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U S A T H A M A

U.S. Army Toxic and Hazardous Materials Agency

PROCEEDINGS
FOR THE

13TH ANNUAL ENVIRONMENTAL QUALITY R&D SYMPOSIUM

"Working Towards a Better Environment - A Progress Report"

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

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15-17 November 1988
Williamsburg Hilton and
National Conference Center
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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. 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.

The response to the 1988 Call for Papers was very enthusiastic. Because the number of abstracts received far 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.

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Keynote Address
By

MG Peter J. Offringa
Assistant Chief of Engineers
Office of the Chief of Engineers

Presented at
Thirteenth Annual Environmental Quality
Research and Development Symposium
15-17 November 1988

KEYNOTE ADDRESS - MG PETER J. OFFRINGA, ASSISTANT CHIEF OF ENGINEERS

VIEWGRAPH 1 - "WORKING TOWARD A BETTER ENVIRONMENT"

- o For many symposium participants, this will represent the only opportunity for direct contact with DA/DOD senior leadership.

- o Based on previous keynote addresses, statements of what is expected of these participants regarding their role in the DA Environmental Program has been observed to have a noticeable positive impact.

- o This keynote address also provides an opportunity to emphasize any policy aspects and guidance that should be considered and implemented throughout the DA chain of command.

VIEWGRAPH 2 - "PROGRAM INTEGRATION"

- o With transfer of USATHAMA to the Corps, the Army has centralized the management of the entire Army environmental program.

- o Symposium participants will be eager to know and or be assured on a firsthand basis from the Program Manager what can be expected due to the recent reorganization of resources to conduct the DA Environmental Program:

  - The DA Environmental Program centrally managed and directed - IR - Compliance - Training - Support - R&D.

  - The Environmental Program will focus on total program requirements - Past - Current - Future.

  - Significance of USATHAMA becoming a part of the Corps of Engineers. Program Integration for the first time. Requirements + Resources + Management System = Success.

  - Changes from the current way of doing business - Total program management and support - CERCLA/RCRA.

- o Recognition of other DOD service attendees as well as those from other federal departments would also be appreciated:

  - Interface with other services/agencies. Air Force, Navy, EPA, Contractor Support, etc.

  - Means for technology exchange such as the IRTCC and the Tri-Services Joint R&D project program recently initiated.

  - Other services' input to the DA Program - Great cooperative efforts in technology development/integration.

VIEWGRAPH 3 - "CHALLENGES"

- o Theme of symposium is "WORKING TOWARDS A BETTER ENVIRONMENT".
- o Challenge - doing so with limited resources available.
- o Role of R&D - provide new ways to do a better job at a lower cost.
- o It is also the role of R&D to transfer this technology to the users. The role of the user is to implement the technology.
- o Users should be receptive to change. Changes in technology and procedures are necessary to meet this challenge.
- o Teamwork is essential. R&D developers and the users must work together.
- o Importance of this symposium. Attendees have excellent opportunities for:
  - Obtaining a better understanding of environmental policies and how they are being implemented.
  - Technology exchange - between developers from different agencies.
    - between users from different agencies.
    - between users and developers.

VIEWGRAPH 4 - "PROGRAM GROWTH"

- o Program growth by various categories is shown in viewgraph.
- o Per statements made by Mr. Parker, DASD-E, in presentations at the American Defense Preparedness Association 16th Environmental Symposium on 18 Oct 88:
  - Current DOD IR program cost estimate: $10-15 billion.
  - Time to complete DOD IR: "well into 21st century".
  - The annual budget could reach billions in peak years.
- o We are faced with long term environmental damage liabilities. These liabilities will increase the IR Program cost if:
  - We don't do the job right the first time.
  - We are unable to do the job in a timely manner.

VIEWGRAPH 5 - "INSTALLATION RESTORATION TECHNOLOGIES"

- o Current treatment technologies are effective and have resulted from your efforts.

- o Regulatory requirements can be expected to become more stringent (based on our experience with environmental regulation in this country). More stringent regulation means higher cost.

- o Even remediation practices which are currently accepted may have to be modified because of emerging restrictions.

VIEWGRAPH 6 - "EXAMPLES OF DA HAZMIN INITIATIVES"

- o Hazardous Waste Minimization is the ultimate solution to the environmental pollution problem. To the greatest extent possible, we must prevent problems.

- o Reducing or eliminating hazardous waste can be accomplished by:

  - Changes in installation management practices.

  - Operational changes; the way we do business.

  - Development of new processes and technology.

VIEWGRAPH 7 - "DA HAZMIN PROGRAM"

- o Explanation of Numbers: DA HAZMIN Program.

  - % Reduction Goal: The % reduction of the base year 85.

  - Waste Produced: The goal tracked waste produced for that year. Does not include demil waste, building rubble, and spill cleanup waste.

  - HAZMIN Goal: Production goal for that year based on the % reduction of the base year.

- o These wastes are generated in the development, production and procurement, and maintenance of necessary material to insure that the soldier is the best equipped and best trained in the world.

- o Congress intended that all hazardous waste generators reduce the quantities of hazardous waste to be disposed of when it amended the Resource Conservation and Recovery Act (RCRA) in 1984.

- o In mid-1985, EPA began promulgating regulations to meet that intent. These regulations:

  - have increased the cost of hazardous waste treatment.

  - have expanded the liabilities for improper hazardous waste management.

  - require that generators develop and carry out a program of hazardous waste reduction and minimization.

- The results of our HAZMIN program efforts are reflected in Viewgraph 2.

o To continue to progress in this program:

  - We must emphasize the potential for substituting non-hazardous materials for those that are hazardous in the development of new systems.

  - We must make the necessary process changes to reduce the generation of hazardous wastes in the production of these systems.

  - We must find ways to recover and reuse hazardous materials in the supply and maintenance cycles of these systems.

o The R&D community must provide improved HAZMIN technology to allow us to achieve our goals by using the principles of material substitution, process change and recovery and reuse.

o The challenge to the R&D community will be to continue to provide technical innovation in a limited resource environment.

o The IR program managers and performers must support the R&D community by close coordination and a willingness to accept and make technological changes.

o When new technology is ready, assistance from the developer is essential to allow the user to properly implement it.

o While we are making a strong effort to reduce hazardous waste generation, we must still be concerned with remedial action to correct past problems.

VIEWGRAPH 8 - "U.S. ARMY INSTALLATION RESTORATION PROGRAM"

o Current challenge is large.

  - 1391 properties.

  - 14 National Priority List (NPL) sites.

  - 9 proposed NPL sites.

o Concerns

  - Cost in dollars and time for cleanup.

  - Future liabilities.

  - Regulatory compliance.

VIEWGRAPH - 9 - "IRP PROFILE"

- o Slide shows phases of a site remediation.
- o Emphasis on the time required to execute even a single site.
- o Time is money.
- o Multiplied by the number of sites. All 1391 Army properties must have at least a PA/SI.

VIEWGRAPH 10 - "IRP GOALS"

- o Our goals are ambitious
  - Complete all PA/SIs by the end of this fiscal year.
  - Complete RI/FS by FY92.
  - Complete remediation actions by FY94.
- o Achievement of this goal will require teamwork.

VIEWGRAPH 11 - "BUILDING BLOCKS FOR SUCCESS"

- o Teamwork is an Army tradition. This tradition must be extended and maintained in the Army's environmental program.
  - The R&D community must continue to direct its efforts carefully to meet the user's needs in the most timely and cost effective manner.
  - The users must continue to be receptive to change and willing to cooperate with our R&D community in the implementation of new technology.
  - We must all coordinate our activities to:

    eliminate unnecessary activities
    eliminate duplication of effort
    optimize our effectiveness by learning from our mistakes as well as our successes.
- o This coordination must be continually extended to include our counterparts in the other services and other federal agencies.
- o Recognition suggested (in this regard) for:
  - An ongoing effort to develop improved environmental monitoring capabilities that is being jointly conducted by DOD/EPA/DOE.
  - A new initiative started in October 1988 by the Army/Navy/Air Force to establish joint projects for development of new IR and HAZMIN technologies of mutual interest.

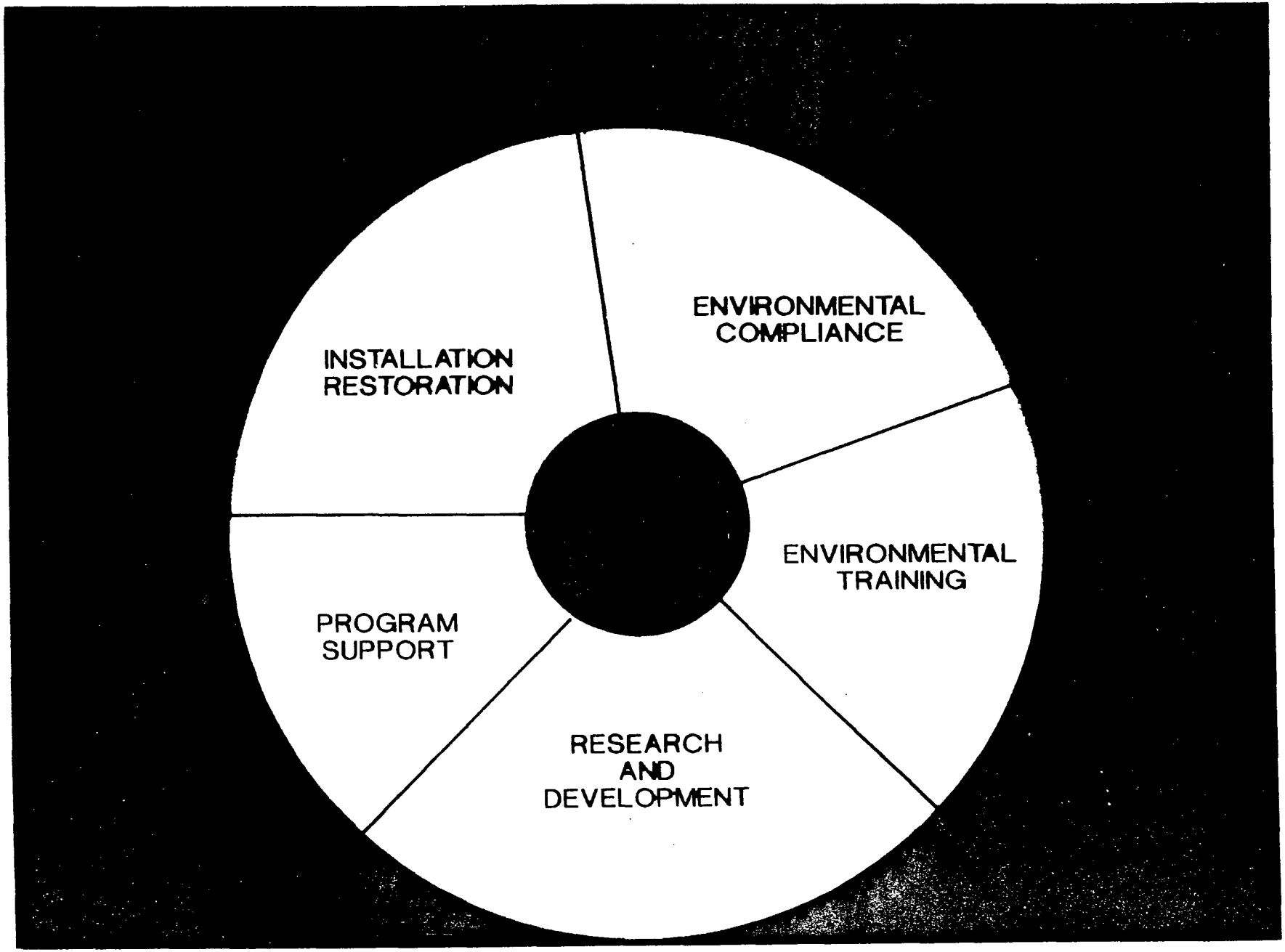
- I will return to my challenge to all of you here, it is imperative that great strides be made in the future to develop innovative processes not only to address the current problems at hand but also to reduce or eliminate generation of hazardous wastes in the future. Again, I applaud your progress to date and I am particularly pleased to see such a cross section of organizations - developers, users, managers and scientists - creating the forum necessary to facilitate technology transfer to achieve our goals.

VIEWGRAPHS

"WORKING TOWARD A BETTER ENVIRONMENT"

Major General Peter J. Offringa

Assistant Chief of Engineers


INSTALLATION
RESTORATION
ENVIRONMENTAL
COMPLIANCE
ENVIRONMENTAL
TRAINING
PROGRAM
SUPPORT
RESEARCH
AND
DEVELOPMENT

CHALLENGES

1391 Installations

7000+ Former Sites

11,000 Underground Storage Tanks

Tons of Hazardous Waste Generated Each Year

400+ Lagoons

Noise

Permits

Asbestos

PCB's

Radon Gas

54 Environmental Law (more to come)

10 EPA Regions

50 States

Thousands of Communities and Municipalities

Base Closures

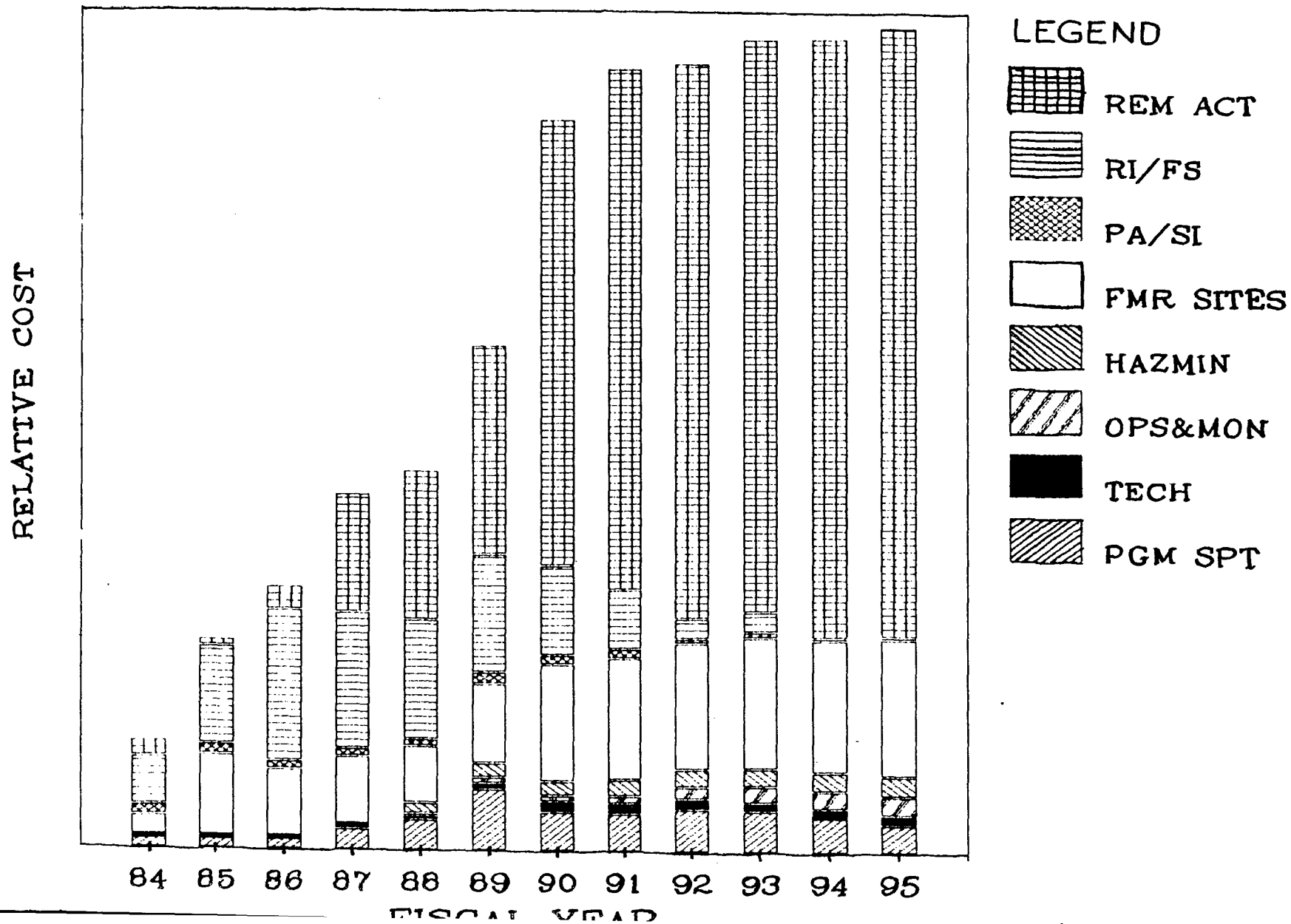
Cost Growth

Indictments

Chem Demil

Notices of Violation

PROGRAM GROWTH



EXAMPLES OF DA HAZMIN INITIATIVES

INSTALLATION MANAGEMENT PRACTICES

- AUTOMATED HAZARDOUS MATERIALS/HAZARDOUS WASTE TRACKING SYSTEM
- INSTITUTION OF STRINGENT HAZARDOUS MATERIAL ORDERING PROCEDURES

INSTALLATION OPERATIONAL CHANGES

- EQUIPMENT RECONFIGURATION IN MUNITION ASSEMBLY LINES
- RECOVERY AND REUSE OF PAINT SOLVENTS

NEW TECHNOLOGY DEVELOPMENT AND ADOPTION

- PLASTIC MEDIA BLASTING
- REFORMULATION OF CHEMICAL PAINT STRIPPERS

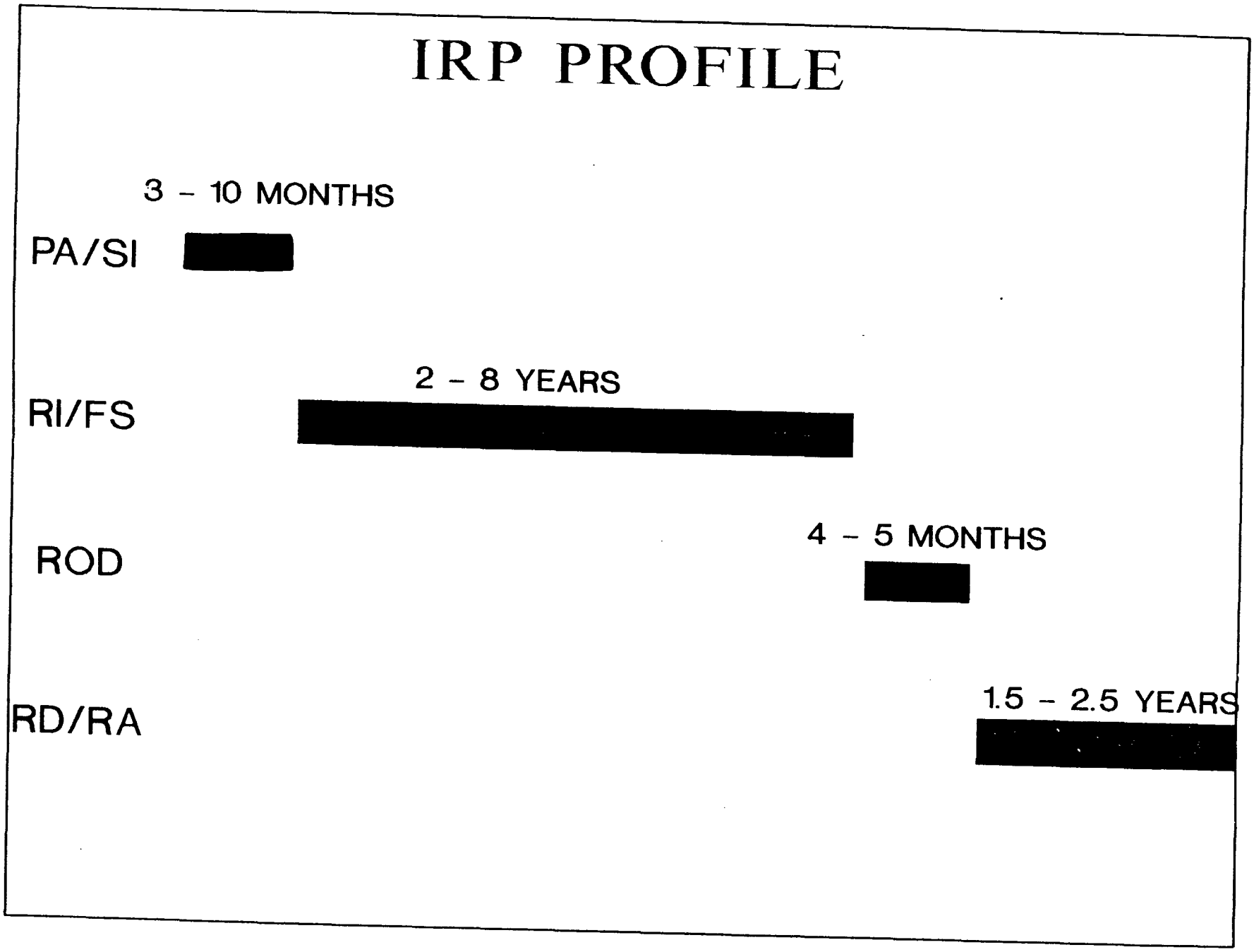
DA HAZMIN PROGRAM

GOAL: BY 1992, REDUCE PRODUCTION OF WASTE BY 50%
(1985 BASE YEAR)

U.S. ARMY
INSTALLATION RESTORATION PROGRAM

- 14 NPL SITES
  - 9 PROPOSED NPL SITES
    - 1391 PROPERTIES REQUIRING ASSESSMENT
      - CONCERNS
        - COST OF AND TIME FOR CLEAN-UP
        - LONG TERM LIABILITIES
        - REGULATORY COMPLIANCE (EPA/STATE/LOCAL)

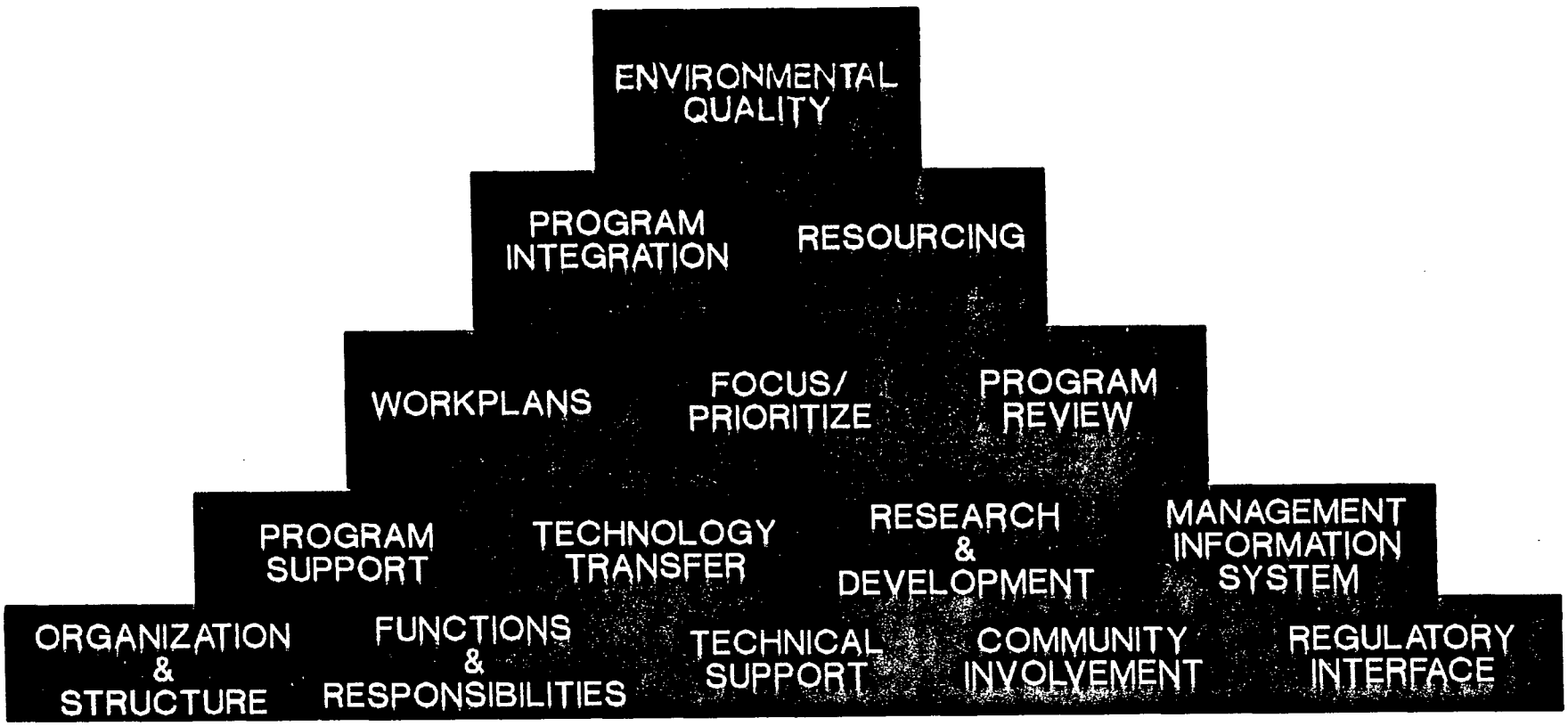
IRP PROFILE



IRP GOALS

COMPLETE	PA/SI's	FY 89
COMPLETE	RI/FS's	FY 92
INITIATE	RA's	FY 94

BUILDING BLOCKS FOR SUCCESS



Working Towards a Better Environment: a Progress Report

By

Bob O. Benn
Office, Chief of Engineers
Directorate of Research and Development

Presented at
Thirteenth Annual Environmental Quality
Research and Development Symposium
15-17 November 1988

NARRATIVE FOR ENVIRONMENTAL QUALITY TECHNOLOGY VIEWGRAPHS

VIEWGRAPH 4. THIS SLIDE IS SYMBOLIC OF THE MANY FACTORS WHICH DRIVE THE ARMY ENVIRONMENTAL POLICY. THESE LEGISLATIVE DRIVERS ARE INCREASING AT A NEARLY EXPONENTIAL RATE. FROM THE CLEAN AIR AND CLEAN WATER ACTS TO THE RESOURCE CONSERVATION AND RECOVERY ACT AND THE SUPERFUND REAUTHORIZATION ACT - ALL OF THESE LEGISLATIVE DRIVERS IMPACT ON WHAT THE ARMY CAN AND MUST DO WITH REGARD TO ENVIRONMENTAL ISSUES.

VIEWGRAPH 5. WHEN DISCUSSING THE ENVIRONMENTAL QUALITY TECHNOLOGY PROGRAM, THREE BASIC DIVISIONS ARE ADDRESSED:

* HAZARDOUS WASTE CONTAINMENT/CLEANUP - WHICH IS THE MISSION OF THE INSTALLATION RESTORATION PROGRAM

* HAZARDOUS WASTE CONTROL - WHICH IS A CRITICAL MISSION TO PREVENT FUTURE CONTAINMENT/CLEAN-UP REQUIREMENTS. AMONG THE AREAS REQUIRING ATTENTION ARE

- UNDERGROUND STORAGE TANKS
- THE PRESENCE AND REMOVAL OF ASBESTOS
- HAZARDOUS WASTE MINIMIZATION
- NON-HAZARDOUS WASTES, AND
- THE ONGOING GENERATION OF INDUSTRIAL WASTES

* IN THE AREA OF ENVIRONMENTAL MANAGEMENT ARE THOSE ISSUES ADDRESSING NOISE CONTROL AND TRAINING RANGE RESTORATION

VIEWGRAPH 6. OF THE CURRENT PROJECTS, MANY HAVE BEEN FOUND TO REQUIRE SOME SORT OF REMEDIAL ACTION - OFTEN AT MANY SITES. THERE ARE CURRENTLY OVER 250 SITES IN NEED OF SUCH REMEDIATION. THE TYPES OF PROBLEMS EXISTING AT THESE SITES INCLUDE CONTAMINATED SOIL AREAS AND LANDFILLS - THE MOST FREQUENTLY OCCURRING PROBLEM AREAS. ALSO REPRESENTED ARE LAGOONS, BUILDINGS, BURNING GROUNDS, AND A VARIETY OF OTHER PROBLEMS.

VIEWGRAPH 7. OVER THE YEARS, RESEARCH AND DEVELOPMENT HAS LED TO TECHNOLOGIES CAPABLE OF REMEDIATION AT SUCH SITES. INCINERATION HAS BEEN DEVELOPED AS A SUCCESSFUL TECHNIQUE FOR THE TREATMENT OF EXPLOSIVE-CONTAMINATED SOIL - OTHER TECHNOLOGY OPTIONS SUCH AS CAPPING, STABILIZATION, AND VOLATILIZATION HAVE BEEN EMPLOYED TO TREAT AND MANAGE CONTAMINATED SOILS.

GROUNDWATER HAS BEEN PROVEN TO BE SUCCESSFULLY TREATED BY DEVELOPED TECHNOLOGIES SUCH AS AIR STRIPPING, CARBON ADSORPTION, AND ION EXCHANGE.

CONTAMINATED STRUCTURES HAVE BEEN DECONTAMINATED BY DESTRUCTIVE MEANS INCLUDING OPEN BURNING AND DISMANTLING AND LANDFILL.

ALTHOUGH THERE ARE SUCCESSFUL METHODS OF TREATING MANY OF THE HAZARDOUS WASTE SITES, MANY OF THE ACCEPTED TECHNOLOGIES ARE IMPLEMENTED AT A HIGH PRICE - BE IT IN DOLLARS OR ADDITIONAL ENVIRONMENTAL CONCERNS. FOR THESE REASONS, R&D IS CONTINUING TO PROVIDE TECHNOLOGIES WHICH CAN BE IMPLEMENTED MORE COST EFFECTIVELY AND WITH LESS PROBABILITY FOR FURTHER ENVIRONMENTAL CONCERNS.

FOR EXAMPLE, EFFORTS ARE UNDERWAY TO DEVELOP HEAVY METAL SEPARATION TECHNIQUES AND AIR POLLUTION CONTROL TECHNIQUES FOR APPLICATION IN THE OPERATION OF EXISTING INCINERATION AND DEVOLATILIZATION TECHNIQUES. OTHER, LESS EXPENSIVE TECHNIQUES ARE BEING INVESTIGATED TO REPLACE INCINERATION AND EXISTING VOLATILIZATION TECHNOLOGIES FOR SOIL TREATMENT.

WITH RESPECT TO GROUNDWATER, IN-SITU BIOLOGICAL TREATMENT IS BEING INVESTIGATED AS A LOWER COST ALTERNATIVE TO EXISTING PUMP AND TREAT METHODS. TO ELIMINATE CONCERNS ASSOCIATED WITH CONVENTIONAL GROUNDWATER TREATMENT TECHNIQUES, OFF-GAS TREATMENT TECHNIQUES ARE BEING DEVELOPED.

RATHER THAN DESTROY CONTAMINATED BUILDINGS AND LANDFILL RESIDUES, R&D IS BEING CONDUCTED TO NON-DESTRUCTIVELY DECONTAMINATE STRUCTURES TO ALLOW FOR THEIR REUSE.

VIEWGRAPH 8. THIS AND THE FOLLOWING SLIDES GRAPHICALLY DEPICT THE DEVELOPMENT OF TECHNOLOGIES WITH APPLICATION TO INSTALLATION RESTORATION. IN THIS SLIDE, THE DEVELOPMENT OF TECHNOLOGIES APPROPRIATE TO THE DECONTAMINATION OF SOLVENT-CONTAMINATED SOIL ARE SHOWN. EARLY RELIABLE TREATMENT METHODS WERE LIMITED TO DIG AND HAUL TECHNIQUES WHEREBY THE CONTAMINATED SOIL WAS REMOVED FROM THE EXISTING SITE AND HAULED AWAY FOR DISPOSAL IN A DESIGNATED HAZARDOUS WASTE LANDFILL. THIS TECHNIQUE, IN ADDITION TO BEING COSTLY, DOES NOT ELIMINATE THE HAZARDOUS WASTE AND CAUSES THE WASTE TO REMAIN A FUTURE LIABILITY. DUE TO DEVELOPMENTS IN THE R&D OF ADVANCED TECHNOLOGIES TO TREAT SOLVENT-CONTAMINATED SOILS, THE DIG AND HAUL PRACTICES ARE BEING REPLACED BY IN-PLACE VOLATILIZATION TECHNOLOGIES AND LOW TEMPERATURE THERMAL STRIPPING OF VOLATILE ORGANIC COMPOUNDS. IN THE FUTURE, DEVELOPMENT OF BIOLOGICAL TREATMENT TO BE CONDUCTED IN-PLACE IS SEEN AS AN ATTRACTIVE ALTERNATIVE.

VIEWGRAPH 9. UNTIL THE MID 1980's, AN ESTABLISHED METHOD FOR MANAGING EXPLOSIVE-CONTAMINATED SOILS WAS TO CAP EXISTING LAGOONS CONTAINING THE CONTAMINATED SOILS. THE DEVELOPMENT OF INCINERATION AS A SAFE AND EFFECTIVE TECHNIQUE FOR THE DECONTAMINATION OF THESE SOILS WAS SEEN AS A VERY POSITIVE FACTOR IN INSTALLATION RESTORATION. R&D OF INCINERATION FOR EXPLOSIVE-CONTAMINATED SOILS LED TO THE IMPLEMENTATION OF INCINERATION TO TREAT CONTAMINATED SOILS AT CORNHUSKER AAP AND, MORE RECENTLY, LOUISIANA AAP. ALTHOUGH THE DEVELOPMENT OF INCINERATION WAS A DRAMATIC IMPROVEMENT IN TREATMENT CAPABILITIES, ITS HIGH COSTS PRECIPITATED THE DEVELOPMENT OF LESS EXPENSIVE METHODS TO DECONTAMINATE SOILS CONTAMINATED WITH EXPLOSIVES. COMPOSTING, A POTENTIALLY CHEAPER BUT EFFECTIVE TECHNIQUE HAS BEEN DEVELOPED THROUGH THE PILOT PHASE AT LOUISIANA AAP AND BADGER AAP AND HAS SHOWN TO BE EFFECTIVE. IN THE FUTURE, IT IS PROJECTED THAT TECHNIQUES EMPLOYING CHEMICAL PRINCIPLES CAN BE AS EFFECTIVE AT A LOWER COST.

VIEWGRAPH 10. THE CONTAMINATION OF GROUNDWATER HAS PRESENTED A DIFFICULT PROBLEM TO THE ARMY. ONCE GROUNDWATER HAS BEEN CONTAMINATED, ALTERNATIVE SOURCES OF DRINKING WATER HAVE BEEN REQUIRED FOR THOSE AFFECTED DUE TO THE LACK OF ADEQUATE TREATMENT CAPABILITIES. IN THE MID 1980's, PHYSICAL TREATMENT TECHNIQUES EMPLOYING

CARBON ADSORPTION, ION EXCHANGE, AND AIR STRIPPING WERE DEVELOPED FOR THE TREATMENT OF CONTAMINATED GROUNDWATER AND HAVE BEEN SUCCESSFULLY EMPLOYED IN THE TREATMENT OF THIS GROUNDWATER. LOOKING TO THE FUTURE, R&D IS BEING PERFORMED TO DEVELOP IN-PLACE METHODS OF GROUNDWATER TREATMENT. SUCH TECHNIQUES, SUCH AS THOSE EMPLOYING IN-SITU BIODEGRADATION OF CONTAMINANTS, WILL ELIMINATE THE NEED FOR PUMPING THE CONTAMINATED GROUNDWATER FROM THE AQUIFER, TREATING IT, AND THEN DISCHARGING THE TREATED WATER -- THE SIMPLIFICATION OF THE PROCESS IN THIS WAY WILL CONTRIBUTE TO OVERALL LOWER TREATMENT COSTS.

VIEWGRAPH 11. ONE OF THE GOALS OF ENVIRONMENTAL R&D IS THE ACCEPTANCE AND IMPLEMENTATION OF DEVELOPED TECHNOLOGIES TO PERFORM NEEDED REMEDIAL ACTIVITIES. THE GENERAL TECHNOLOGIES SHOWN IN THIS SLIDE ILLUSTRATE THE POTENTIAL FOR HANDOFFS OF THE RESULTS OF R&D EFFORTS. COMPOSTING HAS BEEN SUCCESSFULLY DEMONSTRATED ON SOILS CONTAMINATED WITH RDX, TNT, AND NITROCELLULOSE. THERMAL STRIPPING WAS SUCCESSFUL IN REMOVING VOLATILE ORGANIC COMPOUNDS FROM CONTAMINATED SOILS AND WILL BE PROVEN WITH SOILS CONTAMINATED WITH JP-4 FUEL. SUCCESSFUL DEMONSTRATIONS OF THE DECONTAMINATION OF EXPLOSIVE AND CHEMICAL AGENT-CONTAMINATED STRUCTURES WERE CONDUCTED AT CORNHUSKER ARMY AMMUNITION PLANT AND DUGWAY PROVING GROUND.

VIEWGRAPH 12. THE MAGNITUDE OF THE HAZARDOUS WASTE GENERATION PROBLEM AND THE COSTS AND LIABILITIES ASSOCIATED WITH ITS TREATMENT AND DISPOSAL MAKE HAZARDOUS WASTE MINIMIZATION A CRITICAL MISSION. R&D PLAYS AN IMPORTANT ROLE IN HAZARDOUS WASTE MINIMIZATION TO PROVIDE TECHNOLOGIES TO ACHIEVE WASTE REDUCTION GOALS. WITH LIMITED TECHNOLOGY CAPABILITY, HAZARDOUS WASTE TREATMENT WAS NEARLY ALWAYS AN "END-OF-PIPE" ACTIVITY MEANING THE TREATMENT OF WASTES WAS A CONSIDERATION ONLY ONCE THE WASTES WERE GENERATED. WITH AN R&D INVESTMENT IN TECHNOLOGY DEVELOPMENT, METHODS FOR MATERIALS SUBSTITUTION, RECOVERY AND REUSE, AND TREATMENT HAVE THE POTENTIAL TO EFFECTIVELY ACHIEVE HAZARDOUS WASTE MINIMIZATION GOALS OF A 50% REDUCTION IN HAZARDOUS WASTE GENERATION BY FY 92.

VIEWGRAPH 13. IN LIGHT OF THE INFORMATION PRESENTED IN THE PREVIOUS SLIDES, HAZARDOUS WASTE CONTROL IS A MAJOR EFFORT IN THE ENVIRONMENTAL QUALITY PROGRAM. R&D EFFORTS OVER THE YEARS HAVE RESULTED IN EXISTING SOLUTIONS FOR THE MANAGEMENT OF WASTES RESULTING FORM THE PRODUCTION OF MUNITIONS AND OTHER INDUSTRIAL OPERATIONS. EXAMPLES OF THESE SOLUTIONS INCLUDE THE DEVELOPMENT OF BIOLOGICAL AND PHYSICAL CONCEPTS FOR THE TREATMENT OF WASTEWATER RESULTING FROM THE PRODUCTION OF RDX, HMX, AND NITROGUANIDINE. METHODS HAVE BEEN DEVELOPED TO RECOVER THE VALUE OF WASTE PROPELLANTS AND EXPLOSIVES. AND METHODS ARE BEING DEVELOPED AND IMPLEMENTED TO REDUCE AND TREAT HAZARDOUS WASTES RESULTING FROM INDUSTRIAL OPERATIONS INCLUDING PAINT APPLICATION AND REMOVAL. CONTINUED R&D EFFORTS WILL RESULT IN THE DEVELOPMENT OF TECHNOLOGIES TO TREAT WASTES RESULTING FROM NEW TYPES OF MUNITIONS, TO REUSE ENERGETIC WASTES IN THE PRODUCTION CYCLE, AND TO PROVIDE INNOVATIVE METHODS TO REDUCE WASTES AS A RESULT OF METAL FINISHING AND PAINT STRIPPING.

VIEWGRAPH 14. AS WITH THE DEVELOPMENT OF TECHNOLOGIES TO PROVIDE SOLUTIONS FOR HAZARDOUS WASTE CONTAINMENT/CLEANUP PROBLEMS, THE ACCEPTANCE AND IMPLEMENTATION OF R&D DEVELOPMENT PRODUCTS IN THE AREA OF HAZARDOUS WASTE CONTROL AND MINIMIZATION IS A CRITICAL FACTOR. SOME OF THE AREAS WHICH CAN BE CONSIDERED AS TECHNOLOGY HANDOFFS ARE THE DEVELOPMENT OF A BIOLOGICAL TREATMENT PROCESS FOR THE TREATMENT OF WASTEWATER RESULTING FROM THE PRODUCTION OF BALL POWDER AT BADGER ARMY AMMUNITION PLANT, THE DEMONSTRATION OF PAINT WASTE INCINERATION IN SUPPORT OF WASTE MANAGEMENT AT ARMY DEPOTS, AND THE DEVELOPMENT, DEMONSTRATION, AND IMPLEMENTATION OF ALTERNATE PAINT STRIPPERS SUCH AS LESS TOXIC CHEMICAL STRIPPERS AND PLASTIC MEDIA.

VIEWGRAPHS

CORPS OF ENGINEERS MISSIONS

MILITARY

- Military Engineering
  - MOBILITY/COUNTERMOBILITY
  - ENGINEER MODELS
  - ALBE
  - TOPOGRAPHY
  - SUSTAINMENT ENGINEERING
  - SPACE TECHNOLOGY
  - ATMOSPHERIC EFFECTS
- Base Support
  - DESIGN
  - CONSTRUCTION
  - OPERATIONS AND MAINTENANCE
- Environmental Quality
  - INSTALLATION RESTORATION
  - HAZARDOUS WASTE CONTROL
  - ENVIRONMENTAL MANAGEMENT

CIVIL WORKS

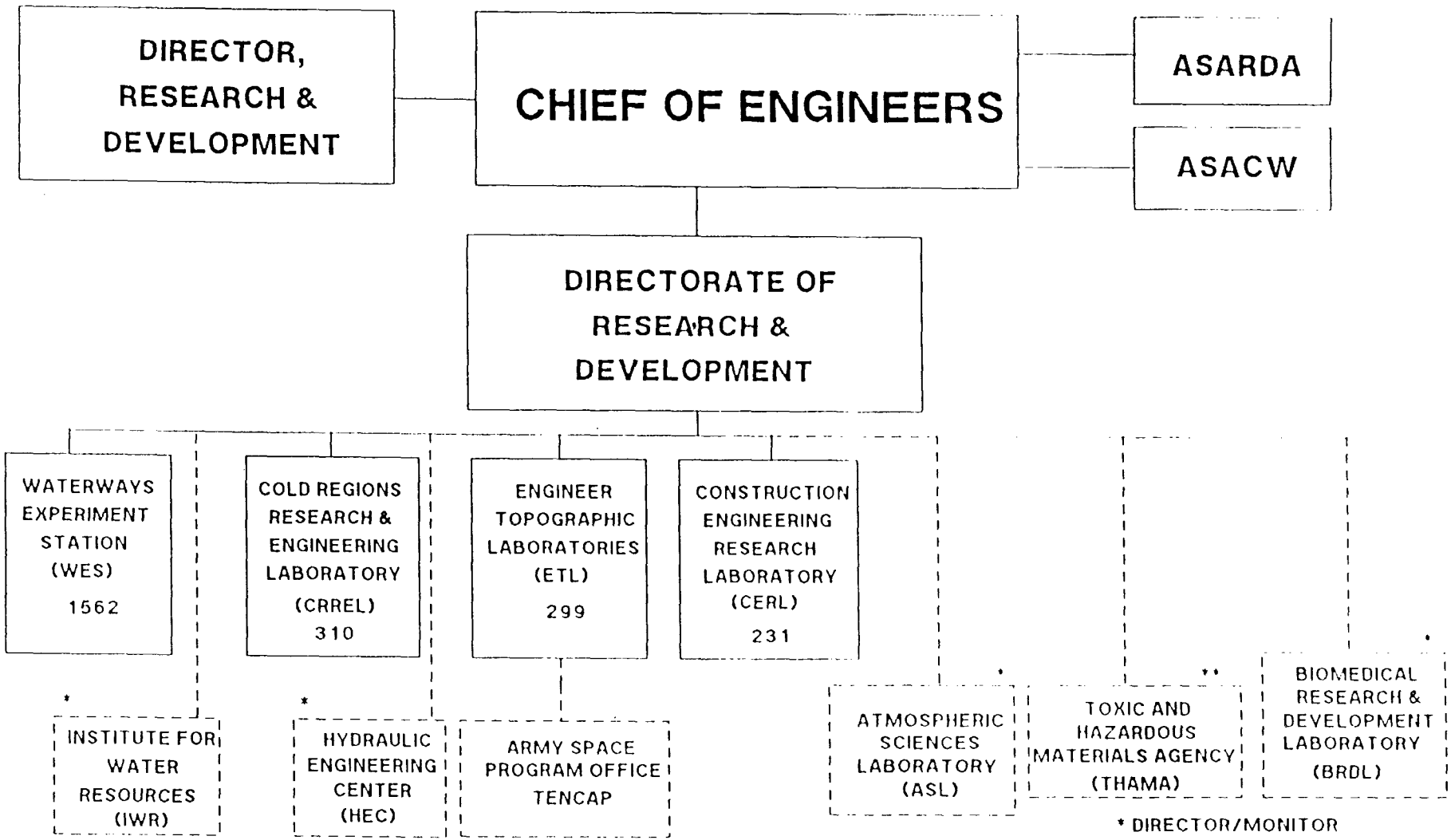
- FLOOD CONTROL AND NAVIGATION
- COASTAL ENGINEERING
- ENVIRONMENTAL QUALITY
- CONSTRUCTION, OPERATIONS AND MAINTENANCE
- MATERIALS
- WATER RESOURCE PLANNING
- SURVEYING AND SATELLITE APPLICATIONS

CHIEF OF ENGINEERS-- RESEARCH AND DEVELOPMENT EXECUTION

FUNCTIONS/RESPONSIBILITIES

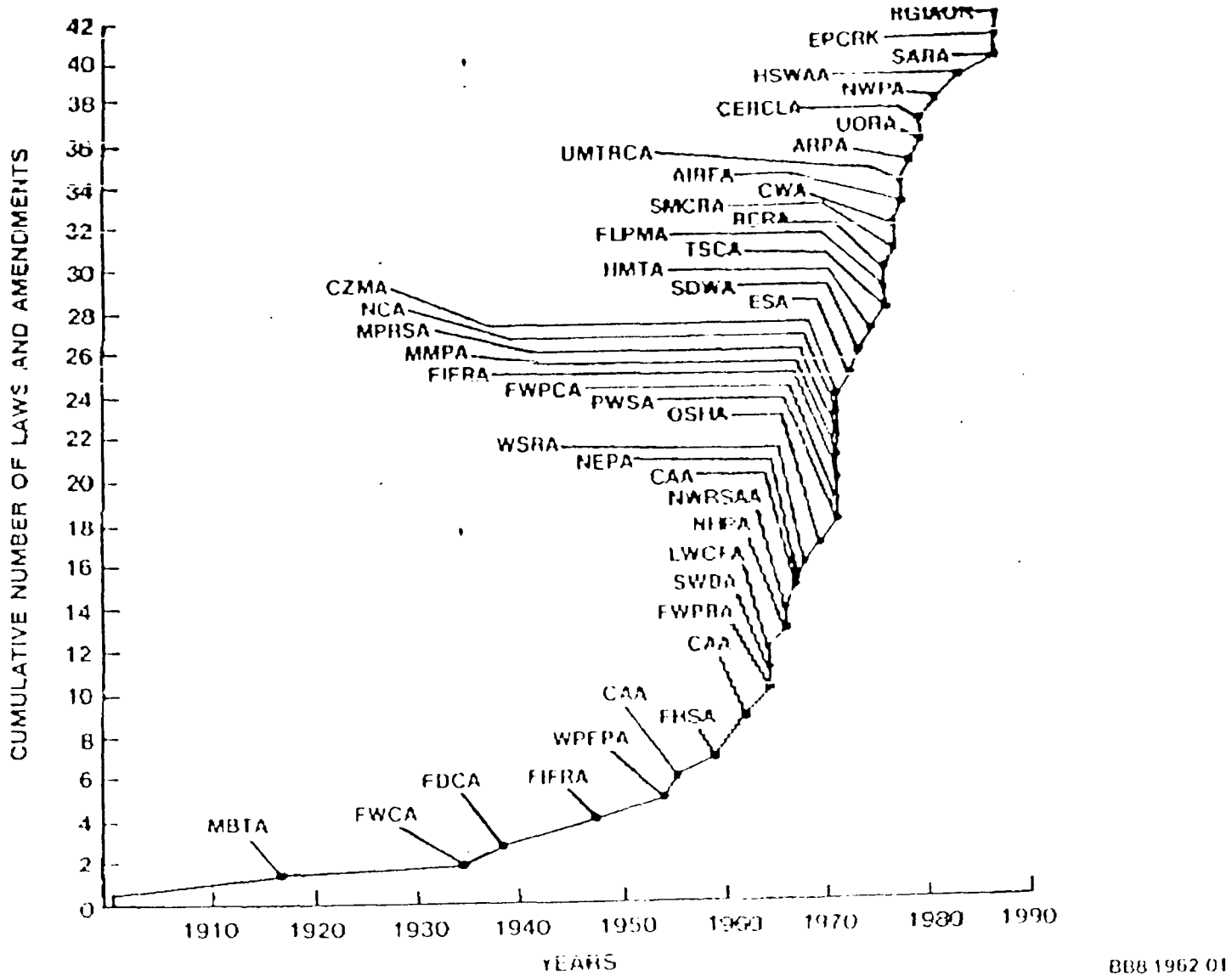
- ASA(RDA) DIRECTOR/MONITOR FOR MILITARY R&D
- DIRECTOR FOR CIVIL WORKS R&D
- MANAGES CORPS LABORATORIES
- CHIEF OF ENGINEERS STAFF

LABORATORY STRUCTURE

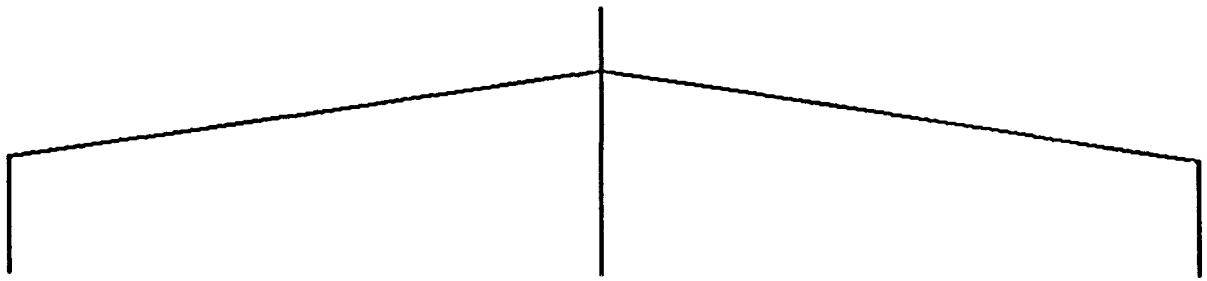


FILE PENNDRW
REV 2 NOV 88

FEDERAL ENVIRONMENTAL LEGISLATIVE POWER CURVE



ENVIRONMENTAL QUALITY TECHNOLOGY



HAZARDOUS WASTE CONTAINMENT/CLEANUP

- INSTALLATION RESTORATION

HAZARDOUS WASTE CONTROL

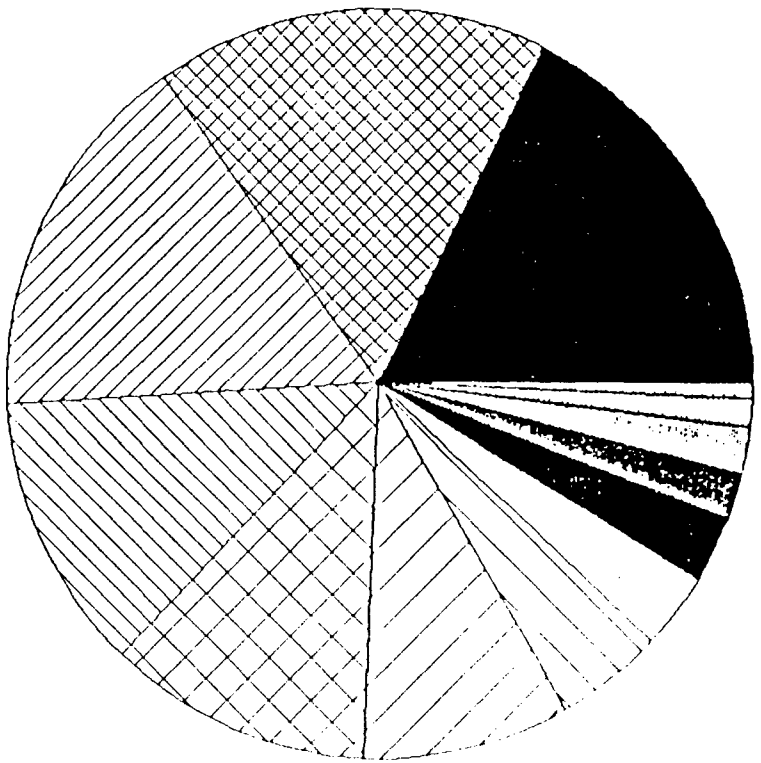
- UNDERGROUND STORAGE TANKS
- ASBESTOS
- HAZMIN
- NON-HAZARDOUS WASTES
- INDUSTRIAL WASTES

ENVIRONMENTAL MANAGEMENT

- NOISE CONTROL
- TRAINING RANGE RESTORATION

HAZARDOUS WASTE CONTAINMENT/CLEANUP

TYPES OF PROBLEMS (PERCENT OF TOTAL SITES)



- CONTAMINATED SOIL AREA 17.8%
- LANDFILLS 17.0%
- LAGOONS 16.2%
- BUILDINGS 11.9%
- BURNING GROUNDS 11.5
- OTHERS (ONE OF A KIND AREAS) 8.9%
- SUMPS 4.7%
- PITS 3.3%
- STORAGE TANKS 2.9%
- STORAGE PADS 2.0%
- SEWERAGE WASTE TREATMENT PLANTS 2.0%
- WASTE TREATMENT PLANT 1.2%
- SALVAGE YARDS 0.6%

HAZARDOUS WASTE CONTAINMENT/CLEANUP

EXISTING SOLUTIONS

SOIL

- INCINERATION
- EXCAVATE/LANDFILL
- CAPPING
- STABILIZATION
- DEVOLATILIZATION

GROUNDWATER

- AIR STRIPPING OF VOLATILES
- CONTAINMENT BARRIERS
- CARBON ADSORPTION
- ION EXCHANGE

STRUCTURES

- OPEN BURNING
- DESTROY/LANDFILL

FUTURE CAPABILITIES

SOIL

- HEAVY METAL SEPARATION
- REDUCE COST OF AIR POLLUTION CONTROLS
- LOWER COST ALTERNATIVES TO INCINERATION

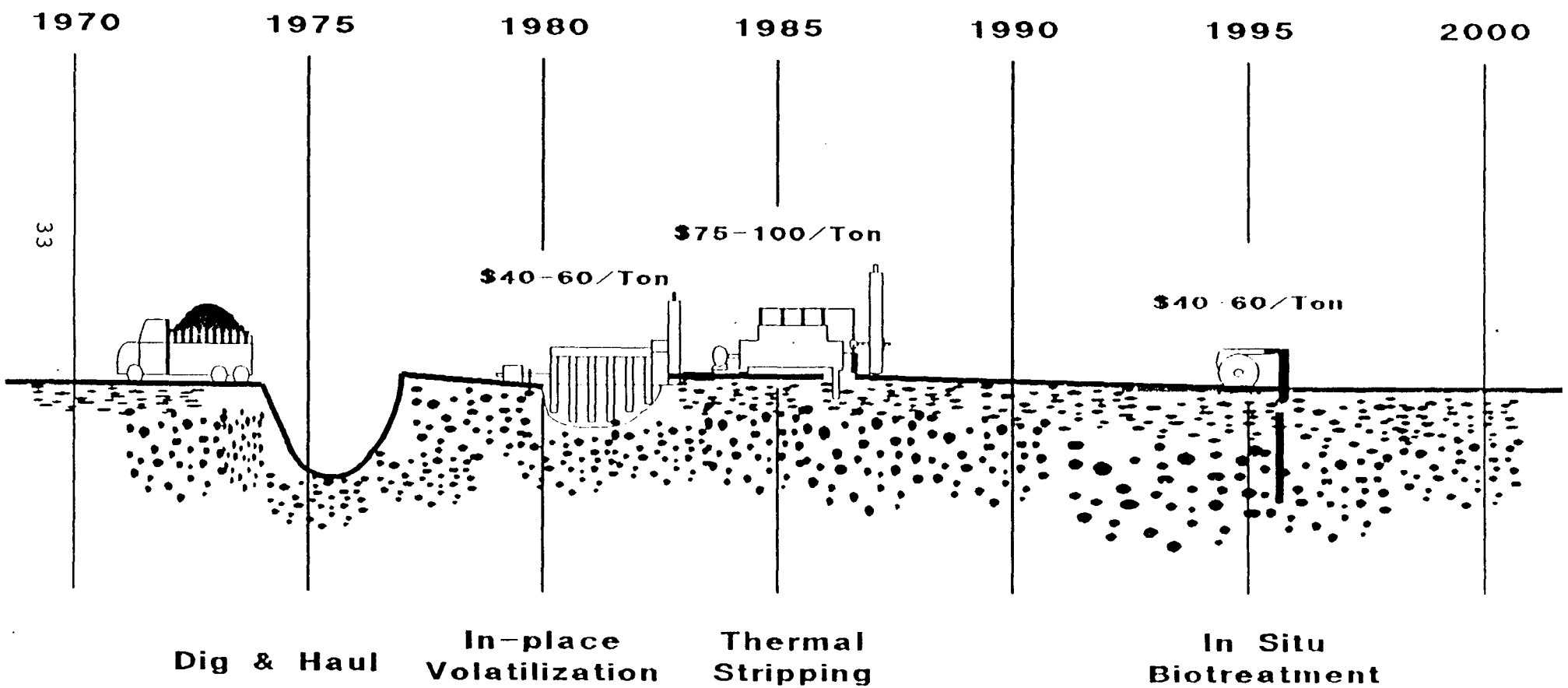
GROUNDWATER

- IN-PLACE MICROBIAL TREATMENT
- TREATMENT OF OFF-GAS FROM AIR STRIPPING
- REPLACEMENT OF CARBON AS FILTRATION MEDIA

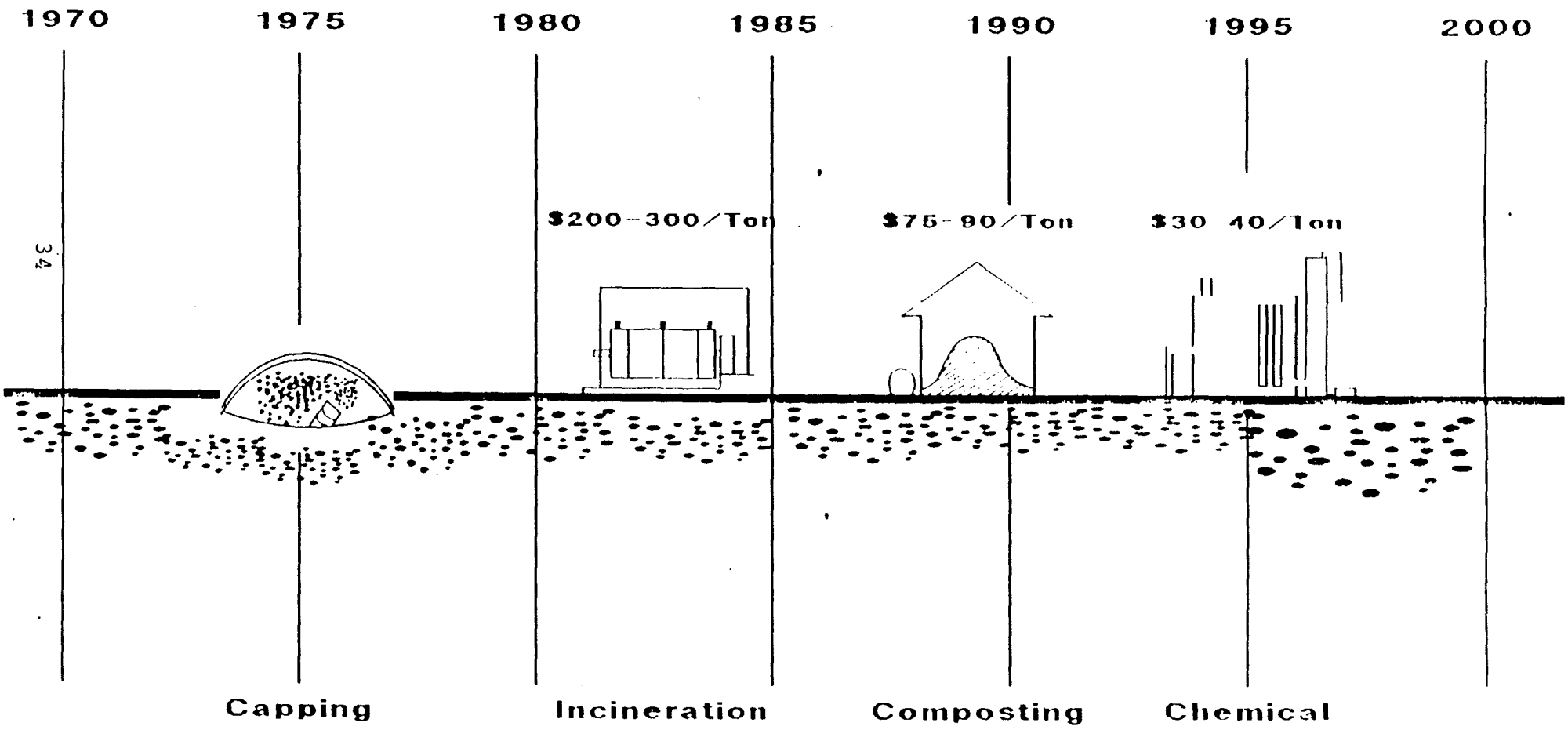
STRUCTURES

- NON-DESTRUCTIVE DECONTAMINATION

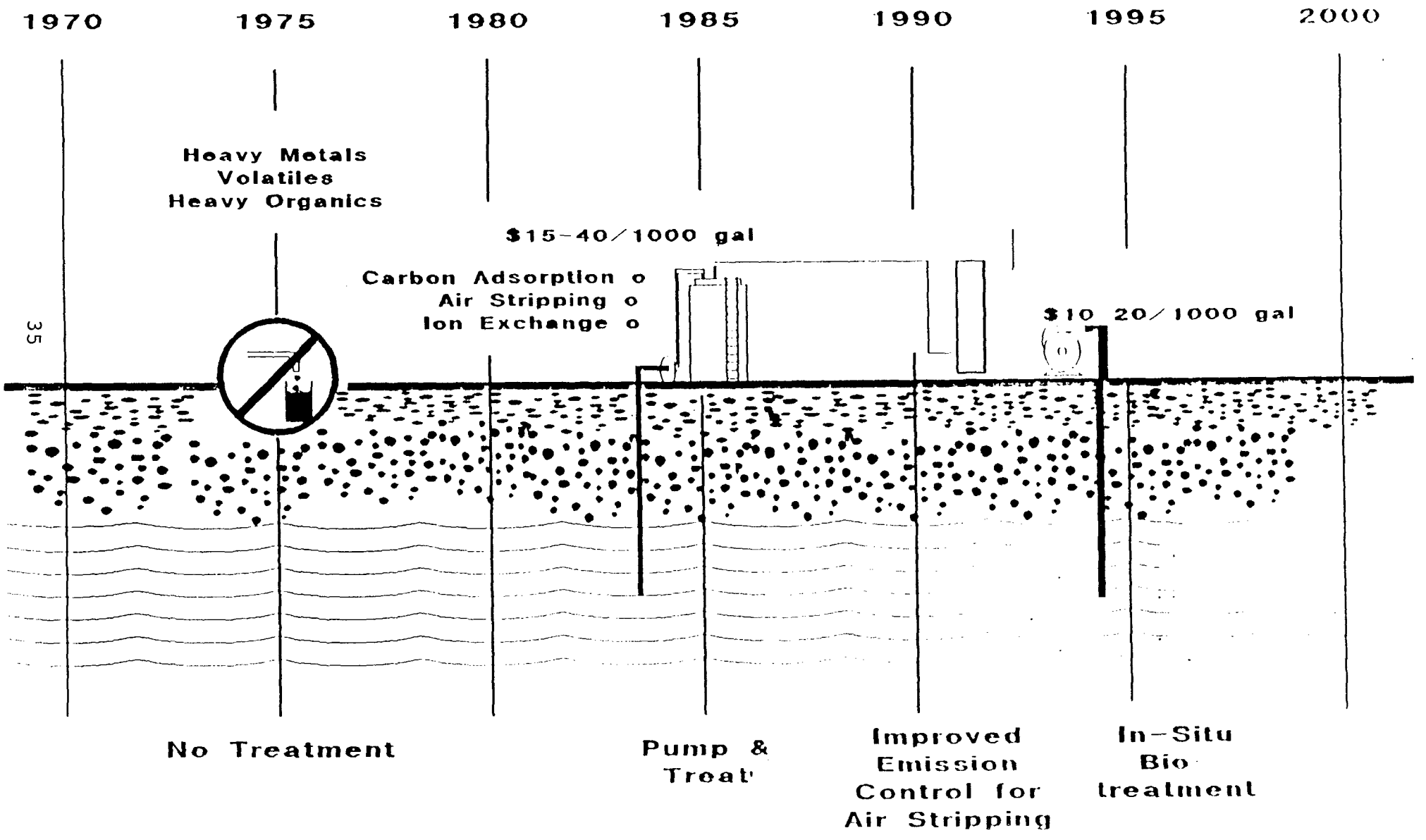
Solvent–Contaminated Soils



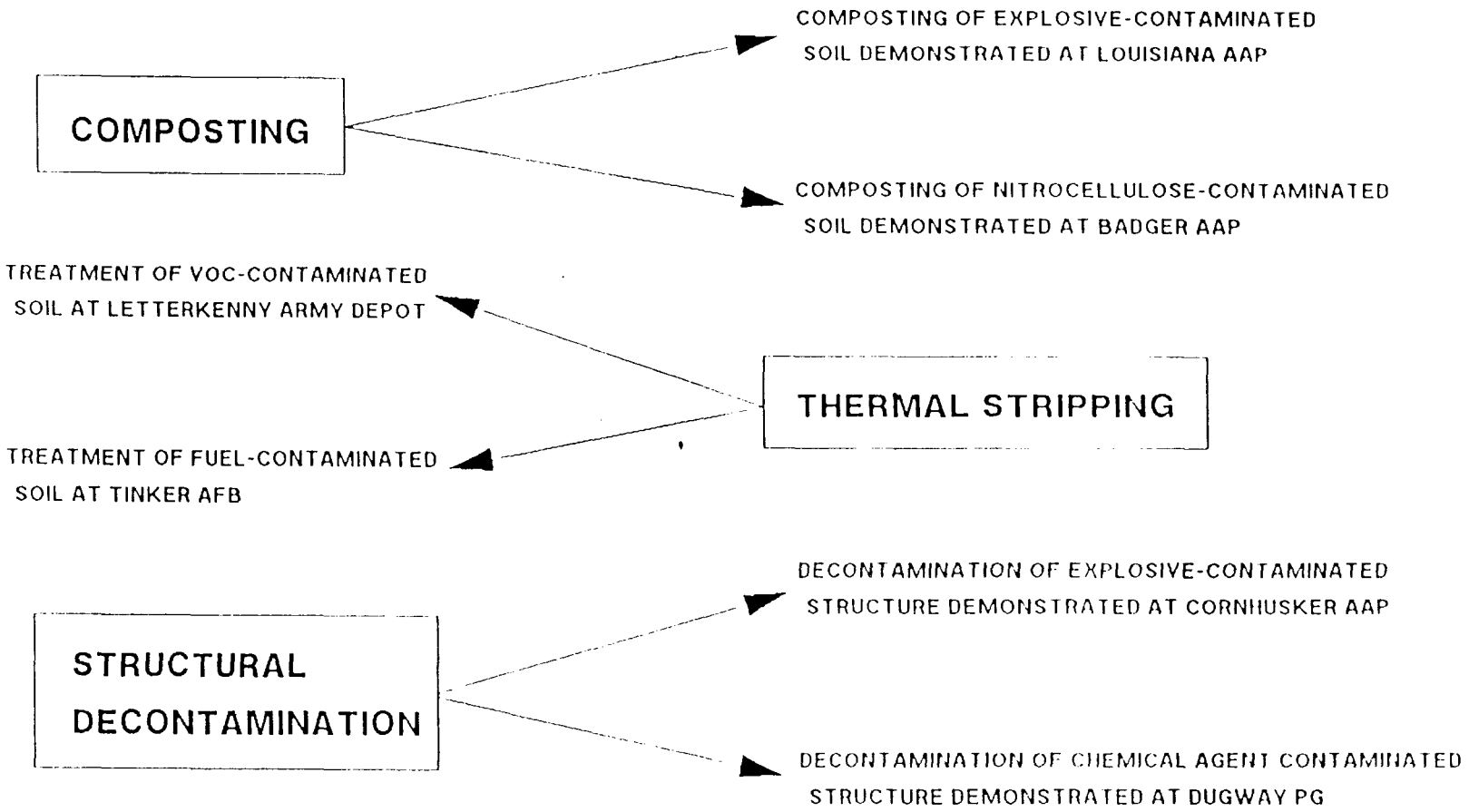
Explosive-Contaminated Soils



Groundwater Contamination



HAZARDOUS WASTE CONTAINMENT/CLEANUP TECHNOLOGY HANDOFFS



HAZARDOUS WASTE MINIMIZATION

LIMITED TECHNOLOGIES

HAZARDOUS WASTE TREATMENT → "END OF PIPE" TREATMENT

TECHNOLOGY INVESTMENT

- MATERIALS SUBSTITUTION FOR:
  - INDUSTRIAL CHEMICALS
  - PAINTS/VARNISHES
  - PRESERVATIVES
  - PESTICIDES
  - CLEANING COMPOUNDS
- RECOVERY AND REUSE OF:
  - INDUSTRIAL CHEMICALS
  - OIL/GREASES/FUEL OIL
  - DRUMS/CANS
  - EXPLOSIVE WASTES
  - GASES
  - CLEANING COMPOUNDS
  - PHOTOGRAPHIC SUPPLIES
  - BATTERUES
- TREATMENT OF:
  - INDUSTRIAL CHEMICALS
  - GASES
  - PHOTOGRAPHIC SUPPLIES
  - BATTERIES
  - TRANSFORMERS (PCB'S)
  - CAPACITORS
  - EXPLOSIVE WASTES

GOAL

HAZARDOUS WASTE REDUCTION → SUBSTITUTE, RECOVER, RECYCLE, TREATMENT

AMC/ARMY GOAL = 50% REDUCTION OF HAZARDOUS WASTE GENERATION BY FY 92
(FY 85 IS BASE YEAR)

HAZARDOUS WASTE CONTROL

EXISTING SOLUTIONS

FUTURE CAPABILITIES

MUNITIONS-RELATED WASTES

- BIOLOGICAL TREATMENT OF RDX/HMX WASTEWATER
- PHYSICAL TREATMENT OF NITROGUANIDINE WASTEWATER
- BIOLOGICAL TREATMENT AND DISPOSAL OF NITROCELLULOSE FINES
- ADVANCED SINGLE, DOUBLE AND TRIPLE BASED MUNITIONS WASTE CONTROL

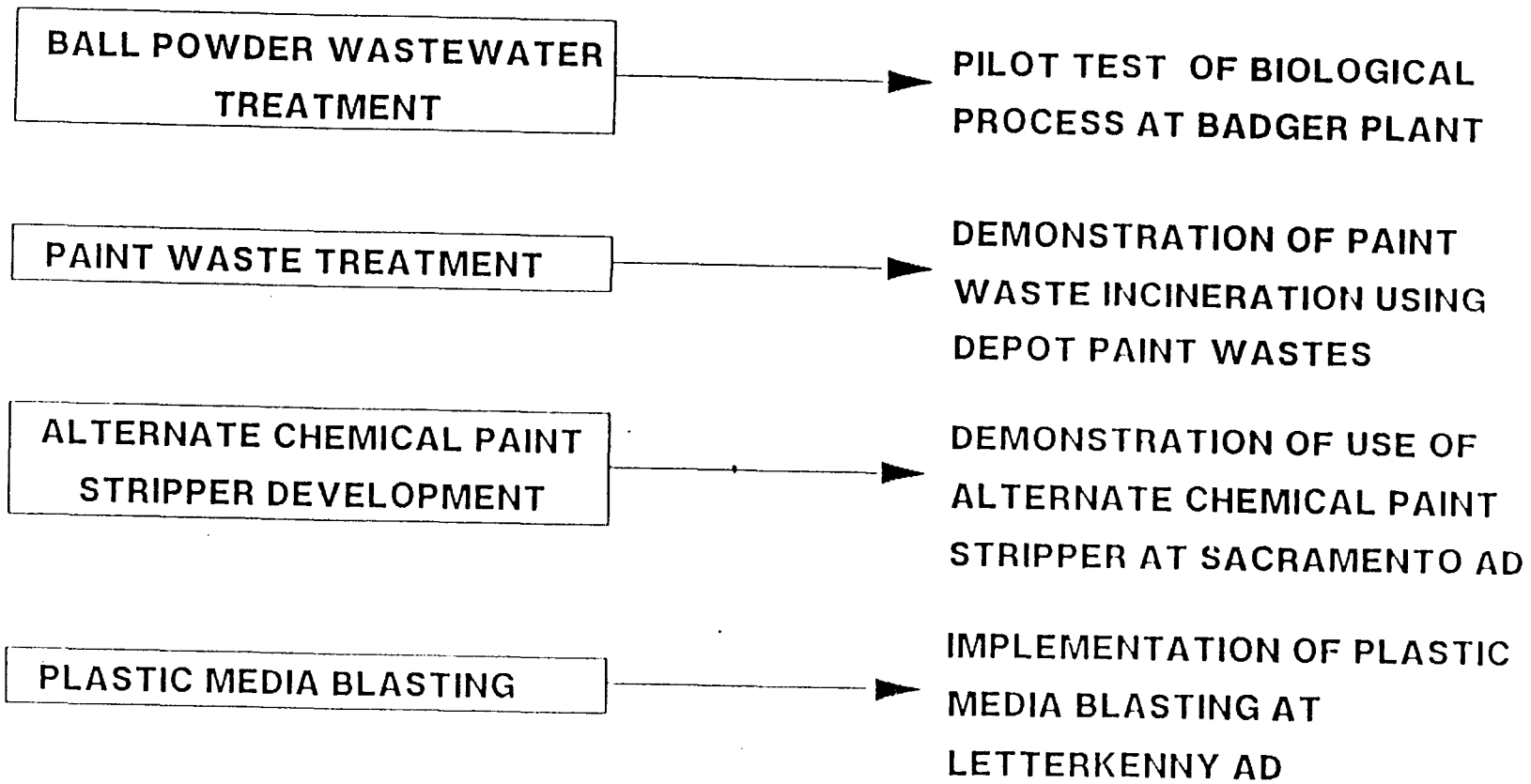
RECOVERY/REUSE OF MUNITIONS RELATED WASTES

- RESOLVATION AND EXTRACTION OF WASTE PROPELLANTS
- REUSE OF WASTE EXPLOSIVES AS FUEL OIL SUPPLEMENTS
- RECOVERY OF WASTE TNT
- REUSE OF ENERGETIC WASTES IN PRODUCTION CYCLE
- DEMILITARIZATION OF LIQUID PROPELLANTS

NON-MUNITIONS RELATED INDUSTRIAL WASTES

- PLASTIC MEDIA BEAD BLASTING
- PAINT WASTE INCINERATION
- ALTERNATE CHEMICAL PAINT STRIPPERS
- VOC EMISSIONS CONTROL
- ALUMINUM ION VAPOR DEPOSITION
- FLUIDIZED BED PAINT STRIPPING

HAZARDOUS WASTE CONTROL TECHNOLOGY HANDOFFS



IMPLEMENTATION OF THE DEPARTMENT OF THE ARMY ENVIRONMENTAL PROGRAM

BY
LEWIS D. WALKER
OFFICE OF THE ASSISTANT SECRETARY OF THE ARMY
(INSTALLATIONS AND LOGISTICS)

PRESENTED TO
THE
THIRTEENTH ANNUAL ENVIRONMENTAL QUALITY R&D SYMPOSIUM
WILLIAMSBURG, VIRGINIA
NOVEMBER 16, 1988

GOOD MORNING! THANK YOU VERY MUCH FOR THE INVITATION TO SPEAK ONCE AGAIN TO THE ENVIRONMENTAL QUALITY RESEARCH AND DEVELOPMENT SYMPOSIUM. I HAD INTENDED TO ATTEND THE ENTIRE SYMPOSIUM THIS YEAR BUT A CONFLICT HAS LIMITED MY ATTENDANCE TO JUST THIS SESSION. IN FACT, I HAVE TO BE BACK IN RICHMOND AT 1030 THIS MORNING TO CONTINUE A SPECIAL REVIEW OF SENIOR EXECUTIVE SERVICE POSITIONS.

