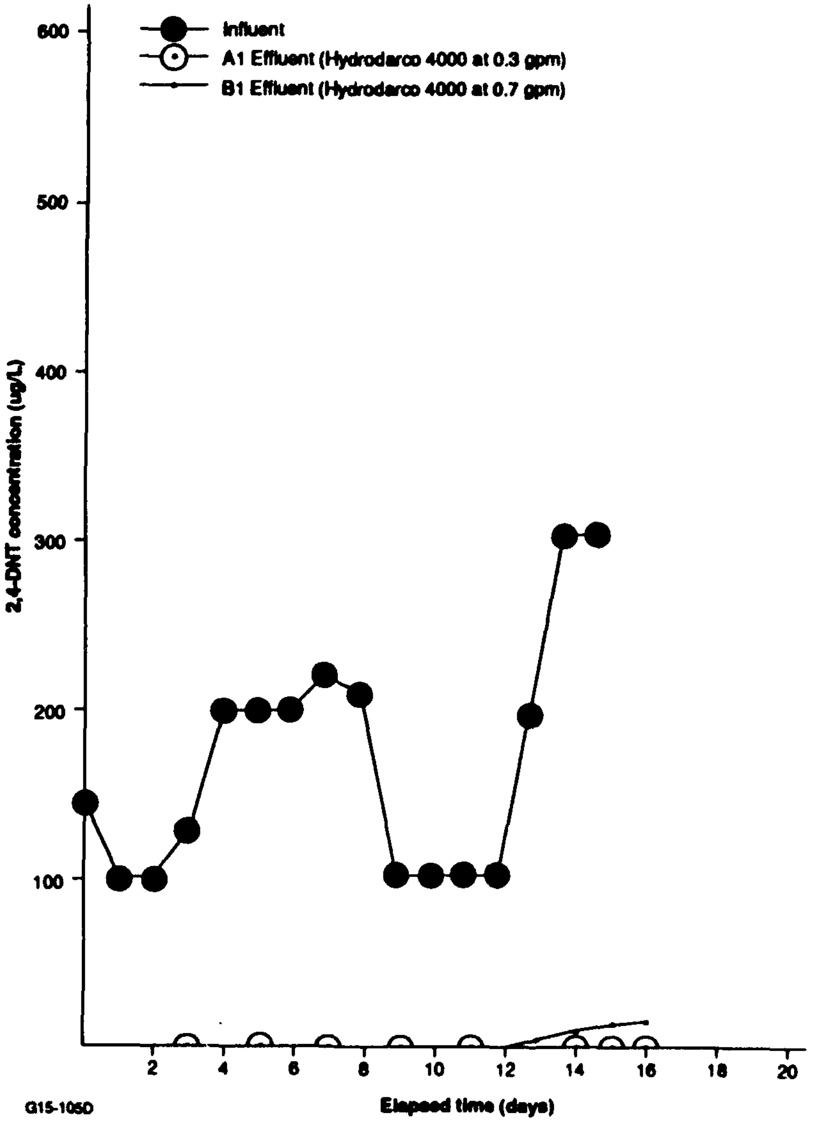

Figure 12. 2,4-DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.

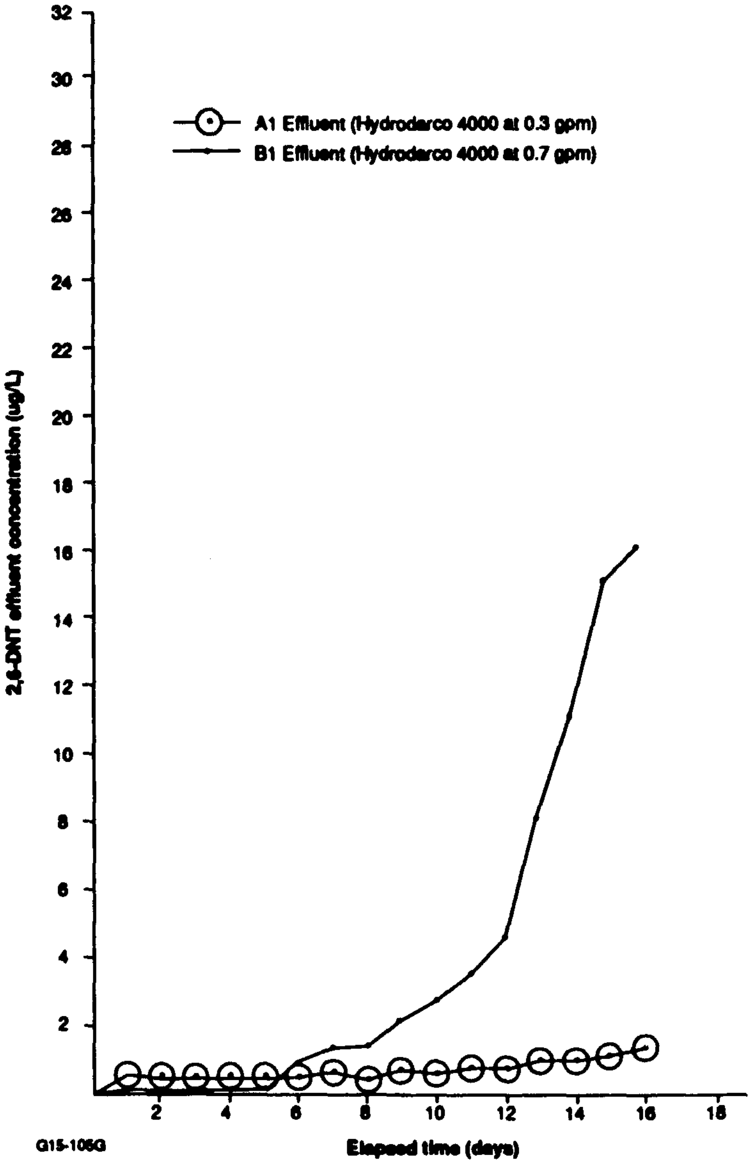

Figure 13. 2,6 DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.

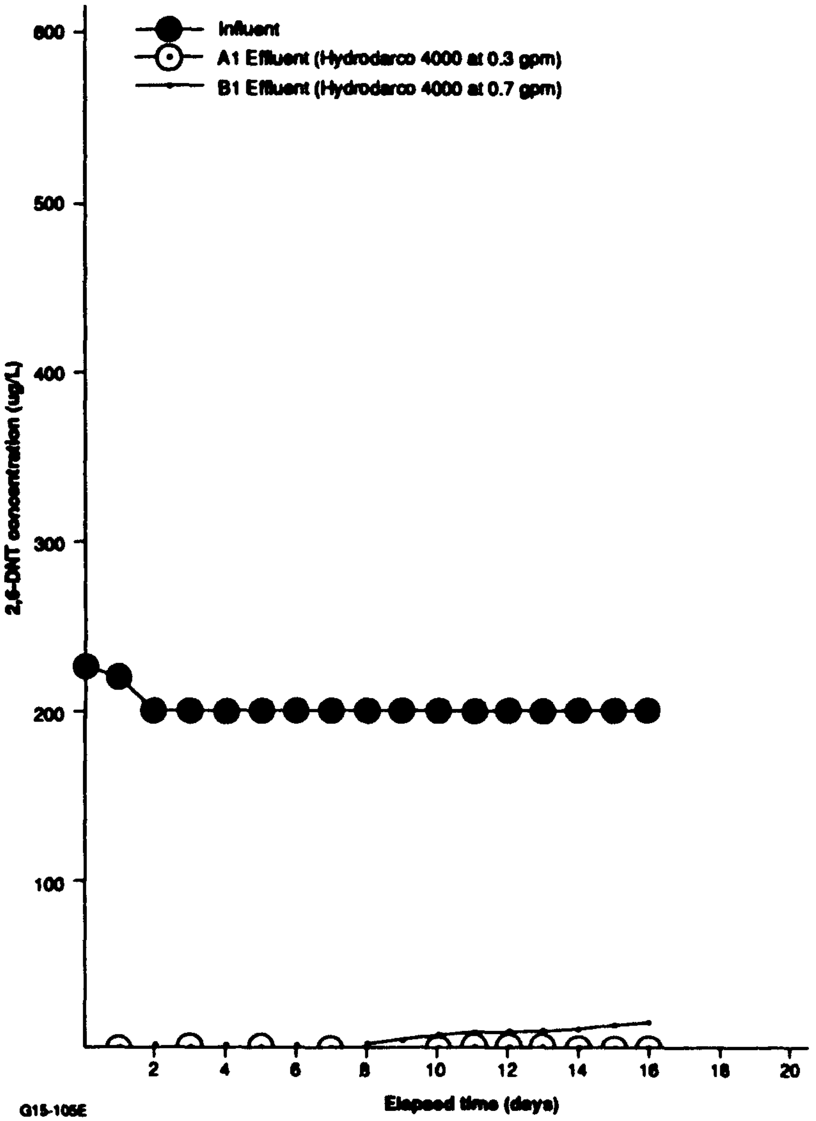

Figure 14. 2,6-DNT concentration using early morning data (0600-0800) from field laboratory results for run two (starting 8 March 1989) at BAAP.

portions of each run. In most test runs effluent explosives levels rose gradually through the duration of the experiment. However, in no run did the effluent concentration of either 2,4-DNT or 2,6-DNT exceed 10 percent of the respective (average) influent concentration before it became necessary to terminate the run. In the first run, which examined both selected carbons at identical influent flow rates of 0.5 gpm, effluent levels of 2,4-DNT reached 40 ug/L (Filtrasorb 300) and 14 ug/L (Hydrodarco 4000) at the end of 16 days of operation. Effluent levels for 2,6-DNT at this point were 24 ug/L (Filtrasorb 300) and 15 ug/L (Hydrodarco 4000).

The second run employed a higher flow rate through one column train (0.7 gpm). Since the output of the monitor well was limited to approximately 1.0 gpm, the other column train operated at 0.3 gpm. In this run, both column trains employed Hydrodarco 4000 carbon, which had provided the lower final effluent concentrations for both contaminants in run one. At the end of 16 days, effluent 2,4-DNT levels were 0.48 ug/L at 0.3 gpm, and 10 ug/L at 0.7 gpm. Effluent levels for 2,6-DNT were 0.12 ug/L and 1.6 ug/L, respectively. As with run one, complete breakthrough was not observed, and with the concurrence of USATHAMA run two was terminated at this point.

It should be noted that a major contributing factor to the inability to obtain breakthrough within available time periods was the low influent concentration of the contaminants of concern, at approximately two orders of magnitude lower than anticipated. The average influent 2,4-DNT concentration for the second run was 50 percent lower than the first run. Similarly, the average influent 2,6-DNT concentration for the second run was 33 percent lower than the first run.

Samples were taken of the primary columns effluent and shipped to WESTON's Analytics Division for 2,4-DNT and 2,6-DNT analysis. Samples representing approximately 10 percent of the field laboratory samples taken and analyzed were collected. Volatile organic compound analyses were performed on the influent to determine their level. Table 7 presents WESTON Analytics Division data obtained during run one while Table 8 presents a comparison between the WESTON Analytics Division data and field lab data for run two.

Table 8 shows that generally good agreement was obtained between the mobile (field) laboratory analyses and those performed by WESTON's Analytics Division, particularly considering the difference in detection limits between the analytical methods.

Tables 9 and 10 summarize operating characteristics for runs one and two. Based upon the flow rate, observed (average) influent concentrations, and total operating time, the total mass loading of each explosive to each column was calculated. Based upon the total amount of carbon in each column and the specific adsorption capacity of the carbon for the explosive (as determined from the isotherm tests) the total column capacity for each explosive was calculated. Finally, from the mass of explosive applied and the capacity of the column, the percent utilization of column

Table 7

WESTON'S Analytics Division Results For
2,4-DNT and 2,6-DNT from Run One Starting on
15 February 1989 at BAAP

Sample ID	Concentrations in µg/L	
	2,4-DNT	2,6-DNT
Column A1 (Calgon Filtrasorb 300)		
15 Feb. 1989 10:00 AM[a]	<0.458	<0.017 [0.013(j)][b]
16 Feb. 1989 10:00 AM	<0.458	0.048
17 Feb. 1989 10:00 AM	<0.458	0.200
Column B1 (Hydrodarco 4000)		
15 Feb. 1989 10:00 AM[a]	c	c
16 Feb. 1989 10:00 AM	<0.458	0.102
17 Feb. 1989 10:00 AM	<0.458	0.063

[a] 15 Feb. 10:00 AM 6 hours into GAC Test.
16 Feb. 10:00 AM 30 hours into GAC Test.
17 Feb. 10:00 AM 54 hours into GAC Test.

[b] <0.017 is the USATHAMA certified lower detection limit; however, lower limits can be detected and 0.013(j) represents the estimated value.

[c] Sample bottle was accidentally broken by the laboratory during extraction procedure.

Table 8

WESTON'S Analytics Division Results VS. WESTON Field Laboratory Results for Run Two at BAAP

Sample ID	Hours into Test	Lionville Laboratory Results Concentration in ug/L		Field Laboratory Results Concentration in ug/L	
		2,4-DNT	2,6-DNT	2,4-DNT[a]	2,6-DNT
Column A1 (Hydrodarco 4000 at 0.3 gpm)					
8 March 1989, 16:00	2	18.10	9.80	0.7[b]	0.6[b]
9 March 1989, 16:00	26	<0.46	0.30	0.4	0.4
10 March 1989, 16:00	50	<0.46	0.27	—	—
11 March 1989, 16:00	74	<0.46	0.26	0.3	0.3
12 March 1989, 16:00	98	<0.46	0.20	0.25	0.25
Column B1 (Hydrodarco 4000 at 0.7 gpm)					
8 March 1989, 16:00	2	0.50	0.19	0.2[b]	0.2[b]
9 March 1989, 4:00	14	<0.46	0.14	ND[c]	0.1[c]
9 March 1989, 16:00	26	<0.46	0.08	ND	0.1
10 March 1989, 4:00	38	<0.46	0.07	ND[c]	0.1[c]
10 March 1989, 16:00	50	<0.46	0.06	—	—
11 March 1989, 4:00	62	<0.46	0.05	ND[d]	0.1[d]
11 March 1989, 16:00	74	<0.46	0.05	ND	0.1
12 March 1989, 4:00	86	<0.46	0.05	ND[d]	0.1[d]
12 March 1989, 16:00	98	<0.46	0.04		

[a] ND = Below detection limit.
[b] Sample taken at 14:00 hours on 8 March 1989.
[c] Samples taken at 6:00 hours.
[d] Samples taken at 8:00 hours.

Table 9

Activated Carbon Column Operating and Performance Data for Run One at BAAP

Hydrodarco 4000 VS. Calgon Filtrasorb 300

Column outer diameter = 5 inches (0.42 ft)
Column inner diameter = 4.25 inches (0.35 ft)
Column area = 0.100 ft^2
Bed Volume (at 2-ft depth) = 0.200 ft^3 (1.50 gallons)

	Hydrodarco 4000	Filtrasorb 300
Flow Rate	0.5 gpm	0.5 gpm
Surface Loading Rate	5.0 gpm/ft^2	5.0 gpm/ft^2
Contact Time	3.0 min.	3.0 min.
Hydraulic Loading	2.50 gpm/ft^3	2.50 gpm/ft^3
2,4-DNT Influent Concentration (avg.)	0.42 mg/L	0.42 mg/L
2,6-DNT Influent Concentration (avg.)	0.3 mg/L	0.3 mg/L
2,4-DNT Capacity (Rate)*	0.12 lb/lb	0.05 lb/lb
2,6-DNT Capacity (Rate)*	0.016 lb/lb	0.044 lb/lb
Weight of Carbon in Column	4.8 lb	5.8 lb
Column 2,4-DNT Capcity (wt)	0.576 lb	0.290 lb
Column 2,6-DNT Capcity (wt)	0.077 lb	0.255 lb
Total 2,4-DNT Loading to Column (lbs)	0.045	0.045
Total 2,6-DNT Loading to Column (lbs)	0.029	0.029
2,4-DNT Capacity Utilized	7.8%	15.5%
2,6-DNT Capacity Utilized	37.7%	11.4%
Run Time (days)	16	16

*From isotherm data.

Table 10

Activated Carbon Column Operating and Performance Data for Hydrodarco 4000 from Runs One and Two at BAAP

Column outer diameter = 5 inches (0.42 ft)
column inner diameter = 4.25 inches (0.35 ft)
Column area = 0.100 ft^2
Bed Volume (at 2-ft depth) = 0.200 ft^3 (1.50 gallons)

Flow Rate	0.3 gpm (Run Two)	0.5 gpm (Run One)	0.7 gpm (Run Two)
Surface Loading Rate	3.0 gpm/ft^2	5.0 gpm/ft^2	7.0 gpm/ft^2
Contact Time	5.0 min.	3.0 min.	2.2 min.
Hydraulic Loading	1.50 gpm/ft^3	2.50 gpm/ft^3	3.50 gpm/ft^3
2,4-DNT Influent Concentration (avg.)	0.17 mg/L	0.42 mg/L	0.17 mg/L
2,6-DNT Influent Concentration (avg.)	0.2 mg/L	0.3 mg/L	0.2 mg/L
2,4-DNT Capacity (Rate)*	0.06 lb/lb	0.12 lb/lb	0.06 lb/lb
2,6-DNT Capacity (Rate)*	0.013 lb/lb	0.016 lb/lb	0.013 lb/lb
Weight of Carbon in Column	4.8 lb	4.8 lb	4.8 lb
Column 2,4-DNT Capacity (wt)	0.288 lb	0.576 lb	0.288 lb
Column 2,6-DNT Capacity (wt)	0.062 lb	0.077 lb	0.062 lb
Total 2,4-DNT Loading to Column (lbs)	0.0098	0.045	0.023
Total 2,6-DNT Loading to Column (lbs)	0.012	0.029	0.027
2,4-DNT Capacity Utilized	3.4%	7.8%	8.0%
2,6-DNT Capacity Utilized	19.4%	37.7%	43.5%
Run Time (days)	16	16	16

*From isotherm data.

capacity was calculated. As noted previously, the effluent (i.e., not adsorbed) fraction of the explosives did not exceed 10 percent and most of the time was substantially lower. Therefore, for this calculation the difference between the total mass of explosive applied and that adsorbed (as would be estimated by integration under the respective concentration curves in Figures 8 through 14) was considered minor.

Tables 9 shows that, after 16 days of operation at the indicated loading, relatively small fractions of each carbon's capacity for each explosive were utilized. Table 10 suggests the same conclusions for all three loading rates using Hydrodarco 4000. It should be noted that, even though the maximum hydraulic loading in run two was higher than in run one, the explosives concentrations in the groundwater had fallen as compared to run one, resulting in a lower mass loading rate of explosives to the column. Longer activated carbon column contact times (which in this study did not exceed 5 minutes) may provide even longer column lives for a given influent concentration.

Based upon the data obtained in this study, the preferred carbon for removing 2,4-DNT and 2,6-DNT from pretreated groundwater at BAAP would be Hydrodarco 4000.

The design and operating conclusions discussed above strictly apply only to groundwater containing 2,4-DNT and 2,6-DNT, i.e., groundwater that did not contain other contaminants or from which other contaminants have previously been removed. In this study, an air stripper was employed to remove volatile contaminants so that adsorption of explosives alone could be evaluated. While it was not the intent of this study to evaluate the need for an air stripper in a full-scale system, one experimental run was planned to examine the concurrent removal of explosives and volatiles. However, the extension of the initial runs, made necessary by the unexpectedly low influent explosives concentrations, precluded completion of this experiment. Consequently, no conclusions are drawn concerning the relative need for an air stripper in conjunction with GAC columns for treatment of BAAP groundwater.

CONCLUSIONS

The following conclusions and recommendations are drawn from this study:

- The concurrent removal of 2,4-DNT and 2,6-DNT from groundwater using continuous flow granular activated carbon columns is feasible. At influent explosives concentrations encountered in this study, removals of 90 percent or better were maintained for at least 16 days at surface loading rates of up to 7.0 gpm/ ft^2 and bed contact times of 3 to 5 minutes. Longer column lives could likely be achieved at higher bed contact times.

- Based upon the isotherm tests performed in this study, the best performing carbons of the five studied were Calgon Filtrasorb 300 and Hydrodarco 4000. Subsequent testing of these two carbons in continuous flow column testing indicated that Hydrodarco 4000 performed slightly better than Filtrasorb 300, as judged by effluent explosives concentrations at comparable bed run lengths.

- Based upon testing performed in this study, there is little potential for airborne emissions of 2,4-DNT or 2,6-DNT in the exhaust of an air stripper used to remove volatile compounds. However, analysis of the condensate that collected in the downward leg of the air stripper exhaust indicated that entrained mist in the exhaust will exhibit essentially the same explosives concentrations as the air stripper influent. Therefore, careful attention should be paid to the efficiency of the demister used in such applications.

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MICROWAVE-HEATED-ACID DISSOLUTION OF METALS FROM CONTAMINATED SOILS AND SEDIMENTS

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INTRODUCTION

Microwave ovens have been used to digest biological samples for over two decades (Abu-Samra et al. 1975, Barret et al. 1978). Investigators have also used microwave-heated-acid digestions for the dissolution of metals from geological materials (Matthes et al. 1983, Nadkarni 1984, Smith et al. 1985, Fisher 1986, Lamothe et al. 1986, Mahan et al. 1987), and comparisons between microwave digestions and the established EPA-protocol for the extraction of metals from a laboratory control sample and an environmental reference standard have been reported (Kammin and Brandt, 1989a,b). Most microwave dissolution procedures developed for soil and sediment samples employ a closed vessel system; thus digestion occurs under both elevated temperature and pressure.

We have developed a microwave-nitric acid digestion sample preparation method and compared it to the hot plate acid digestion procedure (R9) prescribed by the United States Army Toxic and Hazardous Material Agency (USATHAMA). Comparisons were made in regard to sample preparation time, overall simplicity, field compatibility, spike recovery, and metal extraction efficiency. An analysis of extraction efficiency for the microwave/HNO_3 procedure was also performed with a National Institute of Standards and Technology (NIST) environmental reference river sediment standard SRM-2704. Neither the microwave or hot plate digestion is designed to extract the metals retained in the lattices of aluminosilicate minerals. However, potentially available metals should be extracted by both procedures.

Our method uses a slightly modified residential microwave oven, 120-mL Teflon digestion vessels, 10 mL of concentrated HNO_3 per sample, and a rotating carousel for the dissolution of metals from half-gram samples. Guildelines are provided for employing residential microwave ovens for closed vessel digestions of 12 soils and/or sediment samples in less than 13 minutes. Details of the analytical procedure and a more thorough discussion of the results are presented elsewhere (Hewitt and Reynolds in press).

EXPERIMENTAL

Geological Samples

The two sample materials used in this metal extraction study were 1) the National Institute of Standards and Technology (NIST) standard reference material 2704 (SRM-2704) Buffalo River sediment, and 2) a Rocky Mountain Arsenal (RMA) standard soil (available through the Program

Manager's Office, Rocky Mountain Arsenal, Commerce City, Colorado). Digests of both the NIST SRM-2074 and the RMA standard were analyzed for metal concentrations, and a spike recovery test was also performed with the RMA soil.

Digestion Apparatus

A 750-W, residential microwave oven (Sanyo) was used for our digestion experiments. This oven has a 0.04-m^3 cavity, rear exhaust vents, and a plastic-enamel interior. To facilitate air exchange inside the oven cavity, the rear-exhaust vents were covered by a Lucite manifold that housed a 105-mm-diameter, 1.8-m^3/min, cooling fan. The fan pulled air through the oven vents and channeled the exhaust from the manifold to a laboratory exhaust hood. A commercially available, wind-up carousel rotated the digestion vessels to ensure that all samples received equal dosages of microwave energy. Digestions were performed in 120-mL Teflon (FEP) vessels. A set of 12 digestion vessels with a holding tray, relief valves, vent tubing and capping station were obtained from the CEM Corp., Indian Trail, N.C.

Heating Cycles

Both the energy delivered to the oven cavity and the energy absorbed by the oven contents are critical factors in the development of a digestion procedure. Failure to understand and control these parameters could lead to vessel ruptures and oven malfunctions, which are potentially hazardous to the operators (Gilman and Grooms 1988).

Kingston and Jassie (1986, 1988) provide guidelines for determining the power delivered by microwave ovens and for predicting the power absorbed by different digestion solutions. The apparent power absorbed is given by

$$P = CpK\Delta Tm/t \qquad (1)$$

where P = apparent power absorbed (W)
Cp = heat capacity (cal/g–°C)
K = constant for converting calories to watts
ΔT = change in temperature (°C)
m = mass (g)
t = time (sec).

Kingston and Jassie (1988) recommend that microwave-oven-power determination be performed by heating 1 kg of water in a thick-walled Teflon or polyethylene vessel for at least 2 minutes at full power, stirring and measuring the temperature. Table 1 shows the results obtained for the calibration of our microwave oven. Since an oven's magnetron degrades with use, the apparent power should be remeasured periodically.

Due to heat loss and changes in heat capacity of a solution, equation 1 fails to predict the power absorbed at high temperatures and after heating for periods longer than several minutes (Kingston and Jassie 1988). Consequently, the ability to predict solution temperatures using equation 1 is very limited. Experimental heat absorption curves for different digestion solutions as a function of mass have been published (Kingston and Jassie 1988).

The microwave digestion procedure used was similar to the method developed by CEM Corp. for the extraction of metals from soils (Application Note GM-1, Revision 6-88, CEM). The only al-

TABLE 1. Calibration of microwave oven by measurement of apparent power absorbed by 1 kg of water.

t (sec)	Ti (°C)	Tf (°C)	ΔT	P (W)*
90	20	33	13	604
120	20	37	17	593
150	20	42	22	614
180	21	47	26	604
210	21	51	30	598
240	21	56	35	610

$\bar{X} = 604$

* Calculated using equation (1).

terations were the length of the microwave heating periods and absence of hydrogen peroxide. The heating cycles were changed to compensate for the greater level of power delivered by our oven compared to the CEM oven. Hydrogen peroxide was omitted in order to simplify the method for field deployment. Similarities between the methods were the 0.5-g sample size, twelve 120-mL vessels, 10 mL of 16 M HNO_3/vessel, and oven geometry. In order to theoretically maintain the same temperatures and pressures in our system as prescribed for the CEM system, heating times were multiplied by the ratio of the power of the CEM oven and our oven (570/604):

CEM Corp.: Step 1, 2:30 min. at "HI"; Step 2, 10:00 min. at 80%
CRREL: Step 1, 2:20 min. at "HI"; Step 2, 9:25 min. at 80%

Pressure is a function of the organic composition of samples. Ultimate pressures and temperatures will vary from sample to sample.

Analysis

Metals investigated were silver (Ag), arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl) and zinc (Zn). Metal concentrations in extracts were determined by graphite furnace atomic absorption (GFAA) spectroscopy except for Hg which was done by cold vapor atomic absorption (CVAA) spectroscopy. Analyses were performed on a Perkin-Elmer (PE) model 403 atomic absorption spectrophotometer coupled with a PE model 2200 heated graphite atomizer. With the exception of Hg, all analyte concentrations in the digests were determined by the method of single standard addition (Perkin-Elmer 1983) to limit matrix interferences. Mercury concentrations were established by direct comparison to the aqueous standards.

Sample Digestion Procedure

A 0.5-g portion of sample was weighed to the nearest milligram and transferred to Teflon microwave digestion vessel, Redistilled HNO_3(10 mL) was added, and the lids were tightened with the capping station. The capping station, which sealed the digestion vessels with a constant 16.3-Nm torque, was also used to open the vessels in a controlled manner. Sealed vessels were positioned in the microwave tray and the vent tubes attached. Once all 12 positions were filled, the tray was positioned in the middle of the microwave oven on top of a rotating carousel. With the oven door closed and the manifold fan on, the two-step heating program was initiated.

After microwave treatment, the entire tray of vessels was placed in a room temperature water bath for 15 minutes to cool and reduce internal pressure. Once cooled, the individual vessels were opened by the capping station inside a laboratory exhaust hood to contain nitric acid fumes. A particulate residue remained after the digestion of both soil and sediment. Digests were diluted to 100 mL by adding deionized water. After swirling the diluted digests, 5-mL aliquots were taken for analysis and filtered through a 0.45-µm filter using a 10-mL syringe. Filtration was not necessary for the Hg determinations because this analyte is removed from the aqueous solution as vapor prior to detection. Procedural blanks were prepared by taking 10 mL of HNO_3 through the digestion, dilution and filtering steps.

TABLE 2. Detection levels (2× baseline noise).

Analyte	Detection Limit (µg/L)
Ag	≤0.5
As	≤0.4
Ba	≤2
Cd	≤0.2
Cr	≤0.4
Cu	≤0.5
Hg	≤0.005
Ni	≤0.3
Pb	≤0.5
Se	≤1.0
Tl	≤0.5
Zn	≤0.3

To prevent volatilization of Hg, Se and As, soil and sediment samples were not oven dried prior to digestion. Analyte concentrations were based on dry weight after correcting for moisture content determined from paired samples. The SRM-2704 was used as received. The more heterogeneous RMA soil required gentle grinding, which was performed with the bottom of a quartz beaker while retaining the soil in an aluminum weighing dish. Large particles (>1 mm dia.) of the RMA soil were discarded.

Spike recovery samples were prepared by adding 50-µL aliquots of aqueous standards to weighed portions of RMA standard soil in the digestion vessel. The spiked 2:1 soil to aqueous slurry (w/v) equilibrated for approximately one hour prior to the addition of 10 mL of HNO_3 for digestion. In general, spiking concentration were greater than 2× the native levels determined. This minimized the effect of uncertainty in the estimation of the native concentrations.

Blanks digested in vessels that previously had been used to digest the NIST SRM-2704, the RMA standard soil or the spiked RMA standard soil and only rinsed with deionized water showed no detectable cross-contamination. No analyte concentrations for the procedural blanks or cross-contamination checks were above levels corresponding to twice the baseline noise (Table 2). Since analyte concentrations determined in the soil and sediment digests were typically two orders of magnitude above the baseline noise, this level was considered an acceptable detection limit. Therefore, concentrations for samples were not blank corrected.

RESULTS AND DISCUSSION

The microwave/HNO_3 digestion procedure used for the extraction of metals from soil and sediments took less than 13 minutes. An individual employing several 12-position sample carousels with vessels could digest and prepare for analysis approximately 100 samples daily. The method requires only a balance, microwave oven, digestion vessels, capping station, concentrated HNO_3 acid, reagent grade water, and disposable syringes and filters.

The limited number of additional required support facilities, such as electricity and an exhaust hood, make this sample preparation method compatible to field-mobile laboratories. The micro-

TABLE 3. Metal concentrations reported for the RMA standard soil using USATHAMA method R9 by another laboratory and those determined using the microwave/HNO_3 digestion procedure.

	RMA Standard Soil (µg/g)						
	Ba	Cu	Cr	Hg	Ni	Pb	Zn
USATHAMA R9	139.8	9	8.8	0.008	10.1	13	43.1
Microwave/ HNO_3	149	10.3	10.2	0.0066	13.8	8.7	37.7
	143	10.6	11.6	0.0072	6.6	9.5	50.0
	131	10.6	12.3	0.0073	13.5	9.3	44.5
	133	10.3	10.7		12.4	9.0	43.6
	143	10.1	10.8		11.7	9.6	37.2
$\bar{X}$ =	140	10.4	11.1	0.0070	11.6	9.2	42.6
Std. Dev.	7.6	0.22	0.83	0.0004	2.9	0.37	5.3

wave/HNO_3 digestion method requires only hood space for the capping station and exhaust hose, whereas hot plate methods require hood space for all simultaneous digestions. Additionally, this microwave procedure uses only HNO_3, thereby simplifying the wet chemistry. Other advantages of the microwave/HNO_3 digestion are that it is more routine, less subjective with respect to operator judgment, and does not expose the sample to dry heat. Hot plate digestion methods may require repetitive additions and heating cycles until organic decomposition is judged complete. Because hot plate digestions are performed in open vessels, each evaporation cycle can leave portions of the substrate dry, even though complete dryness does not occur. Soil or sediment digests that are partially or totally dried may lose volatile analytes. Volatilization losses from organo-mercury compounds in soils dried at 60°C (Iskandar et al. 1972) or digested in open systems (Van Delft and Vos 1988) have been documented.

RMA Standard Soil

The levels of metals determined in the microwave/HNO_3 digests and those reported by another laboratory using the USATHAMA-R9 digestion procedure for the RMA standard soil are compared in Table 3. For Ba, Cr, Cu, Hg, Ni, Pb, and Zn, the concentrations established using the microwave digestion procedure ranged from 127% to 71%, with an average of 102%, compared to those obtained by hot-plate digestions. The interlaboratory–intermethod comparison shows that both digestion procedures extract similar quantities of metals from the RMA soil.

RMA Standard Soil Spike Recoveries

Mean recoveries of the analytes spiked onto the RMA standard soil ranged from 86 to 102%, with an average of 96% (Table 4) excluding Sb. There was no discernible recovery of Sb. The results in Table 4 show quantitative recoveries; thus the microwave digestion was not susceptible to losses or contamination of the analytes determined. Quantitative recoveries of As, Hg, and Se demonstrated that microwave digestion in closed vessels was an acceptable method for volatile metals. Organic forms of Hg have also been shown to be qualitatively recovered with a microwave-heated acid digestion in a closed vessel (Van Delft and Vos 1988).

Table 4. Spike recoveries from RMA standard soil using microwave/HNO_3 digestion.

Analyte	Average % Recovery and Std. Dev.
Ag	98.8 ± 1.2
As	96 ± 14
Ba	96.6 ± 8.4
Cd	102 ± 3.2
Cr	90.2 ± 4.3
Cu	93.8 ± 1.3
Hg	96.3 ± 3.2
Ni	98 ± 11
Pb	94.3 ± 0.8
Se	97.7 ± 2.8
Tl	97.3 ± 2.3
Zn	86 ± 17

NIST SRM-2704

Table 5 shows the results for the concentrations of metals determined in the microwave/HNO_3 digest of the NIST SRM-2704 river sediment. Mean recoveries of the NIST certified values for As, Cd, Cu, Pb, Tl and Zn averaged 102%, and ranged from 106% to 97.6%. The average Ni recovery was approximately 87% of the NIST certified value, and Ba, Cr, and Hg were only 22%, 63%, and 73%, respectively. NIST certification of metal concentrations in the

Table 5. NIST certified values and determined metal concentrations for the microwave/HNO_3 digestion of the SRM-2704 river sediment.

	As	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Tl	Zn
					(μg/g)					
NIST	23.4	414	3.45	135	98.6	1.44	44.1	161	1.2	438
	±0.8*	12	0.22	5	5.0	0.07	3.0	17	0.2	12
Microw/	23.7	81	3.63	87.8	98.7	1.10	38.1	164	1.37	463
HNO_3	23.1	89	3.65	82.7	95.4	1.09	39.2	168	1.18	425
	23.6	108	3.60	83.0	94.7	0.96	39.3	172	1.27	451
$\bar{X}$ =	23.5	92.6	3.63	84.5	96.3	1.05	38.9	168	1.27	446
	±0.6*	27.2	0.04	5.6	4.2	0.15	1.3	7.8	0.19	38.1
% Recovery										
$\bar{X}$ =	100	22.4	105	62.6	97.6	72.9	87.4	104	106	102
Std. Dev.	1.4	3.3	1.1	2.1	2.2	5.4	2.8	2.5	7.9	4.5

* 95% uncertainty limits.

SRM-2704 sediment was based on at least two independent methods, usually neutron activation analysis and a wet digestion method using HF in conjunction with other acids prior to analysis by atomic absorption spectroscopy or inductively coupled plasma. Clearly, both techniques are designed to measure total metal concentrations. In contrast, the microwave/HNO_3 extraction does not dissolve metal contained in the lattice of many aluminosilicates. Kammin and Brandt (1989a,b) compared microwave digestion to EPA SW-846 method 3050 and reported that both the microwave and hot plate methods recovered similar amounts of metals from an EPA laboratory control sample, yet neither method quantitatively recovered all metals from the NIST SRM-1646 estuarine sediment compared to the NIST certified values.

It is well documented that digestion methods employing HNO_3 or HNO_3/HCl mixtures and heated with either a hot plate or microwave oven do not extract total quantities of many native metals from geological samples. In general, wet digestions, excluding HF, extract only the fraction of metals potentially available to natural biological and leaching processes, and do not attack the aluminosilicate matrix (Que Hee and Boyle 1988). This fraction represents the hazardous waste contribution because the preponderance of anthropogenic metals in soil and sediments are associated with the organic fraction and clay surfaces. Thus, HF digestion methods are not required to determine the increase in soil metal concentrations caused by hazardous waste contamination.

CONCLUSIONS

Our results suggest that for the metals tested, other than Sb, extraction of hazardous-waste-contaminated soils and sediments using a closed vessel microwave digestion can be accomplished in about 13 minutes, with efficiencies comparable to that of hot plate protocols. Extraction can be performed with residential microwave ovens; however, we recommend, for safety reasons, that only commercial systems be employed for method development. Our microwave/HNO_3 digestion is more routine and is less prone to volatile metal losses than open vessel hot plate digestions. Microwave/HNO_3 digestions do not extract total quantities of all native metals in geological materials, yet can be used effectively to determine contaminant-derived concentrations of metals.

Compared to the USATHAMA procedure R9 for the digestion of contaminated soil and sediments for metal analysis, closed vessel microwave digestions are quicker, simpler, and require less wet chemistry and less equipment. For these reasons, microwave procedures are adaptable to the field and should be considered for program validation. A sound program would require well-prepared geological materials for intercalibration among laboratories. Appropriate sample materials should be available in sets consisting of both uncontaminated and contaminated samples. Soils and sediments having a range of properties would be needed to effectively evaluate any digestion procedure.