FIRST OF ALL, LET ME START OUT BY SAYING THAT I BELIEVE THE DEPARTMENT OF THE ARMY ENVIRONMENTAL PROGRAM IS ON THE RIGHT TRACK, BUT THAT WE HAVE TREMENDOUS CHALLENGES AHEAD OF US. IT WILL TAKE THE CONCERTED EFFORTS BY ALL OF US, BUT PARTICULARLY THE EFFORTS OF THE R&D COMMUNITY, TO HELP US EXPAND THE NARROW FOCUS OF TUNNEL VISION THAT WE TEND TO SETTLE IN WITH, TO BREAK THROUGH AND ENCOMPASS THE LARGER PROBLEM AND HOPEFULLY COME UP WITH THE LARGER SOLUTION. I WILL EXPAND UPON SOME IDEAS ALONG THIS LINE IN A FEW MOMENTS.

I AM DEEPLY GRATIFIED THAT WE ARE GETTING THE DA ENVIRONMENTAL MANAGEMENT STRUCTURE IN PLACE TO BETTER FOCUS ON THE ENVIRONMENTAL PROBLEMS. I HAVE EVERY CONFIDENCE IN MAJOR GENERAL OFFRINGA AND AM PLEASED THAT HE IS THE ASSISTANT CHIEF OF ENGINEERS AND THE PROGRAM MANAGER FOR ENVIRONMENT. HE IS INTERESTED AND ENTHUSIASTIC, AND BEST OF ALL, HE IS COMMITTED TO BETTER ENVIRONMENTAL MANAGEMENT. THIS COMMITMENT HAS CARRIED OVER IN THE ORGANIZATIONAL STRUCTURE. BRINGING THE ARMY ENVIRONMENTAL OFFICE BACK UP TO THE ARMY STAFF LEVEL IN THE FORM OF A STAFF SUPPORT AGENCY HAS VASTLY IMPROVED THE RESPONSIVENESS TO TASKINGS. HOPEFULLY, WE CAN SOON GET THE ENTIRE ARMY ENVIRONMENTAL OFFICE LOCATED TOGETHER IN OR VERY NEAR THE PENTAGON.

THE TRANSFER OF THE U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY (USATHAMA) AS A FIELD OPERATING AGENCY TO THE ASSISTANT CHIEF OF ENGINEERS JUST LAST MONTH ALONG WITH AN EXPANDED MISSION, WILL ALSO IMPROVE THE SUPPORT STRUCTURE FOR THE WORLD-WIDE ARMY ENVIRONMENTAL MISSION AND PROGRAMS.

THE INSTALLATION RESTORATION PROGRAM IS PROCEEDING VERY WELL. IN FY 89, THE ARMY'S SHARE OF THE $500 MILLION DEFENSE ENVIRONMENTAL RESTORATION ACCOUNT IS $204.6 MILLION FOR ACTIVE ARMY SITES AND $37.1 MILLION FOR FORMERLY USED DEFENSE SITES (FUDS), FOR WHICH ARMY HAS EXECUTIVE AGENCY PROPONENCY FOR DOD. I AM PARTICULARLY HAPPY TO SEE THAT THE CLEANUP PORTION OF THE FY 89 FUNDS HAS INCREASED TO 45% OF THE TOTAL, COMPARED TO 34% IN FY 88. THIS MEANS THAT WE ARE SPENDING MORE RESOURCES TO CLEAN UP THE PROBLEM RATHER THAN STUDYING THE PROBLEM. ALTHOUGH THE STUDY PHASE IS IMPORTANT, CONGRESS IS ANXIOUS TO SEE PROGRESS IN ACTUAL CLEANUP.

ONE OF OUR CURRENT ENDEAVORS IS TO NEGOTIATE INTERAGENCY AGREEMENTS (IAGs) WITH EPA AND THE STATES FOR OUR NPL AND PROPOSED NPL SITES. WITH THE ASSISTANCE OF THE ARMY ENVIRONMENTAL OFFICE AND USATHAMA, WE FORMALLY KICKED OFF THIS ENDEAVOR WITH AN IAG WORKSHOP ON SEPTEMBER 13. MY PERSONAL GOAL WAS TO HAVE IAGs COMPLETED AT FOUR OF OUR INSTALLATIONS BY THE END OF THE CALENDAR YEAR. THIS GOAL PROVED TO

BE A LITTLE TOO AMBITIOUS. DESPITE VALIANT ATTEMPTS BY EVERYONE CONCERNED IN ATTEMPTING TO MAKE THIS HAPPEN, THE ISSUES OF STATE OVERSIGHT COST REIMBURSEMENT AND RESERVATION OF STATE'S RIGHTS PROVED TO BE ISSUES THAT PREVENTED IMMEDIATE AGREEMENTS. THESE ISSUES ARE CURRENTLY BEING ADDRESSED AT THE DOD LEVEL AND RESOLUTION WILL HOPEFULLY BE FORTHCOMING SOON.

IN THE CASE OF RCRA VIOLATIONS, DOD HAS ISSUED A POLICY THAT WHERE RCRA PROBLEMS CANNOT BE CORRECTED WITHIN A 3-TO-6 MONTH PERIOD, THE INSTALLATION SHOULD NEGOTIATE A FEDERAL FACILITY COMPLIANCE AGREEMENT (FFCA) WITH EPA AND THE STATE. WE HAVE THUS FAR SIGNED FFCAs FOR IOWA ARMY AMMUNITION PLANT AND PICATINNY ARSENAL. NEGOTIATIONS ARE CURRENTLY UNDERWAY FOR FFCAs AT LAKE CITY ARMY AMMUNITION PLANT, WEST POINT AND BAYONNE MILITARY OCEAN TERMINAL.

BECAUSE OF PROBLEMS WITH NOVs, THE ARMY HAS INITIATED AN ENVIRONMENTAL COMPLIANCE ACHIEVEMENT PROGRAM (ECAP) TO FOCUS IN ON ACHIEVING COMPLIANCE AT ALL OUR FACILITIES. THE ARMY ENVIRONMENTAL OFFICE IS TAKING A COMPREHENSIVE LOOK AT THE IMPEDIMENTS TO COMPLIANCE AND DEVELOPING RECOMMENDATIONS TO OVERCOME THESE IMPEDIMENTS. I AM PERSONALLY PUSHING FOR A SEPARATE FENCED ACCOUNT TO FUND RCRA NEEDS WITHIN THE ARMY. UNLIKE THE DERA WHICH IS DEDICATED TO CERCLA TYPE CLEANUPS, THERE PRESENTLY IS NO DEDICATED MONIES FOR RCRA COMPLIANCE. RCRA ISSUES MUST COMPETE WITH ALL OTHER BASE OPERATIONS NEEDS USING OPERATION AND MAINTENANCE, ARMY FUNDS. IN SOME CASES, DEPENDING ON HOW THE INSTALLATION IS FUNDED, RCRA COMPLIANCE IS HANDLED THROUGH ARMY INDUSTRIAL FUND (AIF) ACCOUNTS OR THROUGH RESEARCH AND DEVELOPMENT, TEST AND EVALUATION (RDTE) FUNDING. A FENCED ACCOUNT FOR RCRA CORRECTIVE ACTIONS WOULD DO MUCH TO ASSIST THE ARMY IN MEETING TOTAL COMPLIANCE OBJECTIVES. COMPLIANCE WITH RCRA NOW MAY PREVENT CERCLA PROBLEMS IN THE FUTURE.

THE SENIOR ARMY ENVIRONMENTAL LEADERSHIP IS MEETING NEXT WEEK (21-22 NOVEMBER) TO FOCUS ON SPECIFIC LONG-TERM GOALS AND OBJECTIVES FOR THE ECAP. THE RESULTS OF THIS SENIOR ENVIRONMENTAL LEADERSHIP CONFERENCE WILL HELP FOCUS OUR EFFORTS WELL INTO THE 1990's.

MOST OF YOU ARE AWARE OF THE HAZARDOUS WASTE MINIMIZATION PROGRAM. ALL SERVICES HAVE INITIATED A PROGRAM AND I AM SURE THAT GENERAL OFFRINGA MADE SPECIFIC REFERENCE TO THIS PROGRAM IN HIS KEYNOTE ADDRESS. HAZMIN HAS GOT TO BE A KEY ELEMENT OF OUR OVERALL ENVIRONMENTAL MANAGEMENT STRATEGY.

WE GAIN TREMENDOUS ADVANTAGES IN CUTTING DOWN ON LIABILITY AS WELL AS THE COST OF DISPOSAL IF WE DECREASE THE GENERATION OF HAZARDOUS WASTE THAT MUST ULTIMATELY BE DISPOSED OF. IN FY 88, THE ARMY SPENT $21.7 MILLION FOR CONTRACT HAZARDOUS WASTE DISPOSAL THROUGH THE DEFENSE REUTILIZATION AND MARKETING SERVICE. THIS IS EXPECTED TO JUMP TO $32 MILLION IN FY 89. WHEN YOU CONSIDER THAT THIS IS ONLY APPROXIMATELY 15% OF THE TOTAL ARMY HAZARDOUS WASTE GENERATED, THERE IS AMPLE INCENTIVE TO MINIMIZE GENERATION ON COST ALONE. THE GROWING COST OF DISPOSAL, COMBINED WITH THE POTENTIAL FOR LIABILITY ASSOCIATED WITH REQUIREMENTS FOR FUTURE CLEANUPS, MANDATES THE FOCUS ON SOURCE REDUCTION AND RECYCLING METHODS TO REDUCE REQUIREMENTS FOR HAZARDOUS

WASTE DISPOSAL. THE "FRONT END" APPROACH TO HAZARDOUS WASTE REDUCTION WILL SERVE TO PROVIDE MAXIMUM PROTECTION TO HUMAN HEALTH AND THE ENVIRONMENT.

TO ASSIST THE HAZMIN EFFORT, THE ARMY HAS IDENTIFIED A CERTAIN PORTION OF THE DERA TO SERVE AS "SEED MONEY" FOR INSTALLATION HAZARDOUS WASTE MINIMIZATION PROGRAMS. THE ARMY AUTHORIZED 7.5 MILLION DOLLARS IN FYs 87 AND 88, AND 8.4 MILLION DOLLARS IS PROGRAMMED IN FY 89 FOR USE IN INSTALLATION MINIMIZATION EQUIPMENT PURCHASES, STUDIES AND RESEARCH AND DEVELOPMENT.

GENERAL OFFRINGA AND I CO-CHAIR A HAZARDOUS WASTE MINIMIZATION (HAZMIN) WORKGROUP. THE OBJECTIVE OF THIS WORKGROUP IS TO ANALYZE THE PROCEDURES, EFFECTIVENESS, AND IMPEDIMENTS PERTAINING TO MINIMIZATION OF THE ARMY'S HAZARDOUS WASTE GENERATIONS. THE INTERDISCIPLINARY WORKGROUP MEMBERS PROVIDE A "CORPORATE-LEVEL" VIEW TO ISSUES SUCH AS ACQUISITION, BUDGETING, CONTRACTING, RESEARCH, LOGISTICS, LEGAL AND HEALTH. WITHIN THE NEXT COUPLE OF MONTHS THE ARMY HOPES TO ISSUE FORMAL POLICY CONCERNING REQUIREMENTS FOR IMPLEMENTING AN ARMY-WIDE HAZMIN PROGRAM. THE POLICY STATEMENT IS CURRENTLY UNDER REVIEW BY TOP ARMY MANAGEMENT. THIS POLICY WILL HOPEFULLY FORMALIZE WHAT IS ALREADY UNDERWAY AT THE INSTALLATIONS. IT STATES THAT THE ARMY'S POLICY IS TO REDUCE THE QUANTITY OR VOLUME AND TOXICITY OF HAZARDOUS WASTES GENERATED BY ARMY OPERATIONS AND ACTIVITIES WHERE EVER IT IS ECONOMICALLY PRACTICABLE. EMPHASIS SHALL BE PLACED ON SOURCE REDUCTION METHODS. WHERE SOURCE REDUCTION IS NOT FEASIBLE OR ECONOMICALLY PRACTICABLE, THE ARMY SHALL PROMOTE RECYCLING, ON-SITE TREATMENT, AND OTHER ALTERNATIVES TO REDUCE THE QUANTITY OR VOLUME AND TOXICITY OF HAZARDOUS WASTES. IN ADDITION, THE POLICY ESTABLISHES A GOAL WHICH GENERAL OFFRINGA ALREADY HAS MENTIONED TO ACHIEVE A 50 PERCENT SOURCE REDUCTION OF THE QUANTITY OF HAZARDOUS WASTES GENERATED BY DECEMBER 31, 1992, WHEN COMPARED TO A BASELINE OF CALENDAR YEAR 1985.

TODAY, WE TEND TO CONCENTRATE OUR EFFORTS IN THE HAZARDOUS WASTE AREA AND PERHAPS RIGHTFULLY SO. IT WASN'T TOO MANY YEARS AGO, HOWEVER, THAT SURFACE WATER POLLUTION AND AIR POLLUTION WERE THE AREAS OF INTEREST. WE CAN'T FORGET THAT WE STILL HAVE MAJOR CHALLENGES IN THESE AREAS AS WELL. I RECENTLY RECEIVED A MEMORANDUM FROM MR. PARKER ASKING THE ARMY TO EVALUATE THE IMPACT OF A PROPOSED AMENDMENT TO THE CLEAN AIR ACT. THE NAVY HAD BRIEFED HIM ON POSSIBLE ECONOMIC IMPACTS THAT COULD RUN INTO THE BILLIONS OF DOLLARS FOR BOILER PLANT RETROFITS FOR DOD ALONE TO MEET TIGHTENED AIR EMISSION STANDARDS.

ENVIRONMENTAL NOISE IS STILL AN ISSUE, PARTICULARLY IN EUROPE. THE NOISE FROM LOW FLYING AIRCRAFT IS THE NUMBER 1 ENVIRONMENTAL ISSUE ACCORDING TO THE GERMAN MINISTRY OF DEFENSE. ALTHOUGH NOT STATUTORILY MANDATED, OUR GOAL HERE IN CONUS IS TO HAVE ALL ICUZ SURVEYS COMPLETED BY THE END OF THIS FISCAL YEAR (FY 89). THESE SURVEYS HAVE DONE MUCH TO ASSIST MASTER PLANNERS, BOTH ON THE INSTALLATION AND IN THE SURROUNDING CIVILIAN COMMUNITIES, TO APPROPRIATELY ZONE LAND AREAS TO PRECLUDE AS MUCH AS POSSIBLE INCOMPATIBLE LAND USES RESULTING FROM HIGH AMBIENT LEVELS OF NOISE DUE TO MILITARY OPERATIONS. MOST NOISE IS GENERATED BY MILITARY AIRCRAFT, TRAINING RANGE ACTIVITIES AND EXPLOSIVE DEMOLITION OF AMMUNITION.

OTHER ENVIRONMENTAL ENDEAVORS INCLUDE THE ASBESTOS AND RADON PROGRAMS.

THE ARMY CONTINUES WITH ITS PROGRAM OF IDENTIFYING AND REMOVING, WHERE REQUIRED, FRIABLE ASBESTOS, WITH PARTICULAR EMPHASIS ON CHILD CARE FACILITIES, SCHOOLS, LIVING AND WORK AREAS. ARMY POLICY PROHIBITS THE USE OF ASBESTOS IN NEW CONSTRUCTION AND REQUIRES REMOVAL OF EXISTING ASBESTOS IF IT IS PRESENT IN FRIABLE FORM SUBJECT TO AIRBORNE RELEASE.

THE ARMY IS EMBARKING ON AN AMBITIOUS NEW PROGRAM TO IDENTIFY ALL ARMY-OWNED OR OPERATED BUILDINGS CONTAINING INDOOR RADON CONCENTRATIONS AT LEVELS IN EXCESS OF FOUR PICOCURIES PER LITER OF AIR (AS AN ANNUAL AVERAGE). THIS PROGRAM WILL BEGIN WITH THIS FALL'S HEATING SEASON. PRIORITY OF ASSESSMENT WILL GO TO BUILDINGS USED AS HOSPITALS, CHILD CARE FACILITIES, LIVING FACILITIES (BOTH FAMILY QUARTERS AND TROOP HOUSING) AND WORK AREAS THAT ARE OPERATED 24 HOURS PER DAY. MITIGATION ACTIVITIES WILL DEPEND ON LEVELS MEASURED ABOVE FOUR PICOCURIES PER LITER AND WILL BE HANDLED ON A "WORST-FIRST" BASIS.

IT HAS COME TO MY ATTENTION THAT DESPITE OUR BEST EFFORTS AND INTENTIONS TO COMMUNICATE POLICIES AND PROCEDURES, INSTALLATION PERSONNEL OFTEN WIND UP "REINVENTING THE WHEEL." THE CASE IN POINT IS UNDERGROUND STORAGE TANK INSPECTION AND EVALUATION. ONE INSTALLATION WILL GO THROUGH THE PROCESS OF CONTRACTING FOR A COMPLETE "START FROM SCRATCH" EVALUATION. THE INFORMATION ON PROCEDURES, HOWEVER, IS NEVER MADE AVAILABLE TO OTHER INSTALLATIONS ON PROCEDURES. CONSEQUENTLY, ANOTHER COMPREHENSIVE CONTRACT IS LET TO DO SIMILAR WORK THAT MIGHT NOT BE NECESSARY. CONSEQUENTLY, I HAVE TASKED THE ASSISTANT CHIEF OF ENGINEERS TO CONSIDER ESTABLISHING AND IDENTIFYING "CENTERS OF EXCELLENCE" WITHIN THE ARMY FOR UNDERGROUND STORAGE TANKS, ASBESTOS AND RADON. THIS WOULD ALLOW INSTALLATIONS TO CONTACT A SINGLE AGENCY TO RECEIVE TECHNICAL ADVICE AND INPUT ON A SPECIFIED PROGRAM. HOPEFULLY, CONSISTENCY AND EFFICIENCY WILL RESULT AND FRUSTRATION LEVELS WILL BE LOWERED AT THE INSTALLATION LEVEL.

AT THE BEGINNING OF MY TALK, I MENTIONED THAT THE R&D COMMUNITY IS CRUCIAL TO THE EFFORTS OF PRESENT AND FUTURE ENVIRONMENTAL COMPLIANCE. CERTAINLY, R&D IS VITAL TO SUCH THINGS AS PROCESS CHANGES AND MATERIAL SUBSTITUTION IN HAZMIN INITIATIVES. ALSO THE DEVELOPMENT OF TRACKING SYSTEMS AND ECONOMIC ANALYSIS TOOLS IS EXTREMELY IMPORTANT. BUT THE CHALLENGE TO THE R&D COMMUNITY WILL TRANSCEND THESE ENDEAVORS. WE WILL HAVE TO EXPAND OUR CREATIVE TALENTS TO THINK GLOBALLY ON SUCH ISSUES AS HAZARDOUS WASTE DISPOSAL PROCEDURES IN THE FUTURE. WITH THE LAND BANS FOR VARIOUS MATERIALS, IT IS GOING TO BE INCREASINGLY DIFFICULT AND EXPENSIVE TO DISPOSE OF HAZARDOUS WASTE IN THE FUTURE. MAYBE WE OUGHT TO THINK ABOUT REGIONAL INCINERATION DISPOSAL FACILITIES. THE WESTERN AREA DEMIL FACILITY (WADF) AT HAWTHORNE ARMY AMMUNITION PLANT WAS BUILT BY THE NAVY TO DEMILITARIZE CONVENTIONAL AMMUNITION. IT HAS NEVER BEEN OPERATED FOR A NUMBER OF REASONS BUT SITS THERE WITH AN $80 MILLION SUNK COST. MAYBE WE NEED TO EVALUATE ITS CAPABILITY TO DISPOSE OF HAZARDOUS WASTE FROM ARMY OR MILITARY INSTALLATIONS IN THE WESTERN UNITED STATES. RIGHT NOW NOBODY WANTS TO HAVE A LANDFILL OR AN INCINERATOR LOCATED IN THEIR BACKYARD. MAYBE WE NEED TO SEE WHAT CAN

BE DONE TO CHANGE PERCEPTIONS. ANOTHER PERCEPTION THAT WILL HAVE TO BE CHANGED IS OUR "THROW-AWAY" SOCIETY. ALTHOUGH HAZARDOUS WASTE WILL REMAIN A MAJOR CHALLENGE, I BELIEVE THE DISPOSAL OF NON-HAZARDOUS SOLID WASTE WILL EVENTUALLY APPROACH HAZARDOUS WASTE AS A CHALLENGE. LANDFILLS ARE BEING CLOSED OUT AND ONLY LIMITED LAND AREA IS AVAILABLE FOR NEW LANDFILLS. PERCEPTIONS WILL HAVE TO BE CHANGED IN PACKAGING AND RECYCLING.

THE MILITARY R&D COMMUNITY IS VERY ADEPT AT NETWORKING WITH THEIR CIVILIAN COUNTERPARTS. SEVERAL OF OUR LABORATORIES HAVE COOPERATIVE AGREEMENTS OR AFFILIATIONS WITH UNIVERSITIES. ONE INITIATIVE THAT I HAVE COORDINATED WITH THE ASSISTANT SECRETARY OF THE ARMY FOR RESEARCH, DEVELOPMENT AND ACQUISITION IS TO HAVE THE ARMY SCIENCE BOARD REVIEW THE ARMY'S PROGRAMS IN TOXIC AND HAZARDOUS WASTE MANAGEMENT. ALTHOUGH I STATED EARLIER THAT OUR INSTALLATION RESTORATION PROGRAM IS PROCEEDING VERY WELL, I THINK WE OWE IT TO THE AMERICAN TAXPAYER TO SEE IF WE CAN MAKE IMPROVEMENTS IN OUR STUDY OR REMEDIATION APPROACHES THROUGH AN INDEPENDENT REVIEW. AFTER ALL, THE ARMY IS SPENDING MILLIONS OF DOLLARS ON THIS PROGRAM WHICH WOULD OTHERWISE BE AVAILABLE FOR OTHER USES. THE ARMY SCIENCE BOARD WILL ALSO ASSESS THE HAZMIN PROGRAM AND LOOK AT CURRENT DISPOSAL PROCEDURES FOR HAZARDOUS AND TOXIC WASTES AND EVALUATE OPTIONS FOR FUTURE DISPOSAL FOR BOTH HAZARDOUS AND SOLID WASTE.

THESE ARE A FEW OF MY THOUGHTS. WE HAVE TO BE PROACTIVE IN OUR COMMITMENT TO BRINGING OUR INSTALLATIONS INTO FULL COMPLIANCE WITH ENVIRONMENTAL LAWS AND REGULATIONS. WITH INCREASING PUBLIC AND CONGRESSIONAL SCRUTINY OF THE DEPARTMENT OF DEFENSE'S ENVIRONMENTAL PROGRAMS, WE HAVE TO CONTINUE TO WORK HARD TO ESTABLISH AND MAINTAIN CREDIBILITY. WORKING TOGETHER, WE NOT ONLY CAN ASPIRE TOWARD BETTER ENVIRONMENT, BUT ACHIEVE A BETTER ENVIRONMENT.

THANK YOU VERY MUCH. IF THERE IS TIME AVAILABLE, I WOULD BE HAPPY TO ANSWER QUESTIONS.

Waste Minimization Case Histories at Three U.S. Air Force Air Training Command Bases

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INTRODUCTION

MOTIVATION FOR WASTE MINIMIZATION

There are many reasons why waste minimization has become a subject of interest for the U.S. Air Force (USAF) (U.S. Congress, 1986). First, waste minimization is mandated by the Resource Conservation and Recovery Act (RCRA), in that certification as to the presence and adequacy of a minimization program is incorporated into the manifests attached to hazardous waste containers by generators. Also, waste minimization is a parameter in RCRA Part B permits and is a detail item in biannual reports.

Second, there are substantial cost savings associated with waste minimization. When the quantity of hazardous waste generated decreases, costs for treatment and disposal concomitantly fall. There are also cost savings associated with productivity improvements, which are almost always realized when effective waste minimization programs are emplaced.

Third, there is substantial liability associated with hazardous materials and waste. An organization has to deal with Occupational Safety and Health (OSHA) liability that arises from employee exposure to these materials, as well as transportation liability. Perhaps most significant is the long-term liability associated with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Superfund) and with the cleanup costs associated with secure landfill failure. In recent failures of secure, approved landfills, original generators are being held liable for cleanup costs.

Last, substantial public relations benefits are associated with waste minimization. The perception of an installation or agency by the public (as well as regulatory agencies) is always enhanced by an effectively publicized program. The essentially proactive nature of waste minimization and the environmental consciousness it represents can have a real effect in modifying public opinion.

HISTORY OF THE AIR TRAINING COMMAND PROGRAM

In 1987, the USAF Air Training Command (ATC) made the decision to carry out waste minimization programs at several of its bases. That decision was implemented by an Interagency Agreement between ATC and the Department of Energy (DOE) which allowed the use of DOE's Oak Ridge maintenance and operations contractor, Martin Marietta Energy Systems (MMES). MMES' Hazardous Waste Remedial Actions Program (HAZWRAP) has managed the program for ATC; much of the project's technical work has been carried out by DOE's contractors, Lee Wan and Associates, Inc. and Automated Sciences Group, Inc. Technical fieldwork began in early 1988; the program is still under way.

THE BASES

Lowry Air Force Base

Lowry Air Force Base (AFB) is in the northeast quadrant of Colorado and is located between the cities of Denver and Aurora. After about 30 years as an active flying base, Lowry's runways closed on June 30, 1966. Since then, the Base has evolved into one of the largest training complexes in the world, offering more than 370 technical courses to more than 33,000 students each year.

Lowry Technical Training Center is one of six major training centers in the ATC. Its primary mission is to provide military training and technical skill training in five career areas to all branches of the Armed Forces, other U.S. government agencies, and 33 allied nations. The 3400th Technical Training Wing is the largest part of the Center.

The 345th Air Base Group (ABG) supports Lowry's training mission by providing security and law enforcement, administrative support, civil engineering activities, and facilities and grounds maintenance. The Civil Engineering organization is the largest component of the ABG, providing industrial, real estate, and construction support and managing on-Base housing and fire protection. The Transportation organization provides vehicle maintenance and management and traffic management. The vehicle maintenance branch keeps more than 300 vehicles in serviceable condition. The Supply organization controls all supply activities on the Base. The Consolidated Maintenance squadron creates, fabricates, maintains, and inspects all of the equipment used in the Lowry training mission. This includes keeping track of more than 2,800 classroom trainers and aids, more than 11,000 pieces of precision measuring equipment, 8 aircraft trainers, and 12 aircraft on static display. The squadron also maintains the technical administration library and determines the requirements for administrative publications and forms. The Lowry Corrosion Control Facility is jointly managed by the Civil Engineering paint shop and the Consolidated Maintenance corrosion control shop. Typical work performed includes stripping and painting of Aerospace Ground Equipment (AGE), mockups, and training equipment.

The Air Force Accounting and Finance Center is located on the Base. It provides centralized pay service to all Air Force members and accounts for and reports on all money appropriated to the Air Force by Congress.

Keesler Air Force Base

Keesler AFB is located in southeastern Mississippi within the city of Biloxi. It was founded in 1941 to train airplane mechanics, engine mechanics, and basic trainees. The Base became known as the "Electronics Center of the Air Force" in 1947 when aircraft mechanic training was

moved to other centers and the Air Force's radar school relocated to Keesler from Boca Raton, Florida. All operations at the Base are under the overall umbrella of the Keesler Technical Training Center. The primary missions of the Base are technical training, medical care, weather reconnaissance, and airborne command and control.

The 3300th Technical Training Wing (TTW) is responsible for technical training at the Base. The wing conducts courses in computer science, command and control systems operation, avionics, communications operations, weapons control, manpower management, air traffic control, communications/electronics, personnel, and administration. Courses are taught for members of the USAF, other branches of the Department of Defense (DoD), and foreign countries. The Wing is divided into five technical training groups, each of which is responsible for specific areas of instruction.

Keesler's Resource Management Complex, which includes its maintenance force, supports flying units and is responsible for maintaining instructional equipment used in student training. The Transportation squadron supplies Base transportation needs; its vehicle maintenance branch services approximately 520 pieces of equipment. Base Supply provides virtually all of the equipment, supplies, spare parts, and fuel needed by Base operations. Direct flight line refueling services are provided to all military aircraft and government vehicles; some 7 million gallons of jet fuel and over 300,000 gallons of gasoline and diesel fuel are dispensed annually.

The 3380th ABG provides administrative, personnel, religious, operations and training, civil engineering, and security police support to the more than 32,000 people who use Base facilities. The Civil Engineer squadron maintains Keesler's more than 325 buildings and 1957 military family housing units and is responsible for Base compliance with all hazardous waste requirements.

One of Keesler's principal flying units is TAC's 7th Airborne Command and Control Squadron. The Squadron's EC-130E aircraft have been modified to carry an Airborne Battlefield Command and Control Center, which is designed and implemented to provide continuous control of tactical air operations in forward battle areas and behind enemy lines.

The second of Keesler's principal flying units is the Military Airlift Command's 53rd Weather Reconnaissance Squadron, known to many as the "Hurricane Hunters." The squadron collects data on the atmosphere over millions of square miles of the Caribbean Sea, Gulf of Mexico, and the Atlantic and Pacific Oceans. While best known for missions into the eyes of hurricanes to provide weather data to the National Hurricane Center for forecasts and warnings, the squadron also flies in support of TAC by providing weather reconnaissance for fighter aircraft deployment overseas. The unit also flies in support of the U.S. space shuttle; filming shuttle liftoff until solid-rocket booster separation and then tracking one of the two boosters to splashdown.

The Air Force Reserve's 403rd Rescue and Weather Reconnaissance Wing is the third of Keesler's principal flying units. The Wing is charged with providing worldwide search and recovery of aerospace personnel, along with aerial weather reconnaissance in the Atlantic Ocean, Gulf of Mexico, Caribbean Sea, and the eastern and central Pacific Ocean.

Randolph Air Force Base

Randolph AFB is located approximately 14 miles northeast of San Antonio, Texas, in Bexar County, adjacent to Universal City. As with other Air Force bases, Randolph has a designated host unit (the landlord) and several tenant organizations. This type of organization results in a fairly broad mission description. The 12th Flying Training Wing is the host unit at Randolph; it conducts instructor pilot training in the Cessna T-37 and the Northrop T-38 jet trainers. The wing is organized into four major subdivisions: Operations, Maintenance, Resource Management, and the 12th ABG.

Operations manages Randolph's primary flying mission - training instructors for ATC and Air Force flying training programs. Maintenance is responsible for providing a mission-ready fleet of T-37 and T-38 aircraft for pilot instructor training. Included in this maintenance function is the operation of large facilities that perform major repairs on aircraft and that employ approximately 900 military and civilian personnel. Resource Management is responsible for supply, transportation, comptroller, and logistics planning. The supply squadron manages 45,000 line items valued at $11.5 million. The fuels management operation dispenses over 1.3 million gallons of aviation fuel monthly. Overall, the supply squadron serves more than 30 on-Base tenant groups in addition to off-Base locations. The 12th ABG supports the Flying Training Wing and tenant units by providing military and civilian personnel management, administrative services, security police protection, recreational activities, housing, and food services. Other responsibilities include building upkeep, environmental protection, and energy conservation.

THE WASTE MINIMIZATION STUDY PROGRAM USED AT AIR TRAINING COMMAND BASES

Development of waste minimization programs requires a thorough understanding of current materials handling, accounting, and distribution practices; scheduling functions; and waste management practices used at an installation. Production techniques, auxiliary unit operations, and operator practices must be analyzed relative to their respective contribution to waste generation. The availability and feasibility of waste exchanges, on-site recycling, and commercial recyclers must be evaluated, and the cost-effectiveness of these options must be determined. Current and anticipated regulatory requirements under RCRA, the Clean

Water Act (CWA), the Clean Air Act (CAA), the Superfund Amendments and Reauthorization Act (SARA), and the Toxic Substances Control Act (TSCA) must be incorporated to develop a functional waste minimization program.

At Randolph, Keesler, and Lowry AFBs, two independent investigations were conducted simultaneously. Site visits were conducted to determine the potential for application of source reduction and recycle techniques within the site operations. Market analyses were simultaneously conducted to identify potential recycle options that were commercially available for either on-site or off-site use. The results of these investigations were combined with cost analysis and regulatory requirements to formulate the elements of the waste minimization program at each installation. The search for source reduction options focused on four fundamental techniques: (1) process and product elimination, (2) input material alteration or substitution, (3) technology alteration, and (4) procedural alterations.

SITE VISIT METHODOLOGY

Although waste reduction studies may be performed by a variety of mechanisms, the approach we used was the waste reduction audit. This audit uses many tools and concepts of the environmental compliance audit but differs from those audits with respect to the overall objective. The objective of the waste reduction audit is the identification of options with the potential for waste minimization; compliance is not addressed.

In these studies, records were reviewed, personnel were interviewed, and operations were analyzed as in an environmental compliance audit. The studies were made up of several discrete steps: preinvestigation data collection and analysis, initial site visit and waste reduction audit, options analysis and market analysis, options review and second site visit, implementation plans development, and final report.

Preinvestigation Analysis

Preinvestigation data collection and analysis involved assembly of pertinent documentation that included base layout plans, process area layouts and schematics, the Installation Restoration Program (IRP) Phase I report, description of major unit operations, RCRA annual generator reports and manifests, National Pollution Discharge Elimination System (NPDES) permits and applications, and if possible, inventory records. Major waste streams and respective generation points were identified. Materials flow schematics that track materials from acquisition to waste disposal were developed to the extent possible. A base-specific waste reduction audit plan was developed. Completion of the preinvestigation data collection and analysis step resulted in:

- waste stream identification and compilation,
- initial materials flow schematics,
- identification of potential waste reduction options,

- o a site-specific audit checklist,
- o audit questionnaires, and
- o a site-specific audit plan.

Initial Base Visit

The initial base visit was conducted to confirm results of the preinvestigation analysis, further define materials flows, and develop detailed data on supply and distribution practices, material-handling practices, inventory controls, operator practices, equipment condition and operation, equipment layout, feed variables, waste management practices, and quality assurance/quality control (QA/QC) conformance criteria. Data were developed by a combination of records searches, interviews with key personnel, and visual inspection of unit operations and material-handling techniques during operation.

Before the base visit, a base-specific waste reduction study plan was developed. This base-specific plan identified:

- o specific records to be reviewed,
- o specific personnel for interviews,
- o material-handling locations and practices to be studied,
- o unit operations and operator practices to be investigated,
- o waste management operations to be studied, and
- o an activities schedule.

The initial area of investigation was the supply organization. The analysis of this function was carried out in three discrete parts: materials receipt and handling, materials inventory control/storage, and materials distribution.

The second area subject to study was base unit operations. Efforts here were directed at developing data that allowed formulation of strategies for technology alterations, process modification, materials substitution or elimination, on-base recycling, procedural modifications, hazardous waste delisting, or product and process elimination.

Technology alterations include changes in process conditions, equipment modifications, process automation, or replacement of process operations with those that are more efficient and consequently generate less waste. Process modification includes equipment replacement, modification of process conditions, and development of in-line recycling. Materials substitution includes use of reclaimed or nonreclaimed materials as feedstocks, replacement with less toxic materials, and alteration of input materials. Procedural alterations include personnel training, careful observation of operating practices, waste stream segregation, and strict distribution controls.

The study proceeded through the major waste-generating unit operations in stepwise fashion. Thus, for a given unit operation, the waste reduction study involved:

- o records analysis,
- o analysis of operating practice, and
- o process analysis.

The third phase of the initial base visit was analysis of waste management practices. Compliance issues were not addressed in this effort. This phase investigated the potential for application of source reduction techniques or recycle techniques within waste management. This portion of the survey was separated into analysis of waste management processes, waste characterization, and analysis of management practices. Operations were analyzed, and mass balances were prepared at RCRA treatment, storage, and disposal (TSD) facilities and accumulation areas, NPDES wastewater treatment units, and air discharge point sources and treatment units.

The primary result of the waste reduction study was a comprehensive view of waste generation at the base, which was compiled into logbooks that detail materials management practices and process conditions, etc.

Options Analysis

The third step in the waste reduction study, the development and analysis of options, was made up of four elements: (1) base-specific process and procedures analysis, (2) development of waste-reduction alternatives, (3) development of options rationale and cost analysis, and (4) initial ranking of options.

Upon completion of the initial base visit, material flow schematics were revised to reflect the information obtained. A mass balance that tracks hazardous materials from acquisition to waste disposition was developed. The materials flow schematic and mass balance study was used to identify major materials losses that are indicative of unaccounted for waste generation, poor materials-handling procedures, and poor administrative controls. Use of materials schematics readily identified potential downstream impacts that may result from source reduction efforts and readily identified waste-stream mixing points that are potential waste reduction areas (through waste segregation).

Development of waste reduction alternatives involved generation of potential alternatives, estimation of maximum achievable reductions, market analysis, and impact analysis. An outline of the elements involved in each is provided below:

- o Generation of Alternatives
  - Revise initial options list on the basis of survey information
  - Select options on the basis of industry practice
  - Select technology alteration on the basis of engineering analysis
  - Evaluate in-plant recycle alternatives
  - Evaluate off-base recycle options
  - Evaluate standard operating procedures (SOPs) versus current practice

- Evaluate administrative controls
- Evaluate feed material alteration
- Compare generated options with proven practice
- Develop preliminary options for source reduction and recycle

o Estimation of Achievable Reduction
- Analyze material flow schematic - maximum achievement
- Evaluate waste and feed ratios at waste generation points
- Evaluate efficiency factors based on industry practice
- Evaluate efficiency factors based on engineering analysis
- Determine percent recovery by reclamation
- Evaluate reuse potential
- Analyze energy recovery potential
- Analyze delisting potential

o Market Analysis
- Analyze waste exchange
- Analyze energy recovery - local market survey
- Analyze commercial recycle - market survey
- Analyze available equipment modification
- Analyze product substitution - market and requirements

o Impact Analysis
- Evaluate implementability, availability, and maintainability
- Analyze downstream effects
- Evaluate schedule impacts
- Evaluate regulatory impacts.

The development of an options rationale with a cost analysis required incorporation of all cost elements related to both waste minimization and current waste management practices. Raw materials, labor, processing, and disposal costs had to be tabulated. Capital and operating costs associated with technology alterations or recycle were calculated. Impacts on labor requirements were considered, and cost elements were calculated. Options that considered feed material alteration evaluated not only raw material unit cost differences but also costs associated with technical factors that result from the alteration, such as use differences, process condition alterations, and product quality differences. Waste reduction achieved through procedural alterations considered annual costs associated with implementation of controls and the reduction of the probability of upsets (i.e., spills) that could result in "one-time" waste generation and associated cost increases. Cost analysis considered discrete generation point costs, unit costs, and systems-related costs.

The results of the options evaluation and cost analysis were combined to develop an initial ranking of options. The following evaluation criteria were considered in the development of the option ranking:

- o Reductions achievable,
- o Costs (capital, operating, and waste disposal),
- o Ease of implementation,
- o Systems impacts,
- o Schedule delays - implementation schedule, and
- o Regulatory requirements.

The final result of the options ranking was a preliminary document that provided waste reduction line diagrams, an options ranking profile, descriptions and rationale related to the selected options, and cost analysis for the three audit survey areas: supply, unit operations, and waste management.

Second Base Visit

The findings of the options analysis were presented to appropriate base personnel in the follow-up visit. The primary purposes of this visit were to present the reduction options selected and to determine the ease and schedule for implementation of viable options with base personnel responsible for the affected functions. Additional information was collected as applicable. The second base visit was held in a workshop-type atmosphere in which base personnel who are responsible for implementation of selected alternatives provided input into the operations-level feasibility of the selected alternatives. Maximum communication between audit team members and base personnel was a necessity. The required communication was facilitated through presentation of a summary of findings and a list of discussion subjects by the audit team before the second visit.

The primary result of the second visit was definition of constraints related to the preliminary selected options. These findings were used to develop implementation plans and revised waste reduction options.

Revision of Options and Implementation Plans

The fifth step in the waste reduction audits was the revision of options based on results of the second base visits and development of preliminary implementation plans. Material flow schematics were finalized. Achievable reductions, impacts, and cost analysis were revised as necessary on the basis of implementation concerns. The result of this process was a revised set of source reduction and recycle options applicable to supply, operations, and waste management, which is both cost-effective and readily implemented.

The second portion of this analysis was development of preliminary implementation plans. The elements of these implementation plans are:

- purpose,
- elements of the reduction option,
- responsible parties and functions,
- implementation action items,
- schedule,
- estimated results, and
- measurement criteria.

The elements of the implementation plan develop from the initial options analysis, the second base visit, and the revisions. Implementation plans were developed with input from the base after its review and evaluation of

recommended options. An overall approach was developed that incorporated the elements into the implementation plan, established schedules, and projected results. Measurement criteria, which can be economics-based, volume-based, or performance-based, were established for each option before implementation.

Final Report

The final reports summarize the results of the waste reduction study. They encompass the entire project activity and present options selected, rationale, methodology, cost, and implementation.

Minimization guidelines are developed that describe the project methodology used in waste reduction studies. The intended use of these guidelines is to provide the installation with a concise set of instructions which will allow it to maintain and update the waste minimization program without the need for outside help. Material flow schematics, audit checklists, and questionnaire development are presented in this product. The guidelines also describe the study approach, control variables for investigation, data analysis criteria and methods, various cost analysis methods that are applicable, emerging waste reduction techniques, and development of implementation plans and measurement criteria.

Two training workshops are used to present information provided in the final report and the guidelines; these workshops are ongoing as this paper is being written. The focus of these workshops is to provide personnel training at a working level to those responsible for implementation of minimization technologies. The structure of these workshops varies depending on installation needs and requirements, but in general, one is oriented toward management and one is oriented toward production-level personnel.

FINDINGS AT LOWRY, KEESLER, AND RANDOLPH AIR FORCE BASES

LOWRY AIR FORCE BASE

Activities Reviewed

The activities reviewed at Lowry included the following:

- Base Supply,
- Corrosion Control,
- Print Shop,
- Photographic School,
- Vehicle Maintenance, and
- Miscellaneous Support Functions
  The Training Aids Facility
  The Air Force Accounting and Finance Center

Meteorology
The Auto Hobby Shop
The Lowry Heritage Museum
The Medical/Dental Facility
The Base Photography Laboratory.

Base Supply

A fundamental problem associated with Supply was the minimum of oversight for hazardous materials before their arrival on-base. If an item had not been previously identified by an Issue Exception (IEX) Code 8 or 9 designation, detection was dependent upon institutional or special knowledge of individuals within the Base's supply system. The IEX Code itself was inadequate to control hazardous materials because the codes are based on health and safety criteria, not on the RCRA lists and definitions. A second factor affecting the supply system is a problem with the national stock number system because an item ordered by national stock number from a depot or the General Services Administration may not be the item required or received. There can be broad chemical diversity among items considered as acceptable substitutes. Another major concern with the procurement system is the practice of minimum order quantity. As some contracts are currently written, some items must be purchased in a minimum lot size (such as case lots). This practice often results in lower initial unit costs, but forces the disposal of unused quantities as hazardous waste. These disposal costs often far outweigh the initial cost savings. Inventory management practices also result in inadvertent generation of hazardous wastes. Solvents, paints, strippers, and photosensitive chemicals need to be stored out of direct sunlight and in areas that are not subject to extreme temperatures.

The reduction alternatives considered feasible for Supply include:

- Change National Stock Numbers to reflect hazard;
- Implement a handling protocol that recognizes hazardous materials when ordered and that continually readdresses the supply system to ensure that no item is received on Base without being assessed as a potential hazard;
- Institute a Base Environmental Engineer (BEE)/Base Civil Engineer (BCE) review of all local purchase contracts to ensure identification and prior approval before purchase agreement is initiated;
- Require Material Safety Data Sheets (MSDSs) on all purchase items, both local and government issue;
- Require receipt of MSDS before payment;
- Remove minimum order requirements on purchase contracts;
- Review benchstock levels on a quarterly basis and establish a flexible reorder system that permits purchase of only the quantity of hazardous materials necessary to reach maximum benchstock level;
- Develop an inventory control reporting system that compiles quarterly and annual purchase of hazardous materials by item and location (user);
- Purchase commonly used hazardous materials such as paints and solvents in bulk (where appropriate);
- Limit the purchase of spray cans containing chlorinated solvents and Extraction Procedure (EP) toxic materials;

- o Label chemical storage areas by material type and segregate paint by type/color to prevent misuse; and
- o Store paints, solvents, and other susceptible chemical stocks in properly protected environments.

Implementation of the proposed reduction techniques should significantly reduce the amount of hazardous waste generated by outdated and unuseable materials. At Lowry, the estimate is that this savings would amount to the equivalent of about 19 drums of waste; as much as $21,400 in annual savings for both product replacement and disposal cost. The recommendations listed above are both Air Force-wide and Base-specific. Obviously, those recommendations that require Air Force or Major Command (in this case, the ATC) policy changes cannot be implemented by the Base until those changes occur. Some of the recommendations, however, can be implemented locally and without significant workload increases:

- o Ensure BEE/BCE review of all local purchase items that may be hazardous before purchase,
- o Require MSDSs on all items purchased locally,
- o Require receipt of MSDSs before payment,
- o Review benchstock levels on a quarterly basis,
- o Remove minimum order requirements for purchase and issue,
- o Develop a reporting system to track ordering and use of hazardous materials by individual units.
- o Label chemical storage areas by material type and segregate paint by type/color to prevent misuse; and
- o Store paints, solvents, and other susceptible chemical stocks in properly protected environments.

The recommendations developed for the rest of the activities at Lowry (discussed below) are entirely implementable at the Base level. These recommendations are displayed in Table 1.

Corrosion Control

Corrosion Control is a euphemism for paint removal and application. The reduction techniques recommended for corrosion control include materials substitution, installation of filtration, and counterflow rinsing on a caustic vat line; reclamation of stripping agent; more extensive use of abrasive sanding techniques, improved cleaning of equipment, and installation of more efficient spraying equipment; standardization and reuse of solvents; and improved paint storage.

Print Shop

Substitution and reclamation of solvents offer the best potential reduction options.

Photographic School

Little hazardous waste is produced by the school. The only reduction techniques available are the substitution of cleaning compounds and improved silver recovery.

Table 1. Waste minimization recommendations at Lowry Air Force Base

Location/Process	Baseline (gal)	Volume reduction (gal)	Annual cost savings ($)	Payback period	Description of benefit
CORROSION CONTROL					
1. Substitute material caustic vat	700	--	--		Nonhazardous material disposal
2. Filter caustic vat	700	500	1,000	8 years	Extend vat life
3. Rinse caustic vat	--	--	--		Prevent waste discharge
4. Use abrasive stripping	230	120	3,300	Instant	Reduce waste
5. Reclaim stripper	230	130	3,600	1.9 years	Reduce waste
6. Delist filters	1,400	1,400	2,800	10 years	Reduce baseline
7. Use airless spray	700	1,400	2,800	1 year	Reduce waste
8. Electrostatic paint equipment	700	600	10,000	9 months	Reduce waste and feedstock
9. Solvent use reduction	400	200	400	Instant	Reduce waste
10. Solvent reclamation	400	100	1,250	4.2 years	Reduce waste and feedstock
11. Storage of paint	1,045	1,045	21,400	Instant	Saves supply dollars
PRINT SHOP					
1. Substitution of solvents	500	--	--	--	Reduce toxicity
2. Treatment of spent solvents	500	400	3,500	2 years	Recycling of waste

Table 1 (continued)

Location/Process	Baseline (gal)	Volume reduction (gal)	Annual cost savings ($)	Payback period	Description of benefit
VEHICLE MAINTENANCE					
1. Substitute in caustic vat	1,200	900	330	Instant	Reduce waste
2. Filter caustic vat	1,200	900	3,500	2 years	Reduce potential waste
3. Use airless spray equipment	240	120	300	2 years	Reduce filter and waterfall waste
4. Substitute solvents	540	540	100	Instant	Reduce baseline
5. Use of less toxic coatings	--	--	--	--	Reduce filter problems and lessens solvent needs.
MISCELLANEOUS FUNCTIONS					
1. Training aids revise paint program	60	40	1,450	3 years	Reduce toxicity waste and feedstock usage
2. Accounting and finance center substitute solvent	60	60	180	Instant	Energy recovery
3. Metrology solvent waste exchange	20	18	120	Instant	Reuse of solvent
4. Auto Hobby Shop solvent substitution	60	60	180	Instant	Energy reuse
5. Heritage Museum	--	--	--	Instant	Proper management procedure
6. Medical/dental silver recovery	--	--	25	<3 years	Reduce silver in wastewater

Table 1 (continued)

Location/Process	Baseline (gal)	Volume reduction (gal)	Annual cost savings ($)	Payback period	Description of benefit
PHOTOGRAPHY SCHOOL					
1. Material substitution for chromate-containing system cleaner	2-4	100%	None	Instant	Elimination of hexavalent chromium discharge to publicly owned treatment works (POTW)
2. Addition of a tailing chemical recovery cartridge (CRC)	--	--	25	<3 years	Reduce effluent silver concentration in waste water
Total potential savings - ($56,260) (0.75)[a] = $42,200					

[a]Factor applied to account for overlap of savings when multiple options were combined for a single shop.

Vehicle Maintenance

Substitution of solvents, use of more efficient paint spraying equipment, and the use of less toxic paints are the options with the best potential at this facility.

Miscellaneous Support Functions

These functions all produce varying amounts of hazardous waste. This production, however, is relatively small.

Summary

The recommended options will result in a 75% waste volume reduction and a $42,200 annual savings. Payback periods range from instant to over 10 years.

KEESLER AIR FORCE BASE

Activities Reviewed

The following activities were reviewed at Keesler AFB:

- Base Supply
- Corrosion Control
- Training Aids Fabrication
  - Paint Shop
  - Printed Circuits Shop
- Print Shop
- Medical Facilities
- Vehicle Maintenance
- Miscellaneous Support Functions
  - Nondestructive Inspection
  - Entomology Shop and Golf Course
  - Battery and Electronics Shop
  - Aerospace Ground Equipment
  - Auto Hobby Shop
  - Central Heating Plant.

Base Supply

The Base Supply organization at Keesler has a demonstrated record of excellent performance in minimizing hazardous waste generation. The organization works closely and responsibly with the BEE and with the BCE Environmental Coordinator to prevent the unnecessary introduction and inadvertent generation of hazardous waste. In spite of management involvement and attention to waste minimization, some areas still require additional attention. The first area of concern is the inadvertent receipt of hazardous materials by local purchase. The second major source

of hazardous waste generation is the same problem noted at Lowry AFB - the National Stock Number system and the definition of what constitutes an acceptable substitute. A brief examination of the National Institute for Occupation, Safety, and Health (NIOSH) listing of NSN items indicated a broad chemical diversity among items considered as acceptable substitutes. Some items contained no defined hazardous constituents, while others were composed almost entirely of hazardous materials. Another concern is the practice of minimum order quantity. As some contracts are currently written, certain items must be purchased in a minimum lot size that may result in lower initial cost, but which results in the disposal of unused quantities as hazardous waste. A final concern is inventory management, where improper storage of sensitive materials results in degradation and resultant disposal of unused materials as hazardous waste.

The recommendations for waste reduction at Base Supply at Keesler are essentially identical to those discussed for Lowry AFB, supplemented with the introduction of a hazardous material surcharge system and the use of a suggestion program with rewards as an incentive. The surcharge system and the suggestion program are described in the "Administrative Reduction Techniques" section of this paper.

Corrosion Control

The principal reduction techniques recommended are materials substitution (substituting ethanolamine-, phenyl cellusolve-, or butyl cellusolve-based strippers for phenolic-based ones) and reclamation (by filtration) of paint strippers, solvent reclamation, and changes in paint application equipment.

Training Aids Fabrication

The principal reduction techniques recommended for the Paint Booth involve the modification of procedures and equipment (by modifying the water curtain apparatus to function as a wastewater treatment system) so that paint booth water curtains attain exemption from RCRA, resulting in the elimination of the waste stream. These changes also result in the direct reuse of cleanup solvents.

The primary reduction technique applicable to the Printed Circuits Shop is the replacement of ferric chloride with peroxide/sulfuric acid etchant. A modification in fabrication operations will provide substantial waste reduction if expanded production is pursued.

Print Shop

Reduction options at the Base Print Shop are limited because of the small amount of hazardous waste generated. Substitution of a blanket wash and film processor cleaning fluid along with better silver recovery are the only economically justified options.

Medical Facilities

At the Medical Center Complex, better hazardous material management will result in reduction of waste generation rates. Controls similar to those on pharmaceuticals would result in a model program. Spill training and more outside oversight would also be beneficial.

Vehicle Maintenance

Material substitution and equipment changes, along with the burning of waste oil for energy recovery, would reduce the production of hazardous waste from this operation to essentially zero.

Miscellaneous Support Functions

Materials substitution, equipment changes, and burning oil for energy recovery can also be applied at Nondestructive Inspection, Aerospace Ground Equipment, and the Auto Hobby Shop. By employing more carefully designed pesticide use, the Golf Course can reduce pesticide requirements by one-third.

Summary

The recommended options discussed above and displayed in Table 2 will result in a 39,406-gallon per year waste reduction and a $100,120 annual cost savings. Payback periods range from instant to about 2.5 years.

RANDOLPH AIR FORCE BASE

Activities Reviewed

The activities that contribute significantly to hazardous waste generation at Randolph and that were reviewed as part of the study at that Base include:

- Base Supply,
- Metals Cleaning and Treatment,
- Corrosion Control and Painting Operations (Hangar 48),
- Lear-Siegler (T-37 and T-38 depot-level maintenance) Operations, and
- Miscellaneous Support Functions
  Nondestructive Inspection
  Precision Measurement Equipment Laboratory (PMEL)
  Battery and Electronics Shop
  Wheel and Tire Shop
  Operational Maintenance Hangars
  Base Photography
  Vehicle Maintenance.

Table 2. Waste minimization recommendations at Keesler Air Force Base[a]

Process/option	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
CORROSION CONTROL					
Abrasive removal of dust	390 lbs/year	390 lbs	100	2 years	Elimination of HW stream
Conversion solution - reuse rinse	20 gal/year	20 gal	100	Immediate	Eliminates disposal
Coating application	110 gal/year	65 gal	120		Reduces overspray
overspray: reduction	168 gal/year	105 gal	3,400	2.1 years	Reduces overspray
in filters and feedstock					
Reclamation of solvent and procedural change	350 gal/year	110 gal	1,800	2.3 years	Reduces solvent waste; transforms waste form to solids
Hand applied stripper reclamation	200 gal/year	80 gal	500	1.8 years	Reduces stripper waste; converts to solid form
Vat stripper and rinse reclamation	5,100 gal/year	3900 gal	38,000	0.6 years	Reduction in volume; elimination of toxic solvents

Table 2 (continued)

Process/option	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
TA FABRICATION					
Surface pretreatment - neutralization	200 gal/year	200 gal	700	Immediate	Eliminate HW stream
Cleanup solvent reuse	100 gal/year	150 gal	300	Immediate	Reduction wash stream
Spray painting washwaters - retrofit	750 gal/year	750 gal	2,000	<1.0 years	Eliminate HW stream
Fixer/developer - discharge to POTW	24 gal/year	24 gal	70	Immediate	Discharge to POTW
Circuit fabrication etchant - substitute and reclaim	96 gal/year	90 gal	900	<1.0 years	Eliminates HW Stream
Increased circuit production - THP boards	825 gal/year	675 gal	12,000	NA	State-of-the-art technology
Increased circuit production - THP boards	1,200 gal/year	900 gal	ND	ND	State-of-the-art technology
Superoxide cartridges - not generated at TA - for neutralization of H_3PO_4	420 lbs/year	340 lbs	700	<1.0 years	Elimination of two HW streams

Table 2 (continued)

Process/option	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
PRINT SHOP					
Substitute film processor cleaning	232 gal/year	232 gal	500	Immediate	Reduct chromate discharge to POTW
Improved silver recovery	215 gal/year	215 gal	500	Immediate	Eliminate silver discharge to POTW
Substitute blanker wash and deglazer solution	55 gal/year	30 gal	250	Immediate	Reduce disposal of very toxic waste
MEDICAL FACILITIES					
Establish HM oversight committee	--	--	--	Immediate	Reduce HM usage and spill potential
Establish spill training	--	--	--	Immediate	Reduce HW generation from spills
Use base supply model for ordering HM	--	--	--	Immediate	Reduce HM ordering and use
Improved silver recovery	--	--	--	Immediate	Eliminate silver discharge to POTW

Table 2 (continued)

Process/option	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
VEHICLE MAINTENANCE					
Substitute PD 680 and burn	220 gal/year	220 gal	1,102	<1 year	Eliminate waste stream
Change spray equipment	1,610 gal/year	805 gal	3,591	1-2.5 years	Improve efficiencies; reduce filter waste
Standardize solvents	110 gal/year	110 gal	935	--	Reduce waste stream
Use waterborne acrylic paints	2,600 lbs/year	110 gal	7,183	Immediate	Eliminate solvent and filter wastes
Burn oil for energy recovery	5,000 gal/year	5,000 gal	4,000	Immediate	Eliminate potential waste stream
Institute proper container disposal	430 gal/year	--	--	Immediate	Reduce waste and compliance liability

Table 2 (continued)

Process/option	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
NONDESTRUCTION INSPECTION					
Substitute THF for TCA	10 gal/year	10 gal	73	<1 year	Eliminate potential waste stream
Replace developer	50 gal/year	50 gal	213	Immediate	Eliminate waste stream
Burn PD 680 for energy recovery	50 gal/year	50 gal	40	Immediate	Eliminate waste stream
ENTOMOLOGY AND GOLD COURSE					
Substitute material and change procedures	--	--	500 (est.)	<1 year	Reduce pesticide use rate
AEROSPACE GROUND EQUIPMENT					
Burn waste oil for energy recovery	16,000 gal/year	16,000 gal	12,800	<1 year	Eliminate disposal problems
Substitute PD 680	40 gal/year	20 gal	170	Immediate	

Table 2 (continued)

Process/option	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
AUTO HOBBY SHOP					
Burn waste oil for energy recovery	11,000 gal/year	11,000 gal	7,573	<1 year	Eliminates disposal problems
Maintain Safety-Kleen	--	--	--	--	Reduced management
Total estimated savings based on waste minimization recommendations:				$100,120.	

[a]HM - hazardous materials, HW - hazardous waste, NA - not applicable, ND - not determined, POTW - publicly owned treatment works, TA - training aids, TCA - 1,1,1-trichloroethane, THF - tetrahydrafuron, THP - tetrahydraphenol.

Base Supply

The fundamental issues affecting Supply at Randolph AFB were essentially the same ones as at Keesler and Lowry, and the recommended reduction options were likewise the same. In addition, we suggested the following for Randolph AFB:

- o Institute a bar-code identification system to track hazardous materials inventories,
- o Develop and implement a hazardous materials training program and procedures for Base Supply personnel,
- o Use safety handling equipment to minimize container damage,
- o Purchase hazardous materials in polyethylene or other polymeric containers instead of metal containers,
- o Enforce return of unused chemicals to Base Supply, and
- o Develop a controlled inter-Base hazardous material exchange program.

Metals Cleaning and Treatment

The reduction techniques recommended for this activity include:

- o Chemical vat filtration,
- o Counter-flow rinsing,
- o An altered disposal technique (to take advantage of the totally enclosed facility exemption of 40 CFR 264.1),
- o Elimination of unnecessary process steps, and
- o Materials substitution.

Corrosion Control and Hangar 48 Painting Operations

The discussions of these two operations are combined, even though they are carried out at separate locations on the Base, because the recommendations concerning them have a large degree of overlap. The reduction options suggested included the following:

- o Materials substitution (the use of water-based acrylic paints on AGE equipment and static displays, the use of high-solids urethanes and non-EP toxic materials-containing coatings, and the use of alternate materials for pretreatment and paint stripping),
- o Process changes (the use of electrostatic spraying and powder coating techniques),
- o Recycle and reuse of solvents, and
- o Institution of a delisting petition (for air filters).

Lear-Siegler (depot-level maintenance of T-37s and T-38s) Operations

The principal recommendations for this activity were process changes to eliminate intermediate rinsing and steam cleaning during the paint stripping process. Regeneration (by filtration) of paint-stripper

mixtures along with segregation and separate treatment of rinse waters were also recommended. Reuse of regenerated stripper by combining it with fresh stripper was recommended.

Miscellaneous Support Functions

The principal reduction technique applicable to these operations is the use of higher-flash-point PD-680 solvent, which avoids the "ignitability" characterization of those wastes. A mobile filtration system to regenerate spent PD-680 was recommended. Waste exchange of a Freon-based solvent between the Precision Measurement Equipment Laboratory and the Electronics Shop was recommended, as was elimination of chromate-based developers at NDI.

Summary

The options recommended at Randolph, which are discussed above and displayed in Table 3, will result in a 60% waste volume reduction and a $644,000 annual savings. Payback periods range from instant to over 10 years.

COMMONALITIES

Certain waste minimization options are applicable at all of the installations examined as part of this study. Because of that generality, we feel that it is likely that the options will be applicable at most AFBs and that they may well be a "core" of waste minimization around which each base may build its detailed waste minimization program. These options are discussed below and are separated into general activity areas.

Supply

The problems with the Air Force supply system that contribute to the generation of hazardous waste and the options to remedy those problems are general to the point of being universal. As discussed previously, some of these options can be implemented only at the Command or Service level. These include:

- Change NSN to reflect hazard;
- Implement a handling protocol that recognizes hazardous materials when ordered and that continually readdresses the supply system to ensure no item is received on base without being assessed as a potential hazard;
- Require MSDSs on all chemical purchase items, both local and government issue;
- Develop an inventory control reporting system that compiles quarterly and annual purchase of hazardous materials by item and location (user);
- Purchase commonly used hazardous materials such as paints and solvents in bulk (where appropriate); and
- Limit the purchase of spray cans containing chlorinated solvents and EP toxic materials.

Table 3. Waste minimization recommendations at Randolph Air Force Base[a]

Location/process	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
METAL CLEANING					
1. Improved racking and rinsing techniques	Solution drag-out 4-10 gal/1,000 sq ft of parts	3.6-9.2 gal/1,000 sq ft of parts (90% reduction in drag-out)	6,000	10 years	Reduced disposal frequency. Extended bath life.
2. Filtration on metal-cleaning vats - totally enclosed facility	1,950 gal of sludge a year	1,800 gal of sludge/year	21,275	<<1 year	Allows use of RCRA exception (no permit required). Reduced disposal volume.
- counter-flow rinsing	97,000 gal EPTOX wastewater	67,900 gal EPTOX wastewater	125	Very long	Volume reduction of wastewater.
3. Elimination of two vats from the metal-finishing line.	22,000 gal/year caustic and oxidizer solutions	22,000 gal/year	27,000	Instant	Elimination of engine damage.
4. Materials substitution in organics line	105 gal/year		700	Instant	Elimination of PD 680 disposal. Elimination of paint stripper. Reduced damage to parts.
- PD 680 change		55 gal/year			
- cold paint stripper		20 gal/year			
- TCA spec change		10 gal/year			
- filtration	1,350 gal fluids/year	640 gal/year	8,500	1 year	Vat life extension. Increased cleaning efficiency.