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FEASIBILITY OF BIODEGRADING TRINITROTOLUENE (TNT) CONTAMINATED SOILS

PRESENTED AT THE 14TH ANNUAL
ARMY ENVIRONMENTAL R&D SYMPOSIUM

Presented by

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Study sponsored by

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010

Williamsburg, Virginia
November 14 -16, 1989

PROGRAM OVERVIEW

(1) Literature review
  - composting
  - white rot fungus
  - recent findings using bacterial based systems

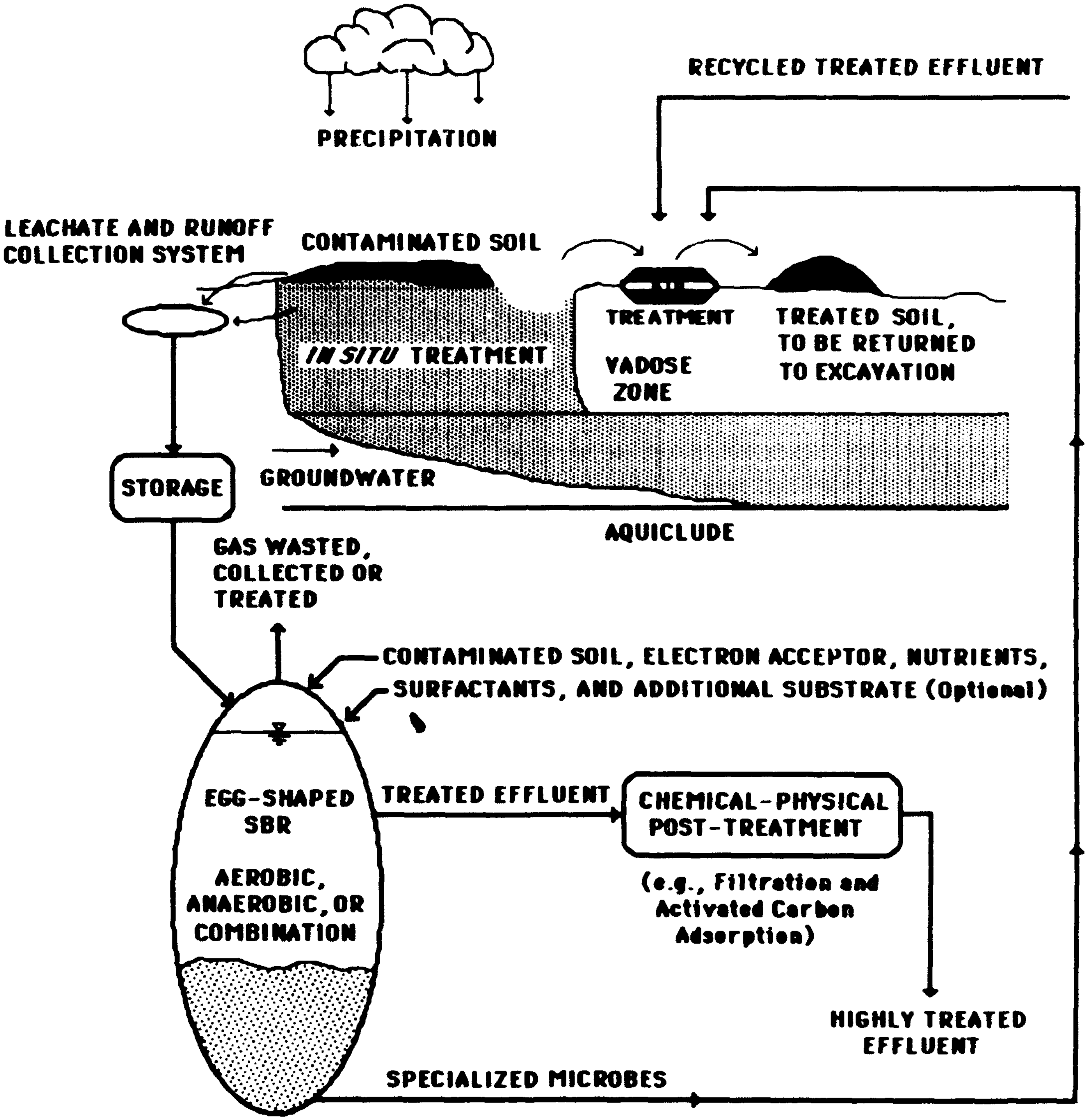
(2) Surfactant selection

(3) Site selection/Sample collection - Joliet Arsenal

(4) Design and construction of TNT fed SBR, periodic fixed film reactor, and the soil slurry reactor

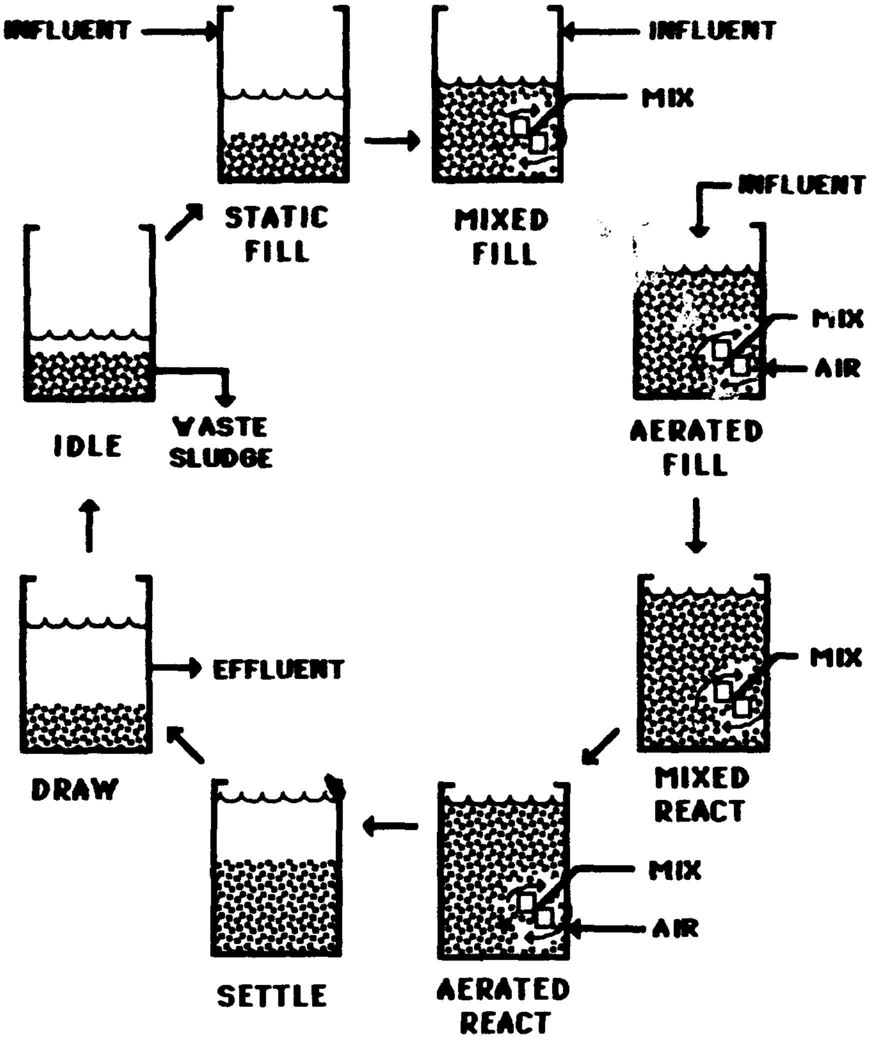
(5) Analysis of TNT, microbial growth, and growth potential

(6) Investigation of low cost alternatives

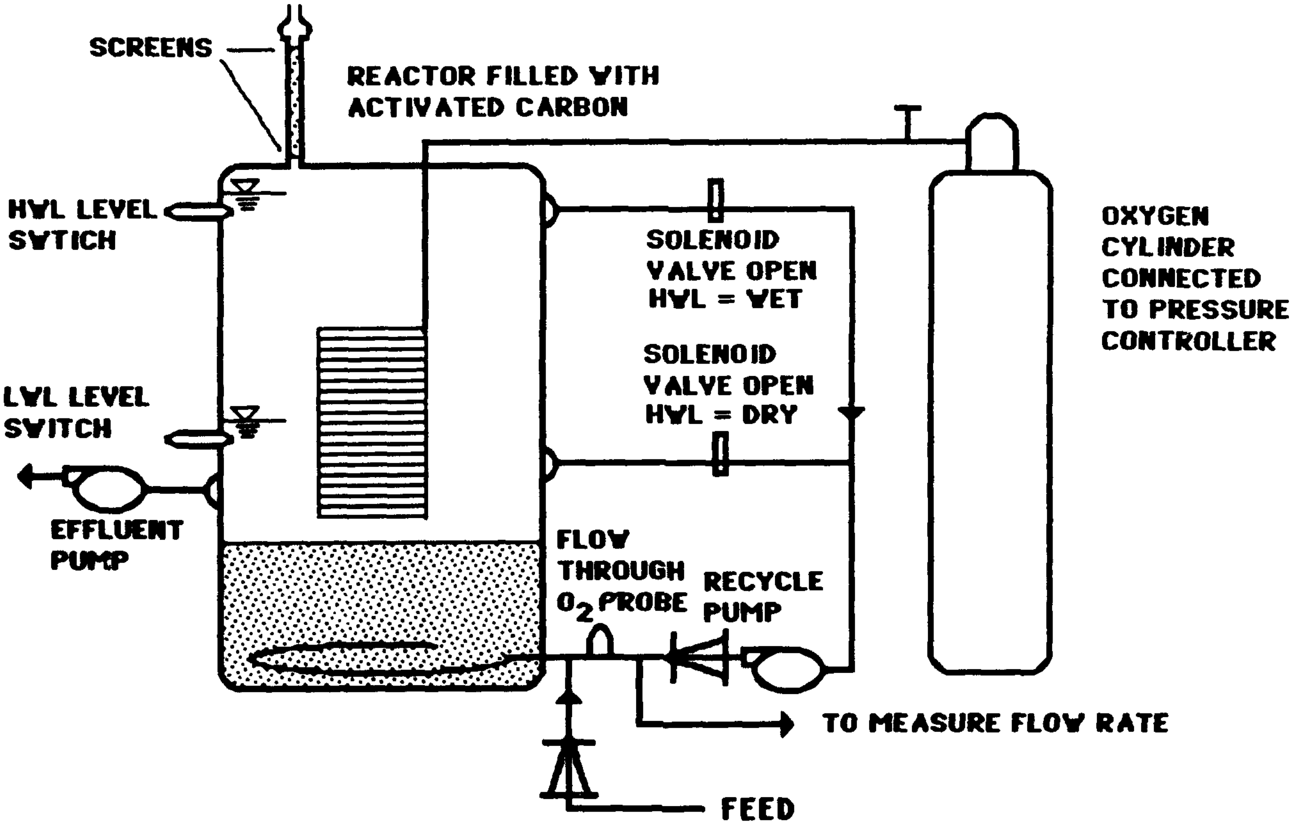


ON-SITE AND *IN SITU* TREATMENT OF LEACHATES AND CONTAMINATED SOILS

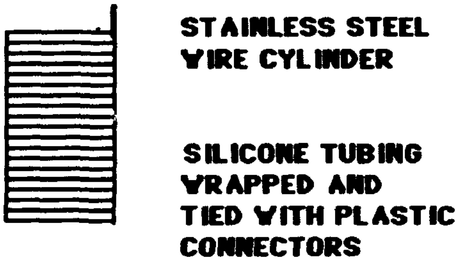
Bioremediation Techniques and Applications on Leachates



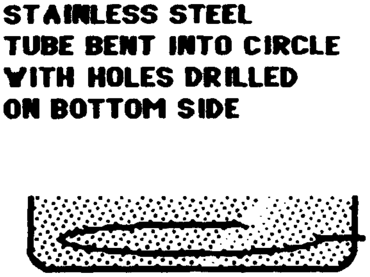
SBR Operation for each Tank for One Cycle for the Periods STATIC FILL (no mixing or aeration), MIXED FILL (mixing without aeration), AERATED FILL, MIXED REACT, AERATED REACT, SETTLE, DRAW, and IDLE.



SYSTEM ILLUSTRATION



DETAIL SILICONE TUBING OXYGENATION SYSTEM



DETAIL BOTTOM INLET

PERIODIC FIXED FILM REACTOR

Bioremediation Techniques and Applications on Soils, and Sediments

Bioremediation Treatment Systems Range from Passive to Aggressive:

(1) Nutrients - e.g., N and P

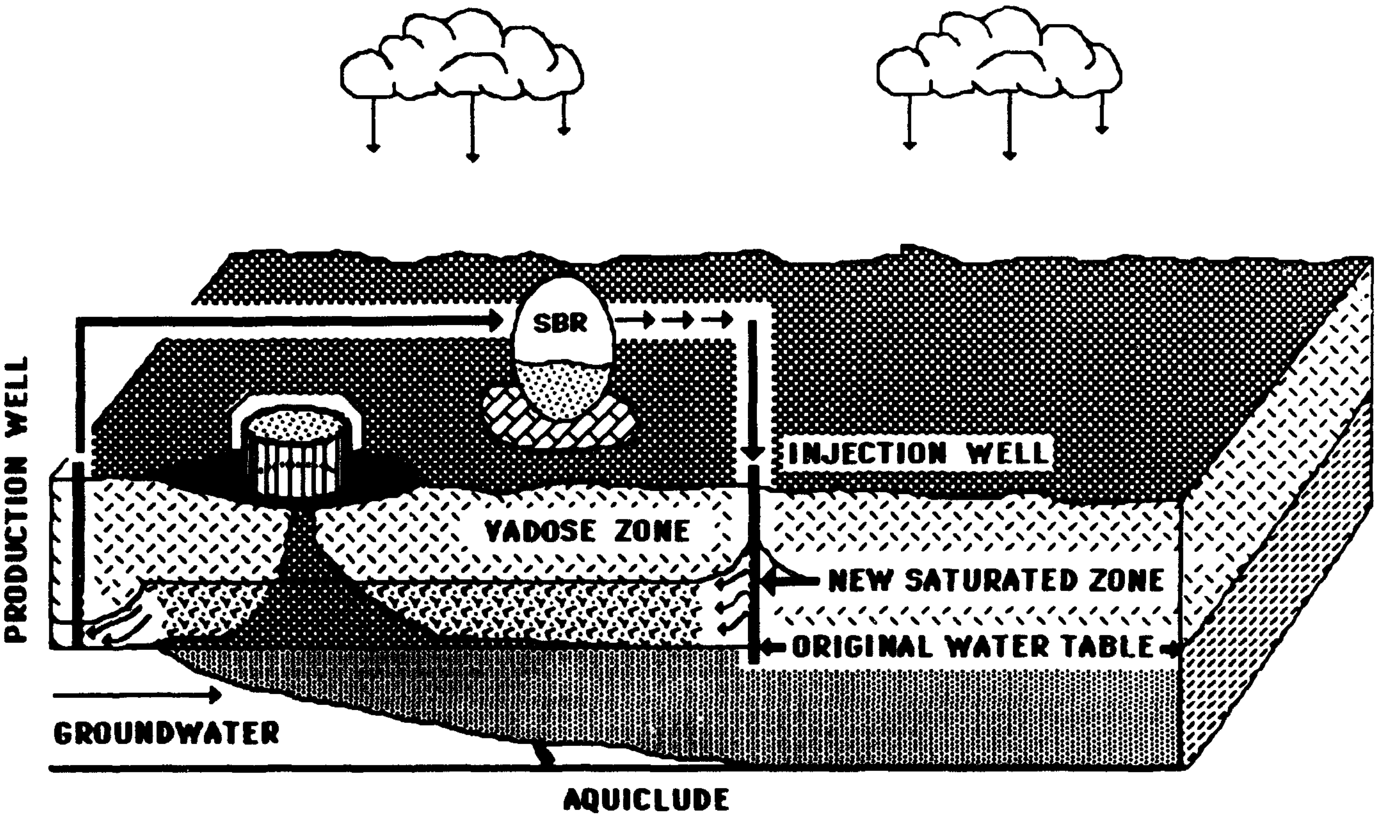
(2) Electron acceptors - NO_3, O_2, H_2O_2, or possibly O_3

(3) Surfactants - to increase bioavailability of sorbed organics

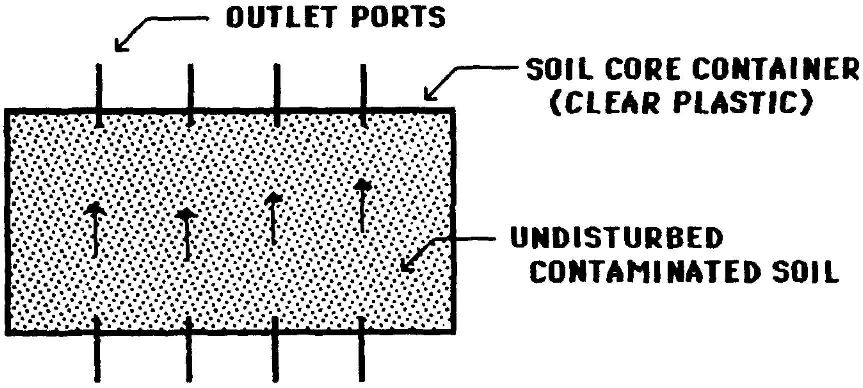
(4) Microbes - stress to select proper distribution; many also produce surfactants

(5) Additional organics - to promote cometabolism of contaminants

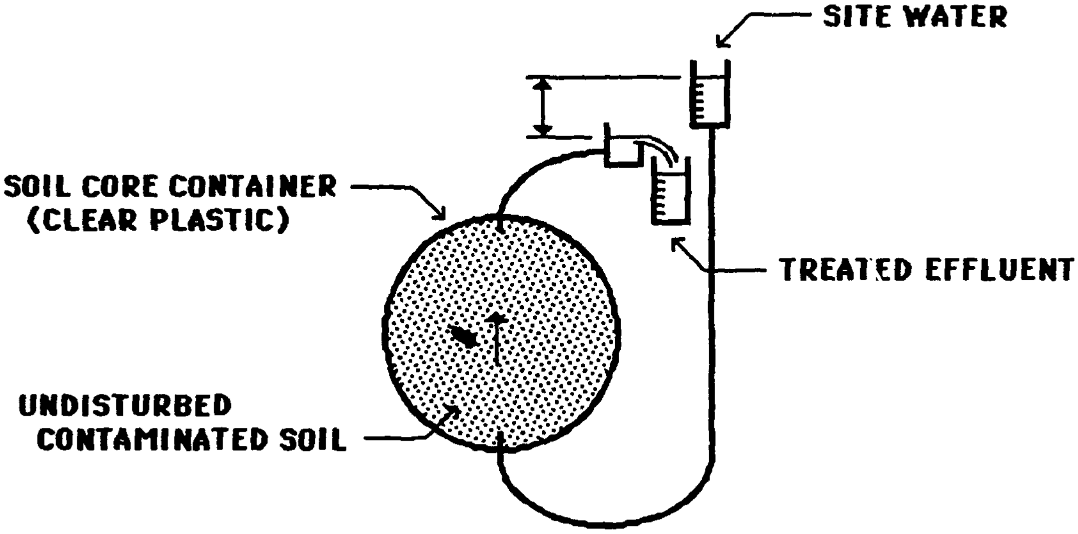
(6) Mixing - to minimize diffusion limitations



PASSIVE *IN SITU* TREATMENT OF CONTAMINATED SOILS

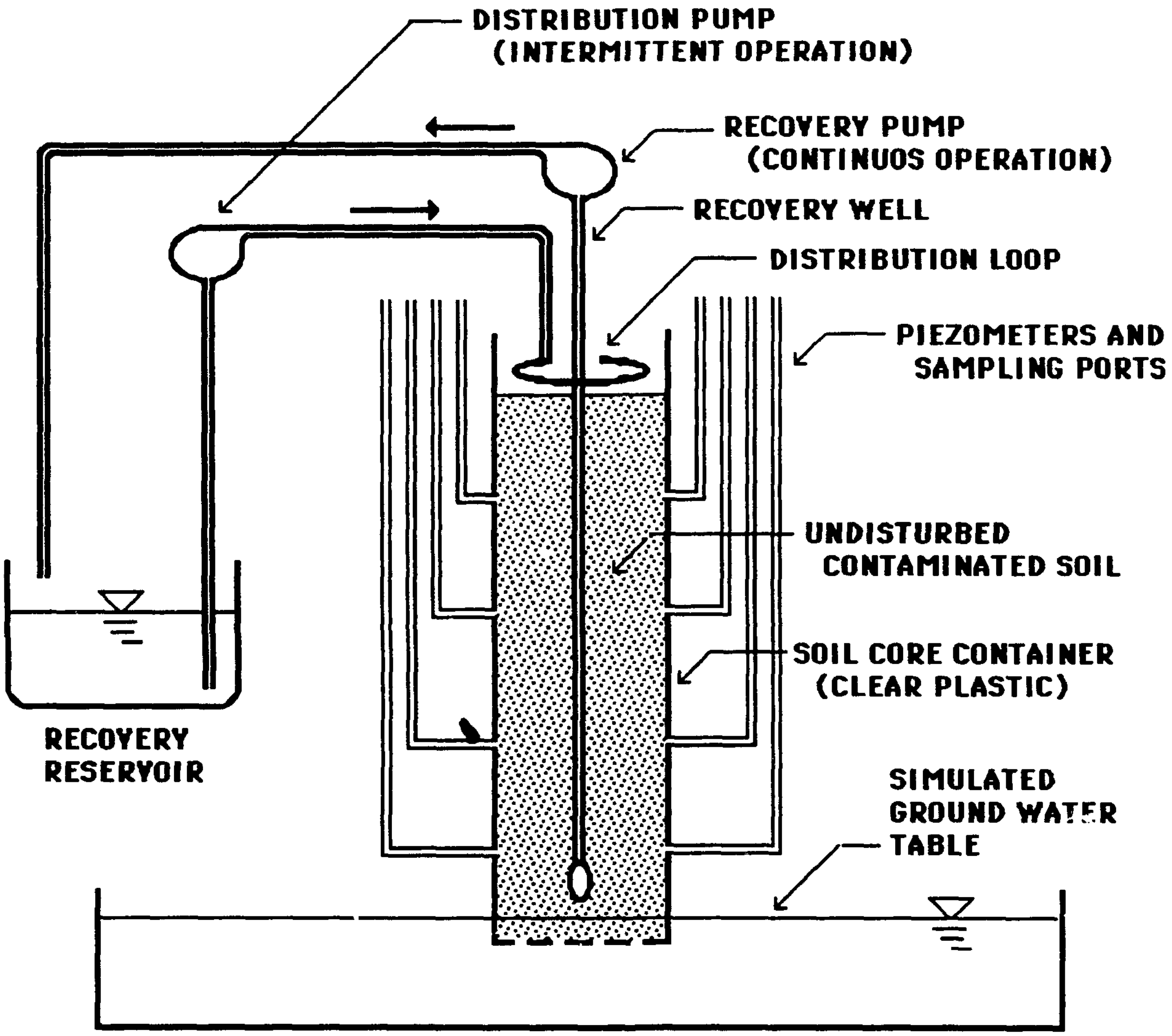


FRONT VIEW

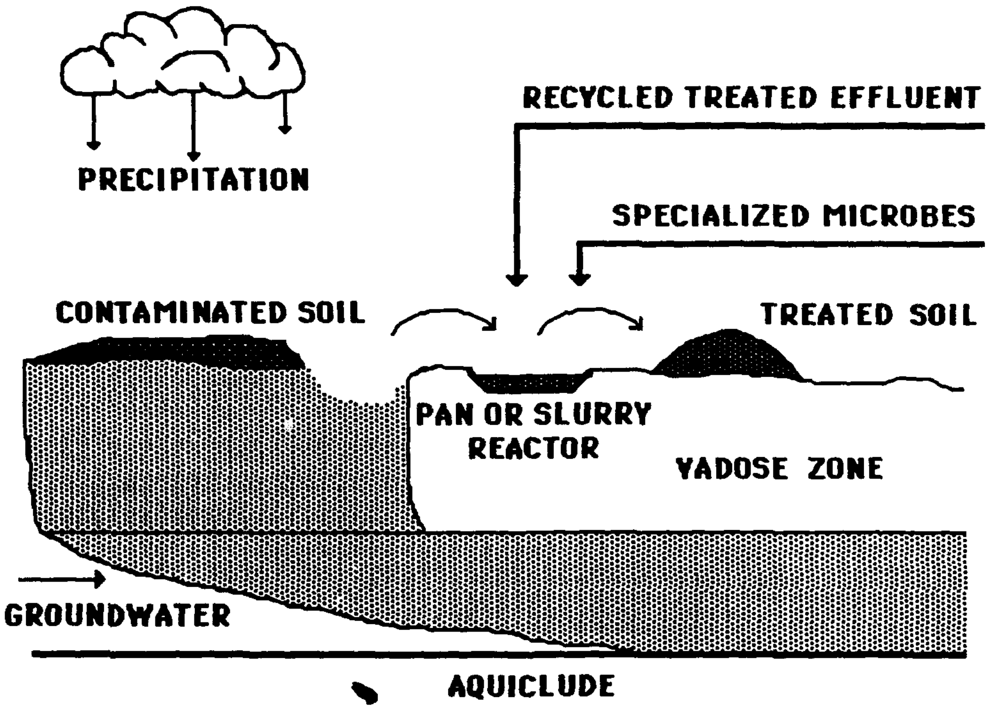


SIDE VIEW

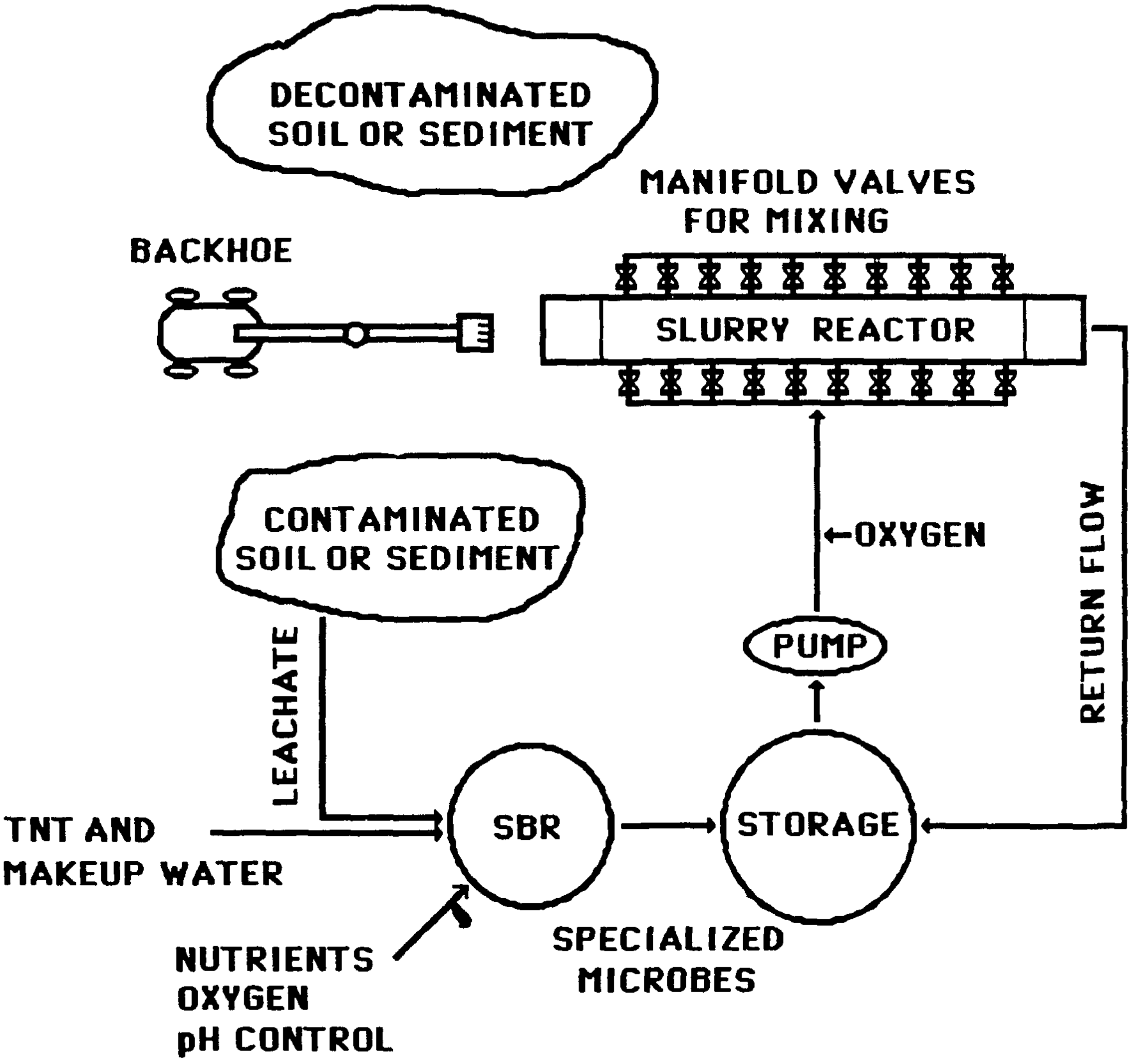
IN SITU SOIL TREATMENT LABORATORY REACTOR SCHEMATIC FOR SATURATED HORIZONTAL FLOW



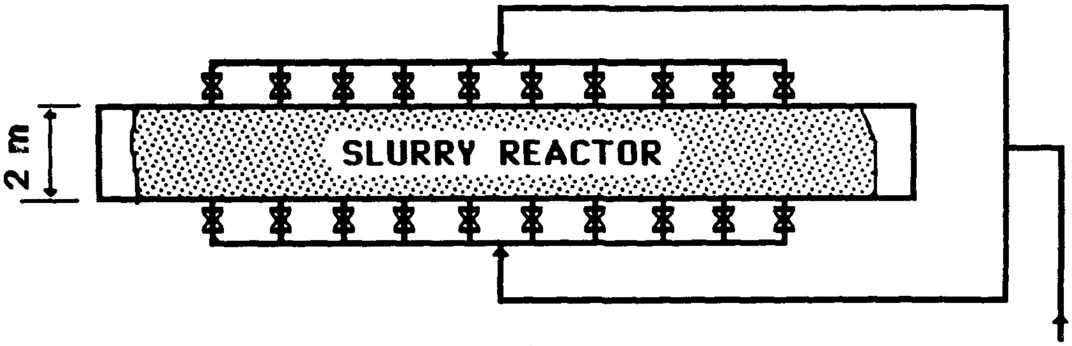
IN SITU SOIL TREATMENT LABORATORY REACTOR SCHEMATIC FOR PERIODIC FLOODING OF UNSATURATED SOIL



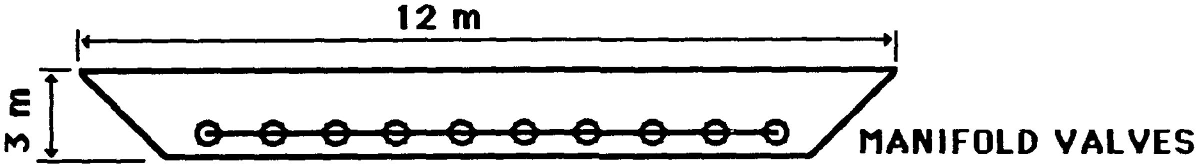
AGGRESSIVE ON-SITE TREATMENT OF CONTAMINATED SOILS WITH PAN OR SLURRY REACTORS



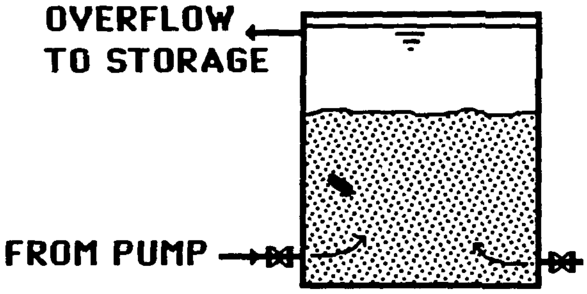
ON-SITE SOIL SLURRY REACTOR FOR SOILS OR SEDIMENTS



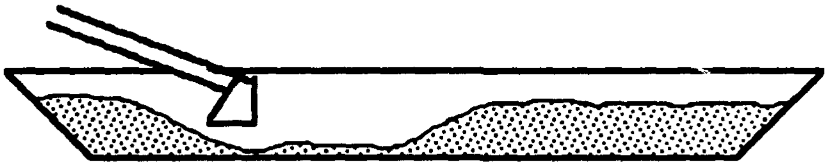
TOP VIEW SLURRY REACTOR
FILLED WITH SOIL OR SEDIMENT



SIDE VIEW SLURRY REACTOR

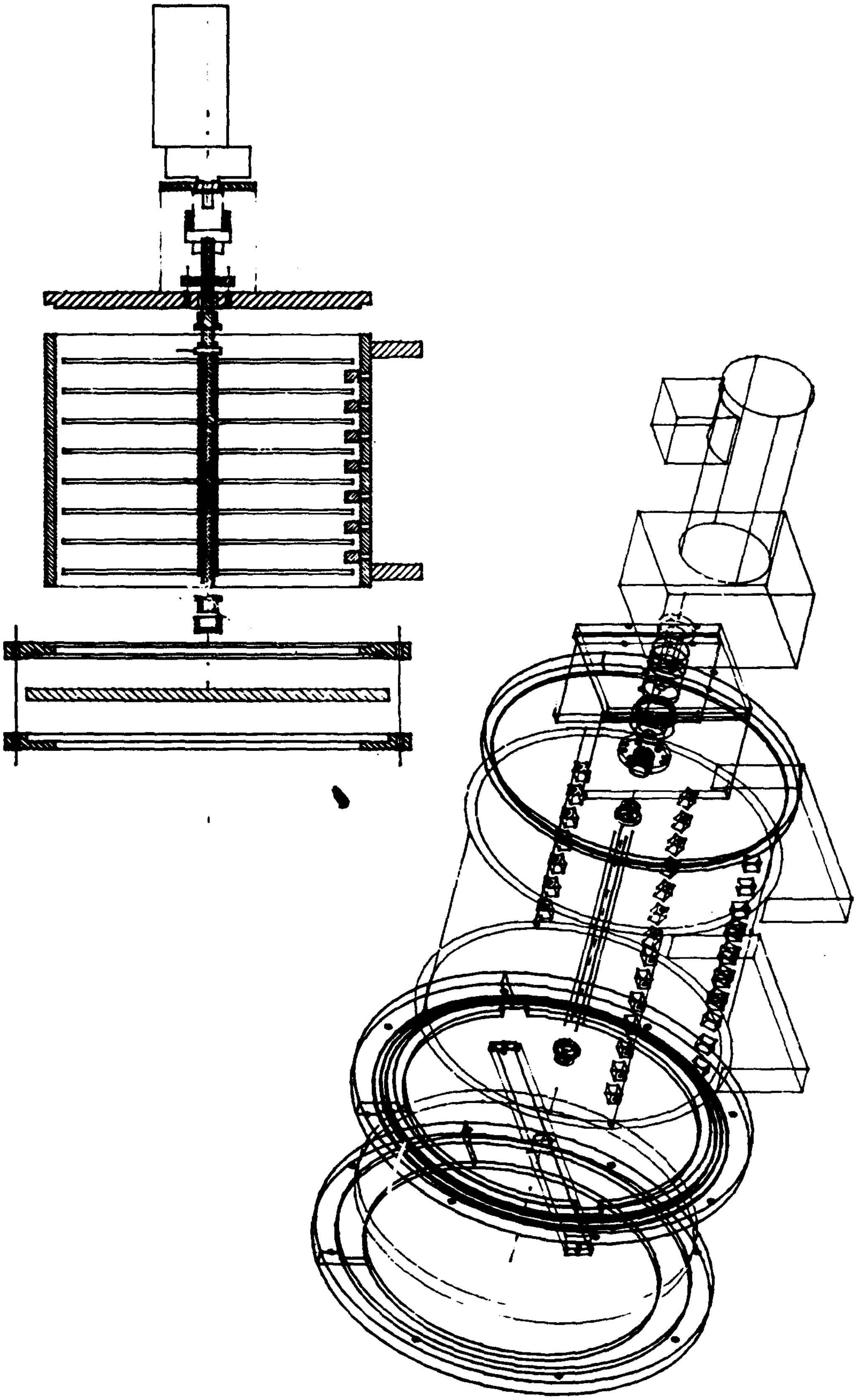


END VIEW SLURRY REACTOR
FLUIDIZED DURING TREATMENT



BACKHOE REMOVING TREATED SOIL OR SEDIMENT

DETAILS OF SLURRY REACTOR



PRELIMINARY RESULTS

(1) Literature review
  - composting
  - white rot fungus
  - recent findings using bacterial based systems

(2) Surfactant selection

(3) Site selection/Sample collection - Joliet Arsenal

(4) Design and construction of TNT fed SBR, periodic fixed film reactor, and the soil slurry reactor

(5) *Analysis of TNT, microbial growth, and growth potential*

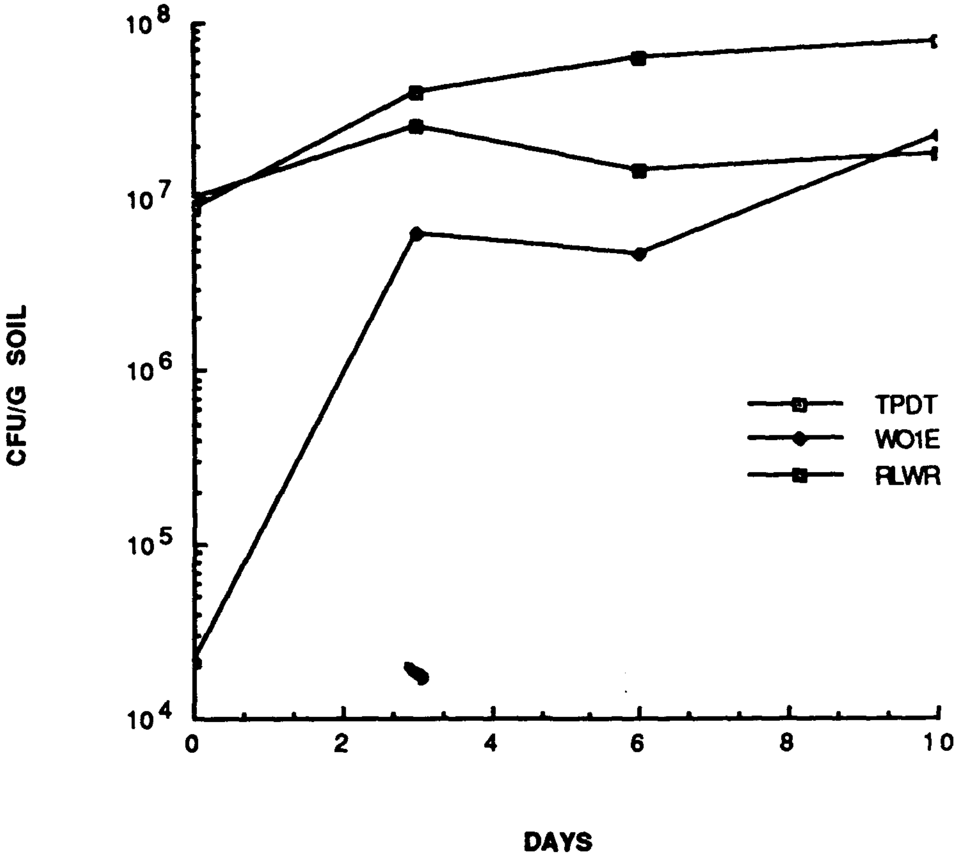
(6) Investigation of low cost alternatives

TNT ANALYSIS - JOLIET ARSENAL

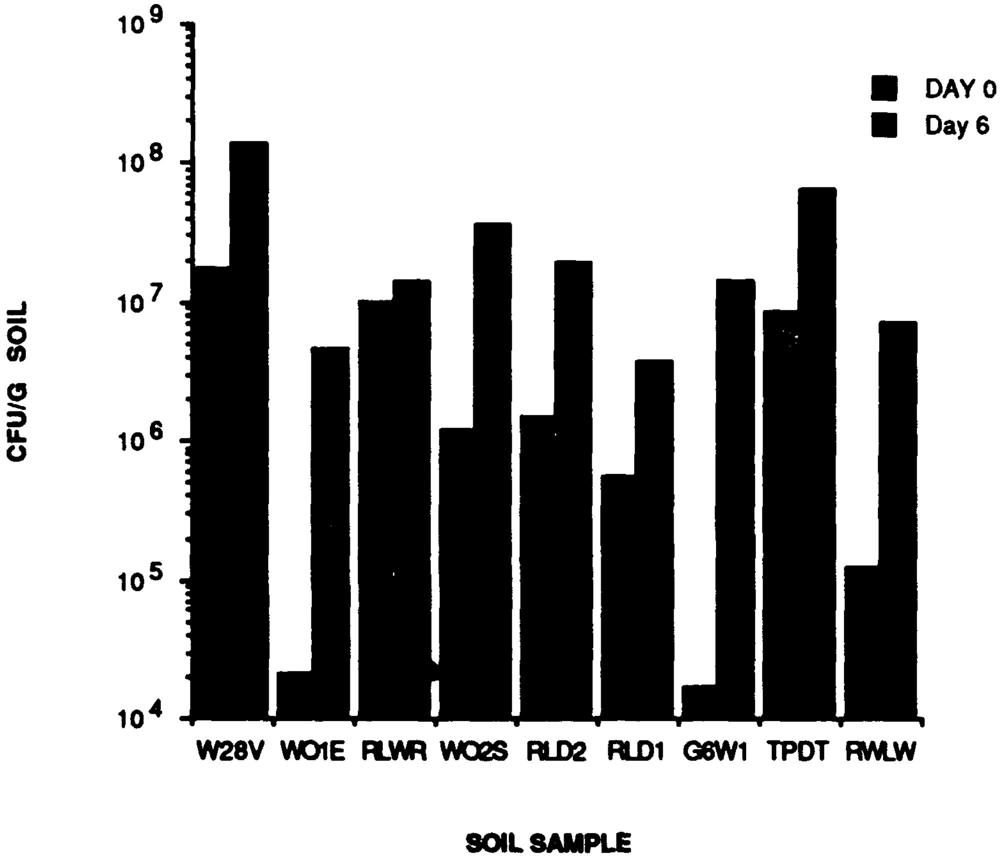
ABBREVIATION	SAMPLE DESCRIPTION	CONCENTRATION, PPM
TPDT*	TNT PRODUCTION LINE DELUGE TANK	144,000
G6W2	WASHOUT #2	35,000 40,000
WO1E	WASHOUT #1 EDGE	130
RLWR	RED LAGOON WATER RUNOFF EDGE	140
WO2S	WASHOUT #2 SIDEWALL	40
RLD2	RED LAGOON DRY #2	15
W28V	8R INTERFACE WASHOUT #2	~2
RLD1	RED LAGOON DRY #1	N/A
RWLW	RED WATER LAGOON WATER	N/A
G6W1	WASHOUT #1	N/A

* sample not plated

MICROBIAL GROWTH ANALYSIS OF SELECTED SOIL SAMPLES FROM JOLIET ARSENAL



GROWTH POTENTIAL OF TNT CONTAMINATED SOIL SAMPLES FROM JOLIET ARSENAL



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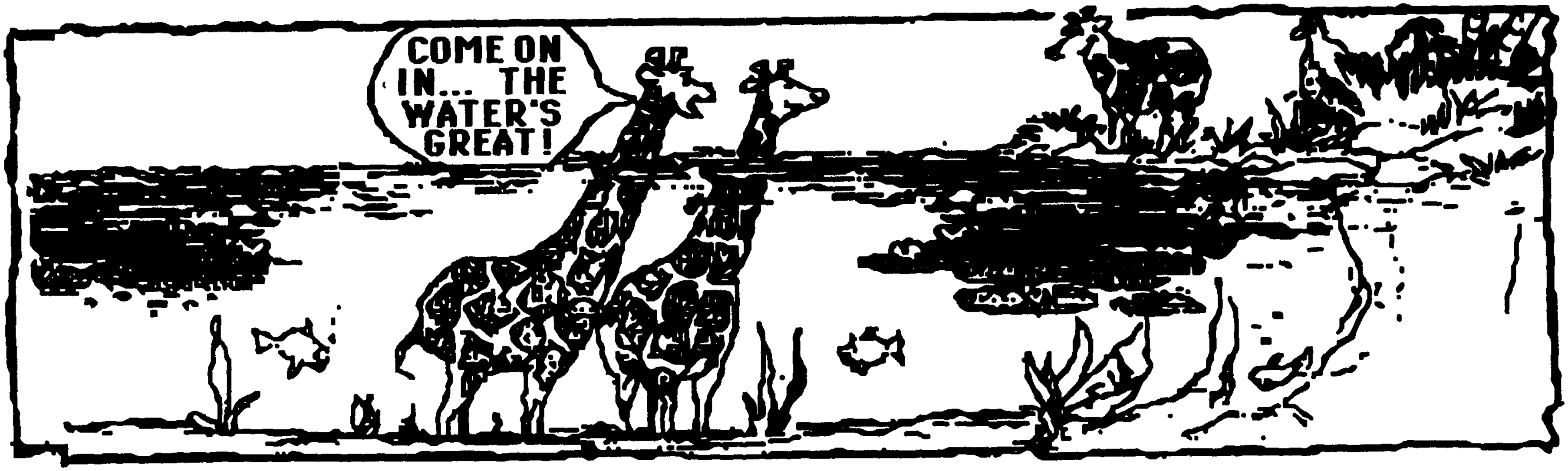

A BIG PART OF THE REASON YOU DON'T
SEE A LOT OF SHORT-NECKED GIRAFFES

IN SITU OPTICAL DETECTION OF EXPLOSIVES IN GROUNDWATER

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We have been working to develop a system for optical in situ detection of nitroaromatics and nitramines in groundwater. The system is to consist of a transportable spectrometer which can be coupled to remote sampling locations through fiber optics. The goal is to provide a tool for screening groundwater samples in the field to aid in locating contaminant plumes. This manuscript will review the current status of our work in this area, summarizing the approaches that we have tried and the results we have achieved to date. More detail can be found in reports and journal articles describing our research (Zhang et al 1988a,b,1989a,b,c, Zhang and Seitz 1989).

A practical method needs to be able to detect levels in the part per billion range. The requirement that the method be implemented remotely through fiber optics further complicates the problem, because light attenuation in the fiber can cause a large decrease in measured intensities. This is particularly severe in the ultraviolet region of the spectrum where optical fibers have high attenuation. Direct in situ spectroscopic detection of nitroaromatics and nitramines with the required sensitivity isn't feasible even with the most sophisticated available spectroscopic methods. Therefore, it is necessary to couple the remote spectroscopic measurement to an indicator phase that interacts with the nitro compounds to render them detectable through optical fibers.

Our approach has been to first develop indicator phases which allow for sensitive optical detection of nitro compounds, then to consider how the changes in the indicator phase optical properties can be measured remotely through fiber optics. After remote measurements have been demonstrated in a laboratory context, instrumentation that can be deployed in the field will be developed.

We have tried three approaches to indicator development. They share the common feature that a permeable polymer is used to "extract" the nitro compound from the sample. This polymer then serves as the medium for the optical measurement. The first approach was to try to directly detect nitro compounds by measuring their absorbance in the ultraviolet after extraction. The second approach, which has been the most successful, has been to formulate the polymer phase to contain a reagent that reacts irreversibly with nitroaromatics to form a product that absorbs in the visible region of the spectrum. The third approach has been to formulate the polymer to contain a fluorescent reagent whose emission is quenched by nitro compounds. These three approaches are considered separately below.

Extraction/Direct Absorption Spectroscopy

This approach is illustrated schematically in figure 1. A polymer phase is coupled to fiber optics so that the absorbance of the polymer phase can be measured. The polymer phase has to serve two functions. The first is to separate the analyte, i.e. the nitroaromatic or nitramine compound. from the sample matrix so that the measurement is not affected by

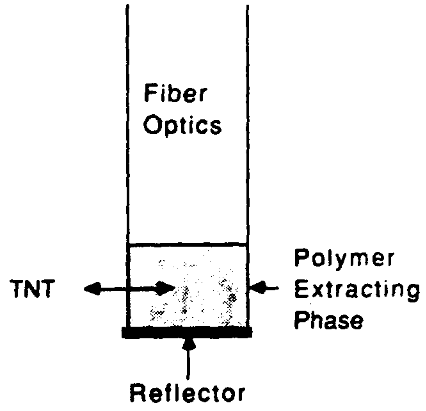


Figure 1: Schematic of Extraction/ Direct Absorption Measurement. TNT reversibly partitions into a polymer extractant. TNT absorbance in the extractant is measured directly through fiber optics.

the optical properties of the sample. In particular, natural organic matter absorbs strongly in the far ultraviolet where the common explosives have their maximum absorption.

The second function of the polymer phase is to preconcentrate the analyte to lower the limit of detection. The need for this can be illustrated by a hypothetical calculation for 2,4,6-trinitrotoluene (TNT). TNT has a molar absorptivity of 1.9×10^4 L/mol cm at 235 nm. If the pathlength is 1 cm and the minimum detectable absorbance is 0.01, then the detection limit for TNT is approximately 0.5 ppm in the absence of preconcentration. A preconcentration factor of 100 will reduce the detection limit to 5 ppb, low enough to be useful for the intended application.

Because TNT and other nitro compounds absorb in the far ultraviolet, it was necessary to find a polymer system that is transparent in this region. The choices are limited. We chose to evaluate poly(vinyl alcohol) (PVOH) crosslinked with glutaraldehyde (Higuchi and Iijima 1985). This forms a firm clear gel with the necessary uv transparency. However, the preconcentration factor for TNT was only 1.4, not nearly enough for the intended application. The reason for the low preconcentration factor is because the PVOH gel is predominantly water. It was established that it was not feasible to lower the water content sufficiently to get a significant improvement in preconcentration factor. Because of this and the fact that we anticipated difficulties in making remote optical measurements at 235 nm, we abandoned this approach.

If it could be implemented successfully with the necessary sensitivity limits, the extraction/direct absorption approach offers several attractive features. Because the only process involved is partitioning between the sample and polymer phase, this method of detection is inherently reversible, allowing for continuous in situ sensing. Although the PVOH gel did not significantly preconcentrate TNT, other polymer phases that we have used preconcentrate TNT by a factor of more than 100, large enough to get the necessary detectability. However, these polymers do not have the necessary uv transparency. Thus, the first problem is still to find a polymer formulation that combines the necessary optical properties with the required preconcentration factor.

Extraction/Indicator Reaction/Absorption

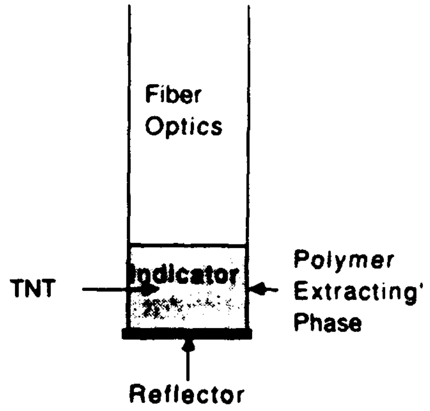
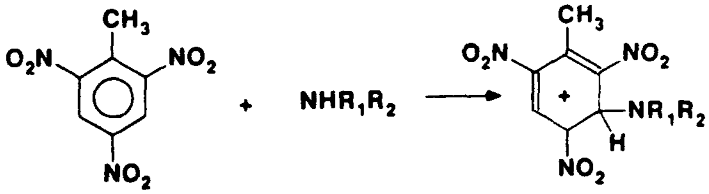


Figure 2: Schematic of Measurement in which TNT is irreversibly extracted into a polymer phase where it reacts with an indicator to from an absorbing product. The absorbance of the product is measured through fiber optics.

The second approach is shown schematically in figure 2. As before, the analyte is "extracted" into a polymer phase. However, in this approach the polymer is formulated to include an indicator that reacts with the analyte to form a colored product. Because the reaction with the indicator is irreversible, this approach is not amenable to continuous measurements. Instead, it offers the possibility of low detection limits because the colored product accumulates in the membrane with time. The longer the membrane is exposed to the sample, the lower the detection limit.

Primary amines have previously been used as indicators for polynitroaromatics (Glover and Keyser 1968). The reaction involves the formation of a colored Meisenheimer anion:



Because the product absorbs well out in the visible, it can be detected remotely through fiber optics without having to contend with large light losses due to fiber attenuation. Because the absorption spectrum of the product depends on polynitroaromatic structure, different explosives can potentially be distinguished using this approach. When the polynitroaromatic is TNT, maximum absorption is observed at 510 nm (Zhang et al 1988b, 1989a).

The polymer phase that we have employed is poly(vinyl chloride) (PVC) plasticized with dioctyl phthalate (Zhang et al 1988b, 1989a). The choice of PVC is critical. Many PVCs are prepared by emulsion polymerization and contain significant amounts of residual surfactant. The surfactant provides a site for water nucleation causing plasticized PVC to become cloudy after a couple hours of contact with water. Bulk polymerized PVC does not contain surfactant and remains clear indefinitely in water.

The plasticizer gives PVC fluidity so that it essentially acts as a bulk phase "solvent" for TNT. In one experiment the coefficient for TNT partitioning into plasticized PVC from water was measured to be 270.

The plasticized PVC is easily formulated as a membrane by solvent casting. PVC and plasticizer are dissolved in tetrahydrofuran (THF). The THF is allowed to slowly evaporate leaving a clear flexible membrane. A large section of membrane can be prepared at one time and can be cut into smaller pieces for multiple measurements. The amine indicator is readily incorporated into membrane by simply dissolving it along with PVC and plasticizer in THF prior to solvent casting. The crucial property of the amine is that it be chemically compatible with PVC so that it doesn't get extracted in the aqueous sample and doesn't tend to form a separate phase. The amine that has yielded the most stable membranes is Jeffamine T-403, a commercially available polyether with three amine groups (Zhang et al

1988b, 1989a).

The stability of these membranes to amine loss has been studied by measuring nitrogen content vs time of exposure to water (Zhang et al 1989c). After 46 days, membranes contain significant amounts of amine. Interestingly, amines prepared to have low initial amine contents are more stable to amine loss. After 46 days, they actually have higher nitrogen contents than membranes containing larger inital amounts of amine. We believe that at high initial amine concentrations. the Jeffamine T-403 tends to form a separate phase, which leads to accelerated rates of leaching in water.

Accelerated loss of amine is observed at pH 5 (Zhang et al 1988b, 1989a). We believe that this is due to protonation of the amine which enhances the water solubility of the Jeffamine T-403. This point needs to be further investigated if these membranes are to be used over long exposure times in acidic samples.

The response of the membrane to TNT has been investigated (Zhang et al 1988b,1989a). For a fixed exposure time, membrane absorbance at 510 nm is proportional to TNT concentration. A typical membrane exposed to 1 ppm TNT for 24 hours has an absorbance of 0.22. After two weeks exposure to aqueous solutions containing 10 ppb TNT, membranes are visibly colored. Response times are believed to be limited by slow mass transfer within the TNT membrane. While it would be highly desirable to get more rapid response, this is not easily achieved.

Membrane sensitivity to TNT depends on amine content (Zhang et al 1989c). By using membranes with low amine contents, it should be possible to design membranes for longterm dosimetry. For example, membranes could be formulated to have a specified absorbance value if exposed to 10 ppb TNT for 2 months. Because this application involves long exposure times, it is capable of detecting very low concentrations and thus could be used to detect the leading edge of a TNT plume.

In so far as it has been investigated, the membrane does not appear to be subject to interference from groundwater components. TNT concentrations in spiked groundwater samples have been measured with 95 to 105 percent recovery (Zhang et ll 1988b, 1989a). Also, the method was successfully applied to four waste water samples. Concentrations measured by the membrane were in good agreement with concentrations determined by a standard chromatographic method when TNT was present. The membrane showed no response to samples which did not contain TNT.

The TNT sensitive membrane that we have developed can be used in several ways. After immersion in a sample for a fixed period of time, it can be recovered and the degree of color formation estimated visually in comparison to color standards. This is convenient and readily implemented in the field. However, it is semiquantitative at best. A more quantitative measurement can be made by measuring absorbance with a conventional spectrophotometer using an unexposed membrane as a reference. In addition, one of the goals of our research was to demonstrate that this membrane could be coupled to remote measurements using fiber optics.

<u>In Situ Measurement through Fiber Optics:</u> Geometries for remote optical absorption measurements are shown in figure 3. In the arrangement of figure 3a, source and detection fibers are on the opposite side of the absorber. This geometry has the advantage that the source radiation does not have to be redirected toward the detection fiber. However, it necessarily requires more space than the other arrangements. The arrangement of figure 3b involves separate source and detection fibers placed side by side. This is more compact but requires redirection of the source radiation toward the detection fiber. This can be accomplished by

employing a specular reflector as shown in the figure or by using an absorbing phase that is heterogeneous and acts as a diffuse reflector.

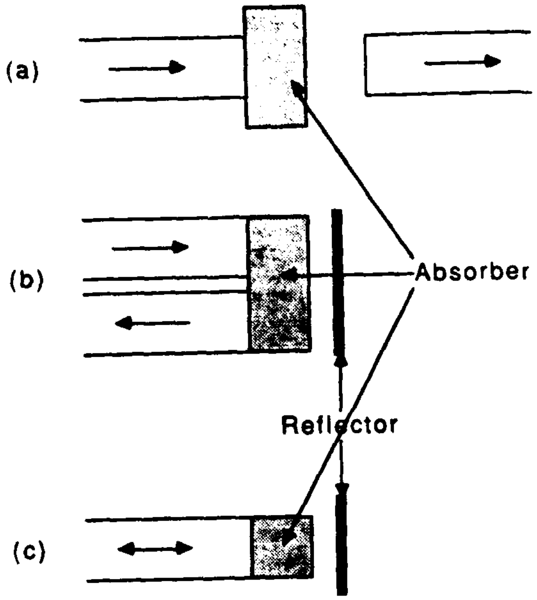


Figure 3: Arrangements for Absorption Measurements through Fiber Optics. (a). Two fiber transmission measurement. (b). Two fiber reflection measurement. (c) Single fiber measurement

The arrangement in figure 3c involves a single fiber to transport light to and from the absorber. This compact arrangement is not subject to error due to fiber misalignment. It also requires redirection of the source radiation. The problem with absorption measurements through a single optical fiber is stray light due to reflection at interfaces in the optical path where there is a change in refractive index. However, recent work has shown the feasibility of single fiber absorption measurements with minimal stray light (Skogerboe and Yeung 1987). Inspired by this study we chose to demonstrate the feasibility of remote fiber optic TNT detection using the single fiber geometry of figure 3c (Zhang et al 1989b, Zhang and Seitz 1989). To minimize the effect of stray light refractive index matching fluid was applied at interfaces to minimize reflections, and a specular reflector was positioned behind the membrane to maximize the intensity of interest. These measures kept stray light to a manageable level such that low absorbances were readily measured.

The single fiber absorption arrangement is a single beam measurement, which does not allow a reference measurement at the same wavelength. Instead, it is necessary to use a different wavelength where no absorption occurs as a reference. This approach has been employed previously in the first reported fiber optic chemical sensor based on changes in absorption (Peterson et al 1980). The use of a separate wavelength to serve as a reference will not completely account for drift that is wavelength dependent. However, it is quite adequate for the intended measurement. By measuring the ratio of the reference intensity to the intensity at 500 nm where the product of the indicator reaction absorbs strongly, we were able to demonstrate that concentrations as low as 100 ppb could be measured remotely through fiber optics (Zhang et al 1989b, Zhang and Seitz 1989).

We demonstrated the feasibility of remote in situ TNT detection using a laboratory spectrofluorometer to provide both source radiation and detection. The next goal is to develop instrumentation which can be deployed in the field. We plan to build a spectrometer in which two LEDs will be the radiation sources at the sample and reference wavelengths. By using LEDs as sources, we anticipate that the resulting spectrometer will be both compact and inexpensive. Although we demonstrated the feasibility of remote TNT measurements using a single optical fiber, we expect to use a two-fiber arrangement for the field instrument to avoid altogether the problem of stray radiation.

Halogenated hydrocarbons have also been detected remotely through fiber optics by measuring the rate at which they react with an indicator to form an absorbing product (Angel et al 1989). The two fiber arrangement shown in figure 3b was used for this measurement. Because the product absorbs at wavelengths close to the wavelengths where the product of the TNT-amine reaction absorbs, the instrument developed for field TNT measurements may also be suitable for remote in situ halogenated hydrocarbon detection merely by changing the indicator phase.

Extraction/Fluorescence Quenching

The amine-containing PVC membranes only respond to polynitroaromatics. They do not response to nitramines. Because we have not been able to identify an indicator that reacts with nitramines to form an absorbing product, we have explored an alternative approach that takes advantage of the observation that nitro compounds are good quenchers of fluorescence. The concept is illustrated in figure 4. Like the previous approaches, it is based on extraction of the analyte into a polymer phase. The polymer is formulated to include a fluorophor which is susceptible to quenching. Extraction of a nitro compound into the membrane leads to fluorescence quenching which can be detected either as a decrease in intensity or a shortening of the fluorescence lifetime. The sensitivity to a particular compound depends on the extent to which it partitions into the membrane and the efficiency of fluorescence quenching.

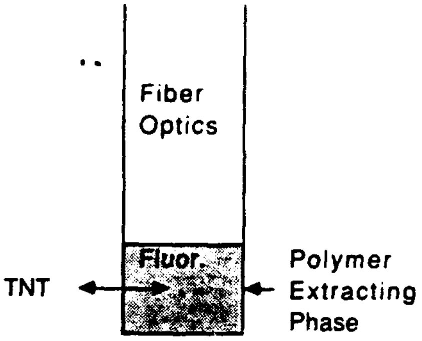


Figure 4: Schematic of Extraction/ Fluorescence Quenching. TNT reversibly partitions into polymer phase and quenches emission from the fluorophor cast into the polymer.

The fluorescence quenching approach offers the advantage that it is inherently reversible and thus can be used for continuous sensing. It is not selective, responding in the same way to all nitro compounds that are extracted into the membrane. However, it can still be used to screen samples for the presence of explosive contaminants. We are particularly interested in developing a system that will respond to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), because this compound is stable and migrates rapidly in groundwater. Research on the fluorescence quenching approach is currently in progress. A detailed report will be prepared in spring 1990. This manuscript will only summarize the most important results.

Plasticized PVC is a poor medium for fluorescence because the chlorine atoms quench fluorescence via the external heavy atom effect. Therefore, we have employed plasticized cellulose triacetate as the polymer phase. It is easily cast into membranes using cyclohexanone as the solvent. Initial work was performed using dioctyl phthalate as the plasticizer. However, we have learned that polar plasticizers increase the affinity of the resulting membrane for nitro compounds. For example, the coefficient for RDX partitioning into the cellulose triacetate from water is 7 for dioctyl phthalate as the plasticizer and 50 for isodecyldiphenyl phosphate.

The fluorophor that gives the most sensitive response is pyrenebutyric acid. Pyrene derivatives have long fluorescence lifetimes because the electronic transition from the first excited singlet state to the ground state is spin forbidden. This allows more time for the excited state to interact with quenchers, thereby enhancing the susceptibility to quenching.

The problem with the fluorescence quenching approach is sensitivity. Our best systems respond to RDX and TNT concentrations in the 1 to 10 ppm range. We have not been able to get detection limits below 1 ppm. Because the response process is reversible, we do not get any further accumulation of analyte in the membrane once equilibrium is reached. Conceivably, sensitivity can be enhanced by adding an indicator which reacts with RDX. This reaction does not have to produce a colored product, but must leave at least one of the nitro groups intact so that fluorescence will still be quenched. The purpose of the reaction would be to get a larger buildup of quencher in the membrane.

If we succeed in developing a membrane with adequate sensitivity, we anticipate that the remote in situ measurement will be based on measurements of changes in fluorescence lifetime accompanying quenching. Lifetime measurements are not affected by factors such as source drift and slow loss of indicator that affect absolute intensity measurements. The source would be an inexpensive nitrogen laser since the 337.1 nm line of this laser efficiently excites pyrenebutyric acid. Since the fluorescence lifetime of pyrenebutyric acid is on the order of 150 nanoseconds, it is relatively easy to measure compared to typical fluorescence lifetimes which fall in the 1 to 10 nanosecond range. Nitrogen lasers put out pulses which only last for a few nanoseconds and thus are well suited for the proposed measurements. The intensity is high enough for remote measurements through fiber optics even though fiber attenuation is quite significant at 337.1 nm.

Conclusions

We have investigated three approaches to the detection of trace levels of explosives in groundwater. We have developed a membrane that can sensitively detect TNT and other polynitroaromatics in groundwater and can be used for in situ optical measurements through fiber optics. As soon as an instrument for field use is constructed, the performance of this system can be evaluated at contaminated sites.

We have also evaluated approaches to explosive detection based on fluorescence quenching and direct detection of nitro compound absorbance. In both cases, significant improvements in sensitivity are required to be able to detect typical contaminant levels in groundwater.

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THE U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY'S R&D PROGRAMS IN ANALYTICAL CHEMISTRY AND INSTRUMENTS

Kenneth T. Lang
U.S. Army Toxic and Hazardous Materials Agency

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is responsible for identifying and cleaning up environmental chemical contamination throughout the Army. A portion of USATHAMA's thrust to accomplish this objective is an ongoing, multifaceted research and development program aimed at making the investigative and verification of environmental cleanup activities more timely and cost effective without sacrificing quality. This presentation will be an overview of several USATHAMA programs designed to accomplish this goal

FY 89 R & D WORKPLAN

R & D PROGRAM	PERFORMER	STATUS
GLOW DISCHARGE/ION TRAP MASS SPECTROMETRY	ORNL	ONGOING
SAMPLE HOLDING TIME STUDY	ORNL	COMPLETED
SOIL SAMPLE COLLECTION, PRESERVATION, AND ANALYSIS PROCEDURE FOR VOC's	ORNL	ONGOING
DEVELOPMENT OF MONOCLONAL ANTIBODIES FOR TETRYL, BENZENE, DIELDRIN AND p-CHLOROPHENYLMETHYLSULFONE	WESTINGHOUSE BATTELLE SoRI	COMPLETED ONGOING ONGOING

FY 89 R & D WORKPLAN (CONT)

R & D PROGRAM	PERFORMER	STATUS
EVALUATION OF FIELD PORTABLE INSTRUMENTS & METHODS	ORNL	COMPLETED
RDX FIELD DETECTOR KIT	BATTELLE	DISCONTINUED
METHOD DEVELOPMENT FOR EXPLOSIVES IN PLANTS	CRREL	COMPLETED
EFFECTS OF WELL CASING MATERIALS IN ENVIRONMENTAL MONITORING	CRREL	COMPLETED PHASE I
METHOD DEVELOPMENT FOR NITROCELLULOSE IN SOIL & WATER	CRREL	ONGOING

FY 89 R & D WORKPLAN (CONT)

R & D PROGRAM	PERFORMER	STATUS
IN SITU DETECTION OF RDX USING FIBER OPTICS	UNH	DISCONTINUED
VALIDATION OF TNT DETECTOR KIT	CRREL	COMPLETED
COMPARISON OF GLASSWARE CLEANING PROCEDURES	CRREL	COMPLETED

FY 90 R & D WORKPLAN

R & D PROGRAM	PERFORMER
GLOW DISCHARGE/ION TRAP MASS SPECTROMETRY	ORNL
FTIR REMOTE SENSING	ANL
FIELD PREPARATION OF SAMPLES	CRREL
LC/MS INTERFACE FOR EXPLOSIVES	AEHA
SOIL-GAS DIFFUSION SAMPLER (TERRATROG)	IITRI

FY 90 R & D WORKPLAN (CONT)

R & D PROGRAM	PERFORMER
EFFECTS OF WELL CASING MATERIALS IN ENVIRONMENTAL MONITORING	CRREL
SOIL SAMPLE COLLECTION, PRESERVATION, AND ANALYSIS FOR VOC's	ORNL
DEVELOPMENT OF MONOCLONAL ANTIBODY FIELD DETECTOR KITS	TBD
TECHNOLOGY REVIEW OF RDX CHEMISTRY RE. FIELD DETECTION	TBD

FY 90 R & D WORKPLAN (CONT)

R & D PROGRAM	PERFORMER
METHOD DEVELOPMENT FOR DEGRADATION PRODUCTS OF EXPLOSIVES AND PROPELLANTS	CRREL
EVALUATION OF SUPERCRITICAL FLUID FOR ANALYSIS OF EXPLOSIVES & HYDRAZINES	CRREL

OTHER NON-R&D PROJECTS

SIMPLIFIED SOIL FIELD TEST PROCEDURE FOR TNT

FIELD TEST OF TNT FIBER OPTICS DETECTION SYSTEM

COMPARISON OF LOW-LEVEL METHODS FOR NITROAROMATICS AND NITRAMINES IN WATER

SALTING-OUT EXTRACTION PROCEDURE FOR EXPLOSIVES

EVALUATION OF "SLOPE TESTING METOHD" FOR UPDATING ACCURACY CORRECTIONS ON CONTROL CHARTS

EXPLOSIVE FIELD DETECTOR KITS

OBJECTIVE: To develop field detector kits for the detection of explosives in soil and water

- Indicator tube for the detection of TNT completed
- Detector kit for RDX under development

DEVELOPMENT OF MONOCLONAL ANTIBODIES

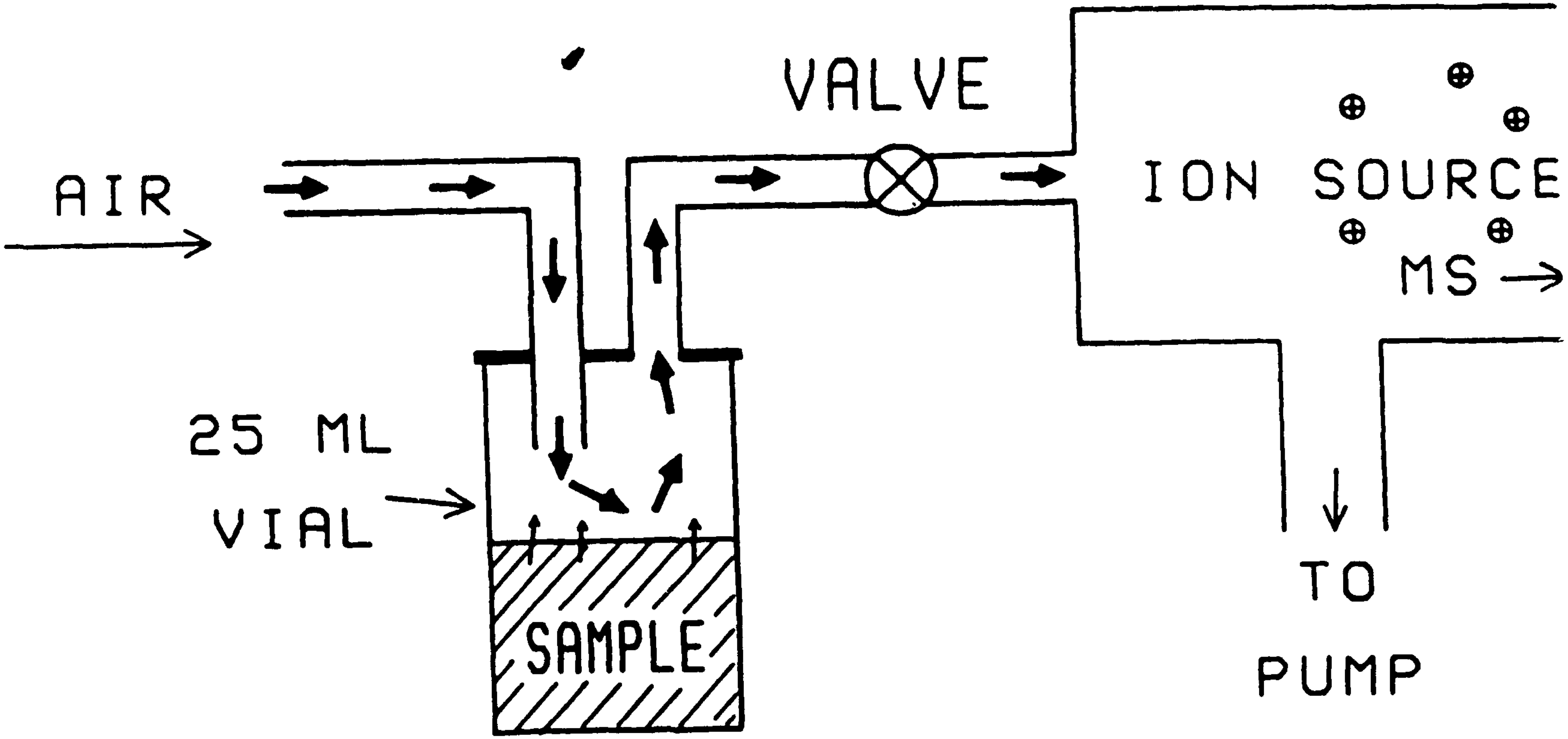
COMPOUNDS TARGETED:

- TETRYL
- BENZENE
- DIELDRIN
- PARA-CHLOROPHENYLMETHYLSULFONE

FTIR REMOTE SENSING

OBJECTIVE: To develop technology for the detection of toxic and hazardous materials real–time in ambient air during remedial actions

GLOW DISCHARGE SAMPLE INLET



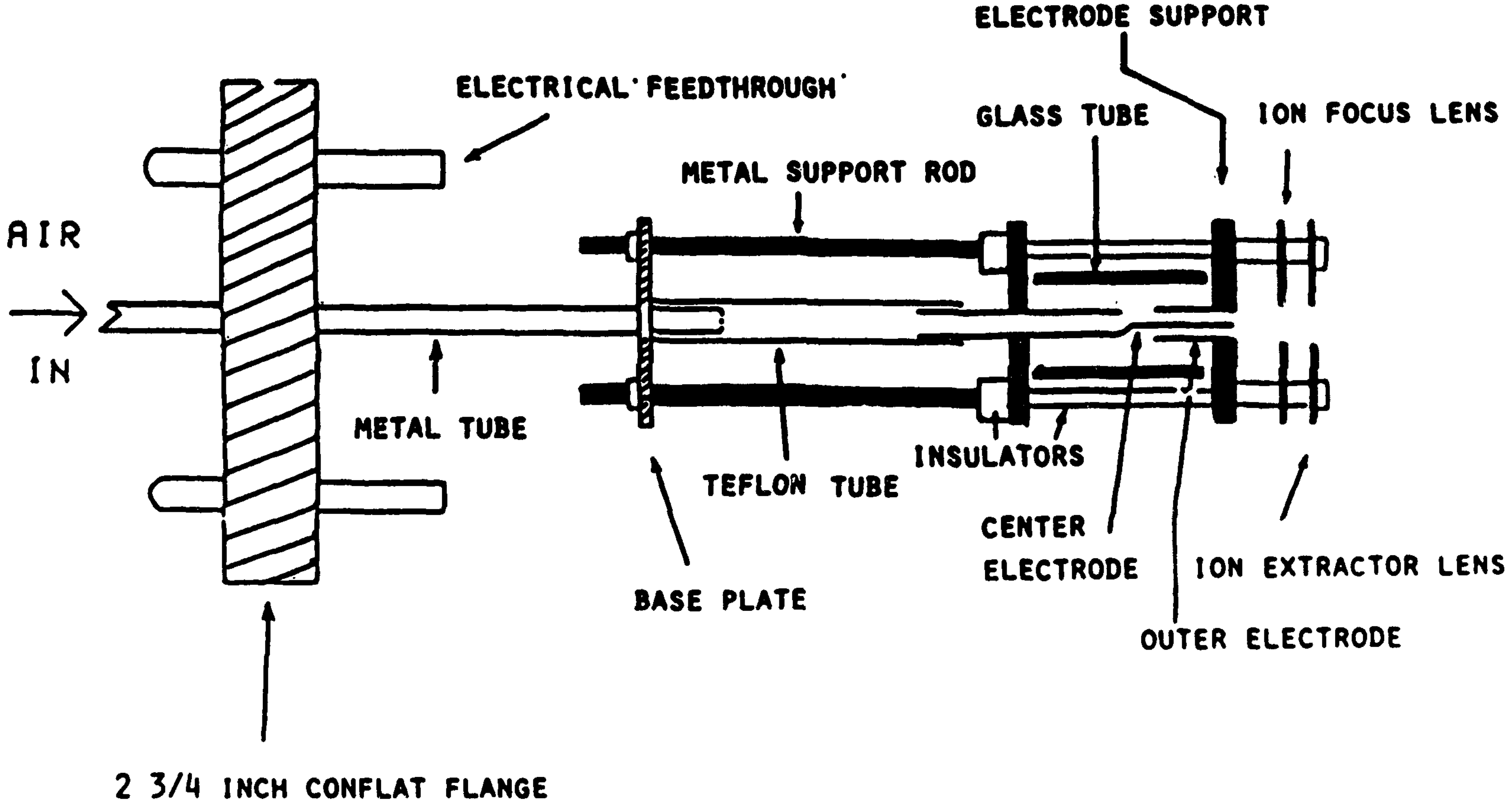
EVALUATION OF GLOW DISCHARGE AND ION TRAP MASS SPECTROMETRY

OBJECTIVE: To develop rapid, cost effective mass spectrometry techniques to replace the current EPA methods for volatiles and semivolatiles in soil and water.

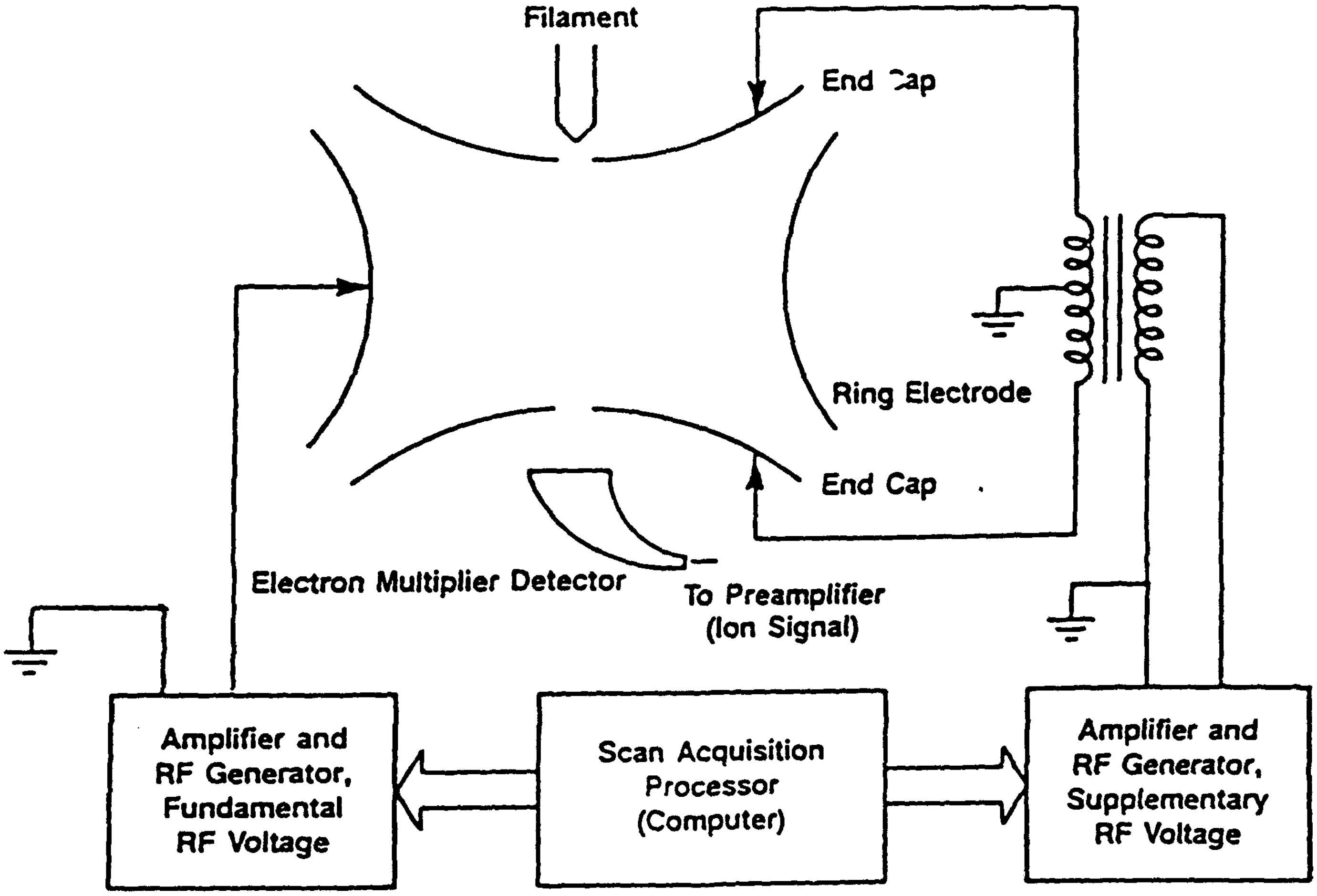
- Can now Analyze 8 samples/day using EPA GC/MS methodology
- Successful to date analyzing up to 200 samples per day with GD and ITMS
- Potential to develop fieldable ITMS

GLOW DISCHARGE IONIZATION SOURCE FEATURES

1. SIMPLE DESIGN
2. EASY TO OPERATE, LOW MAINTENANCE
3. RELIABLE
4. NO FILAMENT OR RADIACTIVE FOIL
5. HIGH IONIZATION EFFICIENCY
6. CHEMICAL IONIZATION OR FRAGMENTATION (similar to EI)
7. SAMPLE AMBIENT AIR DIRECTLY
8. INSIGNIFICANT WATER CLUSTER FORMATION


ELECTRODE SUPPORT
ELECTRICAL FEEDTHROUGH
GLASS TUBE
ION FOCUS LENS
METAL SUPPORT ROD
AIR
IN
METAL TUBE
INSULATORS
TEFLON TUBE
CENTER ELECTRODE
BASE PLATE
ION EXTRACTOR LENS
OUTER ELECTRODE
2 3/4 INCH CONFLAT FLANGE

Ion Trap MS/MS Configuration



DOE HAZARDOUS WASTE REMEDIAL ACTIONS PROGRAM (HAZWRAP)
WASTE TECHNOLOGY DEMONSTRATION PROGRAM

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ABSTRACT

One element of the Department of Energy (DOE) Hazardous Waste Remedial Actions Program (HAZWRAP) is to support the demonstration of waste treatment technologies, both in-house and commercial, to determine the applicability of these technologies in remediating waste problems common to the DOE Defense Programs (DP) installations. A number of innovative technologies have the potential for dealing with DOE-DP Comprehensive Environmental Resource, Conservation, and Liability Act (CERCLA) -related and Resource Conservation and Recovery Act (RCRA) -related waste problems more economically and/or in a more socially acceptable manner than do current processes. It is the goal of HAZWRAP to critically review emerging technologies and to develop those with the greatest potential for significant impact to the DOE-DP waste management program.

Twenty-two technology demonstrations are in various project stages, ranging from recent initiation to nearing completion. These waste treatment technologies relate to the following general technology needs of DOE-DP:

Treatment/Disposal of Hazardous Mixed Wastes
Waste Minimization Methods
Standards/Methods for Site Remediation/Stabilization/Closure
Improved Burial Practices and Waste Forms
Pathways Analysis

Each of the ongoing technology demonstration projects is identified and the objectives, status, and project duration are discussed.

INTRODUCTION

One function of the Department of Energy (DOE) Hazardous Waste Remedial Actions Program (HAZWRAP) is to support the field demonstration of waste treatment technologies, both in-house and commercial, to determine the applicability of these technologies in remediating waste problems common to the DOE Defense Programs (DP) installations. A number of innovative technologies have the potential for dealing with DOE-DP Comprehensive Environmental Response, Compensation, and Liability Act-related and Resource Conservation and Recovery Act-related waste problems more

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economically and/or in a more socially acceptable manner than do current processes. It is the goal of HAZWRAP to critically review emerging technologies and to demonstrate those with the greatest potential for significant effect on the DOE-DP waste management program.

The Technology Demonstration (TD) Program is sponsored by the DOE Headquarters Office of Defense Waste and Transportation Management (ODWTM) through the Hazardous Waste and Remedial Actions Division (HWRAD). Funding is provided through two major management programs: the Hazardous Waste Compliance Technology Program and the Environmental Restoration Program.

A parallel function of HAZWRAP is to promote and expedite research and development (R&D) of selected new technology ideas, through the laboratory stages, for application in the elimination, minimization, destruction, stabilization, or delisting of hazardous and mixed wastes resulting from DOE-DP activities. The techniques are developed by DOE laboratories in cooperation with other governmental agencies and/or the private sector where applicable. The TD Program supports the field demonstration of these technologies when the R&D is completed. The R&D Program is funded by ODWTM through the Waste Research and Development Division and is managed by HAZWRAP.

The TD Program is managed by HWRAD and the HAZWRAP Program Manager. The HAZWRAP Support Contractor Office, staffed by Martin Marietta Energy Systems, Inc., personnel, supports the HAZWRAP Program Manager and HWRAD in their leadership roles. The program formally interfaces with key representatives of the eight field offices and their contractors, and frequent contact is made to establish and maintain program priorities and direction. These relationships are depicted in Fig. 1.

The TD Program began in FY 1986 when discussions were conducted with DOE Operations Offices concerning their particular waste treatment needs. In October 1986 a team of representatives from the eight field offices and Headquarters met to select candidate waste treatment demonstrations. Of the 18 candidate waste treatment problems presented, 3 were selected for demonstration.

In each of the following years the TD Program Manager convened a meeting of the designated Operations Office representatives to review the progress of each of the ongoing projects and to discuss new candidate projects. Each office was requested to provide information on new, high-priority candidate projects that were evaluated and ranked by the representatives based on criteria reviewed and revised as needed at each meeting. At the conclusion of each meeting, a ranked list of the new candidate projects was established. For projects with a high ranking, the TD Program Manager requested that the proposing site submit more detailed information, including costs, schedule, and technical detail. On the basis of this input, the TD Program Manager reviewed each new candidate project with consideration of cost, schedule, and the project's technical differences and compared it with other new candidate and ongoing projects. The results of the TD Program Manager's deliberations were then communicated to Headquarters as recommendations for funding. These recommendations often included a restructuring of the coming fiscal year budget to accommodate the rapidly evolving needs of DP waste management activities.

SECRETARY OF ENERGY

ASSISTANT SECRETARY FOR DEFENSE PROGRAMS

OFFICE OF DEFENSE WASTE AND TRANSPORTATION MANAGEMENT

HAZARDOUS WASTE AND REMEDIAL ACTIONS DIVISION

HAZARDOUS WASTE REMEDIAL ACTIONS PROGRAM PROGRAM MANAGER

--- Support Contractor Office
(TD Program Manager)
(Martin Marietta)

ALBUQUERQUE OPERATIONS --- | --- OAK RIDGE OPERATIONS

CHICAGO OPERATIONS --- | --- RICHLAND OPERATIONS

IDAHO OPERATIONS --- | --- SAN FRANCISCO OPERATIONS

NEVADA OPERATIONS --- | --- SAVANNAH RIVER OPERATIONS

Fig. 1. Organization structure for conduct of the Hazardous Waste Remedial Actions Program.