Table 3 (continued)

Location/process	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
PAINTING					
5. Filtration and counterflow rinsing in hot paint stripping line	660 gal/year of EPTOX sludge	360 gal/year of EPTOX sludge	6,700	2.1-1.7 years	Reduced handling. Waste volume reduction.
6. Filtration of stripper BMB 4411	660 gal/year sludge	300 gal/year sludge	7,000	<1 year	Waste volume reduction. Reduced handling.
7. Filtration of water curtains	2,400 gal/change-out x 6=14,400 gal/year		Assuming barreling of wastes, annual cost savings are $105,000.	Instant	Reduction in waste volume.
8. Paint substitution (water-based acrylics for urethanes) on AGE			25,900-78,500/ year	Instant	Allows reuse of water curtain. Reduction in solvent use.
9. Alteration in painting techniques - powder coatings - electrostatic spraying		65% volume reduction in paint used	7,000	<1 year	Reduction in paint use. Reduction in solvent use. Reduction in water curtain load.

Table 3 (continued)

Location/process	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
HANGER 48					
10. Use of air-assisted airless spraying	17,000 gal air filters	9,000 gal filters	95,000, assuming barreling of wastes	<<<1 year	Reduction in filter waste. Reduction in paint use.
	1,400 gal/year paint	900 gal/year paint	27,000	Instant	
11. Rag recycling - use of commercial shop towels - replacement of MEK with MIBK	1,650 gal/year rags		16,500 or 17,400	2 months 2 months	Reduction in waste disposal.
12. Changes in cleaning procedures (painting equipment)	1,370 gal solvents	900 gal solvents	12,000	Instant	Reduced solvent use, disposal cost.
13. Solvent reclamation	450 gal solvents	340 gal solvents	3,700	1.6 years	Reduction in solvent disposal. Reduction in new solvent requirements.

Table 3 (continued)

Location/process	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
HANGER 46 (LST)					
14. Elimination of paint stripping rinse, rinse water segregation	45,000 gal spent stripper/ water mixture	15,000 gal spent stripper/ water mixture	163,000	Instant	Reduction in stripper/ water waste volume.
15. Treatment of segregated wastewater	17,000 gal	12,300 gal	40,000	10 months	Reduction in waste volume.
16. Reclamation of collected stripper (assumes one reuse)	12,000 gal stripper	5,400 gal stripper	90,000	1 month	Reduction in stripper requirements.
MISCELLANEOUS SUPPORT					
17. Product substitution in nondestructive inspection (developer substitution)	55 gal/year	55 gal/year	600/year	Instant	Replacement of toxic material by nontoxic material.
18. Waste exchange in PMEL-2	55 gal Freon 13	55 gal/year	1,200	Instant	Reduction in Freon requirement. Reduction in waste volume.
19. Material substitution, filtration of PD 680 in OMS shops	1,000 gal PD 680	800 gal PD 680	6,000	Instant	Elimination of RCRA characteristic waste.

Table 3 (continued)

Location/process	Baseline	Volume reduction	Annual cost savings ($)	Payback period	Description of benefit
ACTIONS REQUIRING SPEC CHANGES AND/OR TEST PROGRAMS					
20. Use of tetrahydrafuran as a substitute for methylene chloride-based strippers			11,000	5 months	Improved stripping efficiency.
21. Use of phosphate-based conversion coating to replace alodine					Eliminate alodine disposal. Eliminate use of carcinogen. Eliminate safety hazard.
22. Delisting of air filters from Hanger 48	17,000 gal filters		190,000	2 months	Eliminates need for RCRA disposal of air filters.
Randolph AFB annual cost savings: $621,000 - assuming current waste disposal practices					

[a]AGE - Aerospace Ground Equipment, LST - _____, MEK - methylethyl ketone, MIBK - methylisobutyl ketone, OMS - Organizational Maintenance Shop, RCRA - Resource Conservation and Recovery Act, TCA - 1,1,1=trichloroethane,

The Supply-related options that can be implemented by a Base are the following:

- o Before purchase, ensure BEE/BCE review of all local purchase items that may be hazardous,
- o Require MSDSs on all chemicals purchased locally,
- o Require receipt of MSDSs before payment,
- o Review benchstock levels on a quarterly basis and establish a flexible reorder system that permits purchase of only the quantity of hazardous materials necessary to reach maximum benchstock level,
- o Remove minimum-order requirements for purchase and issue,
- o Develop a reporting system to track ordering and use of hazardous materials by individual units,
- o Label chemical storage areas by material type and segregate paint by type/color to prevent misuse, and
- o Store paints, solvents, and other susceptible chemical stocks in properly protected environments.

Metal Cleaning and Paint Removal

In this activity area, the following options are generally applicable:

- o Conversion to nonchemical paint removal systems where possible,
- o Reclamation of strippers (filtration),
- o Use of non-RCRA regulated strippers and/or use of less hazardous strippers,
- o Reclamation and reuse of solvents (either by filtration or distillation),
- o Counterflow rinsing, and
- o Waste segregation.

Painting

Painting is an activity area in which several generally applicable waste reduction options are available:

- o Alteration of spraying technology away from high-pressure to airless or low-pressure equipment,
- o Solvent standardization,
- o Solvent reclamation (usually by filtration, occasionally by distillation),
- o Use of high-solids paints,
- o Use of water-based coating systems where possible, and
- o Waste segregation.

Miscellaneous Activities

Two options for waste reduction are applicable to a wide variety of situations at AFBs:

- o Waste exchange and
- o Change of PD-680 formulation to a flash point greater than 143°F (this allows the solvent to escape the "ignitability" designation under RCRA).

Other widely applicable reduction options include the following:

- o Product substitution (nondestructive inspection developer),
- o Improvement in silver recovery (photography),
- o Burning oil for energy recovery (vehicle maintenance), and
- o Use of water-based paints where possible (AGE painting).

INSTITUTIONAL WASTE MINIMIZATION OPTIONS

The supply system options discussed previously are only a part of the available opportunity for waste minimization at the institutional level. Institutional programs that can have a pronounced positive effect include goal setting, reporting systems, surcharge programs, training, incentive programs, publicity, and punitive programs. These various programs are discussed in another paper by the same authors (Vogel and Suffern, 1988).

CONCLUSIONS

Substantial waste minimization benefits have been identified at Randolph, Keesler, and Lowry AFBs. The amount of savings varies widely from base to base and correlates with the size of the flight mission and the size of the industrial support mission. There are many commonalities in the available waste minimization options, but to realize the maximum benefit, each base needed to be studied as a separate entity.

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HAZARDOUS WASTE MINIMIZATION (HAZMIN) STUDIES AT AMC INSTALLATIONS - A Summary of Findings, Michael D. Robison, Stephen L. Kistner, Ching-San Huang and David C. Guzewich, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, Md 21010-5422.

1. INTRODUCTION. In 1984, Resource Conservation and Recovery Act (RCRA) (reference 1) required that major (> 1000 kg/month) generators of hazardous waste (HW) sign a statement in their manifests certifying that they have a program in place to reduce the volume and/or toxicity of their waste generation. AMC followed with guidance and policy to its installations (reference 2) for HAZMIN. Goals of HW reduction were established in 14 categories based on calendar year (CY) 1985 baseline data (see the Table) and AMC installations were required to formulate and submit individual HAZMIN plans, along with semi-annual reports to AMC. To assist its installations, AMC requested USAEHA to provide technical support in the form of HAZMIN studies , with site visits, beginning with one visit in fiscal year (FY) 87. The purposes of these visits were to evaluate installation HAZMIN programs, look at each source of HW generation to examine HAZMIN opportunities, and to initiate technology transfer between installations. As of this writing (Oct 88), site visits have been completed at 21 installations with final reports completed for 13 (see references in paragraph 4). Four additional HAZMIN studies are scheduled for FY 89. USAEHA is also performing similar HAZMIN studies for Forces Command (FORSCOM), U.S. Army Training and Doctrine Command (TRADOC), Defense Logistics Agency (DLA), and the National Guard Bureau (NGB).

2. SUMMARY OF FINDINGS. For the most part, every installation surveyed made some good efforts towards reducing its HW generation, but many efforts still must be made if the AMC goals are to be reached. Many of the feasible HAZMIN techniques shown were identified by installation personnel. The accounting of HW generation/HAZMIN has been made difficult for several reasons: in some cases sources of HW were found which should have been added to baseline amounts, while in other cases sources of waste which may not have been hazardous were reported; non-uniform accounting for recycled wastes; differences in regulation interpretation; differences in State HW regulations; and difficulties in separating HW generation from HW minimization. The last problem is significant because of the varying and sometimes confusing ideas and policies about HAZMIN and how they relate to HW generation. In many cases HAZMIN techniques do not reduce HW generation rates but may reduce toxicity (use of alternated strippers), or reduce the amount of waste which is to be landfilled as final disposal (incineration of materials leaving only ash for disposal). It should be noted that the findings in this paper rely solely on the site specific reports and may not reflect existing conditions or generalities of HAZMIN. Additionally, many of the problems discussed here are not necessarily restricted to AMC installations, but are relevant to most Department of Defense (DoD) facilities.

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TABLE

AMC PROCESS HW REDUCTION GOALS[1]

PROCESS, OPERATION, OR CONDITION	PERCENT HW REDUCTION DESIRED BY 1992
Electroplating	50%
Paint stripping	
Plastic beads use	60%
Other means	40%
Painting	50%
Cleaning/degreasing	40%
Transportation vehicle maintenance	30%
Electrical maintenance	60%
Metal working	15%
Fueling operations	30%
Battery shop operations	50%
Propellant/explosives/pyrotechnics production	35%
Load-assembly-pack operations	15%
Waste treatment sludges	60%
Other treatment-generated HW	40%
Other operations or processes	40%

[1]From the CY 1987 AMC Hazardous Waste Minimization Plan

a. Electroplating.

(1) Five installations reporting electroplating HW

(2) Baseline generation: 1.5 M kg
13 waste streams identified

(3) Baseline HAZMIN:

(a) 7 streams with none or little
(b) 1 stream uses closed loop recycle (Chrome Napper) recycle
(c) 2 streams are treated at an Industrial Wastewater Treatment Plant (IWWTP)
(d) 3 streams remove solids to extend bath lives (filtration, electrolytic purification cell [EPC])

(4) Feasible HAZMIN identified:

(a) 1 stream needed verification as HW
(b) 4 streams could have extended lives by filtering baths
(c) 3 streams containing acid or alkalai solutions could be used at IWWTP for pH control

(5) Further research needed:

(a) Regeneration of spent plating baths
(b) Switch to aluminum plating
(c) Reuse of acid and alkalai baths

(6) Discussion. Simple filtration can extend the life of most plating baths and reduce annual HW generation. Use of a closed loop system (like the Chrome Napper system at Lone Star Army Ammunition Plant [LSAAP]) has been very effective in reducing HW generation. Housekeeping efforts have been good, overall. There is a high possibility of meeting the AMC 50 percent reduction goal.

b. Paint Stripping.

(1) 10 installations reporting paint stripping HW

(2) Baseline generation: 330,000 kg
16 waste streams identified

(3) Baseline HAZMIN:

(a) 9 streams with none or little
(b) 2 streams recycle spent stripper solutions offpost
(c) 1 stream disposed through Defense Reutilization and Marketing Office (DRMO) for use in an offpost kiln
(d) 3 streams extend stripper lives by solids removal

(4) Feasible HAZMIN identified:

(a) 3 streams (sand blast debris) needed verification as HW or development of a blasting time vs. HW constituent (heavy metal) link
(b) 6 streams could have extended lives by filtering and reuse by on site distillation equipment
(c) 2 streams were applicable for substitution of stripper

(5) Further research needed:

(a) Fixation of stripper/paint sludges
(b) Development of non-HW thinners

(6) Discussion. Filtration can extend the life of many stripper solutions. Development of effective substitutions would be the ideal solution, in combination with non-metal based paint use. It should be noted that off post recycle of stripper solutions does not reduce HW generation as far as the installation is concerned since each time the solution is sent off post it counts as generation primarily because it has to be manifested to the recycler. For example, if an installation generates 100 gallons/month of spent stripper and has this picked up by a recycling service, the annual generation would be 1,200 gallons. If the stripper is recycled onsite (distilled), the regulations and regulators indicate that the annual generation rate would be 100 gallons (plus a small amount of still bottoms and make-up thinner which then becomes waste), that is, the regulators indicate that the waste thinner should only be counted once if it is recycled onsite. This is one of the anomalies of the accounting process which must be addressed and settled. Also, recycling provisions in the HW regulations are interpreted differently from installation to installation and the data for recycled materials reflects this.
The data obtained during the USAEHA HAZMIN's does not indicate any substantial reduction in HW generation in this category. However, in most cases off post recycle is the best method, given the number of individual shops involved and the lack of on-site expertise in using distillation equipment.

c. Painting.

(1) 8 installations reporting painting HW

(2) Baseline generation: 420,000 kg
17 waste streams identified

(3) Baseline HAZMIN:

(a) 9 streams with none or little

(b) 7 streams substitution of non-metal based paints

(c) 1 stream (filters) incinerated

(4) Feasible HAZMIN identified:

(a) 8 streams paint substitution

(b) 1 streams needed verification of it actually being HW

(5) Further research needed: Dewatering spray paint booth sludges

(6) Discussion. Substitution of metal based paints with non-metal based types should allow the 50 percent reduction goal to be easily met. Some primers still contain metals (chromium).

d. Cleaning/Degreasing.

(1) 8 installations reporting HW in this category

(2) Baseline generation: 480,000 kg
17 waste streams identified

(3) Baseline HAZMIN:

(a) 2 streams with none or little
(b) 2 streams switched to non-hazardous degreaser
(c) 9 streams are recycled off post at a cost to the installation
(d) 2 streams are used in off post kiln as a fuel source
(e) 2 streams are sold (Stratford Army Engine Plant [SAEP])

(4) Feasible HAZMIN identified: 2 streams could be distilled/reused, either on-post or through an off post recycler

(5) Further research needed:

(a) Non-hazardous substitutes. Note: USAEHA has performed limited toxicity and biogradability tests on CITRIKLEEN[R]. CITRIKLEEN was found to be as toxic (in static bioassays) as many of the typical solvents such as trichloroethylene (TCE) and methylene chloride and showed a 5-day biochemical oxygen demand (BOD_5) of 689,000 mg/L. It was shown to be biodegradable but unchecked discharges of CITRIKLEEN to the sanitary sewer may cause problems for biological treatment because of its high BOD_5. The point here is that many of the new "non-hazardous" substitutes should be used cautiously and with complete knowledge of potential effects. For more information or a copy of the completed report, contact Pete Cunanan at AUTOVON 584-3289.

(b) Regional DoD distillation

(6) Discussion. Recycling through an off-post recycler may be cost effective in many cases when compared to on-post recycling. However, the installation's HW generation rate is not reduced because the material is manifested off-post. On post recycle would reduce the generation rate to that of the distillation bottoms, since the original material only has to be counted once as HW (see the earlier discussion in paragraph 2b). But, recycling off post does meet the spirit of HAZMIN since the material is not being disposed of as a HW. The AMC HW reduction goal of 40 percent may not be met because of this. In fact, several of the good HAZMIN techniques are not reflected in HW generation reduction rates. Generally, all materials which are recycled are still counted (legally) as HW in figuring generation rates, although the material is not being disposed of as a HW. So, while the HW generation rate has not been reduced, the waste has effectively been reduce to zero generation in terms of the quantity disposed in a landfill. Recycling thus is excellent HAZMIN. However, the goals established are for the HW generation rate. Some additional considerations need to be established to credit recycling efforts.

[R]Citrikleen is a registered trademark of Penetone Corporation - a subsidiary of West Chemical Products, Inc., Tenafly, New Jersey. Use of a trademark name does not imply endorsement by the U.S. Army but is merely intended as identification of a specific product.

e. Transportation.

(1) 12 installations reporting transportation related HW

(2) Baseline generation: 1,200,000 kg (about 500,000 kg used oil)
22 waste streams identified

(3) Baseline HAZMIN:

(a) 11 streams with none or little (4 were used oil)
(b) 3 streams are burned off post
(c) 3 streams are recycled through off-post contractor
(d) 1 stream had a HW reduction though process modification
(e) 1 stream (used oil at Riverbank Army Ammunition Plant [RBAAP]) given away to the State of Oregon
(f) 1 stream was reblended/reused
(g) 1 stream was distilled through a DRMO contract
(h) 1 stream was segregated and sold

(4) Feasible HAZMIN identified:

(a) 5 streams could be segregated into HW and non-HW streams (normally, solvents and used oils)
(b) 2 streams were anti-freeze and should not have been counted as a HW

(5) Further research needed: Burning used oil as fuel

(6) Discussion. The used oil regulations vary from state to state. In California, Delaware, Florida, Illinois, Massachusetts, Michigan, Missouri, New Jersey, Oklahoma, South Carolina, Texas, and Vermont used oil is a listed HW. However, RBAAP used initiative and sold its oil to Oregon for it use. Comments on spent degreasers can be found in the previous discussion section. AMC's 30 percent goal should be reachable even if additional states or the U.S. Environmental Protection Agency (EPA) determine that used oils are listed wastes. AMC HAZMIN's are supposed to address used oil, even if it is not a listed HW. This differs somewhat from the recent draft Department of the Army (DA) policy for which the DA goal of 50 percent reduction from CY 85 rates are not to be affected by wastes listed as hazardous after 1985. This may need resolving from an accounting standpoint, but certainly AMC installations should be given credit for used oil generation reductions.

f. Electrical Maintenance.

(1) 7 installations reporting HW in this category

(2) Baseline generation: 21,000 kg
8 waste streams identified (6 polychlorinated biphenyl [PCB] related)

(3) Baseline HAZMIN:

(a) All of the installations are generating PCB wastes as they drain and replace transformer fluids. In the future, no PCB wastes should be generated at these installations.

(b) 1 stream (solvent) was small and no HAZMIN was performed

(c) 1 stream completely recycles electronic scrap

(4) Discussion. The 60 percent AMC reduction goal is very reachable, assuming the original data counted PCB's as HW (which it is not under RCRA).

g. Metal Working.

(1) 7 installations reporting metal working related HW

(2) Baseline generation: 1,600,000 kg
14 waste streams identified

(3) Baseline HAZMIN:

(a) 10 streams with none or little
(b) 2 streams have reduced HW generation through improved controls
(c) 1 stream (magnesium, thorium turnings) are recycled.
(d) 1 oily waste stream (Mississippi Army Ammunition Plant [MSAAP]) is gravity settled then de-emulsified through acid cracking to concentrate the waste stream

(4) Feasible HAZMIN identified:

(a) Many or all of the coolant oils can be filtered and their lives thusly extended
(b) The oily waste mixture, once filtered to remove metal particulates, may no longer be a HW
(c) Some of the oily wastes were assumed to be hazardous without testing. Verification testing is in order for these.
(d) Oily wastes which contain water and are tested as HW should be dewatered to reduce volume (MSAAP had planned to purchase a centrifuge for this purpose

(5) Further research needed: Use of some of the salts and nutrient containing coatings used in metallic shell making as fertilizers.

(6) Discussion. Most of this category consists of cutting oils and other machining oils. Reaching the 15 percent reduction goal should be achievable with simple segregation, filtration, dewatering and reuse of the oils. Verification testing should also be made for all oily wastes.

h. Fueling Operations.

(1) 3 installations reported HW generation in this category

(2) Baseline generation: 10,000 kg

(3) Baseline HAZMIN: None

(4) Feasible HAZMIN identified: Use as a supplementary fuel in a boiler

(5) Further research needed: None identified

(6) Discussion. All of this category consists of contaminated or excessed fuel requiring disposal and are generally one-time or periodic generations. Other types of waste which might appear in this category would be tank bottoms and tank cleaning sludges. Spills debris should be associated with this category, but most HAZMIN's either place this amount in the "Other" category or do not include any data on spill debris clean-up. One-time or irregularly generations are not normally included in HAZMIN plans, but spill debris clean-up and associated liability costs can be significantly reduced by improved spill control facilities and improved spill response mechanisms.

i. Battery Shop Operations.

(1) 7 installations reporting battery shop related HW

(2) Baseline generation: 10,000 kg
8 waste streams identified

(3) Baseline HAZMIN:

(a) 4 streams (electrolyte) are used at a IWWTP for pH adjustment

(b) 1 stream (electrolyte) was neutralized, then discharge to industrial sewer

(c) 2 streams (intact batteries) were given to off-post recycler (no HW generation)

(d) 1 stream (Ni-Cad batteries, intact) were sent to an off-post recycler

(4) Feasible HAZMIN identified: None

(5) Further research needed: Simple neutralization often will not render the electrolyte non-hazardous because of lead content. Research may be needed to determine the amount of lead leached into electrolyte versus time-in-use of a battery.

(6) Discussion. There are several HAZMIN options for battery shop operations. Something suitable should be available for nearly all installations.

j. Propellant/explosives/pyrotechnics production (PEP).

(1) 9 installations reported PEP related HW

(2) Baseline generation:
ashes: 1,020,000 kg (10 sources)
reject, off-spec, obsolete munitions: 5,020,000 kg (15 sources)
other: 1,217,500 kg (17 sources)
(see discussion)

(3) Baseline HAZMIN:

(a) Ashes: 5 with none or little
4 use burning pans to reduce soil contamination
1 installation compacts its ashes to reduce volume

(b) Munitions: 1 source with no or little HAZMIN
9 sources use open burning/open detonation (OB/OD) for burning to reduce volume
3 sources are incinerated or otherwise burned
1 source (Lake City Army Ammunition Plant [LCAAP]) OB with IWWTP design for waste pyrotechnics
1 volume reduction facility (Pine Bluff Arsenal [PBA])

(c) Other: 5 sources thermally treated by OB/OD
6 sources with no or little HAZMIN
1 source segregated to keep out non-hazardous materials
3 sources sent off post for recycling
1 source (lab solvents at Holston Army Ammunition Plant [HSAAP]) sent to IWWTP
1 source burned for energy recovery (HSAAP)

(4) Feasible HAZMIN identified:

(a) Use of OB/OD pans at every site

(b) Verification of ash sources as actually being a HW

(5) Further research needed:

(a) Fixation of ashes which are determined to be HW

(b) Reuse of obsolete, off spec, or otherwise reject munitions

(6) Discussion. This category represents the second largest generation of all the categories. Most munitions which cannot be used for whatever reason are thermally degraded to reduce to volume. The amount of material sent to the OB/OD is counted as a HW, this method actually increases HW generation because the resulting ash has, in most cases, been considered hazardous although laboratory analysis is often lacking to support this. Burning or incineration reduces the final disposal to landfill, which is good HAZMIN. But again, there should be a measure of this when interpreting HW and HAZMIN information.

k. Load and Pack (LAP).

(1) Several installations reported LAP related HW. The reports often did not include wastes in this category if treated by IWWTP under an National Pollutant Discharge Elimination System (NPDES) permit. Also, in some cases, LAP and PEP wastes and wastewaters were lumped together into one category.

(2) Baseline generation: The waste streams for which data was available totalled more than 40 M kg/year, all treated under a NPDES (or State equivalent) permit.

(3) Baseline HAZMIN: Treatment at IWWTP

(4) Feasible HAZMIN identified: None

(5) Further research needed:

(a) Recycle and reuse of wastewaters

(b) Water conservation methods

(6) Discussion. Some LAP wastes may be listed under the PEP category. Some installations do some of each and the USAEHA HAZMIN's didn't differentiate each source. Many were lumped together from several sources. In terms of HW generation, treatment offers no incentive for reduction, although it does offer good HAZMIN in terms of reducing both toxicity and the need for land disposal. Pink waters generated by trinitrotoluene (TNT) related facilities are listed hazardous wastes, and data are generally reported correctly as such. However, other wastewaters not specifically listed may be HW and should also be counted as such in generation data. Many industrial wastewaters (acid production, metal finishing) meet the corrosivity criteria ($2 > pH > 12.5$). Strictly speaking, these wastewaters should be included in baseline calculations but often were not since they are not immediately thought of as HW. More generally, when an installation looks at its baseline generation, all wastes, which would be HW if nothing would be done to them, should be included - not just those which were reported as such in 1985.

1. Waste Treatment Sludges.

(1) 11 installations reported waste treatment sludges as HW

(2) Baseline generation: 11,175,300 kg
22 sources

(3) Baseline HAZMIN:

(a) 8 sources with none or little
(b) 1 sources was chemically fixed and then delisting petition submitted (LSAAP)
(c) 1 source was delisted (Watervliet Arsenal [WVA])
(d) 1 source was petitioned for delisting (LCAAP)
(e) 1 source under going removal (waste pond closure)
(f) 6 sources were dewatered
(g) 1 source thermally destroyed at OB/OD
(h) 1 source recycled, sold, or destroyed at OB/OD depending on quality
(i) 1 source was segregated into HW and non-HW components
(j) 1 source was dewatered and delisted (HSAAP)

(4) Feasible HAZMIN identified:

(a) 4 sources could be dewatered for volume reduction
(b) 4 sources are possible candidates for delisting
(c) 2 sources can be chemically fixed and delisted

(5) Further research needed:

(a) Fixation of various sludges, especially metal contaminated types
(b) Continued research into dewatering techniques

(6) Discussion. Dewatering of all HW sludges is normally cost effective and should be considered in nearly every case. Many of the sludges associated with munitions have proven not to be reactive and can probably be delisted, as HSAAP did. It should be noted that delisting does not mean a reduction in generation rates since delisting is only temporary and must periodically be reviewed. Of course, in most cases the delisted waste remains that way after the periodic review. Measures to reduce the source of the waste should still be pursued. Chemical fixation of many of the metal plating sludges should be considered, although research is needed in this area. Considering the large volume of sludges generated, the 60 percent reduction goal should be reachable.

m. Other Treatment HW.

(1) 5 installations reported HW in this category

(2) Baseline generation: 120,000 kg spent carbon (6 sources)
275,000 kg waste oil/alum mixture (1 source)

(3) Baseline HAZMIN:

(a) 4 sources with none or little

(b) 1 source incinerated

(c) 1 source sent offpost for regeneration (Radford Army Ammunition Plant [RDAAP])

(d) 1 source decreased through better management

(4) Feasible HAZMIN identified:

(a) 1 source a candidate for off post regeneration

(b) 1 source a candidate for treatment substitution (air stripping for carbon column treatment)

(c) 1 source can be dewatered

(d) 3 sources identified as possible candidates for delisting

(5) Further research needed: Regeneration of explosive contaminated carbon

(6) Discussion. If spent carbon can be regenerated in a practicable manner, then the 40 percent reduction goal should be reachable.

n. Other Operations and Processes.

(1) 11 installations reported HW in this category

(2) Baseline generation: 100,000 kg
23 sources

(3) Baseline HAZMIN:

(a) Most photographic wastes are recycled for silver recovery

(b) Spill debris are disposed of in various manners

(c) Other wastes are typically generated sporadically and disposed of through DRMO

(d) RBAAP uses a unique HAZMIN technique. It operates a combination triple rinse and drum crusher facility. In California, any drum which originally contained a hazardous material is a listed HW unless it is triple rinsed in accordance with California regulations. Rinse waters are directed to the RBAAP IWWTP for treatment.

(4) Feasible HAZMIN:

(a) Improved Spill Prevention Control and Countermeasure Plan (SPCCP) and Installation Spill Contingency Plan (ISCP) and other management practices

(b) Testing of non-listed sludges for HW constituents

(5) Discussion. Many of the wastes in this category were discovered by USAEHA and therefore not included in baseline data. In many cases, especially for spill debris, the waste has been assumed hazardous. Increased verification should be included in future HAZMIN. Spill prevention control procedures are spotty and could lead to increases in HW generation for this category. RBAAP is the only installation that reported empty containers in its baseline data. No reason was given for this apparent oversight. Other installations with an IWWTP should take RBAAP's lead with its unique triple rinse system.

3. CONCLUSIONS.

a. Most of the installations surveyed have made good attempts at HAZMIN.

b. Many low cost HAZMIN opportunities are available, including filtering plating, thinning, and degreasing solutions to increase usable life; expanding the use of burning pans to every OB/OD ground; eliminating, as far as possible, all use of metal-based paints; segregating HW's from non-hazardous types; and increasing verifications of wastes perhaps incorrectly assumed to be hazardous.

c. Other good general HAZMIN opportunities include dewatering of sludges, enhancing spill prevention and control measures, using closed loop electroplating systems, using available IWWTP systems to their fullest potential, and use of onsite distillation equipment.

d. Research areas of significance include finding ways to reuse or recycle obsolete, off-spec or reject munitions; development of non-hazardous thinners, degreasers, and strippers; chemical fixation of various ashes and sludges; enhance dewatering of sludges; burning various petroleum-oil-lubricants (POL) products as supplemental fuel sources; and regeneration of explosive-laden carbons.

e. Off post recycle of spent solvents, thinners, and strippers and use of IWWTP do not provide incentive to reduce HW generation and the data appears to indicate that HW generation in these categories has not been reduced despite good HAZMIN efforts.

f. Technology transfer of information between installations could be improved. Many installations have taken good initiative with innovative disposal techniques, but the accomplishments have not necessarily been widely broadcast.

g. We do not feel that the baseline or subsequent year data are truly representative of the actual HW generation rates of AMC installations. In many cases, a number of additional sources of waste were identified during the site visits that should have been part of the 1985 baseline amounts. Other wastes should not have been counted as HW at all (ethylene glycol, for example) or could have been tested with a good possibility of the waste turning out not to be hazardous. Also, reporting of generation rates differed from installation to installation.

h. We also do not feel the data is truly representative of all the HAZMIN in effect. Much of the accounting problem stems from differing interpretation of the regulations and how HAZMIN data should be viewed. The relationship between HW generation and HAZMIN efforts is not clearly defined. Comparing HW generation rates between years to determine the benefit of a HAZMIN program does not present the entire picture. We suggest that the generation rate comparison be supplemented with a second measure: a comparison of the generated HW with the sum of all materials which need to be landfilled as final disposal. For example, recycling is a very good HAZMIN technique but is not necessarily reflected in lowered generation rates.

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g. Memorandum, USAEHA, HSHB-ME-SH, 3 June 1987, Subject: Hazardous Waste Study No. 37-26-1656-87, Hazardous Waste Minimization, Riverbank Army Ammunition Plant, Riverbank, California, 2-5 March 1987.

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PROVEN PERFORMANCE OF THE SODIUM SULFIDE/FERROUS SULFATE METALS TREATMENT SYSTEM

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Background

Electroplating facilities for the Air Force range from small operations with one or two baths (500 - 1500 gallons) to shops with over 40,000 square feet of tank space (Reference 1). The principal contaminants in the wastewater from these processes are chromium, nickel, copper, cadmium, lead and zinc. Complexing and chelating agents are added to metal finishing solutions for brightening, cleaning, and to inhibit or prevent precipitation of the metals. These agents include tartrates, phosphates, ethylenediaminetetraacetic acid (EDTA), and ammonia (Reference 2).

These metals and other chemicals are carried into the rinse water which must be treated at the Industrial Waste Treatment Plant (IWTP) at the Air Logistic Centers (ALC) on five Air Force Bases (AFB). The discharge limits for the IWTP at Tinker AFB for the metals of concern are listed in Table 1. The effluent from the IWTP must meet these limits to comply with the National Pollutant Discharge Elimination (NPDES) Permit (Reference 3).

TABLE 1. TINKER AFB NPDES PERMIT REQUIREMENTS

Constituent	Concentration (mg/L)	
	1988	1989
Cadmium, total	0.03	0.015
Chromium, total	1.0	0.1
Chromium, hexavalent	0.1	0.05
Copper, total	0.1	0.05
Lead, total	0.1	0.05
Nickel, total	1.0	0.5
Zinc, total	1.0	0.5

Conventional treatment methods for these wastewaters result in the generation of large quantities of sludge. The sludges require special handling and costly disposal at approved

hazardous waste disposal facilities. These costs are rising continuously. Tinker AFB was paying $168 per ton one year ago. They now pay $220 per ton. This is an increase of over $110,000 per year for that facility. Costs are expected to continue to rise as more stringent requlations are promulgated. Sludge reduction can decrease these costs to manageable levels. Methods of reducing the sludge include reduction in amount of wastewater, treatment optimization, plating chemical conservation, and sludge dewatering.

A program was initiated by the Air Force Engineering and Services Center under contract to EG&G Idaho to determine the feasibility of the use of sodium sulfide and ferrous sulfate to reduce the hexavalent chromium, precipitate the metals, and decrease sludge production and chemical usage. Phase I of the program determined the feasibility of the process in a bench-scale field verification study using the influent to the Tinker AFB Industrial Waste Treatment Plant (IWTP). Phase II of the program was a 5 gpm pilot-scale field study on actual industrial wastewater at Tinker AFB. Phase III of the program is a full-scale field verification study, now ongoing at Tinker AFB. Results of that study will be available in a report Dec 88.

Scope

A pilot-scale field verification plant (Figure 1.) was

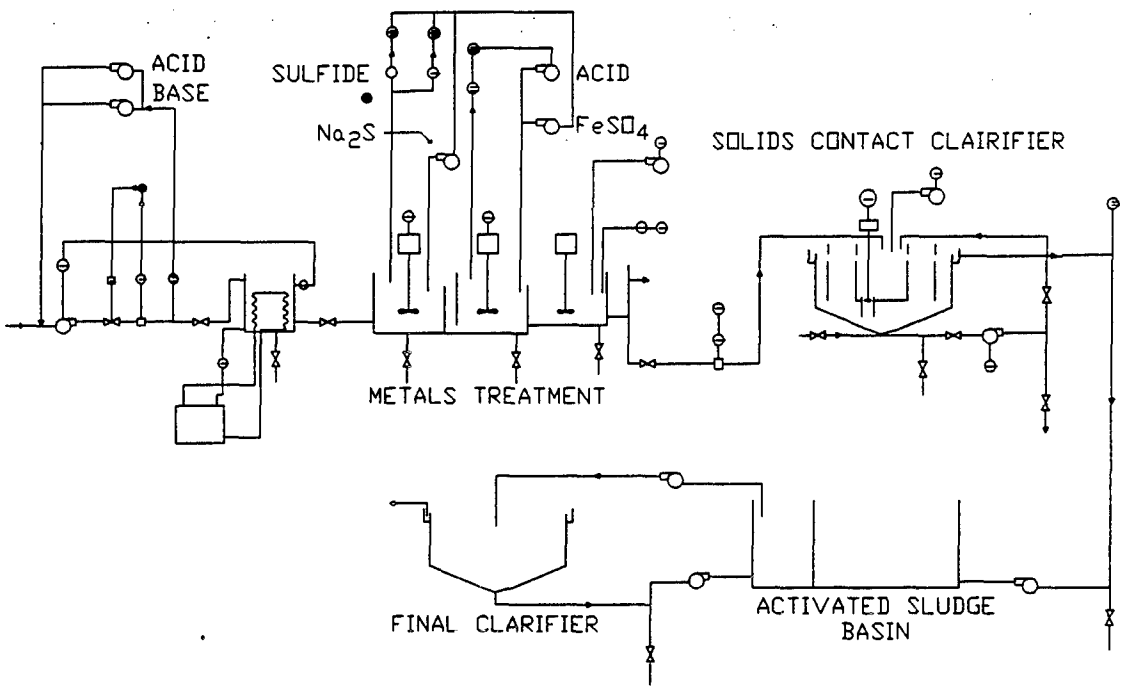


FIGURE 1. PILOT-SCALE FIELD VERIFICATION PLANT

constructed at the Tinker AFB IWTP. Included with the plant wasan analytical support trailer. Tests conducted at the pilot

plant included determination of the optimum sulfide, ferrous, and polymer concentrations; determination of the effect of phosphate, cyanide, EDTA, and added metals on the reduction of hexavalent chromium and total metal removal; and determination of the optimum parameters for operation of the solids contact clarifier. It was necessary to develop an operating system that used a solids contact clarifier, since Tinker AFB was chosen as the demonstration site and their process used a similar system. The impact of flow rate and temperature were also investigated, as was the effect of the sodium sulfide/ferrous sulfate chromium reduction metal removal process on the activated sludge organic removal process. A comparison of the amount of sludge produced by the sodium sulfide/ferrous sulfate method to the acid/sulfur dioxide/lime method was obtained by operating the pilot plant using sulfuric acid, sulfur dioxide, and lime. In addition, a procedure was established for switching the present process to the sodium sulfide/ferrous sulfate process.

The solids contact clarifier at the Tinker AFB IWTP was designed by Walker Process Corporation. A schematic of the solids contact clarifier is shown in Figure 2. The effluent of Mixer

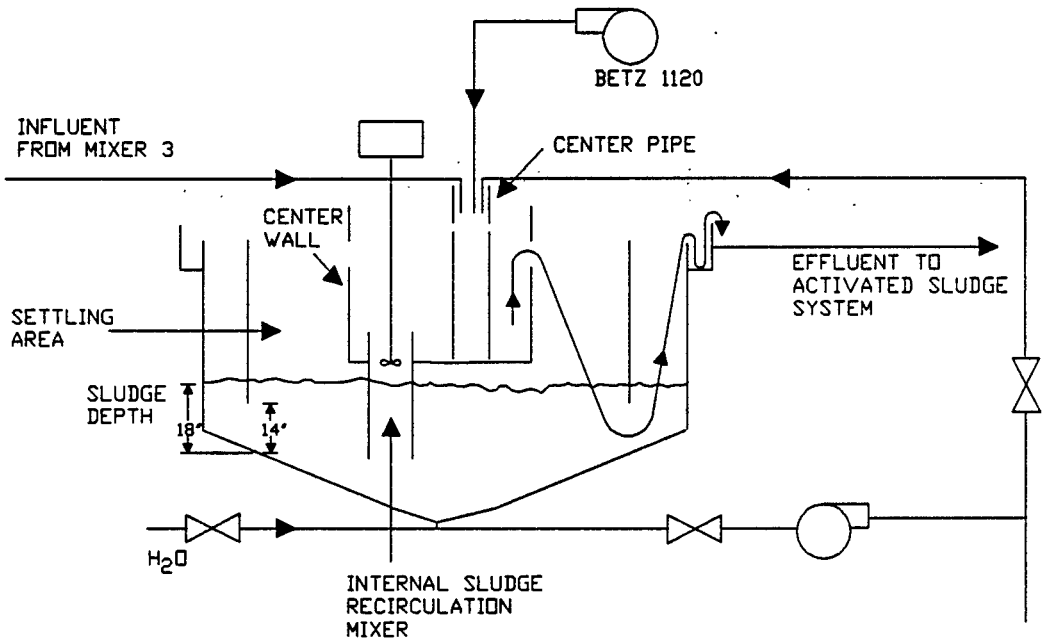


FIGURE 2. SCHEMATIC OF THE SOLIDS CONTACT CLARIFIER

Basin-3 flows to the center well of the solids contact clarifier, where it is mixed with an anionic polymer, and an external sludge recirculation flow. A flash mixer in the center well pulls the sludge from the bottom of the solids contact clarifier for an internal sludge recirculation. The sludge is mixed in this centerwell as a seed or aid for flocculation. The mixture flows from the top of the center well to an intermediate settling ring or skirt. In normal operation of the solids

contact clarifier the sludge depth is kept below this skirt. However, with the sodium sulfide/ferrous sulfate process it was found that a sludge depth greater than the bottom of the skirt was required; such that the effluent could flow under the intermediate skirt through the sludge bed and up thought an outer ring and over the weir of the solids contact clarifier. In this manner, the treated wastewater is filtered through the sludge blanket to remove the fine particulates. External sludge recirculation (10 to 20 percent of the IWTP influent) is required, along with the internal sludge recirculation, to achieve 80 to 90 percent solids in the center cell. The high concentration of solids is required to achieve metal removal below NPDES permit requirements.

After the solids contact clarifier was operating at optimum conditions, the effect of orthophosphate (100 mg/L) ethylenediaminetetraacetic acid (50 mg/L), and mixed metals on chromium reduction was determined. With chemical feeds at the levels represented in Table 2, and with the solids contact clarifier operated at optimum conditions, these additives had no effect on the chromium reduction, metal removal, or activated sludge. Influent wastewater temperatures from 41 to 95 F had no effect, nor did flows proportional to 500,000 and 2,000,000 gal/day.

Results

The sodium sulfide/ferrous sulfate process with the activated sludge process was successfully used on the pilot scale to treat Tinker AFB IWTP influent for reduction of hexavalent chromium, total metal removal and organic removal to less than NPDES permit requirements. The sulfide, ferrous and polymer requirements were optimized as well as the pH for this process. In addition the SCC operation was optimized. The optimum operating conditions are summarized in Table 2. The effects of chemical and physical parameters on the process operation was also investigated in the pilot plant. The general conclusions from these investigations are:

TABLE 2. CHEMICAL REQUIREMENTS

Sodium Sulfide	2 mg/L S^{-2} per 1 mg/L Cr^{+6}
Ferrous Sulfate	1.5 mg/L Fe^{+2} per 1 mg/L Cr^{+6}
Betz 1195 Cationic Polymer	20 mg/L
Betz 1120 Anionic Polymer	0.5 mg/L
pH Mixer-2	7.2 - 7.5

1. Control of pH is required in Mixer-2 after the addition of the ferrous sulfate. Although the hexavalent chromium was reduced to less than 0.1 mg/L Cr^{+6} in a pH range of 7.2 to 8.4, there was less scatter and less

chance of exceeding NPDES permit requirements if the pH was controlled between 7.2 and 7.5.

2. Control of the influent pH is not required to maintain chromium reduction. Control is required to maintain an influent pH greater than 7.2 to prevent off-gassing of hydrogen sulfide gas.

3. The process will produce an effluent at the SCC which will meet the NPDES permit metal requirement as long as the chemical feed requirements are met and the SCC is operated at the optimum conditions.

4. Optimum operating requirements for the SCC require a sludge depth greater than the bottom of the intermediate ring so that fines in the effluent is are filtered; an external sludge recirculation rate of 10 to 20% of the influent flow with an internal sludge recirculation to maintain a high suspended solids concentration in the inner mixer chamber (80-90% suspended solids by volume).

5. Even though cyanide, at 10 mg/L, was carried through the SCC at 1.81 mg/L, this concentration did not effect the activated sludge system and was reduced to 0.5 mg/L at the effluent of the final clarifier. In addition, cyanide did not effect the metal removal at the SCC.

6. Orthophosphate concentrations of 100 mg/L, and EDTA concentrations of 50 mg/L had no effects on the hexavalent chromium reduction or the total metal removal in the SCC.

7. Addition of 5 mg/L metal ions in addition to those present in the influent had no effect on the hexavalent chromium reduction or the total metal removal in the SCC.

8. If the SCC is operated at optimum conditions, the activated sludge system will not be affected by the sodium sulfide/ferrous sulfate system.

9. The activated sludge system will perform best if sound basin management is followed. This includes control of the oxygen feed, organic loading, flow, and the solids inventory.

10. Flow proportional/equivalent to 1.75 million gpd through the Tinker AFB IWTP had no effect on the pilot scale system ability to meet NPDES permit requirements.

11. Temperature from 41°F to 95°F did not affect the pilot-scale process.

12. The continuous flow analyzer works well to monitor the SCC effluent for hexavalent chromium, but requires excessive maintenance (due to plugging by dirt and greases in the influent wastewater) when used to control the feeds by monitoring the influent hexavalent chromium.

13. The streaming current detector is an effective method of measuring the current at the effluent of Mixer-3 and its operation is relatively maintenance free. It appears to be a good method for controlling cationic polymer feed.

14. Although respiration monitoring is a good indication of the health (activity) of the activated sludge system, the respirometer was not rugged enough in the pilot plant for use without excessive maintenance.

15. The mechanics for chromium reduction with the sodium sulfide ferrous sulfate process is complex with multiple reaction pathways. The reaction is concentration dependent on several species (i.e., S^{-2}, Fe^{+2}, and bridging ligands). There is an inverse concentration dependence on S^{-2} and Fe^{+2} with several sulfur species formed in the process.

Preliminary Cost Comparisons

The cost comparisons between the acid/sulfur dioxide/lime process and the sodium sulfide/ferrous sulfate process are based on operating logs at Tinker AFB for Jan thru Jun 1988. During this time 4,454 lb of hexavalent chromium and 141,913,000 gal of industrial wastewater was treated. The sludge produced by the sodium sulfide/ferrous sulfate process is 180 tons per year compared to 1880 tons per year produced by the acid/sulfur dioxide/lime process.

Tinker AFB is considering recycling the treated industrial waste back to their cleaning and electroplating processes. With the lime process, the wastewater requires softening to remove calcium to 150 mg/L calcium carbonate. Jar tests were run to determine the volume of soda ash (Na_2CO_3) required for softening. Approximately 828 tons/yr of soda ash would be required and would produce approximately 828 tons of sludge. These costs are included in the cost comparison.

The cost for the sodium sulfide/ferrous sulfate process is based on the use of dry chemicals and the treatment of the same volume of water and hexavalent chromium as in the acid/lime process. Potential savings for the process is $370,000/yr if the treated water is discharged, as it is presently. If the treated water was to be recycled back to the industrial processes, the potential savings would be $655,000/yr.

Recommendations

The sodium sulfide/ferrous sulfate process was used to treat the Tinker AFB IWTP influent wastewater on the pilot scale with the effluent meeting NPDES Permit Requirements. The process requires control of the chemical feeds and proper operation of the SCC. The SCC operation includes maintaining a sufficient sludge depth and external sludge recirculation. When operated properly, the process can result in a substantial cost savings. The process should be implemented in the Tinker AFB IWTP and its operation demonstrated. An operation and maintenance manual should be prepared to describe the process operation. Implementation will require installation of an external sludge recirculation pump and pH controls.

Conclusion

Based on the results of phase II, the pilot scale study, phase III, the full scale study was initiated. The full scale operation was begun in Jul 88. Phase III has been extremely successful and a report will be available in Dec 88. The Air Force is in the process of obtaining a patent for the process.

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Title: Implementation of Plastic Media Blasting at Army Depots

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Introduction

A major source of hazardous waste at Army depots is residual material from paint removal operations. Chemical stripping, in particular, produces large quantities of hazardous waste. A technology which may reduce the quantity of waste being produced is Plastic Media Blasting (PMB). PMB, which strips paint by propelling small plastic particles at the surface to be depainted, was developed by the Air Force for use on aircraft. PMB produces far less waste than chemical stripping because it is a dry process and the plastic media can be reused several times. Thus, the only waste from a PMB operation is removed paint and a small amount of broken down plastic media. PMB also generates less waste than other blasting media such as sand and walnut shells. Army depots already use PMB for some applications. However, the Army's depainting needs are diverse and some uncertainties about this relatively new process have hindered broader application. Before the depots can determine how PMB can best be used, more information on the strengths and limitations of the process must be gathered.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) has completed a pilot test program at Letterkenny Army depot. Tests were run in a glovebox modified for PMB use and in a new walk-in blasting facility purchased by USATHAMA. A wide variety of Army material was depainted using PMB. Data on paint removal rates, media recycle rates, waste generation and substrate damage was collected. Detailed economic comparisons of presently used methods and PMB were performed. The information gathered from the pilot tests will be given to the depots so that they can determine if their facility would benefit from the use of PMB.

Results of Pilot Testing

a. Optimum Plastic Media - 17 different types of commercially available plastic media was evaluated and compared. Test results did not conclusively indicate that one single brand of media performed (based on paint removal and media consumption) better than all others. Test results did show, however, that for Army depot use, plastic media with a 3.5 to 4.0 moh hardness rating and a 20 to 40 U.S. sieve size achieved the best combination of paint removal and media consumption rates.

b. Optimum Blast Conditions - Blasting pressures between 40 and 50 psi yielded the best results in terms of paint removal rate and waste generation. The optimum standoff distance was found to be approximately 18 inches.

c. Damage to Substates - Steel and aluminum parts with thickness down to 1/8 inch were depainted with PMB without warping, pitting or otherwise damaging the surface. More delicate surfaces such as fiberglass can also be depainted without substate damage provided the operator is trained in the proper techniques.

d. Waste Generation: Based on six months of production data, plastic media blasting was found to produce 50% less to waste than walnut shell blasting and 70% less than chemical stripping. PMB produced 70% less waste than glass bead blasting.

e. Economics: Chemical stripping was found to be 20% less expensive than PMB for small parts. For small parts (less than one foot square) use of a chemical dip tank is less labor intensive than PMB. Although the waste disposal costs with PMB are less, the labor costs are the primary expense for depainting small parts. For larger parts PMB was found to have approximately the same cost as glass beads and to be slightly more expensive than using walnut shells. The economic analysis were based on the present hazardous waste disposal costs payed at Letterkenny Army depot which is 18 cents per pound. As disposal costs become higher, which is already the case at many depots, PMB will become increasingly economical. Economic comparisons are made using new and efficiently operating chemical dip tanks and blasting equipment. When PMB is considered as a replacement for older equipment, the economics can be considerably different. For example, by replacing an obsolete blast room at Letterkenny with a new PMB booth, approximately $100,000 will be saved each year. The savings is realized from reduced disposal costs (about 75% reduction) and reduced labor costs because the new facility has an automatic media recovery system.

f. Rust Removal - Blasting with plastic above was effective at removing light rust but was not effective at removing heavier rust. A mixture of 20% glass beads and 80% plastic media was effective at removing all rust. The addition of 20% glass beads did not significantly increase the waste generation. However, the glass bead and plastic combination is not suitable for blasting delicate surfaces.

g. Materials Suitable for PMB Use - A wide variety of materials were effectively depainted with PMB. Among the materials PMB was effective on were artillery projectiles, communication shelters, decontamination units, 8v engine parts, smoke generator parts, various frames, fiberglass nose cones and shipping containers. Generally, PMB was found to be a suitable paint removal method for any equipment which is usually walnut shell blasted or chemically stripped. PMB is not a suitable replacement for highly abrasive media such as steel shot.

Conclusions

Further implementation of PMB will result in significant reductions in waste generation at the depots. For installations where hazardous waste can be disposed of for 18 cents a pound or less, PMB will be slightly more expensive than other paint removal methods. As disposal costs rise, PMB will become more economically attractive. In cases where blasting equipment must be replaced in any event, equipment which compatible with PMB should be purchased. The data generated at Letterkenny Army depot will now be provided to the other major Army depots. Assistance will be provided to the depots in determining where the use of PMB will be beneficial.

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Demonstration Testing of Plastic Media Blasting at Letterkenny Army Depot, Arthur D. Little, Inc. December 1988.

McCLELLAN AIR FORCE BASE PLATING SHOP RINSE WATER RECYCLE SYSTEM[a]

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ABSTRACT

The Idaho National Engineering Laboratory performed an assessment on the technical and economic viability of a total recycle of the rinse water generated by the Sacramento Air Logistics Center Plating Shop, located in Builidng 243-G of McClellan Air Force Base. A proposed conceptual design using ion exchange beds for the recycle of plating shop rinse water is presented and evaluated. Laboratory studies indicated that the proposed recycle system meets all functional and operational requirements that were identified. But concern over the amount of waste generated during the process of regenerating the ion exchange columns prompted an evaluation of a reverse osmosis unit, which would function as a pretreatment before the ion exchange process. Further studies indicated that the addition of this pretreatment process would improve the performance of the recycle system, but that the cost of construction and operation would be significantly higher. Based on technical and economic evaluations, the ion exchange system is the recommended recycle system for the plating shop.

PROJECT DESCRIPTION

The Sacramento Air Logistics Center (SM-ALC), located at McClellan Air Force Base (AFB) in Sacramento, California, requested that the Idaho National Engineering Laboratory (INEL) perform an assessment of the technical and economic viability of a total recycle of the rinse water generated by the SM-ALC Plating Shop operation.

The project was motivated by McClellan AFB concerns over the quantity of water consumed during normal, daily plating operations (Slide 1). In addition, state and local enviromental regulations (e.g., California Proposition 65) that have been proposed regarding waste water treatment and disposal are increasingly stringent. The possible need for an upgrade of the McClellan AFB Industrial Waste Water Treatment Plant (IWWTP), where the rinse water from the plating shop is currently processed, would result in the curtailing or shutdown of plating shop operations. Therefore, the primary motivations for the assessment is the conservation of water and the continued operation of the plating shop.

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A recycle system for the plating shop rinse water could provide a number of benefits to the plating shop operation. The water consumption at the plating shop (approximately 180,000 gal/day), which represents about one-third of the total water consumption at McClellan AFB, could be reduced by 80 to 90%. This reduction by the plating shop would represent significant water conservation for McClellan AFB and the city of Sacramento. Also, a recycle system would eliminate the waste water stream to the IWWTP and effectuate an independent plating operation. If modifications to the IWWTP should become necessary to meet future enviromental regulations, the plating operation will not be affected. A recycle system that provides pure water and minimizes contaminants in the plating solution, would give flexibility to the plating operation if future regulations should require cleaner rinses. If rinsing control points remained the same, the use of purer water in rinsing could reduce water flows. A total recycle of the plating shop rinse water would allow AFB expansions, with little impact on public water utility. Finally, McClellan AFB public relations would be significantly improved by this upgrade.

DESIGN CONSIDERATIONS

Considerations in the adoption of a recycle system for the plating shop included available space for the system, the point of treatment, and future demands. The space available for the recycle system is 1,950 ft^2 inside the shop and 2,800 ft^2 outside. The inside space currently is used as a sandblasting area and will have to be renovated. The outside area currently is occupied by the bag-filter system for the sandblasting operation. It was decided that the point of treatment would be at end-of-pipe or at the waste water collection sumps (Slide 2). The waste water from the plating operation is divided into five streams: cadmium, chrome, acid/base, cyanide, and miscellaneous. The miscellaneous waste stream is the largest stream and is composed of any waste not classified under the other four streams. The miscellaneous waste may still contain traces of the other streams because most of the shop drains and condensate from the ventilation system for the plating tanks are routed to this tank or sump. The cadmium waste stream is currently processed by evaporation, with the condensate reused as rinse water and the concentrate used in the plating tank for evaporation makeup. The chrome waste stream is currently processed by ion exchange with the regeneration stream treated and transferred by underground pipe to the IWWTP. The rinse water recycle design will incorporate the option to process all five streams in the recycle system, but if current systems are functioning, they will remain in operation. Future design demands are included in the functional requirements for the recycle system.

Funtional Requirements

The functional requirements for the recycle process are as follows:

1. System must deliver water, deionized to the 1 to 2 micro-mhos (500K-1M ohm) range.

2. System must operate continuously (24 h/day) at 120,000 to 270,000 gpd (nominal) and be capable of operating at 325,000 gpd (maximum).

3. System must have an anticipated life of 20 yr.

4. System must be capable of converting liquid hazardous waste streams, the result of processing, to dry waste forms suitable for legal disposal.

5. System must have all necessary support components for removing dissolved solids such as toxic plating liquids, as well as particulates and trace organics.

6. System must be capable of returning to the use of service water if a long-term failure occurs in the ion exchange system.

7. System must be designed to comply with all existing applicable industrial, Federal, State of California, U.S. Department of Defense and U.S. Air Force codes and standards; McClellan AFB is classified Seismic Zone 3.

8. In the event of a power failure, system must be fail-safe and must not endanger the environment nor personnel.

Operational Requirements

The operational requirements for the recycle system are:

1) The system must operate automatically wherever possible to minimize operational manpower requirements.

2) The system must be capable of operating 24 h/day, 7 days/week.

3) Sufficient spare equipment must be available in the system to prevent operational shutdown due to normal anticipated equipment failure (e.g., pump seal failure), or to normal routine equipment maintenance.

4) The system must be capable of maintaining flow requirements at all times within its designed flow rate (120,000 to 325,000 gal/day), taking into account anticipated plating shop workload fluctuations during the 24-h period.

5) System must be designed to minimize personnel exposure to hazardous materials.

6) System must be designed to prevent adverse environmental impact due to system failure (e.g., containment of leaks), or to failure of services (e.g., electrical failure to building).

7) All system piping must be above grade.

TECHNICAL AND ECONOMIC ASSESSMENTS

Technical Assessment

After evaluating various options available for recycle of the plating shop rinse water, INEL has recommended that an ion exchange system be incorporated into the plating shop (Slide 3). All streams will be routed to the recycle system, with the option of processing the cadmium and chrome streams independently. The recycle process will prefilter the waste stream to remove suspended solids and organics. After prefiltering, the stream will be processed through the fixed-bed, ion exchange system and the resulting deionized water, will be collected in a storage tank for use as needed by the plating shop operation. The fixed-bed, ion exchange columns will be regenerated upon depletion. The regeneration solution will be collected and processed through the waste processing system. The resulting dry solid waste will be drummed and disposed of as solid hazardous waste.

The prefilter consists of a disposable filter medium that separates suspended solids from the solution and parallel carbon beds that removes organics from the solution. The ion exchange system consists of a feed tank with sufficient capacity to manage any surges in the flow from the plating operation, parallel fixed-bed, ion exchange units, and associated piping and pumps. The regeneration system consists of acid and base tanks, in-line mixers for blending the acid or base to desired concentration, a deionized water tank to provide water for rinsing and mixing, and associated piping and pumps. The deionized-water storage tank is a lined tank with parallel pumps to assure a constant water flow. The evaporator system consists of a feed tank with sufficient storage capacity, a preheater that heats the feed and condenses the steam from the evaporators, a rising film evaporator, a wiped film evaporator, demisters, and drums for the storage and disposal of the hazardous waste.

The proposed recycle system meets all the functional and operational requirements that were identified, but concern over the amount of waste generated from regeneration of the ion exchange columns has prompted an evaluation of a reverse osmosis unit that would function as a pretreatment before the ion exchange process. The two alternatives were considered in a technical assessment. Scheme 1 was the proposed ion exchange system with the cadmium treatment process still functioning and Scheme 2 was the proposed ion exchange system with a reverse osmosis unit as a pretreatment system. Laboratory studies were performed to verify the operability and performance of both schemes.

Laboratory Study of Ion Exchange

The ion exchange experimental setup consisted of a 100-gal feed tank, feed pump, prefilter, flow meter, cation resin bed, anion resin bed, conductivity meter, deionized water drum, regeneration acid and base containers, regeneration pump, and regeneration waste drum. The resin beds were scaled based on a cation bed, with an area flow rate of 10 gal/min/ft^2 as prescribed by the Illinois Water Treatment Company. A

1-in.-diameter glass column was used with a resin height of 10 in. for the cation column. A 1-1/4-in.-diameter glass column with a bed height of 10 in. was used for the anion column. A graph of the last four of the 19 performed runs (Slide 4) demonstrated the ability of the system to consistently produce a 2-micro-mho deionized water. Results from these tests verified that resin beds (a cation bed of 5 ft 10 in. high by 8 ft diameter and an anion bed of 15 ft-10 in. high by 9 ft 6 in. diameter), would be adequate to handle a 325,000 gal/day stream that has about a 250-ppm ion concentration. The regeneration of the bed would be required about once a week.

Laboratory Study of Reverse Osmosis

The reverse osmosis experimental setup consisted of a pressurized feed tank, reverse osmosis unit, permeate collection container, retentate control valve, and retentate collection container. Measurements for the system were pressure upstream and downstream of the reverse osmosis unit, differential pressure across the unit, permeate flow rate, retentate flow rate and permeate conductivity. The reverse osmosis unit was a high-pressure filter holder with a reverse osmosis membrane. A flow diverter was inserted into the holder to create a flow, parallel to the membrane surface. That was to simulate normal flow in a commercial reverse osmosis unit.

Two important design parameters for application of reverse osmosis in the recycle system are rejection and reduction. Rejection and reduction are defined as follows:

$$\text{Rejection} = \frac{C_F - C_P}{C_F} \times 100\%$$

$$\text{Reduction} = \frac{C_P}{C_F} \times 100\%$$

C_F = Concentration of feed

C_P = Concentration of permeate

Results of the reverse osmosis experiments indicated that a rejection of 90% can be achieved (Slide 5) and based on an evaporation experiment, precipitation will occur around 80%. Therefore, the operation parameters recommended from this study are a rejection of 90% and a reduction of 80%. Qualification of this statement is that the study was conducted with three different membranes that are commercially available at this time and that fouling of the membrane is assumed to occur at the point of precipitation.

Laboratory Results

Assessment of the process for each scheme indicated that both schemes will meet all functional and operational requirements that have been identified, space requirements for construction, and point-of-treatment specifications. Since both schemes have the ion exchange and evaporators as the final stages of the process to produce deionized water and solid waste, all requirements will be met. The space required for the addition of a reverse osmosis unit is approximately 9 ft high by 9 ft wide by 32 ft long and is speculated as being available. Both schemes were designed as end-of-pipe treatment. Differences in the schemes are in the process flow to the evaporators, the amount of solid waste generated, and the number of regenerations for the ion exchange beds (Slide 6). For Scheme 1, these values were 8,600 gal/day, 1,500 lb/day of waste, and 55 regenerations per year. For Scheme 2, these values were 6,500 gal/day, 700 lb/day of waste, and three regenerations per year. The performance of the reverse osmosis unit was 90% rejection and 80% reduction. The reduction in the amount of waste generated makes the addition of the reverse osmosis unite very appealing. However, the increased flow to the evaporator as a result of the reverse osmosis process will increase the costs of construction and operation. The solid waste disposal costs would perhaps offset the evaporator costs. An economical assessment was required before any conclusions could be made.

Economic Assessment

The two schemes were considered in an economic assessment (Slides 7a through d). Summary of the construction and operational costs indicated that Scheme 1 (ion exchange unit only) is much less costly but the amount of solid waste generated was about twice that of Scheme 2. Scheme 2, which would include a reverse osmosis unit before the ion exchange unit , was further investigated to determine what the design parameters would have to be for the economic consideration of a reverse osmosis unit. The primary design criteria, which regulated the equipment and operational costs were the rejection and the reduction parameters. The reduction affects the operational costs for regeneration of the ion exchange columns. A graph of the total cost of a system with a reverse osmosis unit with different rejection and reduction parameters (Slide 8) indicates that reduction affects costs significantly, whereas rejection affects costs only slightly. Comparison of these costs with the costs of Scheme 1 (Slide 9) indicated that the reverse osmosis performance would have to be very good (with a reduction of 99% and rejection of 99%) in order to have a lower overall cost at the end of the 20-yr life of the recycle system.

CONCLUSION

In conclusion, INEL recommends the ion exchange system as an end-of-pipe water recycle system for the plating shop. This recommendation is based on technical and economic evaluations. Technically, the ion exchange system will meet all functional and operational requirements that have been identified, can be constructed in the avialable space, and can provide end-of-pipe treatment for varying

waste stream flows and concentrations. Economically, the system will be the least expensive in overall total cost for the 20-yr life of the recycle system. A major concern will be the amount of dry solid waste, containing trace amounts of hazardous constituents, that will be generated by this process. Future requirements may call for the adoption of a process to recycle the hazardous constituents. However, for the current needs of our customer, this approach can provide a system that will satisfy immediate concerns until the proposed construction of a new plating facility is implemented. The ion exchange system can be incorporated into the new plating facility to provide the pure, quality water needed by the plating operation.