Following review and approval of the recommendations by Headquarters and the HAZWRAP Program Manager, the TD Program Manager established contact with the appropriate Operations Offices to develop detailed plans for the project. The sites were encouraged to include in the planning the exploration of private industry for new and innovative technological solutions. A common method for this search was the procurement request for proposal (RFP) process. The TD Program Manager closely followed the progress of each project, ensuring that plans were executed within cost and schedule, the technical intent of the project was maintained, and the transfer of the technology was completed.

In August 1987 a second meeting was convened to select more waste treatment problems for demonstration starting in FY 1988. In July 1988 a third meeting was held that combined the ranking of projects for the Compliance Technology Program and the Environmental Restoration Program for initiation in FY 1989. The TD Program has grown from 4 projects in FY 1987 to 22 projects in FY 1989.

TECHNOLOGY DEMONSTRATION PROJECTS

Currently, twenty-two technology demonstrations are in various project stages, ranging from recent initiation to nearing completion. These waste treatment technologies relate to the following general technology needs of DOE-DP:

- Treatment/Disposal of Hazardous Mixed Wastes
- Waste Minimization Methods
- Standards/Methods for Site Remediation/Stabilization/Closure
- Improved Burial Practices and Waste Forms
- Pathways Analysis

Each of the ongoing technology demonstration projects is identified and a brief description of the technology is given in Table I. A more detailed description, including objective, status, and expected project duration, is included in Table II. A listing of acronyms pertaining to DOE Operations Offices and DOE laboratories and plants is given in Table III.

Table II. Description of Ongoing Technology Demonstration Projects

PROJECT TITLE: SUPERCRITICAL WATER OXIDATION OF HAZARDOUS CHEMICAL WASTES (PHASE IV)

LOCATION: Los Alamos National Laboratory
Los Alamos, New Mexico

PROJECT OBJECTIVE: To demonstrate the feasibility of the supercritical water oxidation concept for the destruction of hydrocarbon and oxygenated wastes.

WASTE PROBLEM: Liquid wastes containing water, hydrocarbons, and oxygenated compounds are common to most DOE-DP facilities. Technology, in addition to incineration, for the destruction of the hazardous chemical contents of these liquid wastes is desired.

TECHNOLOGY: Above a certain temperature and pressure (647 K and 22.13 MPa), water becomes a fluid that is neither a liquid nor a gas but has some of the characteristics of both. In this state, the solvent properties of water reverse so that nonpolar, organic compounds become soluble and inorganic salts become insoluble. Under these conditions, oxidation of hazardous organic chemicals, such as chlorinated solvents and other hydrocarbons, takes place rapidly and completely. Carbon is converted to carbon dioxide, hydrogen is converted to water, and other components of the hazardous hydrocarbon are converted to an oxidized state. No oxides of nitrogen are generated, however. These properties of supercritical water will be utilized in a process tailored to the needs of DOE-DP facilities.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 9/91

PROJECT STATUS: This is a new project that will demonstrate a waste technology developed by a HAZWRAP R&D project. A demonstration reactor has been designed, and procurement of component parts is under way. Relevant regulatory requirements are being monitored, although no permits appear to be needed at this time. Contact is being maintained with several private companies that have interests in development of this technology.

Table II. (Continued)

PROJECT TITLE: DEVELOPMENT OF A GAS CYLINDER DISPOSAL PLANT (PHASE IV)

LOCATION: Los Alamos National Laboratory
Los Alamos, New Mexico

PROJECT OBJECTIVE: To demonstrate a system for safely disposing of gas cylinders that are damaged or leaking or whose contents are unknown.

WASTE PROBLEM: Most DOE facilities urgently need a practical method of handling and disposing of the contents of leaking or damaged gas cylinders or cylinders whose contents are unknown. Current safety considerations and environmental regulations have made the past practices of cylinder disposal unacceptable.

TECHNOLOGY: Technology exists within the commercial sector for the recontainerization of the contents of leaking or damaged cylinders or of the unknown contents of a cylinder. Contracts will be placed for the design and fabrication of a mobile system to handle one cylinder at a time. The system under consideration consists of a pressure vessel into which the problem gas cylinder is placed. The pressure vessel can be purged with an inert gas or evacuated with a vacuum pump. After the atmosphere of the pressure vessel has been prepared, a hole is drilled into the side of the problem cylinder with a hydraulically driven, remotely controlled drill located within the pressure vessel. Contents of the cylinder are released into the pressure vessel where the gas can be sampled and identified. Once identified, the gas can be repacked into a new cylinder.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 9/91

PROJECT STATUS: This is a new project that will demonstrate technology developed by a HAZWRAP R&D project. Commercial gas cylinder recontainerization, treatment, and disposing capabilities, both existing and under development, have been identified. Los Alamos is negotiating a contract for handling and disposal of these problem cylinders, which lend themselves to sampling and analysis and subsequent shipment to off-site treatment facilities. Existing recontainerization technology for unknown/unshippable cylinders has been determined to be available from two sources. Several issues related to procurement and testing of these technologies remain to be resolved.

Table I. Summary of FY 1989 Technology Demonstration Projects

TREATMENT/DISPOSAL OF HAZARDOUS AND MIXED WASTE

- Supercritical Water Oxidation, Phase IV (ALO/LANL) - Demonstration of certain hydrocarbon oxidation reactions in supercritical water for management of hazardous chemical wastes.
- Gas Cylinder Disposal Plant Development, Phase IV (ALO/LANL) - Demonstration of a process for the safe disposal of the contents of unidentified or damaged gas cylinders.
- Treatment/Disposal of Reactive Metals, Phase IV (CHO/ANL) - Demonstration of a spray-burning process for converting reactive metal wastes to a glass product suitable for land disposal.
- Lead Decontamination (IDO/INEL) - Demonstration of a melt-refining system to decontaminate lead.
- Plasma Centrifuge Reactor (IDO/INEL) - Demonstration of use of high-temperature plasma centrifuge reactor to melt and process entire drums of organic-contaminated soils.
- Hexone Tanks (RLO/WHC) - Demonstration of technologies for treatment and disposal of hazardous organic liquids containing radioactive materials and stored in two deteriorating underground tanks.

WASTE MINIMIZATION METHODS

- Substitution for Chlorinated Solvent Degreasers (ORO/Y-12) - Large-scale demonstration of the substitution of aqueous solvents for chlorinated hydrocarbons currently used, including demonstration of recycling methods for spent aqueous solvents.
- Waste Acid Detoxification/Reclamation, Phase IV (RLO/PNL) - Demonstration of processes that reduce the volume, quantity, and toxicity of metal-bearing waste acids generated from metal-finishing operations.
- Liquid Carbon Dioxide Cleaning (ALO/RFP) - Demonstration of a liquid carbon dioxide process for final cleaning of highly complex stainless steel weapons parts that cannot be cleaned with conventional aqueous methods.

STANDARDS/METHODS FOR SITE REMEDIATION/STABILIZATION/CLOSURE

- Trichloroethylene (TCE)-Contaminated Groundwater (ALO/KCP) - Demonstration of destruction of TCE contained in pumped groundwater by a hydrogen peroxide, ozone, ultraviolet (uv) light treatment system.
- Central Facilities Landfill-II (IDO/INEL) - Demonstration of technologies for nonintrusive locating and monitoring of buried hazardous wastes and for remediating localized hazardous waste contamination.
- Destruction of Volatile Organic Chemicals (VOCs) in Groundwater (ORO/ORNL) - Demonstration of several technologies for the destruction of VOCs contained in groundwater.
- Low-Level Waste Crib (116-B-6-1) (RLO/PNL) - Demonstration of in situ vitrification (ISV) technology to fix fission products and immobilize or destroy hazardous chemicals in soil at a mixed waste site.

Table I. (Continued)

STANDARDS/METHODS FOR SITE REMEDIATION/STABILIZATION/CLOSURE (Continued)

- <u>Gasoline Spill (SAN/LLNL)</u> - Demonstration of vacuum venting technology for recovering and processing gasoline constituents from soil and groundwater
- <u>Site 300 TCE Spill (SAN/LLNL)</u> - Demonstration of vacuum venting for the removal of TCE from soil and perched groundwater.
- <u>Groundwater Biological Treatment (RLO/PNL)</u> - Demonstration of groundwater biodenitrification and carbon tetrachloride biodegradation using indigenous organisms.
- <u>C&P Area Burning Rubble Pit (SRO/SRL)</u> - Demonstration of bioreclamation of soil and groundwater contaminated with chlorinated hydrocarbons using indigenous bacteria enhanced by vegetation.
- <u>Underground Tank Remediation by In Situ Vitrification (RLO/PNL)</u> - Demonstration of the applicability of the in situ vitrification (ISV) technology for vitrifying contaminated underground storage tanks in place.

IMPROVED BURIAL PRACTICES AND WASTE FORMS

- <u>Landfill Cap Verification (ALO/SNLA)</u> - Field and laboratory studies to observe and simulate fluid movement beneath a landfill cap; results will be used to validate a model.
- <u>Encapsulation Development - Phase IV (CHO/BNL)</u> - Investigation of encapsulation materials for potential application to hazardous waste disposal.

PATHWAYS ANALYSIS

- <u>In Situ Detection of Organics - Phase IV (SAN/LLNL)</u> - Development of remote fiber spectroscopy system for detecting and monitoring selected hazardous organic compounds.
- <u>Retardation Factors for VOCs (SAN/LLNL)</u> - Demonstration of method for determining VOC distribution coefficients and retardation factors from soil and water samples collected from monitoring wells.

Table II. (Continued)

PROJECT TITLE: TREATMENT/DISPOSAL OF REACTIVE METALS (PHASE IV)

LOCATION: Argonne National Laboratory
Argonne, Illinois

PROJECT OBJECTIVE: To demonstrate a spray-burning process for converting large quantities of reactive metal waste contaminated with radioactive materials into a glass product suitable for land disposal.

WASTE PROBLEM: Large quantities of waste sodium contaminated with radioactive isotopes of cesium, strontium, and sodium are stored at Idaho and at Hanford. It is estimated that approximately 530 tons is stored, and over 20 tons per year is produced at Hanford. Sodium is reactive with both water and oxygen and must be converted into other chemical forms before disposal.

TECHNOLOGY: The integrated glass formation system for disposal of reactive metal wastes will combine a spray-burn system for handling large quantities of reactive metal wastes, a glass-forming powder delivery system, and a cyclonic reactor to generate an appropriate glass product. The glass-forming powder delivery system and the cyclonic reactor, which were developed at Argonne, will be integrated with the spray-burn system available from a commercial vendor. The process will be demonstrated at the facility of a commercial vendor, who will be selected by the DOE procurement process. Successful completion of the demonstration at the vendor facility will be followed by an evaluation of the process at an appropriate waste sodium storage facility.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 9/91

PROJECT STATUS: This is a new project that will demonstrate technology developed by a HAZWRAP R&D project. Work progressed on the selection process for a subcontractor to perform the demonstration under the technical guidance of ANL. Intent to award a contract was published, and 20 commercial firms expressed interest in performing the demonstration. The Statement of Work and RFPs are being finalized and will be mailed to all potential bidders by July 1, 1989.

Table II (Continued)

PROJECT TITLE: RADIOACTIVE LEAD DECONTAMINATION DEMONSTRATION

LOCATION: Idaho National Engineering Laboratory
Idaho Falls, Idaho

PROJECT OBJECTIVE: To demonstrate melting/refining as a viable method for the decontamination of lead contaminated with radioactive material.

WASTE PROBLEM: Lead, in various forms, sizes, and shapes, has been used as shielding at virtually all DOE facilities dealing with radioactivity. This contaminated lead is subject to Environmental Protection Agency (EPA) regulations and cannot be disposed of through land burial. The only solution is to decontaminate the lead.

TECHNOLOGY: Bench-scale lead decontamination tests that involved beta/gamma surface contamination have been conducted at INEL with excellent results. This demonstration will use a 10-ton facility to melt/refine lead, in various forms and shapes, to reduce uranium contamination to levels that would permit release of lead for reuse or resale.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 6/90

PROJECT STATUS: This is a new demonstration project started in FY 1989. Necessary equipment and materials have been acquired for conducting small-scale refining tests in July 1989 on lead contaminated with both uranium and radioactive isotopes. Solidification tests will be conducted on the dross generated during these tests.

Table II (Continued)

PROJECT TITLE: PLASMA ARC FURNACE DEMONSTRATION

NOTE: This is a cooperative demonstration effort between the DOE HAZWRAP TD Program and the EPA Superfund Innovative Technology Evaluation (SITE) Program.

LOCATION: DOE Component Development Integration Facility (CDIF)
MSE, Inc.
Butte, Montana

PROJECT OBJECTIVE: To establish the efficacy of the Plasma Arc Furnace technology developed by Retech, Inc., Ukiah, California, to destroy the organic and immobilize the inorganic constituents of hazardous wastes. Phase 1 constitutes the SITE portion of the demonstration and will use soils from the Butte area that contain hazardous organic chemicals and tailings from the mining operations that contain various metals. Phase II constitutes the HAZWRAP portion and will utilize hazardous waste mixtures of interest to DOE.

TECHNOLOGY: This process destroys organic wastes and reduces the volume of inorganic wastes. Solid and liquid wastes are fed into a rotating reservoir within a centrifugal reactor. Wastes are indirectly heated by a plasma torch; the high temperatures achieved during this process volatilize liquid components of the waste and achieve high destruction efficiencies. Organic constituents are converted to carbon monoxide, hydrogen, and hydrochloric acid, and in some cases, to carbon dioxide and water. The volatilized components are captured and treated in a gas scrubber unit. The inorganic constituents of the waste (soils, metals, etc.) are converted to a vitrified mass.

PROJECT INITIATION: 10/88 PROJECT COMPLETION: 7/90

PROJECT STATUS: This is a new demonstration project started in FY 1989. Modifications at the CDIF to prepare a site for the plasma equipment have been completed. The components of the Retech Plasma Centrifuge Reactor were transported to Butte in June. Installation of the components of the reactor was completed in early October. Equipment shakedown testing is scheduled for late October. The DOE/EPA tests are scheduled to begin in December 1989.

Table II (Continued)

PROJECT TITLE: HEXONE TANK WASTE TREATMENT DEMONSTRATION

LOCATION: Hanford Reservation
Westinghouse Hanford Company
Richland, Washington

PROJECT OBJECTIVE: To demonstrate technology for the removal and disposal of organic solvents contaminated with radioactive material and contained in underground storage tanks (USTs).

WASTE PROBLEM: Two deteriorating USTs at the Hanford Reservation contain a total of 34,000 gal of a radioactively contaminated hazardous organic mixture, consisting of hexone, normal paraffin hydrocarbons, tributyl phosphate complexes, and water. To comply with both EPA and Nuclear Regulatory Commission regulations, this mixed waste must first be separated into two fractions that can be handled separately. Total radioactivity contained in the two tanks is estimated at 0.25 Ci of mixed fission products.

TECHNOLOGY: This remediation demonstration focuses on three technologies: (1) radioactive decontamination of the liquid through in situ steam stripping or distillation of the organics from the tanks, (2) destruction of the collected organics by incineration, and (3) solidification of the radioactive tars and residuals for subsequent disposal as solid radioactive mixed waste in a permitted area.

PROJECT INITIATION: 5/87 PROJECT COMPLETION: 12/90

PROJECT STATUS: Contents of both USTs have been sampled and analyzed. Pilot-scale tests to select the most efficient method for decontamination of the liquid were conducted; the process selected was distillation. Field-scale equipment has been designed, and fabrication is nearly complete. Five railroad tank cars have been acquired for temporary storage of the cleaned hexone before its incineration. Distillation activities are expected to begin in August 1989. The procurement process for hexone incineration services has started.

Table II (Continued)

PROJECT TITLE: CHLORINATED SOLVENT SUBSTITUTION AT THE Y-12 PLANT

LOCATION: Oak Ridge Y-12 Plant
Oak Ridge, Tennessee

PROJECT OBJECTIVE: To demonstrate the substitution of a nonhazardous degreasing process (using water and a detergent) for a process using a chlorinated solvent currently in use in maintenance operations.

WASTE PROBLEM: Some degreasing operations at the Y-12 Plant utilize a system that uses a chlorinated solvent (HydroSeal) plus freon in an ultrasonic bath. This solvent contains methylene chloride, which is an EPA-recognized carcinogen and which will also soon be covered under DOE Order 5480.10 (Carcinogen Control Program). Successful substitution will reduce chlorinated solvent disposal problems and also demonstrate compliance with waste minimization plans.

TECHNOLOGY: This demonstration will seek a process from the private sector that will replace the current process that uses a chlorinated solvent. Procurement, installation, and testing of the new process are major phases of the demonstration. This project will interface with the nationwide DOE-DP nuclear weapons complex chlorinated solvent substitution programs through established working committees.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 9/90

PROJECT STATUS: This is a new demonstration project started in FY 1989. Specifications and cost estimates are being prepared on the ultrasonic cleaning system that will be utilized in the demonstration. An outline was prepared and work begun on preparation of a report documenting work that has been conducted over the past several years at the Y-12 Plant on the replacement of chlorinated solvents. Involvement of project personnel with the DOE Chlorinated Hydrocarbon Solvents Coordinating Committee continues.

Table II (Continued)

PROJECT TITLE: WASTE ACID DETOXIFICATION AND RECLAMATION (PHASE IV)

LOCATION: Pacific Northwest Laboratory
Richland, Washington

PROJECT OBJECTIVE: To demonstrate processes that reduce the volume, quantity, and toxicity of metal-bearing waste acids generated from metal-finishing operations.

WASTE PROBLEM: Metal-finishing operations at DOE-DP facilities produce quantities of waste acids contaminated with radioactive materials. Detoxification and reclamation of these acids will produce an economic benefit in that the reclaimed acid can be recycled, and the amount of material for disposal is considerably reduced.

TECHNOLOGY: By using distillation, precipitation, and filtration processes, the following goals will be achieved: (1) principal metal ions such as Zr, Cu, and U will be removed from waste acid without reducing acid concentration; (2) the resulting rejuvenated acid will be recycled; (3) anions such as nitrates and fluorides as acid from wastes will be reclaimed by distillation with sulfuric acid; and (4) a residual sulfate waste with low concentrations of nitrates, heavy metals, and radionuclides will be produced.

PROJECT INITIATION: 12/38   PROJECT COMPLETION: 9/91

PROJECT STATUS: This is a new project that will demonstrate technology developed by a HAZWRAP R&D project. Precipitation and distillation were identified as the most feasible processes for reclaiming metals and recycling spent acids. Copper and zirconium were removed from actual spent acid streams with 85% recovery using oxalic acid and sodium fluoride, respectively. Vacuum distillation in a batch packed column demonstrated 80% recovery of acid and a 40% reduction in waste volume from a process stream containing uranium, nitric acid, and sulfuric acid. A 10 gal/h system has been designed, and construction will be completed this year. The system will test simulated spent acid streams from various DOE plants in FY 1990. The equipment will be transferred to an operating facility for on-site demonstration in FY 1991.

Table II. (Continued)

PROJECT TITLE: LIQUID CARBON DIOXIDE CLEANING

LOCATION: Rocky Flats Plant
Golden, Colorado

PROJECT OBJECTIVE: To demonstrate a liquid carbon dioxide cleaning process for final cleaning of complex stainless steel weapons parts that cannot be cleaned by conventional aqueous methods.

WASTE PROBLEM: In order to minimize the production of chlorinated hydrocarbon solvent wastes in weapons production activities, it is desired to development a suitable cleaning process using non-hazardous materials.

TECHNOLOGY: This process uses a flow of liquid carbon dioxide to dissolve and wash away organic contaminants from stainless steel components. The contaminants are initially disolved in the liquid carbon dioxide and later precipitated upon rarefaction of the solution by depressurization. The depressurized fluid is then scrubbed, repressurized, and recycled for reuse.

PROJECT INITIATION: 9/89   PROJECT COMPLETION: 6/91

PROJECT STATUS: This is a new demonstration started in September 1989. Steps are underway to procure the liquid carbon dioxide system.

Table II (Continued)

PROJECT TITLE: TRICHLOROETHYLENE-CONTAMINATED GROUNDWATER TREATMENT DEMONSTRATION

LOCATION: DOE Kansas City Plant
Allied-Signal Aerospace Company
Kansas City, Missouri

PROJECT OBJECTIVE: To demonstrate the destruction of chlorinated hydrocarbons contained in pumped groundwater by liquid-phase treatment with hydrogen peroxide, ozone, and uv radiation.

WASTE PROBLEM: This demonstration is being conducted on TCE-contaminated groundwater located below a tank farm at the DOE Kansas City Plant. The top of the water table lies 10 to 15 ft below the ground surface, and the zone extends downward to a depth of about 35 ft. TCE concentrations in the pumped groundwater reach several parts per million.

TECHNOLOGY: Groundwater is extracted through water recovery wells and is passed through a hydrogen peroxide, ozone, uv treatment system. The cleaned water is being discharged to the city sanitary sewer system.

PROJECT INITIATION: 5/88 PROJECT COMPLETION: 9/90

PROJECT STATUS: The treatment unit has been operational for approximately 12 months. To date, approximately 1.5 million gal of groundwater has been successfully treated. The uv/ozone treatment unit has been producing effluent water that meets all permitted discharge standards. Problems have been encountered, however, with iron and manganese oxidizing within the system and clogging the sparger tubes and coating the uv lamp sheaths. The manufacturer is currently working on the system and making modifications to increase the treatment efficiency and the ozone generation capability.

Table II (Continued)

PROJECT TITLE: CENTRAL FACILITIES LANDFILL-II REMEDIATION DEMONSTRATION

LOCATION: Idaho National Engineering Laboratory
Idaho Falls, Idaho

PROJECT OBJECTIVE: To demonstrate technology for the nonintrusive locating and monitoring of buried hazardous wastes and to investigate technology for the remediation of localized hazardous waste contamination.

WASTE PROBLEM: The Central Facilities Area (CFA) Landfill-II received various hazardous wastes over the period of operation from 1951 to 1982. The types of waste received include waste solvents contained in drums. The quantities of EPA hazardous waste are fairly well known, but the burial locations are not.

TECHNOLOGY: The objective of this project is to find new methods to identify and control localized contaminated areas rather than to remediate the entire landfill. The project includes three phases: (1) obtain site characterization information, (2) obtain and demonstrate technology for nonintrusive locating and monitoring of localized waste sites, and (3) obtain and demonstrate innovative localized remediation technology. Technology will be sought from the private sector through RFPs.

PROJECT INITIATION: 5/87 PROJECT COMPLETION: 9/90

PROJECT STATUS: The hydrogeological characterization of the site was completed. Six shallow monitoring wells were drilled and instrumented. Drilling problems were encountered in the two deep wells in the form of a heaving sand layer at 628 ft below land surface; completion of these wells was delayed. The RFP to private industry for technology applicable to this project was issued in December 1988 and the contract issued in June 1989. The survey technologies used included a variety of geophysical methods combined with a localized soil gas survey. The geophysical methods included magnetometry, electromagnetometry (EM), transient electromagnetometry (TEM), ground-penetrating radar (GPR), and complex resistivity. In addition, a field test of the Ultrasonic Ranging and Data System (USRADS) combined with a magnetometer and an EM31 terrain conductivity meter was conducted in June 1989 by ORNL. A report comparing the various survey technologies is being prepared.

Table II (Continued)

PROJECT TITLE: DESTRUCTION OF VOLATILE ORGANIC CHEMICALS IN GROUNDWATER

LOCATION: Oak Ridge National Laboratory
Oak Ridge, Tennessee

PROJECT OBJECTIVE: To demonstrate several of the most promising treatment methodologies available from the private sector for the removal or destruction of VOCs in groundwater.

WASTE PROBLEM: The presence of trace quantities of VOCs in groundwater at DOE facilities is a common and pervasive problem.

TECHNOLOGY: This project consists of the off-site demonstration, on a pilot scale, of several of the most promising treatment methodologies available from the private sector for the removal or destruction of VOCs in groundwaters from the Oak Ridge Reservation. Results should facilitate the comparison of the performance, capability, and costs of the selected methodologies.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 9/90

PROJECT STATUS: This is a new demonstration project started in FY 1989. A request for expressions of interest was issued to the private sector; responses were requested by the end of June 1989. A draft Statement of Work was prepared and is under review.

Table II (Continued)

PROJECT TITLE: LOW-LEVEL WASTE CRIB (116-B-6-1) REMEDIATION DEMONSTRATION

LOCATION: Pacific Northwest Laboratory
Richland, Washington

PROJECT OBJECTIVE: To demonstrate the most appropriate technology to "fix" fission products and immobilize or destroy hazardous chemicals in the soil at a mixed hazardous waste site.

WASTE PROBLEM: This low-level waste crib (116-B-6-1) received radioactive wastes from equipment decontamination from 1951 to 1968. In addition to fission products, this crib also contains sodium dichromate, sodium oxalate, and sodium sulfomate. The crib is approximately 14 by 18 ft.

TECHNOLOGY: Based upon preliminary site characterization information, the ISV process appears suitable for treatment and stabilization of this site. The ISV technology involves conversion of contaminated soil into a durable glass and crystalline waste form through melting by joule heating. An electric current is passed between electrodes placed in the soil, creating temperatures sufficient to melt the soil (about 1700°C) and to produce, upon cooling, a vitreous mass of relatively high strength and chemical integrity. The project will include (1) a remedial investigation to locate, identify, and quantify the contaminants present in the crib; (2) verification that the ISV technology is applicable to remediate the site; and (3) a demonstration of the ISV technology at the site.

PROJECT INITIATION: 2/88 PROJECT COMPLETION: 9/91

PROJECT STATUS: A GPR survey was performed to provide a more accurate determination of the location and depth of the crib and surrounding underground structures. Following this survey, boreholes were drilled into and adjacent to the crib to obtain soil samples for chemical and radionuclide characterization. Preliminary data indicate that the major part of the contamination is located just below the crib (at about 14 ft) and decreases to background at a depth of about 25 ft. An engineering scale ISV test was performed to verify that ISV is capable of vitrifying the contaminants, soil, and wooden timbers expected at the crib site; the results confirmed that ISV technology is applicable. Preparations are under way at the site, and the ISV system was moved onsite in September. Drilling of the water monitoring wells, required by EPA and the state, will begin in October.

Table II (Continued)

PROJECT TITLE: GASOLINE SPILL REMEDIATION DEMONSTRATION

LOCATION: Lawrence Livermore National Laboratory
Livermore, California

PROJECT OBJECTIVE: To demonstrate innovative in situ processing technology to remove and process organics (gasoline) from affected soil and groundwater for restoration of the quality of water in the affected water-bearing zones.

WASTE PROBLEM: This demonstration is being conducted on a reasonably well-defined spill of leaded gasoline that leaked from a UST over a period of several months in 1978 to 1979. Gasoline constituents penetrated to a depth of about 130 ft and expanded over a diameter of about 120 ft. Concentrations of the constituents of gasoline in the soil range from a few parts per billion to 80,000 ppb, depending upon depth. Concentrations in the groundwater are in the several-parts-per-billion range.

TECHNOLOGY: The demonstration will include mobilization and removal of gasoline constituents from soil, both water-saturated and water-unsaturated, to depths of 150 ft by use of an induced venting process. This process involves application of a partial vacuum created by a vacuum blower system connected to a venting well. The gas flow containing gasoline vapors, air, and water coming from the venting well will be processed through air strippers, with the organic vapors vented through a thermal oxidizer. To treat the water-saturated zones, the water table will be depressed by use of dewatering pumps at the base of the venting well. Induced venting will operate concurrently with the dewatering operation.

PROJECT INITIATION: 4/87 PROJECT COMPLETION: 9/90

PROJECT STATUS: A multiply completed extraction well was installed, and each of the five individually screened intervals in the unsaturated zone was tested for fuel hydrocarbon concentrations. A vacuum extraction system with thermal oxidizer was put into operation, with monitoring of vapor concentrations at the wellhead and after the oxidizer. Calculations based upon flow rates and hydrocarbon concentrations indicate that about 5000 gal of fuel has been removed through September 1989. This has been accomplished over an accumulated operation time of about 1400 hours. These operations demonstrated the effectiveness of vacuum extraction for removing fuel hydrocarbons from the unsaturated zone. Hydrocarbon concentrations in the uppermost zone (20 to 25 ft) declined significantly (from >2600 ppm to <50 ppm). Deeper zones have not shown significant decreases. Consequently, extractions in the recent months have been focused on zones 2 through 5.

Table II (Continued)

PROJECT TITLE: SITE 300 TRICHLOROETHYLENE SPILL REMEDIATION DEMONSTRATION

LOCATION: Lawrence Livermore National Laboratory
Livermore, California

PROJECT OBJECTIVE: To demonstrate the technique of induced vacuum venting for the removal of TCE from soil and perched groundwater.

WASTE PROBLEM: This demonstration is to be conducted on TCE leakage from a process system line that has contaminated a soil interval about 14 ft thick and about 25 ft below the surface. The lateral extent of the contamination covers an area about 300 ft in diameter. The lower portion of the contaminated soil lies in a perched water zone.

TECHNOLOGY: This project will demonstrate a process involving induced venting by applying vacuum to a series of wells completed and screened in the affected soil interval. The induced gas flow through the soil, created by the partial vacuum maintained on the well bore, will cause the trapped TCE to volatilize and move toward the well bore in an areal sweep process. Entrained TCE in the effluent air stream from the wells will be disposed of through surface-mounted processing equipment. The soil will be dewatered to near the bottom of the contaminated soil interval to expose the soil to the venting process.

PROJECT INITIATION: 5/88 PROJECT COMPLETION: 9/90

PROJECT STATUS: Two pilot remediation systems were constructed and installed at the Building 834 Complex. The systems consist of a dual-tank air sparging unit for extraction and treatment of groundwater and an induced vacuum unit for extraction and discharge of TCE vapors from the unsaturated zone. The first system was installed near the southern, downgradient end of the TCE plume. In 6.5 months of operation, about 20,000 gal of water was extracted. TCE concentrations in the extracted water have declined from 19 ppm (by weight) to about 0.2 ppm. TCE concentrations in the extracted vapors have declined from about 6 ppm (by volume) to about 2 ppm. The second system is installed near the center of the 834 Complex in the vicinity of the TCE leaks, where TCE concentrations in water range up to 400 ppm (by weight). About 4300 gal of water containing about 10 pounds of TCE has been extracted. Extracted vapors contain up to 730 ppm (by volume); about 500 pounds of TCE has been removed. Thus far, the project demonstrated that air sparging and induced vacuum extraction are effective methods to remove TCE from groundwater and from sparingly permeable soil and rock.

Table II (Continued)

PROJECT TITLE: GROUNDWATER BIOLOGICAL TREATMENT DEMONSTRATION

LOCATION: Pacific Northwest Laboratory
Richland, Washington

PROJECT OBJECTIVE: To demonstrate a biological process for the destruction of nitrates and organic contam[illegible] groundwater.

WASTE PROBLEM: Liquid wastes have been generated over the 40 years of Hanford site operations. Some of these liquid wastes that were discharged to the soil contained radioactive and hazardous chemicals as well as nitrates. Groundwater from the U1/U2 crib area contains nitrate in excess of 400 ppm and up to 600 ppb of carbon tetrachloride. This groundwater also contains uranium and other heavy metals.

TECHNOLOGY: This project will demonstrate technology to destroy nitrates and specific organic contaminants in groundwater using facultative anaerobic microorganisms. Laboratory tests have been conducted using microorganisms capable of simultaneous destruction of both nitrates and carbon tetrachloride. Tests will be conducted using a pilot-scale bioreactor system, developed in FY 1988 for another project, first on simulated groundwater and then on actual groundwater at the U1/U2 crib area.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 3/91

PROJECT STATUS: This is a new technology demonstration project started in FY 1989. Initial tests with simulated groundwater (nonradioactive) are partially complete. Tests are being performed with a pilot-scale bioreactor system consisting of a bioreactor, clarifier, feed tanks, and associated control and monitoring equipment. Denitrification tests were completed in April 1989, and the results demonstrated that the system could be operated at feed rates exceeding design while producing an effluent nitrate concentration below drinking water standards. Carbon tetrachloride destruction tests were initiated in May 1989. These tests using simulated groundwater will continue through FY 1989; tests with groundwater from the U1/U2 crib site will begin in FY 1990.

Table II (Continued)

PROJECT TITLE: C&P AREA BURNING RUBBLE PIT BIORECLAMATION PROJECT

LOCATION: Savannah River Site
Aiken, South Carolina

PROJECT OBJECTIVE: To develop and implement an environmental project for demonstrating/evaluating the potential of in situ bioreclamation for cleanup of shallow subsurface contamination and bioreactor bioreclamation of deep subsurface contamination resulting from disposal of chlorinated hydrocarbons in an unlined waste disposal facility.

WASTE PROBLEM: Disposal of liquid chemical wastes in the past consisted of discharge and/or burning in small, shallow, unlined basins. Over the period from 1956 to 1974, burning rubble pits at the Savannah River Plant were used in this manner. The soil (at a depth of 1.5 ft) has detectable amounts of perchloroethylene (PCE) and TCE at levels of 44.8 and 5.5 micrograms per gram of soil, respectively; the groundwater contains these same contaminants at much lower levels.

TECHNOLOGY: The first subtask is a demonstration of in situ bioreclamation of contaminated soil using microorganisms enhanced by vegetation. Indigenous bacteria have been isolated that aerobically degrade chlorinated alkenes and alkanes to carbon dioxide, hydrochloric acid, and water. These microorganisms will be selectively enhanced in subsurface soils by planting and cultivating certain types of vegetation. The second subtask is a demonstration of bioreclamation of contaminated groundwater using a bioreactor containing indigenous bacteria.

PROJECT INITIATION: 2/88 PROJECT COMPLETION: 9/91

PROJECT STATUS: Soil samples and plants were taken from the site to set up laboratory vegetation microcosm studies. The soil samples were characterized for particle size distribution, nutrient content, and cation exchange capacity. Rhizosphere and edaphosphere soils were collected so that microbial degradation of PCE could be evaluated. Live plants from the site were transferred to greenhouses for study. Laboratory studies are continuing with a new series of bioreactor tests.

Table II (Continued)

PROJECT TITLE: UNDERGROUND TANK REMEDIATION BY IN SITU VITRIFICATION

LOCATION: Pacific Northwest Laboratory
Richland, Washington

PROJECT OBJECTIVE: To demonstrate the applicability of the in situ vitrification (ISV) technology for the in place remediation of abandoned underground storage tanks previously used for storage of hazardous and mixed wastes.

WASTE PROBLEM: Many underground storage tanks contaminated with radioactive or mixed wastes exist at a number of DOE DP facilities and now require remediation. Current options, including (1) retrieval, treatment, and disposal of tank residues, (2) exhumation, decontamination, and disposal of the tank itself, and (3) treatment and disposal of the soil contaminated by tank leaks, are projected to be exceptionally costly. Lower cost, acceptable alternatives are needed.

TECHNOLOGY: The ISV technology involves conversion of contaminated soils/solid material into a durable crystalline/metallic form through melting by joule heating. An electric current is passed between electrodes placed in the soil and the tank, creating temperatures sufficient to melt the soil and metallic solids and to produce, upon cooling, a vitrified mass of relatively high strength and chemical integrity.

PROJECT INITIATION: 8/89 PROJECT COMPLETION: 9/92

PROJECT STATUS: This is a new project initiated in August 1989. The first task of the project involved the subsurface melting of a small, instrumented, steel cylinder (10" dia by 13" long) encased in concrete (1.5" thick), and containing surrogate sludge traced with radioactivity. This test was accomplished in mid-September and the vitrified mass was excavated in late September. All of the tank sludge contents seemed to have been vitrified and incorporated into the melt; no detectable radioactivity was found in the surrounding soil. A larger instrumented tank will be vitrified early in 1990.

Table II (Continued)

PROJECT TITLE: LANDFILL CAP VERIFICATION DEMONSTRATION

LOCATION: Sandia National Laboratories
Albuquerque, New Mexico

PROJECT OBJECTIVE: To investigate the performance of an impermeable composite-cap closure of a chemical waste landfill in the mitigation of contaminant migration in the vadose zone resulting from water infiltration.

WASTE PROBLEM: This demonstration is to be conducted on an unlined landfill used for shallow burial of a variety of wastes. This landfill will be capped for closure with funds from other sources in FY 1990. The landfill is situated in unsaturated alluvium (primarily sand and gravel) about 500 ft above the water table. Hazardous wastes contained at this site include mineral acids, oxidizing and reducing agents, organic compounds, metals, inorganic salts, and chromic acid in concentrations up to several hundred parts per million in near-surface soil. This landfill was in operation from 1962 until 1980.

TECHNOLOGY: The demonstration consists of a field test of the effectiveness of the cap method by direct measurement of water infiltration adjacent to and beneath the cap. Measurements include moisture content, soil moisture tension, and permeability. Complementary laboratory measurements include soil moisture retention and moisture flow experiments.

PROJECT INITIATION: 12/88 PROJECT COMPLETION: 9/90

PROJECT STATUS: This is a new demonstration project started in FY 1989. Primary activities were the collection of all available data on the landfill site and the development of new data on surface sediments and geological features. A laboratory permeameter was constructed and tested for the determination of saturated hydraulic conductivity on samples collected at the site. Neutron probes for in situ moisture determination were acquired, and field testing is under way. Construction of tensiometers and thermocouple psychrometers for in situ determination of capillary pressure head is under way. A location adjacent to the landfill was established as a site for development, field testing, and calibration of instruments.

Table II (Continued)

PROJECT TITLE: ENCAPSULATION DEVELOPMENT - PHASE IV

LOCATION: Brookhaven National Laboratory
Upton, Long Island, New York

PROGRAM OBJECTIVE: To demonstrate the application of encapsulation materials and technology developed in the HAZWRAP R&D Program for the treatment of selected hazardous chemical wastes.

WASTE PROBLEM: Many of the DOE-DP plants and laboratories produce hazardous chemical and mixed waste streams. Disposal of these stored wastes is a problem common to the DOE-DP complex.

TECHNOLOGY: Specific wastes, such as incinerator ash, sludges, and toxic metals, have been selected as potential candidates for application of new or improved encapsulation materials that are not currently being used for the encapsulation of radioactive and/or hazardous waste materials. These encapsulation materials include polyethylene, sulfur cement, and polyester-styrene.

PROJECT INITIATION: 1/89 PROJECT COMPLETION: 9/92

PROJECT STATUS: This is a new project started in FY 1989 to demonstrate technology developed in the HAZWRAP R&D Program. The feasibility of using polyethylene as a solidification agent for nitrate salt wastes has been demonstrated on a bench-scale. High volumetric efficiencies (70 wt%) were obtained using a single screw-type extruder at 120° C. The EPA Extraction Procedure test indicated that the nitrate release from this encapsulated form was an order of magnitude lower than the regulatory limit for drinking water standards. Confirmatory work is currently under way using actual nitrate salt waste from the DOE Rocky Flats Plant. Planning for the demonstration activity is under way.

Table II (Continued)

PROJECT TITLE: IN SITU DETECTION OF ORGANICS - PHASE IV

LOCATION: Lawrence Livermore National Laboratory
Livermore, California

PROJECT OBJECTIVE: To demonstrate the application of a fiber-optic-based system for monitoring contaminant species in groundwater. Development of optrodes (optical chemical sensors) chemistries for detecting TCE and chloroform was carried out in the HAZWRAP R&D Program.

WASTE PROBLEM: The problem of monitoring groundwater at multiple in situ locations for selected hazardous organic compounds with remote instrumentation exists at most DOE-DP sites.

TECHNOLOGY: Optical chemical sensors have been developed that are compatible with optical fiber spectrometers. Optrodes have been developed that are selective for TCE in the presence of chloroform. The instrumental system will be demonstrated under field conditions with actual waste streams and in underground water locations.

PROJECT INITIATION: 1/89 PROJECT COMPLETION: 9/92

PROJECT STATUS: This is a new project started in FY 1989 to demonstrate technology developed in the HAZWRAP R&D Program. Much of the work has involved planning the project, obtaining and modifying equipment for field use, and calibrating optrodes. Several cabled optrodes have been fabricated and are ready for field application. Most of the low-level (below 1 ppm) calibrations are completed, and higher level (above 1 ppm) calibrations have been started.

Table II (Continued)

PROJECT TITLE: FIELD-BASED MEASUREMENT OF RETARDATION FACTORS

LOCATION: Lawrence Livermore National Laboratory
Livermore, California

PROJECT OBJECTIVE: To demonstrate field-based measurement techniques for determining the distribution of solutes between solid and liquid phases in a heterogeneous geological setting. Methods will be developed to incorporate the spatial variability of the field-measured distribution into predictive modeling of the rate of plum movement, extent of site contamination, and the effectiveness of remedial processes.

WASTE PROBLEM: There is a need for improved models for use in predicting plume movement/distribution in geologic formations.

TECHNOLOGY: Analytical data will be derived from the numerous monitoring and extraction wells being installed at LLNL. These data will be used to improve the accuracy of the retardation factors currently used in various models used to predict movement of contaminants in underground geologic formations.

PROJECT INITIATION: 1/89 PROJECT COMPLETION: 9/90

PROJECT STATUS: This is a new technology demonstration project started in FY 1989. An algorithm was developed to calculate the field-based retardation factors. Sensitivity analyses were done involving parameters such as bulk soil density, skeletal density, and distribution coefficient to quantitatively establish the degree of accuracy needed in individual parameters to ensure desired accuracy in the final retardation factors. Comparison of solid structure determinations were performed on LLNL soils to evaluate such methods as wet weight/dry weight analyses, mercury porosimetry, dry gas pycnometry, and fluid volume displacement. Comparisons of VOC extraction techniques used during EPA Method 8010/8020 analysis have begun to identify methods that yield the best estimate of total VOCs in well core samples. Procedures were examined to improve field and laboratory handling of saturated core samples to minimize loss of VOCs.