CONCERNS AND BENEFITS OF A RECYCLE SYSTEM IN THE PLATING SHOP

CONCERNS:

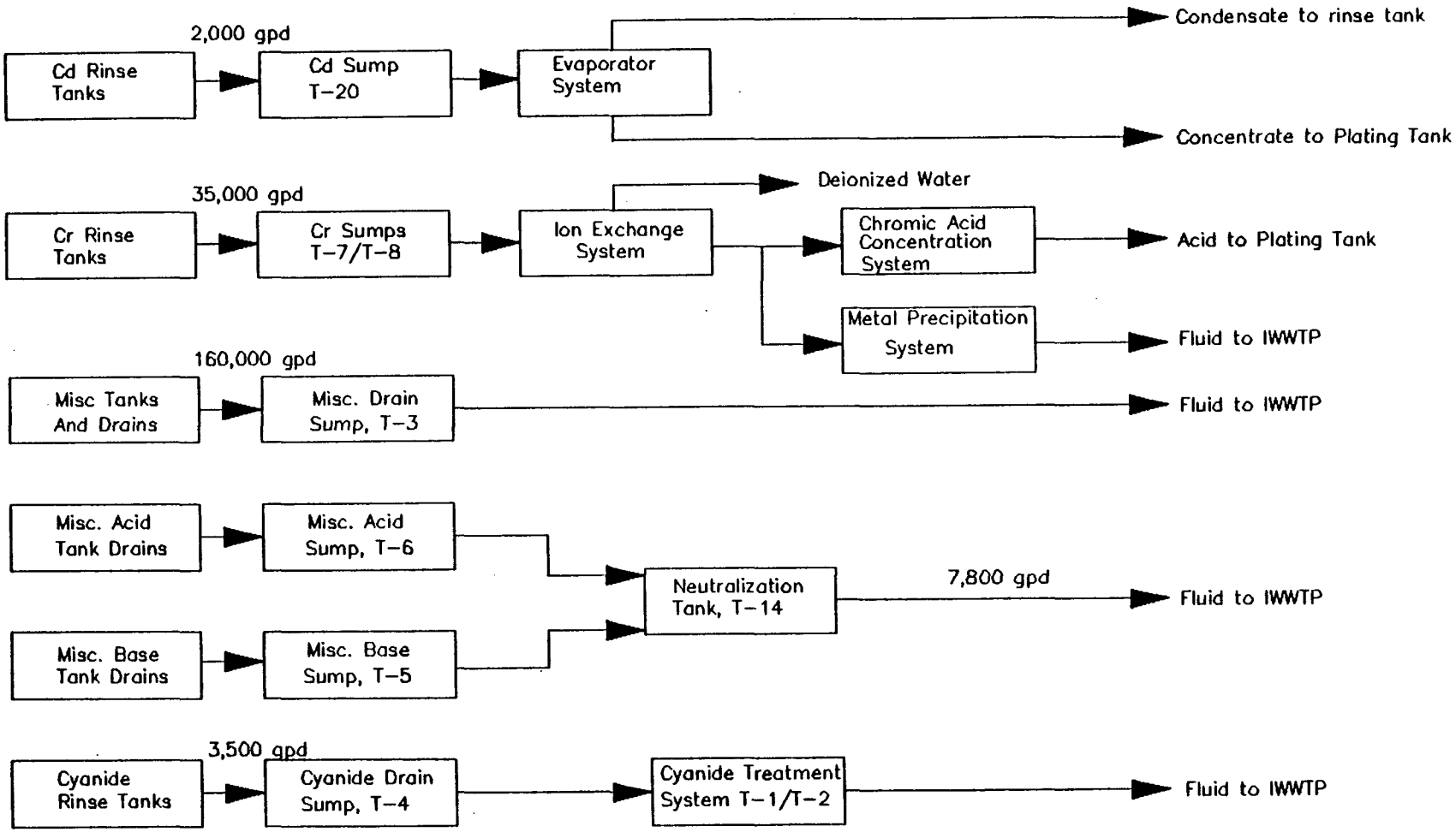
- QUANTITY OF WATER CONSUMED DAILY (180,000 GAL/DAY)
- INDUSTRIAL WASTE WATER TREATMENT PLANT OPERATION TERMINATED TO COMPLY WITH ENVIRONMENTAL REGULATIONS AND PLATING OPERATION TERMINATED UNTIL MODIFICATIONS ARE COMPLETED AND PERMIT RECEIVED
- CONTINUOUS OPERATION OF PLATING SHOP

BENEFITS:

- 80-90 PERCENT REDUCTION IN WATER CONSUMPTION
- INDEPENDENCE FROM INDUSTRIAL WASTE WATER TREATMENT PLANT
- DEIONIZED WATER FOR UTILIZATION IN PLATING OPERATION

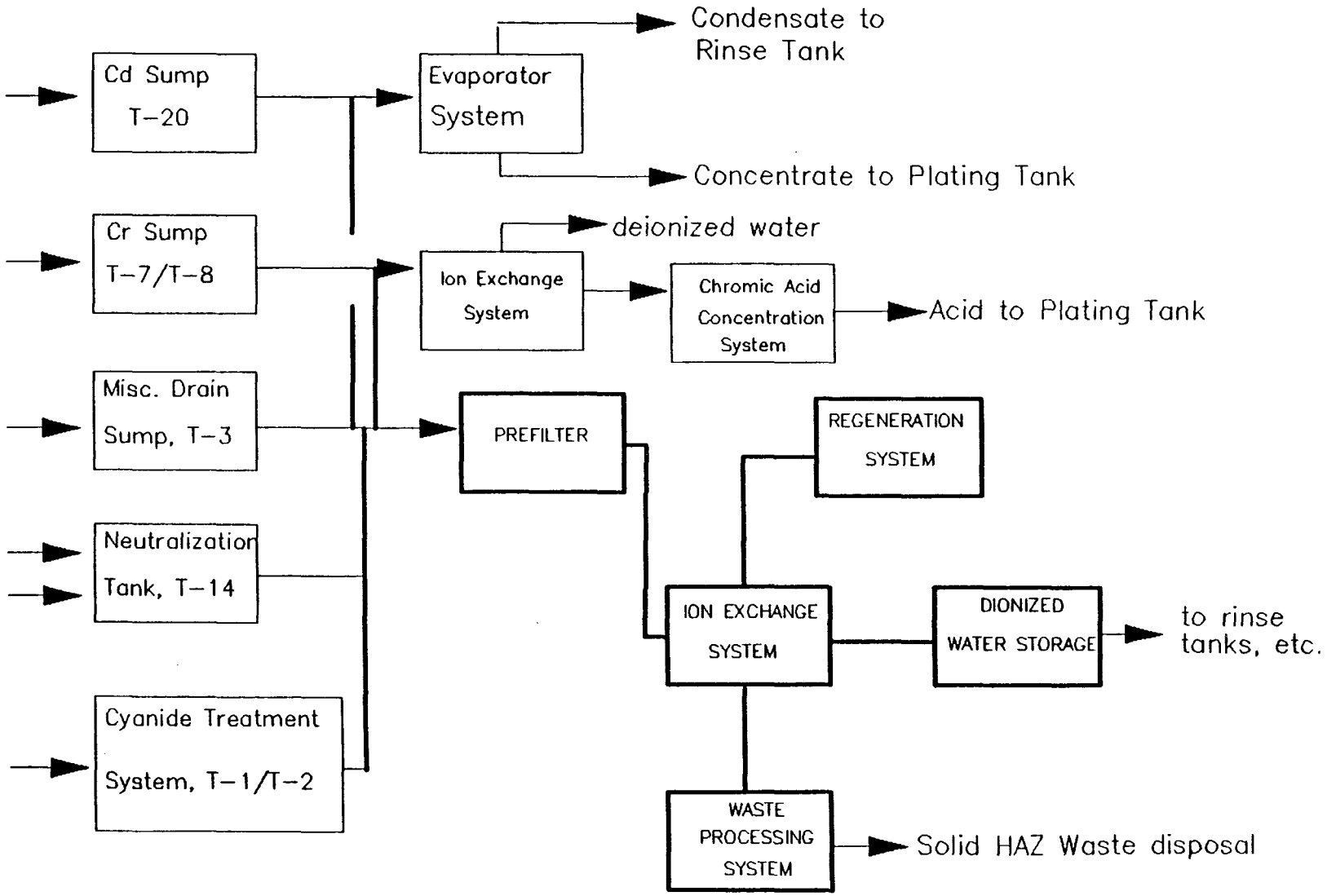
SLIDE 1

BLOCK DIAGRAM OF CURRENT PLATING SHOP EFFLUENT PROCESSING



SLIDE 2

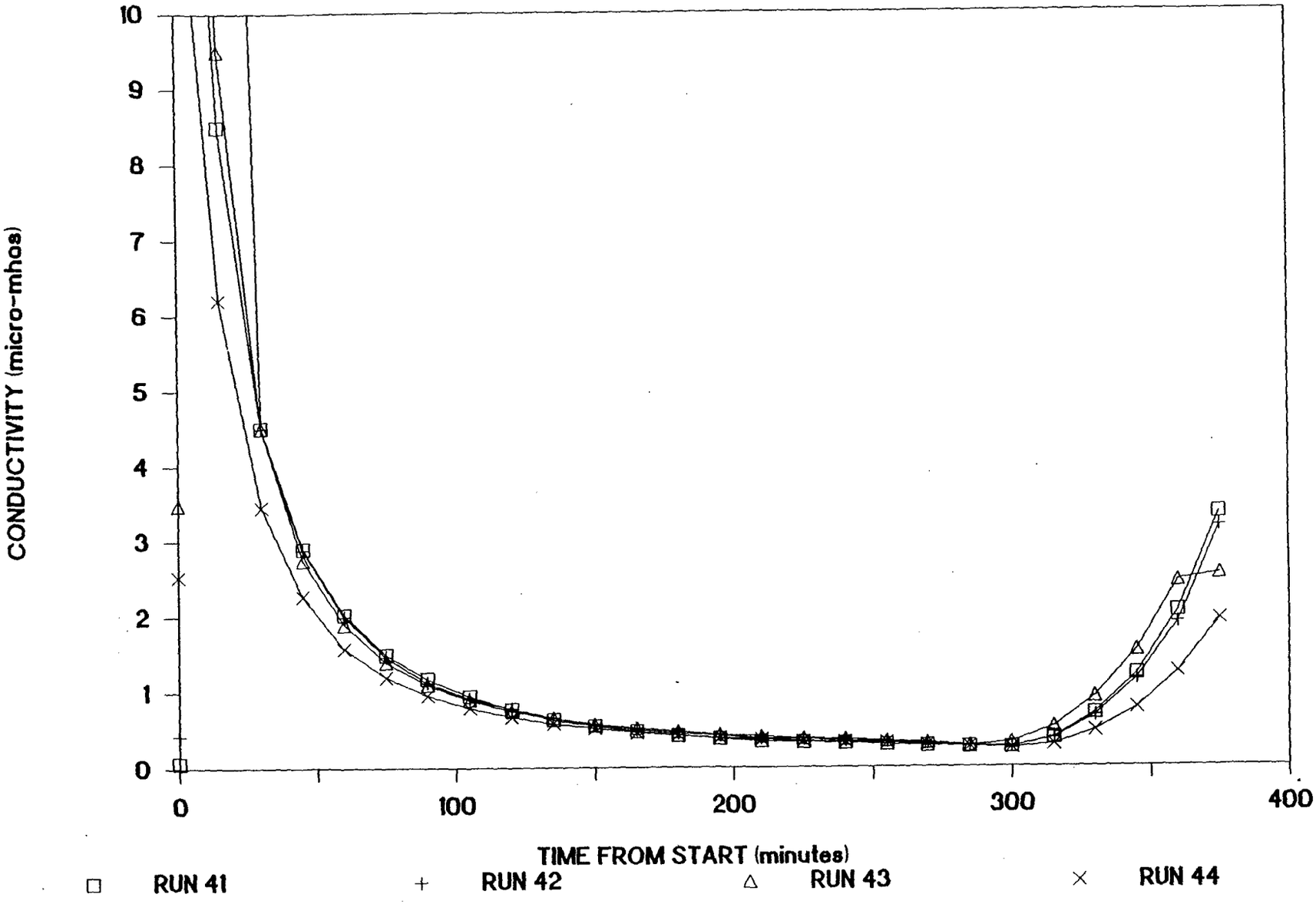
BLOCK DIAGRAM OF PROPOSED PLATING SHOP EFFLUENT PROCESSING



SLIDE 3

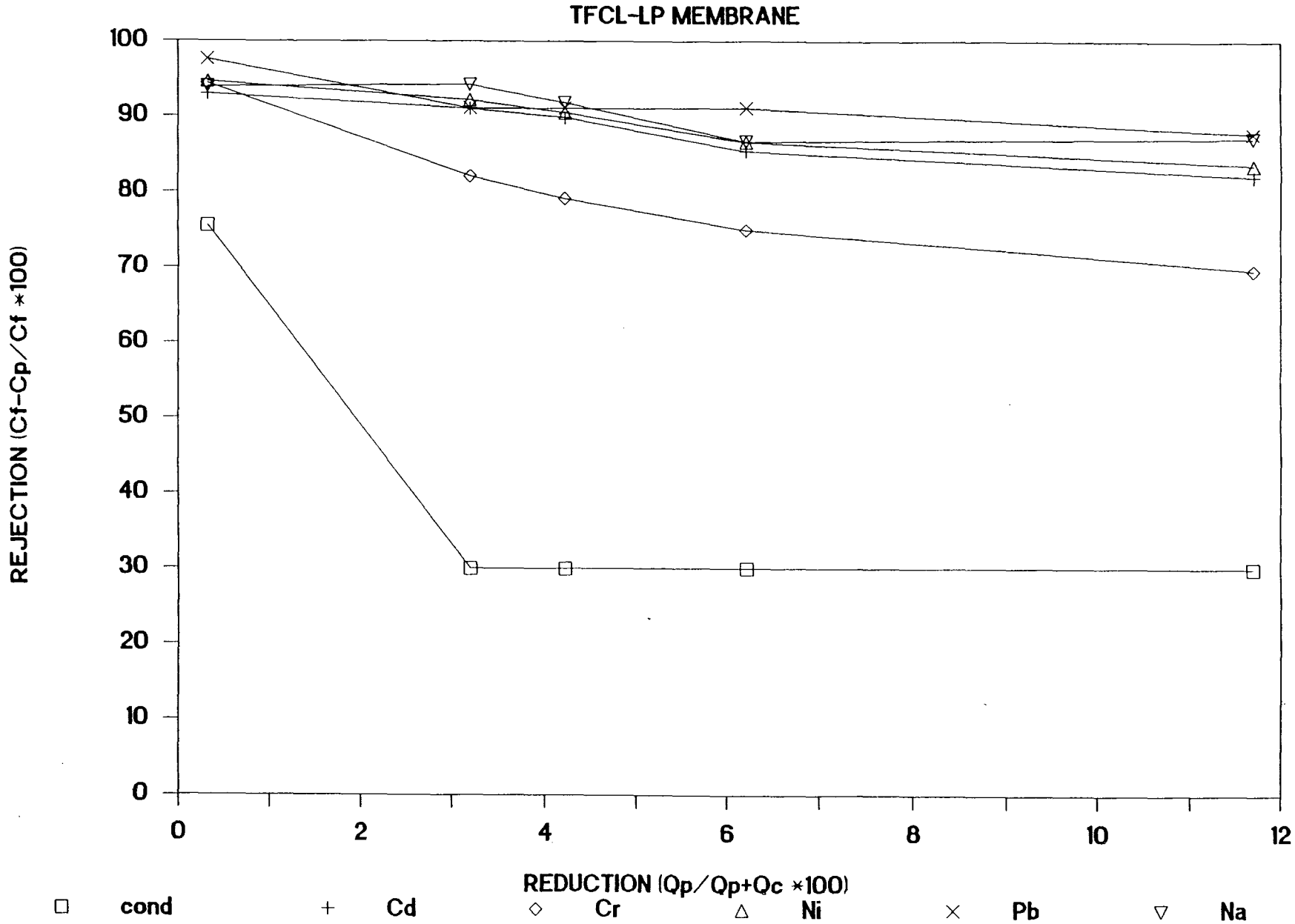
ION EXCHANGE SYSTEM CONDUCTIVITY TESTS

RUNS 41, 42, 43, AND 44.



SLIDE 4

REDUCTION AND REJECTION



SLIDE 5

TECHNICAL ASSESSMENT--PROCESS FLOWS DIFFERENCES IN SCHEME ALTERNATIVES

PARAMETERS	SCHEME 1	SCHEME 2
FLOW RATE TO EVAPORATORS (GPD)	8600	65,000
SOLID WASTE (LB/DAY)	1500	700
NUMBER OF REGENERATION PER YEAR	55	3

SLIDE 6

COST COMPARISON FOR SCHEMES

ITEM LABOR MATERIAL	SCHEME 1	SCHEME 2
BUILDING MODIFICATION		
	13,240	13,240
	67,000	67,000
RESIN BEDS		
	4,800	4,800
	320,200	320,200
OTHER TANKS		
	12,560	12,560
	110,000	110,000
PUMPS AND PIPING		
	54,260	54,260
	59,400	59,400
RISING FILM EVAPORATOR		
	600	600
	150,000	940,000
WIPED FILM EVAPORATOR		
	600	600
	350,000	2,420,000
FILTER SYSTEM		
	8,480	8,480
	54,000	54,000
CARBON SYSTEM		
	0	0
	239,200	211,600
OTHER		
	2,640	2,640
	370,000	370,000
REVERSE OSMOSIS		
	0	81,500
	0	600,000
SUBTOTALS		
LABOR	97,180	178,680
MATERIAL	1,719,800	5,152,200
OVERHEAD AND PROFIT	320,400	320,400
TOTAL	2,137,380	5,651,280

SLIDE 7a

ESTIMATED MATERIALS, CHEMICALS, POWER, AND STEAM (ANNUAL BASIS)

ITEMS	SCHEME 1	SCHEME 2
OPERATOR COSTS:		
MAN HOURS	2,022	3,762
DOLLARS ($27/HR)	54,600	101,570
MATERIALS:		
FILTER MEDIA	13,000	11,000
SAFETY EQUIPMENT	1,000	1,000
ACTIVATED CARBON	213,000	177,000
55 GALLON DRUMS ($42)	35,000	16,207
MEMBRANE	0	60,000
CHEMICALS:		
NAOH ($215/T)	21,000	320
HCL ($90/T, 36%)	22,000	340
CALIBRATION CHEM	2,000	500
MEMBRANE CLEANER	0	5,000
ELECTRICAL POWER:		
480 V @ $.08/KW	7,680	15,380
STEAM:		
$10/MBTU	106,000	1,316,699
HAZARDOUS WASTE DISPOSAL		
$226/DRUM;450 LB/DRUM	188,400	87,210
AMOUNT (LB/DAY)	1,500	695
TOTAL:	663,680	1,792,227

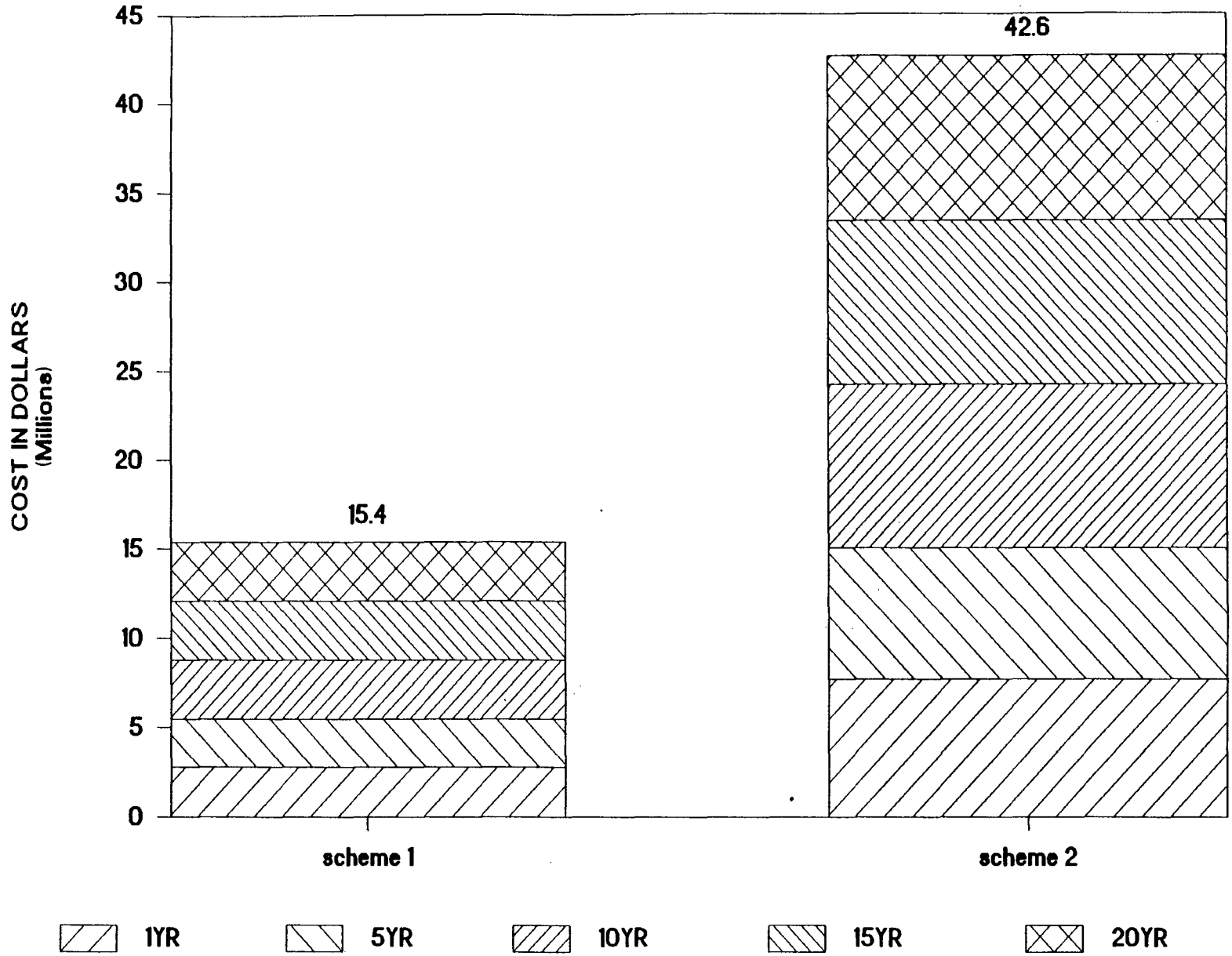
SLIDE 7b

ESTIMATES OF COSTS FOR FIRST YEAR, 5 YEARS, AND 10 YEARS

SCHEME	CONSTRUCT COST	ANNUAL OP COST	FIRST YR $ TOTAL	WASTE LB/DAY	5 YR $ TOTAL	10 YR $ TOTAL
SCHEME 1	2,137,380	663,680	2,801,060	1500	5,455,780	8,774,180
SCHEME 2	5,651,280	1,792,227	7,443,507	695	14,612,413	23,573,546

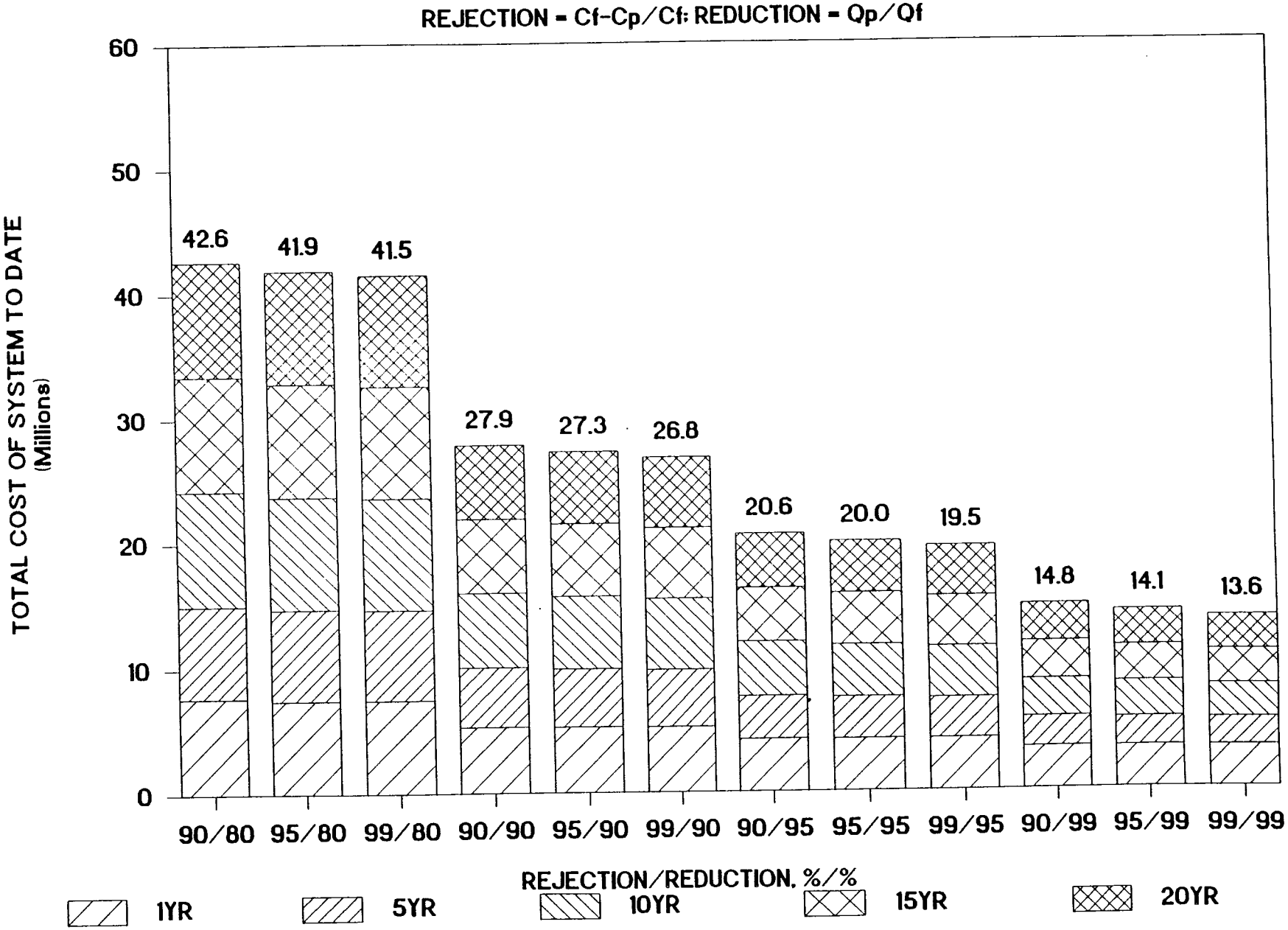
SLIDE 7c

20 YEAR ACCUMULATIVE TOTALS



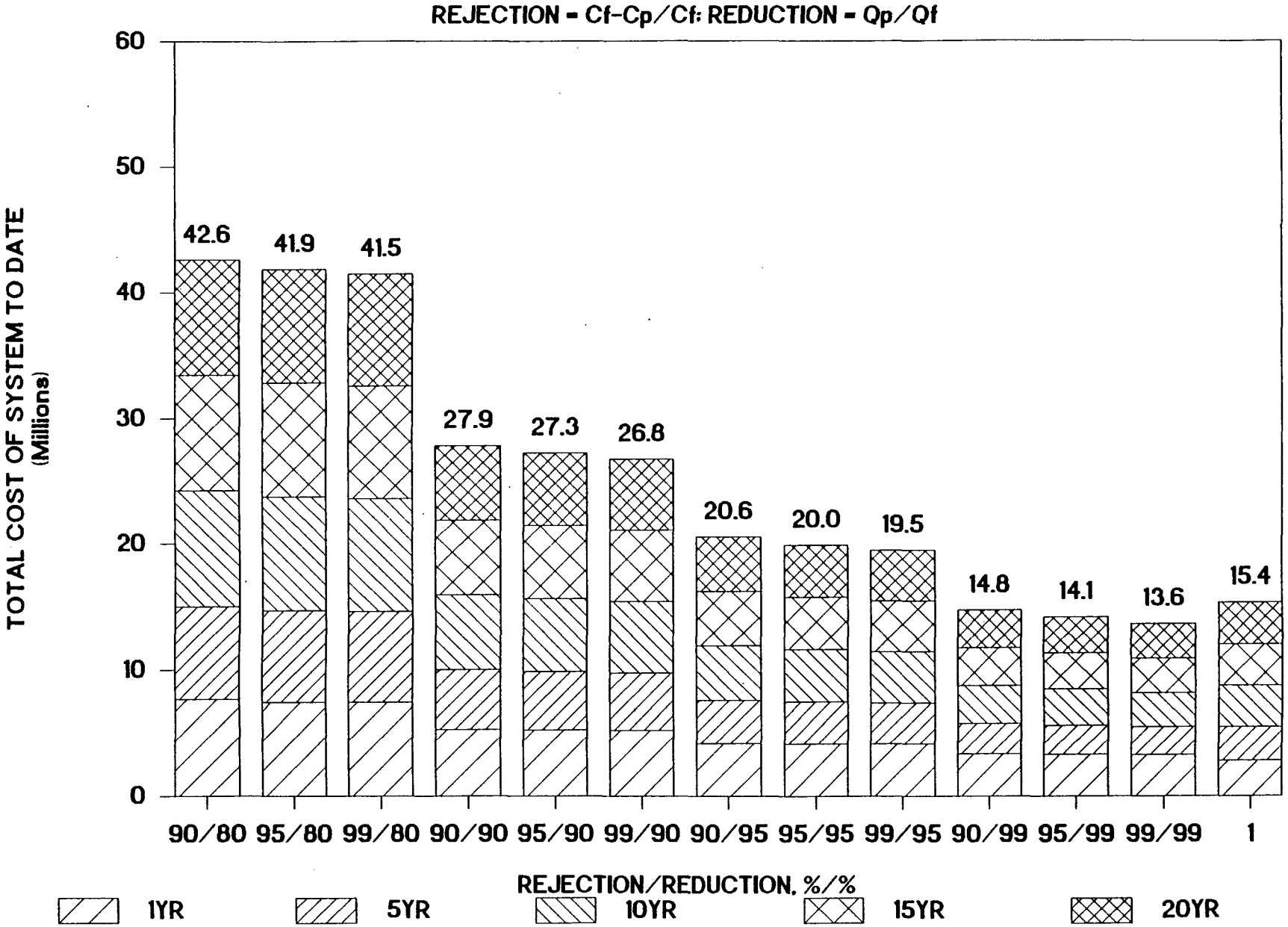
SLIDE 7d

COST EVALUATION OF RO PERFORMANCE



SLIDE 8

COST EVALUATION OF RO PERFORMANCE



SLIDE 9

COMPOSTING OF EXPLOSIVES CONTAMINATED SEDIMENTS

Richard T. Williams and P. Scott Ziegenfuss,
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and Gregory B. Mohrman and Wayne E. Sisk, U.S. Army
Toxic and Hazardous Materials Agency

A field-scale demonstration was conducted to investigate composting as a technology for remediating explosives contaminated sediments. Test sediments contained approximately 76,000 ppm of total explosives, including TNT (66% of total explosive), RDX (25%), HMX (9%), and tetryl (0.3%). The mixture that was composted consisted of straw/horse manure, alfalfa, horse feed, and sediment. Two 12 cubic yard piles were constructed, one was maintained at approximately 35°C and the second at approximately 55°C. After 22 weeks, total explosives were reduced by 99% (from 17,872 to 74 ppm) in the thermophilic (55°C) pile. Transformation products peaked in concentration at approximately 20 days and subsequently fell to near detection limits.

INTRODUCTION

The manufacture and handling of explosives and propellants has resulted in soil and sediment contamination at U.S. Army munitions facilities, often as a result of previously acceptable waste disposal practices. The United States Army is currently investigating several technologies for decontaminating propellant- and explosives-contaminated soils. Among these candidate technologies is composting.

Composting is a process during which organic materials are biodegraded, resulting in the production of organic and/or inorganic transformation products and energy in the form of heat. This heat is trapped within the compost matrix, leading to the self-heating that is characteristic of composting. Composting for the purpose of hazardous substance destruction is initiated by mixing a matrix contaminated with biodegradable compounds (explosives in the present study) with organic carbon sources and bulking agents, which are added to enhance the porosity of the mixture to be composted.

Contaminants of concern at the Louisiana Army Ammunition Plant (LAAP) include 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), and N-methyl-N,2,4,6-tetranitroaniline (tetryl). These explosives are found as contaminants in lagoon sediments as a result of the disposal of "pink water", which is generated during munitions packing and loading operations.

Previous research has indicated that TNT is microbially transformed, but is not completely mineralized to inorganic products [1,2,3]. Conditions that have been found to enhance the biotransformation of TNT include high organic carbon concentration and aerobic conditions [4]. Microbes generally catalyze nitro-group reduction of the TNT molecule [5]. A number of TNT biotransformation products are known. Evidence exists that these metabolic transformation products adsorb strongly to organic materials [6].

Anaerobic conditions and high organic carbon content have been found to enhance the biotransformation of RDX and HMX [4,7]. Laboratory-scale composting studies with ^{14}C-RDX have demonstrated high levels of $^{14}CO_2$ production (37 to 46 percent of initial ^{14}C activity added), suggesting ring cleavage and complete mineralization [8].

The primary objective of this study [9] was to evaluate the utility of aerated static pile composting as a technology for remediating soils and sediments contaminated with the explosives TNT, HMX, RDX, and tetryl. Secondary objectives included a comparison of the efficacy of mesophilic (35°C) versus thermophilic (55°C) composting, evaluating different materials handling and process control strategies, and determining transformation products when Standard Analytical Reference Materials (SARMs) were available.

MATERIALS AND METHODS

Two 8-inch-thick concrete test pads were constructed 20 feet apart adjacent to the pink water lagoons at LAAP. Drainage channels in the pads were connected to a sump located below grade. Water from the sump was reapplied to the compost piles.

The mixture to be composted was prepared using horse manure and soiled bedding (straw), alfalfa, horse feed (Purina Balanced Blend 14), and contaminated sediment. Sawdust, wood chips, and baled straw were used to construct bases and insulating covers (see Figure 1).

A mechanical feed system, developed initially to meter explosives-contaminated soil into an incinerator, was used to homogenize sediment and to mix the material to be composted.

Dual-channel strip-chart recorders (Omega Engineering) were used to continuously record compost temperatures. Two landfill thermocouple probes (Atkins Technical) were placed in each pile. One probe was placed 2 feet inside each pile, 3 feet above pad level, and 2 feet from the blower end of the pile. The other probes were inserted into the center of each pile. A landfill probe equipped with a hand held digital thermometer was used to monitor temperatures daily at 6 locations in each pile.

Each compost pile contained a system of perforated and nonperforated ADS polyethylene drainage tubing (4-inch diameter) placed on top of a wood chip base and connected to an explosion-proof radial-blade blower. The blowers were used to pull air through the compost piles. Blower cycling was controlled by both timer and temperature feedback systems. The temperature feedback system consisted of soil thermistors that measured compost temperature and panel-mounted Fenwal series 551 thermistor sensing temperature controllers.

The mixture to be composted was prepared as follows. Sediment (excavated and homogenized 2 weeks previously and analyzed for explosives concentration) was reprocessed through the feed system once. Horse feed was mixed into the sediment on the mixing pad using an excavator bucket. Straw/manure, alfalfa, and 35 pounds of fertilizer that contained nitrogen, potassium, and phosphorus (13/13/13) were added to the mixture. The mixture was mixed using an excavator and front-end loaders for 30 minutes. The mixture was processed through the feed system once. Each load of compost was moistened with water as it was delivered to the pads. Approximately 400 gallons of water were applied to each compost pile.

Pile construction was completed and the temperature control systems and recorders started on 25 February 1988. Samples were analyzed for contaminant concentration nine times over a 153-day test period. The compost piles were individually dismantled, remixed, and remoistened at day 33, 60, and 111.

Analyses for lead, selenium, and arsenic were conducted by procedures in Standard Methods for Chemical Analysis of Water and Wastes (U.S. EPA 600/4-79-020, 1979). Compost samples were analyzed for TNT, RDX, HMX, tetryl, and transformation products by USATHAMA Method LW02, modified for the extraction and analysis of compost.

RESULTS

The sediment contained TNT (56,800 mg/kg), RDX (17,900 mg/kg), HMX (2,390 mg/kg), and tetryl (650 mg/kg). The sediment was combined with the other components of the mixture to be composted according to the materials balance presented in Table 1.

Total explosives concentrations in piles 3 and 4 at the beginning of the study were 16,460 and 17,870 mg/kg, respectively. After 153 days, the concentration of total solvent extractable explosives in pile 4 was 74 mg/kg. A linear plot of total explosives concentration versus time for the thermophilic pile is presented in Figure 2. The mean and standard deviation at each time point represents at least three and as many as nine replicate samples.

Day zero compost samples were analyzed for TNT transformation products. Concentrations of transformation products in these samples peaked in concentration at approximately 20 days and subsequently fell to near detection limits.

The appearance of the compost changed considerably over the 153-day test period. When the compost was initially mixed, it had a highly fibrous appearance, a rough texture, and it smelled conspicuously of the manure, urine, and feed used to prepare it. After approximately 100 days, the compost had become more soil-like and less fibrous in appearance. At the end of the test period, the compost had both the appearance and smell of loamy soil.

DISCUSSION

The concentration of solvent-extractable total explosives was significantly reduced during the 153-day test period. Fate mechanisms that may have been responsible for contaminant reduction include sorption of explosives and transformation products to the compost matrix, incorporation of explosives and transformation products into environmentally stable molecules, and mineralization of explosives to carbon dioxide, water, and other inorganics.

Previously published literature indicates that biotransformation of TNT, RDX, and HMX does occur. However, with the exception of RDX [8], significant mineralization of these compounds has not been demonstrated. Work by Kaplan and Kaplan [6] indicated that incorporation of chemically reactive transformation products into compost matrices increased with increasing compost age and was the primary fate process involved in explosives composting. These studies were, however, conducted at laboratory scale in externally heated flasks. Consequently, microbial community development and the corresponding metabolic activity may have been less than that observed in a large scale compost. The significance of mineralization in the present study cannot be determined from the data generated.

Previous research on explosives composting with ^{14}C-labeled test materials has demonstrated extensive (and apparently nonreversible) binding of ^{14}C activity to a compost matrix over time [3,8]. In one study [8], less than 1 percent of the initial ^{14}C activity (spiked as ^{14}C-TNT into compost) was recovered as $^{14}CO_2$ after 6 weeks of composting, while 66 percent of the ^{14}C activity became bound to the compost matrix and was unextractable. The production of organic transformation products from TNT, RDX, and HMX is well documented [10,11]. In the present study, TNT transformation products were detected in initial compost samples, increased in concentration over the first several weeks of the test period, and decreased to low mg/kg levels thereafter. These data do not support one environmental fate process over another.

The results of this field demonstration indicate that composting is a feasible technology for reducing the extractable explosives/transformation products concentrations in contaminated soils and sediments. Consequently, composting may be a suitable technology for remediating explosives-contaminated soil and sediment. The compost residue, however, must be acceptable for disposal in a manner which makes composting cost effective. Additional chemical characterization of the residue as well as residue toxicity studies are recommended.

Acknowledgement - The authors thank W. Sniffen, L. Morse, E. Schaefer, G. Perry, and E. McGovern for technical support. This work was sponsored by the U.S. Army (contract purchase order No. DAAK11-85-D-0007). The views, opinions, and findings contained in this publication are those of the authors and should not be construed as an official Department of the Army position, policy, or decision unless so designated by other documentation.

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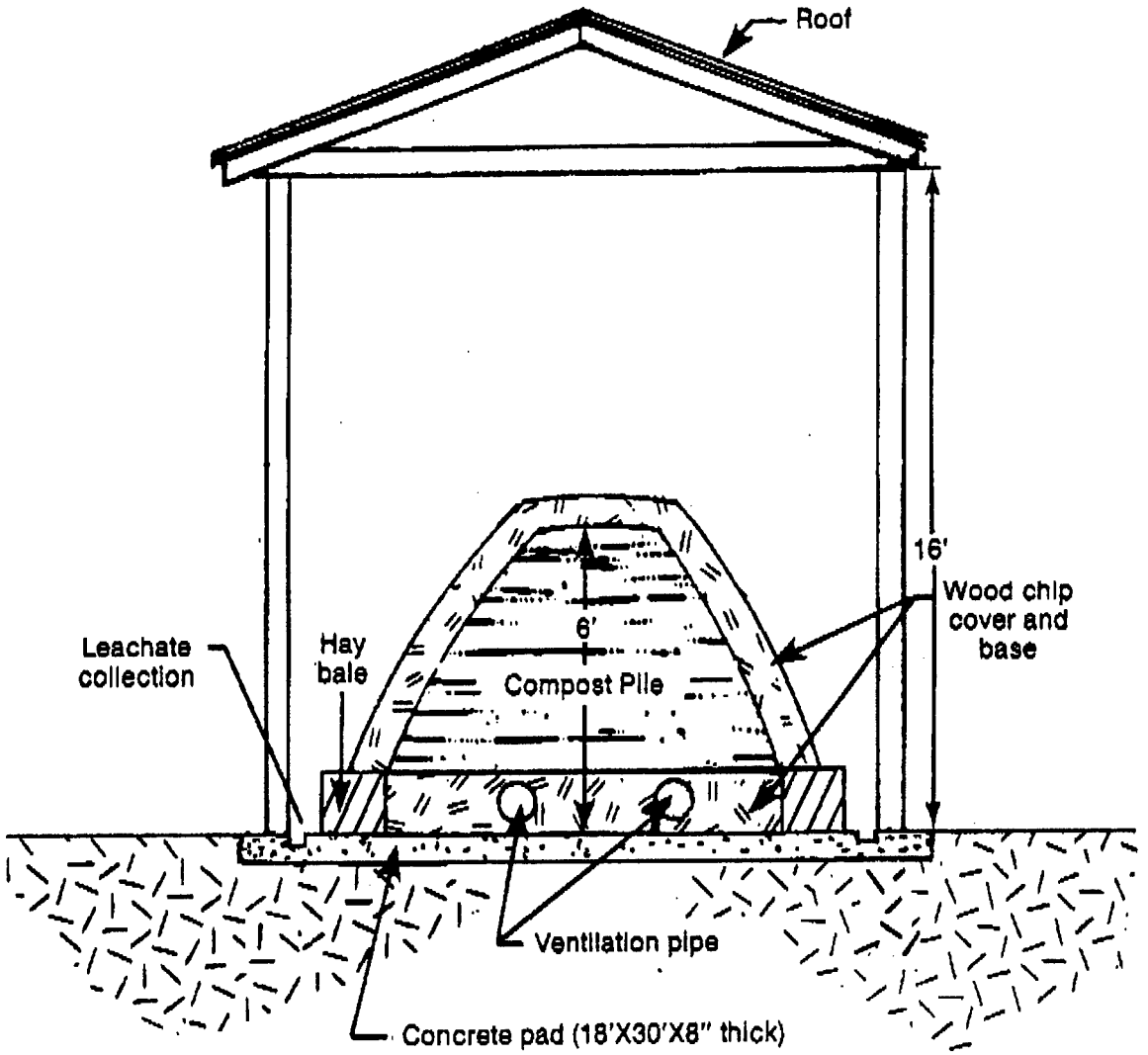
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TABLE 1

Materials Balance of Mixture to be Composted

Material	Volume (cu yd)	Mass (lb)	Volume (percent)	Mass (percent)
Sediment	1	2,300	3	24
Alfalfa	13	940	38	10
Straw/manure	16	2,480	47	25
Horse feed	4	4,000	12	41
Total	34	9,720	100	100



Note: Schematic only, not to scale.

Figure 1. Cross-sectional schematic of compost pile with roof, Louisiana Army Ammunition Plant.

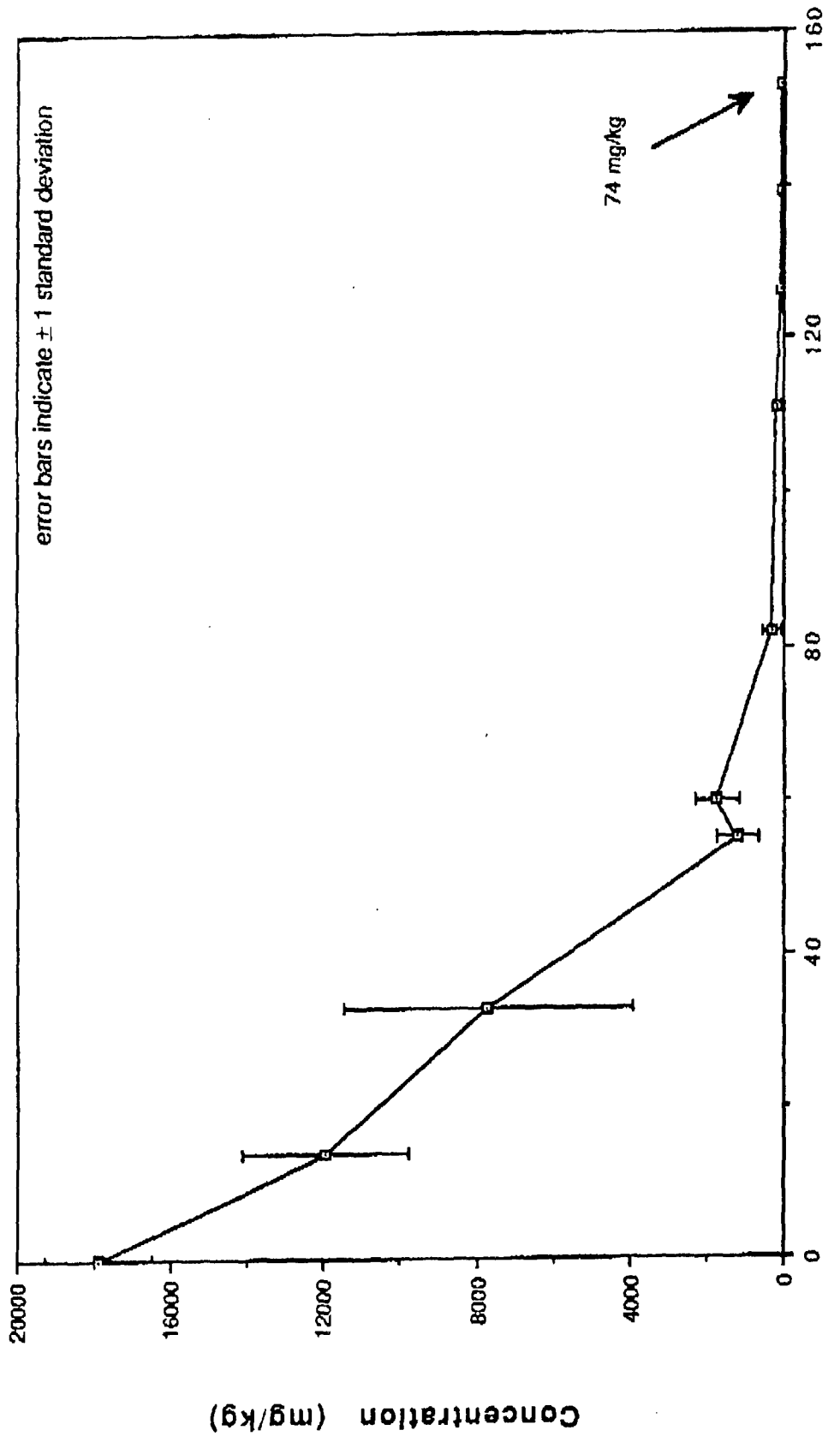


Figure 2. Concentration of Total Explosives in Thermophilic Compost Pile.

ANNULAR CENTRIFUGAL CONTACTORS AS RAPID OIL-WATER SEPARATION DEVICES[1]

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ABSTRACT: The results of preliminary tests to apply devices known as annular centrifugal contactors to the rapid separation of oil-water mixtures are presented. Separation efficiencies of oil from water of >99% have been demonstrated on both light and heavy oils. Equilibrium within the separating zone of the contactor is reached within seconds. Dynamic testing in which water to oil flow ratios of 1:5 and 5:1 have been conducted without loss of performance. The laboratory scaled contactors tested have total throughput of 80 cc/min. The design and construction of larger devices with total throughputs of hundreds of gallons per minute is feasible. Such contactors would be compact units capable of allowing rapid recovery from a broad range of hydrocarbon spills on waterways. The efficiency of these contactors is such that water discharged can be returned directly to the environment. Recovered hydrocarbons may be useful without further refinement.

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1. This work was performed under DOE contract DE-AC07-76ID01570.

INTRODUCTION

Annular Centrifugal Contactor technology began approximately twenty years ago as faster methods of solvent extraction were explored by radiochemists (Rydberg 1969). Early devices consisted of a phase mixer coupled to a motor driven centrifuge for rapid phase separation. Centrifugal contactors are devices which allow mixing and subsequent disengagement of two phases within a single unit. Many designs have been studied for applications ranging from the pharmaceutical industry to nuclear fuel reprocessing. An evaluation and comparison of various centrifugal contactor designs with other types of solvent extraction devices was made at Battelle labs over ten years ago (Browne and Geier 1977).

Since that time, contactor design and technology has been pursued primarily by those associated with nuclear fuel reprocessing. Chemical engineers at Argonne National Laboratory, Savannah River Laboratory and Oak Ridge National Laboratory have studied and refined the design of these devices for more than eighteen years. As such, much information is available in the form of progress reports from each laboratory which details the contributions of those engineers to contactor technology.

EXPERIMENTAL

The Chemical Engineering Division of Argonne National Laboratory designed the miniature annular centrifugal contactors used in these studies (Leonard, Bernstein, Zeigler and Pelto 1980). A schematic drawing of one of these contactors is shown in Figure 1. This particular contactor employed a 2.1 cm (outside diameter) rotor, 3.5 cm in length.

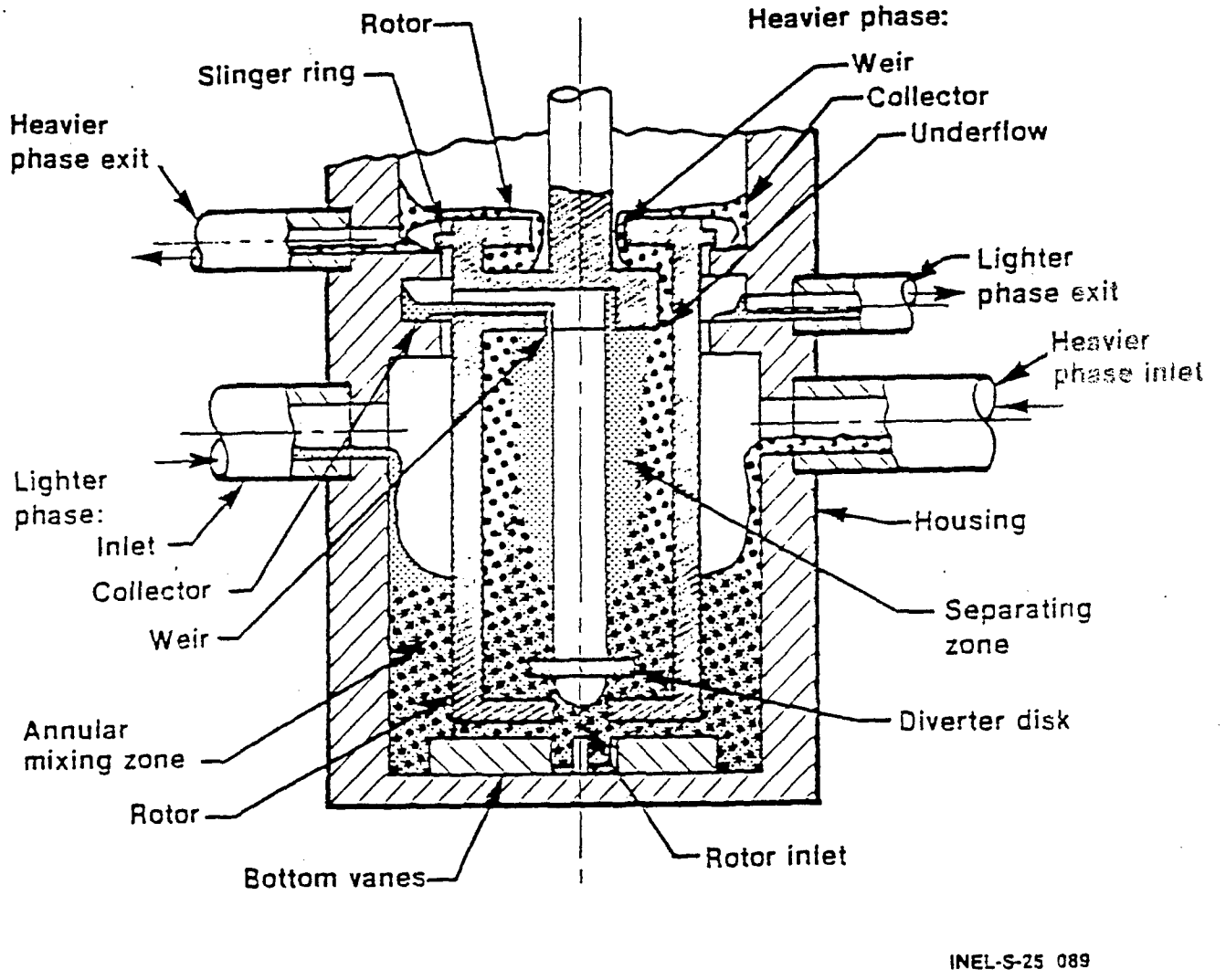


Figure 1. Schematic of the Annular Centrifugal Contactor.

In operation, aqueous and organic solvents are pumped into the side inlet ports, and are mixed by skin friction in the annulus between the rotor and the casing. Radial vanes in the base of the casing inhibit fluid rotation beneath the rotor and direct the mixture upward into the rotor. Vertical baffles inside the rotor quickly accelerate the rising mixture to rotor speed. The mixed phases are centrifuged, producing a double vortex with the heavier phase at the perimeter. Internal circular weirs direct the separated phases to collector rings in the housing from which each phase exits through a tangential port near the top.

As this device was developed for rapid solvent extraction applications, the figure shows separate organic and aqueous phases entering the annulus. Laboratory tests to determine the contactor's efficiency as an oil-water separator were made by introducing the two phases separately. However this was only an experimental convenience to allow controlled study of the affect of various organic to aqueous flow rates. Mixing in the annulus is quite vigorous under all rotor speeds tested and would more than simulate oil-water mixtures introduced into the unit from environmental pickup devices and pumps. Under actual spill recovery operations the oil-water mixture would be fed into both inlet ports of the contactor, simultaneously. The additional mixing of the oil and water in the annulus does not affect separation performance. In fact, it may help establish the equilibrium for centrifugal separation inside the rotor.

The laboratory contactors used for these tests are fitted with a bottom drain and valve to allow emptying of the contactor between

experiments. Experiments were conducted to bypass the annular mixing chamber by plumbing the oil and water into the bottom drain using a "T" connection. Under these conditions, equilibrium could not be attained under any conditions of rotor speed and pumping rates. Cross-contamination of the two phases was extensive and further efforts to bypass the annular mixing zone were abandoned.

The first series of tests were conducted on No. 1 diesel fuel. Separate phases were pumped to the inlets of the contactor body using positive displacement piston pumps from Fluid Metering Inc. Total flow rates did not exceed 80 cc/min. A clear plastic body was used to allow visual identification of flooding in the annulus and to observe the extent of two phase mixing. Various flow ratios were tested by varying the pumping rate of a single pump while the contactor was running at equilibrium. The rotor speed for this series of tests was 2900 rpm. Bromcresol green (0.04%) indicator solution was added to the water to enhance visual detection of phase cross-contamination. A series of visual standards were prepared ranging from 1 to 5% oil in water and water in oil. All estimates of phase separation were visually determined by comparison to these standards. The results of this test set are typical of most experiments run and are presented in Table 1. Organic to aqueous ratios (o/a) were adjusted by reducing the pumping rate of one phase while leaving the other phase flow-rate fixed. As such maximum flow was tested only at o/a = 1. However, capacity values at various o/a ratios from 0.1 to 10 have been reported to range from 80-200 cc/min. for contactors of this size and design (Leonard, Bernstein, Zeigler and Pelto 1980b). The maximum throughput appears at o/a ratio = 2.0.

TABLE 1

Organic / Aqueous (o/a) ratio	Flow rate cc/min.	Visual Phase purity % Aqueous	Organic (No.1 Diesel)
10	44	100	90
5	48	100	>95
3.3	52	100	>98
2.5	56	100	>98
2.0	60	100	>98
0.1	44	100	100
0.2	48	100	100
0.4	56	100	100
0.75	70	100	>95
0.9	76	100	>98
1	80	100	>98

Tests were then conducted on S.A.E. 30-30W motor oil to evaluate the contactor's efficiency on heavier (higher viscosity) oils. The experiment was conducted as described for No. 1 diesel after several operating parameters were established. Rotor speed was lowered to 1900 rpm and total throughput rates were halved to 40 cc/min. Equilibrium was rapid and stable throughout various o/a ratios. However, the detergent additives in the motor oil caused some irreversible emulsification which made estimates of separation efficiency difficult. Therefore, further testing employed a standard grade of mechanical vacuum pump oil as the

higher viscosity organic phase. The viscosity was not labelled however the advertised pour point is -15° C. It appears slightly less viscous than S.A.E. 30-30W at room temperature.

Oil-water separation tests made using mechanical pump oil were quite successful at rotor speeds of 1800-2400 rpm and flow rates of 40 cc/min total. Testing also indicated that high viscosity products could be efficiently separated from water with very little cross phase entrainment when detergent additives were not present. As before, flow rates were varied from o/a = 0.25 to 4.0 with no loss of contactor equilibrium.

An Argonne modification to the above tested annular centrifugal contactor employed a 4.4 cm long rotor. Tests were also conducted with this contactor on No. 1 diesel and mechanical pump oil. It appears that the longer rotor allows higher total throughput although no effort was made to exceed 80 cc/min on the No. 1 diesel tests. Separation performance was as good or better than with the contactor employing a 3.5 cm long rotor. Tests on mechanical pump oil showed improved performance and throughput. After reaching equilibrium at a total oil-water throughput of 40 cc/min and o/a = 1, the pumping rate could rapidly be increased a factor of 2 to 80 cc/min without loss of equilibrium or separation efficiency. The optimum rotor speeds were 2400 rpm and 4200 rpm for separations employing mechanical pump oil and No. 1 diesel, respectively.

FUTURE STUDIES

Larger scale studies and demonstrations are planned. Engineers at Oak

Ridge National Laboratory have gained considerable experience operating 12 cm diameter rotor contactors. These larger units have throughput of 5-9 gallons per minute (Demuth, Jubin and Ladd 1988). A set of engineering drawings of the 12 cm rotor contactor are being updated and will be sent to the INEL. Current plans are to build one of these contactors and test its efficiency and capacity using a surface skimmer oil pickup device.

The ultimate goal of this program is to design, build, and test an annular centrifugal contactor capable of separating oils, solvents and fuel with a throughput of 200-400 gpm.

The engineers at Oak Ridge National Laboratory have developed a empirical formula for estimating contactor capacity:

$$Q = .044d^{2.443}$$

Where Q is total throughput in L/m and d is rotor diameter in cm. This relationship shows that the contactor capacity can be dramatically increased by a small increase in rotor diameter. Naturally there are other factors which impact upon throughput, primarily rotor speed, but in general this formula should suffice for estimating purposes. Table 2 provides a number of convenient sizes and their calculated throughput.

TABLE 2

Rotor diameter	Estimated Total Throughput
16" (40 cm)	95 gpm (360 L/m)
20" (50 cm)	164 gpm (622 L/m)
24" (60 cm)	257 gpm (972 L/m)
30" (76 cm)	457 gpm (1731 L/m)

CONCLUSIONS AND RECOMMENDATIONS

The results of these brief laboratory experiments are quite favorable. Equilibrium within the contactor is reached within seconds and phase separation approaches 100% under proper conditions of rotor speed and pumping rate. Scale-up to larger devices is feasible with only minor engineering effort since no design modifications from the 12 cm diameter rotor contactor are anticipated. These larger units have the additional feature of an air weir which allows further control of the organic/aqueous interface within the separating zone of the rotor. (The laboratory scale contactors tested are too small to allow for incorporation of this feature.)

Therefore, continued development of this device should be pursued as an environmental tool to be used in conjunction with surface skimmers to recover from organic spills in lakes, oceans and waterways. It also has potential applications as a selective solvent extraction device for the removal of hazardous metals from impoundments and process waste streams.

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TREATMENT OF HEAVY METALS CONTAMINATED SOILS BY ROASTING

By

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INTRODUCTION

Roasting was first identified as a promising technology for the treatment of heavy metals contaminated soils in a study conducted by WESTON for the U.S. Army Toxic and Hazardous Materials Agency in 1987. This study identified all conventional, developing, and conceptual technologies which could be applied to treat the metals contaminated soil that may be found on Army installations as part of a remedial action. These technologies were evaluated and "soils roasting" was identified as a technology which showed promise for application to these types of sites. The roasting technology has not yet been applied to heavy metals contaminated soils but has been studied primarily in Japan for the treatment of heavy metals contaminated waste materials. The technology has also reportedly been applied to long-term immobilization of radioactive isotopes.

The available data and work reported from Japan indicate that this technology has excellent potential for remedial application on heavy metal contaminated soils. USATHAMA did not opt to pursue laboratory development studies due to the higher priority placed on organic and explosives contaminated materials that pose the more immediate problems in USATHAMA installation restoration efforts. However, the problem of metals contaminated soils treatment remains a large one which has not yet been effectively solved.

The primary method historically used for the management of heavy metals contaminated soils and residues has been land disposal or solidification/stabilization prior to landfilling. The high costs and risks associated with land disposal and future RCRA landfill prohibitions necessitate the exploration of environmentally sound alternatives to land disposal.

Roy F. Weston, Inc. (WESTON) has decided to pursue Roasting as an internally funded research and development project because we believe that Roasting has the potential for a high degree of effectiveness and may be implemented using conventional rotary kiln or other thermal process equipment. This initiative is compatible and complementary to the current WESTON initiatives in low and high temperature thermal treatment of organics contaminated soils.

This project is intended to determine the feasibility and effectiveness of Roasting for the treatment of contaminated soils. Once effectiveness is established on the laboratory scale, further development or U.S. EPA site efforts would be pursued, by means of internal WESTON, private, or government funding mechanisms. Given WESTON's experience with rotary kiln incineration technology, scale-up and full-scale system implementations are readily achievable.

BACKGROUND

Numerous Superfund, RCRA corrective action, and other remedial action sites have metals contaminated soil requiring cleanup. Still more of these remedial action sites contain soil contaminated with a combination of metals and organic compounds or explosives. Since metals cannot be biologically degraded or otherwise destroyed using techniques applied to organic contaminants, no effective commercial alternative to hazardous waste stabilization or landfilling currently exists.

Several regulatory developments in recent years have changed the climate for land disposal of hazardous wastes and waste materials from hazardous waste cleanups. These include the HWSA amendments to the original RCRA statute which requires that EPA institute a ban on land disposal of hazardous wastes containing high levels of heavy metals. In addition, the SARA amendments to the Superfund legislation promote the use of technologies which reduce toxicity, mobility, or volume and discourage the use of off- site land disposal. These developments, coupled with a growing recognition of the potential long-term liabilities associated with land disposal, have created a need for effective metals contaminated soil treatment.

In an effort to identify options for the treatment of heavy metals containing soils/residues, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) initiated the original evaluation of treatment technologies which may be candidates for further development. WESTON, under contract to USATHAMA, performed an in-depth engineering study to identify and evaluate the most promising technologies for treatment of heavy metals contaminated soils.

Existing site investigation data indicated that chromium (Cr), cadmium (Cd), and lead (Pb) are the metal species most often present at elevated levels at Army installations. Therefore, the evaluation of treatment technologies was based on soil containing these metals.

State and federal regulatory requirements for contaminated soil remediation were reviewed to identify any target soil metal concentrations which should be achieved by a remedial treatment

process. This review indicated that specific treatment objectives for metals contaminated soils currently do not exist. Treatment objectives are typically based on a site-specific evaluation of migration potential and an assessment of potential impacts. The achievement of EP toxicity limits is considered a minimum treatment target based on current hazardous waste disposal regulations and the achievement of background levels is considered a maximum target. Based on this regulatory framework, it was determined that any technology selected for possible development should at a minimum, be capable of treating the metals contaminated soils to reduce their leachability to levels well below EP toxicity limits.

This study resulted in the identification of 21 treatment technologies. Most of these technologies may be considered to be innovative methods for the treatment of metals contaminated soils.

These technologies are listed in Table 1, along with the approach to metals "treatment" employed (i.e., immobilization, removal, etc.) and the type of treatment employed (i.e., chemical, biological, etc.)

The technology evaluation, discussed in greater detail in previous papers, resulted in selection of three technologies for detailed evaluation (see Table 2) and in the recommendations that the Roasting technology be developed for immobilization of metals. Roasting was found to offer the potential for high performance, long-term effectiveness through incorporation of metals in a ceramic-like matrix, and cost-effectiveness at high throughout rates.

TECHNOLOGY DESCRIPTION

In the Roasting process, the heavy metals in the feed material are immobilized in a crystalline inorganic matrix. As the contaminated soil material is heated, it passes through the following stages:

(a) Evaporation of the residual water.

(b) Decomposition of hydroxides and salts to form the corresponding oxides.

(c) Sintering, the fusing together of solid particles without reaching the liquid state, occurs at about two-thirds of the melting temperatures (absolute-°K).

(d) Melting of heavy metal oxides (around 2,000°C).

The Roasting process heats the feed material to between sintering and melting temperatures where heavy metals are immobilized

in the semi-solid slag. X-ray diffraction photographs of the sintered slag show that the metals are in the dispersed phase while the silica melts to form the continuous phase.

Since immobilization is the objective of this process, volatilization of metals should be minimized. To achieve this, silicates in the form of clay minerals may be added to the melt if not present in the waste or soils. These additives yield a more viscous melt and raise the boiling point of the metal compounds in the melt. Roasting of contaminated soils has not been studied, but naturally occurring silicates in soil may provide the same benefit as the silicate additives (i.e., lowering the viscosity of the melt and boiling point of the metals) for soil treatment.

In related projects, experiments showed that kaolin alone processed at 750-775°C yielded a product from which alumina could be easily extracted using HCl. However, kaolin processed at temperatures >1,000°C prevents the extraction of alumina from the product. This phenomenon is similar to the predicted mechanism of metal immobilization in roasting slag.

Since the technology involves immobilization of the metals in a nearly molten stage, a roasting furnace that can handle this slag would be required. The rotary kiln, a commonly available furnace used extensively in the cement industry and capable of operating at slagging temperatures with a minimum of fouling, is suggested for use in the full scale process. Additives like kaolin are inexpensive and widely available in the United States.

The preliminary conceptual design (see Figure 1) developed by WESTON uses a process wherein the contaminated soil would be excavated and screened to remove oversized rocks. This screening is necessary to meet the equipment tolerances for subsequent processing of additives and soils through a mixer. The mixture of screened soil and the additives would then be fed to the rotary kiln to be roasted. Moisture would be driven off into the vapor phase and would exit the kiln with the combustion gases. Organic compounds may be oxidized or driven off into the vapor phase, depending on their volatility, combustibility and retention time in the kiln. The gases from the kiln would be passed through a dust control device to control particulate emissions. The molten slag would be cooled in a grate cooler and the product subsequently reduced in size using a jaw crusher to improve handling characteristics. Based on analytical data, the crushed slag could either be used to backfill the excavated area or transported for disposal. This design concept is presented in Figure 1. If the soil contains

volatile organic compounds in addition to metals, Roasting may be combined with Low Temperature Thermal Treatment (LT^3), as shown in Figure 2, to improve thermal efficiency and reduce operating cost.

The only experimental data currently available are for simulated metal hydroxide sludge. While these data indicate that the metals are not significantly mobilized when subject to acid leaching, the test procedures do not resemble the applicable EP toxicity extraction procedures or Toxicity Characteristic Leaching Procedure (TCLP) which would be applied in the United States. No information is available to indicate that full scale operations have been conducted. Thus, laboratory experiments are essential to demonstrate that the concept is viable before pursuing further development.

OBJECTIVES OF THE STUDY

The overall objective of the research and development study is to demonstrate that the Roasting technology can successfully immobilize heavy metals in various soils types, rendering the soils nonhazardous and acceptable for backfilling onsite. The performance standard which will be used to measure success in achieving this objective will be the TCLP because EPA has indicated its intention to utilize this procedure in place of EP toxicity in the future. The concentration of metals in the leachate must be below the TCLP limits at a minimum. Hopefully, leachate concentrations will be one to two orders of magnitude below those limits.

Secondary objectives of the study are to determine the effects of soil type, soil additive type, operating temperature, and roasting (residence) time on performance. The data from this study can be used to confirm the commercial viability of Roasting and to establish the basic parameters which govern performance.

TECHNICAL SCOPE

Tests will be conducted by preparing metals "contaminated" soil, mixing additives for each batch test, and roasting the various compositions in a laboratory furnace. Key parameters expected to affect performance are:

- Soil-type and characteristics.
- Additive type.
- Soil to additive ratio.
- Roasting temperature.
- Roasting (residence) time.

Soil type will affect performance since clay, silt, and sand components of the soil may behave differently. The higher

temperature melting components may remain in a separate phase and be surrounded by the phases formed by the more mobile additive. Clay soil, however, may itself contain minerals which will contribute to a stable crystalline product of roasting. Thus, two soil types (clayey and sandy) have been identified as candidate soil types for the initial testing. Performance of Roasting for clay soils will vary with the particular clay type, but will generally be better than for sandy soils. A smaller number of test conditions will be specified for clay soils.

The specific metal compounds or species present in the soil typically affect its hazardous properties, including toxicity and mobility. More soluble metal salts will be used to spike the soil since these compounds are more mobile and represent a worst case for demonstrating effective treatment by immobilization. A compound with a chromium valence state of +6 will be selected since this is the more toxic and mobile valence state. Suggested metal salts are:

- Potassium dichromate ($K_2Cr_2O_7$).
- Lead nitrate ($Pb(NO_3)_2$).
- Cadmium nitrate ($Cd(NO_3)_2$).

A synthetic contaminated soil will be formulated/prepared to achieve the target total metal concentrations which are based on a review of metals contaminated soil data conducted by WESTON for USATHAMA ("Heavy Metals-Contaminated Soil Treatment: Conceptual Development," February 1987). The maximum total metal concentrations observed were as follows:

- Chromium - 3,000 mg/kg.
- Lead - 5,000 mg/kg.
- Cadmium - 500 mg/kg.

The target metal concentrations for the study will be 75 percent of the maximum observed values.

The weight ratio of additive to soil is important because the crystalline phase formed by the additive in the product must be present in sufficient quantities to incorporate the metals in the crystalline product or encapsulate the metals to prevent their migration. During the first phase of testing, where the objective is to identify the additive most effective at the lowest temperature, a conservatively high ratio of soil to additive will be used for all tests. The ratio will be varied in Phase 2 to identify the relationship of ratio and temperature to performance.

Roasting temperature is a key test parameter. The additive and soil mixture will pass through the following stages as the temperature increases:

(1) Evaporation of residual water.

(2) Decomposition of hydroxides and salts to form the corresponding oxides.

(3) Sintering - the fusing together of solid particles without reaching the molten state.

While in the third stage (sintering), the mobility of the additive minerals and some soil minerals greatly increases resulting in the formation of a fused crystalline structure. The fused mixture may contain mixed phases, possibly including noncrystalline glass phases. An adequate roasting temperature will allow sufficient mixing of the more mobile additives with the contaminated soil to incorporate metals into the crystalline structure. Roasting temperature will be varied in Phases 1 and 2.

Duration of roasting, or roasting time, may be an important parameter since the mixture may not fully melt but instead undergo accelerated movement within the solid phase. Longer roasting time should, up to a point, result in a more uniform product.

Treatment effectiveness will be determined by measurement, before and after roasting, of the metals' leachability using TCLP.

The laboratory test program is currently underway as of this writing and completion is anticipated in early 1989. Following completion of the laboratory testing, the project team will evaluate the results in order to assess the ability of the technology to meet the overall objectives of metals immobilization in the roasting product. The relationships between performance and the key parameters varied during the study will be determined and presented in graphic form and, if appropriate, in theoretical or empirical correlations.

If the performance data confirm that Roasting is an effective treatment technology which will immobilize the metals in a stable matrix, the data will be evaluated to determine what the likely operating conditions would be in the full-scale Roasting operation. The conceptual design and preliminary cost estimates developed for the USATHAMA study will be revised based on the new test data and the anticipated full-scale operating conditions. These results will be used to assess whether further development and scale-up of the full-scale operation are viable and should be pursued further.

Table 1

Technologies Identified for Metals Treatment In Soils/Sludges

Technology	Treatment/Approach	Development Status	Comments
In situ vitrification	Thermal/Immobilization	Full scale	Electrodes to heat and glassify ground
Onsite vitrification	Thermal/Immobilization	Full scale	Electrodes to heat and glassify waste stream
Onsite plasma arc (w/ metal recovery)	Thermal/Recovery	Full scale	Destroys organics, gasifies and condenses metals
High temperature fluid wall	Thermal/Immobilization	Full scale	Destroys organics, glassifies metals
Roasting	Thermal/Immobilization	Experimental	Results in fixation in crystaline matrix
Chloride volitilization	Thermal/Recovery	Experimental	Roasting of chloride results in volitilization
Onsite precipitation	Chemical/Immobilization	Conceptual	Use of wastewater precipitation techniques to immobilize metals in excavated soil or sludge
In situ precipitation	Chemical/Immobilization	Conceptual	Use of wastewater precipitation techniques applied directly to the soil in place
In situ precipitation by vapor phase application	Chemical/Immobilization	Conceptual	Same as above except gaseous precipitants
Onsite extraction	Chemical/Mobilization	Pilot scale	Chelators or surfactants used to mobilize metals. Needs associated recovery technique

Table 1
(continued)

Technology	Treatment/Approach	Development Status	Comments
In situ extraction	Chemical/Mobilization	Experimental	Same as above except applied in situ with solution recovered through groundwater
Vegetative Uptake	Biological	Conceptual	Metals accumulate in plants, ultimate fate not addressed
High gradient magnetic separation	Physical/Recovery	Pilot Scale	High magnetic gradient used to deflect magnetic or paramagnetic particles containing metals
Stabilization (admixing)	Physical/Immobilization	Full scale	Chemical fixation in a cementious or pozzolanic mixture
Macro-encapsulation	Physical/Isolation	Pilot scale	Coating with a low permeability mixture
Micro-encapsulation	Physical/Isolation	Full scale	Mixing and extruding in a low permeability material
Geologic isolation	Physical/Isolation	Full scale	Not a treatment
Secure landfill	Physical/Isolation	Full scale	Not a treatment
In situ adsorption	Chemical/Immobilization	Experimental	Materials absorbed and immobilized
In situ ion exchange	Chemical/Immobilization	Conceptual	Ion exchange materials incorporated into soil
Onsite ion exchange	Chemical/Recovery	Conceptual	Transfer metals from soil to ion exchange resins by means of water slurry. Needs associated recovery technique

Table 2

Comparative Ranking and Cost of Technologies

Criteria/Technology	Rating Factor	Microencap-sulation	Roasting	Extraction
1. Effectiveness	4	3	3	2
2. Long-term performance	3	2.5	3	3
3. Residual treatment/ disposal	3	2	2.5	1
4. Throughout	2	3	3	3
5. Materials Handling	1	1.5	2	1.5
6. Air controls	1	2	2	3
7. Flexibility	2	3	2.5	2
8. Ease of operations and maintenance	1	2	2	1.5
9. Transportability	2	2.5	1	2
10. Reliability	2	3	3	2
11. Safety	3	2	2	2.5
12. Environmental risk	3	3	3	2
13. Development time	1	2	1.5	1.5
14. Proprietary status	1	1.5	3	3
15. Permit/institutional	1	2	1	1
16. Project cost	3	1	2	2
TOTAL NUMERICAL SCORE		76.5	80.5	69
Estimated Total Project Cost(1):				
10,000 Tons of Soil		$ 6,810,000	$ 5,700,000	$ 5,050,000
100,000 tons of Soil		$29,625,000	$10,950,000	$10,270,000

(1) = Based on one year duration of operations, 1987 dollars.