Table III. Acronyms Relating to DOE Operations Offices and DOE Laboratories and Plants

ALO = Albuquerque Operations Office, Albuquerque, New Mexico
ANL = Argonne National Laboratory, Chicago, Illinois
BNL = Brookhaven National Laboratory, Upton, Long Island, New York
CHO = Chicago Operations Office, Chicago, Illinois
IDO = Idaho Operations Office, Idaho Fall, Idaho
INEL = Idaho National Engineering Laboratory, Idaho Falls, Idaho
KCP = DOE Kansas City Plant, Kansas City, Missouri
LANL = Los Alamos National Laboratory, Los Alamos, New Mexico
LLNL = Lawrence Livermore National Laboratory, Livermore, California
ORO = Oak Ridge Operations Office, Oak Ridge, Tennessee
ORNL = Oak Ridge National Laboratory, Oak Ridge, Tennessee
PNL = Pacific Northwest Laboratories, Richland, Washington
RFP = Rocky Flats Plant, Golden, Colorado
RLO = Richland Operations Office, Richland, Washington
SAN = San Francisco Operations Office, San Francisco, California
SRL = Savannah River Laboratory, Aiken, South Carolina
SNLA = Sandia National Laboratory-Albuquerque, Albuquerque, New Mexico
SRO = Savannah River Operations Office, Aiken, South Carolina
WHC = Westinghouse Hanford Company
Y-12 = DOE Y-12 Plant, Oak Ridge, Tennessee

ASSESSING THE IMPACT OF HAZARDOUS WASTE DISPOSAL SITES ON THE ENVIRONMENT: CASE STUDIES OF ECOLOGICAL RISK ASSESSMENTS AT SELECTED NAVY HAZARDOUS WASTE DISPOSAL SITES[#]

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ABSTRACT

The current status of ecological risk assessments being conducted for hazardous waste disposal sites located at Naval Air Station (NAS) Whidbey Island, WA, and Naval Construction Battalion Center (NCBC) Davisville, RI, are reported. The sites being investigated at NAS Whidbey Island include a fire fighting training area, a pesticide disposal site, and the air station's runway ditches. Toxicological impacts are being evaluated using starling (*Sturnus vulgaris*) nesting and reproductive biology as an indication of contaminant migration into the food chain. Toxicological impacts are also being monitored in small mammals, hawks, owls, herons, and selected prey species located on or near the hazardous waste disposal sites.

The sites being investigated at NCBC Davisville are a landfill and disposal site located directly adjacent to Allen Harbor and Narragansett Bay. Ecological impacts are being assessed by characterizing the sediment and water quality in Allen Harbor and nearby Narragansett Bay and evaluating the toxicological impact on quahog clams (*Mercenaria mercenaria*), soft shell clams (*Mya arenaria*), oysters (*Crassostrea virginica*), mussels (*Mytilus edulis*), and amphipods (*Ampelisca abdita*). In addition, biomarker assays are being conducted to evaluate the mutagenic potential of sediments collected from Allen Harbor and the surrounding Narragansett Bay.

The sampling designs and rationale being used for the investigations at NCBC Davisville and NAS Whidbey Island are presented. The procedures for incorporating the toxicology data into the remedial investigation and feasibility study process, and supporting the development of risk management plans are also discussed.

[#] Paper presented at the 14th Annual Army Environmental R&D Symposium, 14-16 November 1989, Williamsburg, Va

INTRODUCTION

Remedial actions conducted at hazardous waste disposal sites must meet cleanup levels that will insure protection of human health and the environment (Comprehensive Environmental Response Compensation and Liability Act, 42 U.S.C. 9604 (a)). The development and application of biological assessment methods to determine the impact of disposal sites on the environment is the focus of the research described in this paper. Biological assessment techniques are required to provide the data necessary to conduct ecological risk assessments of the impact of disposal sites on the surrounding environment. Ecological risk assessment involves quantitative estimation of the likelihood of adverse ecological impact resulting from exposure to toxic substances (Beck and Conner 1987). Ecological risk assessments are accomplished by collecting data relating exposure levels to biological effects (Gentile et al. 1989) and provide a framework for interpreting and predicting potential adverse impacts (Phelps and Beck 1989). With appropriate assessment techniques it will be possible to obtain direct measures of environmental health and implement monitoring programs to assess and verify the environmental risks of hazardous waste disposal sites.

Demonstrations of biological assessments aimed at assessing the ecological risk of hazardous waste disposal sites are currently being conducted at the Naval Air Station (NAS) Whidbey Island, Washington, and the Naval Construction Battalion Center (NCBC) Davisville, Rhode Island. At NAS Whidbey Island the impacts of three disposal sites on wildlife and the surrounding environment are being evaluated. The sites being investigated are a former fire school, a pesticide disposal area and the runway ditches. At NCBC Davisville a landfill and disposal area located directly adjacent to Allen Harbor in Narragansett Bay are being investigated to determine the impact of leachate from the disposal sites on shellfish and sediment quality of Narragansett Bay.

The toxicological assessment for NAS Whidbey Island is being performed by The Institute of Wildlife and Environmental Toxicology (TIWET), from Clemson University, Clemson, SC, in cooperation with Huxley College of Environmental Studies, Western Washington University, Bellingham, WA. The risk assessment at NCBC Davisville is being executed under a cooperative research agreement between the Naval Ocean Systems Center, San Diego, CA, and the Environmental Protection Agency Environmental Research Laboratory, Narragansett, RI, with the cooperation and assistance of the Narragansett Bay Project, Providence, RI, the Food and Drug Administration Northeast Technical Services Unit, Davisville, RI, and the University of Rhode Island Graduate School of Oceanography, Narragansett, RI.

RELATIONSHIP OF TOXICITY ASSESSMENTS TO THE REMEDIAL INVESTIGATION PROCESS

The relationship of toxicity assessments to the remedial investigation and feasibility study (RI/FS) process at hazardous waste sites is outlined in Figure 1 (Johnston and Lapota 1989, Lapota et al. 1989). The RI/FS can consist of three phases: information gathering, verification and evaluation of site conditions, and, if required, remediation. Onsite investigations carried out in accordance with EPA Superfund Guidance (EPA 1986) are primarily concerned with quantifying site contamination levels, and relating those levels to potential health risks. The objective of the toxicology studies described in this paper is to determine the toxicological impact of the disposal site on the surrounding environment.

During the toxicology study data are collected to determine exposure levels and the consequences of exposure to receptor organisms. The toxicology study seeks to answer the question: Is there a toxicological impact? If the answer is no, the goal for the second phase of the toxicology study is to confirm the nonimpact and provide monitoring data necessary for site closure. However, if significant toxicological impacts are detected then the goal of the second phase will be to provide a detailed evaluation of the impact. This information will be necessary to determine what corrective action is required and evaluate toxicity reduction during feasibility studies of remedial options. If remediation is required, the toxicity data will be used to measure the effectiveness of cleanup and help determine when remediation can be terminated. Interaction between the toxicology and onsite investigations is required to assure that the data collected are complementary and comparable. Obtaining complementary and comparable data can be accomplished by intercalibrating analytical methods to be used (A in Figure 1), providing significant information feedback to facilitate an accurate description of toxicological effects and contaminant source and loading (B and C in Figure 1), and the selection of appropriate cleanup levels (D in Figure 1) (Johnston and Lapota 1989, Lapota et al. 1989).

DESCRIPTIONS OF SITE INVESTIGATIONS

Toxicology Demonstration Project at NAS Whidbey Island, WA

The Naval Air Station (NAS) Whidbey Island has been proposed for addition to the National Priorities List (NPL). Twenty eight sites have been recommended for investigation as part of the Navy's Installation Restoration Program (NEESA 1984a, SCS Engineers 1987). NAS Whidbey Island is located in a fairly pristine area of the Puget Sound and provides habitat for a variety of game birds, water fowl, and mammals. The endangered peregrine falcon and the threatened bald eagle have been sighted in areas on NAS Whidbey Island and a great blue heron colony is also located on the air station. Beaches and bays around NAS

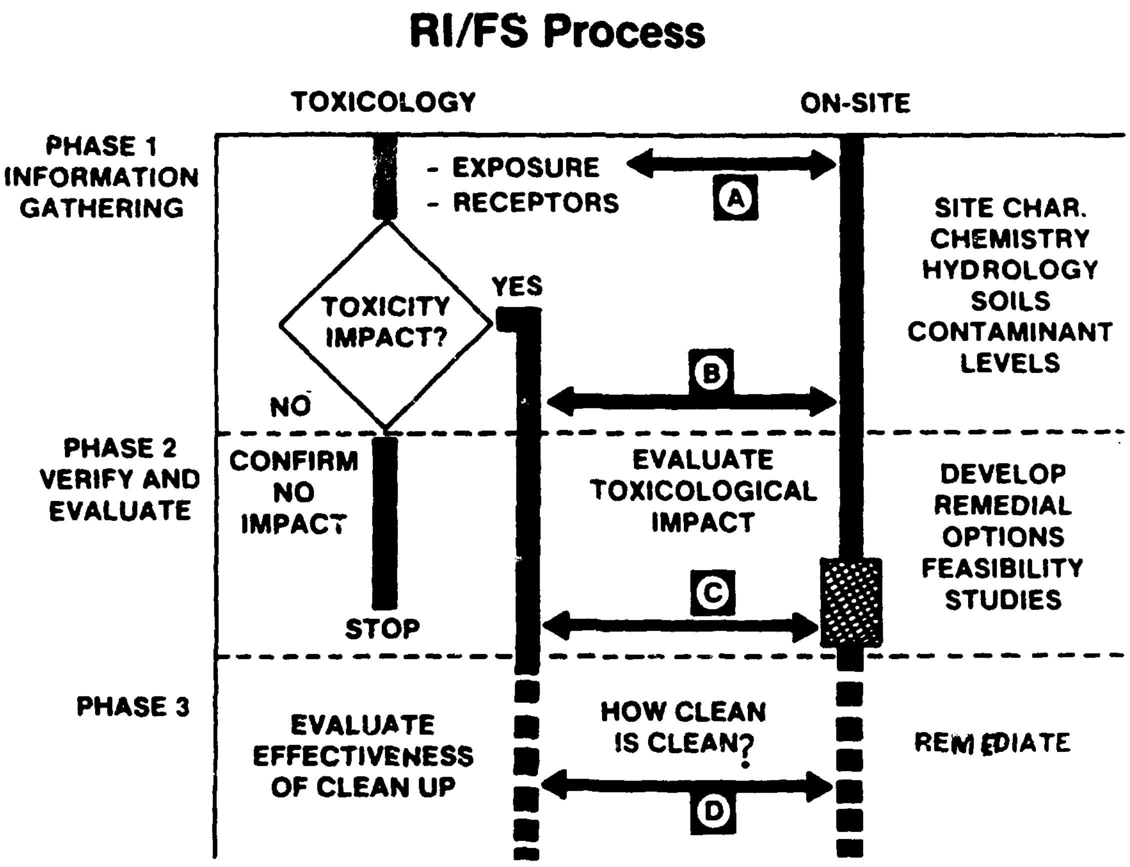

Figure 1. Integration of toxicological assessment information into the Remedial Investigation and Feasibility Study (RI/FS) process (Johnston and Lapota 1989).

Whidbey Island are popular fishing and shellfish gathering areas. Past disposal practices may have contaminated lowland areas and the accumulation of persistent and biomagnifying contaminants could affect higher order predators and humans (NEESA 1984a). The primary purpose of the toxicological investigation is to determine if contaminants from disposal sites are significantly impacting wildlife and degrading environmental quality. The study will also demonstrate the effectiveness of in situ toxicological assessment techniques.

The sites selected for toxicological assessment are the Clover Valley Fire School, the Pesticide Disposal Area, and the Runway Ditches. These sites were selected for evaluation based on the possible presence of surface contamination and concern for migration of contaminants into the food chain (TIWET 1989).

The contaminants of concern at the Clover Valley Fire School include aromatic hydrocarbons and heavy metals released when waste oils were burned during fire fighting training exercises conducted between 1951 and 1966. An estimated 50,000 to 75,000 gallons of waste fuels contaminated with solvents, oils, and paint strippers were burned and disposed of at the fire school (NEESA 1984a). The Pesticide Disposal Area was used for rinsing equipment used during insecticide and herbicide applications. During the period between 1973 and 1983 a variety of pesticides, including 2,4D, malathion, and chlordane were disposed in a dry well located at the site (NEESA 1984a). The network of ditches around the air station's runways comprises the third site being investigated. The ditches run south and east of the runway and collect runoff from the flight line as well as from storm sewers near the hangar operations area, and eventually discharge into a marshy area around Dugualla Bay in the Puget Sound. Since 1965 jet fuels, waste cleaning solvents, caustic agents, motor oils, paints, and paint thinners have been periodically spilled around the air station's flight line and hangars and washed into the runway ditches (NEESA 1984)..

The approach of the toxicological investigation of impacts from the disposal sites is designed to assess the extent and nature of possible contamination using free-living species residing on the sites of interest (TIWET 1989). Assessments of reproductive success and biochemical function are being made between populations sampled on the disposal sites and populations sampled from sites which have no known history of contamination. To accomplish this goal several parallel lines of inquiry among different animal species are being conducted. Additionally, organic chemical analyses of soil and invertebrates will be conducted to determine which contaminants are likely to be incorporated into the food chain.

Food chains are frequent pathways for environmental contaminants to penetrate into biological communities. Numerous studies from both agricultural (Anderson et al. 1982, Telford et al. 1982, Stoewsand et al. 1986) and natural settings (Cooke 1973, Rudd et al. 1981) have demonstrated extensive contamination from anthropogenic sources.

A representation of a simplified food web, emphasizing the monitored species is shown in Figure 2. This generalized figure shows the complexity of the ecosystem at NAS Whidbey Island. Plants may accumulate soil contaminants and expose herbivorous insects (e.g., grasshoppers) and mammals (e.g., voles), and omnivorous mammals (e.g., mice), which in turn will expose animals feeding on higher levels of the food web. The primary route of exposure is being assessed with the European starling (Sturnus vulgaris). Starlings feed on carnivorous insects, herbaceous insects, grubs, earthworms, and larvae of various insects which may be living in close association with the soil. Many of the latter organisms are particularly important as detritivore-decomposer organisms. Plant materials become important food sources on a seasonal basis (Feare 1984). Consequently, starlings may be exposed to a wide array of contaminants in the grazing (e.g., grasshoppers, catepillars) and detritivore food chains (e.g., earthworms). Other possible routes of exposure are being assessed by evaluating toxicological impacts on small mammals, primarily mice, voles and shrews, and birds of prey, such as the northern harrier (Circus cyaneus) and great blue heron (Ardea herodias).

The primary investigatory tool used at the Clover Valley Fire School and the Pesticide Disposal Area is the enhanced avian bioassay. The starling presents numerous advantages as an indicator wildlife species. In general, birds possess characteristics which tend to maximize their exposure to *environmental contaminants*. First, birds possess high metabolic rates with attendant elevated food intake rates. Secondly, their complex air sac respiration system (Fedde 1976) is structurally unique and maximizes inhalation exposure. Finally, birds frequently dust bathe and use surface water for bathing. Behaviors such as these would likely result in increased dermal exposures through contact with contaminated soils and surface water.

The starling is an introduced species which is abundant throughout most of North America (Robbins et al. 1983) and is frequently considered a pest. Starlings are easily induced to nest in artificial nest boxes (Figure 3) facilitating experimental manipulations and assuring investigators of a viable experimental population to work with (Robinson et al. 1988). Starlings usually feed within 200 m of their nest site (Feare 1984) and frequently feed closer if resources allow (Tinbergen 1981). Thus starlings should forage a substantial amount of time within the confines of the study sites. At nesting time the parents may have difficulty maintaining a positive energy balance when striving to feed their offspring. At this crucial juncture starlings are representative of most songbirds. Starlings have proven to be excellent research subjects in field studies exploring the effect of organophosphorus pesticides on wildlife (Robinson et al. 1988). The USEPA has recently issued a guidance document for starling nest box studies for use in determining

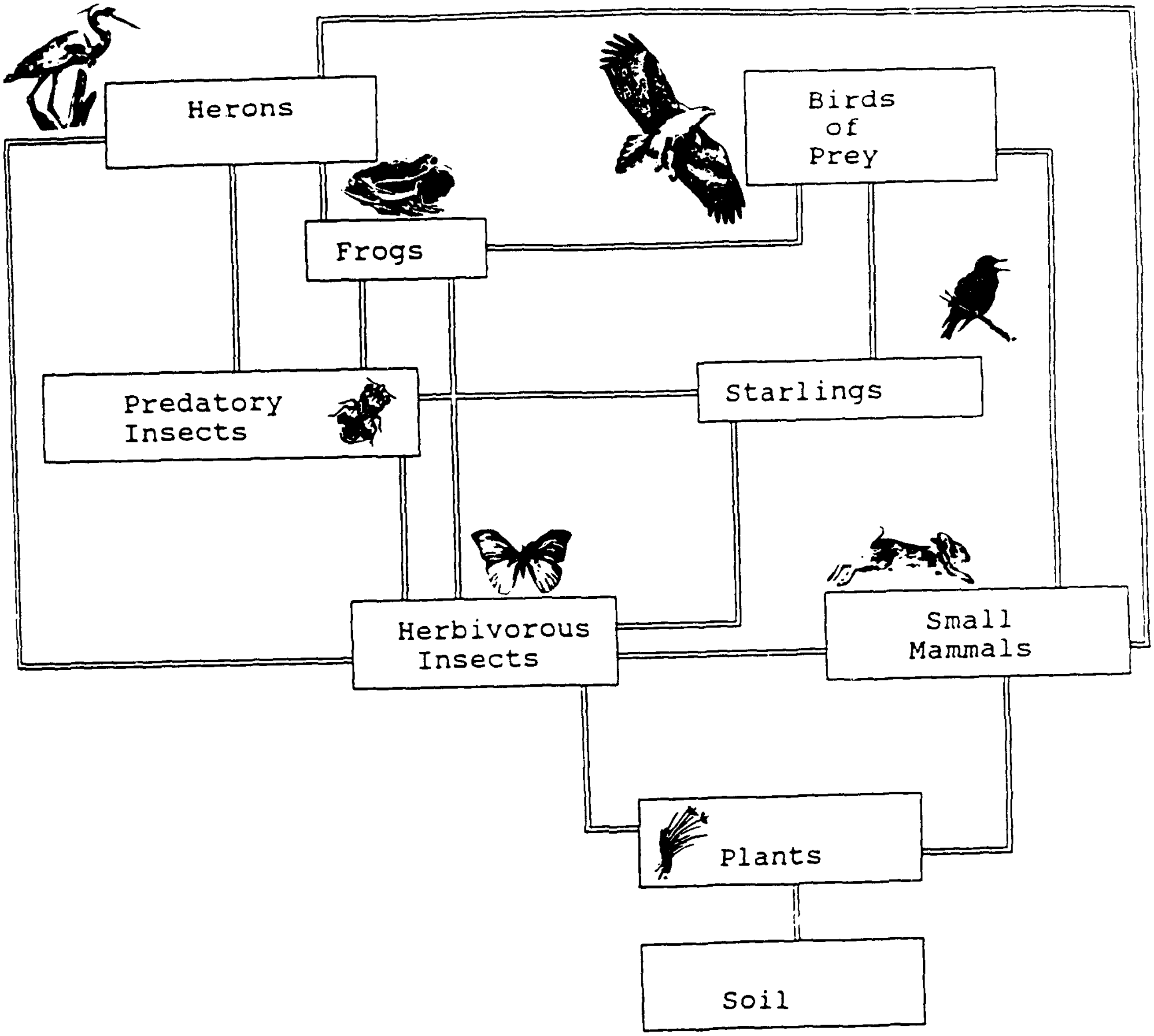

Figure 2. A diagram illustrating a simplified food web for NAS Whidbey Island. The soil compartment represents both the physical components of the soil and decomposer organisms such as earthworms. This extremely important component connects with virtually every other compartment. The small mammal compartment includes both herbivorous (e.g., voles) and carnivorous species (e.g., shrews). The birds of prey compartment contains both diurnal and nocturnal species (TIWET 1989).

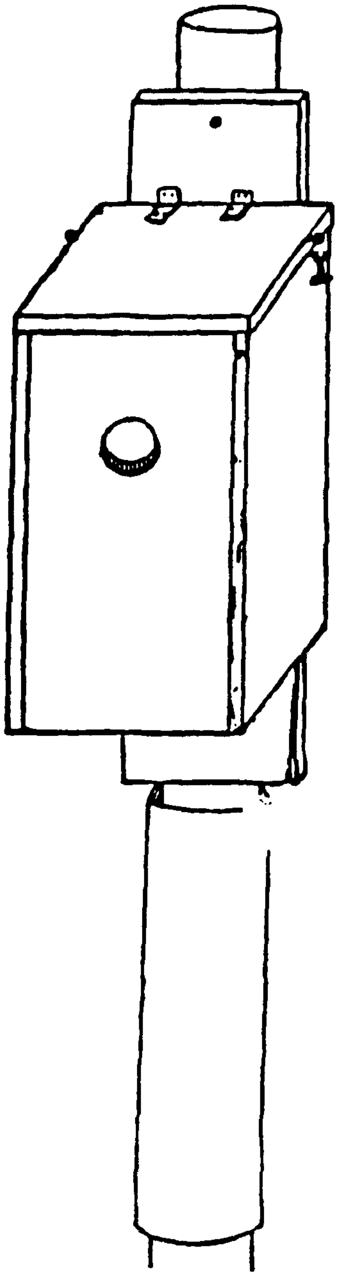

Figure 3. Nest box design used in the enhanced starling bioassay (IWT 1988).

effects of pesticides on nontarget organisms in agricultural settings (IWT 1989). The study at NAS Whidbey Island is the first use of the starling bioassay for assessing impacts of hazardous waste disposal sites.

Starling nest boxes have been erected at the Clover Valley Fire School and the Pesticide Disposal Area (Figure 4). An exposure gradient was created by placing the nest boxes in transects radiating out from the focal point of contamination in concentric rings. Starlings defend a territory which is normally less than 0.5 m in diameter around the nest hole (Kessel 1957), but on occasion the defended area extends to 10.0 m (Feare 1984), especially just before egg-laying. Therefore nest boxes on all sites were spaced a minimum of 12 meters apart (Figure 4) to reduce the possibility of intraspecific conflict. Statistical analyses of ecological endpoints such as clutch size, hatching success and fledging success will be conducted to determine differences along the exposure transects and differences between the disposal sites and three references sites located in Western Washington (TIWET 1989).

Based on past studies (Whitten et al. 1989, Robinson 1988, Brewer et al. 1988, 1989) up to 80% occupancy can be expected, with an average of four nestlings per box. During the first year of the study high occupancy was not achieved because nest boxes were erected too late in the season. In order to determine what food items adults starlings are feeding to nestlings, approximately 10% of the active boxes on each site were sampled for invertebrate prey items by taking crop samples. Crop sampling involves placing a restrictive ligature about the throat of the nestling. The ligature is tight enough to prevent swallowing but loose enough to avoid injuring the nestling. Ligatures are left in place for a short period of time (maximum one hour) and the food items are collected and analyzed for species composition and tissue burdens of contaminants in the juveniles' diet. Since post-fledging survival is key to parental reproductive success and the long-term survival of songbird populations, a subsample of juvenile hatchlings were banded before fledging. If there is no effect of the study sites on fledging survival and subsequent behavior, then return rates should be equal to those at the reference sites.

Small mammals have also been shown to be excellent indicator organisms in field studies of various contaminants (e.g., Anderson and Barrett 1982, Maly and Barrett 1984, Barrett 1988, Hall et al. 1989). Small mammals such as mice and shrews, live on the soil surface and some species burrow within the litter and upper levels of the soil itself, thereby maximizing chances of dermal exposure. Their diet is varied, and ranges from nearly strict herbivory (e.g., some voles, *Microtus* spp.) to an omnivorous (e.g., deer mice, *Peromyscus maniculatus*) and completely carnivorous condition (e.g., the shrews, Soricidae). Studies of small mammals were initiated on all three sites during spring and summer of 1989.

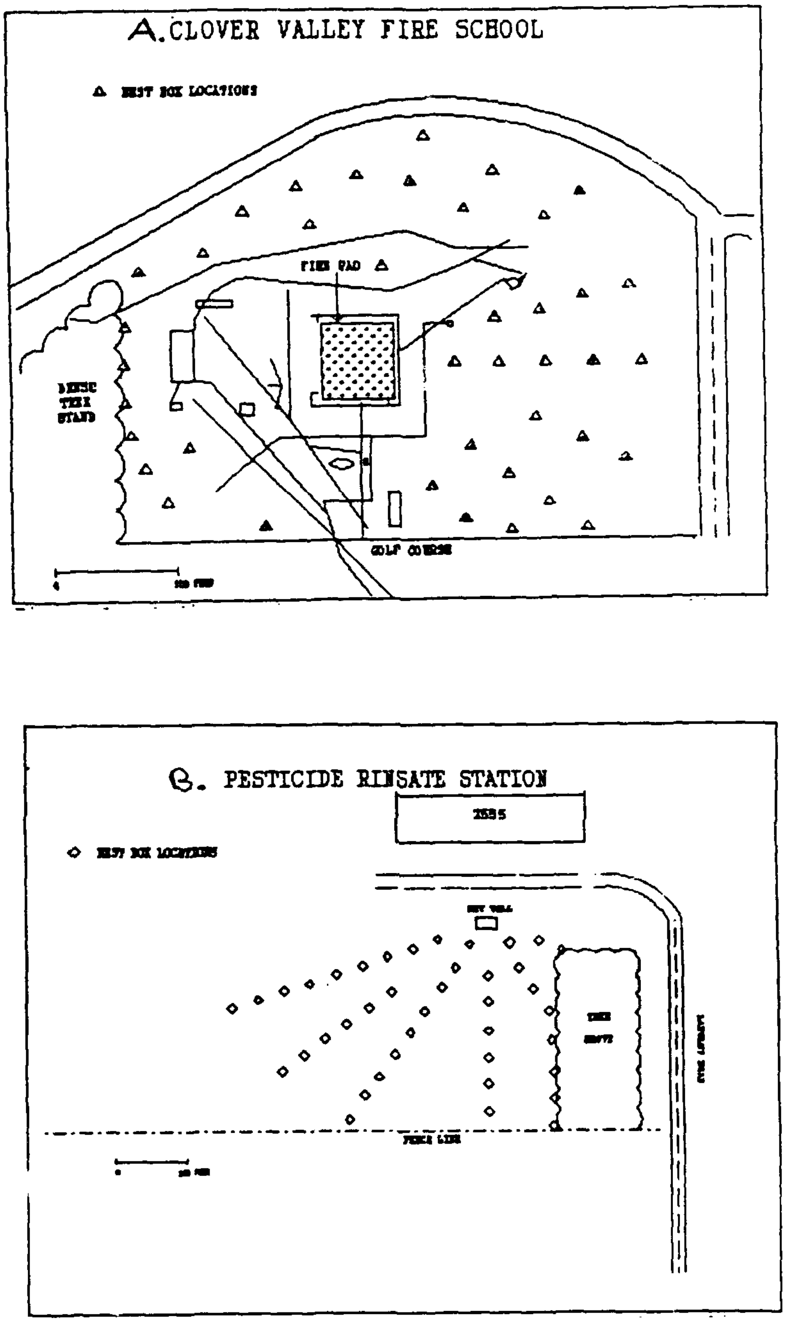

Figure 4. A digram illustrating the placement of starling nest boxes at the Clover Valley Fire School (A) and the Pesticide Disposal Area (B) (TIWET 1989).

Raptors, by virtue of feeding on higher trophic levels may be indicators of contaminants which move up through the food chain (Moriarity and Walker 1987). Red-tailed hawks (*Buteo jamaicensis*, great-horned owls (*Bubo virginianus*), western screech owls (*Otus kennicottii*), and northern harriers (*Circus cyaneus*) are being evaluated for radio-tracking to determine their feeding and foraging ranges. Owls and raptors feed quite extensively on small mammals and occasionally on songbirds. The pathway of contaminants from soil to vegetation to herbivore to carnivore is being evaluated by monitoring biochemcial responses in the raptors.

Herons are similar to raptors in their position on the food chain. Herons consume fish, amphibians, and small rodents. Observations on heron foraging will be conducted to determine where adults are feeding and prey items. The great blue heron colony will be visited twice to acquire nondestructive samples (e.g. fecal matter, discarded eggshells, and dead nestlings that have fallen from the nest). Methods using the chorio-allantoic membrane (CAM) of discarded eggshells has proven to be a useful technique in assessing the chemical burden of heron chicks in a nondestructive bioassay (Norman et al. 1989). Data obtained from the heron colony at NAS Whidbey Island will be compared to data previously collected from other heron colonies in the Puget Sound. If preliminary investigations indicate abnormal concentrations of contaminants, more in-depth studies will be planned for ensuing years. If no indications of impact are determined, a monitoring program will be established to verify on-going health of the heron colony.

The use of wildlife populations for the monitoring of chemical contaminant availability in the environment is enhanced by the evaluation of "marker enzymes" which respond to the presence of contaminants in the body (Lee et al. 1980, Payne et al. 1987, Rattner et al. 1989). These enzymes are found in the blood, liver, and brain of most species (Walker 1978). Marker enzyme response to contaminants can provide a measurable toxicological endpoint. A biochemical response, once traced back to an offending contaminant, can then serve as an indicator of toxic insult as well as a method to monitor mitigation attempts on the contaminated site. Biochemical evaluation of the wildlife on NAS Whidbey Island will entail the measurement of several bioindicator enzymes from the liver, brain, and plasma tissues of starlings, mice, and amphibians. In addition, tissue burdens of contaminants of concern will be analyzed to obtain a complete picture of exposure and toxicological effects. The complete sampling plan and protocols for the toxicology study at NAS Whidbey Island are documented in the work plan (TIWET 1989).

Risk Assessment Pilot Project at NCBC Davisville, RI

Allen Harbor, located in Narragansett Bay at the Naval Construction Battalion Center (NCBC) Davisville, RI, has been closed for shellfishing by the Rhode Island Department of Environmental Management due to suspected hazardous waste contamination from a landfill and disposal area adjacent to the harbor. The landfill, about 15 acres in size, received a wide variety of wastes including sewage sludge, solvents and paints, chromic acid, PCB contaminated waste oils, preservatives, basting grit, and other municipal and industrial wastes generated at NCBC Davisville and NAS Quonset Point between 1946 to 1972 (NEESA 1984b). Another site, located on Calf Pasture Point, was used for disposal of calcium hypochlorite, decontaminating solution, and chloride (NEESA 1984b). Previous analyses of sediment and bivalve tissues from Allen Harbor have shown increased levels of heavy metals and organics (TRC Environmental Consultants, Inc. 1986). The purpose of the risk assessment pilot project is to determine the impact of the disposal sites on environmental quality and shellfish resources in Allen Harbor and to develop and field validate ecological risk assessment methods.

During the first phase of the risk assessment consists of three components: waste site characterization, exposure assessment, and effects assessment. The site characterization portion of the study centers primarily on identification of chemicals residing in the disposal sites (TRC Inc 1988). The exposure assessment focuses on quantification of contaminant levels in the sediment and water column of Allen Harbor and reference areas in Narragansett Bay (EPA-ERL 1989a). The biological effects assessment evaluates toxicity responses of selected organisms, determines physiological and histological conditions of shellfish, and examines chemical bioaccumulation in shellfish tissues (EPA-ERL 1989a).

The primary responsibility for characterizing the Allen Harbor landfill resides with TRC Inc (TRC Inc 1988). Sample splits obtained from groundwater, visible seeps on the face of the landfill, and sediment samples adjacent to the face of the landfill were obtained for analysis by both Environmental Protection Agency Environmental Research Laboratory (EPA-ERL) and TRC Inc. The intercalibration exercise between EPA-ERL and TRC Inc ensures a good description of potential contaminant fluxes into Allen Harbor, accomplishes a quality assurance and quality control (QA/QC) check between EPA-ERL and TRC Inc, and assures that the two data sets will be complementary and comparable. In addition, the Food and Drug Administration Northeast Technical Services Unit (FDA-NETSU) and the University of Rhode Island Graduate School of Oceanography (URI-GSO) are also participating in the intercalibration procedure.

The degree of exposure to resident biota to contaminants from the Allen Harbor landfill is being identified by a qualitative and quantitative description of the contaminants in sediments and seawater. The approach for sediment characterization consists of collection and analysis of an extensive grid of samples within Allen Harbor (Figure 5) and in reference stations in Narragansett Bay (Figure 6). One-gallon scoop samples were collected interidally at four locations each within Allen Harbor, Marsh Point (MP in Figure 6), and at two locations at Coggeshell Cove (CC in Figure 6) on Prudence Island. Soft shell clams (*Mya arenaria*) were also collected at these locations.

Subtidal sediments were collected on a grid of eleven stations within Allen Harbor, at seven stations along a "T" transect out of Allen Harbor (Figure 5) and at Mount View (MV), Greenwich Bay (GB), North Jamestown (NJ), and Potter Cove (PC) (Figure 6). A Smith-McIntyre grab sampler was used to obtain five grabs per station in Allen Harbor and vicinity (Figure 5). The top 2 cm of sediment was saved from each grab for subsequent analysis. The four stations representing mid-bay conditions (Figure 6) were sampled using five replicate grabs per five locations per station for a total of twenty five grabs per station. This scheme ensured comparability of data for statistical purposes.

Additional subtidal sediments were obtained at five selected stations within Allen Harbor by gravity coring to a depth of 30 cm, the estimated depth of disturbance due to shellfishing activity. Subsamples were taken from these cores at three depths (top, middle and bottom), and were composited by depth for subsequent analysis. To reduce the number of sample analyses, a subset of both intertidal and subtidal stations were selected for initial chemical determinations. If these results indicate the need for more detailed analysis the archived samples are available for examination. Since all sample were obtained in a single collection, comparability of results will be maintained. In addition, this method of sampling guarantees available material for other purposes. Aliquots from each of five replicate grabs were composited (1 gal total) for each of the Allen Harbor and mid-bay stations, thus reducing the number of chemical analyses needed without sacrificing the ability to detect strong chemical signals.

Chemical analyses were conducted for a "working list" (Table 1) of contaminants developed based on previously identified problem compound in marine environments, existing information on the disposal sites, and information generated by the extensive analytical screen conducted on a preliminary subset of samples. In addition to the analyses identified in Table 1, sediment and tissue samples (from Allen Harbor and from MV) were analyzed for organotin compounds by the Naval Ocean Systems Center (NOSC).

Water column samples were collected in Allen Harbor and at the MV station. Analysis of these samples was related to the analysis of seeps on the face of the landfill. Timing of sampling was scheduled so that samples were collected during

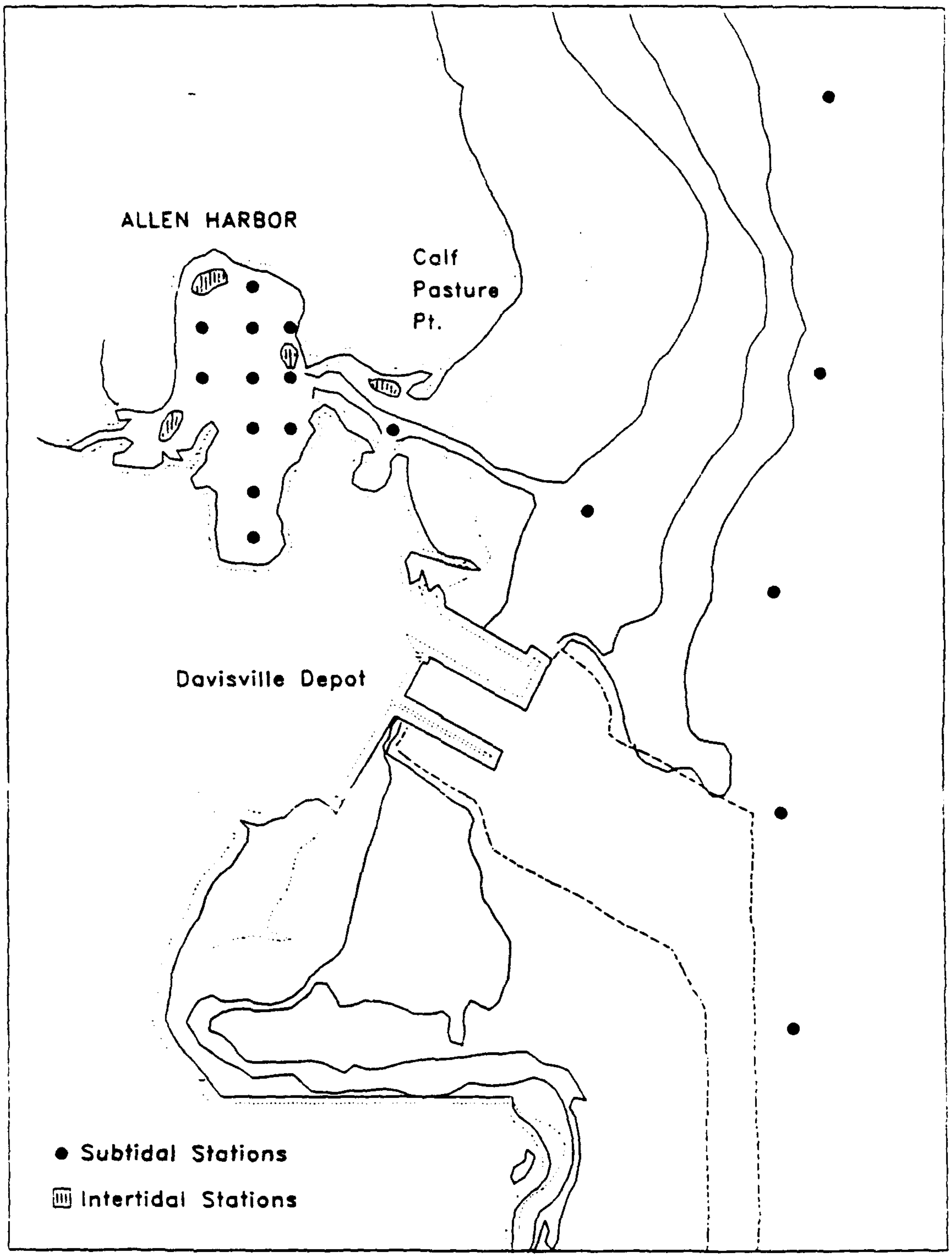

Figure 5. Station locations for characterizing sediments and shellfish in Allen Harbor and nearby Narragansett Bay (EPA-ERL 1989).

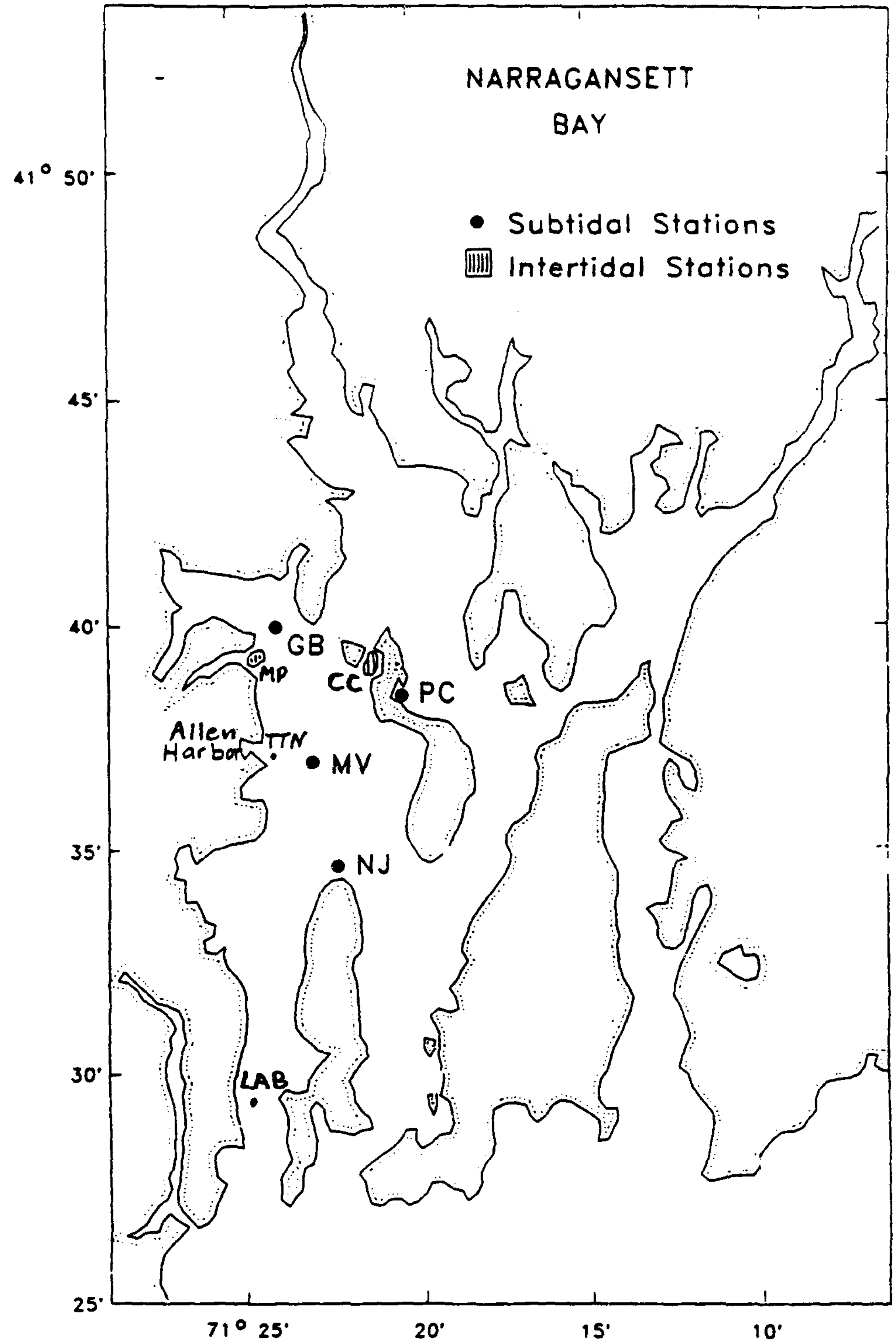

Figure 6. Reference stations locations for characterizing sediments and shellfish in Narragansett Bay (EPA-ERL 1989).