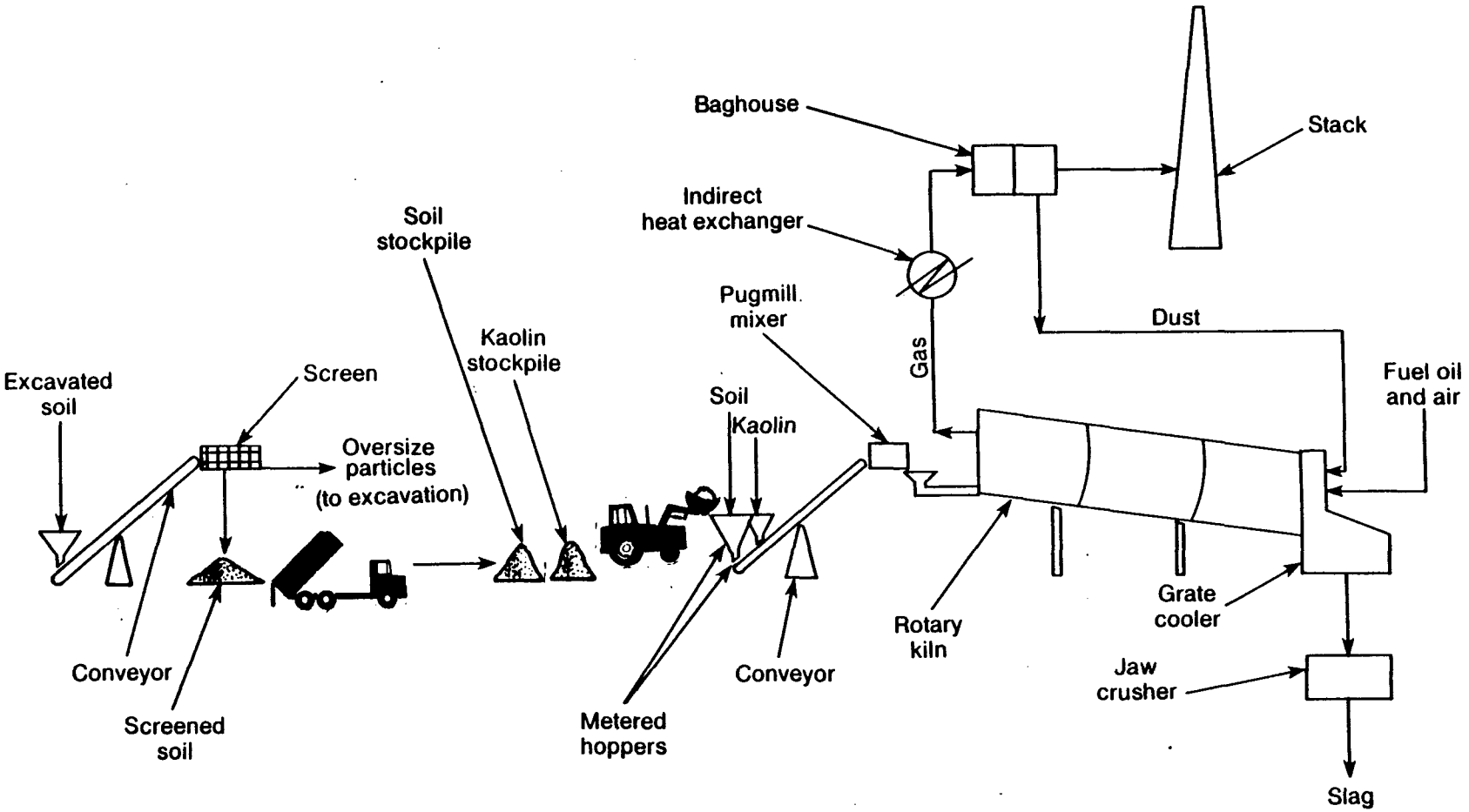


FIGURE 1 **Flow diagram with major equipment for treatment of of soils with metal contaminants only - by roasting.**

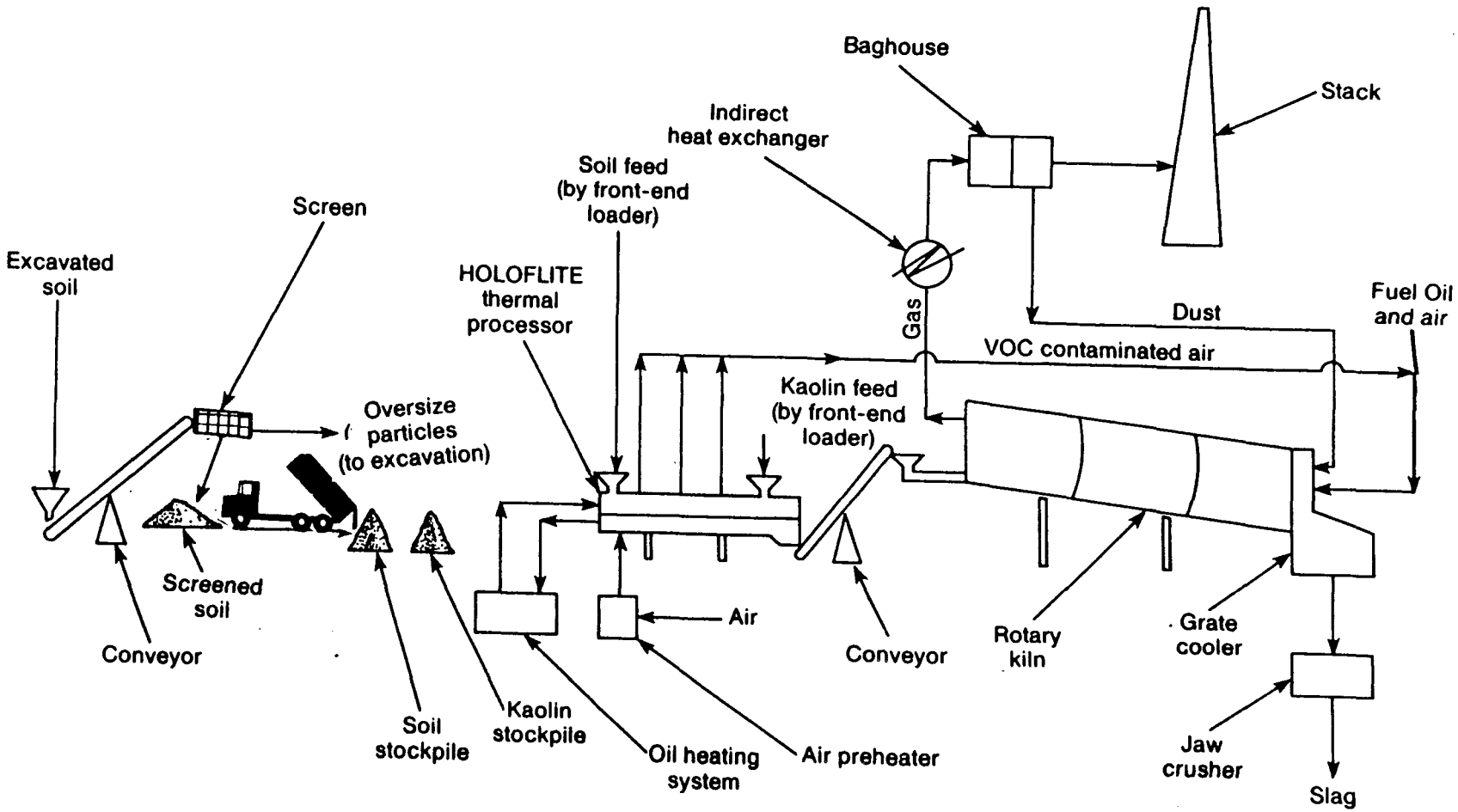


FIGURE 2 **Flow diagram with major equipment for treatment of soils with VOC and metal contaminants - Low Temperature Thermal Stripping followed by roasting.**

HAZARDOUS ORGANIC WASTE DESTRUCTION BY ELECTROCHEMICAL OXIDATION

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INTRODUCTION AND SUMMARY

Generation of hazardous chemical wastes has been proceeding in this country for over a century, and of radioactive mixed wastes for over 40 years. Until very recently, disposal of such wastes was by landfill burial, or frequently by dumping them into streams and sewers. The capacity of the ecological system to detoxify the very high levels of human-generated dumped wastes is being strained, as evidenced by the current concern over the effects of chlorofluorocarbons on the ozone layer, acid rain effects, and other warning signs. Obviously, generated wastes must be held to a minimum, and those which cannot be avoided must be disposed of in landfills isolated from the environment by impermeable barriers, or preferably, destroyed entirely.

The destruction as opposed to stoage of hazardous organic wastes generally involves some form of oxidation, whether it be biological or chemical. The technique of incineration which is most frequently applied consists of a reaction of the wastes with molecular oxygen at high temperatures. These high temperatures are necessary because the oxidation takes place in the gas phase, as the organic wastes volatilize or pyrolyze to gases and react with gaseous molecular oxygen. The major problem with high temperature oxidations which occur during incineration is the formation of toxic coupling products from chlorinated phenols (dioxins), corrosive gases (hydrogen chloride and fluoride), and flyash. Incomplete combustion can also be a source of trouble. Apart from these purely technical reasons, incinerators take up to 7 years to receive appropriate regulatory approval, and are notoriously difficult to operate to achieve very low levels of toxic emissions over a prolonged period, when they may be burning widely variable waste compositions. Incinerators are excellent for the disposal of flammable solvents, for instance, but do not work nearly so well for wastes containing water, acids, alkalies, highly chlorinated solvents, or high proportions of soil and dirt.

For these reasons, Battelle-Northwest, via its Northwest Hazardous Waste Research, Development, and Demonstration Center (NWHWRD&D Center) funded a project to investigate an electrochemical method for oxidation of hazardous and mixed wastes. Electrochemical oxidation (ECO) has been successfully applied for destruction of very dilute solutions of chlorinated solvents in water, and for cleanup of more concentrated phenolic pulp wastes. Our work was intended to examine the ECO approach to destruction or organic wastes which are found on the Hanford site and in the Pacific Northwest generally. Not surprisingly, many of these wastes are also found elsewhere, particularly at military installations, as they comprise solvents, paints, laboratory chemicals, and other chemical processing wastes.

Electrochemical oxidation of organic materials is the subject of a very large amount of prior research (e.g., 1) and electrochemistry per se has been investigated for the past century and is the basis of many high-volume industrial processes (2) as well as inorganic syntheses (3). However, this research is generally not applicable to the subject of organic waste destruction, because of its emphasis on synthesis and its frequent use of a single pure starting material. Concentrated organic wastes are almost always mixtures, and the electrochemical cell conditions for total oxidation are far different from those required for a single electron conversion of a molecule of a pure compound, for example.

Electrochemical oxidation (ECO) takes place in the liquid phase during electrolysis and does not require vaporization of the organic material. Although it is a process that takes place at ambient temperature and atmospheric pressure, the chemical activity of the oxygen form (hydroxyl radical) is very high compared to that of molecular oxygen in air. Thus, very rapid and complete oxidation takes place with none of the problems of incineration. An example of an ECO process involving an acidic anolyte (anode solution) containing a nickel salt (nickel acts as a facilitator for the oxidation) is shown in Figure 1. In this simplified representation, an organic waste is mixed with a solution of sulfuric or nitric acid containing nickel sulfate or nitrate, respectively, and pumped continuously through the anode or oxidizing side of an electrochemical cell. The cathode side is also acidic and contains the same acid as the anode side. The two parts of the cell are isolated physically by means of a plastic membrane which, however, is permeable to some ions. Hydrogen is generated at the cathode, and can in principle be converted back to electricity by combustion in a fuel cell; oxidation at the anode results in conversion of the organic material to carbon dioxide, water, and inorganic ions from any organic sulfur, nitrogen, chlorine, etc., present in the waste.

The ECO-system for oxidation of hazardous chemical wastes was investigated in the small laboratory system shown in Figure 2. The cell (in exploded view) is shown in Figure 3. The laboratory system is capable of almost linear scale-up from grams/hr (the existing system shown in Figures 2 and 3) to almost any level, by increasing the anode surface area and by plugging in additional cells. The flow cell (an Electro-Synthesis Company Microcell) was fitted with a stainless-steel cathode and a platinum on titanium anode for most experiments. A Riapore 1035 anionic membrane separated the anode and cathode compartments. The anode and cathode each had an available electrode surface area of 20 cm^2. The anolytes used in the experimental work included a metal ion, such as cobalt, manganese, or nickel, dissolved in 4 N nitric acid to a total volume of 300 ml. Other nitric acid concentrations were used in some experiments and 4 N sulfuric acid was also used with cobalt. The catholytes consisted of the same concentrations and total volume of the acid used in the anolyte with no addition of metal salts. The anolyte was heated and stirred. A burette inverted over water was used to measure cathode gas evolution, and an inverted separatory funnel was used to measure the larger volume of anode gas produced. Flow of anolyte and catholyte through the cell was achieved by two Teflon pumps (Saturn model SP 2000 with Minarik motor controllers). Direct current power was supplied by a Hewlett-Packard model 6281A DC power supply with a maximum capacity of 6 A. Teflon tubing was used to connect all of the system components and Galtek sample valves were used to extract samples during system operation.

During a typical experimental run, 300 ml of anolyte and catholyte were added to the cleaned and leak-checked system. The circulating pumps, heaters, and stirrer were turned on, and the system was brought to the desired temperature. Temperatures of 22(ambient), 35 and 50°C were used in the experimental runs. When the system was up to temperature, 5 ml of organic material were added and allowed to mix with and fully dissolve into the anolyte. An initial sample was taken before the power supply was turned on to serve as the basis for subsequent organic concentration determinations. The power supply was then turned on and adjusted to provide 6 A to the cell; the time, voltage, and amperage were noted on the data sheets. Samples were taken at 30-min intervals for gas chromatographic (GC) analyses. Gas evolution from the catholyte and anolyte was noted and gas samples taken for GC analysis.

The random error associated with the injection of the sample into the GC was <5%, about the same as that anticipated from sample inhomogeneity. GC analysis was more difficult for the sulfuric acid samples because sulfuric acid attacked the organic packing in the columns and had therefore to be neutralized before injection, which resulted in a precipitate that had to be removed by centrifuging prior to injection into the GC.

Initial laboratory research was concentrated on the oxidation of hexone (4) (MIBK, methyl isobutyl ketone, 5-methyl-2-pentanone), since it is slightly water-soluble (1.67% at 25°C), and since approximately 125,000 l of hexone slightly contaminated with radioactive iodine is stored at Hanford. Some 40 experiments were performed in total, including 4 with continuous addition of hexone, to determine the optimum reaction temperature the most efficient metal ion and its concentration, the effect of different acids and acid concentrations, anode and cathode materials, and the effects of metal ion contaminants.

The oxidation rate of hexone in the continuous addition mode using 1.0M nickel or cobalt in nitric acid proved to be remarkably constant at 2.74 - 3.1 g hexone oxidized/hr in a 300 ml system. This was achieved with a current of 6 amps and a DC voltage of 5.4. The batch system results showed a much greater temperature and concentration effect, and a 2-3 fold higher power consumption (Figure 4). The hexone oxidation rate (in continuous mode) coupled with a low electrical and equipment cost are very favorable, and fully justify further development of the ECO process for organic waste destruction. The intermediate products from hexone oxidation were acetic acid and acetone, as confirmed by GC-mass spectrometry (GC-MS) and shown in Figure 5. Nickel was found to be the most effective ad-ion, with a positive temperature effect between 35 and 50°C. Power requirements for hexone conversion to acetone and acetic acid and thence to carbon dioxide and water were about 10 KW/Kg, or, at a power cost of 4c/KW, approximately 40 cents/kg. In view of the current regulatory climate regarding waste transportation, storage, or incineration, this cost is not unreasonable.

Further work on the ECO system was performed with other, less tractable and water-insoluble compounds and mixtures. Experiments were performed with Photrex (1,1,2-trifluoro-1,2,2-trichloroethane), chloroform, Lindane (hexachlorocyclohexane, Gammexane), phenol, diglyme (diethyleneglycol dimethyl ether), and quinoline as examples of other organic wastes which might be encountered in an actual, "real-life" organic waste mixture. In

other experiments major emphasis was on chlorinated hydrocarbons such as tri- and perchloroethylenes (TCE and PCE, respectively), which represent a major waste disposal problem, and mixtures with aromatic hydrocarbons (toluene and o-xylene).

Liquid samples were taken in these experiments as previously described, but with heterogeneous solvent/anolyte mixtures, accurate GC analysis was very difficult. For soluble solvents such as diglyme, of course, this situation did not occur, but with toluene and xylene it was necessary to relate all components of the mixture to one (toluene) taken as unity. Also, in experiments using an alkaline anolyte, carbon dioxide evolution could not be used as a measure of organic compound oxidation, since it was absorbed in the anolyte. In experiments in which chlorinated solvents were used as test materials, an accurate measure of the degree of degradation was obtained by quantitative analysis of the inorganic chloride produced. Chloride ion was determined by the addition of an excess of 0.1 M silver nitrate solution (15 ml) to 5 ml of sample solution, followed by gravimetric determination. (Titration using a fluorescein indicator was initially attempted, but the end point could not be determined accurately due to the acidity of the solution and interference by nickel ions.)

Overall, the ECO system operated consistently well, with only one mishap caused by inadvertent exchange of the platinized titanium anode by one of stainless steel: The steel anode corroded through within 3 hr and allowed acid anolyte to escape into the glass container placed underneath the system. Generally, there was no detectable corrosion of the anode, and the steel cathode showed $<$ 1 mm depth of corrosion after completion of all of the experiments. The ion-selective membrane separating the cathode and anode compartments of the cell developed a yellow color and an odor indicating that it was absorbing some of the organic material, but only in the case of chlorobenzene was the organic material detected in the cathode side of the cell, showing membrane permeation. There was no membrane clogging by oxides of nickel (as was observed with a silver ad-ion). Cell temperature was maintained at ambient ($22^{\circ}C$) to minimize loss of volatile organic vapors. Some loss of organic material as vapor or as entrained liquid during anode gas evolution was inevitable as most of the substances tested were volatile liquids.

Nitric acid was primarily used as the catholyte in these experiments, and over a 24 hr period it was reduced to ammonia. The pH of the catholyte gradually increased, with a corresponding drop in cell current. When the catholyte was regenerated by addition of concentrated nitric acid, cell current returned to near the original value. This was repeated up to 3 times during the longer experiments. When 0.5 M sulfuric acid was used as the catholyte, hydrogen gas was evolved. Obviously, in practical applications, sulfuric acid would be used as the catholyte and the hydrogen gas used as a fuel.

Direct GC analysis of the anolyte is a useful tool for determining quantities of water-soluble organic compounds, as has already been noted for hexone destruction. Results shown in Figure 6 show that this is also true for diglyme and quinoline (isopropanol gave non-reproducible results). The quinoline destruction experiment was run in two anolytes: Nickel nitrate and nitric acid, and sodium hydroxide, at widely different initial pH values. It

is noteworthy that the oxidation of quinoline took place much more rapidly in the alkaline anolyte than the acidic one, while the oxidation of diglyme in acid medium was also very rapid, even when an additional 5 ml of diglyme was added 24 hr into the experiment. The phenol solution became black within seconds of starting the current, undoubtedly due to oxidative coupling, and tar was deposited within the system within 5 min. This is the only experiment where the membrane became blocked by products. (ECO of phenolic solutions (pulping wastes) is one of the few examples of a patented process using ECO for organic waste cleanup (5)).

Direct GC analysis of liquid samples of the anolytes to which water-insoluble organics were added, in contrast, gave widely variable results for the actual amounts of organic compounds present, both of consecutive samples and of duplicate GC analyses of the same sample. This was expected because the number of organic droplets included in a given volume of aqueous medium was random. This of course presents a problem in monitoring the course of the experiments. As an example, TCE was run as a test material both with and without added nickel nitrate, and liquid samples taken for GC analysis. No pattern could be distinguished, and the data were apparently random. Photrex was readily detected by GC in a standard solution, but was not detectable even at time zero in the anolyte solution, although two small peaks from unidentified organic volatiles appeared. Lindane was not volatile under our GC conditions and its destruction, as well as that of chlorobenzene, was monitored by carbon dioxide evolution rate.

These scoping experiments clearly demonstrated that oxidation of a wide variety of organic chemicals is possible in the ECO cell; however, the rates of oxidation were widely different, and in at least the case of quinoline, that rate was pH-dependent. The presence of phenol and presumably also of other substances capable of oxidative coupling is detrimental to the smooth operation of the cell. Hence, the various components of organic waste mixtures will be oxidized at different rates in the cell, and some will lead to tar formation. The ECO-system is therefore not a "black box" destruction system like incineration in its present form, but must be tailored to each waste type.

Additional experiments were performed with the common chlorinated toxic solvents, TCE and PCE. To eliminate the possibility that significant amounts of these more volatile compounds were simply being evaporated from the cell by electrolytic oxygen, or entrained in droplets passing over with the evolved gases, we performed carbon dioxide gas and chloride ion analyses in the evolved gas and anolyte samples, respectively. Formation of carbon dioxide is an indication that complete organic oxidation is taking place, as there is no other possible source of carbon in the anode compartment, and formation of inorganic chloride is an indication that electrochemical reactions are taking place as both TCE and PCE are stable in aqueous acid solutions at ambient temperature. Figures 7 and 8 present data on two short-period experiments with TCE as the only added organic compound (in one of which the nickel adion was omitted). In two three-day experiments with a mixture of TCE, PCE, toluene, and o-xylene, the latter two compounds added to simulate a "real-life" waste, a different pattern emerged (Figure 9). In the latter two experiments, the nitric acid catholyte was regenerated daily by addition of concentrated nitric acid to restore the original pH.

In contrast to the marked positive effect of the nickel ad-ion on the EC oxidation of hexone (Figure 4), nickel appeared to have little, or a slight negative effect on TCE oxidation, while increasing the overall TCE concentration in the cell resulted in an increased chloride production rate (Figure 7). Up to 20% of the theoretically available chlorine was converted to chloride ion within 7-8 hr with TCE alone, but with toluene, xylene, and PCE also present, this figure was approached only after an extended run of 70-80 hr. Two apparently identical experiments with the organic mixture showed different, and in one case complex, chloride ion liberation rates over time (Figure 9). Electrons available for waste oxidation do not all go to release chloride ion, of course, and this result probably reflects the stepwise nature of the ECO process, with a single chloride ion per TCE or PCE molecule being released initially, further oxidation then taking place on the carbon skeleton of the intermediate product. Toluene and xylene, being in a much more reduced form than TCE and PCE would take more electrons per molecule for oxidation, and would be expected to slow down the overall oxidation, the power supplied being constant.

Addition of 40 ml of TCE at the beginning of the experiment resulted in only 0.1% of the carbon appearing as carbon dioxide after 22 hr, compared to 4.3 and 5.9%, respectively, in two experiments where only 5 ml was added (and reacted for only 6 hr). This corresponds to a 50-fold decrease in the proportion of carbon dioxide for only an 8-fold increase in the amount of organic additive.

APPLICATIONS

Use of the ECO-system to destroy organic hazardous wastes can be envisaged in several ways: Initially, our objective was the complete conversion of hexone wastes to carbon dioxide and water. The system using an acidic anolyte and a nickel ad-ion was effective for this. During the course of our investigation of other materials, alternative processes were discovered. For destruction of phenolic wastes, for example, the rapid oxidation of dilute phenolic solutions to insoluble tars could be utilized to clean up pulping wastewaters. Phenol could actually be added in some cases to act as a "getter" for other soluble substances which can be oxidized but which do not form insoluble tars on their own, such as sugars and alcohols. Use of an alkaline anolyte can be used to destroy substances such as quinoline and other amines.

Perhaps the most useful discovery in this work was the finding that halogenated compounds can be selectively dehalogenated. In a mixture containing flammable solvents such as toluene and xylene, chlorine was selectively removed from TCE and PCE. This offers the possibility of pre-treating such solvent mixtures to make them more amenable to incineration and reduce their hazard.

Although the work to date has involved concentrated materials, the ECO-system can be applied to dilute solutions, or to slurries of dirt and soil containing small amounts of organic wastes. The advantage of the ECO-system for this application is that oxidation will only take place on the solid surface or in water-permeable sites; incineration destroys the humic acids in

soil throughout the matrix, making the product useless as an agricultural medium and generating additional compounds from humic acid pyrolysis.

Radioactive (mixed) waste destruction is a troublesome problem which could be alleviated by an ECO-system. At Hanford, Complexant Concentrate is a radioactive waste comprising radioisotopes of various types in a highly concentrated inorganic salt mixture, and also containing over 40 g/l of a mixture of chelating agents (EDTA, HEDTA, NTA, and citrate). The chelating agents chemical structures are primarily carboxylate groups joined to aminoalkanes, and are thus highly suited to ECO to carbon dioxide, nitrogen, and water.

These are a few examples of waste types which could benefit from ECO; there are many others.

COST

Electricity cost is frequently quoted as a disadvantage of ECO processes. In view of the high and rising costs for other disposal methods, it is useful to examine some approximate costs for the amount of electricity required to destroy the compounds used in these experiments. Of course, the system was laboratory scale only, and pre- and post treatment costs, pumping, wear and tear, etc., need to be taken into account. The electricity cost for hexone destruction has already been quoted as 40 cents/kg. The cost for TCE and PCE can be determined as follows:

During the course of these experiments, electrons were supplied at the rate of approximately 3.6 Faradays/d (at 4.0 amp); by definition, 1 F will supply one electron equivalent. In the experiment using 40 ml (0.445 moles) of TCE, 13.7% of the available organic chlorine was liberated as chloride ion in 22 hr, corresponding to a requirement for 18.3 F per g/ion of chloride ion. When only 5 ml TCE (0.056 mole) was used, the requirement was 33.9 F/g-ion chloride liberated. In neither case was chloride liberation complete, but increasing the concentration of the insoluble organic TCE had a beneficial effect on efficiency. In terms of electricity cost, assuming 4 cents/KWH, a supply at 6V and 4.0 amp for 22 and 7 hr respectively provided 0.53 KWH and 0.17 KWH at a cost of 2.1 and 0.7 cents. Hence, when 73.2 g (40 ml) TCE was placed in the cell, 13.7% of the chlorine was converted to chloride for 2.1 cents, corresponding to a cost for TCE destruction of $2.09/kg. When only 9.15 g (5 ml) TCE was placed in the cell, with 18.5% of the chlorine converted to chloride in 7 hr, the cost for destruction would have been $3.93 cents/Kg. These figures of course assume a linear rate for dechlorination and take no account of ancillary power and equipment costs.

CONCLUSION

These laboratory results for the ECO-system indicate its potential as a replacement for incineration in certain cases, particularly when there is a need for destruction of chlorinated solvents. The application of ECO to a particular waste requires pre-knowledge of the waste composition, so that the optimum cell conditions can be determined. Once this is done, ECO may offer

a cost-effective and environmentally clean way of destroying organic wastes at the source.

Because of the ease of scale up, mild operating conditions, and ease of turning the system on and off, one of the major advantages of an ECO system for hazardous waste disposal is the fact that minimal operator training is needed. With the current shortage of skilled operators trained in hazardous waste incinerator operation, this makes continued research on ECO desirable.

Work is in progress to increase the efficiency of the general oxidation process, to extend the range of compounds which can be treated, and to define the types of concentrated hazardous chemical wastes which could be most economically and beneficially treated.

ACKNOWLEDGEMENT

This work was supported by funding from the Northwest Hazardous Waste Research, Development and Demonstration Center and the Department of Energy under contract DE-AC-06-76RLO-1830, which support is gratefully acknowledged.

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5. J.D. Becker, "Process for Purification of waste Waters Accumulated from Pulp Production, Particularly from Chlorine Bleaching of Pulp: Electrolysis, Sedimentation," U.S. Patent 4,490,257, Dec. 25, 1984.

FIGURE 1: Simplified Schematic of the Electrochemical Oxidation System.

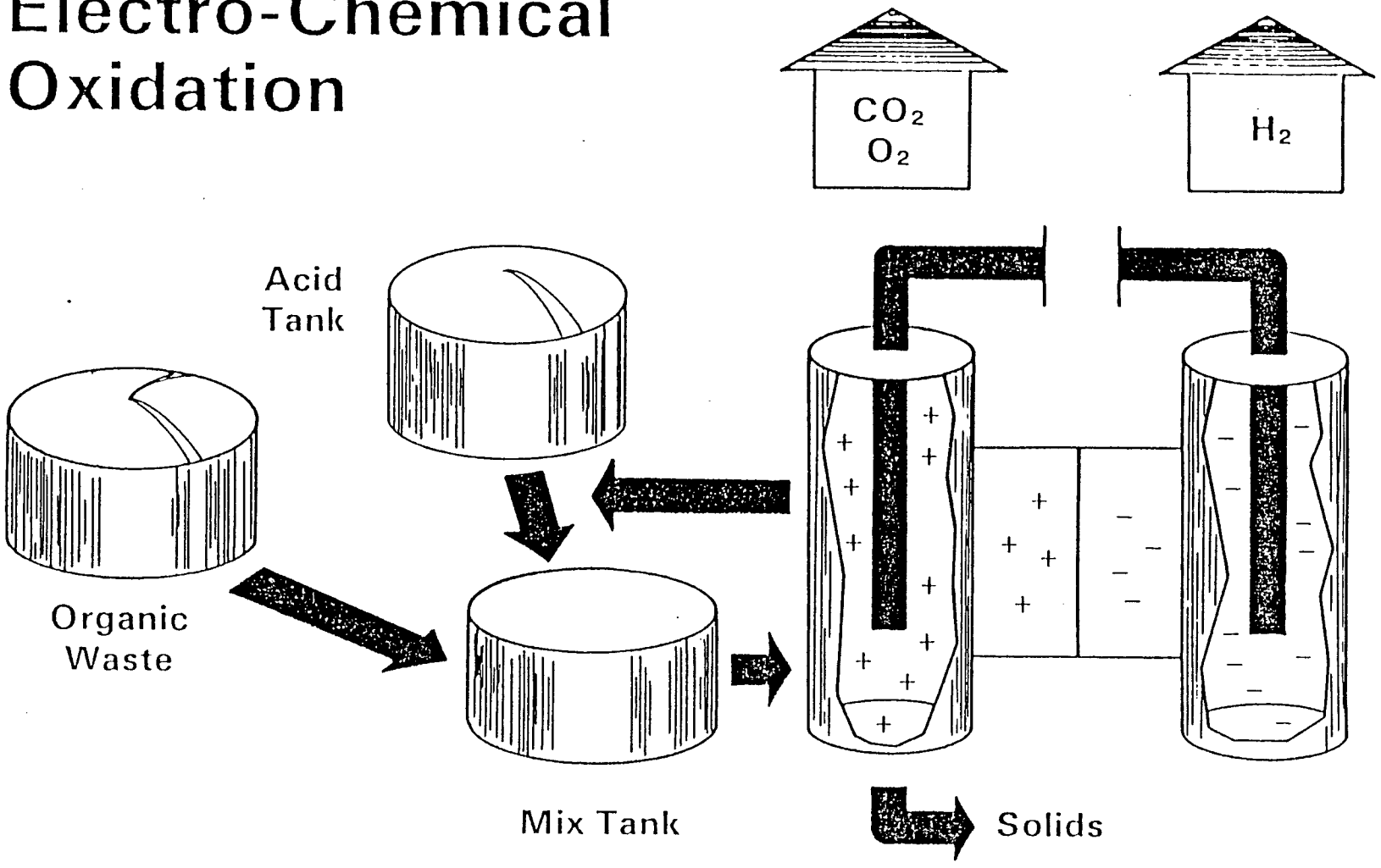


Figure 2: Diagram of the Laboratory Electrochemical Oxidation Apparatus.

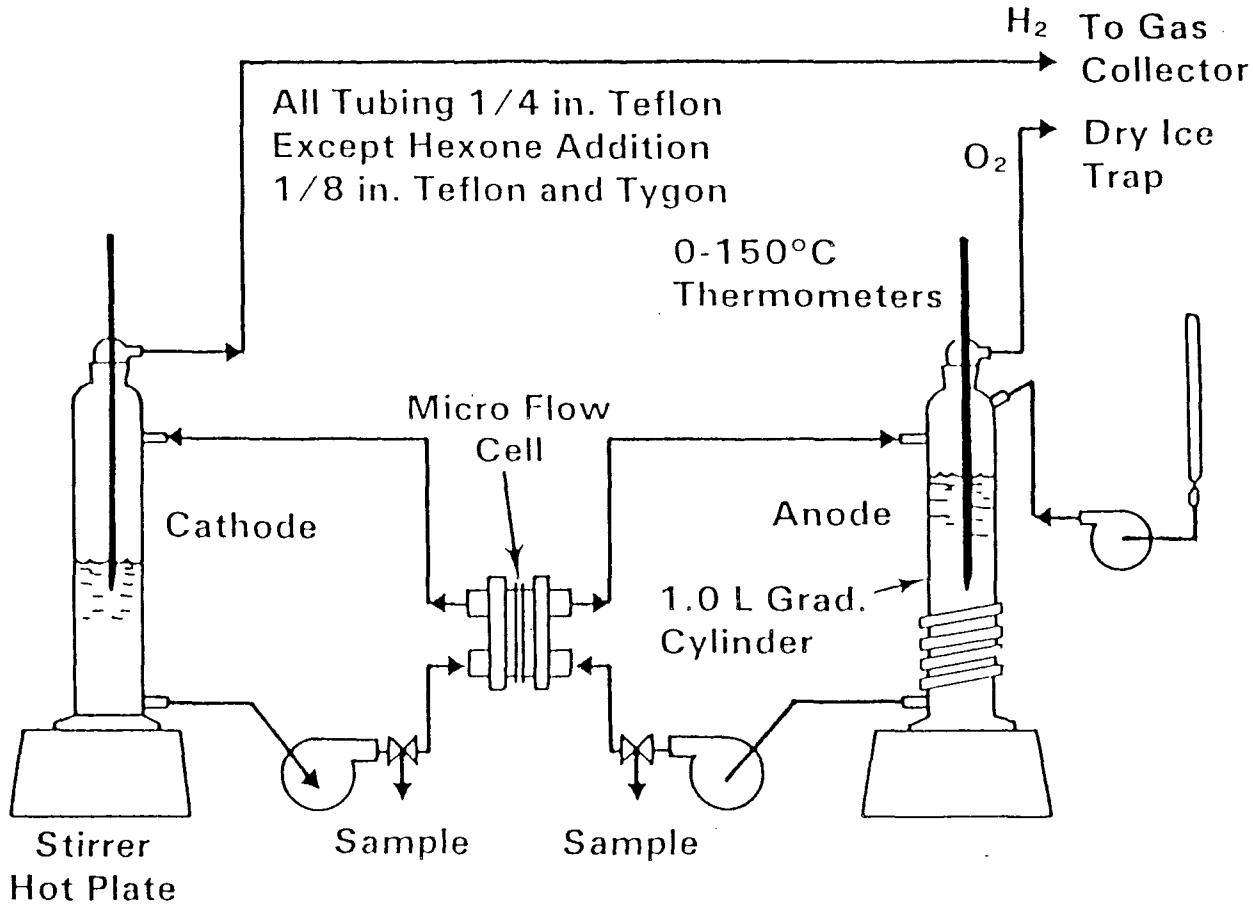
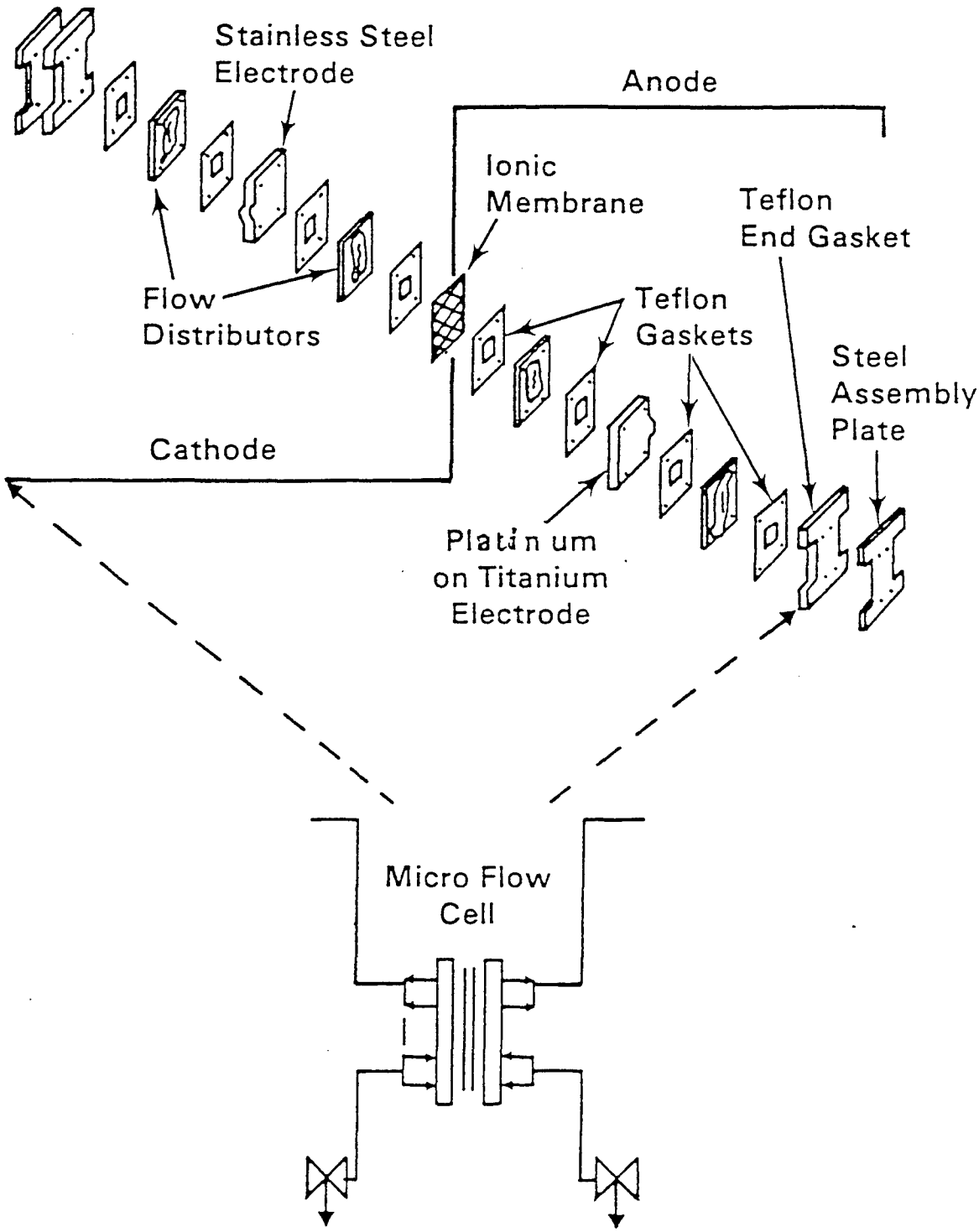


Figure 3: Exploded View of the Electrochemical Oxidation Cell.



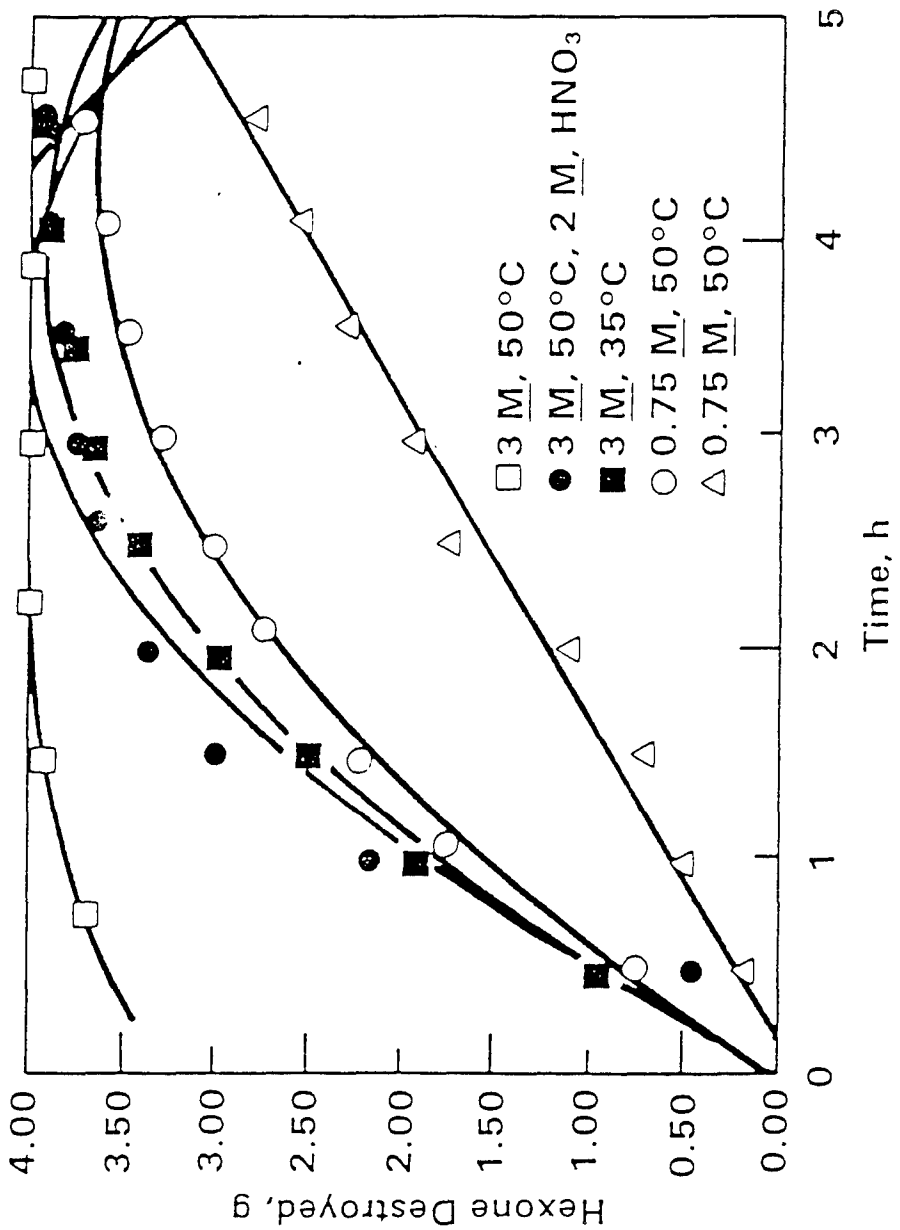


Figure 4: Electrochemical Oxidation of Hexone.

Figure 5: Intermediate Production of Acetone from Hexone During ECO.

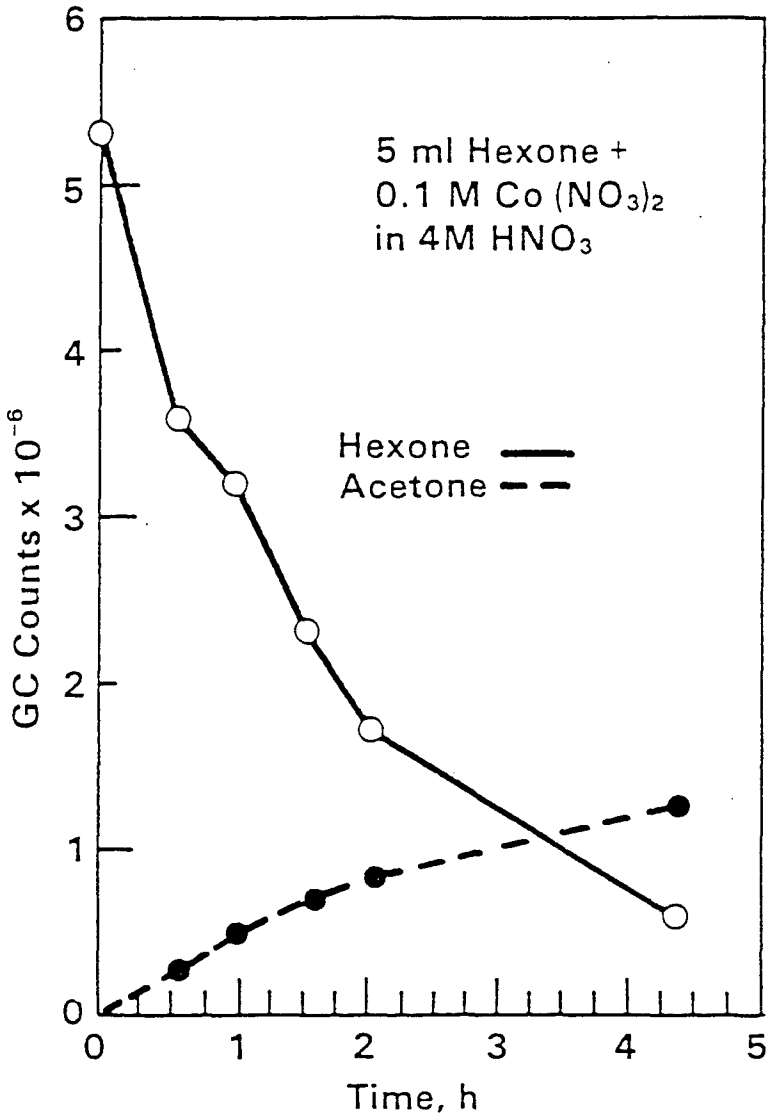


Figure 6: Electrochemical Oxidation of Diglyme and Quinoline.

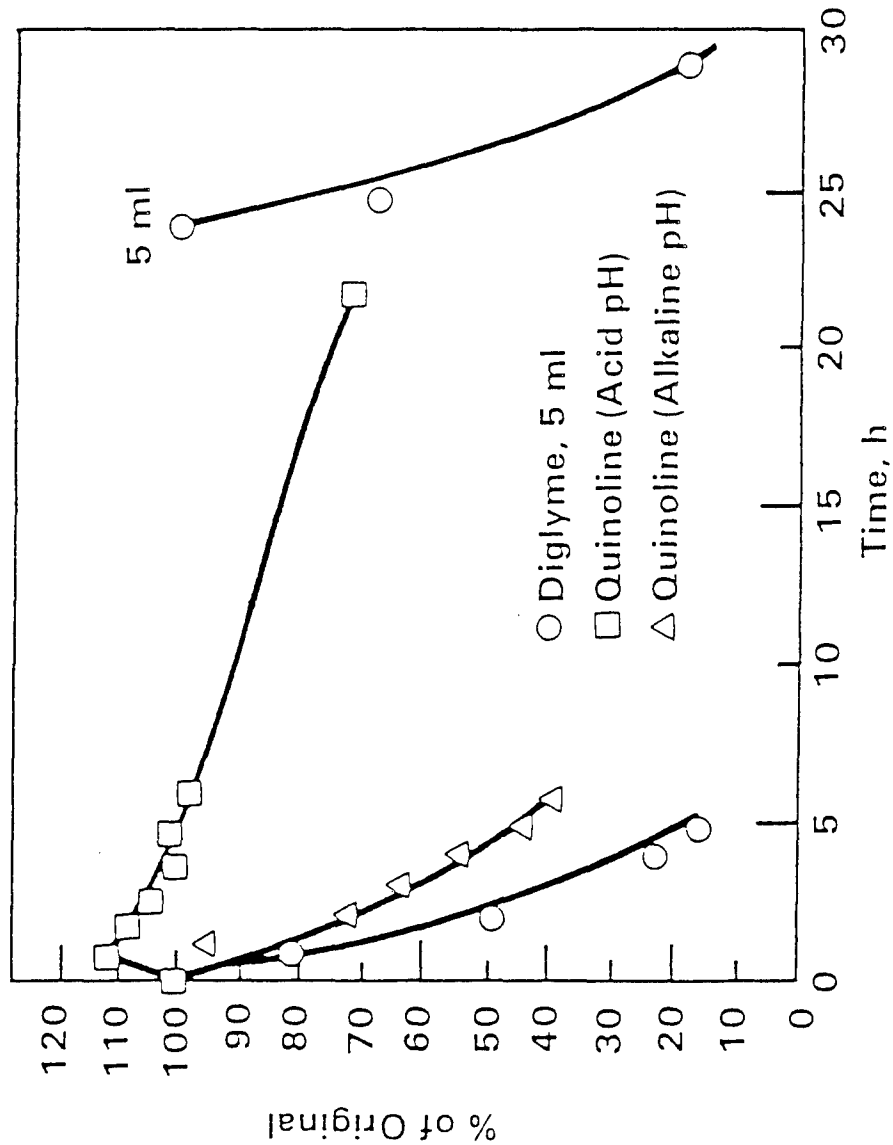


Figure 7: Inorganic Chloride Ion Production from Trichloroethylene During ECO.

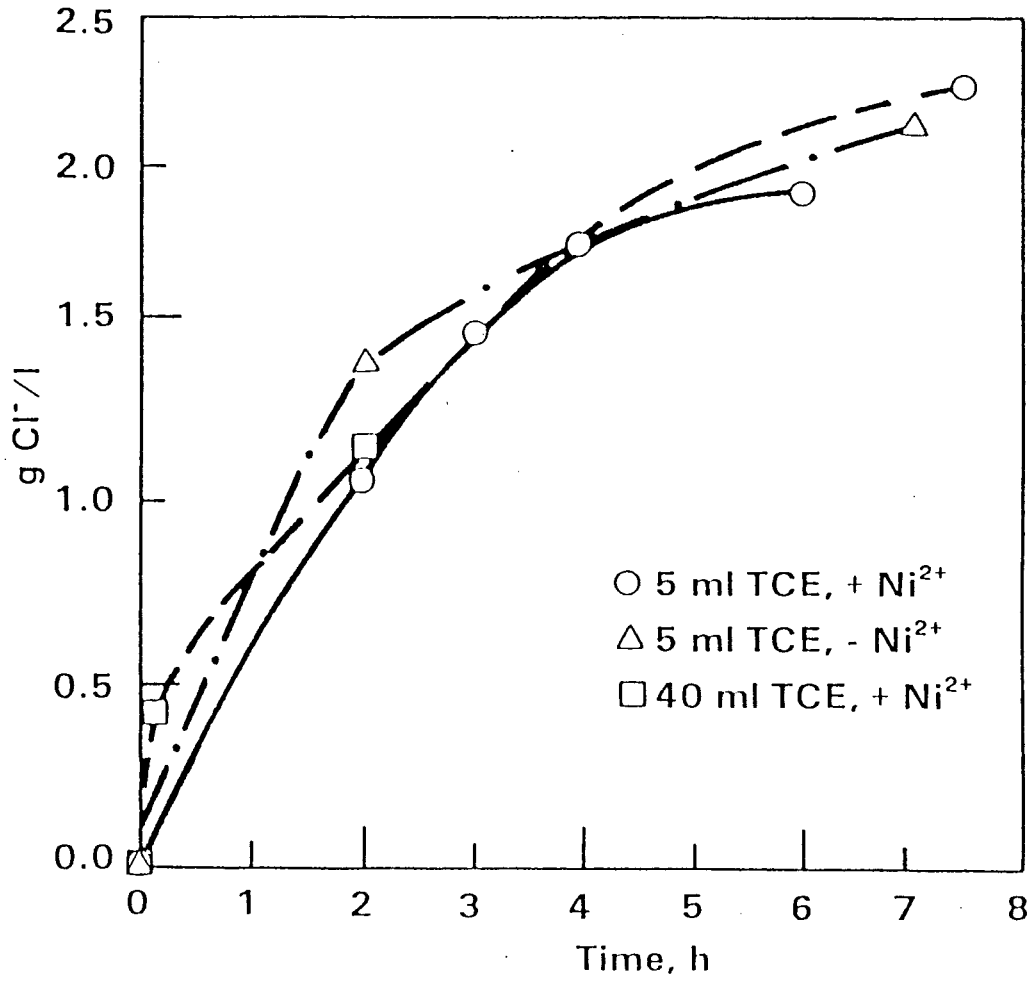


Figure 8: Carbon Dioxide Production from TCE During Electrochemical Oxidation.

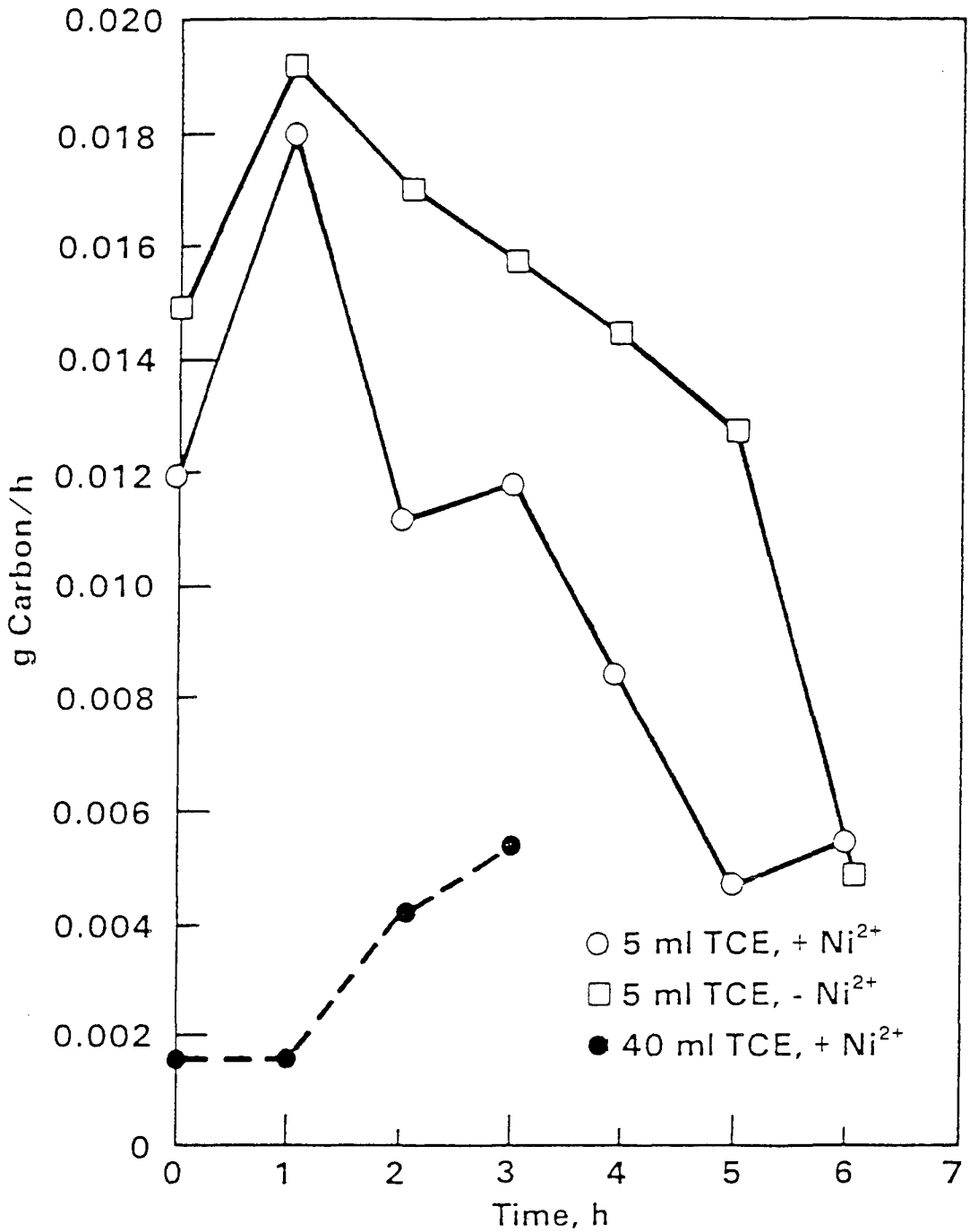
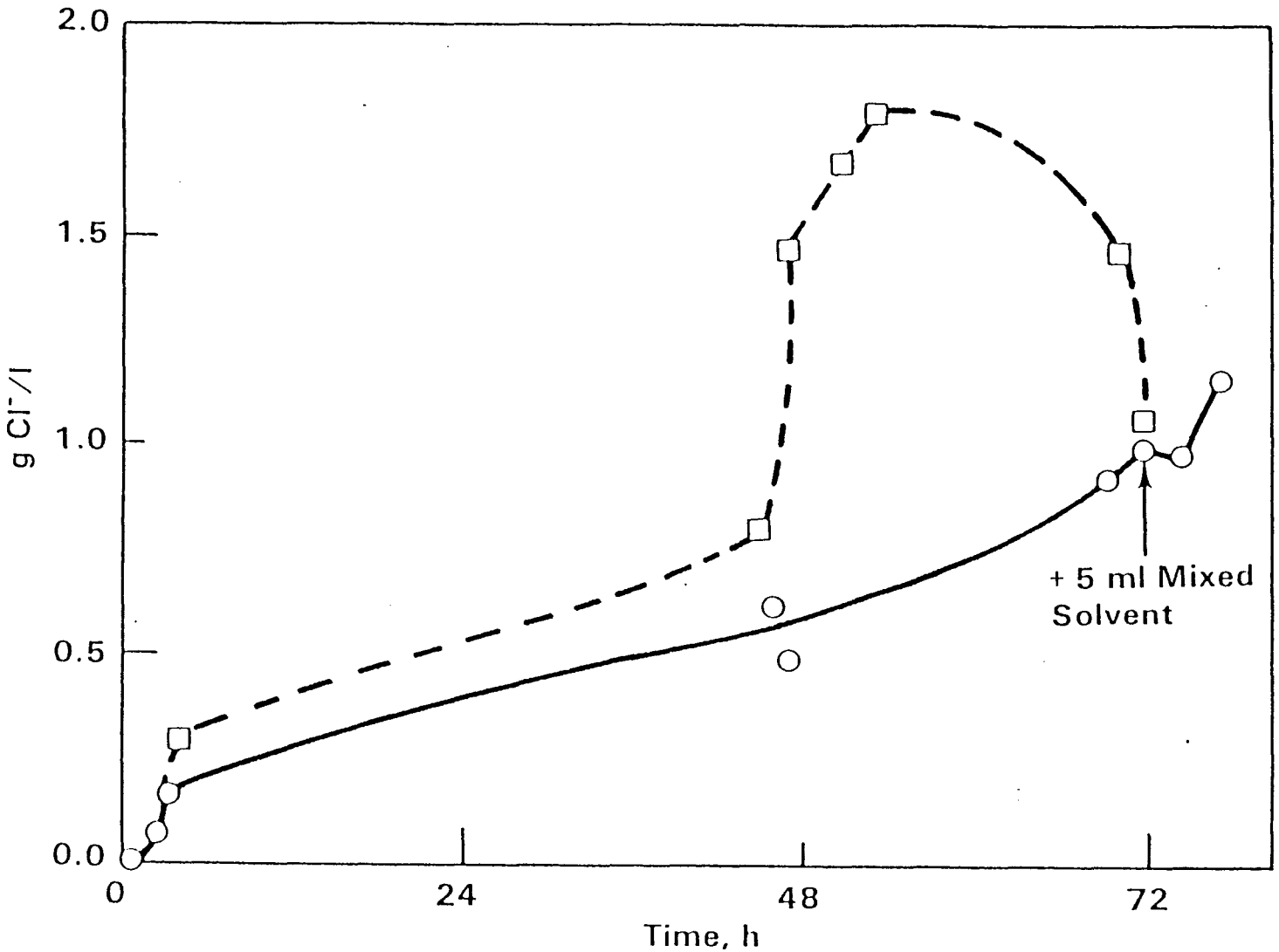


Figure 9: Chloride Production from TCE and PCE in the Presence of Toluene and Xylene.



VACUUM EXTRACTION OF VOLATILE ORGANIC COMPOUNDS FROM SOILS *

by

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INTRODUCTION

Volatile organic compounds (VOCs) are being extracted by applying a vacuum to the soil as part of a remedial action program at the Twin Cities Army Ammunition Plant (TCAAP) in New Brighton, Minnesota, a suburb north of the Minneapolis-St. Paul, Minnesota metropolitan area. This site is part of a National Priority List (NPL) Superfund site. The federal facility has undertaken a remedial action program to eliminate the groundwater contamination from the plant and the surrounding area. Action has been initiated to clean up the site and treat the groundwater which is migrating from the TCAAP.

Two programs are underway to deal with the groundwater contamination by using extraction and treatment and source control at several of the past disposal sites. Two of the past disposal sites are utilizing the technique of volatile organic compound vacuum extraction from the soils. A relatively new technology termed 'In-Situ Volatilization (ISV)' was implemented at the Army plant. ISV removes volatile organics from the soil by mechanically drawing air through the contaminated soil volume. The technique is applied in soil layers above the water table (unsaturated zone). An array of vents (similar to shallow wells) penetrating the affected portion of the vadose zone are connected via manifolding to air blowers. The blowers create a partial vacuum in the vents and pull air, including volatiles, out of the soil.

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* Paper presented by BRUCE E. WENZEL, Ph.D., Environmental Group Leader, Federal Cartridge Co., at USATHAMA 13th Annual Environmental Quality R & D Symposium, Williamsburg, VA, Nov. 15, 1988.

PILOT WORK AT TCAAP

The primary objective for the pilot study was to assess the feasibility of the vacuum extraction technology. The pilot study was conducted by the Roy F. Weston Consulting Engineering firm under a contract with the U.S. Army Toxic and Hazardous Materials (USATHAMA) research demonstration program. A 14-week field program was conducted from November 1984 through February 1985 to study the feasibility of the air-stripping technology as a site remediation alternative. The results of the testing showed great promise, with the concentrations of volatiles extracted ranging as high as 350 ppm of trichloroethylene, which was used as an indicator of the VOC contaminants. During this time period approximately one-half ton of volatiles were estimated to have been removed through the pilot process.

DESIGN ACTIVITIES

During the spring of 1985 the TCAAP was undergoing tremendous political and legal pressures to initiate remedial action at the installation where groundwater contamination had been discovered in 1981. In subsequent years, that contamination was found to be migrating from the installation, contaminating a nearby community water supply.

In the spring of 1985 the Army felt that interim remedial action measures were necessary. These were embarked on in a program begun on June 14, 1985. Source control and groundwater treatment were the interim remedial actions chosen. The first item to be implemented was the ISV system as a method of source control. Following the Army's decision to move ahead on the installation of the vacuum extraction program, a design team was formulated at the TCAAP. The design team was composed of Army representatives from the plant and from USATHAMA, the operating contractor (Federal Cartridge Company) and two consultants (Roy F. Weston, Inc. from the pilot work and Wenck Associates, Inc. as the local design-consulting firm.) In addition, the contractor who was hired to install the system was also queried for advice and assistance for the construction program. The design of the system was performed by the firm of Wenck Associates, Inc. of Wayzata, Minnesota, with the input of the members from the design team. Meetings were held on a weekly basis, or more frequently if necessary, throughout the design process. As much of the pilot plant results as possible were utilized. However, changes, new approaches, and technologies were put into play in the final design of the system.

The two sites to have the system installed were known as Sites D and G. Site D is an area where open burning of unknown amounts of explosives and solvents occurred. Also an unknown amount of metal wastes, chemicals, polychlorinated biphenyls, and solvents were disposed at this site. Site G was a former landfill/-dumpsite where an unknown amount of general refuse wastes, chemicals, volatile organics, and solvents were disposed.

An eighteen-inch clay cap was designed for both sites to avoid any further leaching of precipitates through the soil layers. At Site D, thirty-nine (39) three-inch well vents were planned at a 25-feet spacing in an area of approximately 130 feet by 200 feet. The depth of the vents is mostly 35 feet. At Site G, eighty-nine (89) three-inch well vents were planned at a 25-feet spacing in an area of 190 feet by 360 feet. Depths of the vents are: half 35 feet, a few 45 feet, and most of the remainder 55 feet. Both systems were designed for a capacity of 110 cubic feet per vent. Both systems have four blowers. Each blower at Site D (20 hp) has a capacity of 2200 cubic feet per minute (cfm) while Site G blowers (40 hp) have the capacity of 5700 cfm. Pipe diameters are eight inches for the laterals and eighteen inches for the header at Site D and twenty-four inches for the header at Site G. The design pressure for the blowers is a vacuum head of twenty-four inches of water.

Figure 1 is a schematic of the ISV system at Site G.

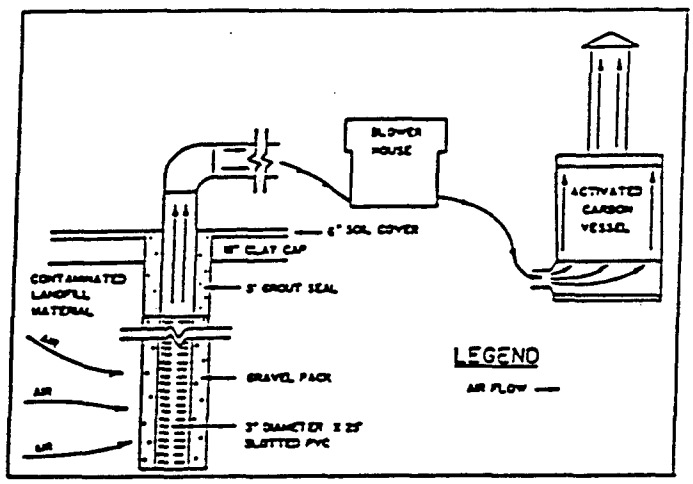
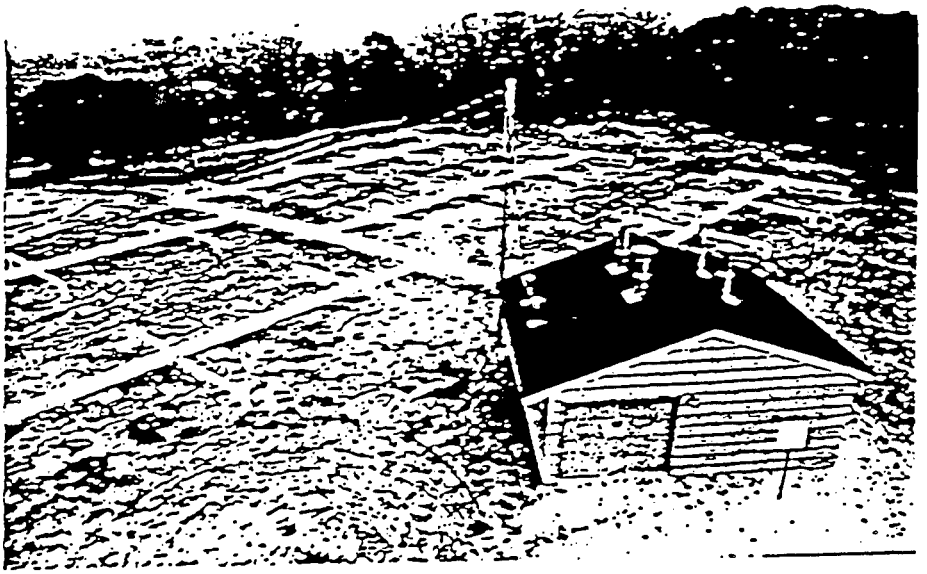


Figure 1
ISV Schematic Site G

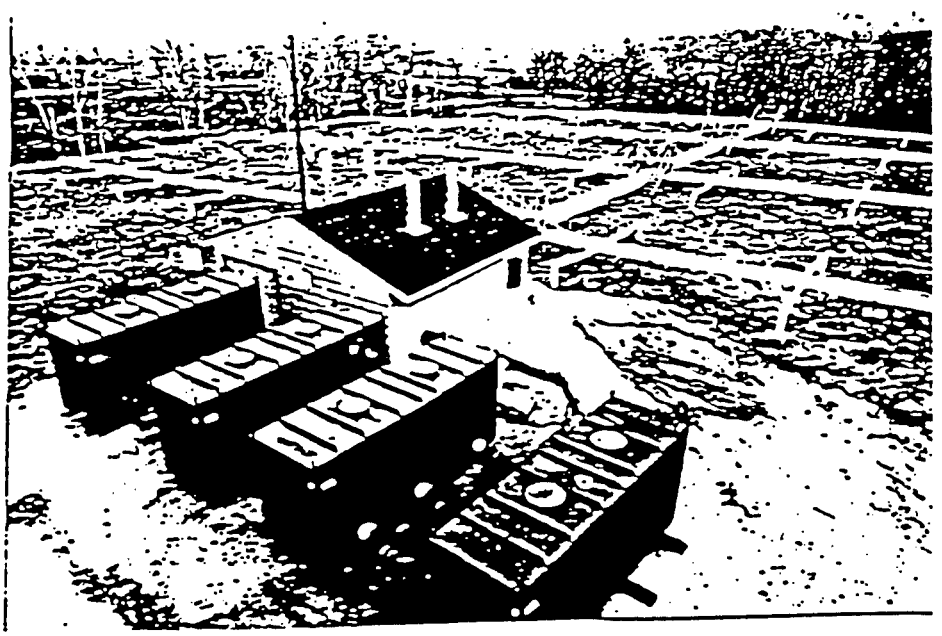
CONSTRUCTION

The construction of the ISV system at these two sites was started in November 1985 and concluded by the end of the calendar year. At one site approximately 1400 cubic yards of PCB contaminated soils needed to be removed to meet the regulatory requirements before the ISV system was installed. Following the excavation of the soils, clay caps were installed. The drilling, placement and fabrication of vents, construction of a building and blower installation with all electrical controls were completed in record construction time during cold weather. The system was completed by the end of 1985 so that it could be put on line in January of 1986.

The following two photographs show the configuration of the systems.



Site D



Site G

OPERATION OF SYSTEMS

Phenomenal success was obtained on volatile removal as soon as the vacuum blowers were started.

The system at Site D was started on January 29, 1986. During the first day of operation, over 1200 pounds of total VOCs were removed. Site D blowers were run for 37 days and removed approximately 20,000 pounds of total VOCs.

Site G system was started on February 20, 1986. During the first day of operation, approximately 4600 pounds of total VOCs were removed. This system was run for 14 days and removed 24,000 pounds of total VOCs. No air emission controls had been chosen to be put onto the system with concurrence of the Minnesota regulatory agency. However, after this phenomenal success and excess air emissions, the systems were both shut down while discussions with the regulatory people ensued. During the next four months the systems were off, a number of different discussions took place with the Minnesota regulatory agency and with the U.S. Environmental Protection Agency. Air quality modeling and studies were performed. Ambient monitoring was conducted during the time the systems were in operation. Site D resumed operations on July 7, 1986, and was allowed to be operated under a controlled type of air emission rate discharge. Site G operation was resumed on August 21, 1986, with carbon adsorption units added to the air exhausts. A complete air monitoring plan has been in operation since the start of treatment. The air emissions at Site G are controlled by activated carbon. Various testing or negotiations were undertaken to reactivate the carbon by on-site incinerator, off-site reactivation, and burning at a local power plant. Presently the carbon is being removed and trucked to an off-site facility for reactivation.

Ambient air monitoring has revealed no air deterioration. Readings have been at background levels on the site downwind of the emissions as well as at the TCAAP boundary.

Total removal rates are shown in Figures 2 & 3 (see page 6).

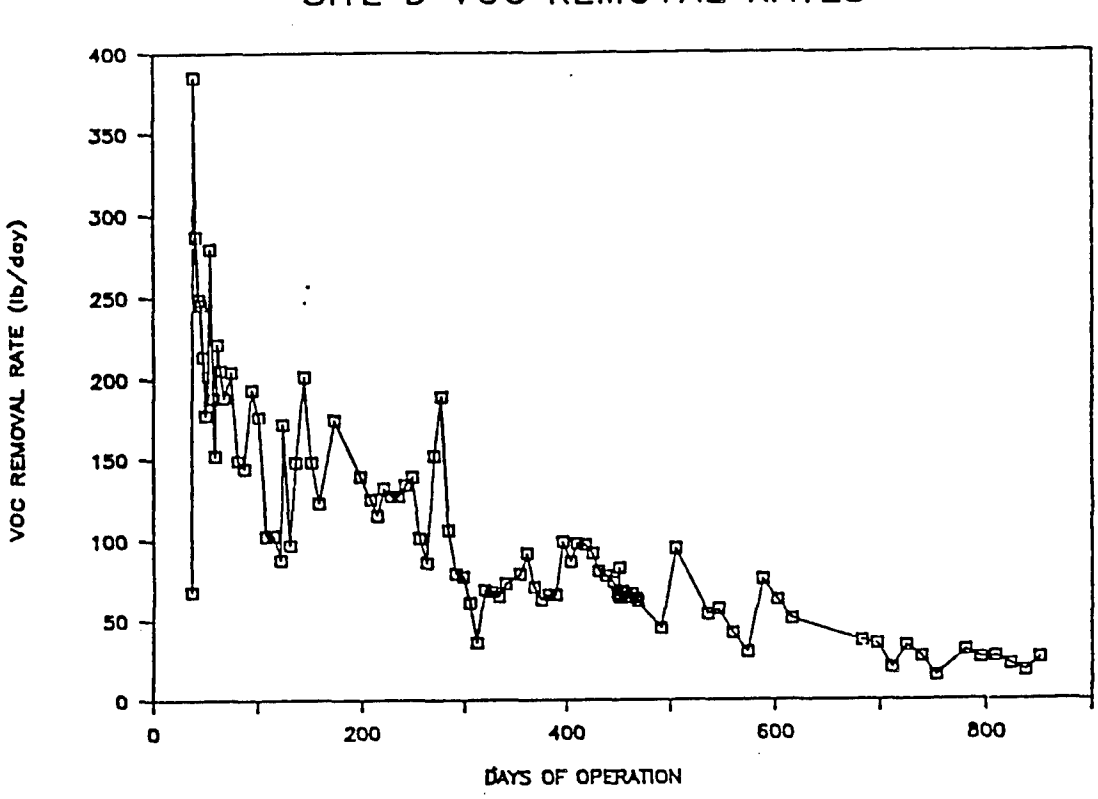


Figure 2

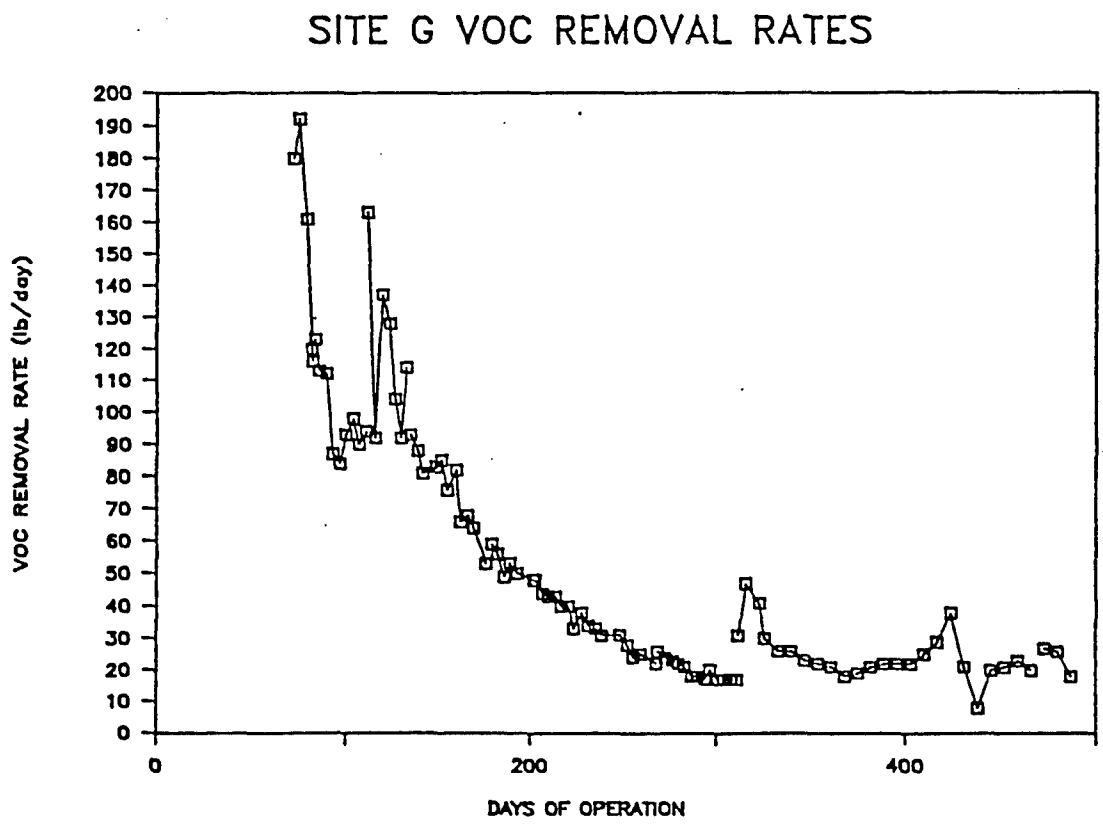


Figure 3

COSTS

The capital costs of the installation at Site D were $167,000. Capital costs at Site G, which included carbon, were $470,000. Operating costs for Site D have varied from $2,000-$3,000 per month. Site G costs with carbon regeneration are about $10,000 per month. During the time of operation the removal at both sites has been in excess of 160,000 pounds of volatiles. For Site D, without carbon, the total costs are estimated at $243,000. With the removal of 87,000 pounds of volatiles this is $2.80 per pound removed. For Site G, the capital costs of $470,000 with an additional $194,000 operating costs for the time of operation (300 days) would bring the cost per pound of VOC removed to approximately $8.

Figures 4 & 5 show the removal costs versus amount of VOCs removed.

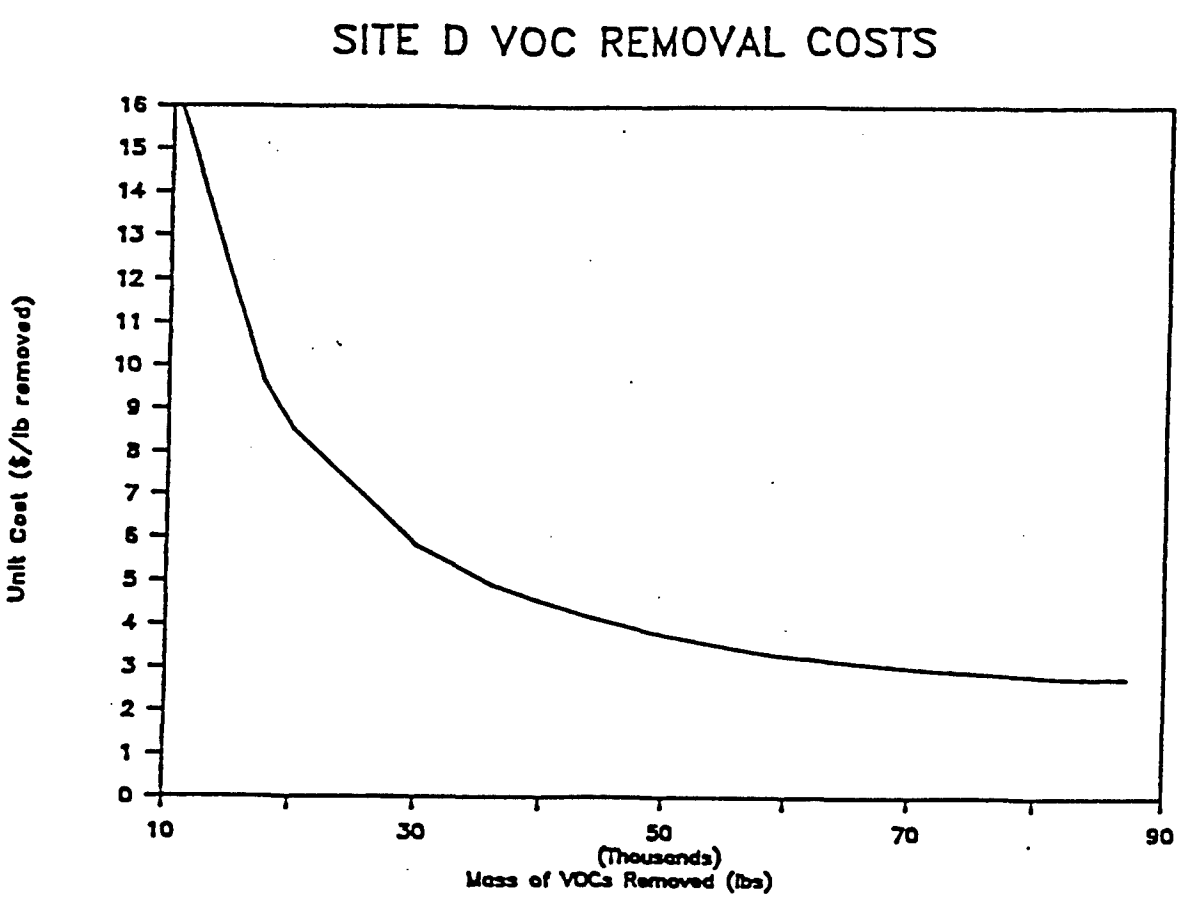


Figure 4

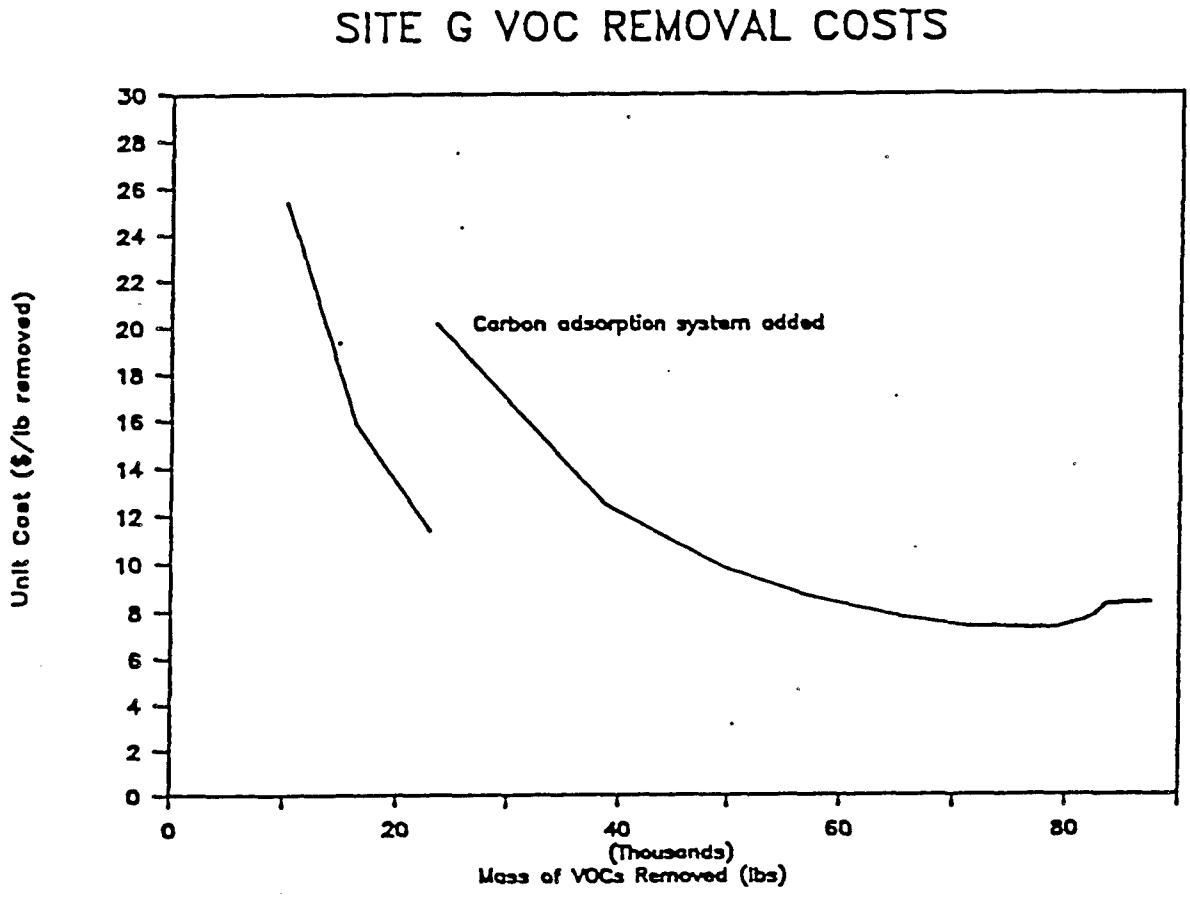


Figure 5

SUMMARY

In conclusion, the vacuum extraction form of soil treatment has been found to be an effective means of performing remedial action at a contaminated soil site. The capital cost investment is low. If the system can be throttled back to maintain the volatile emission rates within the regulatory agency requirements and can be operated with no controls, operating costs are relatively inexpensive. Labor and electrical costs are very low, with the only major item required on the system being the amount of sampling and analysis that would be conducted to verify the amount of volatiles being removed. Even with the usage of carbon, if the ability to regenerate the carbon is available, operating costs can be in the lower range so that total remediation costs can be relatively low in comparison to other forms of remediation such as excavation of soil and hauling it to a hazardous waste landfill.

The consulting firm of Wenck Associates, Inc. of Wayzata, MN and the Twin Cities Army Ammunition Plant were recognized and received the 1987 Grand Award from the MN Consulting Engineers Council for Engineering Excellence for this project.

Low Temperature Thermal Treatment of Volatile Organic Compounds

By

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Thirteenth Annual Environmental Quality
Research and Development Symposium
15-17 November 1988

INTRODUCTION

Leakages are common problems at Army installations where fuel and solvent storage, handling, and transfer operations take place. Surface soils in these high-use areas can often be contaminated from spills and leakages. Jet propulsion fuel (JP-4) and chlorinated organics such as trichloroethene (TCE) are prevalent soil contaminants and threats to groundwater sources at many airfields. Contamination migration control and cleanup are major challenges to installation personnel. The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is evaluating technologies to decontaminate soils.

Previous bench-, pilot-, and full-scale studies have shown that soil decontamination is possible using a low-temperature thermal treatment process to volatilize the contaminants from the soil, followed by high-temperature incineration of the exhaust fumes in an afterburner.

Roy F. Weston, Inc. (WESTON) designed and has received U.S. Patent Number 4,738,206 for the Low Temperature Thermal Treatment (LT^3) process for treating soils contaminated with volatile organic compounds (VOCs) and petroleum hydrocarbons. USATHAMA has commissioned WESTON to demonstrate a pilot study of a full-scale LT^3 process on soils at Tinker Air Force Base in Oklahoma. The pilot study is scheduled to be conducted 19 December 1988 through 10 February 1989.

PREVIOUS STUDIES

Bench-Scale System

The bench-scale unit located in WESTON's Lionville, PA laboratory has been used to determine the feasibility of treating various waste material by the LT^3 process. Past studies have demonstrated positive results in the removal of chlorinated benzenes from soil. Column leach tests of the processed soil showed less than 12 ppm of chlorinated benzene compounds and heavy metal concentrations two orders of magnitude below the EP toxicity action levels.

More recent bench-scale studies examine the feasibility of processing soil contaminated with coal tar and petroleum hydrocarbons. These soils contain several carcinogenic polynuclear aromatic (PNA) compounds. The results from the studies indicated high removal (greater than 96.7 percent) of benzene, toluene, ethyl benzene, and methylene chloride from the soil. The PNAs from the coal tar soil were removed with an average removal efficiency of 97.3 percent.

The soils containing petroleum hydrocarbons were contaminated with an average of 55 parts per million (ppm) PNAs and 100 ppm oil and grease. An average of 99.1 percent of the PNAs and 99.8 percent of the oil and grease were removed.

The bench-scale system is used to predict the capability of the full-scale unit to process a given soil matrix with specific contaminants. By testing the soil on the bench-scale unit, mobilization of the full-scale equipment and inappropriate use of the LT^3 system to solve problems that cannot or should not be processed by this system is avoided.

Pilot-Scale System

The pilot-scale unit was used to demonstrate the decontamination of VOC-contaminated soil at Letterkenny Army Depot. The study was performed under a contract with USATHAMA through the Research and Development (R&D) program. The results were favorable demonstrating the LT^3 as an effective technology for removing VOCs from soil. Greater then 99.9 percent VOC removal from the soil was demonstrated. Stack emissions were in compliance with Federal and State regulations including those for VOCs, HCl, CO, and particulates.[1]

Full-Scale LT^3 System

The encouraging results of bench-scale testing and the pilot program provided the confidence for Weston Services to invest in the construction of a full-scale system.

The full-scale LT^3 system has most recently demonstrated the removal of gasoline and No. 2 fuel oil from soil in Springfield, Illinois. The soil contained benzene, toluene, ethyl benzene, and xylene (BTEX) in a total concentration of 155 ppm. These contaminants were removed at an average of 99.9 percent. The soil also contained PNAs at an average concentration of 6 ppm. The final PNA concentrations averaged less than the detection limit of 0.3 ppm.

The full-scale LT^3 will be used for the demonstration test at Tinker AFB and then will be mobilized to the Crows Landing Naval Air Station located near Modesto, California. The project at

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[1]Test Plan for a Pilot Investigation of Low Temperature Thermal Stripping of Volatile Organic Compounds from soil at Letterkenny Army Depot, June 1985, Prepared for U.S. Army Material Command, U.S. Army Toxic and Hazardous Materials Agency, Contract DAAK11-82-C-0017, Task Order Number 11.

Crows Landing is for the remediation of soils contaminated with petroleum hydrocarbons from a leaking underground storage tank. This program is sponsored by the California Department of Health Services, and the U.S. Navy, and is part of the Superfund Innovative Technology Evaluation (SITE) program.

BACKGROUND OF THE TINKER AIR FORCE BASE DEMONSTRATION

The soils to be processed are located in the sludge dump area in the southwestern portion of Tinker AFB. The sludge dump was in operation during the period from 1961 through 1968. The dump is reported to contain waste oils and liquids from industrial operations and sludge from petroleum lubricants used at the Air Force Base.

An investigation of the sludge dump was conducted in March 1988.[2] Hydrogeological studies indicated a hydrocarbon layer was floating on the groundwater. Analysis of the free-floating product identified the sample as closely resembling jet fuel (JP-4), although it contained other hydrocarbon solvents. High concentrations of solvents, primarily TCE, were also found in the water and soil samples.

Another investigation was made in May 1988[2] to delineate the boundary of the sludge dump area. It was found that the soil was contaminated with petroleum hydrocarbons and solvents to a depth of approximately 12 feet. As a result of the investigations at the site, it was estimated that approximately 900 cubic yards of sludge-contaminated soil is present in the dump.

OBJECTIVES OF THE DEMONSTRATION AT TINKER AIR FORCE BASE

The objectives of the demonstration at Tinker AFB are to evaluate the LT^3 process to demonstrate the following:

- The effectiveness of the LT^3 treatment technology to remove JP-4 and chlorinated solvents from soils.
- The impact on system performance caused by varying operational parameters (e.g., hot oil temperature and soil residence time).
- The impact on system performance when utilizing a stripping agent (e.g., hexane and water) to aid in decontaminating the soils.

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[2]Installation Restoration Program, Tinker Air Force Base, Oklahoma, Landfill 3 Site, Sludge Dump Contaminated Soil Area, Information for Soil Removal and Decontamination, May 1988.

- The optimum range of operational parameters for treating contaminated soils.

- The ability to comply with Federal, State, or local air emissions requirements.

CRITERIA FOR A SUCCESSFUL DEMONSTRATION

The demonstration will be considered to be successful if the analytical results from the processed soil from some of the test runs indicate that the goal cleanup level (GCL) of the contaminants has been achieved. Table 1 lists the existing contaminant concentrations in the soil (based on previous investigations[2]) and indicates the GCL for each contaminant. Some tests will fail thus establishing the upper and lower operating limits for soil residence time and hot oil temperature. On- and off-site analysis will be conducted on the samples collected during the demonstration. Off-site analysis will be performed in the WESTON Analytics Laboratory located in Lionville, Pennsylvania.

The primary goal of the demonstration test is to determine the optimum operating conditions that effectively decontaminate the soil at a practical soil residence time and attainable hot oil temperature. The optimal operating conditions are those that result in a successful analytical test run (i.e., contaminant concentration below GCL) with the lowest soil residence time and lowest hot oil temperature.

A successful test run must also meet the following stack emissions limitations as required by the Oklahoma State Department of Health:

- Less than 4 pounds per hour hydrochloric acid.

- Less than 25 ppm carbon monoxide.

- Less than 0.08 grains particulate per dry standard cubic foot corrected to 12 percent carbon dioxide.

- Less than 100 ppm total hydrocarbons.

PROCESS DESCRIPTION

The foundation of the LT^3 technology is the thermal processor, an indirect heat exchanger used to dry and heat contaminated soils. Heating the soils to approximately 400°F evaporates and strips the moisture and VOCs from the soil. The organic vapors, stripped from the soils, are then processed in an afterburner or fume incinerator independent of the soil matrix.

Table 1

Contaminant Concentrations in Landfill 3
Soil Borings and Cleanup Objectives

Contaminant	Organic Concentration (ug/kg) max.	avg.	Goal Cleanup Level in Extract (ug/L)
Trichloroethene	6100000	743270	70 a
trans-1,2-Dichloroethene	370000	115875	N.A.
Tetrachloroethene	446900	76266	50 b
Toluene	270000	39341	330 b
1,2-Dichlorobenzene	570000	37066	125 b
Bis(2-ethylhexyl) phthalate	120000	30000	N.A.
2-Butanone	97000	18218	750 b
4-Methyl-2-pentanone	117320	16192	N.A.
Total xylenes	131000	13044	150 b
1,4-Dichlorobenzene	59000	12085	10800 a
Methylene chloride	84740	11152	960 b
4-Methylphenol	43000	10750	N.A.
1,2,4-Trichlorobenzene	24000	6675	N.A.
2-Methylnaphthalene	19000	4750	N.A.
2,4-Dimethylphenol	19000	4750	N.A.
2-Methylphenol	19000	4750	N.A.
1,3-Dichlorobenzene	52000	4309	N.A.
Fluoranthene	17000	4250	140 c
2-Hexanone	13000	3250	N.A.
2-Chloroethylvinylether	9200	3064	N.A.
Ethylbenzene	19280	2710	53 b
Acetone	5700	2083	N.A.
Naphthalene	6800	1700	N.A.
Diethyl phthalate	3800	950	N.A.
Chlorobenzene	3200	621	50 b
1,1-Dichloroethene	2200	550	100 a
1,1,1-Trichloroethane	980	352	410 b
Vinyl chloride	1200	314	50 a
Vinyl acetate	1000	250	N.A.
1,2-Dichloroethane	680	233	400 a

a - Remedial Design Bog Creek Farm Site, Superfund Project, Howell Township, New Jersey, U.S. Army Corps of Engineers, DACW 41-88-R-0162.
b - California List, 40 CFR Part 268, Subpart D.
c - Substances Toxic to Aquatic Life, Support B: General Use Waters Quality Standards of Illinois (February, 1986).
N.D. - None detected.
N.A. - Not assigned.

Table 1
(continued)

Contaminant	Organic Concentration (ug/kg) max.	avg.	Goal Cleanup Level in Extract (ug/L)
Benzene	490	123	70 a
Chloroform	11	3	70 a
Carbon disulfide	5	1	4810 b
Benzo(a)anthracene	N.D.	N.D.	8.7 c
Benzo(a)pyrene	N.D.	N.D.	15 c
Benzo(a)fluoranthene	N.D.	N.D.	12 c
Chrysene	N.D.	N.D.	100 c
Dibenzo(a,h)anthracene	N.D.	N.D.	20 c
Acenaphthene	N.D.	N.D.	1200 c
Acenaphthylene	N.D.	N.D.	660 c
Anthracene	N.D.	N.D.	660 c
Benzo(g,h,i)perylene	N.D.	N.D.	51 c
Benzo(k)fluoranthene	N.D.	N.D.	11 c
Fluorene	N.D.	N.D.	140 c
Indeno(1,2,3-c,d)pyrene	N.D.	N.D.	29 c
Phenanthrene	N.D.	N.D.	660 c
Pyrene	N.D.	N.D.	180 c

a - Remedial Design Bog Creek Farm Site, Superfund Project, Howell Township, New Jersey, U.S. Army Corps of Engineers, DACW 41-88-R-0162.
b - California List, 40 CFR Part 268, Subpart D.
c - Substances Toxic to Aquatic Life, Support B: General Use Waters Quality Standards of Illinois (February, 1986).
N.D. - None detected.
N.A. - Not assigned.

The LT^3 system is divided into four main topics of emphasis: soil treatment, hot oil system, emissions control, and water treatment. A schematic diagram of the LT^3 process is shown in Figure 1. The LT^3 process equipment is mounted on three tractor trailer beds for transportation and operation. The unit is suitable for highway transport and may be installed on a site location in 2 days (plus transportation). The general arrangement of the process equipment and the placement of the trailers during operation is shown in Figure 2.

Soil Treatment

Contaminated soil is excavated and stockpiled for feeding into a scalping screen or shredder to remove oversize (greater than 2 inch) material and debris. Classified material is transported by an enclosed drag conveyor to a hopper that directly feeds the thermal processor. The thermal processor is an indirectly heated auger type heat exchanger for solids and slurries. The processor mixes, conveys, agitates, and heats the contaminated soils allowing the moisture and volatiles to evaporate and escape from the soil. An indirectly heated processor was chosen to eliminate contamination of the heating medium and improve thermal efficiency.

The low operating temperature of the process heats the soil to approximately 400°F and minimizes the thermal load compared to incineration and still allows vaporization of the volatiles. Not only is less heat required to process the volatiles, but the soil matrix does not have to be heated to incineration temperatures.

The processor resembles a jacketed screw conveyor with four parallel screws contained in a single jacketed trough. The shaft and screw flights are also hollow to allow the hot oil to be circulated through the shaft and flights as well as the jacket.

In the full-scale LT^3 system two thermal processors, each with 4 18-inch diameter, 20-foot long screws have been stacked in series. They are operated in series to insure adequate residence time and agitation to release volatiles trapped in the interstices of the soil matrix.

After processing, the soil is transferred via enclosed screw conveyors to a dump truck for stockpiling or for use as on-site backfill.

Hot Oil System

The heating system for the hot oil is a conventional closed loop 7.2 million Btu/hr hot oil heater with the associated pumps, tanks, piping, valves, and controls. This system heats the oil to 600°F and can be fired on propane, natural gas, or oil. The oil temperature and flow rate can be adjusted to compensate for varying feed characteristics.

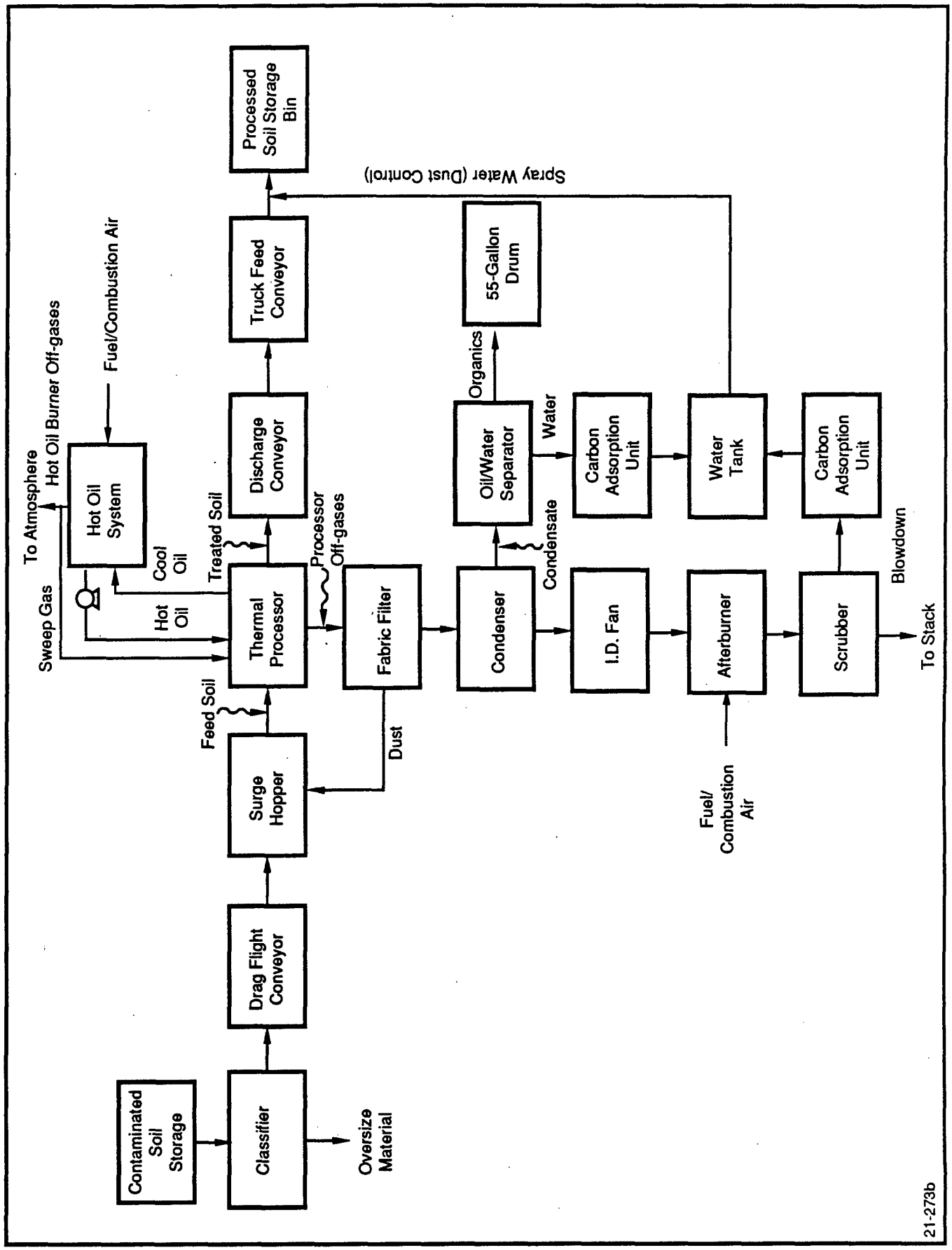
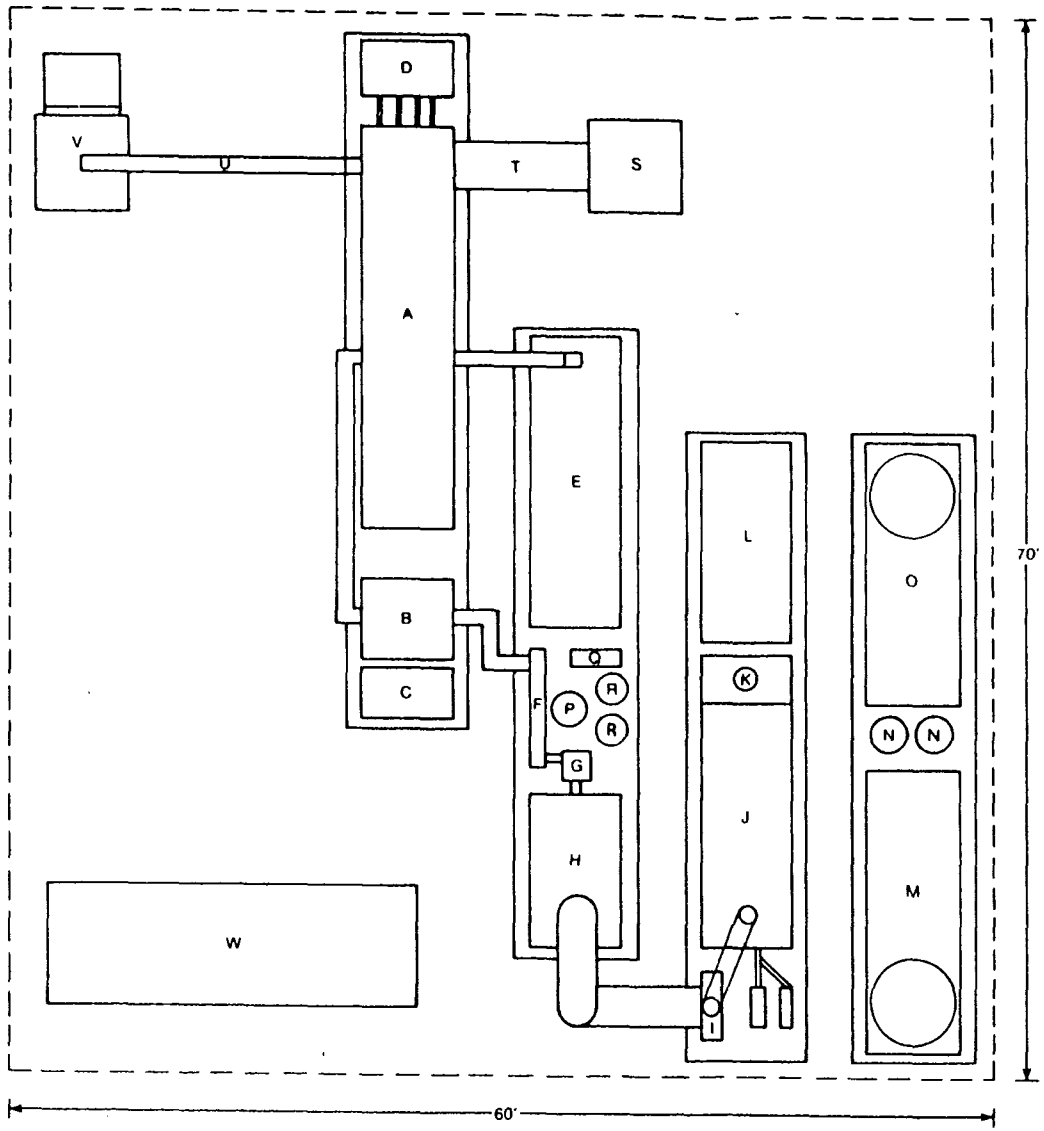


Figure 1 Flow Diagram for the Low Temperature Thermal Treatment System



Equipment

- A Thermal Processors
- B Baghouse
- C Motor Control Center
- D Thermal Processor Drive Units
- E Hot Oil System
- F Condenser
- G Induced Draft Fan
- H Afterburner
- I Scrubber ID Fan
- J Scrubber System
- K Exhaust Stack
- L Caustic Storage Tank
- M Fresh Water System
- N Blowdown Carbon Adsorption Units
- O Blowdown System
- P Recycle Water Tank & Pump
- Q Oil/Water Separator
- R Water Carbon Adsorption Units
- S Clay Shredder
- T Drag Conveyor
- U Discharge Conveyor
- V Dump Truck
- W Continuous Emissions Monitoring Trailer (CEM)

Figure 2 Mobile Low Temperature Thermal Treatment System Layout

Emissions Control System

A portion of the combustion gases released from the hot oil system is used as sweep gas in the thermal processor. The warm sweep gas removes the volatiles from the processor. Sweep gas is introduced to maintain an exhaust gas temperature from the processor of about 300°F to avoid moisture or organic condensation. The sweep gas is a safety measure providing an inert atmosphere to avoid exceeding the lower explosive limit (LEL) of contaminants within the thermal processor and downstream equipment.

This sweep gas carries the volatiles through a fabric filter (baghouse) for particulate emissions control and then into a condenser. The condenser reduces the water load on the subsequent afterburner and condenses some of the volatiles, making it possible to recover selected volatiles as desired.

An acid gas scrubber is included in the system to be operated at Tinker AFB. The scrubber is located immediately downstream of the afterburner. In the first stage of the scrubber, the quencher, the gases are cooled to saturation temperature. In the second stage, the packed bed absorber, acidic gases, such as hydrochloric acid (HCl), are neutralized to sodium chloride (NaCl) and water using sodium hydroxide (NaOH). The scrubber is designed for a minimum HCl removal efficiency of 99 percent. Since salts are generated through the neutralization process, a small purge (blowdown) stream is maintained to prevent the buildup of salts. The scrubber blowdown liquid is collected for on-site treatment and reuse.

Water Treatment

Condensate from the condenser is composed of water and condensed volatile organics. The two phase condensate is separated in an oil-water separator. The separated organic phase (oil) is stored in 55-gallon drums for future transport and processing off-site or for recovery of the organics.

The water, from the oil-water separator and the scrubber blowdown with a low concentration of soluble organics and salts, is treated in a 2-stage carbon adsorption system. The treated water is sprayed on the discharging processed soil to cool the soil and to suppress fugitive dust emissions.

OPERATING CONDITIONS FOR THE DEMONSTRATION TEST

Fifteen test runs will be completed. A test run consists of a minimum of 4 hours of steady-state operation. The test runs are divided into four phases:

- o Determining limits of operation.
- o Optimization.
- o Verification.
- o Enhancement with solvent addition.

A three-by-three matrix has been developed and is shown in Table 2. Three soil residence times (30, 45, and 60 minutes) and three hot oil temperatures (400, 500, and 600°F) will be evaluated. Operating times and temperatures were selected based on the types and concentrations of contaminants in the soil and on past operating experience.

The first test run will be conducted to determine the upper limit of operation (i.e., the highest soil residence time and hot oil temperature). After reviewing the analytical results of the first test, it may be necessary to increase the operating conditions to establish the upper limit. After the upper limit is established, the lower limit will be determined in the same manner (i.e., the lowest soil residence time and hot oil temperature).

Once both the upper and lower limits have been established, the matrix will be adjusted as necessary. The remaining matrix test runs will be conducted to perform the optimization phase of the program. These runs will be conducted to establish the optimum operating conditions for soil decontamination.

The verification phase of the program will be conducted based on the data resulting from the matrix test runs. The optimum test run as determined from the data will be run simultaneously with a stack testing program. The stack test will be conducted to verify that the stack emissions are within the regulatory limits.

Once the optimum conditions have been established, the final test runs will be performed with variations in the soil residence time and hot oil temperature while adding a solvent or stripping agent (hexane and water). These runs will determine whether the efficiency of the LT^3 process can be enhanced by adding these specific stripping agents. Stack testing will be conducted during two of the final test runs.

SAMPLING PROGRAM

Samples of the feed and processed soils and the process streams will be collected and analyzed in the on-site laboratory. The locations of the sampling points are shown in Figure 3. Table 3 indicates the analysis that will be performed on each of the samples.

Table 2 Test Matrix for Determination of Optimum Operating Conditions

Residence time (minutes)	Hot Oil Temperature (°F) 400	500	600
30	Ts=150	Ts=250	Ts=350
45	Ts=200	Ts=300	Ts=400
60	Ts=250	Ts=350	Ts=450

Ts=Estimated Processed Soil Temperature

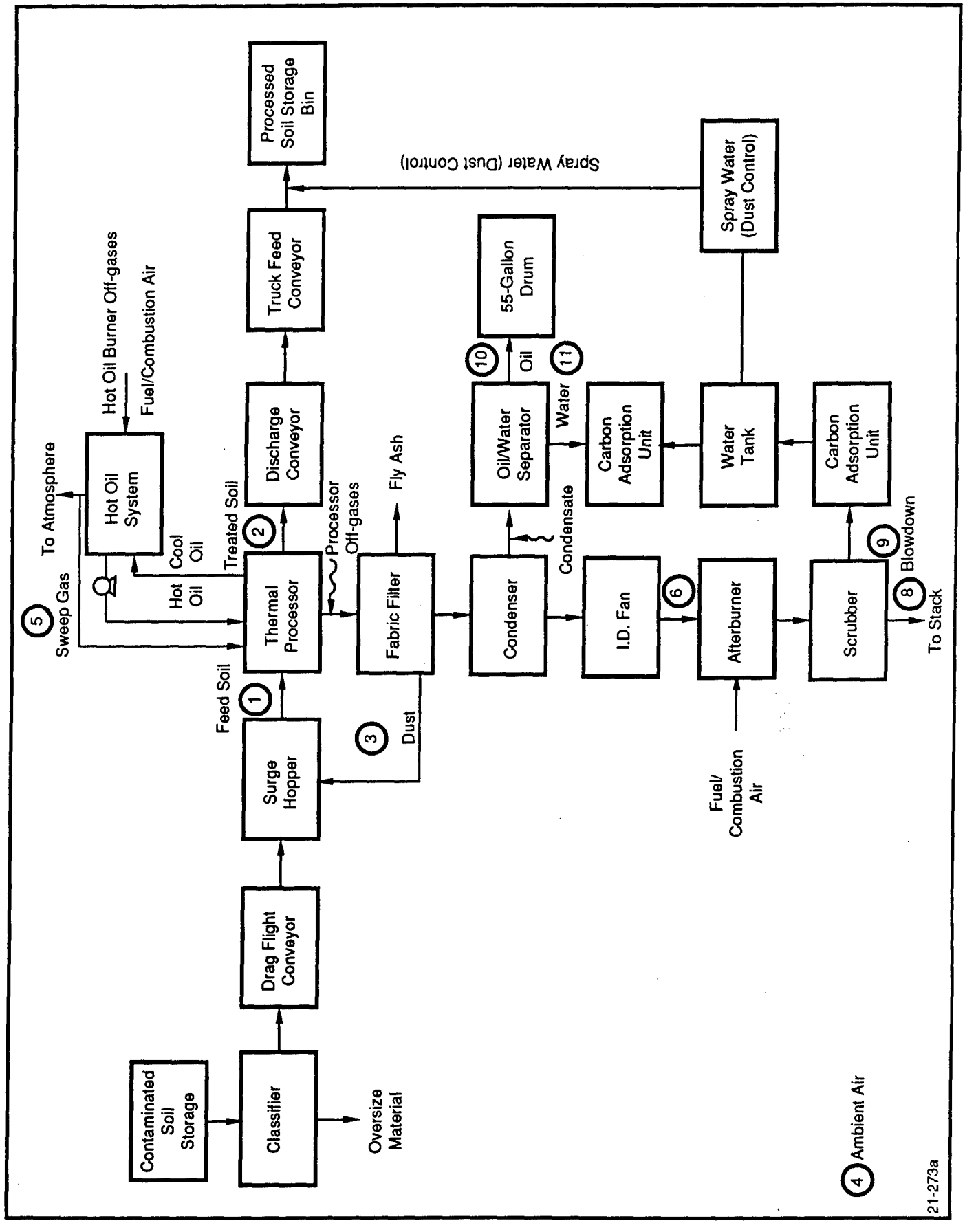


Figure 3 Sample Locations for the Low Temperature Thermal Treatment System

Table 3

Summary of Sample Analysis

Parameters Sampled and Analyzed	Feed Soil	Processed Soil	Dust	Ambient Air	Sweep Air Inlet	Afterburner Inlet	Afterburner Outlet	Stack Gas	Scrubber Blowdown	Condensate Phase Oil	Condensate Phase Water
Volatiles	X	X	X	X		X		X	X	X	X
Semivolatiles	X	X	X			X		X	X	X	X
Oxygen					X	X	X				
Carbon monoxide					X	X	X				
Carbon dioxide					X	X	X				
Total hydrocarbons					X	X	X				
Nitrous oxides								X			
Particulates								X			
Moisture content				X	X	X		X			
HCl								X			

DATA ANALYSIS

After completing the demonstration test, a written report will be submitted to USATHAMA. The report will include test data results and an evaluation of equipment performance based on the initial objectives of the demonstration. The report will address the effectiveness of the LT^3 to remove VOCs from soils; the impact of system performance of varying operational parameters and solvent addition; and the ability to comply with air emissions regulations. The final report will also include recommendations for system optimization, design revisions, and an economic analysis of data for a recommended full-scale treatment system.

USATHAMA Analytical Chemistry Program

By

Kenneth T. Lang
Chief, Analytical Branch
USATHAMA

Presented at
Thirteenth Annual Environmental Quality
Research and Development Symposium
15-17 November 1988

METHODS DEVELOPMENT

Highlights of Previous Work:

- Developed and validated explosives in soil and water
- Evaluated drying techniques on the loss of explosives from soil samples
- Evaluated effects of PVC pipe on the recovery of explosives from groundwater
- Development of a fiber optics technique for the detection of TNT in groundwater
- Compared effects of well casing materials on groundwater monitoring wells
- Developed method for explosives in plant tissues

METHODS DEVELOPMENT

Work Currently in Progress:

- Validate the field TNT detector kit
- Develop method for nitrocellulose in soil and water
- Develop fiber optics method for RDX
- Improve analytical procedure for nitroglycerine in soil and water
- Continuation of method development for explosives in plant tissue
- Conduct leaching study of Well Casing material and expand list of analytes from previous study
- Investigate degradation and biodegradation products of explosives
- POC – Marty Stutz AV 584–3206; (301) 676–7569

SURFACE SAMPLING TECHNIQUES

Objective : To develop a "real-time" and permanent record of explosive and explosive by product contamination on building surfaces and equipment at AAP's.

- A.D. Little developed a procedure for the detection of explosives on surfaces using a UV/still photography technique
- Barringer Research Ltd. designed, constructed, and field tested a "real-time" detection technique using a video camera, a UV illuminator, an image processor, and a TV monitor.
  Draft final report received Aug 88
- POC - Les Brown, AV 584-3206; (301) 676-7569

SOLID SORBENT COLLECTION PROCEDURES

Objective : To develop a sample collection procedure using solid sorbents to preconcentrate analytes of interest in the field to reduce shipping costs, improve holding times and reduce sample loss from breakage.

- Oak Ridge National Laboratories evaluated solid sorbent materials for the collection of explosives, pesticides, and phenols from water and soil.
- Battelle Columbus validated the collection procedures for explosives, pesticides, and phenols. Improved the collection procedures, and the explosive method.
- Army Environmental Hygiene Agency is conducting ruggedness testing of the explosives collection procedure and method.
- Battelle Columbus to continue work on pesticides and phenols.
- POC – Doug Scarborough AV 584-3348; (301) 676-7569

SOLID SORBENT TECHNIQUE for ORGANOCHLORINE PESTICIDES

Objective : To identify and compare solid sorbent material(s) for the absorption of organochlorine pesticides from groundwater samples, and to develop analytical protocols for the determination of organochlorine pesticides. This methodology will provide a means to preconcentrate the analytes of interest in the field resulting in reduced shipping costs, improved holding times and reduced sample loss due to breakage.

- Continuation of work started by Oak Ridge National Laboratories and Battelle Columbus
- Follow-on contract awarded to Battelle Columbus Sep 88
- Final report to be completed April 89
- POC – Durant Graves, AV 584-3206; (301) 676-7569

FIELD PORTABLE INSTRUMENTS and METHODS

Objective : To identify and field test analytical instruments and methods which can be routinely used in the field to obtain "real-time" analytical data from environmental samples.

- Task awared to Oak Ridge National Laboratories April 87
- Literature review completed July 88
- Laboratory testing completed Nov 88
- Field testing at Rocky Mountain Arsenal scheduled for completion Mar 89
- POC – Doug Scarborough AV 584-3348; (301) 676-7569

FIELD SAMPLE PREPARATION TECHNIQUES

Objective : To develop for field use, alternatives to fixed laboratory analytical methods which require extensive, time-consuming sample pretreatment prior to instrumental analysis.

- Award task second quarter FY 89
- Performer – Cold Regions Research and Engineering Laboratory
- Project Completion – first quarter FY 90
- POC – Durant Graves, AV 584-3206; (301) 676-7569

RDX FIELD DETECTOR KIT

Objective : To develop a field detector kit for the detection of RDX in water and soil.

- Contract awarded to Battelle Columbus Sep 88
- Planned completion date Apr 89
- Follow up effort to validate method
- POC – Doug Scarborough, AV 584-3206; (301) 676-7569

DEVELOPMENT OF MONOCLONAL ANTIBODIES FOR TETRYL

Objective : To develop a reliable method for the analysis of tetryl in environmental samples which is more precise and with better accuracy than current instrumental techniques.

- Contract awarded to Westinghouse Bioanalytic Systems, Co. Jun 88
- Planned completion date Feb 89
- Follow up effort to validate method
- POC – Steve Krogsrud, AV 584-3206; (301) 676-7569

DEVELOPMENT of MONOCLONAL ANTIBODIES for RMA

Objective : To produce monoclonal antibodies for use in the analysis of 1) Benzene, 2) Dieldrin, and 3) Para-Chlorophenylmethylsulfone in environmental samples. Use of monoclonal antibodies will provide a more specific analysis than is possible using current methodologies.

- Tasks awarded to Battelle-Columbus and Southern Research Sep 88
- Production of antibody to be completed Dec 88
- Method testing to be completed Mar 89
- Final Report to be completed May 89
- POC - Doug Scarborough, AV 584-3206; (301) 676-7569

HOLDING TIME STUDY

Objective : To establish a valid data base upon which to base how long samples may be retained after collection and prior to analysis without detrimental effects to the analytes of interest.

- Joint DOD/EPA/DOE study, with USATHAMA the lead agency.
- Completed evaluation of explosives and volatiles in soil and water.
- Holding time study results:

	Current	Study
– Explosives, water	7 days	56 days
– Explosives, soil	7 days	56 days
– Volatiles, water	14 days	56 days (pH2)
– Volatiles, soil	7 days	< 3 days

- POC – Mary Ann Ryan, AV 584–3348; (301) 676–7569

DEVELOPMENT OF INTEGRATED VOC METHODOLOGY

Objective : To develop a method for collection, preservation, and analysis of volatile organics in soil which addresses the deficiencies in the current EPA methodology.

- Task awarded to Oak Ridge National Laboratories Aug 88
- Currently evaluating techniques for the collection of soil samples and the potential for adapting them to conventional analytical techniques with significantly reduced sample transfer and manipulation steps
- POC – Mary Ann Ryan, AV 584-3348; (301) 676-7569

EVALUATION OF GLOW DISCHARGE MASS SPECTROMETRY

Objective : To develop a rapid, cost effective mass spectrometry technique to replace the current EPA methods for volatiles and semivolatiles in the soil and water.

- Task awarded to Oak Ridge National Laboratories 4 April 88
- Can now analyze 8 samples per day using EPA GC/MS methodology
- Successful to date analyzing up to 200 samples per day using GD/MS
- POC – Doug Stevenson, AV 584-3348; (301) 676-7569

DEVELOPMENT OF A STANDARD REFERENCE SOIL

Objective : To develop a well characterized, standard matrix soil which can be used by all USATHAMA laboratory contractors to certify analytical methods for soil and for the preparation of daily quality control samples.

- US National Bureau of Standards has begun development of work plan. Coordination meeting between USATHAMA, NBS, and Maryland Department of Agriculture was held in Aug 88
- Planned completion date Jun 89
- POC – Steve Krogsrud AV 584-3206; (301) 676-7569

DEVELOPMENT of STANDARD METHODS

Objective : To identify and evaluate the best analytical methods for the analysis of environmental samples; and to develop a data base on the precision and accuracy of each method in order to establish preliminary performance criteria for contractor laboratories

- Awarded contract to Environmental Science and Engineering Sep 86, and a contract to A D Little Sep 87
- ESE has completed 5 methods and are finalizing 8 additional methods
- ADL has been awarded 7 tasks to date
- POC – Mary Ann Ryan, AV 584-3348; (301) 676-7569

CLASS CONTRACT

Objective : To provide Contractor Laboratory Analytical Support Services for the Installation Restoration Program following strict QA/QC protocol.

- Five year, fixed price contract with five laboratories.
- Analyses certified and conducted IAW USATHAMA QA/QC protocol
- Delivery orders can be awarded usually in 3 weeks or less
- Analyses completed in 30 days or within holding time whichever is less; letter report within 5 days of completing analysis; data entry into IRDMS 30 days following completion of analysis.
- Emergency response within 72 hours of sample receipt.
- POC's – Doug Stevenson/Mary Ann Ryan, AV 584-3348; (301) 676-7569.

Laboratory Investigation of the Toxicity Characteristic Leaching Procedure and the Extraction Procedure Toxicity Characteristic

by

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Waterways Experiment Station, Corps of Engineers
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Vicksburg, Mississippi 39181-0631

ABSTRACT

The 1984 amendments to the Resources Conservation and Recovery Act (RCRA) require that the U.S. Environmental Protection Agency (USEPA) restrict the land disposal of hazardous wastes. USEPA identified four characteristics that could be used to classify a waste as hazardous. These included corrosivity, ignitability, reactivity, and toxicity as defined by the Extraction Procedure Toxicity Characteristic (EP). Waste exhibiting any one of these characteristics is classified as hazardous.

The EP test is used to determine if a waste poses an unacceptable risk to human health and the environment. This test evaluates the potential for a waste to leach eight metals, four pesticides, and two herbicides.

The Toxicity Characteristic Leaching Procedure (TCLP) was developed to address a Congressional mandate to identify additional characteristics of wastes, primarily organic constituents, that may pose a threat to the environment. This testing procedure has been promulgated for use in determining specific treatment standards associated with the land disposal restrictions. The TCLP is also proposed as a replacement procedure for the current EP test. The TCLP procedure expands the list of contaminants from the 14 listed in the EP protocol to a total of 52. The additional contaminants include 20 volatile organics, 16 semi-volatile organics, and 2 pesticides.

This study compared the results of the TCLP with those of the EP to determine the precision of both tests. Two heavy metal synthetic wastes and a perchloroethylene still bottom waste were used in this study. Twelve volatile organic compounds were added to each waste type at two ratios. Two synthetic heavy metal wastes were solidified/stabilized and the perchloroethylene waste was untreated. The EP and TCLP extractions were performed on three samples from each waste. The resulting leachate was analyzed for As, Ag, Ba, Cd, Cu, Ni, Pb, and Zn and the twelve volatile organic compounds. The results of this study indicated that the TCLP and EP extracts were similar for most of the metal contaminants when extraction fluid No. 2 was used for the TCLP, but differ when TCLP extraction fluid No. 1 was used. Concentrations for six of the volatile organic contaminants measured in the TCLP leachates, were significantly higher than those measured in the EP leachates while the TCLP and EP tests produced similar results for the four additional volatile organics evaluated in this study.

ACKNOWLEDGEMENTS

The test described and the resulting data herein, unless otherwise noted, were obtained from research conducted by the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. The study was sponsored by the U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory (HWERL), Cincinnati, Ohio, and by the Office of Solid Waste (OSW), Washington, DC., under Interagency Agreement DW9693014601. Mr. Carlton Wiles, HWERL, was the EPA project officer, and Mr. David Friedman, OSW, provided policy assistance throughout the study. Permission to publish this information was granted by the Chief of Engineers and by the USEPA project sponsor.

INTRODUCTION

In 1976 the Congress of the United States enacted Public Law 94-580, the "Resource Conservation and Recovery Act of 1976" (RCRA). Section 3001 of the Act required that the U.S. Environmental Protection Agency (USEPA) promulgate criteria to differentiate between hazardous and non-hazardous wastes (Government Institutes 1983).

Under RCRA, the USEPA established three methods for delineating a waste as hazardous. First, a waste is defined as hazardous if it is listed in Table 1 of Volume 45 of the May 19 Federal Register (USEPA 1980). Second, a non-listed waste is determined to be an "Acute Hazardous Waste" if the waste is: (a) found to be fatal to humans in low doses, or (b) it is shown in studies to have an oral LD50 (lethal dose to 50 percent of the population tested) in rats of less than 2 mg/l, or a dermal LD50 in rabbits of less than 200 mg (Hill 1986). Third, a non-listed waste is designated as hazardous if it exhibits a characteristic of a hazardous waste as established by the USEPA and outlined in CFR 40 part 261 subpart C (USEPA 1987).

The four characteristics that the USEPA established to designate a non-listed waste as a hazardous waste are ignitability, reactivity, corrosivity and EP toxicity. A waste exhibiting one or more of these characteristics is classified by the USEPA as hazardous. Once a waste is classified as hazardous it must be handled in accordance with RCRA. Each of these four characteristics is outlined in detail in USEPA's SW-846 (USEPA 1982, 1986c).

While ignitability, reactivity, and corrosivity are important characteristics of hazardous waste, no additional discussion of these characteristics is presented in this paper. The focus of this paper is directed towards the characteristics of toxicity as defined by the Extraction Procedure Toxicity Characteristic (EP) and the newly developed Toxicity Characteristic Leaching Procedure (TCLP).

EXTRACTION PROCEDURE TOXICITY CHARACTERISTIC

One of the most significant dangers posed by hazardous waste stems

from the leaching of toxic constituents into groundwater (Government Institutes 1983). The EP is the test procedure promulgated under RCRA which addresses characteristics directly related to the actual toxicity of the waste. During the development of the EP test, the USEPA's "primary concern was that hazardous waste might, unless subjected to regulatory control, be sent to a sanitary (municipal) landfill" (Friedman 1985). Based on this concern, the EP test was designed to simulate the leaching of a solid hazardous waste co-disposed with municipal waste in a sanitary landfill and to evaluate the potential impact of the leachate on ground water contamination.

A waste exhibits EPToxicity if it fails to pass the EP (USEPA 1986c). Assessing this characteristic entails subjecting the waste to a leaching test and analyzing the extract for eight metals, four pesticides, and two herbicides. If the EP extract contains these contaminants above the limits set by the USEPA it is determined to be "hazardous."

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

Regulations defining a waste as hazardous were first promulgated in 1980. At the time that the EP was promulgated, the USEPA recognized that the EP only addresses a small portion of the recognized toxic constituents (Friedman 1985). Almost immediately, the USEPA initiated work to develop a leaching procedure that would address additional toxic constituents of hazardous waste, primarily organic compounds. As a result of the USEPA's research effort, the TCLP extraction has been proposed as a method of addressing the shortcomings of the EP extraction (Friedman 1985). Since the TCLP was first published in the Federal Register (USEPA 1986a), it has undergone several modifications. At the time this study was conducted the June 13, 1986 publication of the TCLP (USEPA 1986b) was the most current. This is the method which was followed throughout this study. More recently the November 7, 1986 version of the TCLP method has been published in the Code of Federal Regulations (USEPA 1987).

LEACHING PROCEDURES

The EP Leaching Procedure

The EP is outlined in "Testing Methods for Evaluating Solid Waste" (USEPA 1982). The EP extraction consists of five steps, each of which is summarized below:

1. Separation Procedure--
   A waste containing unbound liquid is filtered and if the solid phase is less than 0.5% (by weight) of the waste, the solid phase is discarded and the filtrate analyzed for the EP contaminants. If the waste contains more than 0.5% solids, the solid phase is extracted and the liquid phase stored for later use.

2. Structural Integrity Procedure/Particle Size Reduction--
   Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of waste of 3.1

cm2, or, if it consists of a single piece, be subjected to the Structural Integrity Procedure (SIP). The SIP is used to demonstrate the ability of the waste to remain intact after disposal. If the waste does not meet one of these conditions, it must be ground to pass the 9.5-mm sieve.

3. Extraction of Solid Material--
The solid material from step 2 is extracted for 24 to 28 hours in an aqueous medium whose pH is maintained at or below 5.0 using 0.5 N acetic acid. In acidifying to pH 5, no more than 4.0 g of acid solution per gram of material being extracted may be used.

4. Final Separation of the Extraction from the Remaining Solid-- After extraction, the liquid:solid ratio is adjusted to 20:1 and the mixed solid and extraction liquid are separated by filtration. The solid is discarded and the liquid is combined with any filtrate obtained in Step 1. This is the EP extract that is analyzed and compared to the threshold values listed in Table 1 (USEPA 1982).

5. Testing (Analysis) of EP Extract--
Inorganic and organic species are identified and quantified using the appropriate 7000 and 8000 series of methods of analyses. These methods are listed in "Test Methods for Evaluation Solid Waste" (USEPA 1982, 1986b).

The TCLP Leaching Procedure

The TCLP is outlined in the June 1986 Federal Register (USEPA 1986b). Specific modifications to this procedure implemented during this study are described in the "Materials and Methods" section of this paper. The TCLP Procedure is summarized below.

The TCLP Procedure is conducted in two parts. The first consists of a procedure, employed for the extraction of non-volatile compounds. The second is employed for the extraction of volatile compounds.

Procedure When Volatiles are Not Involved--
The TCLP procedure for non-volatile contaminants consists of a five step procedure as described below:

1. Separation Procedure--
A waste containing unbound liquid is filtered and if the solid phase is less than 0.5% of the waste, the solid phase is discarded and the filtrate is analyzed for the desired non-volatile contaminants. If the waste contains more than 0.5%
solids, the solid phase is retained for extraction and the liquid phase is stored for later use.

TABLE 1. MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (mg/l)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10,10-Hexachloro-1 7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1 4-endo, endo-5,8-dimethano-naphthalene)	0.02
D013	Lindane (1.2,3,4,5,6-Hexa-chloro-cyclohexane, gamma isomer	0.4
D014	Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl)ethane)	10.0
D015	Toxaphene (C10H10C18, Technical chlorinated camphene, 67-69% chlorine)	0.5
D016	2,4-D (2,4-Dichlorophenoxyacetic acid)	10.0
D017	2,4,5-TP (Silvex) (2,4,5-Trichlorophenoxypropionic acid)	1.0

2. Particle Size Reduction--

Prior to extraction, the solid material should have a particle size capable of passing a 9.5-mm (0.375-in.) standard sieve or a surface area per gram of material equal to or greater than 3.1 cm2. If the surface area is smaller than the 3.1 cm2, the particle size of the material should be

reduced. Unlike the EP, the SIP is not performed on material subjected to the TCLP.

3. Extraction Fluid Determination--

Prior to extraction, a small sample of the waste is slurried in distilled water. Depending on the pH of this slurry either extraction fluid No. 1 or No. 2 is selected as the extraction fluid to be utilized throughout the non-volatile extraction. Extraction fluid No. 1 is a buffer solution made by combining glacial acetic acid and 1.0 N sodium hydroxide. Extraction fluid No. 2 is an acetic acid solution having a pH of 2.88.

4. Extraction of the Solid Material--

The solid waste is placed in an extraction bottle. Then the appropriate extraction fluid at twenty times the weight of the solid waste is utilized to slurry the solid waste. The waste is extracted for 18 hours.

5. Final Separation of the Extraction from the Remaining Solid--

Following extraction the liquid is separated from the solid by filtration. The solid is discarded and the liquid is combined with any filtrate obtained in Step 1. This is the TCLP Extract that is analyzed for non-volatile contaminants.

Procedure When Volatiles are Involved--

The TCLP procedure for volatile contaminants (Table 2) consists of a four-step procedure as outlined below:

1. Separation Procedure--

A separation procedure, similar to the one used for the non-volatile extraction, is performed. This procedure is described in the "separation procedure" outlined in the section "Procedure When Volatiles are Not Involved."

2. Particle Size Reduction--

The method used to reduce the particle size of the waste extracted for volatile compounds is similar to the particle size reduction method utilized for the non-volatile extraction. This method is described under the non-volatile section.

3. Zero-Head Extraction of the Solid Material--

The solid waste is extracted utilizing extraction fluid No. 1. The waste is placed in a Zero-Head Extraction (ZHE) device and slurried (under zero-head conditions) with the extraction fluid at 20 times the weight of the waste. The waste is
extracted for 18 hours.

TABLE 2. VOLATILE CONTAMINANTS AS LISTED BY THE TCLP*

Compound
Acetone
n-Butyl alcohol
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Methylene chloride
Methyl ethyl ketone
Methyl isobutyl ketone
Tetrachloroethylene
Toluene
1,1,1 Trichloroethane
Trichloroethylene
Trichlorofluoromethane
Xylene

* If any or all of these compounds are of concern, the zero-head space extractor vessel shall be used. If other (non-volatile) compounds are of concern, the conventional bottle extractor shall be used.

4. Final Separation of the Extraction from the Remaining Solid--Following extraction the liquid is filtered as it is removed from the ZHE device. The solid is discarded and the extraction liquid is combined with any filtrate obtained in step 1. This is the TCLP extract that is analyzed for volatile contaminants.

Comparison of the EP and TCLP Procedures

There are many contrasts between the EP and TCLP procedures (Callaway et al. 1987), some of which are quite prominent, while others are buried deep within the procedures. The most obvious dissimilarity is that the TCLP procedure requires the use of the ZHE apparatus for volatile compounds and an extraction fluid selection step. Other differences include:

(1) The TCLP requires that each phase of a multiphase leachate be analyzed separately and then mathematically recombined. The EP does not address multiphasic leachates.

(2) The TCLP requires separation of oily waste samples into a liquid and solid phase. The EP addresses non-filterable oily waste as a solid material.

(3) In the TCLP procedure for non-volatiles, one of two extraction fluids is selected to extract the solid waste sample. The type of extraction fluid is determined in an initial test on the waste and is based

on the waste's alkalinity. Extraction fluid No. 1 is an acetate buffer at a pH of 4.93 +/-0.05. Extraction fluid No. 2 is an acetic acid solution with a pH of 2.88 +/-0.05. The EP utilizes distilled deionized water as an extraction fluid and 0.5 N acetic acid is added to the solid waste/water slurry to maintain the pH at 5.0 +/-0.2. The acetic acid is added as required, up to a maximum of 4 g of 0.5 N acetic acid per 1 g of solid waste extracted.

(4) The TCLP procedure requires the use of 0.6 to 0.8 m glass fiber filter and excludes the use of prefilters. The EP requires the use of 0.45 m cellulose triacetate filters and allows the use of glass fiber prefilters.

(5) The TCLP requires that the particle size of the solid be small enough to pass a 9.5-mm standard sieve. The EP allows the use of the SIP if the sample is monolithic in nature. If the sample is not a monolith, the EP requires that the particle size be small enough to pass a 9.5-mm standard sieve.

(6) The TCLP requires that the ZHE apparatus be used for volatile extractions and also specifies that glass, polytetrafluoroethylene (PTFE), type 316 stainless steel, high-density polyethylene (HDPE), polypropylene or polyvinyl chloride must be utilized as extraction vessels when non-volatile compounds are extracted. The EP is vague about the extraction vessel design.

(7) The TCLP requires rotary agitation in an end-over-end fashion at 30 +/-2 rpm. The EP allows the use of a blade-stirred vessel or a rotary end-over-end agitator.

(8) The extraction period is 18 hours for the TCLP and 24 to 28 hours for the EP.

(9) The EP requires monitoring and adjustment of the pH throughout the extraction, while the TCLP does not.

PURPOSE AND SCOPE

The purpose of this study was to compare the results of the TCLP to those of the EP. This comparison was accomplished by dividing the study into two separate sections. The first evaluated the relative metal-extraction effectiveness of the two methods, while the second investigated the extraction of volatile compounds by the EP and the TCLP.

MATERIALS AND METHODS

The study reported on herein was conducted in four phases: (1) stabilization/solidification (S/S) of the various sludges, (2) curing and preparation of test specimens, (3) extraction of the S/S wastes using the EP and TCLP, and (4) analysis of the extracts. Each phase is discussed in detail below.

STABILIZATION/SOLIDIFICATION OF THE SLUDGES

The three wastes, a synthetic metal sludge (WES), a synthetic metal waste solution (WTC), and a perchloroethylene still bottom waste (PCE), were utilized for this study. Chemical analysis of these wastes is presented in Table 3. The synthetic metal sludge and synthetic metal waste solution were stabilized/solidified (S/S) using the binder to waste ratios presented in Table 4. The perchloroethlene sludge was not S/S. Prior to the initial set, each of the S/S mixtures and the unstabilized/unsolidified prechloroethlene waste were divided into two portions, portion A and portion B. Twelve volatile organic compounds (Table 5) were added to each portion A at a 1.0% (weight) concentration and to each portion B at a 0.1% (weight) concentration. These mixtures were then poured into polyethylene containers and sealed.

SPECIMEN CURING AND PREPARATION

The six mixtures contained in the polyethylene containers were placed in a constant temperature environment at 4o Celsius. These mixtures were cured under these conditions for a period of 14 days. At the end of this curing period the waste materials were crushed in the sealed bottles. Each waste material was then separately ground in a chilled mortar and screened through a 0.375-in. sieve. The resulting fines, for each waste, were placed in glass jars and mixed.

EXTRACTION OF THE WASTES

After each of the wastes (WES 0.1%, WES 1.0%, WTC 0.1%, WTC 1.0%, PCE 0.1% and PCE 1.0%) was homogenized, the wastes were subjected to triplicate EP and TCLP extraction procedures. The EP extractions were performed in closed, tumbled-glass containers. The TCLP extractions were conducted using both the ZHE extraction (for volatile organics) and the nonvolatile extraction method (for metals).

TABLE 3. ANALYSES OF THE SLUDGES

Waste	Parameter	Ionic Species	Concentration (mg/kg wet weight)
WES	Cadmium	Cd+2	4,000
	Chromium	Cr+3	18,000
	Nickel	Ni+2	19,000
	Mercury	Hg+2	200
	Calcium	Ca+2	60,000
	(Total Solids		25%)
WTC	Arsenic	As+3	2,400
	Cadmium	Cu+2	4,600
	Chromium	Cr+3	1,600
	Lead	Pb+2	8,100
	Phenol		3,700
	(Total Solids		3.4%)

TABLE 3. ANALYSES OF THE SLUDGES (Continued)

Waste	Parameter	Ionic Species	Concentration (mg/kg wet weight)
	pH		2.5
	(Bulk Density		1.0 g/cm3))
PCE	Antimony		11.2
	Barium		265
	Beryllium		0.3
	Cadmium		19.1
	Chromium		185
	Copper		2,390
	Nickel		223
	Silver		5.8
	Zinc		1,600
	Arsenic		8.9
	Lead		376
	Mercury		2.0
	Selenium		1.7
	Thallium		1.0
	Total Organic Halogens		4,660
	Chemical Oxygen Demand		887,000
	pH		6.07

TABLE 4. BINDER-TO-WASTE RATIOS USED TO STABILIZE/SOLIDIFY THE WASTES

Waste	Binder Type	Binder-to-Weight-Ratio
WES	Portland Cement	0.3
WTC	Portland Cement	1.0
	Type F Flyash	1.0
	Soil	1.0
PCE	----------	0.0

TABLE 5. ORGANIC COMPOUNDS USED TO SPIKE THE SLUDGES

Organic Compound
Chloroform
1,2 Dichloroethane
1,1,1 Trichloroethane
Carbon Tetrachloride
Trichloroethene
Benzene
1,1,2,2 Tetrachloroethane
Tetrachloroethene
Toluene
Ethlybenzene
Methyl Ethyl Ketone
Methyl Isobutyl Ketone

ANALYTICAL PROCEDURES

This study involved analyzing the EP and TCLP leachates for non-volatiles (metals) and volatile organics. Leachate samples submitted for metal analysis were filtered, digested and analyzed according to the methods outlined by the appropriate extraction method (USEPA 1982, 1986a, 1986c). Leachate samples submitted for volatile analyses were not digested.

STATISTICAL PROCEDURES

Statistical analyses were performed on the data produced during this study using the Statistical Analysis System (SAS) software package provided by SAS Institute (SAS Institute Inc. 1987). An analysis of the variance (ANOVA) multifactor factorial test, as described by Miller and Freund (1985), was conducted on data sets produced by this study. An ANOVA procedure outlined in Chapter 11 of the SAS/STAT user guide (SAS Institute Inc. 1987) was used to perform this statistical procedure.