Table 1. Compounds known to cause problems in marine environments and therefore, routinely analyzed at the U.S. Environmental Research Laboratory at Narragansett, R.I.

Parameter	Matrix	Units***	Detection Limits	Method	Reference	Maximum Holding Time
Volatiles	Sediment tissue seawater	PPB		Purge & Trap GC/MS	**URI SOP's	2 Weeks
Pesticides	Sediment	NG/G	0.6	Extraction/	*EPA	Prior to extraction indefinite if frozen (sediments and organisms) or refrigerated (water) After extraction indefinite if stored in tightly sealed vials with maximum amount of solvent in vial. Must be stored in dark refridgerator.
	tissue	NG/G	0.6	GC-ECD	SOP's	
	seawater	NG/L	0.3			
F-1 (PCBs)	Sediment	NG/G	2	Extraction/	*EPA	
	tissue	NG/G	2	GC-ECD	SOP's	
	seawater	NG/L	1			
F-2 (aromatic)	Sediment	NG/G	0.6	Extraction/	*EPA	
	tissue	NG/G	0.6	GC-MS	SOP's	
	seawater	NG/L	0.3			
F-3 (more-polar)	Sediment	NG/G		Extraction/	*EPA	
	tissue	NG/G		GC-FID	SOP's	
	seawater	NG/L				
Trace Metals						
Cr, Cu Pb, Ni, Ag	Sediment	µg/g	1-3	ICP	*EPA	6 months after extraction
	tissue	µg/g	0.5-1.5	ICP	SOP's	
	seawater	µg/L	0.5-1.0	Graphite AA		
Cd	Sediment	µg/g	1.0	ICP	*EPA	
	tissue	µg/g	0.5	ICP	SOP's	
	seawater	µg/L	0.1	Graphite AA		
Hg	Sediment	µg/g	0.1	Cold vapor AA	*EPA	
	tissue	µg/g	0.05	Cold vapor AA	SOP's	
	seawater	µg/L	0.5	Cold vapor AA		
Zn	Sediment	µg/g	0.5	ICP	*EPA	
	tissue	µg/g	0.3	ICP	SOP's	
	seawater	µg/L	0.05	Graphite AA		
Arsenic	Sediment	µg/g	4	ICP	*EPA	
	tissue	µg/g	2	ICP	SOP's	

*EPA SOP's referenced in appendix 2

**Method listed in section 12

***Sed and tissue on dry wt. basis

"dry" and "wet" periods to identify whether there was a contaminant plume in Allen Harbor. Bacteriological indicators were measured by FDA-NETSU and volatile organics (VOCs) were quantified by URI-GSO.

The biological effects assessment portion of the study included toxicity response demonstrations, measurements of physiological and histological condition of bivalves, and quantification of chemical bioaccumulation in shellfish tissues. Shellfish were emphasized because of their ecological and commercial importance in Allen Harbor and Narragansett Bay. Approximately fifty animals of either quahogs (Mercenaria mercenaria) at subtidal stations or soft shell clams (Mya arenaria) at intertidal stations were collected at each station. Where present, oysters (Crassostrea virginica) were also collected. These samples were used to estimate resource density and condition indices. A subset of samples were processed for chemical analysis of tissue residues and to evaluate health via histopathological observations. The remaining samples were archived for future chemical analysis as required. Past experience has shown that tissue samples may be effectively preserved for many years by careful sealing and freezing (EPA-ERL 1989a).

Because of its dense distribution and economic importance the quahog is being used as the primary organism for evaluating benthic impacts. It is sedentary and filters large volumes of water, making it an ideal organism for evaluating environmental quality. Quahogs were sampled at all subtidal stations (Figures 5 and 6) during the fall of 1988 for observations of resource density and size distribution. At a subset of five stations corresponding to the subset of stations selected for chemical screening, five composites of five animals each were sampled for tissue burdens; twenty five animals were sampled at each station for condition index (shell length/whole weight/tissue wet weight ratios) and for histopathological examination. Quarterly sampling of quahogs will continue for a year at a subset of five stations for histological observations and determination of condition indices (EPA-ERL 1989a).

The soft shell clam is very common in intertidal areas of mid and upper Narragansett Bay including Allen Harbor, and its abundance supports an active recreational fishery. Samples of soft shell clams were obtained at the intertidal stations in Allen Harbor, Marsh Point, Coggeshell Cove and Calf Pasture Point. Observations similar to those for the quahog were made on the soft shell clam including analysis of tissue burdens, condition indices, and histopathology. The latter observations are being made quarterly for one year at three of the stations. Oysters were sampled once at two stations, Allen Harbor and CC. Similar observations are being made on the oysters.

Composite sediment samples from Allen Harbor and MV, GB, NJ, and PC, and selected sediments from the bay-wide Narragansett Bay Project survey were tested with the amphipod (Ampelisca abdita) assay. *A. abdita* is a euryhaline benthic, tube-building, amphipod inhabiting fine intertidal and subtidal sediments. It is a filter feeder which ingests suspended particles and is a common food source for bottom fish. *A. abdita* has been shown to be sensitive to contaminated sediments and can be used to evaluate the relative toxicity of sediments (Redmond 1988). The amphipod assay was used to evaluate the relative toxicity of sediments collected in Allen Harbor and in reference areas of Narragansett Bay (EPA-ERL 1989a).

The physiological condition of water column organisms was examined using cages containing the blue mussel, *Mytilus edulis* (Figure 7). The mussels were collected from a clean reference site in Narragansett Bay and deployed in plastic mesh cages at four stations (four replicate cages/station, fifty animals per cage) for a spring and fall deployment period of twenty eight days. One station was located in Allen Harbor, and outside Allen Harbor in Narragansett Bay at TTN, MV, and LAB (Figure 6). Mussel cages were moored 1 m above the bottom. Clearance rate, assimilation efficiency, and respiration rate were determined for the mussels at the end of the deployment to calculate the scope for growth (SFG) index. The SFG index provides an integrated index of the mussels' physiological well-being and has been shown to highly correlated with environmental conditions and the presence of toxic contaminants (Nelson et al. 1987).

Sediment conditions in Allen Harbor were further evaluated through characterization of benthic community condition using the REMOTS camera system. This work was sponsored by the Narragansett Bay Project and the Allen Harbor stations were included as part of the bay-wide survey (SAIC 1989). Benthic habitat quality, organic enrichment, dissolved oxygen concentration, and the distribution of *Clostridium perfringens* were examined at fifty-nine stations in the bay to provide information on the sediment quality of areas of Narragansett Bay (SAIC 1989).

Biomarkers tests on two of the sediment samples collected for the amphipod assay, one from Allen Harbor and one from Mount View, were conducted to evaluate cytotoxicty and mutagenicity of contaminants in the sediments. The V79 Metabolic Cooperation Assay (V79/MC) was used as a short-term test to identify tumor promoters. The assay is based on the discovery that the tumor promoters inhibit the gap junctional-mediated transfer of materials between cells (EPA-ERL 1989a). The V79/Sister Chromatid Exchange Assay (V79/SC) was used to evaluate the mutagenic effects of the complex mixtures and fractions of contaminants extracted from the sediment. In this assay chromosomal damage is measured by induction of micronuclei in the interphase cell. Micronuclei represent acentric chromosome or chromatid fragments which give rise to one or more small secondary nuclei that are excluded from daughter nuclei. Sister chromatid exchange represents the the breakage and reciprocal exchange of identical DNA material between the two sister chromatids of a chromosome. Both micronuclei and sister

In Situ Array

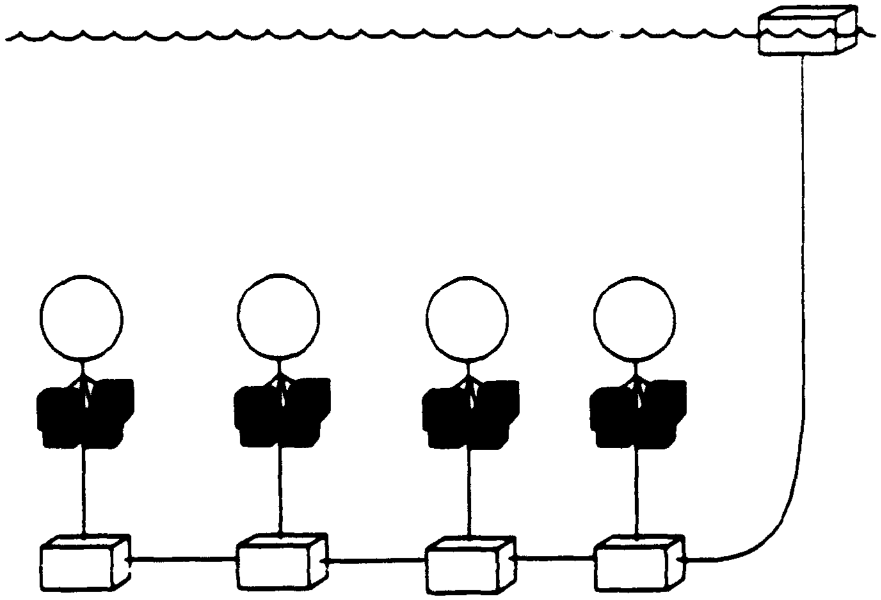

Figure 7. Mussels cages used to deploy mussels at stations located in Narragansett Bay, RI (Nelson et al. 1987).

chromatid exchanges have been found to increase in cells exposed to mutagenic compounds (Mueller et al. 1989).

The results obtained during the first phase of the risk assessment are summarized in the interim (EPA-ERL 1989b) and the draft final reports (EPA-ERL 1990). General observations show no dramatic differences in the chemical composition of the sediments collected from Allen Harbor and those from other areas of Narragansett Bay. Low bacterial counts and no evidence of sediment toxicity from the amphipod assay support this conclusion. The tissue residues and bacterial counts measured in Allen Harbor were also relatively low in comparison to other areas of Narragansett Bay. The histopathological observations and abundance estimates shows that the bivalve population in Allen Harbor is relatively healthy and the benthic community, as measured by the REMOTS system, is relatively undegraded. However, evidence of possible pollution impact on organisms in Allen Harbor was detected in the water column and benthos. Water column pollution stress was detected in sporadic elevated microbial levels and reduced SFG in mussels deployed in Allen Harbor, relative to reference areas. Impacts on benthic dwelling organisms were detected by elevated hemopoietic neoplasia in soft shell clams and elevated levels of tributyltin (TBT) in quahogs. It is not clear that these impacts can be attributed to the landfill and, in fact, are most likely a result of pollution entering Allen Harbor from runoff or boating activities at the marina located in the harbor (Milliken 1989, EPA-ERL 1990).

Work currently planned for the second phase of the risk assessment will address the contributions of the landfill to observable environmental impacts in Allen Harbor by partitioning exposure and toxicity amongst the potential sources. These sources include the landfill itself, runoff from storm drains and nonpoint sources, and effects from increased boating activity during the summer months. Additional sampling will address the relative affliction rates of neoplasia in soft shell clams in Allen Harbor and Narragansett Bay to determine if Allen Harbor is a locus of the disease or whether neoplasia is endemic to soft shell clams in Narragansett Bay. Results of these investigations will be interpreted within an ecological risk assessment framework. A long-term monitoring strategy will be developed to support the risk management plan (EPA-ERL 1989c).

BENEFITS OF ECOLOGICAL RISK ASSESSMENTS

The primary benefit of conducting the studies described in this paper is that direct measures of environmental health are made with actual exposure conditions which are related to biologically significant endpoints. This process provides the risk framework for interpreting and managing impacts from the disposal sites (Phelps and Beck 1989). Ecological risk assessment allows investigators to identify the source and extent of the problem and delineate between hot spots and nonproblem areas that can be prioritized accordingly. Since ecological risk assessment is an emerging science, a potential drawback is that sometimes results can be ambiguous and subject to conflicting interpretations. Therefore, it is very important that decision criteria are selected that consists of: "... well defined, conveniently measured, and easily understood set of endpoints on which to base management action" (Phelps and Beck 1989, p2351). By selecting the proper endpoints for a particular ecosystem uncertainty can be quantified to allow reduction, rather than elimination, of risk and the identification of appropriate cleanup levels (Greenberg 1989).

Ecological risk assessments also provide information on ecotoxicity or how contaminants affect ecosystems. Continued studies of ecotoxicity will lead to the development of methods and databases that can provide a risk assessment framework for other applications and result in biologically-based models to assess risk, rather than the statistical models currently in use (Paustenbach and Keenan 1989). Finally, ecological risk assessments and monitoring programs can provide a direct verification of environmental safety. This information can be used to facilitate site closures and determine how clean a hazardous waste disposal site actually is.

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DEVELOPMENT OF INNOVATIVE PENETROMETER TECHNOLOGY FOR THE DETECTION AND DELINEATION OF CONTAMINATED SOILS

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ABSTRACT

Truck-mounted cone penetrometers capable of quickly and economically measuring soil strength properties from the surface to depths of approximately 50 meters in suitable soils (sand, silts and clays) are in routine use in engineering studies for subgrades and foundations. A project is currently underway to develop contaminant sensors that can be built into soil penetrometer equipment to allow the detection and delineation of contaminants in soils as the penetrometer is forced through the soil. A goal of this research effort is to develop a family of sensors that can be used to produce real-time data on-site as the penetrometer is forced through the soil at speeds as fast as 2 cm/sec. Two types of sensors, a module for measuring soil resistivity and a module for measuring soil fluorescence, are discussed as examples of sensor technology integrated into the penetrometer.

The soil resistivity module uses an array of electrodes mounted on the penetrometer rod to determine the presence of anomalous electrical resistivity in soil adjacent to the penetration hole. Soil contaminants containing easily ionized components such as salt will produce decreased soil resistivity. Changes in resistivity in a uniform soil type can be used as a preliminary indication of soil contamination. The soil resistivity module has successfully located closed landfills and evaporation ponds.

The soil fluorescence module can detect soil contaminants that will fluoresce under ultraviolet light. Fluorescence is a promising approach for the detection of contamination from fuels, lubricants, and certain explosives wastes. The fluorescence module has been successfully employed in a tracer dye study on a dredged material site.

The economy obtained by using a penetrometer rather than a conventional drill-and-sample approach easily justifies the cost of development of additional sensors. Techniques for low-level detection of toxic metals and specific organic contaminants are currently being researched. Spectral characteristics of contaminated soil show great promise in contaminant detection. Combining sensors with a location/positioning capability can produce a system for real-time, on-site mapping of subsurface contamination.

INTRODUCTION

A typical cone penetrometer system designed for foundation investigations consists of a 35.7-mm diameter steel rod terminating in a 60-degree cone. The cone and a section of the rod behind the cone (the sleeve) are instrumented to allow the forces acting on the cone and the sleeve to be measured as the penetrometer is forced through soil or unconsolidated sediments. The tip resistance and the sleeve friction are measured continuously as the penetrometer is advanced through the soil at a standard rate of 2 cm/sec. The force needed to move the rod is produced by a hydraulic load frame mounted on a truck equipped for off-road operation. With a truck loaded to produce a 20-ton reaction mass, penetrations as deep as 40 to 50 meters can be achieved in most normally compacted, uncemented soils. The sleeve friction and tip resistance vary systematically with the soil type (clayey, sandy or mixed silt and sand), and this allows the soil type to be continuously estimated from the cone response data. Cone penetrometer testing is considered the most useful in-situ soil test method available and most countries have established cone penetrometer test standards (Campanella and Robertson, 1982). A cone penetrometer can collect data from penetrations totalling approximately 200 m in one day at a cost of approximately $30 per m. Drilling, sampling and testing would produce only 20 percent of the data within the same time period and would have a unit cost ten times that of a penetrometer.

Since the cone penetration system provides a rapid and economical method for moving instruments and even samplers into the soil, there has been interest in developing geophysical tools or chemical sensors and samplers that could be operated with the standard cone penetrometer equipment. The sensors allow the presence of contaminants to be detected while the soil stratigraphy is being established from the standard cone response (Amann, Berigen and Wollenhaupt, 1986). When the cone penetrometer and specialized sensors are combined with a location/positioning system for the penetrometer truck, the combination will allow for real-time, on-site mapping of contamination in the subsurface.

The purpose of this report is to discuss the operation of two sensor systems that have been used with penetrometer equipment and to provide an outline for the development of a cone penetrometer-based system for detection and delineation of contaminated soils at hazardous waste sites. The goal is to show what has been achieved with this technology to improve our ability to characterize waste sites and to describe the logical next step in specialized penetrometer system development.

CONE PENETROMETER-BASED SENSOR SYSTEMS

The cone penetrometer unit is designed to provide information on the type of soil in the subsurface from strength characteristics measured by internally mounted strain gages as the instrument moves through the soil. The cone is advanced at a uniform rate of 2 cm/sec over 1-m intervals. After each 1-m advance, the cone is halted while an additional 1-m rod segment is added to the rod string. Technically, a sensor can operate either continuously as the rods are advanced or the sensor can be read at 1-m intervals if response time is slow. Both methods of operation would fit into the standard pattern of advance of the cone penetrometer and would not interfere with collection of data on the soil stratigraphy. While it is possible to envision specialized sensors that might require long delays for equilibration or might have a nonreversible response, first efforts in sensor development have emphasized techniques that have rapid, reversible response and can provide a continuous record of soil characteristics. Sensors that involve measurements of electrical properties and spectral properties are prominent candidates for development because they involve rapid, reversible responses that can be related to the presence of anomalous materials (contaminants) in the soil.

Sensors Based on Electrical Properties

Electrical resistance (or conductance) of groundwater is routinely measured as a gross estimate of inorganic contamination. Because electrical resistance of saturated soil is related to the resistance of the pore fluid, it is possible to make estimates of the relative levels of contamination from differences in soil resistivity observed in similar soil types (Rhoades and others, 1989).

Instruments designed to measure soil resistivity from the cone penetrometer typically are built by mounting a series of conductive bands or buttons a few centimeters apart on the exterior of the rod so that soil comes in contact with these electrodes as the rod moves through the soil column. The electrodes are separated by an abrasion-resistant insulator that holds the electrodes in place and maintains the constant diameter of the rod (Figure 1). The measuring surface wipes itself clean as soil is forced across the surface. Response is rapid and no equilibration is required. With close spacing of the electrodes, the volume of soil investigated is small, but resistivity interfaces are very sharply defined.

Electrical resistivity modules have been most successful in locating closed landfills (Amann, Beringen and Wollenhaupt, 1986) or evaporation ponds (Cooper and others, 1988a, 1988b). The high concentrations of inorganic contaminants associated with these targets provide excellent contrast with uncontaminated soils.

The major disadvantage in the use of electrical resistivity measurements involves the effects of the soil. Soils with clay present conduct electricity through soil water and through the outside conductive layer (bound water layer) of the clay itself. Clays and clay-sand mixtures can be conductive even when the pore fluid is resistive (Rider, 1986). Cone resistance and sleeve friction can provide data on the soil type that can assist in many instances in obtaining a correct interpretation of the variation in electrical resistivity.

Sensors Based on Spectral Properties

Sensors based on spectral properties such as fluorescence or absorption have been employed in investigation of contaminants in surface and groundwater, but adaptation of this technology to the cone penetrometer is a new and potentially very useful development. By using fiberoptics it is possible to produce a compact unit that can provide a remote excitation and light collection system that permits examination of spectral properties of fluids or solids without building complex optical equipment into a small probe. Chudyk, Carrabba and Kenny (1985) and Chudyk and others (1989) reported on units developed for measuring fluorescence from organic contaminants in monitoring wells. Lieberman, Inman and Stromvall (1987) showed how a fiber optic fluorescence unit could be used for measuring trace amounts of inorganic contaminants remotely in seawater using fluorogenic ligands.

A prototype fluorescence sensor for the cone penetrometer was fabricated at USAE Waterways Experiment Station and tested in a subsurface dye tracing experiment. The unit has two 0.25 watt mercury vapor lamps, emitting light at the 254 nm wavelength and above, mounted inside a 35.7-mm diameter penetrometer rod (Figure 2). The lamps are positioned behind an 8-mm diameter round sapphire window. The window is 4-mm thick, transparent to ultraviolet and is ground optically flat. The termination of a 500-micrometer diameter optical fiber is mounted directly behind the window so that light from the soil moving past the window is captured by the fiber and passed through 50 meters of fiber to a spectrophotometer or optical multichannel analyzer on the surface. The fluorescence sensor unit attaches to standard penetrometer rod (Figure 3) and can be mounted above the instrumented cone and friction sleeve unit.

In an initial field test to the unit, 8 liters of a non-toxic, fluorescent optical brightener (Fluoretrack II, Formulabs, Escondido, CA) was injected in saturated sand at a depth of 4 m in an area underlain by approximately 10 m of hydraulically placed sand and silt. Over 35 penetrometer pushes were made in a pattern crossing over the penetration point. Data on fluorescence were taken with a Guided Wave Model 260 fiber optic spectrophotometer (Guided Wave, Inc., El Dorado Hills, CA) interfaced with a personal computer. The sensor was calibrated on standards prepared from water-saturated sand samples containing known amounts of optical brightener (Figure 4). The intensity (power in picowatts) of the fluorescence signal was measured at 517 nm at 0.1 sec (0.2 cm depth) intervals as the rod moved downward. Figure 5 shows the pattern of the dye detected with the fluorescence sensor. A water sampler designed for use on the penetrometer was used to collect ground-water samples over the plume and confirm that dye was present in the pattern the sensor indicated.

Laboratory testing conducted with an optical multichannel analyzer indicates that complete spectral data can also be collected. Ultraviolet or visible absorbance as well as fluorescence can be used to detect and delineate soil contamination (Figure 6).

DEVELOPMENT OF A SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (SCAPS)

Advances in sensor technology have pointed to the possibility of developing a real-time, multi-parameter measurement system for detecting and delineating pollutants in soil. The system could couple measurements from a suite of chemical and physical sensors to a location/positioning system. Soil contaminant distribution could be displayed as a series of map overlays as they are collected. This approach would be similar to the system discussed by Lieberman, Clavell and Bower (1989). The systems approach has the advantage that it allows the use of real-time sensor data collected with the penetrometer and associated equipment to guide the intelligent placement of borings for the collection of large volume soil samples and/or the installation of permanent monitoring wells for the collection of groundwater or soil gas. Since the SCAPS equipment would collect and analyze data while the unit is still on-site, gaps in sensor data can be identified and additional data can be collected until the objective of selecting optimum locations for more expensive and time-consuming drilling and sampling is completed. The SCAPS unit can also be equipped to collect small-volume, high-quality water or soil samples to confirm sensor readings. Field-based screening tests on SCAPS samples can be used to provide the justification for a full-scale sampling and analytical program such as would be required by regulatory considerations or litigation.

A full SCAPS system would include the following:

a) A suite of geophysical equipment (magnetometers and ground-penetrating radar) for scanning the area ahead of the penetrometer to avoid hazards from unknown wastes or unmapped utilities.

b) The penetrometer with physical and chemical sensors and real time data acquisition and location/positioning equipment.

c) Data analysis and mapping equipment to present contaminant distribution data in the field.

d) Field sampling and analysis equipment to provide confirmation of sensor data as required.

e) Grouting pumps and injection equipment to seal the penetrometer holes and maintain the integrity of the site.

f) Safety equipment to protect the work crew and ensure containment of toxic or hazardous materials on-site during the site investigation.

By integrating site investigation efforts and undertaking each activity (from sweeping the site for buried hazards to taking samples for regulatory compliance and litigation) in a step-wise progression, we can provide a safe and economical waste site investigation. The key features in accelerating site clean-up efforts are rapid screening with sensors to optimize our monitoring efforts and prompt on-site integration of data so that questions can be answered as fully as possible before critical and expensive decisions on permanent monitoring programs or cleanup activities are made.

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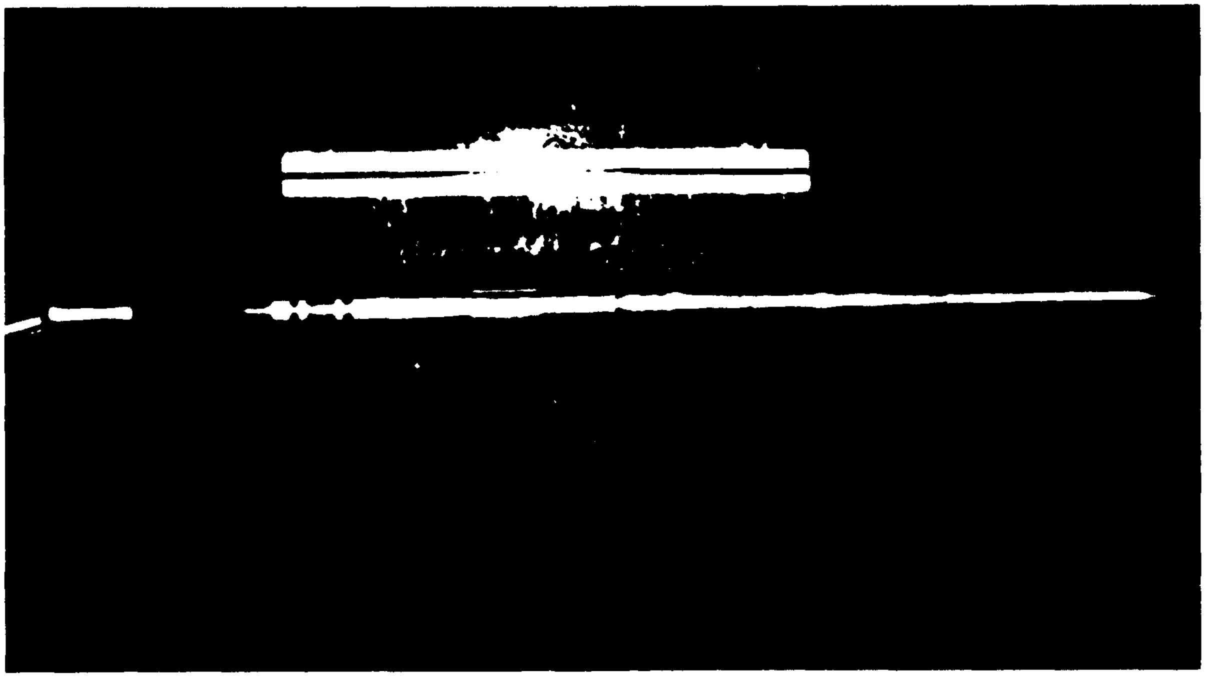

Figure 1. Photo of penetrometer with soil resistivity module attached. The electrodes are formed from stainless steel bands. The dark sections of the module are abrasion-resistant insulators.

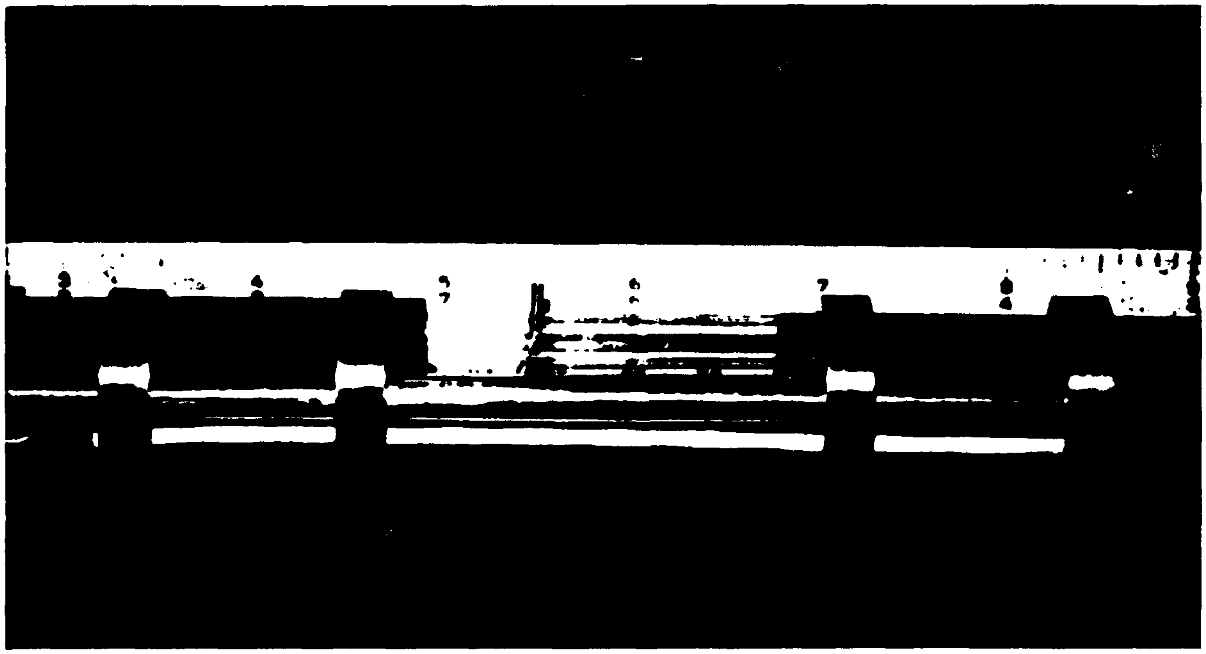

Figure 2. Photo of disassembled fluorescence sensor showing the mercury vapor lamps. The optical fiber termination is located in the tube between the two lamps.

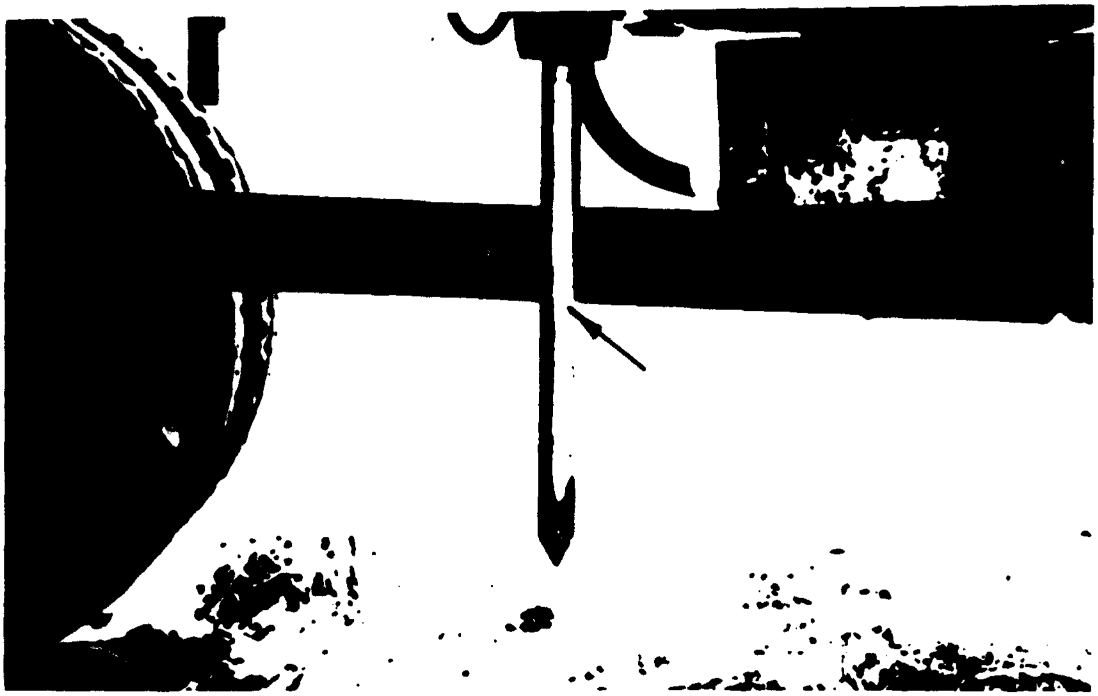

Figure 3. Photo showing the fluorescence sensor mounted on the penetrometer rod. The arrow marks the position of the small window located on a section of the rod that has been milled flat.

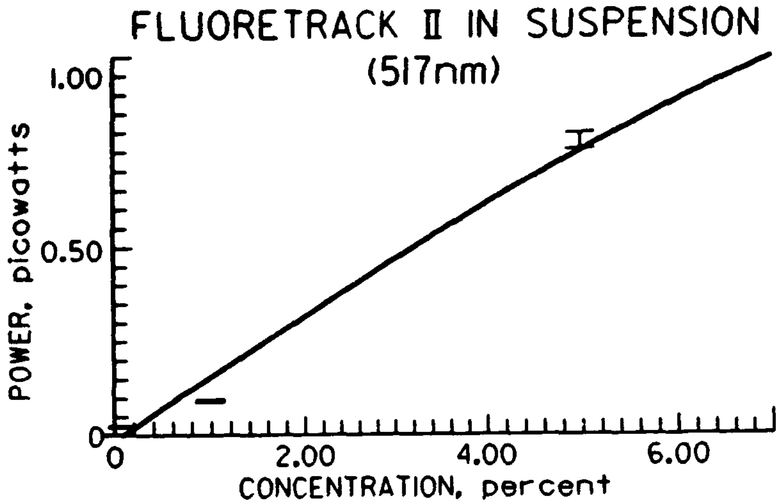

Figure 4. Low-level calibration curve prepared for the fluorescence of Fluoretrack II suspension in sand. Error bars represent one standard deviation from the average reading.

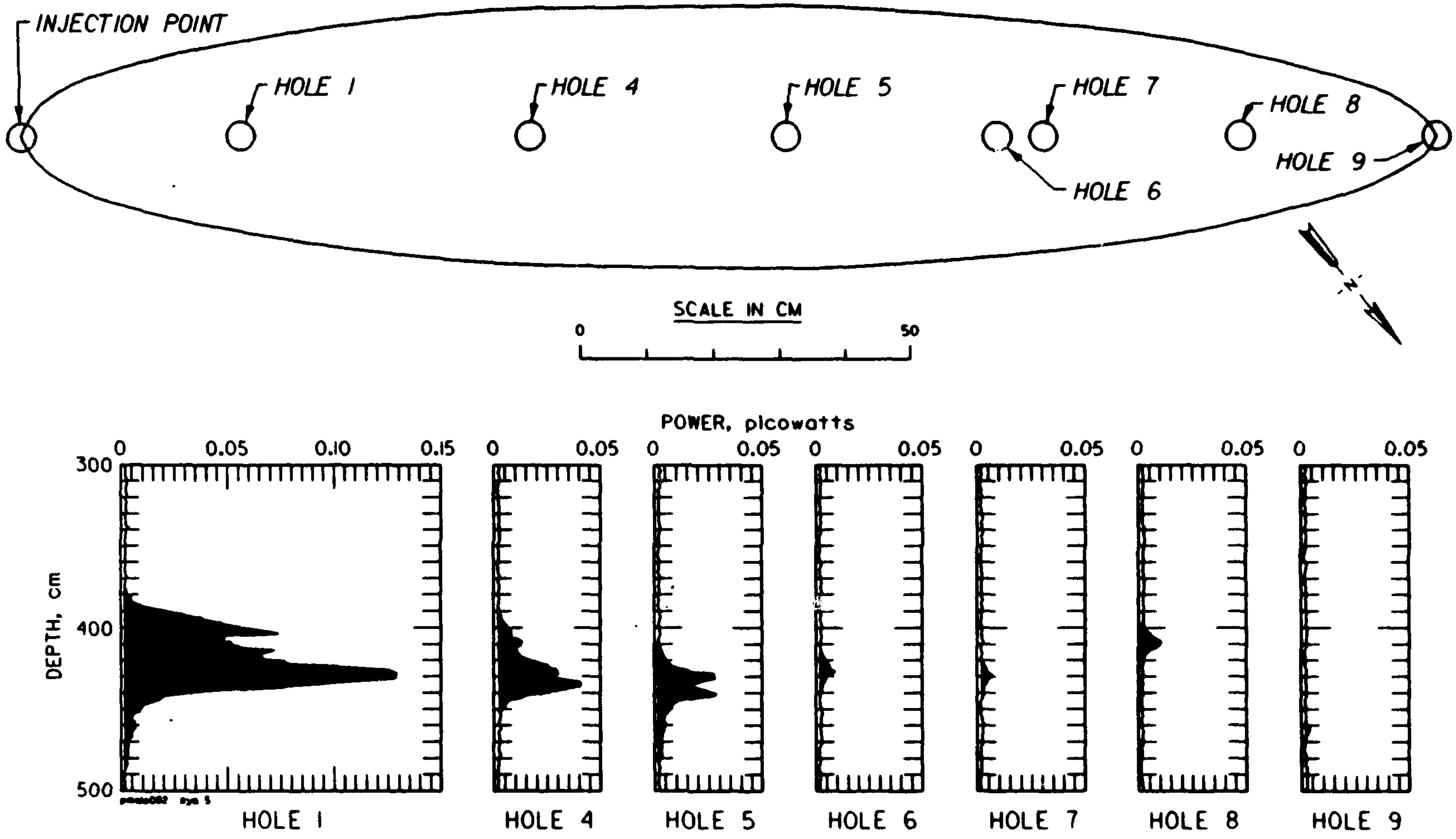

Figure 5. Map view and readouts from the fluorescence sensor showing the dilution and movement of the dye as it is carried away from the injection point. The width of the plume was estimated from readings made across the plume path near Hole 5. The reduction of fluorescence intensity is due to filtration of the suspended solid dye, adsorption of the dissolved dye on clays and silts and dilution by the surrounding groundwater.

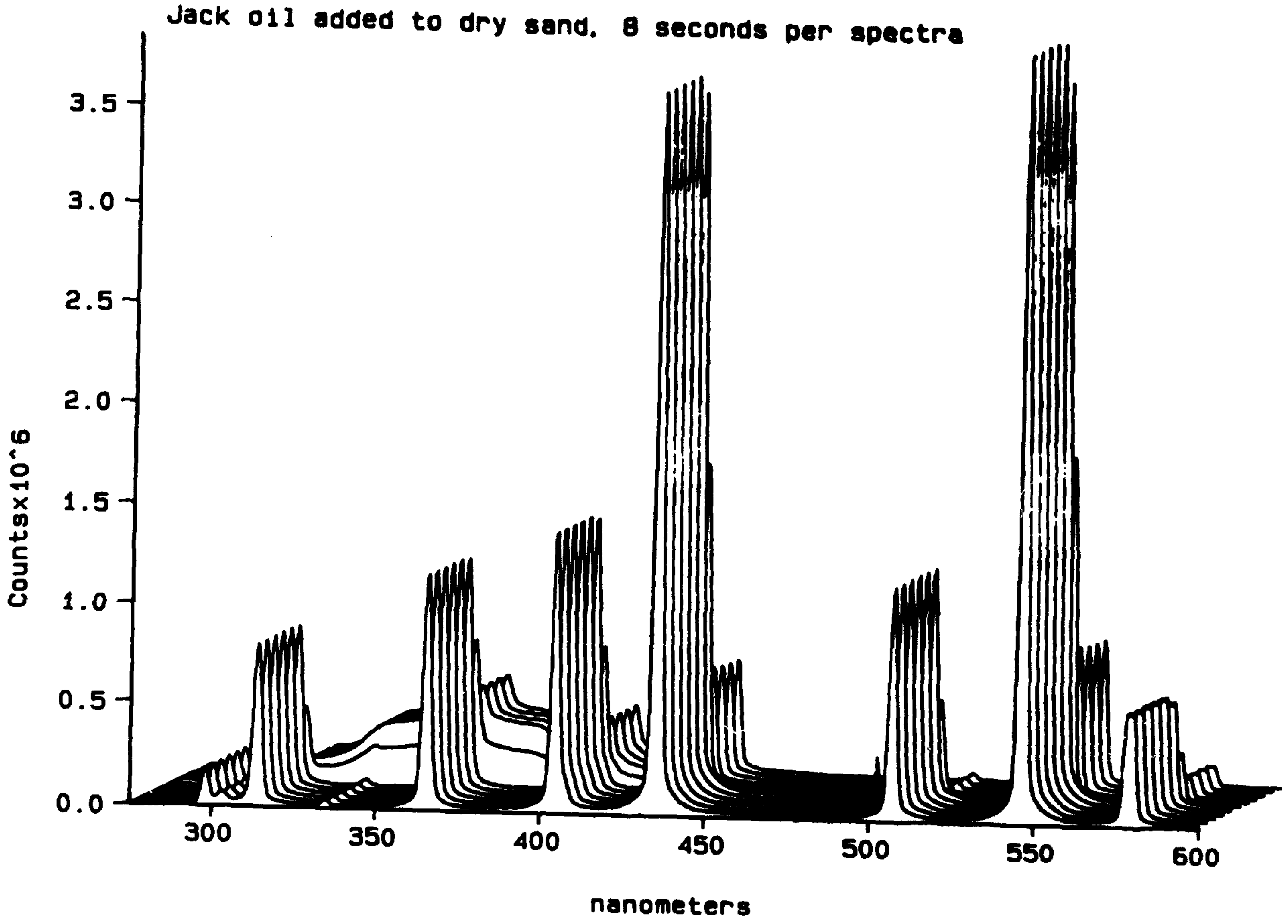

Figure 6. Spectral data collected with an optical multichannel analyzer. The spectra in the foreground were collected in clean sand, the spectra in the background were collected as the sand was contaminated with hydraulic oil. Fluorescence excitation and collection of the reflectance/fluorescence energy was done using the penetrometer fluorescence sensing unit.