When it was determined that the levels of test interaction were significant, a "paired-sample T test" (Miller and Freund 1985) was utilized to determine if the EP and TCLP results differed significantly. A MEANS procedure outlined in Chapter 33 of the SAS/STAT user guide (SAS Institute Inc. 1987) was used to perform this statistical procedure. Decisions whether to reject or accept the null hypothesis were comprised using an alpha level of significance of 0.05 or 20:1 odds.

RESULTS

NON-VOLATILE CONTAMINANTS

The results of the statistical analysis are presented in Table 6. The results for the WES sludge indicated that there is not a significant difference between the EP and TCLP extraction for any of the metals studied. The statistical analysis for the WTC waste data indicates that the EP and TCLP differed significantly in their ability to extract arsenic and lead. The results of the PCE waste extractions indicated that there were statistical differences between amounts of all the non-volatile contaminants measured in the TCLP and EP extracts.

Several values are reported in Table 6 as "DL," indicating that the concentrations of these contaminants were at, or below, the detection limits. As a result the statistical significance of these data cannot be evaluated; consequently, the results for the PCE-arsenic, PCE-silver, and WTC-cadmium data are omitted from the remainder of the discussion.

Figure 1 presents the normalized TCLP and EP extracts expressed as multiples of TCLP values, averaged for the replicate specimens for all three sludges. The extract concentrations that are presented in this figure are normalized to their dry-raw waste concentration. This corrects for any dilution by the interference materials, small changes in the binder ratio, and variations in the moisture content of the extracted materials. Normalized extract concentrations were derived using the following equation.

$$ECn = (EC \times V)/(W \times M \times B) \qquad (1)$$

where

ECn = The normalized extract concentration, mg/kg
EC = The contaminant concentration measured in the TCLP or EP extract, mg/l
V = The volume of extraction fluid, l
W = The weight of the wet treated waste extracted, kg
M = The solids concentration of the solidified/stabilized waste extracted expressed as a decimal
B = The weight fraction of raw waste in the solidified/stabilized/interfered waste mixture, calculated as follows:

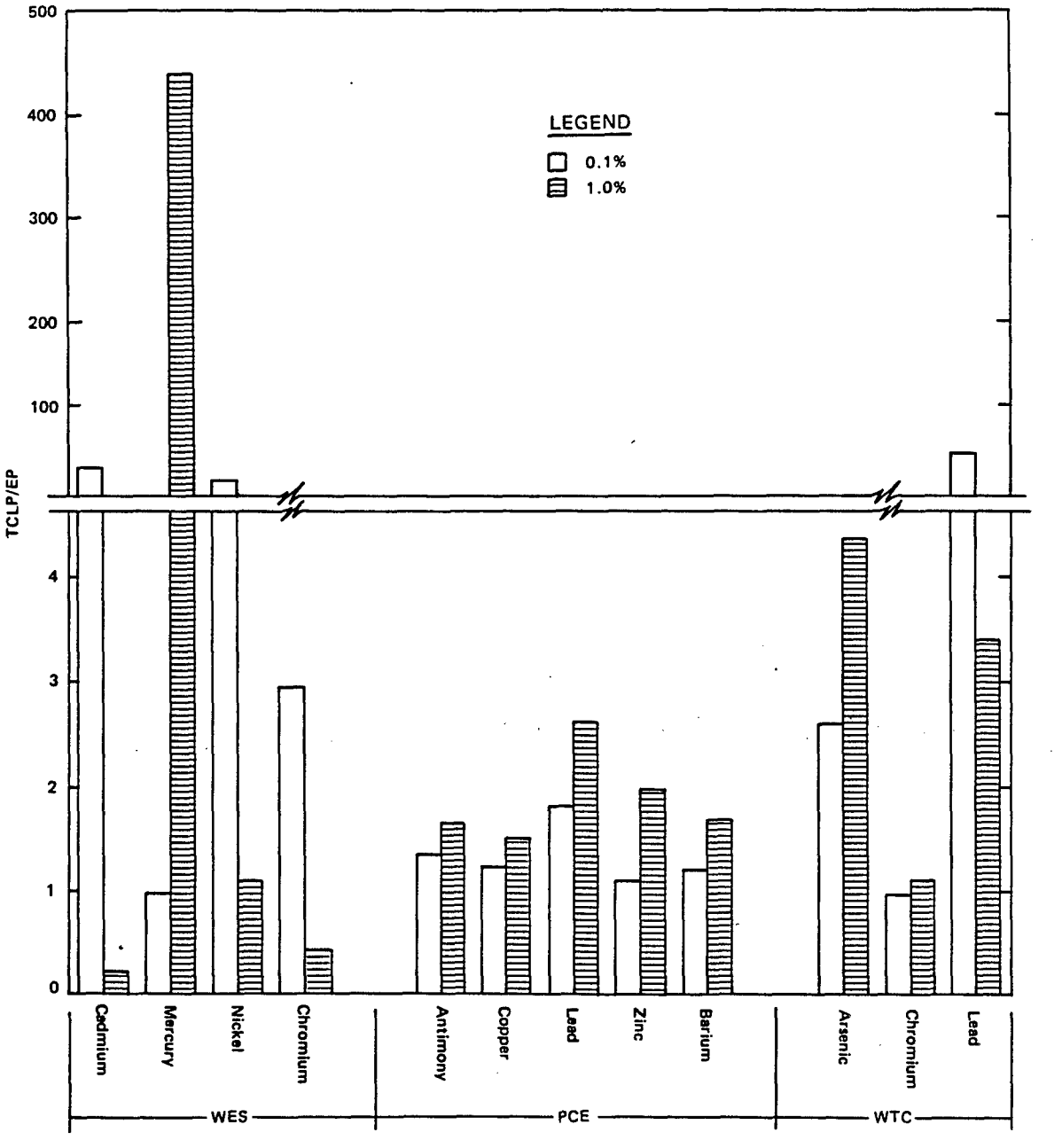


Figure 1. The Average Metal Extract Concentrations Expressed as the Normalized TCLP Concentration Divided by the EP Concentrations.

TABLE 6. RESULTS OF THE STATISTICAL ANALYSIS FOR THE NORMALIZED NON-VOLATILE TCLP AND EP EXTRACTS

Sludge	Metal Contaminant	Extraction* Test	R** Value
WES	Cadmium	N	0.598
	Chromium	N	0.424
	Nickel	N	0.653
	Mercury	N	0.973
WTC	Arsenic	Y	0.973
	Cadmium	DL	
	Chromium	N	0.530
	Lead	Y	0.906
PCE	Antimony	Y	0.947
	Arsenic	DL	
	Copper	Y	0.929
	Lead	Y	0.878
	Silver	DL	
	Zinc	Y	0.902
	Barium	Y	0.913

DL = Detection Limit

* Yes (Y) indicates there is statistical difference between the variable compared at alpha = 0.01. No (N) indicates no statistical difference.

** R values give an indication of how well the statistical model fits the data. As the fit of the model improves, the R value approaches 1.0.

$$B = \frac{\text{weight of raw waste}}{(\text{weight of raw waste} + \text{weight of binder} + \text{weight of interference agent})} \quad (2)$$

The data presented is an average of the three normalized extract values calculated as shown in the equation below:

$$\frac{TCLP}{EP} = \frac{(TCLP_1 + TCLP_2 + TCLP_3)/3}{(EP_1 + EP_2 + EP_3)/3} \quad (3)$$

where:

EP_1, EP_2 and EP_3 = the normalized EP replicate extract concentration for the contaminant of interest, in mg/l

$TCLP_1$, $TCLP_2$, and $TCLP_3$ = the normalized TCLP replicate extract concentration for the contaminant of interest, in mg/l

Thus, for Figures 1,2, and 3 a value of 1.0 indicates that the amount of a particular contaminant measured in the EP extract is equal to the amount of that contaminant measured in the TCLP extract. Values greater than 1.0 indicate that the TCLP extract concentration is greater than the EP extract concentration and values less than 1.0 indicates that the EP concentration is greater than the TCLP.

Figure 1 illustrates that for the PCE sludge the TCLP is generally a more aggressive extraction for the metal contaminants. On the average, the extract from the TCLP contained concentrations of metals approximately twice as large as the metal concentrations measured in the EP extracts. The TCLP and EP results for the WES waste varied in their aggressiveness towards the various contaminants. In some cases the EP was more aggressive than the EP. Due to the inconsistency in aggressiveness of the TCLP for the WES waste, the statistical methods were unable to establish a significance difference between the EP and TCLP extract concentrations.

The generalized non-volatile results for the TCLP and EP extraction for the three sludges evaluated in this study are summarized below:

(1) The results of the statistical analysis indicate that the TCLP and EP extractions produce extracts that are significantly different for the PCE waste. This may be explained by the fact that the PEC sludge had a pH of 6 and was not S/S. Due to the low alkalinity of this sludge, extraction fluid No. 1 was used for the TCLP extraction and little acid was added in the EP extraction. This resulted in the TCLP and EP extraction fluids being substantially different. It is suspected that the results of the TCLP and EP extractions varied as the result of the difference in extraction fluids.

(2) For a majority of the cases studied, the WES and WTC wastes produced TCLP and EP extracts which indicated no evidence of being statistically different. Arsenic and lead were the only contaminants for which the TCLP and EP statistically differed. One possible explanation for this may be attributed to the fact that similar extraction fluids were used. Since both WTC and WES wastes were stabilized/solidified, TCLP extraction fluid No. 2 was utilized due to the sample's high alkalinity. The EP extraction, performed on the WES and WTC wastes also required the maximum quantity of acid addition. When 400 ml of 0.5 N acetic acid is added to 1600 ml of water, the alkaline neutralization capacity of the EP extraction fluid and the TCLP extraction fluid No. 2 are equal. Equal alkaline neutralization capacity offers one explanation as to why the WTC and WES sludges produced TCLP and EP extracts that did not differ statistically.

VOLATILE CONTAMINANTS

Results of the statistical analysis performed on the volatile extracts are presented in Table 7. Statistical analysis on the data for six of the organic constituents (1,2 dichloroethane, carbon tetrachloride, 1,1,2,2 tetrachloroethane, tetrachloroethene, 2-butanone and 4-methyl-2-pentanone).

TABLE 7. RESULTS OF THE STATISTICAL ANALYSIS FOR THE NORMALIZED TCLP AND EP VOLATILE EXTRACT CONCENTRATIONS

Organic Constituent	Extraction Test	R Value**
Chloroform	Y	0.93
1,2 Dichloroethane	N	0.93
1,1,1 Trichloroethane	Y	0.96
Carbon Tetrachloride	DL	0.93
Trichloroethene	Y	0.98
Benzene	Y	0.98
1,1,2,2 Tetrachloroethane	DL	0.98
Tetrachloroethene	N	0.99
Toluene	Y	0.99
Ethylbenzene	Y	0.95
2-Butanone	N	0.96
4-Methyl-2-Pentanone	N	0.98

DL = Detection Limit

* Yes (Y) indicates there is statistical difference between the variable compared at alpha = 0.01. No (N) indicates no statistical difference.

** R values give an indication of how well the statistical model fits the data. As the fit of the model improves, the R value approaches 1.0.

indicated no statistical difference between the EP and TCLP. However, analyses of two of these six organic constituents (1,1.2,2 tetrachloroethane and carbon tetrachloride) indicated that the extract concentrations were at or below the detection limit, thus making analysis of the data difficult. Consequently, only 1,2 dichloroethene, tetrachloroethene 2-butanone, and 4-methyl-2-pentanone appeared to be extracted from the waste equally by the EP or TCLP.

Figures 2 and 3 present the extraction results for the 0.1% and 1.0% spiked sludges (WES, PEC and WTC) expressed as multiples of the TCLP values averaged for the three replicate specimens. These figures illustrate that generally the concentrations of organic contaminants measured in the TCLP extracts are slightly higher than those for the EP. The TCLP organic extract concentration is typically one and a half times higher than those measured in the EP extracts. However, these figures also indicate that the EP generated extracts with higher concentrations for some organics. Compounds detected in the EP extracts at concentrations greater than 1.1 times the TCLP extracts included; 1,2 dichloroethane, benzene, 1,1,2,2-tetrachloroethane, 2-butanone and 4-methyl-2-pentanone, for the 0.1% fortified sludges and, tetrachloroethene and ethlybenzene for the 1.0%.fortified sludges.

Because the ZHE apparatus was used in the TCLP, it was initially hypothesized that the TCLP would generate extracts that contained much higher concentrations of volatile organics than the EP extracts. However, as shown by the data presented in Figures 2 and 3, this was not always the case. In fact, the extracts from the TCLP have only slightly higher

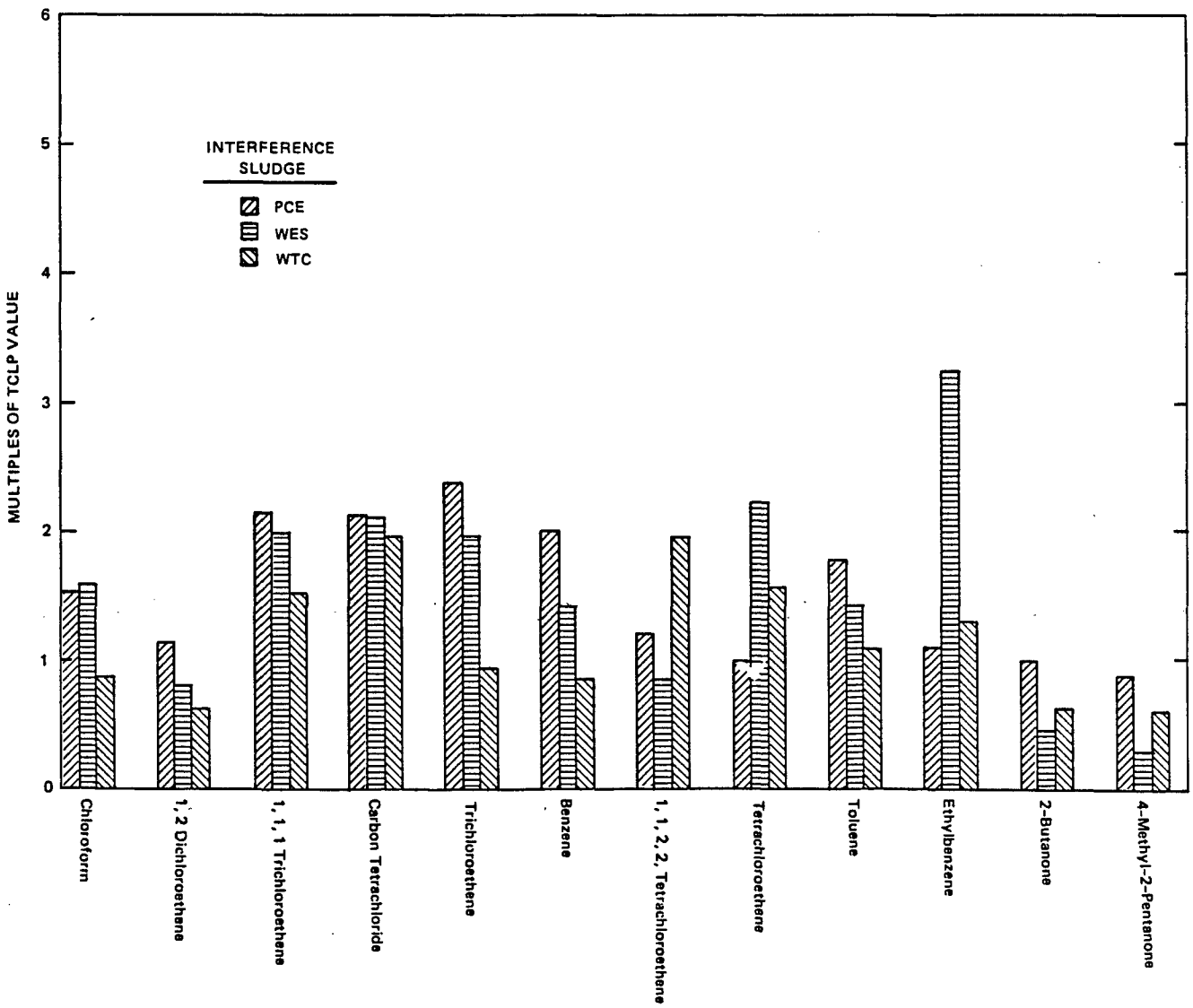


Figure 2. The Average 0.1% Organic Extract Concentrations Expressed as the Normalized TCLP Concentration Divided by the Normalized EP Concentration.

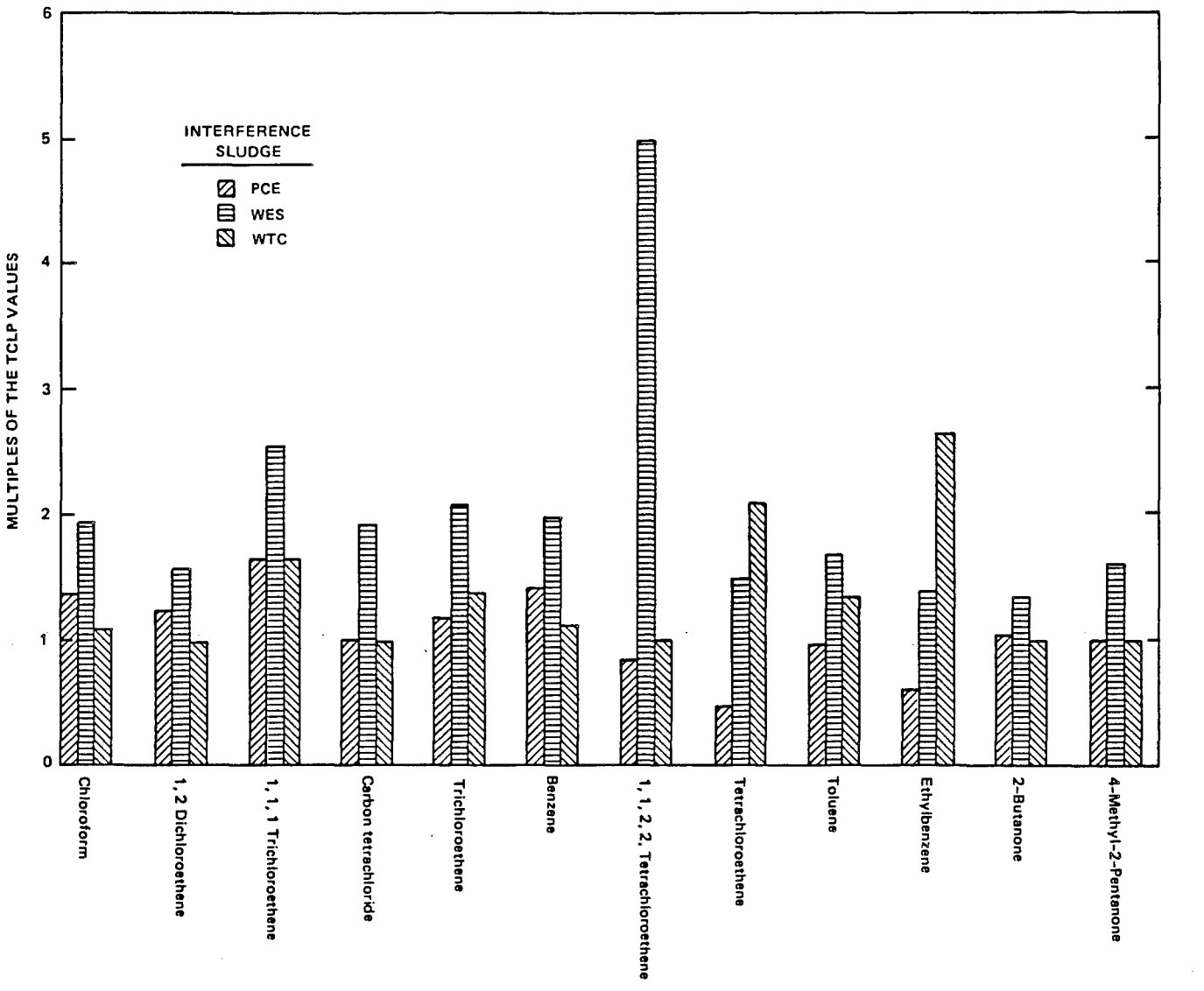


Figure 3. The Average 1.0% Organic Extract Concentrations Expressed as the Normalized TCLP Concentration Divided by the EP Concentration.

concentrations of volatile organics than measured in the EP extracts.

Attempts were made to correlate the EP and TCLP data with various physical properties such as vapor pressure, solubility, pH, and boiling point; however, no correlation between contaminant concentration and any of these variables was found. The data developed during this study appears to refute postulations such as: (1) the more volatile compounds should be detected in the TCLP extracts at greater concentration than the EP extracts, or (2) the difference in pH of the EP and TCLP extraction fluids could account for the extraction of more organic compounds from the waste. Due to the complex nature of the wastes and the many variables involved with the EP and TCLP extractions, no attempts are made to explain why the EP generated extracts with higher concentrations of organics than the TCLP.

PROCEDURAL DIFFICULTIES ENCOUNTERED WITH THE TCLP

The TCLP extraction procedure is more difficult to perform than the EP extraction. Factors which contributed to the TCLP complexity include:

(1) The TCLP requires two extractions, one for volatiles and another for non-volatiles. The EP only requires one extraction.

(2) The TCLP utilizes two extraction fluids and requires an extraction fluid selection step. The EP only requires one extraction fluid.

(3) As indicated by the high degree of contamination observed in the ZHE blanks, the TCLP ZHE apparatus is difficult to clean. It is suspected that the valve on the ZHE may trap small amounts of liquid that may contaminate subsequent extracts.

(4) The TCLP protocol does not give clear directions on the utilization of volatile organic vials (VOV) for extract collection. Excessive turbulence when placing the extract in the VOV could result in the loss of volatile organics.

(5) When the extraction fluid is added to the ZHE apparatus, it is difficult to accurately measure the volume of extraction fluid. Pumping from a graduated cylinder offers one solution but the large open area of the cylinder may permit contamination of the extract fluid.

(6) A major problem uncovered as a result of this study is the large amount of 1,1 dichloroethene (1,1-DCE) that was measured in some of the extracts. Although the sludges were not spiked with 1,1-DCE and no measurable amounts of 1,1-DCE were detected in the bulk analyses of the raw sludges, large amounts of 1,1-DCE were detected in the TCLP and EP extracts. The measurable quantities of 1,1 DCE were only detected in the extracts of the sludges that were S/S. It is suspected that some form of dechlorination reaction, which is favored by the alkaline extraction conditions of the S/S wastes, is resulting in the formation of 1,1-DCE. Similar phenomena have been reported by other researchers (Newcomer et al. 1986).

CONCLUSIONS

This study was conducted to compare the results obtained from performing the TCLP and the EP on identical waste samples. Several EP and TCLP extractions were performed on a number of different wastes subjected to a variety of conditions. Based on the results of this study, the following conclusions can be drawn:

(1) Generally the TCLP was a more aggressive leaching procedure than the EP for the metals and organics investigated in this study.

a. When TCLP extraction fluid No. 2 was used, the EP and TCLP produced similar results for the extraction of metals.

b. When TCLP extraction fluid No. 1 was used, the concentrations of metal contaminants extracted by the EP and TCLP differed with the TCLP generally being the more aggressive extraction.

c. The TCLP ZHE was generally a more aggressive extraction for volatile organics than the EP extraction.

(2) Although the TCLP ZHE was a more aggressive leaching procedure than the EP for the volatile organics, the difference in the concentrations of volatile organics in the TCLP and EP extracts was much less than initially expected.

(3) When the ZHE is used, cross-contamination presented a potential problem.

(4) The TCLP and EP extraction of the solidified/stabilized wastes produced conditions that permitted dechlorination reactions. Significant amounts of 1,1-dichlorethene were detected in the TCLP and EP extracts, although 1-dichloroethene was not detected in the raw wastes extracts. This phenomenon should be addressed in future research.

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PRACTICAL LIMITS TO PUMP AND TREAT TECHNOLOGY FOR AQUIFER REMEDIATION

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If one is challenged to restore a contaminated aquifer, the procedure of pumping contaminated water to the surface for treatment and discharge is a common aquifer remediation technology. The perceived success of pump and treat technology can be misleading if the hydrology and contaminant characteristics at the site are not adequately understood. A failure to understand the processes controlling contaminant transport can result in extremely long pumping periods and, consequently, costly and inefficient remediation.

Ground-water contamination problems vary greatly in all regards, including their size and depth, the nature of the geology, and the characteristics of the contaminants, as well as their source. A thorough understanding of all of these factors is critical in developing cost-effective remediation technology and defining the proper role of pumping and treating within a remedial action plan.

To better understand the ramifications of a pump and treat project, it is helpful to develop a contamination scenario by assigning the conditions of size, geology, and contaminant type. For this discussion, assume that the area of ground-water contamination is ten acres; the aquifer has a thickness of almost 55 feet; the water in storage amounts to 30 percent of the aquifer's volume; and the contaminant is salt water. Under these conditions, it would be possible to exchange the water in this ten acre plume in about a year by pumping at a rate of 100 gallons per minute.

Indeed, it appears that pumping would solve this problem, under these conditions, where the contaminant is very soluble and is not retained on the subsurface materials. In reality, it may be necessary to pump for two or three or more years to reach an acceptable salt concentration due to the "tailing" effect often observed in these types of remedial actions.

Tailing is the slow, nearly asymptotic decrease in contaminant concentration in water flushed through contaminated geologic material. Tailing may be caused by several phenomena. In the simplest case of a highly soluble non-retained contaminant, tailing is due to contaminant migration into the finer pore structure of the geologic material. These finer pores then contain water and contaminants that are only slowly exchanged with the bulk water present in larger pores, and tailing is a result. It is the water and contaminants in the larger pores that is mobilized during pumping.

The problem in trying to remove many of the man-made and natural organic compounds from ground water is that they tend to absorb and adsorb to the organic and mineral components of the aquifer material in much greater quantities than in the liquid phase. Therefore, when water is removed by pumping, the predominant amount of the contamination remains behind on the aquifer material. Obviously, removing the aquifer material instead of the water is not usually a feasible alternative.

Once sorbed to the geologic material, contaminants can desorb and thus be released into the water where they are removable by pumping. However, research has shown that a fraction of the sorbed contaminant is only slowly released into the water. This slow, desorptive release acts in concert with slow contaminant release from the fine pores, discussed above, to cause tailing.

Our challenge of site remediation is complicated exponentially if the contaminants are themselves constituents of a water-insoluble liquid, such as gasoline. In this case, the gasoline will likely become trapped in the pore spaces of the aquifer and cannot readily be pumped out. Its benzene, toluene, and xylene components then partition or "bleed" into the passing ground water at a rate and to a concentration which is characteristic of the contaminants of concern.

One can be deceived in attempting to remove the components of gasoline by pumping at increasingly higher rates since the concentration of these contaminants initially may appear to be reduced or even eliminated. This deception can result from dilution, by bringing larger amounts of uncontaminated water into play; or, by dropping the water table below the source of contamination, or both. It is important to understand that the contaminant cannot be removed faster than it is released into the passing ground water. In any event, if the pumps are stopped for some period of time, the water soluble gasoline components will again dissolve into the ground water and one will find that the contaminant concentrations have returned to their previous levels.

To obtain some insight into the period of time required to remove the constituents of gasoline by pumping, it is necessary to return to the scenario conditions developed above for salt water. Under these conditions, it would be necessary to pump at a rate of 100 gallons per minute for approximately 1500 years to reduce the initial amount of toluene by 80 percent if ten percent of the voids contained gasoline. If it is necessary to reduce the amount even more, in order to meet drinking water or some other standards,

the time required would be lengthened greatly. In some cases the configuration of the plume and the hydrogeology will allow increasing the pumping rate while avoiding the dewatering of the contaminant plume. But even a tenfold increase to a thousand gallons per minute would still require 150 years of pumping in our example. Even if the hydrogeology would permit an unlimited pumping rate, there is a point beyond which the removal of contaminants would not increase due to the constant rate at which a particular contaminant partitions or "bleeds" into the passing ground water.

There is little doubt that pumping and treating ground water is a viable approach to aquifer restoration in some instances, particularly when the aquifer is hydrologically homogeneous and the contaminant or contaminants are highly soluble and have little affinity for sorbing to the aquifer material. It may also have utility when it is necessary to remove the more highly concentrated portions of a contaminant plume, or perhaps even a separate phase such as gasoline floating on ground water. Some comtaminants will also be removed when using wells to intercept contaminated ground water. It will not usually be applicable to the removal of oily wastes or those synthetic organic compounds which tend to highly sorb to the aquifer material. There are many cases, especially where the contamination is very old, where the compounds have found their way into the finer pore structure of the aquifer where their movement back into the water phase will be very slow.

It is important to understand the processes that limit the effectiveness of pump and treat technology in order to develop efficient and cost effective remedial action plans.

EPA TREATABILITY DATABASE

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INTRODUCTION

Since the mid-1970's, EPA has generated a wealth of data on the treatability of organic and inorganic compounds found in industrial and domestic wastewaters, groundwater, leachates, and surface waters. To date, various attempts have been made to organize selected segments of this information, but a comprehensive evaluation and compilation of information encompassing compounds regulated by all pertinent environmental laws has not been undertaken. This major activity was initiated with the overall objective of providing a database on the treatability of priority pollutants and other hazardous compounds in water and wastewater. The database summarizes years of studies on the treatability of priority pollutants and other hazardous compounds Regulated under the Clean Water Act, Safe Drinking Water Act, Resource Conservation and Recovery Act, Toxic Substances Control Act and the Superfund Amendments and Reauthorization Act.

POTENTIAL TECHNICAL USERS

One of the primary purposes of this ongoing project is to have the database as accessible as possible to the technical community.

The database will allow the user to have access to published, peer reviewed, technical literature to assist in determining whether a proposed method of treatment is appropriate for the specific compound present in the waste/water to be treated. This will be a valuable tool to the regulatory agencies who review plans and proposals of waste treatment; practicing environmental engineers who prepare treatment system designs; and public and private research personnel.

It is to be noted that this is not a design program, but a summary of published data presently available. Also, it was not the intent of EPA to develop a program that designs treatment systems. Rather, its purpose is to store in a central location, data from studies on treatment of chemical compounds, and allow for easy access of the information.

CURRENT STATUS

The database is still in the process of development and refinement as of the writing of this paper (10/88), although copies of current version are now available. The existing program has been developed using "dBASE III PLUS" and is compiled using "Clipper". These are software programs for storing and retrieving data. Selection of the software was based on the availability and familarity of dBASE throughout EPA offices. The program was designed to be menu driven with the intent of maintaining ease of operation for users with limited computer knowledge.

To date, there are 389 compounds entered into the database of which approximately half have treatability data (data other than physical/chemical properties). Of the compounds with treatability data, there are approximately 1500 treatability data sets (entries) and 250 isotherm (adsorption) data entries. To obtain these data, over 2000 references have been gathered, of which more than half of these have been reviewed. However, only 200 references to date have passed the quality assurance requirements set up for the project.

The program is designed to be compound specific. All information within the database can be accessed by identifying the compound of concern. A compound name can be selected in three ways; name can be selected from the compound listing, compound name can be typed in, or the CAS (Chemical Abstract Service Registry) number is typed in. A listing of all the compounds in the database can be called to the screen from which the user can make his selection (Figure 1). The listing includes many of the common synonyms for each compound. Therefore, the user need not know the exact name under which the compound was stored in the program; but can use the name that is most familiar. If the user selects a synonym name for the

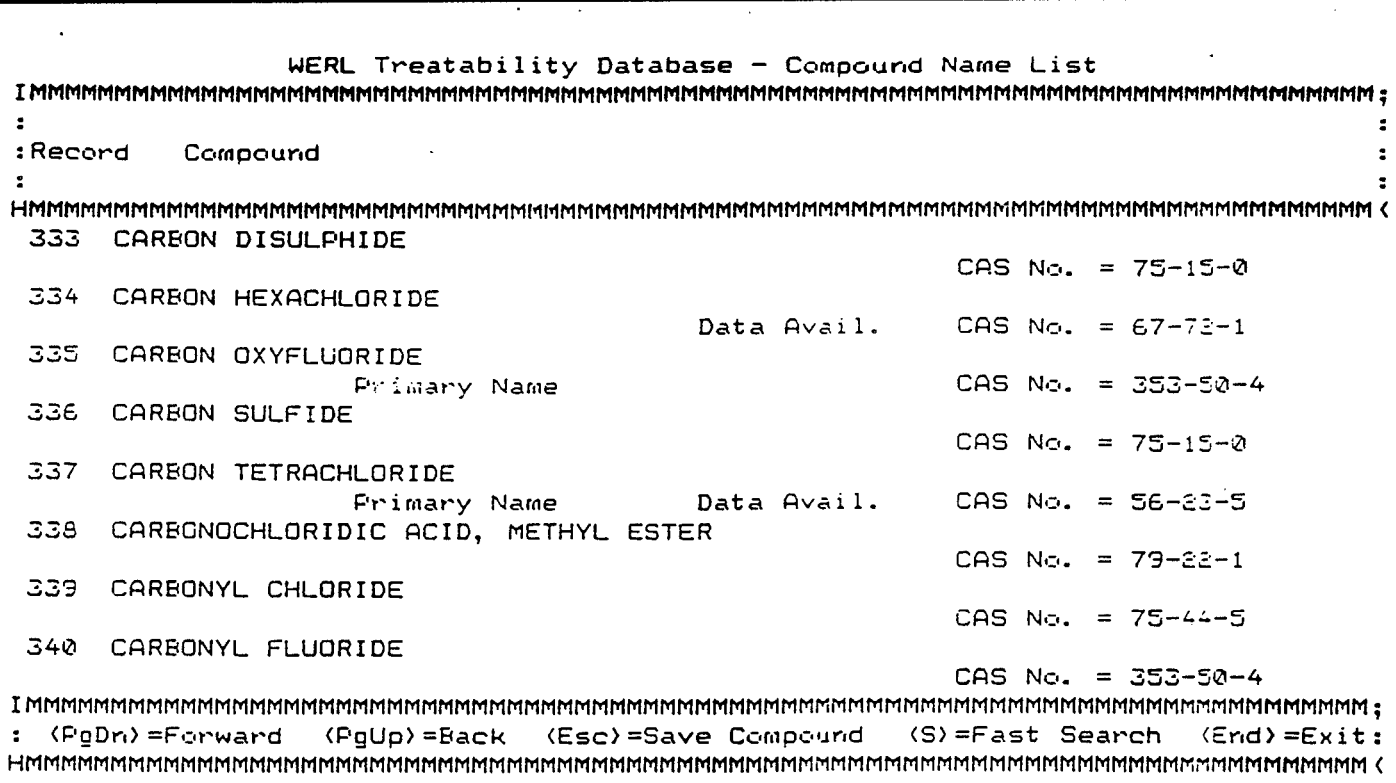


Figure 1. Compound name list.

compound, the program will inform the user of such. The reason for this is, the screens containing the data are always given with the primary name in the heading. Thus, the user would not be confused with the different name. On the compound listing, those names which are primary are identified as such (see Carbon Oxyfluoride above). The listing of compounds also gives the CAS number for each compound and indicates if treatability data exists for the compound (see Carbon Hexachloride and Carbon Tetrachloride in Figure 1).

To move around the compound listing, the user will utilize several keys. The first are <Pg Up> and <Pg Dn>, which moves the screen forward and back. To move more quickly through the names, a fast search command was developed. The user enters <S> followed by the first letter of the compound of concern, and the the screen will automatically move to the first compound starting with that letter. Then using <Pg Up> and <Pg Dn>, the user can locate the specific compound. For example, if the user is searching for information on Carbon Tetrachloride, he can <Pg Dn> through the entire list, or by typing <S> followed by <C> he will be taken to C.I. 41000B (compound 317) and would need only page down twice to get to the screen presented in Figure 1. The compound can be selected from this list by using the <Ecs> key and entering the number to the left of the compound. Therefore, for Carbon Tetrachloride the user would enter 337.

As a user becomes more familiar with the database, a quicker method for obtaining data is to type either the name or CAS number directly on the appropriate screen. When typing in a compound name, the user must type it exactly as it is listed in the database. Special attention must be made to capital & lower case letters, locatior of commas, numbers & blank spaces. If the name does not match character for character the computer will not locate it. Using the CAS number might be a better solution, remembering that the dashes between number sets (ie. 50-00-0) need to be included.

Once the compound is selected, the data for the specific compound will be brought to the screen. The first screen contains basic Chemical Physical Properties (Figure 2). This presents various properties of the compound including molecular weight, melting point, boiling point, vapor pressure, Henry's Law Constant, log octanol/water coefficient, etc.

WERL Treatability Database Ver No. 1.0 09/13/88

CARBON TETRACHLORIDE

CAS NO.: 56-23-5

COMPOUND TYPE: HYDROCARBON,HALOGENATED

FORMULA: C CL4

CHEMICAL AND PHYSICAL PROPERTIES	REF.
MOLECULAR WEIGHT: 153.82	333A
MELTING POINT (C): -23	333A
BOILING POINT (C): 76.5	333A
VAPOR PRESSURE @ T(C), TORR: 113 @ 25	463A
SOLUBILITY IN WATER @ T(C), MG/L: 800 @ 20	1006A
LOG OCTANOL/WATER PARTITION COEFFICIENT: 2.73	1226A
HENRY'S LAW CONSTANT, ATM x M3 MOLE-1:2.93 E-2 @ 25	191C

Figure 2. Chemical & Physical Properties Report.

The second screen presents references for environmental data (Figure 3). It identifies where the user can obtain the specific environmental information for that compound. This is the only information not directly given by the database, although it does identify those compounds which are of environmental concern and provides the user with a reference for more information. Information on the reference is given in the bibliography portion of the program.

ENVIRONMENTAL DATA	REF.
CHRONIC NONCARCENOGENIC SYSTEMIC TOXICITY	4B
RISK ESTIMATES FOR CARCINOGENS	4B
DRINKING WATER HEALTH ADVISORIES/STANDARDS	346B
WATER QUALITY CRITERIA	4B
AQUATIC TOXICITY DATABASE	NA

Figure 3. Environmental Data Report.

The third screen (Figure 4) contains Freundlich isotherm data. Any isotherm data that have been obtained for each specific compound are summarized here. The Freundlich isotherm data as well as the treatability data are presented using certain abbreviations and codes. These codes are summarized in Figure 5. Using Figure 5 and looking at the isotherm data for Carbon Tetrachloride (Figure 4), the user will note that all but one entry is for clean water (distilled) matrix which was spiked with Carbon Tetrachloride. The other entry is for tap water. Also note, that each reference (ie. 30A) is provided with a letter rating. An "A" rating is a peered review article and/or report, a "B" rating indicates a government report, and a "C" rating is a non-peered article.

FREUNDLICH ISOTHERM DATA

ADSORBENT	MATRIX	K	1/N	Ce UNITS	X/M UNITS	REF.
NORIT PEAT CARBOM	C	0.16	0.75	ug/L	mg/gm	30A
NUCHAR WV-G	C	0.22	0.69	ug/L	mg/gm	30A
FILTRASORB 400	C	0.23	0.74	ug/L	mg/gm	30A
HYDRODARCO 1030	C	0.13	0.68	ug/L	mg/gm	30A
FILTRASORB 400	T	0.20	0.60	ug/L	mg/gm	30A
FILTRASORB 300	C	11.1	0.83	mg/L	mg/gm	3B
FILTRASORB 400	C	6.80	0.469	mg/L	mg/gm	1028C

Figure 4. Freundlich Isotherm Data Report.

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Treatment Technologies Code and Abreviation Table

Treatment Technologies

AFF	Aerobic Fixed Flim
AL	Aerobic Lagoons
AS	Activated Sludge
AirS	Air Stripping
AnFF	Anaerobic Fixed Film
AnL	Anaerobic Lagoons
BGAC	Biological Granular Activated Carbon
CAC	Chemically Assisted Clarification
ChOx	Chemical Oxidation (Parantheses shows oxidation chemical ie. ChOx(Oz) - is ozone)
ChPt	Chemical Precipitation
Fil	Filtration
GAC	Activated Carbon (Granular)
IE	Ion Exchange
PACT	Powdered Activiated Carbon Addition to Activated Sludge
RBC	Rotating Biological Contactor
RO	Reverse Osmosis
SBR	Sequential Batch Reactor
SCOx	Super Critical Oxidation
SExt	Solvent Extraction
SS	Steam Stripping
Sed	Sedimentation
TF	Trickling Filter
UF	Ultrafiltration
UV	Ultraviolet Radiation
WOx	Wet Air Oxidation

NOTES:

____ + ____	is the first process unit followed in process train by the second ie. AS + Fil - Activated Sludge followed by Filtration
____ w ____	is the two units together ie. UFwPAC - Ultrafiltration using Powdered Activated Carbon
____(B)	is batch instead of continuous flow

Scale

B - Bench Top P - Pilot plant F - Full scale

Number after letter refers to the plant number in a specific reference (ex. F7 - plant 7 is the seventh full scale plant in the indicated report).

Matrix

C - clean water (ex. distilled)	GW - ground water
S - synthetic wastewater	W - surface water
D - domestic wastewater	T - tap water
ML - municipal leachate	R - RCRA listed wastewater
HL - hazardous leachate	SF - superfund wastewater
I - industrial wastewater	AS-E - activated sludge effluent

Figure 5. Code & Abbreviation Table.

SIC (Standard Industrial Classification) Codes

(For industrial wastewaters a 2 digit SIC code will be given following the letter designation, i.e. I 22 is a Textile Mill Products wastewater. If the SIC code is unknown a U will be shown, I U)

13 - Oil and gas extraction
20 - Food and kindered products
22 - Textile mill products
24 - Lumber and wood products
26 - Paper and allied products
27 - Printing and publishing
28 - Chemicals and allied products
29 - Petroleum refining and related industries
30 - Rubber and misc. plastic products
31 - Leather and leather products
33 - Primary metals industries
36 - Electronic and electric equipment except computer equipment
39 - Misc. manufacturing industries
49 - Electric, gas, and sanitary
99 - Nonclassifiable establishments

Effluent Concentration

Effluent concentration will be given as a arithmetic mean to two significant figures. The number of samples used to calculate the mean is given after conc. as (n).
(ex. 13 (5) - 13 is the mean of 5 sample values)

% Removal

Percent removal will be calculated on a concentration basis. If data are available, it will also be calculated on a mass basis for physical/chemical systems. Those vaules calculated on a mass basis will be noted by a (m). An example would be:

% Removal:	99.95	99.95 is based on concentration
	98(m)	98 is based on mass

Reference Codes

A - Papers in a peer reviewed journal.
B - Government report or database.
C - Reports and/or papers other than in groups A or B not reviewed.
D - Group C papers and/or reports which have been given a 'good' quality rating by a selected peer review.
E - Group C papers and /or reports which have been given a 'poor' quality rating by a selected peer review. This data will only be used when no other data are available.

Figure 5. Code and Abbreviation Table (con't).

The last screen(s) contain the treatability data. The data are broken into six data ranges. These are based on the influent concentration of the various studies. The influent ranges are: 0-100 ug/L, >100-1000 ug/L, >1-10 mg/L, >10-100 mg/L, >100-1000 mg/L, and >1000 mg/L. Data for each concentration are presented on separate computer screens. If no data are available for a certain range, that screen will not appear.

An example of a treatability data screen is presented in Figure 6. The table summarizes the treatment technology, the reference from which the data have been extracted, the scale of the study, the source matrix, effluent concentration and percent removal achieved. For example, the first citation has an influent concentration between 0 and 100 ug/L of Carbon Tetrachloride. The technology shown is GAC (granular activated carbon). It is a full-scale plant (F) treating hazardous leachate (HL). The effluent concentration achieved is less than 10 ug/L which is a removal of greater than 89%. The reference from which this data was obtained is reference 237A.

WERL Treatability Database **Ver. No. 1.0 09/13/88**

CARBON TETRACHLORIDE

CAS NO.: 56-23-5

INFLUENT CONCENTRATION - 0-100 ug/L

TECHNOLOGY	REF.	SCALE	SOURCE MATRIX	EFFLUENT CONCENTRATION (ug/L)	PERCENT REMOVAL
GAC	237A	F	HL	<10 (1)	>89
AS	975B	F4	I 28	<3	>94.8
AS	203A	P	D	13 (14)	81
AS	206D	P	D	<0.2 (20)	>99.67
AS	240A	P	D	4 (12)	90.7
TF	203A	P	D	26 (14)	62
TF	240A	P	D	4 (12)	90.7
AL	203A	P1	D	15 (14)	78
AL	203A	P2	D	11 (14)	84

Figure 6. Treatability Data Report.

Information on the source of the data is also presented in the database; each data set has a reference number associated with it. After viewing data, the user is given the option to obtain information on the references. Typically pertinent operational data along with the bibliography are given for each reference (Figure 7). If the user still requires additional information, he can obtain the reference at a library or contact Mr. Kenneth Dostal at EPA in Cincinnati. Mr. Dostal keeps each of the references on file in his office. His address and telephone number are given in the introduction of the program.

WERL Treatability Database Reference Number: 237A

McDougall, W.J., R.A. Fusco and R.P. O'Brien, "Containment and Treatment of the Love Canal Landfill", Journal WPCF, Vol. 52, No. 12, pp 2914-2924 (December 1980).

Two-stage (series) granular activated carbon columns providing onsite full-scale treatment of the leachate. Each pressurized adsorber contained 20,000 lbs of carbon; no additional operating criteria provided. Units started in November 1978 and data in tables from samples taken in March 1979.

Figure 7. Bibliography.

This database is meant to be a tool for the user. It is not meant to be used for design purposes, but as a summary of available data to date on treatment of specific chemical compounds. Thus, it can be used as a guide to identify the effectiveness of technologies for specific wastes. Private industry or regulatory personnel preparing or reviewing work plans or scopes of work which involve treatment of organic or inorganic compounds will be able to make educated decisions on whether the proper treatment is proposed for a certain waste.

QUALITY ASSURANCE

To insure the accuracy of the data in the database, a rigorous quality assurance (QA) program has been established.

A flow diagram of the program is presented in Figure 8. Each reference is reviewed approximately five times. The first is the "editing rules" review to identify those references which should be included in the database. If the paper passes, the summarized data are reviewed by an internal QA coordinator, after which the reference would receive an external peer review. Having passed these three reviews, the data are submitted to the US EPA for review. The final reviews include checks for accuracy in the computer entry of the data. The QA program established maintains the integrity of each and every data point of the database.

AVAILABILITY

Although the program will continue to be expanded, it is being made available free of charge through EPA's Risk Reduction Engineering Laboratory in Cincinnati on computer disks. It is also expected that there will be regular distributions of the data, possibly biyearly.

The hardware requirements to run the program are as follows:

IBM PC (or Compatible)
PC/MS DOS 2.0 or greater
384K RAM available (or greater)
Printer 10 CPI
Mono or color monitor

Questions or comments should be directed to Mr. Kenneth Dostal at the U.S. EPA-Cincinnati (513-569-7503).

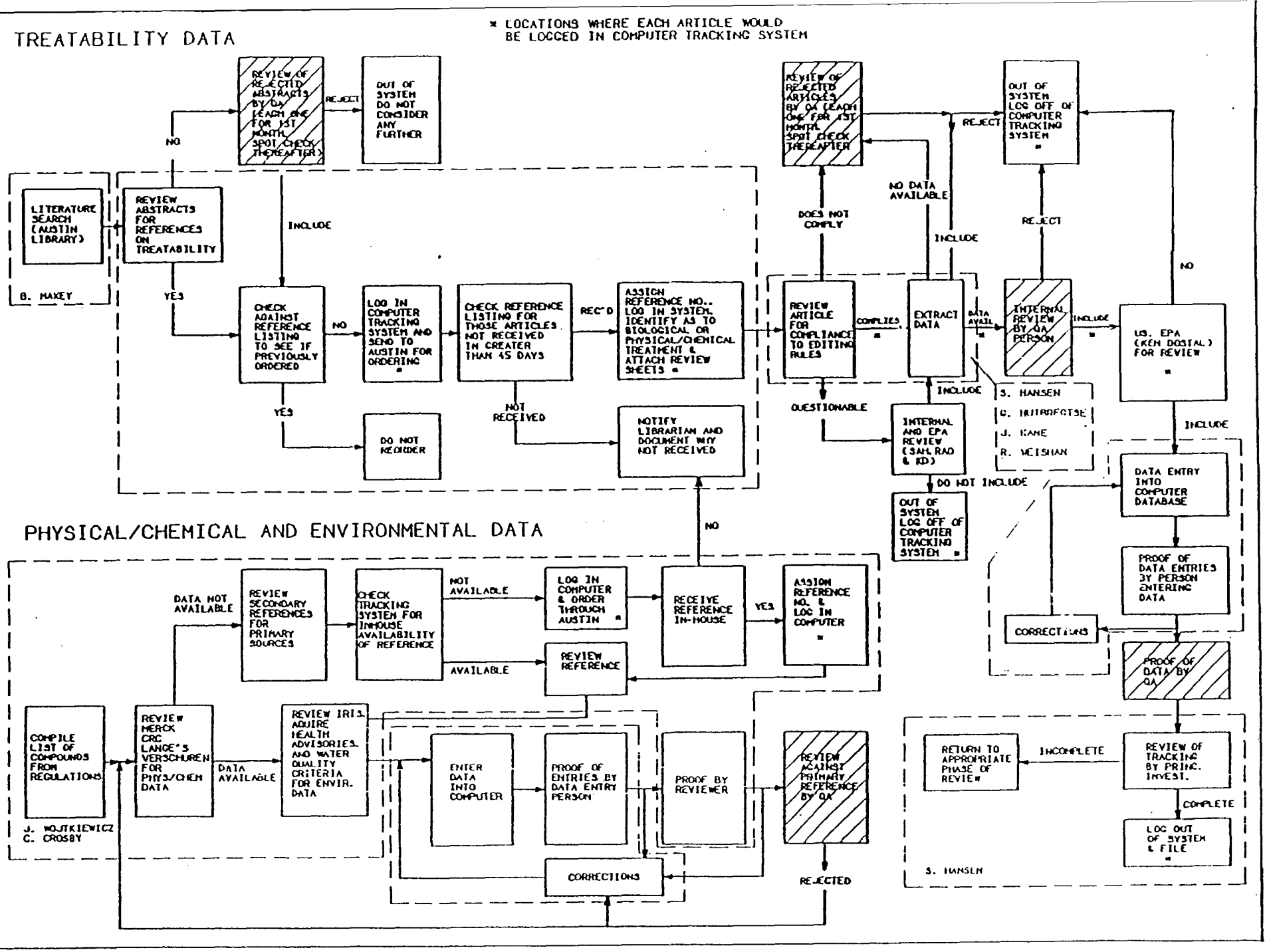


Figure 8. QA Program flow diagram.

NAVY AQUATIC HAZARDOUS WASTE SITES: THE PROBLEM AND POSSIBLE SOLUTIONS[#]

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ABSTRACT

Data on 367 hazardous waste sites at 58 Navy and Marine Corps activities, located in the coastal zone, were reviewed to characterize the contaminants, disposal methods and potentially impacted environments. This report identifies Navy aquatic hazardous waste site problems, assesses technology requirements, and describes remedial pilot projects being initiated at impacted aquatic sites.

The major waste types found fell into several categories: a combination of all hazardous wastes disposed at a single landfill site (27%), toxic organics (43%), petroleum hydrocarbons (26%) and heavy metals (20%). Releases into the environment were by spills or dumping on the ground (56%), landfilling operations (26%), burial in lined pits (10%), leakage from storage tanks (4%) and direct discharge into water bodies (3%). The most frequently threatened aquatic environments were bays (27%), rivers (27%), marshes (16%) and streams (14%). While remedial action options at the waste site are usually available, remedial action in the contaminated aquatic environment risks serious disruption to the community one is trying to protect. Competent risk analysis is required to determine the most effective remediation alternative. Remedial investigation pilot projects being initiated include: verification and evaluation of hydrocarbon degradation (jet fuel) at NAS Patuxent River, MD; wildlife toxicity assessment demonstration project at NAS Whidbey Island, WA; and environmental risk assessment pilot study at NCBC Davisville, RI.

[#]Paper Presented at the 13th Annual Environmental Quality R&D Symposium, November 15-17, 1988, Williamsburg, VA.

INTRODUCTION

Hazardous waste contamination of aquatic environments occurs primarily in coastal and estuarine areas which is where the Navy operates and deploys the majority of its assets. Figure 1 depicts the typical Navy installation. Immediately apparent is that the facility is surrounded by water -- and therefore the effectiveness of the Navy's pollution abatement and clean up programs will be reflected in the water quality and sediment quality of the adjacent water body.

The Navy and Marine Corps share many clean up problems with the Army and Air Force. Soil and groundwater contamination from munitions disposal, spills of volatile organics, polychlorinated biphenyls, plating wastes, heavy metals, petroleum oil and lubricants, as well as other wastes are common to the three services (U.S. Army Corps of Engineers 1985; U.S. Air Force 1985). What makes many of the Navy and Marine Corps waste clean up problems unique is that contaminated sites may impact wetland areas that are on or adjacent to Navy and Marine Corps property. For example, when shore-based storage tanks leak, petroleum products seep into groundwater and the aquatic environment. Contaminants may leach from waterfront disposal sites, such as landfills and burn areas, into surrounding soil, groundwater, and aquatic environments. Similarly, chemical waste spills from plating shops or rework facilities, although initially occurring on land, are washed down storm sewers and drainage channels and ultimately end up in the aquatic environment.

The aquatic environment is the final sink for many contaminants and the ultimate question of impact, depends on the environment's ability to assimilate wastes. Aquatic contamination from waste disposal sites could have a direct effect on human health from the consumption of contaminated seafood, as well as result in bans on commercial fishing, or the impoundment of seafood tainted with high levels of contaminants. Recreational and swimming areas could also be closed because of unsafe levels of contamination. These actions could have a "ripple" effect on local economies dependent on commercial and sport fishing. Additional impacts could be incurred when sediment, contaminated from waste disposal sites, must be dredged. Contaminated sediment will require special removal and disposal methods and could prevent or delay and increase the cost of harbor maintenance. Conscientious management of waste sites impacting aquatic environments requires ability to properly identify threatened habitats and select the necessary steps to mitigate impacts (Pavia 1987).

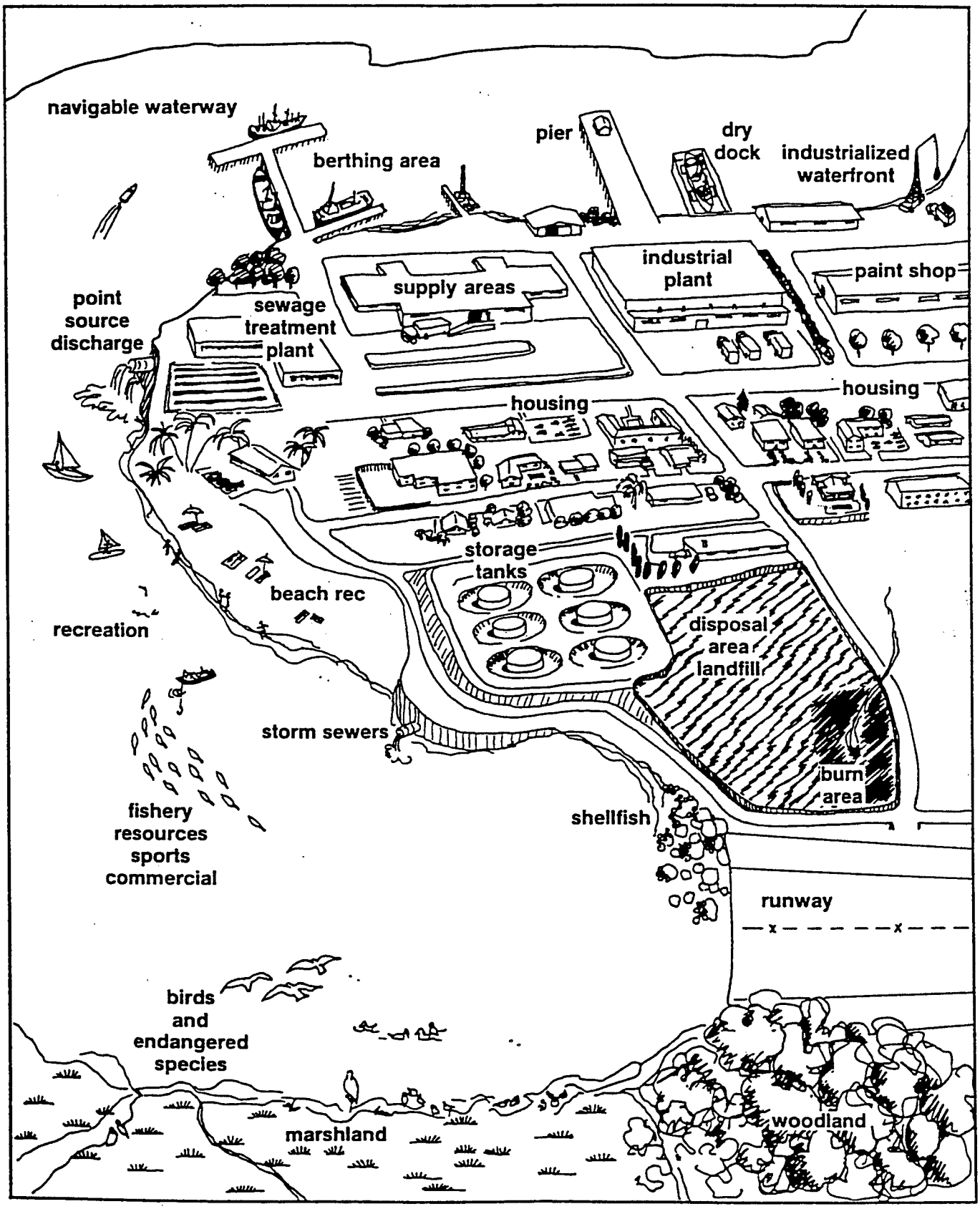


FIGURE 1: Typical Navy installation.

PROBLEM DEFINITION

Potential aquatic site contamination problems were identified and evaluated by: 1) reviewing Initial Assessment Studies (IAS) reports of Navy and Marine Corps Activities located in coastal and estuarine areas to determine types of contaminants present and types of environments being impacted; and 2) visiting sites with identified aquatic site contamination to gain first hand knowledge of the problems. Data on 367 hazardous waste sites at 58 Navy and Marine Corps activities were reviewed. Sites selected for this review were sites recommended for confirmation study and judged to have potential impact on aquatic environments. These sites represent more than half of the sites reviewed by the Initiation Decision Report (IDR) process (Olah 1988).

Contaminants, disposal methods and impacted environments at the sites reviewed were grouped into broad categories to facilitate overall summary and conform to contaminant-medium pairings used in the IDR process (Olah 1988). These categories are described in Table 1. While admittedly subjective, the broad categories were felt to share important characteristics. Those contaminants grouped into a given category tended to co-occur on site and require similar remedial treatment. Disposal methods within a category were felt to be similarly vulnerable to contaminant migration via surface runoff or ground water. Categories of aquatic environments were judged similar in their dilution rate, potential contaminant residence time and subsequent impact on their biological communities. The IAS reports were also examined to determine mode of contaminant transport in order to further distinguish site characteristics. In nearly every case both ground water and surface water transport contaminants into the surrounding environment and can be regarded as a universal site trait.

Figures 2, 3, and 4 summarize the number of sites characterized by particular contaminants, disposal method, and potentially impacted aquatic environment, respectively. Combined wastes, a conglomeration of essentially all hazardous wastes disposed at a single site, accounted for 99 (27%) of the sites reviewed. Of the remaining 268 sites, 158 (43%) were contaminated with toxic organics, 94 (26%) were impacted with petroleum hydrocarbons, and 72 (20%) had evidence of heavy metal contamination. Note that more than one contaminant group was often present at the same site. Other wastes such as ordnance, radionuclides, and asbestos were present at only 11, 3, and 4 sites, respectively (Figure 2).

The primary method of combined waste disposal was by landfill (85 sites: 26%). Most wastes were released into the environment by "spills" or by dumping on the ground (185 sites: 56%). Burial in lined pits (36 sites: 11%), leaks from storage tanks (15 sites: 4%), and discharges directly into water bodies (10 sites: 3%) accounted for the remainder of the releases (Figure 3).

TABLE 1: Contaminant types, disposal methods, impacted environments and their elements.

CONTAMINANT TYPE	ELEMENTS OF GROUP
Combined Wastes	All wastes including, organics, heavy metals, petroleum, oil, lubricants, solvents, paints, sludges, refuse, caustics, acids, etc.
Hydrocarbons	Petroleum-based fuels: deisel, JP-5, JP-4, AVGAS, bunker fuel, and gasoline; Oils, sludges, and lubricants.
Toxic Organics (TOX)	All organic pollutants not associated with petroleum: solvents, paints, pesticides, and PCBs. Also includes otto fuel.
Heavy Metals	Metals most often present were: Cr, Pb, Cd, Cu, Hg, Se, and Ar. Also included were cyanide, ash, coke, blasting grit, and plating wastes.
Ordnance	Includes explosive compounds: RDX, TNT, tetryl, DNT, DNB, picric acid, and nitrobenzene; bomb casings and other munitions.
Radioactive	Isotopes of radium.

DISPOSAL METHOD	ELEMENTS OF GROUP
Landfill	Includes well managed sanitary landfills as well as uncontrolled trash dumps.
Spill	Spills, surface disposal, unlined pits, storage leaks, and burn areas.
Lined Pits	Pits lined with reinforced concrete or equilivent; deep disposal wells.
Leaking Tanks	Above ground tanks, underground tanks, and pipelines.
Water Disposal	Ponds, lagoons, ditches, canals, marinas, and outfalls.

TABLE 1: Continued.

IMPACTED ENVIRONMENT	ELEMENTS OF GROUP
Marshes	Marshes, mangrove swamps, swamps, and shallow estuaries.
Ponds	Ponds, lagoons, springs, sloughs, and canals.
Beaches	Rocky shores, sandy beaches, mudflats, and other intertidal areas.
Streams	Streams and creeks.
Bays	Bays, lakes, sounds, and other inland waters.
Rivers	Rivers, harbors and deep estuaries.
Ocean	Open ocean or gulf.

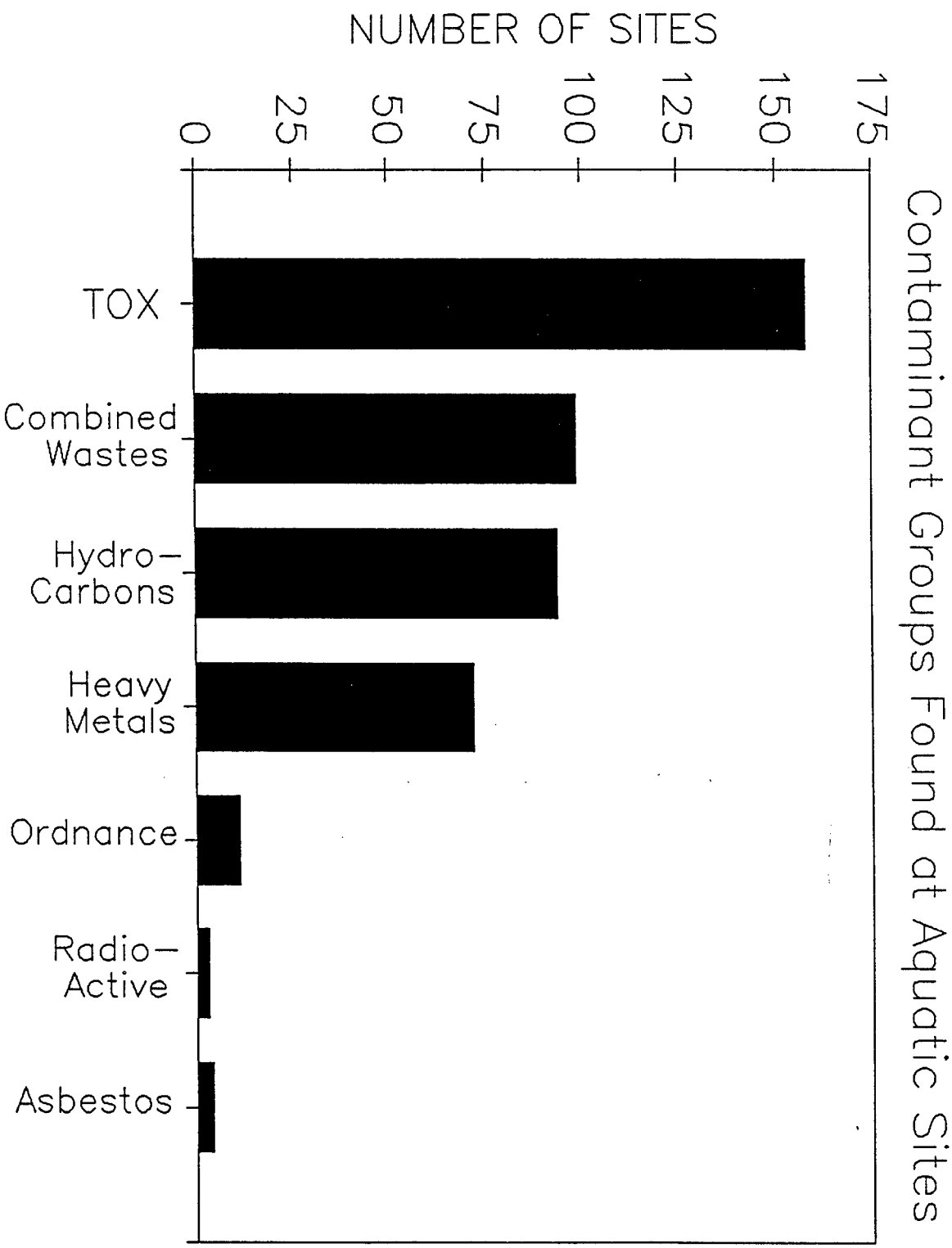


FIGURE 2: Contaminant groups disposed at Navy aquatic hazardous waste sites. (TOX = toxic organics)

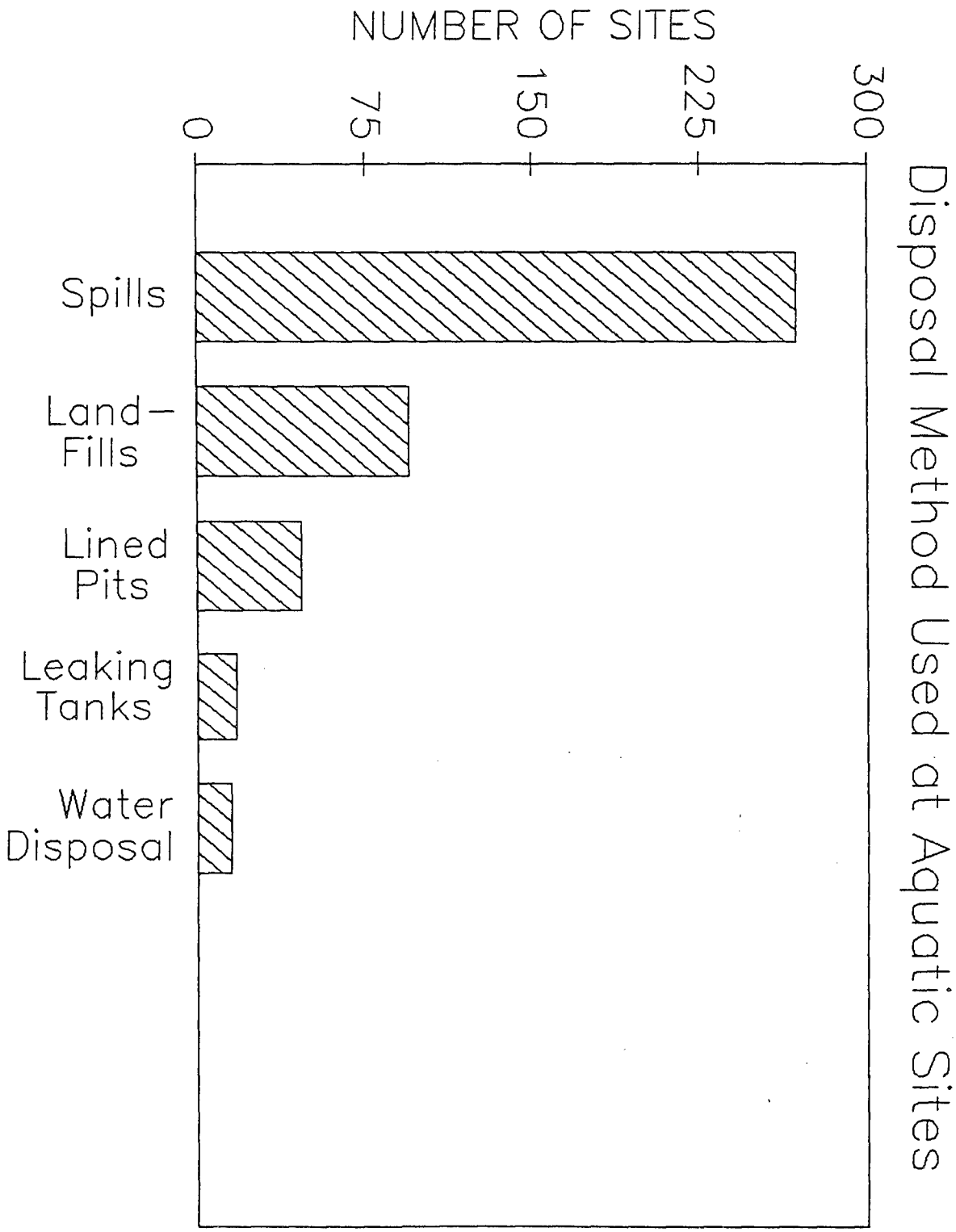


FIGURE 3: Disposal method used at Navy aquatic hazardous waste sites.