USAF AIP STRIPPING AND EMISSIONS CONTROL RESEARCH

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Introduction

Groundwater under airfield facilities is often contaminated with jet fuel hydrocarbons, chlorinated solvents, and degreasers. This contamination has been the result of past disposal practices, leaking storage tanks, and accidental spills. The Air Force has begun remediation of contaminated groundwater through the Installation Restoration Program (IRP). Implementation of IRP has included identifying contaminated areas, determining the type and extent of the contamination, developing technologies for contamination remediation, and selecting the appropriate cleanup activities. The Air Force Engineering and Services Center's Environics Division is responsible for developing and testing new and more cost-effective technologies for cleanup of Air Force contaminated groundwater. Special emphasis has been placed on the removal and destruction of volatile and semi-volatile contaminants because they are the majority of the groundwater contaminants found at Air Force bases. The most commonly used technique for removal of volatile contaminants from groundwater is countercurrent packed tower air stripping. Major problems with this technique include reduced removal efficiencies for low and moderately volatile contaminants, increased blower power requirements and reduced stripping efficiencies from hardness precipitation and biological growth on packing material, and contaminated air emissions. This paper will summarize the results of several laboratory and field tests of innovative air stripping and emissions control techniques to remedy these problems.

A review of USAF air stripping and emissions control research was presented by Ashworth and Elliott (Reference 1) for activities which occurred from the early to mid 1980's. The article discussed investigation of countercurrent and rotary air stripping along with research in activated carbon adsorption and catalytic oxidation for emissions control. In this paper, we will discuss our testing of innovative packing materials for countercurrent air stripping columns, further experimentation of rotary air stripping, and development of new catalysts and adsorption materials for emissions control. We will also discuss our laboratory and pilot-scale research of a novel groundwater remediation technique referred to as crossflow air stripping.

Countercurrent Column Packing Materials

The packings used in air stripping plays a major factor in the design and costs associated with these systems. The most effective packing material causes very high mass transfer of the contaminant from the groundwater to the air, while also causing very low gas-phase pressure drops through the air stripping column. To evaluate the performance of new packing materials, we conducted a field test at a contaminated site at a fuel storage area at Eglin AFB FL. We investigated four different types of packing materials in a 12-inch diameter countercurrent column. The packing materials tested included 5/8-inch Stainless Steel Pall Rings, Koch/Sulzer Type BX plastic gauze packing, Flexeramic Type 48 ceramic packing, and Delta SH plastic packing. The Pall Rings are a random dumped packing while the three others are structured packings.

Our data from the tests showed the Koch/Sulzer packing had the best mass transfer characteristics of the four packing materials. The Delta SH packing showed the lowest gas-phase pressure drops through the tower, therefore, the lowest blower energy costs. An economic comparison is being completed to determine the most advantageous trade-off between packings with high mass transfer characteristics and those with low blower energy requirements. Results from this economic comparison will be published in the technical report for the field testing of the countercurrent column packing materials. (Reference 2).

Rotary Air Stripping

A rotary air stripper is a vapor and liquid contactor which uses centrifugal force to push contaminated water through packing material while air is pushed countercurrent to the flow of water. The centrifugal force spreads out the contaminated groundwater on the packing material causing high mass transfer of the contaminant from the water to the air. The main advantage of the rotary air stripper is the reduction in the height of the stripping equipment. Large tall towers are inherent in conventional packed column air stripping.

Our first tests with a rotary air stripper were conducted at a contaminated site at a US Coast Guard Station at Traverse City MI (Reference 3). In these tests, a 100-gpm rotary air stripper showed removal of the contaminant as a function of the liquid to gas ratio and the speed (rpm) of the spinning rotor. Our data showed the removal efficiency increased with an increase in the gas to liquid ratio up to a value of about 30 (volume/volume). After this value was obtained, very little increases in removal efficiencies were realized with increased gas to liquid ratios. A similar phenomeonon was observed with the influence of the rotor speed on the removal efficiency. Increasing the rotation above approximately 600 rpm produced very small changes in the removal efficiency. In all the tests, high removal efficiencies (>99 percent) were achieved with the highly volatile contaminants (e.g., trichloroethylene and tetrachloroethylene), while relatively low removal efficiencies were observed for the less volatile contaminants (e.g., 1,2-dichloroethane).

In the tests at Traverse City, only one size and type of packed rotor was used and only influent and effluent data could be taken. Because of these restrictions, a limited amount of mass transfer data could be obtained. In our field testing of rotary air stripping at Eglin AFB, we used three different sizes of rotors and two different types of packing materials, along with an internal sampling mechanism. The sizes included 9, 12, and 15-inch outer radii packed rotors. The types of packing materials included a metal sponge and a wire gauze. Using the different packed rotors, data was obtained to develop and compare equations for predicting the mass transfer, pressure drops, and power consumption of the rotary air stripper (Reference 4). The equations can be used to design the size, rotating speed, air-to-water ratios, and energy necessary for a rotary air stripper to meet site specific performance requirements.

Our initial thoughts on the rotary air stripper were that it would be less susceptible to fouling of the packing by hardness precipitation and biological growth due to the high shear forces. This was found to be not valid during our testing at Eglin AFB. Signs of plugging due to mineral deposits were observed in the rotors; however, it should be emphasized that the groundwater at Eglin AFB has a very high iron content (~9 ppm) and may not be a fair evaluation of the machine.

Emissions Control

The emissions from air stripping equipment are contaminated with the pollutants removed from the groundwater. Regulations concerning air stripping tower emissions are becoming increasingly strict. The US EPA Office of Solid Waste and Emergency Response (OSWER) has established guidance on the control of air emissions from air strippers used at Superfund sites for groundwater treatment (Reference 5). Because of stricter regulations and the high costs of emissions control, AFESC has been investigating methods of removing and destroying the contaminants from the air emissions of air stripping towers.

One method of removing the contaminants in air stripper emissions is adsorption. Activated carbon is the most commonly used material in sorption processes. A major disadvantage of this technology is the high cost of regeneration.

To try to reduce regeneration costs, we investigated two molecular sieve adsorbents for removing the contaminants in the emissions at the air stripping testing at Eglin AFB. These molecular sieve adsorbents were tested because of their capability for being regenerated on-site with ozone. The molecular sieve materials tested included Union Carbide's Type 9102 and 1387-53. Our data showed that both molecular sieve materials were unsuccessful adsorbing the contaminants in the air stripping emissions (Reference 2). The unfavorable performance of the molecular sieves may have been due to having too small a pore size to allow the contaminant molecules access to the active adsorption sites.

Another emission control technique we have been investigating is catalytic oxidation. Catalytic oxidation is a combustion process where the contaminant-laden air stream is preheated and passed through a catalyst bed. Final products of the oxidation are typically carbon dioxide, water, and inorganics.

A major problem with catalytic oxidation is the tendency of the catalysts to deactivate due to chlorine and/or sulfur in the emissions. Our testing at Eglin AFB emphasized this point dramatically. In less than a week's operation, all catalysts tested showed signs of deactivation due to sulfur in the groundwater.

To help alleviate this problem, two laboratory studies are now being conducted to investigate catalysts resistant to deactivation. The University of Akron is working on the development of a catalyst that resists deactivation when challenged with a chlorinated air stream. They have found that chromium oxide and vanadium oxide materials have the potential to reach greater than 95 percent conversion of chlorinated organics to water, carbon dioxide and dilute hydrogen chloride (Reference 6). They are continuing their research to find a superior catalyst that is resistant to chlorinated organics and sulphinated compounds that may be present in air stripping emissions.

The second study is being done by the Research Triangle Institute (RTI). They are evaluating off-the-shelf catalyst formulations from five manufacturers. The goal is to find out which catalyst is the best for a given contaminated air stream. After the catalyst has deactivated from constant exposure to a synthesized air stripper emissions stream, RTI will determine what caused the catalyst to deactivate, operating procedures to minimize deactivation, and if the catalyst can be effectively regenerated. This information will be used to do an economic comparison of the different catalysts. Catalyst formulations that are being tested are the ARI Econocat, a copper chromite formulation from Harshaw, Carulite from Carus Chemical, three supported noble metal catalyst formulations from UCI, and a Haldor-Topsoe catalyst.

Crossflow Air Stripping

Crossflow air stripping is a packed column aeration process which involves changing the air flow path of a conventional countercurrent tower. The main change is the placement of baffles inside the tower which causes the air to flow in a crisscross pattern up through the packing. This forces the air to flow at 90 degrees to the flow of contaminated water rather than in completely opposing directions as in a countercurrent tower. Proper selection of baffle spacing can produce a marked reduction in gas velocity, and consequently, a lower gas phase pressure drop thereby reducing blower energy costs compared to conventional countercurrent mode of operation.

Our testing of crossflow air stripping has included laboratory and pilot-scale towers using highly and moderately volatile contaminants (Reference 7). Laboratory tests included a 6-inch diameter tower which had the capability to vary the baffle spacing. Pilot-scale tests included a 12-inch diameter column with a fixed baffle spacing.

Our experiments determined the mass transfer and pressure drop characteristics of the crossflow device. Equations were developed for predicting the crossflow performance. Performance of the crossflow tower was compared to widely used correlations and our equations for designing air stripping equipment.

Results show the crossflow tower can greatly reduce the blower energy costs. However, for the highly volatile compounds, the blower energy cost is not a significant factor in the total cost. Therefore, a countercurrent tower would be just as cost-effective as a crossflow tower. Blower energy costs do have a significant impact on the total cost of air stripping for the low and moderately volatile contaminants. Therefore, the crossflow tower could be more cost-effective for removing these compounds from groundwater.

Conclusions

Air stripping and emissions control of the off-gases continue to be cost-effective treatment technologies for contaminated groundwater. Our future research in air stripping will be geared toward alleviating hardness precipitation and biological growth in air stripper equipment, testing the crossflow air stripper on low volatile contaminants (e.g., napthalene, acetone, phenol), and developing user-friendly personal computer software for designing the most cost-effective air stripping equipment. Our research in emissions control will continue with development and testing of catalysts resistant to deactivation, while also pursuing catalysts which require less energy for oxidation and destruction of the contaminants. These upcoming research efforts should continue to reduce the costs and technical problems associated with groundwater remediation activities.

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THE PRELIMINARY POLLUTANT LIMIT VALUE APPROACH: THE PC-EXECUTABLE PROGRAM VERSION

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INTRODUCTION

The US Army owns property contaminated with chemical agents, munitions, explosives, solvents, paints, smoke residues, or their environmental by-products. The contamination occurs in soil, surface water, or groundwater. Decisions need to be made as to whether remedial actions are required to reduce the amount or extent of contamination, despite often insufficient information concerning the contaminants. These decisions may be internally directed by the Army's Installation Restoration Plan or in response to regulations of the Comprehensive Environmental Response, Compensation and Liability Act of 1980, including 1986 amendments (commonly called "Superfund"), or in response to regulations of the Resource Conservation and Recovery Act.

The Preliminary Pollutant Limit Value (PPLV) approach has been developed and refined at the US Army Biomedical Research and Development Laboratory (Small, 1988). It provides answers to the "How Clean is Clean?" question, which is central to determining the need for or the extent of remedial actions. The PPLV approach is based on linking soil or water contamination levels to a dose which if attained, either through direct exposure to soil or water or through consumption of foodstuffs raised or grown on a contaminated site, would not pose a hazard to the exposed population. The approach consists of the following steps:

- Determine the pollutants of concern.
- Determine one or more soil- or water-use exposure scenarios, each of which is a collection of pathways. The pathways are "word pictures" which trace unique routes by which people are exposed to a pollutant.
- Develop an equation for each pathway that relates a person's intake of a pollutant to its concentration in soil or water.
- Collect the quantitative data involved in these equations.
- Compute the soil or water limits for individual pathways (SPLV), and from these, calculate PPLVs.
- Interpret the results.
- Determine if other considerations (such as aquatic toxicity) might indicate that limits lower than the PPLV should be applied.

The PPLV approach has recently been adapted to a software computer package, the Pollution Hazard Assessment System (PHAS). This paper overviews the PHAS program structure with emphasis on relating how the system supports the steps described above.

PHAS PROGRAM STRUCTURE

PHAS has been programmed in BASIC code, and is capable of being handled on most personal computer configurations. It can be operated on a system as elementary as a computer with 640K memory, two-disk drives, a monochrome monitor, and a line printer. The PHAS has been programmed to be "user-friendly"; procedures are menu-driven, and responses are prompted and monitored for logical or semantic errors.

Figure 1 shows the overall system structure. The component BASIC programs appear as boxes. The OPEN11 program provides the starting and exiting point for PHAS and for moving between programs. The cylindrical shapes indicate disk-stored files. These files can be created by the user at one time and recalled for use at a later time. The files share one of the three common extension designations ".PTH", ".LDS", or ".DAT", whose significance is explained below. The solid arrows between programs or between disk-stored files and programs indicate routes by which disk-stored file information is transferred during PHAS processing.

Generally, quantitative data processing in PHAS is two dimensional. One dimension deals with chemical specificity. For example, a fish bioconcentration factor is a chemical-specific property while a person's daily intake of fish is not. The second dimension deals with data use; some variables are used explicitly in pathway equations while other variables can be used to estimate these explicit variables if published information is not available.

SCENARIO DEVELOPMENT.

Scenario development is accomplished in the program PATWAY11. This program presents a menu of soil- or water-based pathways; these pathways are summarized in Table 1. The operator selects those of interest. PATWAY11 provides a printed "blueprint" of the input needs in terms of variables used in equations and estimations. This "blueprint" should be most useful at the start of a remedial investigation - endangerment assessment exercise, since it identifies data needs for assessments which may be provided from the investigation. PATWAY11 produces two integer indices. One index indicates the pathways selected. The other index indicates the status of variables relative to the scenario (i.e.: needed for a pathway equation, used in estimations, not needed at all). These indices are stored in a .PTH file.

DATA COLLECTION

The non-chemical specific data are processed by the INPUTS11 program. These data include information such as human consumption rates, livestock characteristics (several pathways deal with beef and dairy products), and site soil characteristics. A data set can be created in INPUTS11, or an existing set modified. A non-specific data set can be stored in a .LDS file for future use. A .PTH file, which has the pathway and status indices discussed above, can be used to restrict the extent of data processing only to data pertinent to the .PTH file scenario.

Chemical-specific data are processed by the CHMFIL11 program. These data include physical-chemical properties, partition coefficients for environmental

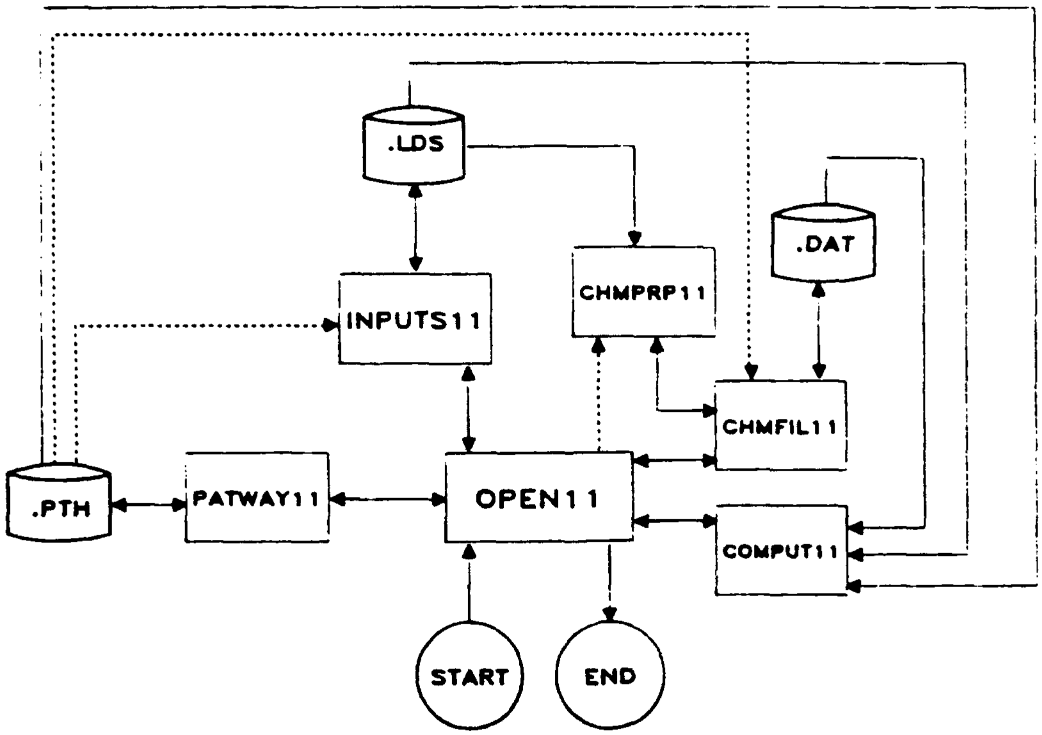


FIGURE 1. PHAS Programs and File Structure

transfer, and toxicologically-based limits for exposure. A new data set can be created here, or an existing data set modified. Moreover, CHMFIL11 can access estimation routines on an as-needed basis; these routines are in CHMPRP11. As with INPUTS11, a .PTH file can be used to regulate data appearance. A developed data set can be stored in a .DAT file for further use. CHMPRP11 can be accessed independently of the other programs in PHAS. This is an "a la carte" mode, where all inputs are manually provided, and no results are stored in a .DAT file.

ASSESSMENT ANALYSIS

The assessment analysis occurs in COMPUT11. Data for COMPUT11 can be obtained in several different ways. At one extreme, it is possible to run COMPUT11 with data in stored .PTH, .LDS, and .DAT files. This is shown in Figure 1 by the lines connecting these files to COMPUT11. At the other extreme, one can enter PATWAY11, INPUTS11, and CHMFIL11, develop the requisite data sets in each program, and then enter COMPUT11. Figure 2 shows a sample result for the hypothetical compound "2,7-Dinitrotoluene" due to exposure via the soil-related pathways with asterisks in Table 1. The first column indicates exposure in mg/day due to the presence of 1 mg/kg of pollutant in soil. The second column shows the SPLVs. The third column indicates exposure in mg/day if the PPLV level of concentration is in soil (mg/L in water); the sum of these exposures is the "Allowable Daily Intake" indicated.

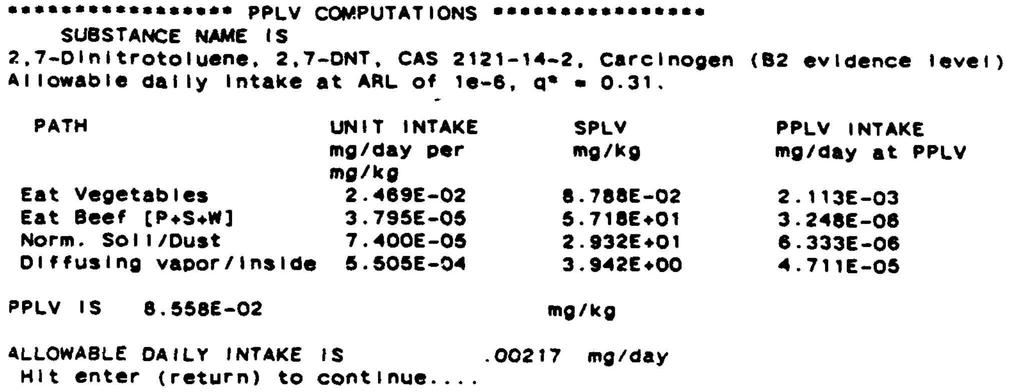
COMPUT11 also lets the user assess if constraints (such as aquatic toxicity) might indicate that limits lower than the PPLV should be applied. This

TABLE 1. PATHWAYS INCLUDED IN PHAS

Description	Environmental Media
Domestic water consumption	Water and soil
Fish consumption	Water and soil
Vegetable consumption	Water and soil*
Beef consumption, pollutant in cow's drinking water only	Water
Beef consumption, pollutant in pasture and water	Water
Beef consumption, pollutant in pasture only	Soil
Beef consumption, pollutant in pasture and soil	Soil
Beef consumption, pollutant in pasture, soil, and water	Soil*
Milk consumption, pollutant in cow's drinking water only	Water
Milk consumption, pollutant in pasture and water	Water
Milk consumption, pollutant in pasture only	Soil
Milk consumption, pollutant in pasture and soil	Soil
Milk consumption, pollutant in pasture, soil, and water	Soil
Exposure to normal dust levels (combined pollutant ingestion, inhalation and skin absorption)	Soil*
Exposure to construction activity levels of dust (combined as above)	Soil
Exposure to vapors diffusing from soil in confined area	Soil*
Exposure to vapors diffusing from soil in open area	Soil
Dermal absorption of pollutant from water on skin surface	Water and soil

---

* Pathways are used in sample printout shown in Figure 2



```
***************** PPLV COMPUTATIONS ****************
    SUBSTANCE NAME IS
2,7-Dinitrotoluene, 2,7-DNT, CAS 2121-14-2, Carcinogen (B2 evidence level)
Allowable daily intake at ARL of 1e-6, q* = 0.31.

  PATH                        UNIT INTAKE      SPLV          PPLV INTAKE
                              mg/day per       mg/kg         mg/day at PPLV
                              mg/kg
 Eat Vegetables                2.469E-02       8.788E-02      2.113E-03
 Eat Beef [P+S+W]              3.795E-05       5.718E+01      3.248E-08
 Norm. Soil/Dust               7.400E-05       2.932E+01      6.333E-06
 Diffusing vapor/inside        5.505E-04       3.942E+00      4.711E-05

PPLV IS   8.558E-02                          mg/kg

ALLOWABLE DAILY INTAKE IS            .00217  mg/day
 Hit enter (return) to continue....
```

FIGURE 2. Sample Assessment Result from COMPUT11

provides a "red flag" the user may want to explore in more detail in an environmental assessment coincident with an endangerment assessment.

APPLICATIONS

The term "preliminary" in the PPLV also applies to the PHAS. It is most useful at the start of an investigation exercise. It can help resolve questions of analysis sensitivity; clearly problems can occur if a proposed analytical method cannot detect the PPLV level of a compound. It can provide guidance as to what information should be sought in a remedial investigation.

The coded pathway equations are designed to be "safe-sided". Thus, for pathways considered within PHAS, the PHAS assessment can be used as a rough check of more complicated formulations proposed for similar pathways in endangerment assessments. The PHAS may be used for endangerment assessments with two caveats: first - the pathways to be considered are included in the PHAS pathway suite (see Table 1), and second - the rationale and assumptions involved in PHAS pathway development apply to the specific site situation. Small, 1988 should be consulted.

AVAILABILITY

At press time, "Version 1.1" of PHAS software has been prepared. The instruction manual is in draft form. Eleven .DAT files for common US Army explosives and propellants have been prepared for this software. The author will provide copies of the software, the draft manual, and supporting technical documentation to interested persons if they will provide the author two blank double-sided, double-density 5-1/4 inch diskettes. The author encourages practice with the software, and welcomes comments as to its use and any shortcomings encountered, either in the software or in the draft manual.

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Small, M. 1988. The Preliminary Pollutant Limit Value Approach: Manual for Users. Technical Report 8918, U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick MD. DTIC AD-A206976.

DISCLAIMER

TREATABILITY STUDY OF FOUR CONTAMINATED WATERS AT ROCKY MOUNTAIN ARSENAL, COMMERCE CITY, COLORADO, USING CHEMICAL OXIDATION WITH ULTRA-VIOLET RADIATION CATALYZATION

by

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ABSTRACT

The U.S. Army Engineer Waterways Experiment Station (WES) and Peroxidation Systems, Inc., Tucson, AZ, conducted a program to assess treatment of four contaminated waters found at Rocky Mountain Arsenal (RMA). One of the purposes of the program was to conduct laboratory and field treatability studies in order to proceed with a response action to treat liquid wastewater resulting from a variety of CERCLA and other RMA planned activities.

The evaluation consisted of chemical oxidation through ultraviolet/hydrogen peroxide (UV/H_2O_2) treatment of the wastewaters using a continuous plug-flow reactor. The four sources of wastewaters included the hydrazine wastewater storage tank, the South Plants wastewater storage tank, the North Boundary ground water, and the South Plants ground water, each with a varying degree of contamination. The wastewaters were representative of a wide range of activities at RMA such as:

- RMA Laboratory Wastewaters.
- Decontamination Pad Liquid Wastes.
- Remedial Investigation/Feasibility Study (RI/FS) Activity Wastes.
- Comprehensive Monitoring Program (CMP) Wastewaters.
- Interim Action Generated Wastes.

Field studies evaluated organic reduction in the four wastewaters. Significant removals of Diisopropylmethylphosphate, Dibromochloropropane, benzene, chloroform, and hydrazine were obtained. UV/H_2O_2 treatment was most effective on the South Plants wastewater storage tank and the North Boundary ground water. Significant removal was also obtained on the hydrazine wastewater storage tank and South Plants

ground water. However, the more concentrated wastewaters will require pretreatment with chemical addition and an adjustment in H_2O_2 dose, run time, UV intensity or perhaps the addition of a process catalyst.

INTRODUCTION

The Rocky Mountain Arsenal (RMA) occupies over 17,000 acres in Adams County, Colorado. Figure 1 shows the Arsenal location in proximity to Denver, Colorado. The property occupied by RMA was purchased by the government in 1942. Throughout World War II, RMA manufactured and assembled chemical intermediate and toxic end-products, and incendiary munitions. During the 1950's, RMA produced GB nerve agent and filled munitions with the agent until late 1969. In 1970, RMA began the demilitarization of chemical warfare material by caustic neutralization and incineration. Since 1960, the RMA also operated an Aerozine 50 rocket fuel production facility owned by the U.S. Air Force at the Arsenal. In addition to these military operations, portions of the Arsenal have been leased to Shell Oil Company for the manufacture of chemicals including pesticides and herbicides. As a result of these activities at the RMA, the migration of contaminants into the environment and, in particular, portions of the shallow alluvial aquifer has occurred.

Since 1988, the Army and Shell Oil Company have been actively pursuing a program to treat wastewater resulting from the assessment and implementation of response actions for control and cleanup of contamination on RMA. As part of this program, the Army tasked the U.S Army Engineer Waterways Experiment Station (WES) to conduct an assessment and to develop the information needed to proceed with a response action to treat liquid wastewater resulting from a variety of CERCLA and other existing and planned RMA activities. Some identified sources of RMA wastewater are:

- RMA laboratory wastewaters
- Decontamination pad liquid wastes
- Remedial Investigation/Feasibility Study (RI/FS) activity wastes
- Comprehensive monitoring program (CMP) wastewater
- Interim action generated wastes

Currently, wastewaters generated from these activities are being treated by RMA using a 10 gpm system comprised of activated carbon, activated alumina, and an air stripper. This existing treatment system (ETS) has been unable to consistently achieve 10 gpm due to a history of operational problems.

A conceptual treatment system has been proposed by WES and is illustrated in Figure 2. Pilot studies of the different treatment processes presented in Figure 2 were performed by WES to develop data and requirements for design of the conceptual wastewater treatment system (CWTS). An evaluation of chemical oxidation coupled with ultraviolet radiation catalyzation for treatment of four contaminated waters was performed as part of the pilot scale studies at RMA. Chemical oxidation with UV irradiation was included as part of the CWTS to improve system flexibility for treating a wide variety of liquid wastes that will be generated during RMA site remediation and monitoring activities. This paper focuses on the UV/hydrogen peroxide process treatability study results.

THE ULTRAVIOLET/HYDROGEN PEROXIDE PROCESS

The UV/hydrogen peroxide oxidation is a treatment process that incorporates the synergistic effects of hydrogen peroxide with ultraviolet radiation to destroy many organic contaminants found in a variety of contaminated wastewaters. One important aspect of the technology is that it is a destruction technology that is capable of reducing many traditionally hard-to-treat contaminants to non-hazardous reaction products, such as water and carbon dioxide.

The mechanism(s) of contaminant destruction during UV/hydrogen peroxide treatment varies depending on contaminant type. Some contaminants are easily degraded by the oxidizing agents alone, with UV radiation having little effect on treatment (IIT Research Institute, 1989, Kuo and Soong, 1984). On the other hand, some compounds are very difficult to chemically oxidize, but, in the presence of UV radiation, absorb the UV radiation, thereby, becoming excited and then moving into a higher energy state becoming susceptible to chemical oxidation. In some cases, UV irradiation alone is capable of destroying a contaminant. Sundstrom et al (1986) found that the addition of a chemical oxidizer had little effect on the destruction of chloroform during photolysis.

Although, individual contaminants may be destroyed by UV irradiation or chemical oxidation alone, most wastewaters contain a variety of contaminants requiring different treatment conditions. The synergistic effect of chemical oxidizers and UV irradiation may decrease reaction time and reduce the formation of chemical intermediates during treatment of these multi-component wastewaters. One distinct advantage of combined UV/hydrogen peroxide treatment is the formation of hydroxyl radicals (OH^-). The hydroxyl radical, a deterioration product of the photolysis of hydrogen peroxide, is a much stronger oxidizer than hydrogen peroxide (Sundstrom et al, 1986).

TECHNICAL APPROACH

A total of six runs were made on each contaminated water source (test influent waters). The runs varied by flow rate and influent hydrogen peroxide dosage. The effect of the hydraulic retention time (HRT) within the reactor and oxidizer concentration were evaluated for each contaminated water. The amount of contact time between the contaminants in the influent and the UV light is dependent on HRT. The longer the HRT, the longer the UV contact time. HRT is function of the flow rate into the reactor and reactor volume as described by the following equation:

$$\mathrm{HRT} = V / Q \qquad (1)$$

where,

HRT = Hydraulic retention time, minutes
Q = flow rate, gallons per minute (gpm)
V = Reactor volume, gallons

Three flow rates, low, medium, and high, were evaluated. With each flow rate, two hydrogen peroxide influent dosages, high and low dosages, were evaluated. Therefore, three HRTs were evaluated with two respective influent hydrogen peroxide dosages associated with each HRT. This allowed the effects of UV contact time (HRT) and varying oxidizer concentrations on the contaminant removal rates to be evaluated.

DESCRIPTION OF STUDY INFLUENTS

The four test influent waters for this study were ground water collected from Sump A of the North Boundary treatment system, ground water from the South Plants complex, a hydrazine contaminated wastewater left over from the decontamination activities of the Aerozine mixing plant, and wastewater from the influent tank of the existing treatment system (ETS). The ETS influent is believed to contain basically the same contaminants and respective concentrations as the majority of the influents that will be treated by the CWTS. The other contaminated waters evaluated during this study represent waters containing the maximum possible degree of contamination the CWTS should ever treat. No pretreatment (i.e. pH adjustment) or catalyst addition was done on any of test influents discussed in this paper.

The principal contaminants of interest for each contaminated water are listed with their respective concentrations in Table 1. Although several other contaminants not listed in Table 1 were detected in most of the test influents for this study at much lower concentrations, only those contaminants listed in Table 1 will be discussed in this paper.

UV/HYDROGEN PEROXIDE REACTOR

The UV/hydrogen peroxide reactor used during this study was a Model CW-40 obtained under contract from Peroxidation Systems Incorporated (PSI), Tucson, Arizona. The reactor had a 55 gallon volume and was equipped with eight ultraviolet lamps that were laid within horizontal quartz tubes. The quartz tubes traversed the reactor and were positioned perpendicular to flow. The quartz tubes were sealed using two rubber O-rings with compression washers. The UV lamps were capable of delivering high or low UV intensities. All of the UV lamps were always set on high UV intensity during this study.

The PSI Reactor CW-40 was a plug flow reactor in which hydrogen peroxide was added directly into the influent line via an injection tee located in front of an in-line static vortex mixer. This mixer allows the waste-water/hydrogen peroxide solution (influent) to be completely mixed before entering the reactor. Influent was fed into the reactor using a stainless steel centrifugal pump. Influent flow rate into the reactor was set using a valve and flowmeter located on the influent line of the system. Electrical power requirements for the reactor was 40 kilowatts.

A 50 percent hydrogen peroxide solution was used during this study. The hydrogen peroxide was supplied using a chemical metering pump capable of accurately delivering the hydrogen peroxide at the required feed rate to the injection tee by simple pump flow rate adjustment.

Hydrogen peroxide feed rates were set only after the reactor temperature had stabilized because hydrogen peroxide deterioration is dependent on temperature. The time required for temperature stabilization varied according to influent flow rate due to the excessive amount of heat given off by the eight UV lamps (the greater the flow, the lower the reactor temperature). Reactor temperature was the controlling factor when determining the minimum influent flow rate (i.e. highest HRT). The reactor temperature was not allowed to exceed 125 ° F as specified by PSI.

The low hydrogen peroxide dose for each run was set first for each flow rate by adjusting the hydrogen peroxide feed pump until the effluent hydrogen peroxide concentration was approximately 10 mg/l. This effluent concentration assured that the oxidation reactions occurring within the reactor were not hydrogen peroxide limited. Once the effluent hydrogen peroxide concentration was 10 mg/l, the influent hydrogen peroxide dosage or concentration was determined based on the hydrogen peroxide feed pump settings (i.e. pump flow rate). The high hydrogen peroxide dosage was determined by approximately tripling the low hydrogen peroxide influent dosage. The hydrogen peroxide feed pump settings were adjusted to increase the hydrogen peroxide flow rate through the injection tee by a factor of three.

Sampling and Analysis of Test Influents and Effluents

Sampling ports were located before the hydrogen peroxide injection tee, after the vortex mixer (pre-UV reactor), and after the UV/hydrogen peroxide reactor (post-treatment). Influent and effluent hydrogen peroxide concentrations were monitored using EM Quant brand test strips. All pH measurements were made in the field using a portable pH meter. Temperature measurements were made using in-line thermometers located on the influent and effluent lines.

Two influent samples were collected during treatment of each contaminated water to insure that the same quality influent was used throughout all six treatment runs. Three effluent samples were used to evaluate effluent quality obtained from each treatment run.

The ETS influent, North Boundary ground water, and South Plants ground water influent and effluent samples were analyzed for volatile contaminants, semi-volatile organic contaminants, and pesticides from the US Environmental Protection Agency's Priority Pollutant list, and other organic contaminants characteristic of waters found at RMA. These chemical analyses were performed by DataChem Incorporated, Salt Lake

City, Utah. The hydrazine wastewater was analyzed for hydrazine and its related compounds by the Analytical Laboratory Group of WES, Vicksburg, Mississippi.

RESULTS

The influent flow rate, HRT, and influent and effluent hydrogen peroxide concentrations, pH, and temperature from each test run are presented in Tables 2 - 5. The results from the treatability test runs for each test influent water are presented in Tables 6 - 9. Tables 6 - 9 present the percent of contaminant removed during each respective treatment run. A discussion of the results of UV/hydrogen peroxide treatment for each test influent water is discussed individually below.

Existing Treatment System Influent

The results of the EST influent UV/hydrogen peroxide runs are presented in Table 6. All six runs resulted in complete destruction of benzene. The percent removals of chloroform from the EST influent runs were all below 50 percent,except for the high HRT, low hydrogen peroxide dose run. The high HRT, low hydrogen peroxide dose run resulted in a 71 percent reduction of chloroform. One explanation is that the lower HRT runs did not allow enough UV contact time to completely remove the chloroform. Sundstrom et al (1987) determined that UV treatment alone was as effective as combined UV and hydrogen peroxide treatment indicating that chloroform is removed primarily through photolysis during UV/hydrogen peroxide treatment. The high HRT, high hydrogen peroxide run achieved approximately half the chloroform removal than the high HRT, low hydrogen peroxide run (see Table 6). The excess hydrogen peroxide not utilized for contaminant oxidation during the high HRT, high hydrogen peroxide dose run could have absorbed much of the available UV energy for degradation into other oxidizer species, water, and oxygen, thereby reducing available UV energy for chloroform destruction.

Excellent percent removals of nemagon were obtained during all test runs (Table 6). The mid-HRTs runs had the lowest percent nemagon removals of all the test runs. Although, the difference between the performance of the mid-HRT runs and the other test runs for removing nemagon is not considered significant.

The two low HRT runs were appreciatively different from each of the other runs in terms of DIMP removal, indicating that the DIMP oxidation reaction kinetics may be dependent on oxidizer concentration. The low hydrogen peroxide dose run had 19 percent less DIMP removed than the high hydrogen peroxide dose. This difference is attributed to the increased amount of hydrogen peroxide and OH^- available for chemical oxidation during the high hydrogen peroxide dose run.

North Boundary Ground Water

The influent DIMP concentrations for the North Boundary ground water were approximately 1.5 orders of magnitude higher then those detected in the ETS influent (Table 1). All of the DIMP percent removals in the North Boundary ground water were in excess of 87 percent for all runs evaluated (Table 7). The percent DIMP removal for the low HRT, low hydrogen peroxide run was better then the ETS influent low HRT, low hydrogen peroxide run (Tables 6 and 7) even though the EST influent had lower concentrations of DIMP. The percent removal of DIMP from the North Boundary ground water was approximately the same with less hydrogen peroxide required, because the North Boundary ground water has fewer organic contaminants requiring chemical oxidation than the ETS influent. Therefore, more chemical oxidizers were available for DIMP oxidation.

Hydrazine Wastewater

The hydrazine wastewater runs resulted in percent removals of UDMH in excess of 69 percent for all runs (Table 8). The higher hydrogen peroxide doses produced higher percent removals for all of the hydrazine wastewater contaminants, except NDMA, than the low hydrogen peroxide dosages. NDMA is an intermediate formed during oxidation of the hydrazine derivative organics (UDMH and MMH).

The IIT Research Institute Inc. (1989) working under contract with the US Air Force investigated the production of NDMH during the oxidation of MMH and UDMH. Their findings indicate that NDMH production is proportional to the extent of oxidation of the hydrazine derivative compounds. Therefore, the greater the extent of UDMH and MMH oxidation, the greater the amount of NDMH produced as an oxidation reaction intermediate.

The formation of NDMA during oxidation of UDMH and MMH is especially apparent during the high HRT, high hydrogen peroxide run. Significant oxidation of the UDMH and MMH took place with little NDMH reduction occurring (the NDMA that was removed was replaced by the NDMA produced during the oxidation of the MMH and UDMH). On the other hand, the runs where little MMH oxidation occurred, such as the high HRT, low hydrogen peroxide run, resulted in high percent removals of NDMA. The observed NDMA removal is probably due to the oxidation of the NDMA originally in the influent prior to treatment and not destruction of the NDMH produced during treatment via UDMH and MMH oxidation.

Hydrazine oxidation was appreciatively better during the high hydrogen peroxide dose runs. Hydrazine and MMH destruction was not enhanced by increased UV irradiation (higher HRTs). Hydrazine and MMH removals were dependent on the amount of hydrogen peroxide available for oxidation (i.e., higher doses). This finding is consistent with IIT Research Institute's conclusions (1989).

Another observation noted by IIT Research Institute during their studies was during UV/hydrogen peroxide treatment of a wastewater contaminated with hydrazine and related hydrazine organic compounds, the pH was significantly lowered as treatment proceeded. They concluded that this was primarily due to the formation of organic acids during oxidation of the hydrazine and related derivative compounds (IITRI 1987). The results of the RMA hydrazine wastewater UV/hydrogen peroxide test runs are consistent with IIT Research Institute's findings. The high HRT, high hydrogen peroxide dose run, in which the greatest percent removal of hydrazine and related compounds occurred, had the largest decrease in pH for all the runs (Table 4).

South Plants Ground Water

Contamination of the South Plants ground water is comprised primarily of volatile organic compounds, mainly benzene (see Table 1). There was little or no removal of any of the organic contaminants achieved during any of the six South Plants ground water runs (Table 9). The high hydrogen peroxide dose runs resulted in the higher percent removals for all of the contaminants, except for benzene during the high HRT runs. This observation suggests that increased hydrogen peroxide doses and treatment time would be required for further removal of the contaminants.

The highest percent removal of benzene occurred during the medium HRT, high hydrogen peroxide run. The lower percent removal of benzene during the high HRT, high hydrogen peroxide run could be attributed to the partial degradation of the other aromatics present in the South Plants ground water into benzene (i.e. benzene is an intermediate). Only 67 percent of the available hydrogen peroxide was utilized during the high HRT, high hydrogen peroxide dose run indicating that the oxidation reactions during this run were not hydrogen peroxide limited. The benzene oxidation reactions occurring during UV/hydrogen peroxide treatment of the South Plants ground water apparently required more reaction time than was allotted during the high HRT, high hydrogen peroxide dose run.

Chloroform percent removals during the low hydrogen peroxide dose runs were higher than those for the high hydrogen peroxide dose runs (Table 9). The chloroform data from the ETS influent runs also resulted in improved removal of chloroform during the low hydrogen peroxide dose runs (Table 6). As observed during the ETS influent runs, deterioration of hydrogen peroxide during photolysis is absorbing UV radiation that would be available for chloroform destruction.

CONCLUSIONS

The following conclusions were made based on the results of this study:

a. Benzene was successfully removed from the existing treatment system influent, with little benzene being removed from the South Plants ground water.

b. Both Nemagon and DIMP were effectively removed during all the test runs in which these chemicals were present.

c. Absorption of the UV radiation by the available hydrogen peroxide during the high HRT, high hydrogen peroxide dose runs resulted in lower chloroform removals than the high HRT, low hydrogen peroxide dose runs.

d. The lower oxidizer requirements of the North Plants ground water resulted in lower hydrogen peroxide doses than the existing treatment system influent and in equal success in the removal of DIMP.

e. The high HRT, high hydrogen peroxide run had the lowest NDMA removal and highest hydrazine, UDMH, MMH removals of all the hydrazine wastewater runs. This run also resulted in the greatest reduction of pH for any of the runs.

COMMENTS

In general, it appears that longer UV contact time and increased hydrogen peroxide doses may have resulted in higher percent removals of all the contaminants. This is especially true for the highly contaminated waters, such as the hydrazine wastewater and South Plants ground water. However, excellent treatment was obtained for the mildly contaminated waters, such as the existing treatment system influent and North Boundary ground water.

The UV/hydrogen peroxide unit selected for use as part of the CWTS should be flexible enough to be operated in both batch and continuous modes of operation. The selected mode operation of UV/hydrogen peroxide reactor used for treatment of a wastewater at the CWTS will depend on the types of contaminant(s) and relative concentrations detected in the influent (this is true for the whole CWTS as well).

Increased hydrogen peroxide dosages should reduce the required HRT, although treatment of some contaminants, such as benzene in the SPGW, is simply reaction rate limited. Other measures to reduce treatment time that were not evaluated doing this study that need to be investigated are the use of cation-based catalysts and lowering the influent pH prior to treatment.

ACKNOWLEDGEMENTS

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Table 1

Selected Organic Analysis of Contaminated Influent Waters

Influent	Analyte	Concentration (ug/l)
Hydrazine Wastewater:		
	Nitrodimethylamine (NDMA)	270.0
	Monomethylhydrazine (MMH)	130.0
	Hydrazine	4200.0
	Unsymmetrical-Dimethylhydrazine (UDMH)	4250.0
Existing Treatment System Water:		
	Benzene	2.3
	Chloroform	5.2
	Nemagon (DBCP)	2.6
	Diisopropyldimethylphosphonate (DIMP)	70.3
North Boundary Ground Water:		
	Diisopropyldimethylphosphonate (DIMP)	806.7
South Plants Ground Water:		
	Benzene	355,000.0
	Carbon Tetrachloride	155.0
	Chloroform	2,500.0
	Toluene	685.0
	Trichloroethylene (TCE)	140.0
	Xylene	160.0

Table 2

Existing Treatment System Influent System Operational Data

Flow (gpm)	Retention Time (min.)	Influent H202 Dosage (mg/l)	Effluent H202 Dosage (mg/l)	Influent Temp. (f)	Effluent Temp. (f)	Influent pH	Effluent pH
14	4	201	30	38	60	9.63	7.75
14	4	72	10	39	58	9.17	7.42
10	6	367	30	38	66	9.54	7.20
10	6	121	10	41	70	9.24	6.59
5	11	970	50	52	93	9.50	7.23
5	11	501	10	53	110	9.66	6.49

Table 3

North Boundary Ground Water System Operational Data

Flowrate (gpm)	Retention Time (min.)	Influent H202 Dosage (mg/l)	Effluent H202 Dosage (mg/l)	Influent Temp. (f)	Effluent Temp. (f)	Influent pH	Effluent pH
13	4	186	50	56	78	7.54	7.33
13	4	38	10	56	78	7.54	7.29
10	6	239	30	56	86	7.50	7.14
10	6	78	10	56	85	7.54	7.20
5	11	998	40	49	105	7.51	7.17
5	11	489	10	49	105	7.51	7.18

Table 4

Hydrazine Wastewater System Operational Data

Flowrate (gpm)	Retention Time (min.)	Influent H202 Dosage (mg/l)	Effluent H202 Dosage (mg/l)	Influent Temp. (f)	Effluent Temp. (f)	Influent pH	Effluent pH
10	6	215	30	34	68	10.50	10.27
10	6	104	10	34	68	10.50	10.36
6	9	519	30	34	80	10.43	10.15
6	9	164	10	35	81	10.50	10.39
3	18	1037	30	34	110	10.46	9.79
3	18	328	10	34	110	10.46	10.23

Table 5

South Plants Ground Water System Operational Data

Flowrate (gpm)	Retention Time (min.)	Influent H202 Dosage (mg/l)	Effluent H202 Dosage (mg/l)	Influent Temp. (f)	Effluent Temp. (f)	Influent pH	Effluent pH
14	4	170	30	52	74	7.61	7.27
14	4	55	10	52	72	7.61	7.08
8	7	152	30	50	84	7.61	7.33
8	7	55	10	50	82	7.61	7.14
3	18	365	120	50	118	7.61	7.24
3	18	122	20	50	118	7.61	7.29

Table 6

Percent Reduction of Contaminants
Existing Treatment System Influent

	High-HRT		Mid-HRT		Low-HRT	
Contaminant	Low H202	High H202	Low H202	High H202	Low H202	High H202
Benzene	100.0	100.0	100.0	100.0	100.0	100.0
Chloroform	71.7	49.4	35.9	34.6	28.8	38.1
Nemagon	100.0	100.0	92.3	89.9	100.0	100.0
DIMP	100.0	100.0	100.0	100.0	76.7	95.4

Table 7

Percent Reduction of Contaminants
North Boundary Ground Water

	High-HRT		Mid-HRT		Low-HRT	
Contaminant	Low H_2O_2	High H_2O_2	Low H_2O_2	High H_2O_2	Low H_2O_2	High H_2O_2
DIMP	99.8	100.0	99.7	98.0	96.8	87.2

Table 8

Percent Reduction of Contaminants
Hydrazine Wastewater

	High-HRT		Mid-HRT		Low-HRT	
Contaminant	Low H2O2	High H2O2	Low H2O2	High H2O2	Low H2O2	High H2O2
NDMA	83.7	25.8	48.4	73.6	62.3	0.0
MMH	10.3	82.1	-2.6	42.3	5.1	0.0
UDMH	68.7	95.0	63.9	87.4	69.6	72.1
Hydrazine	27.1	81.2	26.3	54.5	8.2	17.7

Table 9

Percent Reduction of Contaminants
South Plants Ground Water

	High-HRT		Mid-HRT		Low-HRT	
Contaminant	Low H202	High H202	Low H202	High H202	Low H202	High H202
Benzene	13.6	27.7	21.1	38.0	4.2	-0.1
Carbon Tet.	16.1	14.0	-7.5	1.1	-9.7	-9.7
Chloroform	12.1	9.2	-3.6	-0.7	-2.1	-5.0
Toluene	6.1	10.5	-12.9	-2.2	9.0	10.0
TCE	11.9	9.5	-14.3	-7.1	-7.1	-7.1
Xylene	16.7	20.8	-2.1	4.2	12.5	10.4

THE NAVY'S SHORESIDE ENVIRONMENTAL PROTECTION RDT&E PROGRAM: A STRATEGY FOR ENVIRONMENTAL COMPLIANCE AT NAVAL SHORE FACILITIES

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INTRODUCTION

Increasing environmental compliance requirements are impacting on the operational effectiveness of Navy Shore Facilities. This year the Naval Facilities Engineering Command (NAVFACENGCOM) received numerous requests for research, development, test and evaluation (RDT&E) assistance from Navy Major Claimants. These requests were based on potential operational impacts from the inability to comply with current and impending environmental laws and regulations. Operational impacts identified ranged from the high cost of technical solutions and increased manpower requirements to facility shutdowns and possible criminal and civil liability. RDT&E is required to develop new and innovative technologies to assure cost effective compliance with environmental laws and regulations.

An integrated RDT&E program is required to address a broad range of environmental requirements and to meet the challenge of overall environmental protection. NAVFACENGCOM has established specific goals and thrust areas to facilitate the development of an integrated RDT&E program. These goals and thrust areas are listed in Table 1. The legislative and regulatory mandate for each goal is listed in Table 2. The execution of RDT&E projects aimed at achieving these goals is necessary for the Navy to obtain and maintain cost effective environmental compliance for shoreside facilities and operations.

TABLE 1: NAVY ENVIRONMENTAL RDT&E GOALS (NAVFAC PERSPECTIVE)

I. Zero discharge of hazardous wastes from Navy industrial facilities.

THRUST AREAS:

- Waste Stream Treatment for Industrial Processes
  - . Emptying, Cleaning, and Derusting Bilges and Tanks
  - . Painting and Paint Stripping Operations
  - . Boiler Lay-up and Cleaning Operations
- Ordnance Operations and Waste Disposal
- Lubricants and Other Fluids Change-outs
- IWTP Reagents Use and Reuse

II. Acceptable cleanup levels achieved at all Navy past hazardous waste disposal sites.

THRUST AREAS:

- Remediation Technologies
  - . Biological (In situ and bioreactors)
  - . Chemical
  - . Physical
- Risk Assessment and Risk Management Methodologies
- Site Restoration and Closure Techniques

III. One hundred percent reclamation of industrial and municipal waste water at Navy facilities.

THRUST AREAS:

- Conservation
- Reuse and Reclamation of Waste Water
- Reduction of Water Total Toxic Organics
- Groundwater Protection
- Monitoring and Protection of Drinking Water

IV. Zero air emissions and acceptable noise emissions from Navy shore facilities.

THRUST AREAS:

- Air Emissions Control
- Alternatives to Volatile Organic Carbon (VOC) Coatings
- Control of New and Emerging Air Pollutants
- Noise Reduction and Control
- Alternatives to Chlorofluorocarbon (CFC) Applications

V. Nonpolluting, safe, and state-of-the-science materials and industrial processes for Navy facilities.

THRUST AREAS:
- Improvements for Industrial Processes
  - . Emptying, Cleaning, and Derusting Bilges and Tanks
  - . Painting, Paint Stripping Operations
  - . Boiler Lay-up and Cleaning Operation
- Substitution for Nonhazardous Materials
- Nonpolluting Antifouling Systems

VI. State-of-the-science methods and instrumentation for cost effective monitoring of Navy unique pollutants and contamination.

THRUST AREAS:
- Sensor Development
  - . Sensor Networks
  - . Real Time Sensors for Process Control and Monitoring
- Biomonitoring for Toxicity and Hazard Assessment
- Monitoring Network Design and Implementation

VII. Comprehensive prediction and management of environmental effects from Navy systems and operations.

THRUST AREAS:
- Control of Nonpoint Source Pollution
- Modeling and Prediction of Environmental Effects
- Remote Sensing and Remote Detection
- Site Closure and Excess Property Procedures

TABLE 2: THE STATUTORY AND REGULATORY MANDATE FOR THE NAVY ENVIRONMENTAL RDT&E GOALS (NAVFAC PERSPECTIVE)

I. Zero discharge of hazardous wastes from Navy industrial facilities.

Resource Conservation and Recovery Act (RCRA), Clean Water Act - National Pollution Discharge and Elimination System (CWA-NPDES), Toxic Substances Control Act (TSCA), Federal, Insecticide, Fungicide and Rodenticide Act (FIFRA), National Ocean Pollution Planning Act (NOPPL), Used Oil Recycling Act (UORA)

II. Acceptable cleanup levels achieved at all Navy past hazardous waste disposal sites.

Comprehensive Environmental Response Compensation and Liability Act and Superfund Amendment and Reauthorization Act (CERCLA and SARA), National Contingency Plan (NCP), Hazardous and Solid Waste Amendments (HSWA), Applicable or Relevant and Appropriate Requirements (ARARs)

III. One hundred percent reclamation of industrial and municipal waste water at Navy Facilities.

CWA, Safe Drinking Water Act (SDWA), Water Resources Planning Act (WRPA), State Regulations, economic necessity

IV. Zero air emissions and acceptable noise emissions from Navy shore facilities.

Clean Air Act, TSCA, Noise Ordinances, State Regulations

V. Nonpolluting, safe, and state-of-the-science materials and industrial processes for Navy facilities.

RCRA, Occupational Safety and Health Act (OSHA), NPDES, TSCA, FIFRA, State Regulations, economic necessity

VI. State-of-the-science methods and instrumentation for cost-effective monitoring of Navy pollutants and contamination.

National Environmental Policy Act (NEPA), CERCLA and SARA, RCRA, CWA (Dredging Requirements, National Estuary Program, Nonpoint source, NPDES), Ocean Dumping, State Regulations, economic necessity

VII. Comprehensive prediction and management of environmental effects from Navy systems and operations.

NEPA, Coastal Zone Management Act (CZMA), Endangered Species Act, Farm Bill (nonpoint source), Marine Protection, Research and Sanctuaries Act, Exclusive Economic Zone, Outer Continental Shelf - "Ocean Sanctuary", Floodplain Insurance Act (increased liability in coastal areas)

PROGRAM STRUCTURE

The environmental RDT&E program sponsored by NAVFACENGCOM addresses three program areas: hazardous waste minimization (HAZMIN), Installation Restoration (IR), and Pollution Abatement Ashore (PA). The HAZMIN projects are supported with Navy Defense Environmental Restoration Account (DERA) funds set aside to reduce hazardous waste generation at Navy facilities; the IR projects are also supported with Navy DERA funds; and the PA projects are supported with funds from the RDT&E Program Element 0603721N, Y0817.

HAZMIN and IR program RDT&E is required to develop a technology base capable of minimizing hazardous waste generation and reducing the cost of cleaning up hazardous waste sites. Innovative technology development is required for physical, chemical, and biological treatment of hazardous wastes, methods for risk assessment and risk management of hazardous waste sites, and techniques for site restoration and site closure. The majority of technology development projects can be executed as demonstration projects at specific IR sites. However, RDT&E funds are required to support feasibility studies of specific technologies that are not mature enough for demonstrations. These RDT&E funds are used for selected technology development projects and for integrated strategy development for solving technological problems associated with site restoration and hazardous waste minimization.

PA program RDT&E is required to reduce mission impact and cost of compliance with Federal and State laws and regulations primarily driven by the Clean Water Act, Clean Air Act, and the National Environmental Policy Act.

Major program thrust areas include:

Industrial Improvements. RDT&E is required to identify and implement nonpolluting industrial processes for Navy unique industrial and waterfront facilities. New industrial processes and replacement of toxic chemical processes are required to cost effectively meet Federal and state regulations requiring pretreatment of industrial wastewater.

Monitoring and Assessment. The Navy must develop systems to aquire scientifically sound and legally defensible monitoring and assessment data to document the environmental safety of Navy operations.

Water Conservation and Reuse. RDT&E is required to develop water conservation and reuse technology due to increased demand for water supplies, seawater intrusion into coastal aquifers, and the high cost of potable water supplies. Effective management and use of available water resources will be required. This problem will be especially acute in the Southwest and Florida.

Air Emission Control. RDT&E is required to identify: the substitution of materials and emission control technology for volatile organic compound (VOC) emissions from solvents and paints; the substitution of materials for chlorofluorocarbons (CFC) and halon systems that will be banned to prevent ozone depletion; and technology to mitigate and control noise pollution.

Methods and Instrumentation. RDT&E is required to develop methods and instrumentation to measure unique Navy pollutants. These methods and materials will be required for determining the extent of environmental pollution and the effectiveness of the Navy's pollution abatement program.

Comprehensive Prediction and Management. RDT&E is required to develop methods to integrate environmental information that will provide effective management of harbor areas, wetlands, shorelines, and other natural resources. Modeling and prediction of long term impacts will provide tools necessary for management of the Navy's environmental resources. Methods and technologies needed for Navy compliance with requirements of nonpoint source runoff, coastal zone management, and endangered species legislation are the most urgently needed.

PROGRAM METHODOLOGY

Each project listed in this execution plan has undergone rigorous prioritization by NAVFACENGCOM. Each proposal has been reviewed to assure adherence with project documentation requirements established by NAVFACENGCOM. Representatives from the laboratories were given the opportunity to present their proposals at the R&D Planning and Review Meeting. Each proposal was reviewed and commented on by the Engineer In Charge (EIC) responsible for the respective program area. The projects were then ranked according to their technical merit and applicability to the established goals and thrust areas (Table 1). Only the projects receiving the highest priority are included in the execution plan.

HAZARDOUS WASTE MINIMIZATION

NAVAL CIVIL ENGINEERING LABORATORY

Tracking# Title

HW-89-01 Expert System for Haz Min

OBJECTIVE: Develop expert system for selecting HAZMIN technologies at Navy Facilities:
FY90 EXECUTION: Complete user data package and transition to NEESA.
STATUS: Completed feasibility study and software package.

HW-89-02 Non-Cyanide Electroplating

OBJECTIVE: Develop a process that will minimize or eliminate toxic cyanide waste generation from Navy electroplating processes.
FY90 EXECUTION: Complete initial feasibility study for pulse plating of cadmium on steel.
STATUS: Completed evaluation of closed-loop, non-cyanide, non-acidic cadmium process with promising results.
HW-89-04 Cyanide Minimization

OBJECTIVE: Develop technologies for treating cyanide waste streams.
FY90 EXECUTION: Complete user data package and technical note for electrolytic system at NADP Norfolk; upon final approval initiate evaluation of ion exchange-gas membrane system and selective metal removal for ion exchange recovery systems.
STATUS: Completed operational test of electrolytic treatment system at Norfolk NAVAIRDEP.

HW-89-09 Purification of Metal Finishings

OBJECTIVE: Develop closed loop purification and metal recycling process for electroplating.
FY90 EXECUTION: Defer until completion of higher priority HAZMIN projects.
STATUS: Identified problem areas during technical evaluation of purification/recovery/reuse applications.

HW-89-11 Non Persistent Emulsifiers

OBJECTIVE: Evaluate effectiveness of non-persistent fast-breaking degreasers for bilge and tank cleaning.
FY90 EXECUTION: Defer until completion of FFR and higher priority HAZMIN projects.
STATUS: Draft final feasibility report in review process.

HW-89-12 Recycling Hydroblast Wastewater

OBJECTIVE: Reduce wastewater from hydroblasting by 90%.
FY90 EXECUTION: Implement recycling technology at Norfolk Naval Shipyard and prepare user data package and specifications for transition.
STATUS: Determined final feasibility and completed field tests at Norfolk Naval shipyard with coordination with NAVSSES.

Tracking# Title

HW-89-19 Beneficial Use of Acid/Alkaline

OBJECTIVE: Maximize beneficial use of acid and alkali waste generated at Navy industrial facilities by using the wastes as reagents in IWTPs.
FY90 EXECUTION: Defer until completion of higher priority HAZMIN projects.
STATUS: Completed IFR and determined cost effectiveness of approach.

HW-89-24 Sodium Nitrate Reduction

OBJECTIVE: Develop cost effective method to eliminate sodium nitrite waste from shipyards.
FY90 EXECUTION: Complete final feasibility of chemical and biological treatment methods. Develop plan for operational test at shipyard with NAVSEA concurrence.
STATUS: Initiated laboratory investigation of treatment methodologies.

HW-89-25 Citric Acid Reduction

OBJECTIVE: Reduce volume and disposal cost of Naval shipyard wastes containing citric acid.
FY90 EXECUTION: Determine feasibility of ultra violet hydrogen peroxide treatment.
STATUS: Evaluated ion-exchange process as not feasible.

HW-90-33 Electrodialytic Membrane

OBJECTIVE: Develop electrodialytic membrane technology for treatment and minimization of hazardous wastes containing metals.
FY90 EXECUTION: Defer until completion of other plating waste demonstrations.
STATUS: New Start.

HW-90-34 Shelflife Specifications

OBJECTIVE: Develop recommendations for extension or elimination of shelf life terms for hazardous materials in the Navy supply system.
FY90 EXECUTION: Initiate shelf life performance evaluation and correlate shelf life with performance. If additional funds available, accelerate evaluation timetable.
STATUS: New start. Project has NAVSUP concurrence.

HW-90-35 USAF IWTP Technology

OBJECTIVE: Adapt USAF $FeSO_4/Na_2S$ process to Navy IWTP to enhance heavy metal removal.
FY90 EXECUTION: Conduct sanitary engineering study to determine efficacy of process and develop TEMP for implementation at select IWTPs.
STATUS: New Start. Have obtained NAVAIR concurrence.

NAVAL CIVIL ENGINEERING LABORATORY (continued)

Tracking# Title

HW-90-36 Reduction of Pink Water

OBJECTIVE: Develop effective process for detoxifying pink water, which will cost effectively eliminate hazardous waste and the need for disposing spent activated carbon.
FY90 EXECUTION: Defer until completion of higher priority HAZMIN projects.
STATUS: New Start.

HW-90-37 Super Critical Fluid

OBJECTIVE: Develop super critical fluid technology for the destruction of Navy specific wastes.
FY90 EXECUTION: Defer until completion of higher priority HAZMIN projects. Coordinate with USAF.
STATUS: New Start.

DAVID TAYLOR RESEARCH CENTER

HWM-89-01 Shipboard HAZMIN

OBJECTIVE: Reduce and control consumable material authorized for shipboard use in hull, mechanical and electrical systems and in weapon and combat system equipment.
FY90 EXECUTION: Develop minimization plan for solvents and initiate minimization plan for adhesives.
STATUS: Completed hazardous materials information and database system. Obtained NAVSEA concurrence.

HWM-89-03 Blasting Grit Recycling

OBJECTIVE: Evaluate use of sloped grid, fluidized bed calciner for thermal reclamation of blasting abrasives.
FY90 EXECUTION: Upon final approval, complete reclamation evaluation and analysis report and initiate shipyard evaluations.
STATUS: Initiated evaluation of calciner system.

HWM-89-05 Bilge Oily Waste

OBJECTIVE: Develop shoreside oily waste treatment system to process bilge oily wastes.
FY90 EXECUTION: Complete construction of pilot treatment facility and evaluate effectiveness. Identify technology transfer package.
STATUS: Initiated construction of treatment system and negotiations with the State of New Jersey.

HWM-89-04 Ultra Jet Removal

OBJECTIVE: Develop cost effective system to remove paint from hulls and eliminate or reduce hazardous waste.
FY90 EXECUTION: Complete report on progress to date.
STATUS: Evaluated cavitating jet and cost comparison.

NAVAL AIR PROPULSION CENTER

Tracking# Title

HW-90-40 Freeze Crystallization

OBJECTIVE: Develop freeze crystallization pilot plant for removal and recycling of heavy metals at a NADEP facility.
FY90 EXECUTION: Defer. Obtain funding and approval for specific application at NAVAIR facility.
STATUS: New Start.

NAVAL AIR SYSTEMS COMMAND (NAVAL AIR DEVELOPMENT CENTER)

HW-90-41 Chrome Replacement

OBJECTIVE: Evaluate a material and process substitute for chrome applications on airframe substrate.
FY90 EXECUTION: Initiate development of chrome replacement specification for NAVAIR applications.
STATUS: New Start.

HW-90-42 Alternate Aerospace Coatings

OBJECTIVE: Develop substitute aerospace coatings without heavy metals for use on aircraft systems.
FY90 EXECUTION: Defer until completion of higher priority HAZMIN projects.
STATUS: New Start.

HW-90-43 Paint Reformulation for HAZMIN

OBJECTIVE: Develop reformulation of Navy epoxy and alkyd paints and coatings to remove heavy metals and VOCs.
FY90 EXECUTION: Upon final approval, evaluate epoxy performance on ships and publish specification. Start contract to develop low VOC air dry alkyd paints.
STATUS: Finalized epoxy specification requirements; literature survey of alkyd paints.

INSTALLATION RESTORATION

NAVAL CIVIL ENGINEERING LABORATORY

Tracking# Title

IR-89-02 PCB Decontamination at Guam

OBJECTIVE: Develop cost effective PCB decontamination alternative technology and demonstrate applicability at PWC Guam.
FY90 EXECUTION: Evaluate performance of KPEG process during scale-up and operation of 20 ton system; Develop technology transfer package for KPEG process for other PCB sites . Defer major contract award until additional funds are available .
STATUS: Determined feasibility of pilot system; Project jointly funded with EPA Hazardous Waste Engineering Research Laboratory.

IR-89-03 Bioremediation at 29 Palms

OBJECTIVE: Demonstrate landfarming technology to cleanup a fuel spill at MCAGG 29 Palms.
FY90 EXECUTION: Complete pilot treatment plots and final feasibility study.
STATUS: Completed literature search and technology assessment; Obtained permits for test plan; developed cooperative research with EPA Las Vegas.

IR-89-07 Fuel Cleanup Technology

OBJECTIVE: Evaluate processes to treat contaminated ground water.
FY90 EXECUTION: Complete technology transfer guide for NEESA, which includes scopes of work, cost estimating procedures, regulatory requirements, etc.
STATUS: Completed engineering evaluation cost analysis report.

IR-89-08 Photochemical Cleanup at Lakehurst

OBJECTIVE: Demonstrate the ability to oxidize organics from contaminated groundwater at NAEC Lakehurst.
FY90 EXECUTION: Complete bench scale test and evaluation and develop site test plan for pilot scale unit.
STATUS: Completed work plan and initiated bench scale/treatability studies.

IR-89-09 Bioremediation at Seal Beach

OBJECTIVE: Investigate in situ aerobic and anaerobic degradation of gasoline hydrocarbons at NWS Seal Beach.
FY90 EXECUTION: Complete treatability/feasibility studies and develop pilot scale test.
STATUS: Completed work plan, which includes cooperative research with Stanford University, Orange County Water District, Waterways Experiment Station and NOSC.

Tracking# Title

IR-89-10 Ordnance Bioremediation

OBJECTIVE: Investigate feasibility and efficacy of using bioremediation to decontaminate ordnance wastes at NSB Bangor.
FY90 EXECUTION: Coordinate technology development with USATHAMA; identify technology pilot project at NSB Bangor; defer laboratory tests until Army completes technology assessment.
STATUS: Characterized microbial populations at Site D; evaluated white rot fungus and initiated treatability studies.

IR-88-01 In Situ Bioremediation at Pax River

OBJECTIVE: Test innovative technologies for the cleanup of refined fuel oil site.
FY90 EXECUTION: Obtain funding from CHESDIV; implement four phases of treatment for overall site: oil/water separation, chemical precipitation, colloidal removal, and dissolved product treatment. Continue in situ bioremediation study in controlled area.
STATUS: Remedial investigation and evaluation of biodegradation potential have been completed. So far in situ bioremediation has not been successful.

IR-90-04 Geoprocessing for IR Support

OBJECTIVE: Provide technical foundation and guidelines for Navy-wide IR decision support using geoprocessing technology.
FY90 EXECUTION: Complete geoprocessing application at NAEC Lakehurst and develop technology transfer package.
STATUS: Completed grid and database system for MCAS Kanahoe and NAEC Lakehurst.

IR-90-13 Combined Waste Adsorption

OBJECTIVE: Develop an adsorption process to remove and treat hazardous organics, heavy metals, and mixed refuse from landfills.
FY90 EXECUTION: Defer until completion of higher priority technology development projects.
STATUS: New start.

IR-90-14 Stabilization/Solidification

OBJECTIVE: Develop technology for solidifying and stabilizing hazardous wastes in soils.
FY90 EXECUTION: Complete initial feasibility study and determine cost effective treatment technologies
STATUS: Completed fixation studies at NSY Hunter Point and NCBC Port Hueneme, and obtained cooperative agreement and funding from EPA Risk Reduction Engineering Laboratory.

Tracking# Title

IR-90-24 Target Range Cleanup

OBJECTIVE: Develop technology for cleanup and control of contaminated target butts.
FY90 EXECUTION: Develop site selection criteria and initiate feasibility study.
STATUS: New Start.

IR-90-23 Pipeline Cleanup and Monitoring

OBJECTIVE: Develop in situ pipeline monitoring system for leak detection and monitoring of cleanup.
FY90 EXECUTION: Complete sensor development and participate in the Tri-Service cone penetrometer project.
STATUS: New Start. This project will be done in conjunction with NOSC project NOSC-90-10.

IR-90-25 Electrolysis Oxygen Generation

OBJECTIVE: Evaluate effectiveness of in situ oxygen generation using electrolysis.
FY90 EXECUTION: Complete feasibility study.
STATUS: New Start.

IR-90-26 Electro-Acoustical Soil Cleanup

OBJECTIVE: Evaluate effectiveness of electro-acoustical soil decontamination process for Navy wastes.
FY90 EXECUTION: Coordinate with EPA; defer laboratory studies until completion of EPA technology assessment.
STATUS: New Start; EPA cooperative effort being developed.

IR-90-27 JP-5 Cleanup

OBJECTIVE: Evaluate physical/chemical process to treat JP-5 fuel spills.
FY90 EXECUTION: Defer until completion of demonstration project feasibility study for Patuxent River and 29 Palms.
STATUS: New start; Need technology evaluation for applications at contaminated sites.

IR-89-05 Biotechnical Slope Protection

OBJECTIVE: Investigate applications of biotechnical methods to control runoff from hazardous waste sites.
FY90 EXECUTION: Complete initial feasibility study to determine the effectiveness of vegetation in accumulating toxic components of runoff.
STATUS: Initial feasibility study at NSB Bangor started.

NAVAL OCEAN SYSTEMS CENTER

Tracking# Title

NOSC-89-03 Site Specific Toxicity Assessment

OBJECTIVE: Develop methods and protocols for determining site specific toxicity using a suit of portable biological indicator systems.
FY90 EXECUTION: Complete integration of biochemical and chemical analysis monitoring modules and initiate feasibility demonstration at NAS North Island.
STATUS: Completed initial feasibility study and prepared technical paper for presentation at Ocean '89.

NOSC-89-04 Benthic Flux Device

OBJECTIVE: Build and test a remotely deployed sampling device for in situ measurement of the release of chemical toxicants from contaminated sediments.
FY90 EXECUTION: Complete development and testing of prototype system.
STATUS: Completed systems specification and initiated prototype development.

NOSC-89-05 Tri-Service Bioreactor Technology

OBJECTIVE: Coordinate and plan the Tri-Service bioreactor project and conduct research, development and demonstration of bioreactor technology to remediate hazardous waste sites.
FY90 EXECUTION: Implement the Tri-Service bioreactor program; develop bioreactor application to cleanup hazardous waste sites; complete feasibility study.
STATUS: Completed cell culturing system and initiated feasibility study of bioreactor degradation of JP-5 and otto fuels.

NOSC-89-06 Whidbey Island Toxicology Demo

OBJECTIVE: Conduct toxicology demonstration to assess the impact of hazardous waste disposal sites on wildlife and the environment and evaluate the risks associated with the remediation of the waste site.
FY90 EXECUTION: Complete baseline ecological risk assessment for fire fighting training area, pesticide rinseate site, and the runway ditches. Initiate verification and evaluation of toxicological effects.
STATUS: Initiated toxicological evaluation for hazardous waste sites using enhanced starling assay, monitoring of raptors and great blue herons, and monitoring of prey. Cooperative research with the Institute of Wildlife and Environmental Toxicology, Clemson University, and Huxley College of Environmental Studies, Western Washington University.

Tracking# Title

NOSC-89-07 Davisville Risk Assessment

OBJECTIVE: Conduct ecological risk assessment to determine risk of hazardous waste sites on the environment and select the most cost effective remediation; develop guidelines for conducting ecological risk assessments at impacted aquatic sites.
FY90 EXECUTION: Complete verification and evaluation of toxicological effects from the Allen Harbor Landfill.
STATUS: Developed cooperative research effort with the EPA Environmental Research Laboratory, Food and Drug Administration, and the University of Rhode Island; completed baseline risk assessment for Allen Harbor.

NOSC-90-08 Contaminant Dispersion & Prediction

OBJECTIVE: Validate hydrodynamic and toxicant transport models that predict the transport and fate of contaminants from hazardous waste sites.
FY90 EXECUTION: Integrate acoustic doppler profiler into the marine environmental survey capability and initiate the validation of models for application at hazardous waste sites.
STATUS: New Start. Hydrodynamic and toxicant transport models have been developed for 15 Navy harbors and estuaries. This will be cooperative research between NOSC and DTRC.

NOSC-90-10 Tri-Service Fiber Optic Sensors

OBJECTIVE: Develop a fiber optic-based metal sensor for incorporation into the Tri-Service cone penetrometer system.
FY90 EXECUTION: Evaluate indicators for metal sensor and develop specifications for prototype sensor package. Obtain funding for site demonstration from specific EFD .
STATUS: New start. Tri-Service work plan has been developed. This project will be done in conjunction with NCEL project IR-90-23.

NOSC-90-11 Complexation Capacity

OBJECTIVE: Develop a probe for in situ measurement of the complexation capacity of natural wasters.
FY90 EXECUTION: Defer project until higher priority efforts are completed.
STATUS: New Start.

NOSC-90-12 Remedial Analytical Methods

OBJECTIVE: Develop analytical methods to rapidly measure extent of hazardous waste contamination and determine the effectiveness of remediation at NWC Seal Beach.
FY90 EXECUTION: Develop and demonstrate feasibility of field adaptable analytical methods to support the analytical requirements of the Seal Beach Bioremediation and bioreactor development projects.
STATUS: New start. Cooperative research with NCEL has been developed.

NAVAL OCEAN SYSTEMS CENTER (continued)

Tracking# Title

NOSC-90-15 NRC Special Study

OBJECTIVE: Task the National Research Council, National Academy of Science to develop recommendations for improving aquatic environmental risk assessments of hazardous wastes.
FY90 EXECUTION: Develop tasking and work plan for the NRC. Seek funding from DOD to execute study.
STATUS: New start. Initiated Tri-Service review necessary for DOD funding.

NOSC-90-16 NAS North Island Risk Assessment

OBJECTIVE: Demonstrate risk assessment methods in support of the RI/FS for NAS North Island.
FY90 EXECUTION: Obtain funding from SOUTHWESTDIV as part of the RI/FS.
STATUS: New Start.

POLLUTION ABATEMENT ASHORE

NAVAL CIVIL ENGINEERING LABORATORY

Tracking# Title

PA-89-01 Nonpoint Source Control Technology

OBJECTIVE: Evaluate methods for controlling and mitigating nonpoint source (NPS) runoff from Navy shore facilities.
FY90 EXECUTION: Develop work plan and environmental assessment to evaluate wetlands enhancement technology for NPS runoff control.
STATUS: Initiated environmental assessment for NPS control at COMNAVBASE Norfolk. Developed cooperative research with Virginia Institute of Marine Science, Waterways Experiment Station, LANTDIV, and NOSC.

PA-89-02 VOC Control

OBJECTIVE: Develop technologies to control volatile organic compound (VOC) emissions.
FY90 EXECUTION: Defer development of control technology, priority is on source reduction.
STATUS: New Start.

PA-90-03 Environmental Acceptable Coatings

OBJECTIVE: Develop specifications for use of environmentally acceptable coatings for Navy applications.
FY90 EXECUTION: Complete specification for alkyds/epoxies, initiate evaluation of acrylics/urethanes.
STATUS: Completed initial feasibility report and plan for total Navy compliance with VOC emissions.

PA-90-12 IWTP Sludge Characterization

OBJECTIVE: Determine quantity, nature and status of Navy industrial and sanitary sludges and recommend alternative technologies to meet EPA sludge regulations.
FY90 EXECUTION: Defer until completion of higher priority PA projects. Should refocus proposal on IWTP sludge reduction and resubmit for FY91 plan.
STATUS: New Start.

PA-90-14 Nitric Oxide Emission Reduction

OBJECTIVE: Evaluate low Nitric Oxide (NO_x) retrofit options for mobile utility support equipment (MUSE) generators and for small Navy package boilers and recommend suitable control technologies.
FY90 EXECUTION: Initiate review of appropriate control technologies and development of NO_x emission control implementation strategy for MUSE generators.
STATUS: New Start.

Tracking#   Title

PA-90-22 UST Leak Detection

OBJECTIVE: Develop in situ leak detection capability for Navy bulk underground tanks storing JP-5 and diesel marine fuel.
FY90 EXECUTION: Conduct pilot scale field test of In Situ sensor network and complete final feasibility report.
STATUS: Completed IDR and laboratory scale sensor evaluation. Project has been transitioned from 6.2 program.

PA-90-21 Low Flush Toilets

OBJECTIVE: Test and evaluate the effectiveness of using low flush toilets for water conservation at Naval facilities and develop guidance specification.
FY90 EXECUTION: Develop guidance document for specification of low flush toilets for Navy use. Coordinate and conduct any tests required with funding from EFD (CHESDIV).
STATUS: New Start.

PA-90-25 Pb in Drinking Water Guidance

OBJECTIVE: Evaluate Pb mitigation for potable water systems and develop guidance for Navy application.
FY90 EXECUTION: Complete technology assessment and test and evaluate candidate technologies; perepare guidance document.
STATUS: New Start.

SH-90-02 Fiber Release From Asbestos Cement

OBJECTIVE: Reduce asbestos fiber release caused by asbestos-cement products.
FY90 EXECUTION: Defer
STATUS: New Start.

SH-90-05 Glove Bag for Asbestos Containment

OBJECTIVE: Develop user guide for safe glove bag use.
FY90 EXECUTION: Defer.
STATUS: New Start.

SH-90-06 Asbestos Encapsulation Guide Specs

OBJECTIVE: Develop NAVFAC Guide Specification for asbestos encapsulation.
FY90 EXECUTION: Prepare Draft NAVFAC Guide Specification 09876.
STATUS: Have developed specifications for asbestos removal and disposal (0280C).

NAVAL OCEAN SYSTEMS CENTER

Tracking#   Title

PA-90-16 Pb Analyzer

OBJECTIVE: Develop a sensitive, hand-held, fast-response, heavy metal analyzer for field use.
FY90 EXECUTION: Develop prototype electrode-cell and laboratory-based system. Investigate possibility of obtaining additional funding from EPA to speed development.
STATUS: New Start.

PA-89-09 Expert System for Assessments

OBJECTIVE: Develop an expert system interface for operation of environmental water quality monitoring.
FY90 EXECUTION: Defer until completion of marine environmental survey capability.
STATUS: Completed test and evaluation of expert system.

PA-90-19 AFFF Detection

OBJECTIVE: Develop a simple method for estimating and monitoring Aqueous Film Forming Foam (AFFF) concentrations in effluents from Naval facilities.
FY90 EXECUTION: Identify spectral signature of AFFF and determine if MILSPEC is required for incorporation of marker compound.
STATUS: New Start.

PA-90-17 Sediment Dosing System

OBJECTIVE: Develop an automated mechanical system capable of adding and recovering suspended sediment at specific concentrations using a portable microcosm system.
FY90 EXECUTION: Defer until completion of PA-89-10. Investigate cooperative funding with Army Corps of Engineers.
STATUS: New start. Initiated possible cooperative research with the ACOE to support dredging projects in Pearl Harbor.

PA-90-18 Spectral Radiometry

OBJECTIVE: Develop capability for large-scale, real-time environmental monitoring of Navy coastal areas using remote sensing.
FY90 EXECUTION: Defer until completion of higher priority projects. Develop cooperative research with NCEL.
STATUS: New Start.

PA-90-15 Nonpoint Source Assessment Technology

OBJECTIVE: Develop methods necessary to determine environmental risk and impact of nonpoint source runoff and effectiveness of control measures.
FY90 EXECUTION: Support environmental assessment at Norfolk and development of NPS assessment protocols.
STATUS: This project will be done in conjunction with NCEL project PA-89-01.

Tracking# Title

PA-89-06 Fiber Optic Sensor for Metals

OBJECTIVE: Develop real time, fiber optic-based chemical sensor system for direct field measurement of toxic metals and organic compounds in aqueous samples.
FY90 EXECUTION: Optimize sensor system for metals. Defer development of software and hardware.
STATUS: Completed feasibility study and development of prototype sensor specifications.

PA-89-08 Marine Environmental Survey Capability (MESC)

OBJECTIVE: Develop a modular water quality mapping system that can be used to conduct real-time chemical, biological, and hydrographic parameters in harbors, bays, estuaries, and other near-shore environments.
FY90 EXECUTION: Complete MESC system documentation and initiate development of AUTOCAD interface. Integrate MESC technology into other assessment projects.
STATUS: Completed test and evaluation for MESC system components; completed procurement, system check out, and acceptance testing for new survey craft, RV ECOS.

PA-89-10 Portable Environmental Test System

OBJECTIVE: Develop capability to perform chronic and short term multi-species tests for pollution effects at specific sites using a portable microcosm system.
FY90 EXECUTION: Complete operational testing and user data documentation for portable environmental test system. Incorporate system into environmental assessments.
STATUS: Completed test and evaluation master plan, developed systems specifications and completed ILS plan. Submitted patent application for diluter system.

PA-89-11 Biomonitoring of Navy Effluents

OBJECTIVE: Develop standardized biomonitoring methods for Navy effluents and obtain regulatory acceptance.
FY90 EXECUTION: Assess biomonitoring requirements and initiate development of low cost standardized biomonitoring protocols for Navy effluents.
STATUS: Completed feasibility study of field dosing system.

NAVAL AIR SYSTEMS COMMAND (NAVAL AIR DEVELOPMENT CENTER)

Tracking#	Title
PA-90-20	CFC and Halon Substitution

<u>OBJECTIVE</u>: Test and evaluate substitute materials for chlorofluorocarbon (CFC) cleaners and refrigerants, and halon fire suppression agents suitable for use in aircraft systems.
<u>FY90 EXECUTION</u>: Defer. Obtain funding from OP-45 for centrally funded CFC and halon compliance projects.
<u>STATUS</u>: New Start.

PA-90-23 Replacement of VOC Coatings for Aircraft

<u>OBJECTIVE</u>: Develop low Volatile Organic Compound (VOC) substitute aerospace and specialty coatings for aircraft systems.
<u>FY90 EXECUTION</u>: Defer until additional funds are available.
<u>STATUS</u>: New Start.

CONCLUSION

The Navy has developed an integrated environmental RDT&E program. This program is structured within the framework of seven goal areas:

- Zero discharge of hazardous wastes from Navy industrial facilities
- Acceptable cleanup levels at all Navy hazardous waste disposal sites
- One hundred percent reclamation of wastewater at Navy facilities
- Zero air emisions and acceptable noise emissions from Navy facilities
- State-of-the-science materials and industrial processes for Navy facilities
- State-of-the-science methods and instrumentation for cost effective monitoring of Navy-unique pollutants and contaminants
- Comprehensive prediction and management of environmental effects from Navy systems and operations

This integrated RDT&E program has been developed to address the broad range of environmental requirements which face the Navy [illegible] meet the challenge of overall environmental protection.