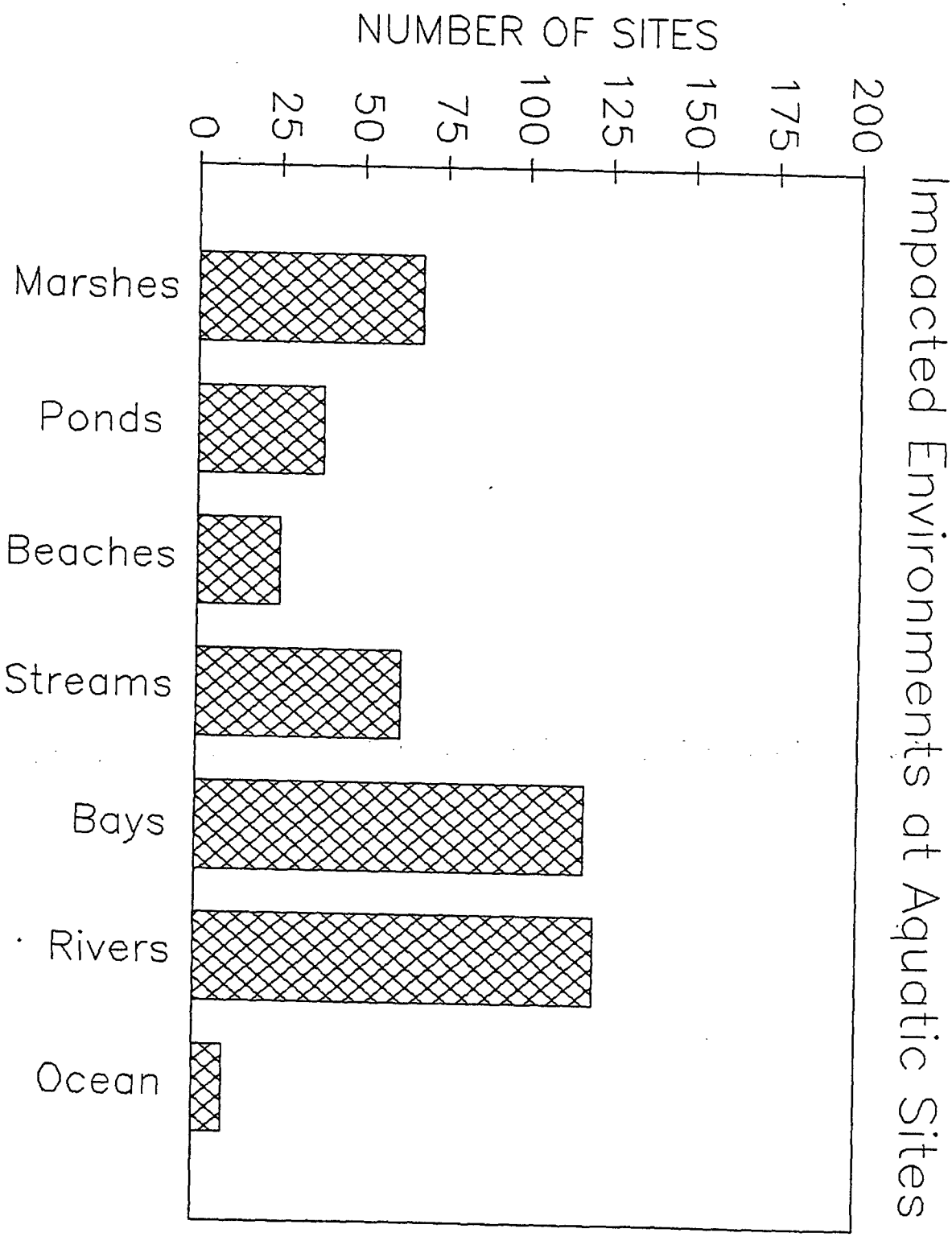


FIGURE 4: Potentially impacted aquatic environments at Navy aquatic hazardous waste sites.

The most frequently threatened environments were bays, rivers, marshes and streams. Potential impacts to bays, mostly in the form of contaminated sediments and possible shellfish contamination, were identified at 100 (27%) of the sites. Impacts to riparian habitats were suggested at 99 (27%) of the sites reviewed. Sixty (16%) of the sites could directly affect surrounding marshlands and 48 sites (14%) threatened streams. Ponds and lagoons, beach and tidal areas, and open ocean areas were threatened at 30 (8%), 19 (5%), and 9 (3%) of the sites, respectively (Figure 4). Some sites could potentially impact more than one environment type, but only the most directly impacted water body was identified here.

To determine whether particular contaminants or disposal methods presented greater hazards to the environment and local human populations than indicated by their numerical occurrence alone, the numerical occurrences of contaminants, disposal methods and impacted environments were multiplied by the Confirmation Study Ranking System (CSRS) scores reported in the IAS reports (NEESA 1982). The CSRS weighting did not appreciably change the distributions shown in Figures 2-4, other than increasing the relative importance of combined wastes disposed in landfills and decreasing the importance of hydrocarbons and toxic organics. This reflects, in part, the much larger volume of combined waste disposed in landfills compared to the hydrocarbons and toxic organics disposed of on the surface (usually through container leakage or spills).

Most all contaminants are found at landfills, while most hydrocarbons, toxic organics and heavy metals are released through spills. Bays, rivers, marshes, and streams, appear most impacted, primarily by combined wastes, toxic organics, hydrocarbons, and heavy metals. Comparable charts of occurrence weighted by CSRS scores did not appreciably affect the relative importance of contaminant groups on impacted aquatic environments.

Results obtained from reviewing Navy and Marine Corps hazardous waste sites are comparable to the National Oceanic and Atmospheric Administration's findings during their review of 435 private sector hazardous waste sites located in coastal environments (Pavia, 1987; Pavia and Harris, 1985). Navy hazardous waste sites described are a representative subset of all Navy and Marine Corps sites: they are not distinguishable by their contaminants, method of disposal or appropriate remedial technology. The problem is not so much the disposal site but rather the surrounding environment which is subjected to runoff and leachate from uncontrolled waste sites located in the coastal zone. While waste sites are relatively small, contained and well defined, impacted environments are large and complex. Water dispersal and biological community interaction tend to spread or concentrate contaminants in complicated patterns. Both waste sites and impacted environments require action but prescribed treatment is different. In many cases, controlling the waste

site or stopping the source of contamination may be sufficient to protect wetland areas. However persistent wastes, such as heavy metals and PCBs, partition into the sediment and can result in long term toxic effects to the ecosystem (Pavia, 1987).

Both waste sites and impacted environments must be characterized to determine what contaminants are present, at what concentrations they occur, and how they are distributed. Both must be monitored over time to judge the efficacy of remedial action at the source (waste site) and consequence to the sink (aquatic environment). For the case of the waste site, laboratory or in situ analysis of contaminants in water, soil or biological samples collected in confirmational studies may adequately map contaminant distribution. For the case of the aquatic environment, additional use of biological indicator species or species assemblages - a "miner's canary" - is needed to provide more realistic measure of biological toxicity of migrating contaminants, particularly if multiple contaminants act synergistically. While remedial action at the waste site is recommended and several options are usually available for particular contaminant-medium pairings, remedial action in the contaminated aquatic environment risks serious disruption to the community one is trying to protect. Rather, competent risk analysis of competing remedial techniques to determine potential impact is required.

One exception to this generalization is possible cleanup of aquatic sediments. Sediments are the ultimate sink for contaminants entering the aquatic environment. Contaminated sediments, whether resulting from Navy or non-Navy wastes, are dredged by the Navy. By law, the environmental impact of dredging must often be assessed and minimized. Academic and private research into terrestrial waste site remedial technologies is growing rapidly (Sayler 1987; Symposium on Reducing Risks from Environmental Chemicals through Biotechnology 1987). While terrestrial techniques might be extended to include contaminated aquatic sediments, relatively little research specifically addresses this area. Effective sediment remedial technologies are important to the Navy because their use would alleviate impact from nearby waste sites and facilitate necessary dredging. Stricter requirements will be enforced for dredging and disposal of contaminated sediments (Tilley et al. 1987; Turner 1987; Fredette et al. 1987; Johns et al. 1987; State of WA 1987; Evans 1988; Lukjanowicz et al. 1988).

TECHNOLOGY ASSESSMENT

An assessment of the technology requirements needed to address aquatic hazardous waste contamination identified three major areas for research and development. These areas are developing technology for making better measurements at aquatic sites, technology for conducting toxicity assessments at aquatic sites, and technology for remediating aquatic site contamination. In order to meet this need the Naval Ocean Systems Center has

initiated research, development, and demonstration to fill in these technology gaps.

Measurement Technology

Organometal Analysis. An analytical method for trace measurement of organotins in seawater has been optimized using hydride reduction to form volatile tin hydrides which are concentrated in a liquid nitrogen cooled trap and volatilized into a hydrogen flame quartz burner followed by detection in an atomic absorption spectrophotometer. This method has been automated and is being modified for analysis of other organometals at hazardous waste site. The objective of this project is to develop and operationally test an automated monitoring system for near real time analysis of organometals in the aquatic environment.

Fiber Optic Chemical Sensors. Many Navy sites are contaminated with toxic organic compounds and or petroleum hydrocarbons. Of special concern are the poly-aromatic or poly-nuclear hydrocarbons which are known carcinogens. Site investigations have documented the presence of these compounds in soils, groundwater and sediments. Most present analytical methods are not suited for rapid in situ field analysis or detailed monitoring required for site investigation and clean up. The objective of this project is to develop portable fiber-optic based sensor system for real-time in situ field measurement of poly-aromatic hydrocarbons in environmental samples for seawater, sediment and groundwater.

Marine Environmental Survey Capability (MESC). Conventional analytical techniques which involve sampling and subsequent laboratory analysis of discrete samples do not provide the temporal and spatial information required to make accurate assessments of dynamic nearshore environments. The objective of the MESC system is to develop a modular water-quality mapping system that can be used to survey chemical, biological, and hydrographic parameters in harbors, bays, and other nearshore environments. The MESC system is designed as a complete, stand-alone, modular system consisting of: (1) a suite of towed and flow-through water quality sensors, (2) an integrated navigational and positioning system, (3) an onboard data acquisition, processing, and display system, and (4) all required support equipment. The system can be deployed from a transportable survey craft or from any platform of opportunity to obtain real-time or near real-time measurements of water quality.

Benthic Flux Measurements. Studies conducted by the Army Corps of Engineers have shown that total sediment toxicant concentration is not always related to measured biological effects. A significant fraction of the toxic compounds may be absorbed on the particulate phase and not available biologically. For constituents that are significantly mobile a greater risk may result from removal of the sediments via dredging than than leaving the material in place. This project will provide a

measurement system that can be used to quantify the actual in situ flux of toxicant from the sediment into the water column to facilitate cost effective clean up strategies. The device will consist of a dome and associated "landing gear" that can be lowered from a small craft and released. Samples will be collected within the dome at pre-programmed times and the system will be retrieved using an acoustic release mechanism. The flux rate will then be calculated from analysis of the increase in toxicant over time.

Contaminant Dispersal and Prediction. The remediation of hazardous sites impacting aquatic environments requires the potential long-term impact to be determined. Selection of the most cost effective solution requires the capability to identify and predict the consequences of remediation before irreversible or costly environmental damage occurs. To do this methods must be demonstrated which will analyze and predict contaminant dispersion from hazardous waste sites impacting aquatic systems. Modeling methods must be validated using time varying hydrodynamic and contaminant data collected before they can be applied as a useful tool to improve monitoring designs and support remedial investigations and feasibility studies (RI/FSs) at sites impacting aquatic systems.

Sediment Plume Mapping. More than forty hazardous wastes sites will require remediation of contaminated sediment. In cases were dredging is required to maintain navigable waterways or to remediate contaminated areas, the impact of material resuspension is unknown and difficult to estimate, due to inadequate sampling techniques which cannot easily locate regions of dispersal. This project will provide a real-time measurement system capable of tracking subsurface plumes of contaminated sediment. The real-time projection will identify where and when to collect water-quality samples to quantify the dispersal of toxicants and estimate the potential effects on the marine environment. The approach is to determine the feasibility of using an acoustic doppler current profiler and high-precision positioning system deployed from a moving vessel to determine the dispersion characteristics of resuspended materials resulting from dredging contaminated sediment.

Toxicity Assessment Technology

Marine Bioindicator Systems. The Navy is required to clean up many hazardous waste sites located in the coastal zone. Chemical methods alone are inadequate to reliably determine the necessity or effectiveness of cleanup operations. The objective of this project is to develop methods and protocols for determining site specific toxicity using a suite of portable biological indicator systems. This system will be used in support of the RI/FS for Naval Air Station North Island, CA. Successful evaluation will result in methodology applicable to other aquatic hazardous waste sites. This project will combine in situ data collection and real time chemical analysis

capability with a portable marine bioindicator system for site-specific toxicity assessments. This capability will facilitate evaluating the effectiveness of cleanup operations at marine hazardous waste sites. The applicability of measuring in situ growth, bioaccumulation, biochemistry and toxicity will be evaluated by comparing effects in a portable bioassay trailer, a portable microcosm and with field bioindicators. The most effective bioindicator system will identified and developed to evaluate cleanup effectiveness.

Portable Environmental Test System (PETS). A major difficulty in compliance with cleanup requirements is the weakness of risk assessment techniques used to evaluate chronic environmental effects. The Navy must test for possible environmental effects of Navy specific toxicants, dredge material and hazardous wastes in the aquatic environment. The PETS is a self-contanined portable microcosm system consisting of aquaria and support equipment designed to test short term and chronic pollutant effects on harbor and shoreline communities of interest to the Navy. The quick response mobile PETS will allow cause and effect determinations of environmental impacts to be made, using environmentally realistic, yet controllable conditions. Such systems are now recognized by the EPA and other regulatory agencies as being a cost-effective means of obtaining realistic environmental assessment information.

Phytoplankton Bioluminescence Assay. Many current bioassay techniques for assessing toxicity are time consuming, labor intensive, expensive, and use inappropriate species to assess toxicity. An assay tool is needed that will address ecological impact at the sublethal level of exposure. The use of mortality as a common endpoint in presently used bioassays for decision making is inadequate for realistic risk assessments. A bioassay, currently being developed at NOSC, using dinoflagellate (algae) bioluminescence, chlorophyll fluorescence, and adenosine triphosphate levels will provide more sensitive sublethal indices of toxicity. The immediate advantages of using this technique are increased sensitivity of the assay compared to animal species, ease of use, less time required to run the assay, and lower cost in conducting the assay.

Site Specific Environmental Quality Assessment Laboratory. The purpose of this project is to develop EPA accepted protocols for optimum generic site toxicity assessments using a suite of organisms. The system will consist of a self-contained, transportable laboratory with tanks. It will include biological, physical, and chemical monitoring. Protocols and species selection will conform to the guidelines of regulatory agencies and the parameters of the specific sites.

Remediation Technology

Bioreactors. The purpose of this project is two-fold: (1) develop small, laboratory scale bioreactors for rapid determination of optimal biodegradation conditions at specific sites and (2) develop prototype bioreactor suitable for scale up to be used as a portable or mobile unit for hazardous waste detoxification onsite. Hazardous waste sites have specific factors affecting biological cleanup. This project will use bioreactors, to evaluate factors specific to the site under investigation, including the nature of the waste material or mixture, type of soil or sediment, proximity to water, existing microbial population, pH, oxygen, and nutrients for optimal onsite remediation. Scaled up versions of successful laboratory bioreactors can be deployed to the specific site where they can be used to monitor the progress of ongoing cleanup. Bioreactor systems can also be engineered to provide closed systems for above ground treatment of wastes using cultured or genetically altered organisms preventing their release into the environment.

Rapid Monitoring of Remedial Detoxification. Conventional analytical methods for the priority pollutants are expensive in time and money and are not adaptable for field use. Detection and identification of hazardous organic substances and monitoring clean-up measures can be expedited by utilizing field adaptable field measurements to screen samples and reduce analytical costs. Structural characteristics of compounds can be used as the basis for identification and estimation of the substance by the presence or absence and intensity of distinctive ultraviolet or infrared absorption bands. Simple chemical measurements using portable, low cost spectrophotometers can be used to screen samples and quantify the presence or absence of the compound(s) of interest, thus reducing the number of samples that must be sent to analytical laboratories for more detailed analysis. The validity of the methods will be verified using artificial mixtures, simulated contaminated samples, laboratory scale bioreactors, and field samples. The feasibility of this approach will be demonstrated with using a laboratory scale bioreactor system.

Complexation Capacity for Heavy Metals. In natural waters there exists an important component which tends to mitigate toxicity called the complexation capacity. Complexation capacity is the tendency of ligands and other organic material (humus) to absorb or retain heavy metals and other toxins. Accurate measurements of the complexation capacity will provide more realistic measures of toxicity at disposal sites and provide useful information for the development of synthetic complexing agents for the cleanup of waste waters.

DEMONSTRATION PROJECTS

Demonstration projects were selected on the basis of three primary criteria: (1) that the demonstration would be scientifically interesting and the results would be applicable to many other Navy and non-Navy hazardous waste sites, (2) the demonstration would be logistically do-able on the basis of manpower, timing, and resources, and (3) the demonstration would be politically acceptable to the activity and Naval Facilities Engineering Command. The current demonstrations and their start dates are: Verification of biodegradation of jet fuels at NAS Patuxent River, MD, July 1987; toxicology demonstration project at NAS Whidbey Island, WA January 1989; and risk assessment pilot study at NCBC Davisville, RI, November 1988.

Verification of Biodegradation at NAS Patuxent River, MD

The scope of this project is to design and execute experiments to evaluate and verify in situ biodegradation of jet fuel spilled in a marsh area by: (1) determining the rate of biological degradation of petroleum hydrocarbons before, during, and after remediation, and (2) identify metabolites associated with biodegradation of petroleum hydrocarbons in soil, sediment, and water. The work is being conducted by Dr. Richard Lee, from the Skidaway Institute of Oceanography, University of Georgia, and in coordination with the Naval Civil Engineering Laboratory.

The hydrocarbon degradation potential was determined for soil and water contaminated with spills and seepage of the jet fuels JP-4 and JP-5 near a fuel farm at NAS Patuxent River, MD. About four acres were contaminated, to a depth of about seven meters, with petroleum products. The deterioration of adjacent wetland habitat and the possible contamination of the Patuxent River, which enters the Chesapeake Bay, are areas of significant concern.

Hydrocarbon degradation rates were determined by adding radiolabeled hydrocarbons to soil or water samples and measuring rates of mineralization (production of $^{14}CO_2$). The radiolabeled hydrocarbons used were benzene, toluene, naphthalene, methylnaphthalenes, fluorene, hexadecane, and phenanthrene. The surface soils at the contaminated site were primarily sand but a layer of peat was also present. The peat appeared to be saturated with oil. Hydrocarbon degradation rates were slower in peat relative to sand. The half-lives of naphthalene in oiled sand, oiled peat and "clean" reference soil were 1, 2 and 31 days, respectively. Similar rates were found with the other jet fuel hydrocarbons. The slow degradation in the "clean" reference soil is presumably due to a low number of hydrocarbon degrading microbes, whereas in the oiled soils hydrocarbon degrading microbes may dominate the microflora. All of the hydrocarbons examined from the jet fuel, e.g. toluene, benzene, and naphthalene, were rapidly degraded in oiled soil. However,

hydrocarbons not present in jet fuels, e.g. hexadecane and fluorene, were more slowly degraded in oiled soils than in "clean" reference soils. It appeared that the soil microbes in the oiled soil have adapted only to jet fuel hydrocarbons and can not degrade other petroleum hydrocarbons, such as heavier weight polycyclic aromatic hydrocarbons and alkanes.

We are currently determining hydrocarbon degradation rates in streams and ponds into which oil is seeping from the contaminated soils.

Toxicology Demonstration Project at NAS Whidbey Is., WA

Naval Air Station Whidbey Island, WA has been nominated for addition to the National Priority List (NPL). A total of 28 sites have been proposed for addition the the NPL. Much of NAS Whidbey Island is forest, grassland or marsh and provides habitat for numerous upland game birds, waterfowl, and other mammals and birds including the endangered peregrine falcon and threatened bald eagle. Beaches and bays around NAS Whidbey Island are popular fishing and shellfish gathering areas. Past disposal sites may potentially contaminate lowland areas and the accumulation of persistent and biomagnifying pollutants in the food chain could affect higher order predators and man.

The objectives of this demonstration project are to conduct a toxicological evaluation to assess impact of hazardous waste to wildlife, evaluate risks associated with remediation of waste sites, and demonstrate the use of an enhanced avian bioassay using starlings as a bioindicator of toxicological impacts. A quadrant of nest boxes will be used to create an exposure gradient to quantify toxicological effects on survival, behavior, bioaccumulation and reproductive success. Toxins of concern will be identified by analysis of feeding behavior and bioaccumulation data.

The Institute of Wildlife Toxicology at Western Washington University (IWT-WWU), Dr. Ron Kendall, Director, will be conducting the research to perform the <u>in situ</u> toxicological evaluation of the impacts from hazardous waste sites on wildlife and the environment. The IWT-WWU has extensive experience in the planning and execution of <u>in situ</u> tests on avian populations, the capability to perform field studies for collection of avian populations, including nest box deployment, rearing of juvenile starlings, and nonlethal serum sampling of raptors, and nondisruptive assessments of great blue heron productivity and health, expertise in trapping and assaying rodents, and expertise for biochemical analysis of tissue samples for specific protein complexes as well as for toxic chemicals and their metabolites (Kendall 1988; Robinson et al. 1988; Brewer et al. 1988).

Successful demonstration of the innovative approach of using

starlings as bioindicators of toxicological impacts, will provide an assessment tool that can be used at other Navy and non-Navy waste sites. The toxicological information will be used to determine the extent and potential impact (if any) of contamination to the environment for input to the RI/FS process. Follow-on studies to determine the effectiveness of remediation, will be conducted if required.

Risk Assessment Pilot Study at NCBC Davisville, RI

Allen Harbor at Naval Construction Battalion Center (NCBC) Davisville, RI has been closed for shellfishing by the Rhode Island state Department of Environmental Management, due to suspected hazardous waste contamination from a landfill adjacent to the harbor. Analysis of sediment and bivalve tissues from Allen Harbor have shown increased levels of heavy metals and organics. The waste sites may be a source of leachate and low-level contamination to the harbor. Information is needed to assess the potential long term impacts and identify risk management procedures. This project will develop and field validate ecological risk assessment methods. Ecological risk assessment involves quantitative estimation of the likelihood of adverse ecological effects resulting from exposure to toxic substances from hazardous waste sites. Ecological effects will be determined using toxicological and bio-markers methodology. The completed risk assessment will support selection of remedial action or risk management of wastes. Monitoring will be conducted to measure the success of remediation technology.

A memorandum of agreement between the Naval Ocean Systems Center and the EPA-Environmental Research Laboratory (EPA-ERL), Narragansett, RI was obtained to provide for cooperative research and development of risk assessment methodologies. The EPA-ERL is a center of excellence for marine coastal and estuarine water quality research and has the lead within the EPA to develop ecological risk assessment methodologies. The pilot study provides a site to use as a case study to develop methods for ecological risk by measuring and defining the extent of hazardous waste impact, assessing the toxicological and biological effect of the impact, and evaluating tools to detoxify and remediate. In addition the project will implement monitoring and assessment to support a risk management plan for Allen Harbor.

The anticipated products from this demonstration are: (1) The risk assessment for Allen Harbor, selection of optimal cost-effective remediation, and verification of the effectiveness of clean up. (2) The evaluation of new and innovative technology for conducting ecological risk assessments developed by conducting cooperative research and monitoring activities. (3) Guidance for ecological risk assessments at other Navy and non-Navy aquatic sites.

RECOMMENDATIONS

The following are felt to be pertinent Navy research and development interests:

(1) Development of chemical sensors (Ostgaard, 1984; Hirschfeld, et al, 1983; Lieberman et al, 1987;) and biochemcial sensors (Pickwell and Steinert, 1984; Viarengo, 1985; Jenkins and Sanders, 1986; Steinert and Pickwell, 1988) to map and monitor contaminants in the water column and underlying sediment, preferably in real time. Real time display would allow directed sampling on site, rather than force reliance on a priori sampling designs associated with subsequent laboratory analysis. Real time analysis could focus on mapping "key" or representative contaminants as tracers to predict the distribution of other contaminants, which could be verified by standard laboratory analysis.

(2) Identification of biological indicator species and assemblages to assess biological toxicity of multiple contaminants (Vernberg and Vernberg, 1974; Vernberg et al. 1977; Wise, 1985; Gentile et al. 1988). This data is a necessary input to risk models which aid in choosing preferred remedial measures (Beck and Conner, 1987). Navy personnel should become familiar with risk assessment methods and their role in remediation.

(3) Development of remediation technologies designed for aquatic sediments. In situ techniques are preferred because they are suitable for environments where dredging may occur as well as those environments where dredging is not an issue. Monitoring and disposal of contaminated dredge spoils will require specialized methodology for assessment of impact as well as possible treatment options.

Figure 5 shows the relationship of the three areas of research to the Remedial Investigation/Feasibiltiy Study process. Improved measurement technology will result in better site investigations and more realistic and achievable remedial options. Advances in remediation technology will assist in the development of feasibility studies and reduce the costs of clean up. The development of toxicity/risk assessment technology is critical to the whole process. Toxicological information can be used to determine the severity of the problem, identify effective remedial options, and determine "How clean is clean?". Therefore methods that allow the direct measurement of environment health will be extremely useful for assuring the environmental safety of hazardous waste disposal sites and compliance with the law.

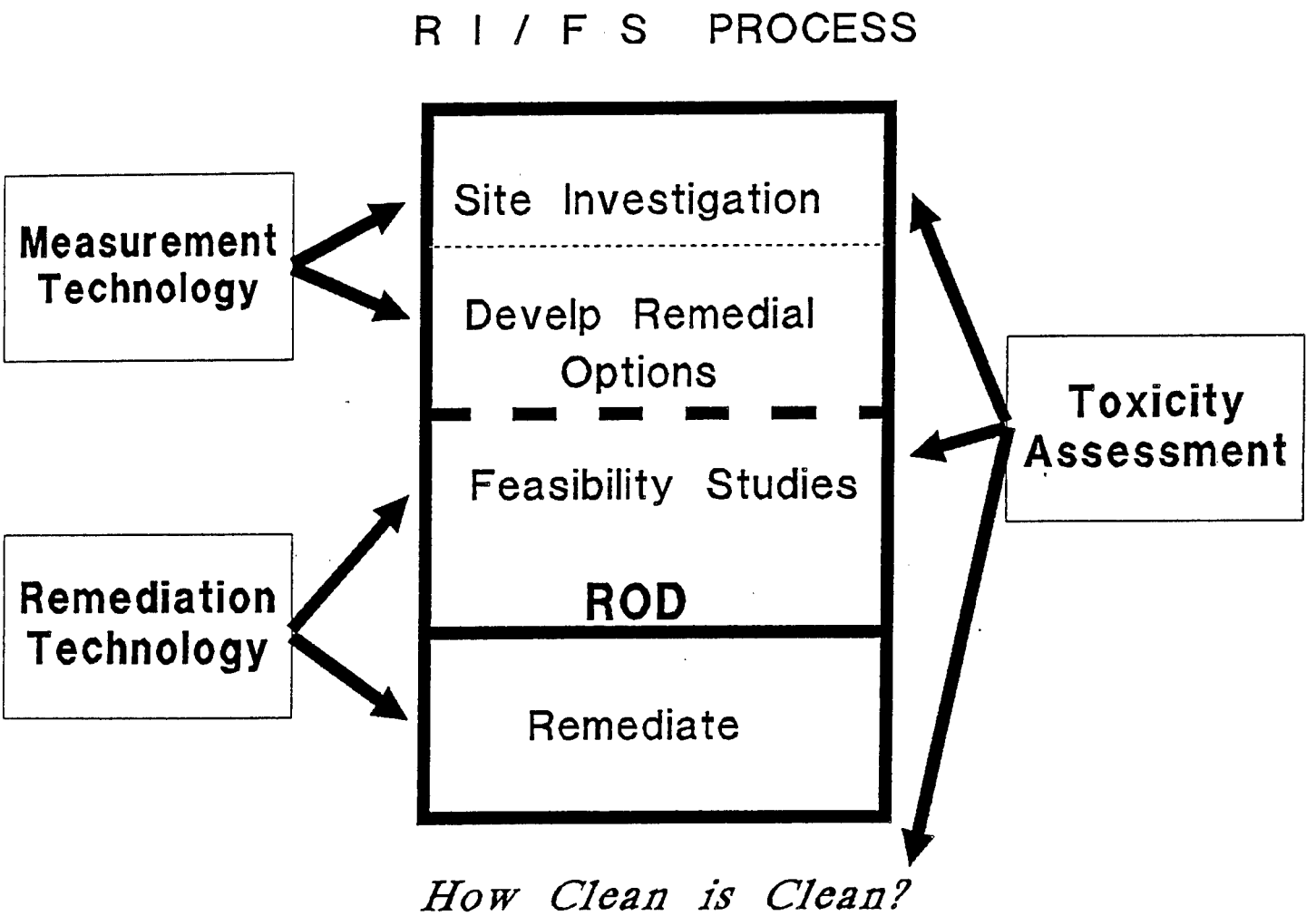


FIGURE 5: The remedial investigation feasibility study (RI/FS) process, includes the site investigation, development of remedial options, performance of feasibility studies, the signing of the record of decision (ROD) and remediation. Develpment of measurement, remediation, and toxicity assessment technology is needed to support the RI/FS process.

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A Field Experiment of Groundwater Transport in a Heterogeneous Aquifer[1]

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Abstract

The Tennessee Valley Authority (TVA) is conducting a large-scale groundwater research project as a part of the Electric Power Research Institute's (EPRI) Solid Waste Environmental Studies (SWES) project. The goal of the SWES project is to develop better methods for simulating the processes that affect the transport and fate of solutes from wastes of fossil fueled power plants. At the TVA test site, nonreactive tracers were injected into the groundwater and will be tracked by sampling several hundred wells for at least two years. Results are providing insight into transport and dispersion processes in very heterogeneous aquifers. Results are intended to provide a basis for verifying or improving models for predicting transport and dispersion of contaminants in saturated groundwater systems. The experimental design and current results are presented.

Introduction

There are three objectives of the large-scale groundwater research project:

- To better define transport and dispersion processes of contaminants in the saturated zone;
- To evaluate and compare the different methods for geohydrologic site characterization of heterogeneous aquifers; and,
- To provide a quality data set to serve as a benchmark for evaluating models of transport and dispersion in the saturated zone.

This project is part of the comprehensive SWES project initiated by EPRI in 1983 to address major aspects of geohydrology and

[1]Sponsored by EPRI; Research Project RP 2485-5

geochemistry related to land disposal of waste from fossil fueled power plants (Figure 1). The field test conducted by TVA is known as the Macrodispersion Experiment (MADE), and is located at Columbus Air Force Base in Mississippi (Figure 2).

The research site is underlain by a shallow alluvial aquifer ranging from 10 to 13 meters in thickness. These terrace deposits consist primarily of sand and gravel with lesser amounts of clay and silt. The aquifer is extremely heterogeneous with localized hydraulic conductivities ranging from 10^6 cm/s to 1 cm/s, with differences of three to four orders of magnitude frequently encountered in the same borehole. The aquifer is underlain by dense clays which form an aquitard. Since November 1983, TVA personnel have conducted numerous subsurface studies to characterize the terrace aquifer. These studies include exploratory drilling and soil sampling, laboratory testing of soil samples, surface and subsurface geophysical surveys, aquifer tests, monitoring of the hydraulic-head field in three dimensions, and mineralogical and water quality analyses.

Several methods have been used to estimate the spatial variability of hydraulic conductivity at the test site. These include:

- Downhole geophysical logging of 57 wells using natural gamma, gamma-gamma, neutron and resistivity techniques;

- Surface geophysical surveys, including electromagnetics, vertical resistivity profiling, streaming potential, and ground penetration radar;

- Particle size analysis of several hundred soil core samples;

- Permeameter tests on 30-inch undisturbed soil cores from seven locations;

- Single well pumping tests combined with flowmeter measurements in fully penetrating wells; and

- Packer permeability tests at several fully-penetrating wells.

Site characterization studies are summarized in Waldrop, et al. (1987). More details may be found in Boggs, et al. (1988), and Rehfeldt, et al. (1988a and b).

Experimental Design

The field experiment consists of injecting a source of tracer into the saturated zone of the aquifer over a 48-hour period. The three-dimensional plume was then tracked for two years. With the exception of relatively minor refinements, the project design is described in Betson, et al. (1985). In October 1986, tracers were

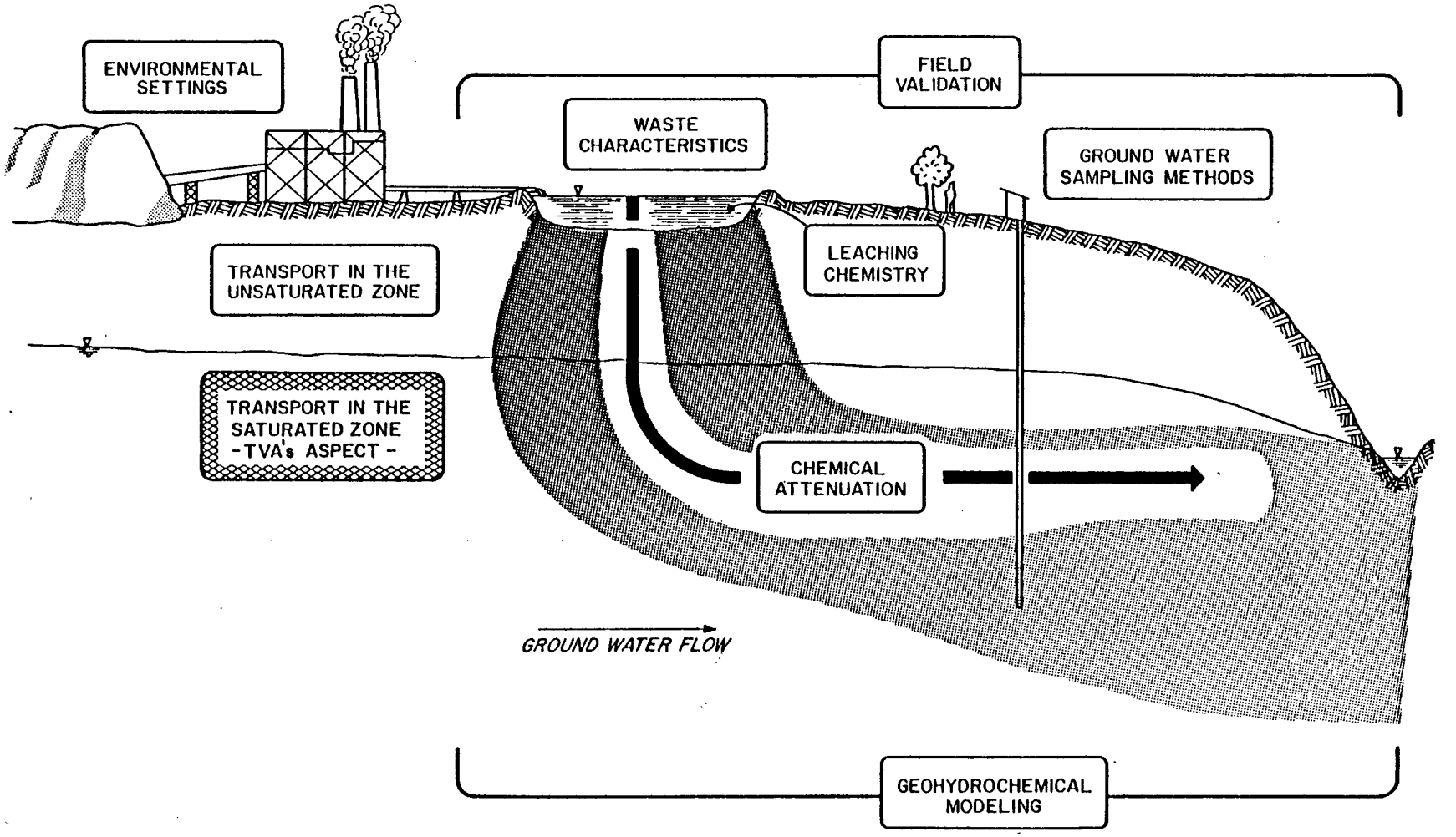


Figure 1. Research Components of EPRI Solid Waste Environmental Studies Project

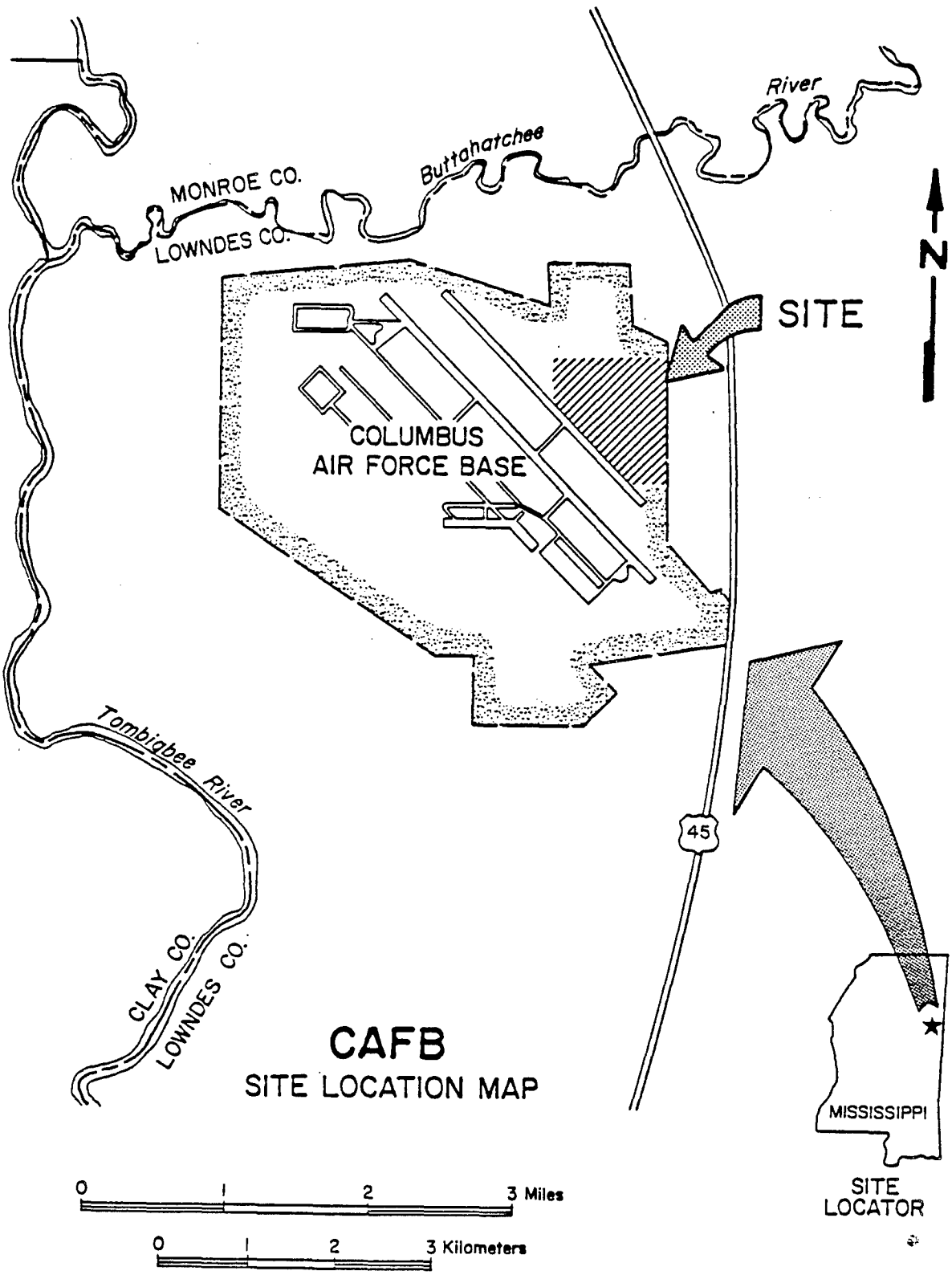


Figure 2. Macrodispersion Experimental Site

injected into five wells spaced one meter apart. These injection wells were screened over about one meter at a depth of about 8 meters. Ten cubic meters of solution were continuously injected over 48 hours to minimize mounding of the groundwater in the vicinity of the injection. Although bromide serves as the primary tracer, three fluorinated benzoic acids, deuterium, and two freons were also injected.

Tracer sampling is accomplished with a grid of sampling wells intended to bound the tracer plume. The sampling grid, as of November 1988, consists of 258 sampling wells distributed as shown in Figure 3. The movement of the plume dictated when and where additional wells were installed. Each of the wells is designed to draw samples of groundwater for analysis of tracer concentrations from as many as 30 individual depths simultaneously.

Vertical hydraulic gradients measured at the site (attributable to the heterogeneity of the aquifer) indicated that extreme care is required to prevent the sampling wells from creating artificial pathways for vertical groundwater movement. These devices, known as Multilevel Samplers (MLS), are designed with sampling tubes inside of the PVC pipe as shown in Figure 4. Sampling tubes exit at different depths through holes in the pipe wall where a short filter is attached to the end of the tube. The MLS are installed by augering to the base of the terrace aquifer, installing the MLS through the hollow-stem auger, removing the auger, and allowing the aquifer materials to collapse around the sampler. All MLS are equipped with external bentonite collars between sampling ports. The bentonite in the nylon collars absorbs water and swells to several times its original volume to further retard artificial vertical movement of groundwater in the annulus.

Sampling of the entire MLS network was conducted at approximately 12 week intervals. A High Performance Liquid Chromatograph was used to determine the concentrations of bromide and fluorinated benzoic acid tracers in each sample. Other tracers were not analyzed. In addition to tracer concentrations collected from the MLS, groundwater levels in 32 piezometers within the tracer test area are measured. Seven of these piezometers and a rain gauge are equipped with continuous recorders to transmit via satellite real-time to a data management center. These data reveal that the water table fluctuates about two to three meters annually. Maximum levels are expected in early March and minimum levels in late summer and early fall.

Sampling Results

Seven complete snapshots of the tracer plume have been conducted to date. Examples of tracer concentrations, presented in Figure 5, portray a very irregular and non-Gaussian plume. Although the zone of peak concentration of the tracer plume has moved only approximately 7 meters in two years, a partial snapshot conducted in

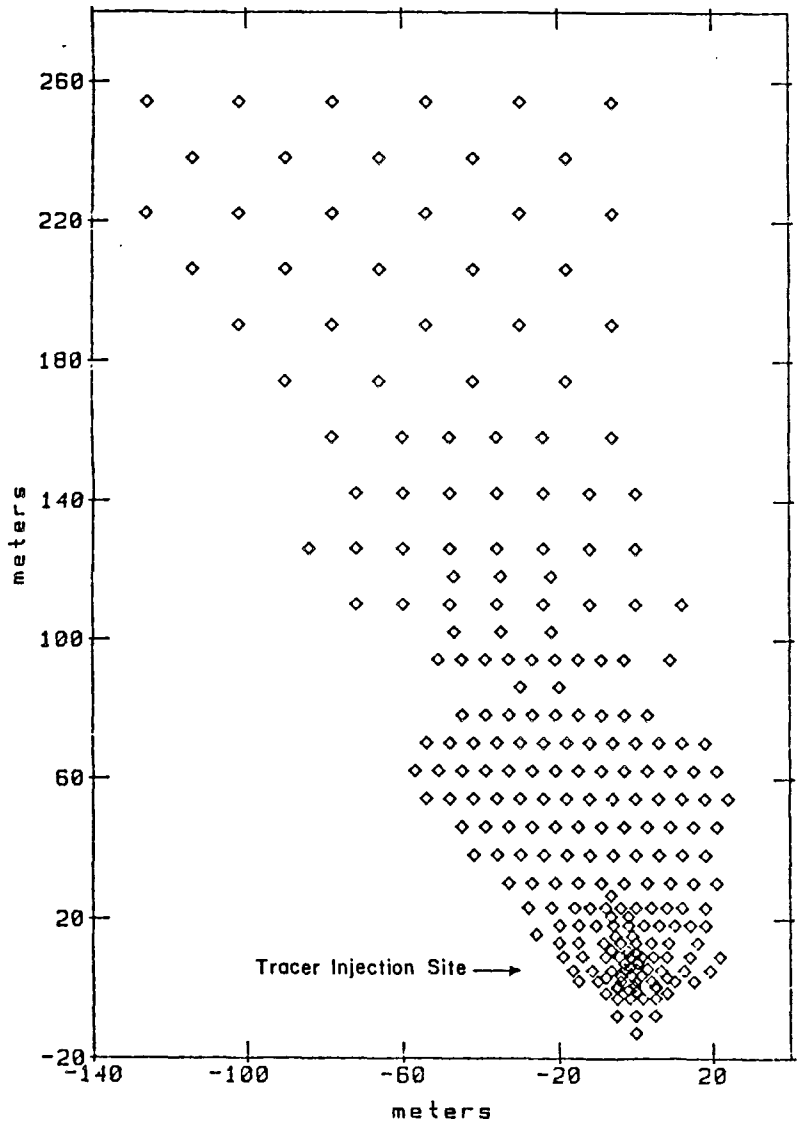


Figure 3. Multilevel Sampling Well Network

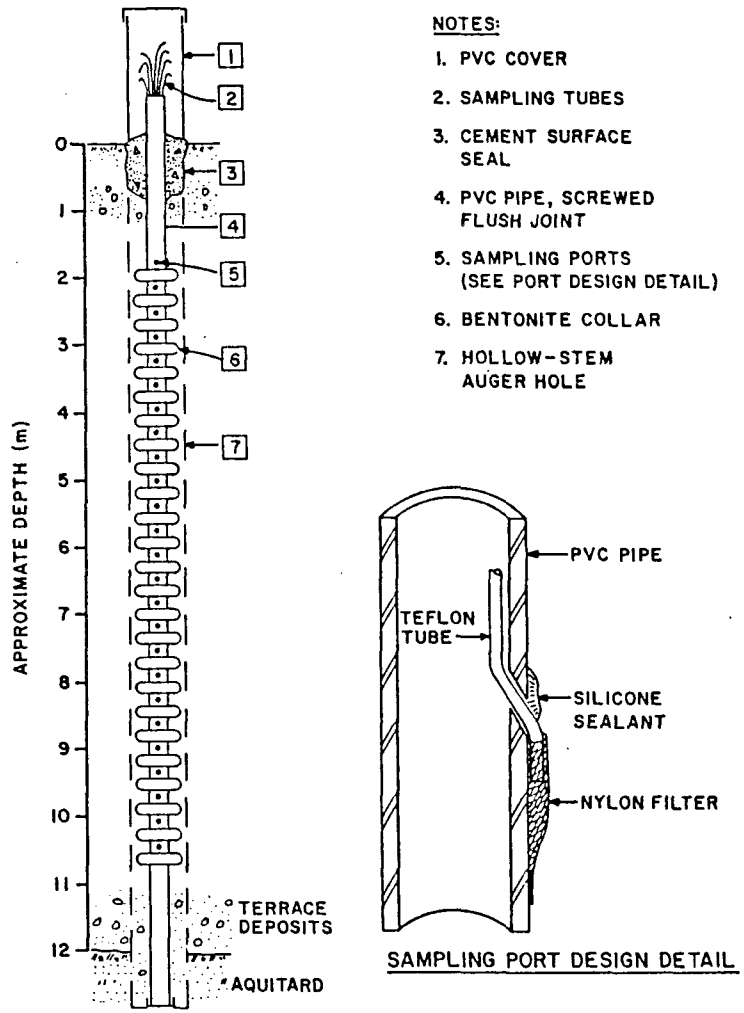


Figure 4. Multilevel Sampling Well Design

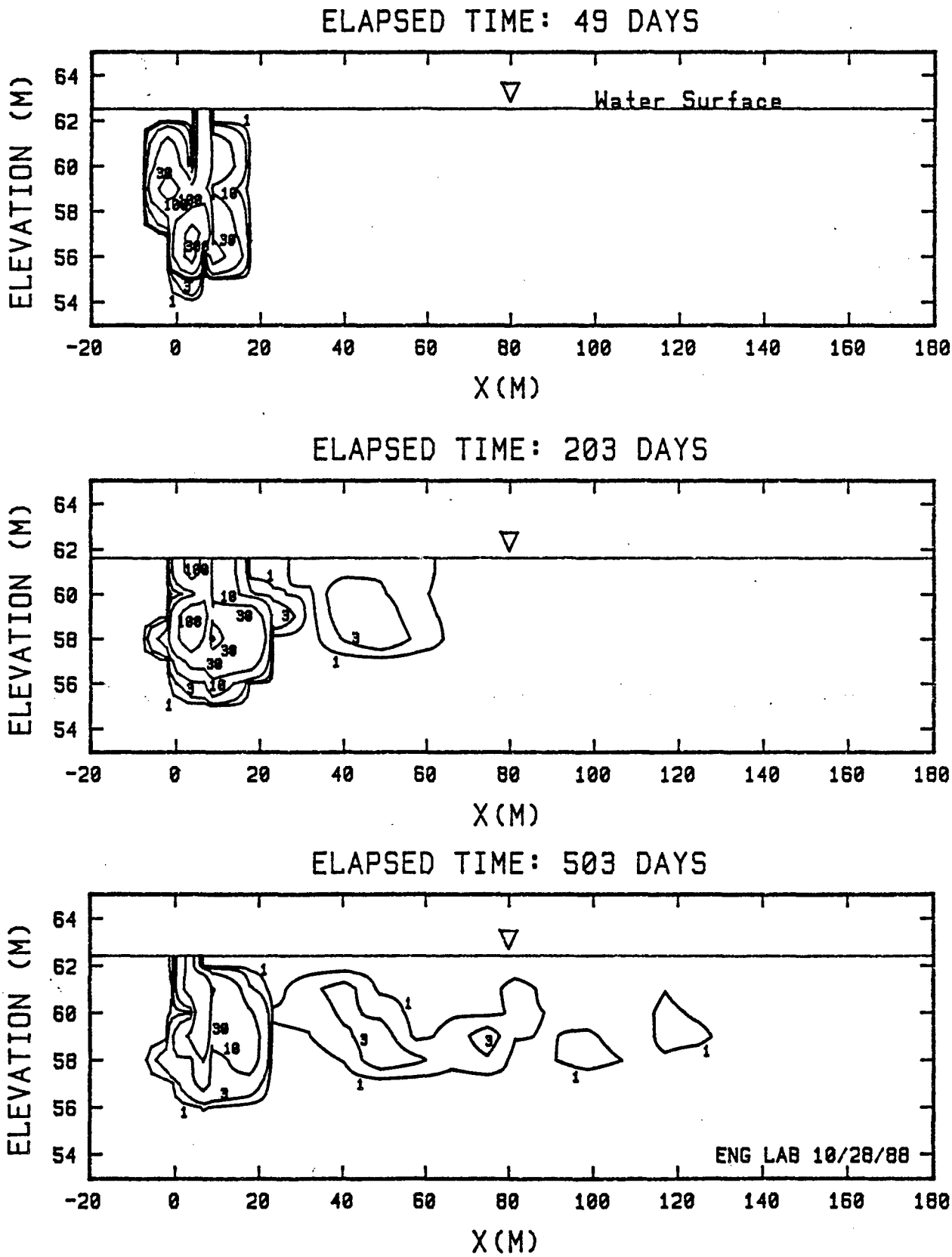


Figure 5. Tracer Concentrations in a Longitudinal Section (mg/L)

June 1988 revealed that the leading edge of the tracer had traveled greater than 260 meters, and thus outdistancing the sampling network. The tracers have evidently meandered in a three-dimensional pattern seeking zones of high hydraulic conductivity which produced a fingering effect. The annual fluctuation of the water table further complicates the transport and dispersion processes. However, these complicating conditions are probably typical of the geohydrological conditions of industrial solid waste facilities, most of which are located adjacent to rivers or other large bodies of water. The net result is an advection rate much greater and more complex than had been predicted. Additional theoretical development to mathematically describe these processes appears necessary.

Data analysis and reporting of the many interesting aspects of this experiment are still in progress. Another tracer injection may be conducted for EPRI in the spring of 1989. The test design will reflect results of tests and analyses currently in progress. Future uses of the test facility beyond the EPRI requirements are unclear at this time. However, considering the tremendous investment in site characterization, installation of equipment, and analysis of transport and dispersion process, additional use of this facility is likely. Furthermore, the heterogeneity which has made the test so difficult to design, conduct, and analyze, also makes the site valuable in that it is typical of real world conditions.

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PILOT-SCALE TESTING OF PAINT WASTE INCINERATION

° Preliminary Results °

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ABSTRACT

U.S. Army depot operations generate large quantities of paint removal and application wastes. These wastes, many of which are hazardous, are currently disposed off-site. Offsite disposal of solids is often by landfilling. Landfilling of hazardous wastes will be banned or highly restricted in the future. USATHAMA has initiated several research activities to evaluate alternative disposal of paint wastes. This paper presents a preliminary evaluation of data collected by PEI Associates, Inc. during pilot-scale incineration tests of selected Army paint wastes. A draft report is currently in preparation. The information presented herin has not yet been reviewed by USATHAMA.

INTRODUCTION

U.S. Army depots are involved in repairing and refurbishing Army vehicles and equipment. These activities involve paint application and removal operations that generate a variety of wastes. In particular, large amounts of waste are generated by paint removal operations such as chemical stripping and mechanical blasting, and by paint application operations which generate waste paint and solvents. These paint wastes contain potentially toxic organic compounds, corrosive liquids, and/or heavy metals, and have thus been classified as hazardous wastes. These wastes are currently disposed offsite under commercial contract. Many of the solid paint wastes are disposed of by landfilling. Disposal is expected to present an increasingly severe problem because land disposal of all hazardous wastes will be restricted in the future. Therefore, the development of alternative technologies to land disposal is needed to assist the depot operations in managing the hazardous waste they generate.

Two previous studies conducted by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) have concluded that incineration of the paint wastes has the greatest treatment potential, both from technical and cost-effectiveness standpoints.[1,2] The most recent study involved bench-scale incineration testing and found that the resulting ash residue would not be hazardous according to the U.S. Environmental Protection Agency (EPA) Toxic Characteristic Leaching Procedure (TCLP) criteria. The study recommended pilot-scale testing of incineration to determine if subsequent treatment of the ash residue is needed and to determine the destruction and removal efficiency (DRE) of organic compounds.

PEI Associates, Inc., has recently conducted pilot-scale testing of paint waste incineration for USATHAMA under Task Order No. 0001 of Contract No. DAAA15-88-D-0001. The objective of this task was to continue development of paint waste treatment technology through pilot-scale rotary-kiln incineration testing. Specifically, the results of the pilot test are being evaluated to assess how the characteristics of the paint waste and incinerator operating conditions affected the following:

- Characteristics of ash residue.
- Amount of ash residue.
- Destruction and removal efficiencies for organic compounds.
- Characteristics of stack gases.

Four types of paint waste were identified in previous USATHAMA reports as being the largest waste streams: 1) spent shot blast media (walnut hulls, plastic, metal, or glass media); 2) paint application waste (waste paint and solvents); 3) spray booth wastes (air filters with trapped paint, floor sweepings, and Nanapeel™, a rubberized spray booth coating); and 4) spent chemical strippers and contained paint sludge. PEI visited the Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania to conduct familiarization sampling and characterize these waste streams. The four general categoriesof paint waste were each found to include several different individual wastes. Ultimately, 14 types of paint waste were sampled, including two types of blast media (plastic and walnut hulls), four types of spray booth waste, four kinds of waste paint and solvents, and two chemical strippers, each with liquid and sludge fractions managed as separate streams. Other wastes generated in smaller quantities were identified but not sampled. In addition to the numerous categories of waste, there was a large variability of characteristics within the same waste. Subsequently, plastic and agricultural blast media (walnut hulls) were chosen for the first pilot-scale test because they account for approximately 50% of the paint waste generated at LEAD. Other paint wastes will be tested in the future.

EXPERIMENTAL PROCEDURES

The pilot-scale incineration tests were conducted in August, 1988, at the John Zink Co. incineration test facility in Tulsa, Oklahoma. This facility has several pilot-scale modular components that can be assembled in various configurations. A schematic of the rotary-kiln incineration system used for these tests is shown in Figure 1. The system consisted of a rotary-kiln incinerator with a screw feeder, a kiln afterburner (secondary combustion chamber), a water quench for the kiln ash, and a stack gas conditionaing tower. Additionally, a venturi scrubber followed by a knockout chamber and a final fume incinerator, as required by the Oklahoma State Department of Health (OSDH) for all tests involving hazardous wastes, were included in the configuration. The maximum heat throughput to the system is 3 million BTU/hour.

The test matrix chosen for the first stage of paint waste incineration is shown in Table 1. Approximately 195 lbs/hr of dry paint waste was fed to the kiln. This dry waste consisted of equal amounts of plastic and agricultural blast media that were manually mixed. It was necessary to add water to this mixture to prevent excessive dusting during mixing and to prevent the dry, fine-grained blast media from being blown through the kiln by the combustion air; the moisture content averaged 37% over all the tests. The waste was also spiked with surrogate organic compounds

(chlorobenzene and ortho-dichlorobenzene) to allow calculation of the destruction and removal efficiencies (DREs) of both volatile and semi-volatile organics. The spiking compound feed rates were 8.7 lbs/hr of chlorobenzene (volatile organic) and 13 lbs/hr of o-dichlorobenzene (semi-volatile organic), which represented 4 and 6%, respectively, of the total feed rate of combustible materials (i.e., not including the moisture content). These compounds are ranked very high on the EPA incinerability index because they are difficult to incinerate; thus, if the performance standard of 99.99% DRE is met for these compounds, other volatile and semi-volatile compounds would also be destroyed by the same incineration conditions.

The operating conditions investigated were temperatures in the kiln and afterburner, and the residence time of waste in the kiln (which could be varied by changing the kiln rotation rate). The kiln operating temperatures were 1500 and 1800°F, and the afterburner temperatures were 1600 and 2000°F. Two tests with residence times of 30 and 60 minutes were conducted for each of the two kiln operating temperatures, giving a total of 4 tests. Each of these tests consisted of 2 two-hour runs.

Several sampling activities were conducted to allow characterization of the feed, ash, and air emissions. Samples of the paint waste feed were collected during each run and analyzed for the metals and organic compounds on the EPA's Toxic Characteristic Leaching Procedure (TCLP) list. Proximate and ultimate analyses were also conducted on the paint waste. The dry kiln ash was sampled from a port near the bottom of the kiln discharge hood before contact with the quench water. Samples of the kiln ash were analyzed for the TCLP metals and organic compounds. In addition, the ash was subjected to the TCLP extraction and the extract analyzed for metals and organic compounds.

Air emission samples were taken from Sample Port A in Figure 2 after passing through a water cooling tower to cool the off-gases to between 600 and 800°F. Volatile organics in the air emissions were measured using the Volatile Organic Sampling Train (VOST) protocol, and the EPA Modified Method 5 sampling train was used to measure semi-volatiles, particulates, and HCl emissions. A metals train was used to measure metal concentrations in the flue gas, and an in-stack impactor was used to measure particle size distribution. In addition to these sampling activities, Continuous Emissions Monitoring (CEM) was conducted in the flue at the kiln afterburner exit for carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), and temperature, and after the venturi scrubber for nitrogen oxides (NOx) and sulfur dioxide (SO_2). Operating conditions of the incineration system such as temperatures, combustion air flow rates, auxiliary fuel feed rates, and percent oxygen in the gases exiting the kiln and afterburner were also periodically monitored.

RESULTS

The results of the proximate and ultimate analyses of the feed material are shown in Table 2. The average, low, and high values are based on one sample for each of the 8 test runs. These results are given on a dry basis and reflect the

characteristics of the mixed blast media before addition of water or spiking compounds. The average heating value of the waste was about 7700 BTU/lb; the 37% moisture content of the actual feed material decreased this value to about 4800 BTU/lb. The ash content ranged from 6.5% to 14.3%, and averaged 11%. The elements of concern with regard to air pollution — sulfur, nitrogen, and chlorine — averaged 0.11%, 12.4%, and 0.09%, respectively. The source of the chlorine content was probably the plastic blast media.

Table 3 summarizes the results of the metals analysis for the feed material on a dry basis. The primary metals of environmental concern that cause the media residue to be hazardous are lead and chromium, with average concentrations of 5066 and 1467 ppm, respectively. Barium was also present in significant amounts, with an average concentration of 504 ppm. Many of the metals in the feed material had a wide range of concentrations over the tests, with lead ranging from 1796 to 8320 ppm, and chromium from 595 to 2340 ppm. This diversity reflects the fact that the metal content of a particular drum of spent blast media is determined by many factors, including the metal content of the pigments in the paint being removed, how readily the paint is removed (paints that are difficult to remove will require more blast media and thus result in lower metal concentrations), and the efficiency of the blasting operation on different kinds of parts.

No significant organics were found in the feed samples. The only compounds found with average concentrations greater than 1 ppm were methanol (11ppm), methyl ethyl ketone (2.6 ppm), 4-methylphenol (1.4 ppm), and acetone (1.3 ppm).

The metal contents in the kiln ash for each test condition averaged over 2 runs each are presented in Table 4, and the metal concentrations in the TCLP extracts of the ash are given in Table 5. Lead, barium, and chromium are the compounds with the highest concentrations in the kiln ash, with lead concentrations ranging from 161 to 2915 ppm, barium from 475 to 2140 ppm, and chromium from 132 to 982 ppm. Arsenic, barium, and silver concentrations increased in the kiln ash as compared with the concentrations in the feed material, while the other metal concentrations decreased in the kiln ash. The only test that produced ash that exceeded the TCLP criteria was Test 3, with a kiln temperature of 1800°F and 60 minutes residence time. The cadmium concentration was 7.1 ppm (TCLP limit = 1 ppm), and the chromium concentration was 32 ppm (TCLP limit = 5 ppm). Concentrations of lead and silver approached the TCLP limits of 5 ppm for each. Although this test had higher concentrations of metals in the TCLP extracts than the other tests, the total metal contents in the ash were not generally greater. This apparent anomaly indicates that for this test condition, the metals in the ash were in a more leachable form than for the other test conditions. Organic compounds in the ash and TCLP extracts were generally below detection limits; concentrations averaged over the 4 tests were always less than 1 ppm.

Sampling of the gas emissions after the kiln afterburner and water cooling tower indicated that more than 99.999% of the organic spiking compounds were destroyed for each test condition, and thus the DRE performance standard of 99.99% was surpassed for both volatile (chlorobenzene) and semi-volatile (o-dichlorobenzene) principal organic hazardous constituents (POHCs).

Particulate loading to the control system after the kiln afterburner was a function of both temperature and kiln residence time, as shown in Table 6. Higher emission rates occurred at lower temperatures and longer residence times. The range of values for uncontrolled particulate loading was from 0.38 gr/dscf for the 1800°F kiln temperature and 30 minute residence time to 2.4 gr/dscf for the 1500°F kiln temperature and 60 minute residence time. These values correspond to 1.3 and 6.5 pounds of particulate emissions per 100 pounds of feed material, respectively. Figure 3 presents the mass emission rates in graphical form. These correlations with operating temperatures and residence times are consistent with general incinerator operating principals.

A graphical summary of the particle size distribution data is presented in Figure 4. At the lower kiln temperature of 1500°F, the majority of particles were larger than 15 microns. At the higher kiln temperatures of 1800°F, a greater mass percentage of particles was found smaller than a given particle size. Therefore, higher kiln and afterburner temperatures resulted in smaller particles, as would be expected. These small particles will need to be considered in designing air pollution control equipment. Figure 4 also shows that for a given temperature, the two residence time lines are fairly close together, which indicates that residence time did not have a large effect on particle size distribution.

Results of the continuous emissions monitoring (CEM) are summarized in Table 7. The average O_2 concentrations for the test conditions ranged from 5.4 to 8.4%, and the CO_2 concentrations ranged from 9.2 to 11.4%. The sets of O_2 and CO_2 data correlate with each other, with higher O_2 values corresponding to lower CO_2 values, as expected. Many CO spikes were observed during the first test, which can be attributed to difficulties during the first day in keeping the incinerator at steady state operating conditions; the average CO concentration for these two runs was 308 ppm. Average CO concentrations during the remaining tests ranged from 14 to 24 ppm.

Average concentrations of SO_2 after the venturi scrubber ranged from 10 to 24 ppm. Average concentrations of NO_x ranged from 72 to 154 ppm, with higher process temperatures creating more NO_x, as expected.

Table 8 summarizes the metals emissions rates in the gas exiting the kiln afterburner, expressed as pounds of metal emitted per 100 pounds of dry feed material. Lead and zinc were the metals emitted in the largest amounts, with lead emissions rates ranging from 0.14 to 0.38 lb/100 lb dry feed and zinc emission rates ranging from 0.046 to 0.16 lb/100 lb dry feed. Barium, cadmium, and chromium also exhibited significant concentrations in the flue gas. The data represent filterable plus condensible metal fractions.

Figure 5 presents in graphical form the percent of metals in the feed that are emitted in the flue gas before any control devices. No correlations have yet been drawn between operating conditions and percent of metals emitted in the flue gas. Arsenic, cadmium, and the compounds of lead are more volatile than the other metals, and thus the percent of metals in the feed emitted in the stack gas is higher for these metals.

CONCLUSIONS

Plastic and agricultural (walnut hulls) shot blast residues were readily incinerated by a conventional rotary-kiln system. Destruction and removal efficiencies (DREs) greater than the performance standard of 99.99% were achieved at all operating conditions for the organic spiking compounds. A significant volume reduction of waste was achieved, and a nonhazardous kiln ash was produced at all operating conditions except for the combination of the higher kiln and afterburner temperatures and longer residence time. The metals in this ash appeared to be more leachable than in other tests, and the TCLP extract exceeded the criteria for cadmium and chromium. Data on the characteristics of air emissions were collected prior to the control device. This data will be used to evalute the applicability of various gas cleaning systems.

USATHAMA plans several other activities to continue development of on-site incineration of paint wastes as an alternative to off-site disposal. Additional pilot tests will be conducted on other types of paint waste, such as chemical strippers, paint booth filters, and waste paints and solvents. A cost evaluation will be conducted to compare the cost of incineration with current disposal practices. For each of the paint wastes, applicable emissions control devices will be determined and the solid residues assessed for hazardous characteristics. Material handling will be evaluated to determine the best method of feeding waste to an incinerator. After these various stages of incinerator testing and evaluation, PEI will make recommendations regarding implementation of this technology at U.S. Army depots.

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APPENDIX:

TABLES AND FIGURES

TABLE 1. TEST MATRIX FOR PAINT WASTE INCINCERATION

Test Number	1	2	3	4
Number of runs	2	2	2	2
Length of run (hrs)	2	2	2	2
Waste feed rate, dry (lb/hr)	195	195	195	195
Temperature in kiln (°F)	1500	1500	1800	1800
Temperaure in secondary chamber (°F)	1600	1600	2000	2000
Residence time (min)	30	60	30	60
Kiln RPM	0.5	0.25	0.5	0.25

TABLE 2. PROXIMATE/ULTIMATE ANALYSIS OF SPENT BLAST MEDIA

Constituent	Average	Low value	High value
Proximate analysis, dry basis (%)			
Volatile matter	70.9	67.6	73.2
Fixed carbon	18.2	16.6	20.3
Ash	11	6.5	14.3
Sulfur	0.11	0.08	0.15
BTU/lb	7680	7480	7900
Ultimate analysis, dry basis (%)			
Carbon	43.3	40.7	46.7
Hydrogen	5.4	5.1	6.0
Nitrogen	12.4	5.1	16.0
Chlorine	0.09	0.07	0.11
Oxygen	27.7	24.4	34.7

TABLE 3. METALS IN INCINERATOR FEED
(1:1 Mix of Plastic Blast Media and Agricultural Blast Media)

Metal	Concentration, ppm		
	Average	Low	High
Arsenic	3.8	1.6	11.4
Barium	504	226	733
Cadmium	106	76.8	150
Chromium	1467	595	2340
Lead	5066	1796	8320
Mercury	<0.13	<0.13	<0.13
Selenium	1.2	<0.08	2.7
Silver	7.4	1.28	30.6

TABLE 4. AVERAGE METALS CONTENT IN KILN ASH, ppm

Metal	Operating Condition			
	TEST 1: Low temp/ long residence	TEST 2: Low temp/ short residence	TEST 3: High temp/ long residence	TEST 4: High temp/ short residence
Arsenic	16.3	24	9.5	8.2
Barium	2140	1712	1290	475
Cadmium	6.4	8.25	4.9	1.7
Chromium	982	775	477	132
Lead	1352	2915	643	161
Mercury	0.065	0.07	0.31	0.065
Selenium	0.0525	0.36	<0.08	0.04
Silver	25.7	48.6	3.5	0.38

TABLE 5. METALS CONTENT IN TCLP EXTRACTS OF ASH, ppm

Metal	Operating Condition				Toxicity Limit
	TEST 1: Low temp/ long residence	TEST 2 Low temp/ short residence	TEST 3 High temp/ long residence	TEST4 High temp/ short residence	
Arsenic	<0.002	<0.002	0.006	0.03	5
Barium	0.66	2	1.5	2.4	100
Cadmium	0.03	0.01	7.1 ✓	0.02	1
Chromium	0.09	<0.002	3 2	0.09	5
Lead	4.6	2.8	4.2	1.2	5
Mercury	<0.0003	<0.0003	<0.003	0.0008	0.2
Selenium	<0.002	<0.002	<0.002	<0.002	1
Silver	0.06	0.07	3.1	0.03	5

TABLE 6. UNCONTROLLED PARTICULATE LOADING

Conditions	gr/dscf @ 7 % O2	Mass emission lb/100 lb feed
TEST 1: Low temp/ Long residence	2.4	6.5
TEST 2: Low temp/ Short residence	1.42	4.1
TEST 3: High temp/ Long residence	0.54	1.7
TEST 4: High temp/ Short residence	0.38	1.3

TABLE 7. SUMMARY OF CEM EMISSION DATA

Conditions	NOX, ppm	SO2, ppm	O2, %	CO2, %	CO, ppm
TEST 1: Low temp/ Long residence	87	20	6.2	10.8	308
TEST 2: Low temp/ Short residence	72	10	6.1	10.8	24
TEST 3: High temp/ Long residence	154	24	8.4	9.2	18
TEST 4: High temp/ Short residence	132	14	5.4	11.4	14

TABLE 8. SUMMARY OF METALS EMISSIONS DATA

Conditions	Metals Emission Rates, lb/100 lb feed					
	Arsenic	Barium	Cadmium	Chromium	Lead	Zinc
TEST 1: Low temp Long residence	0.0005	0.018	0.012	0.018	0.149	0.046
TEST 2: Low temp Short residence	0.00001	0.016	0.008	0.026	0.14	0.09
TEST 3: High temp Long residence	0.001	0.002	0.01	0.004	0.38	0.16
TEST 4: High temp Short residence	0.0005	0.001	0.01	0.005	0.19	0.14

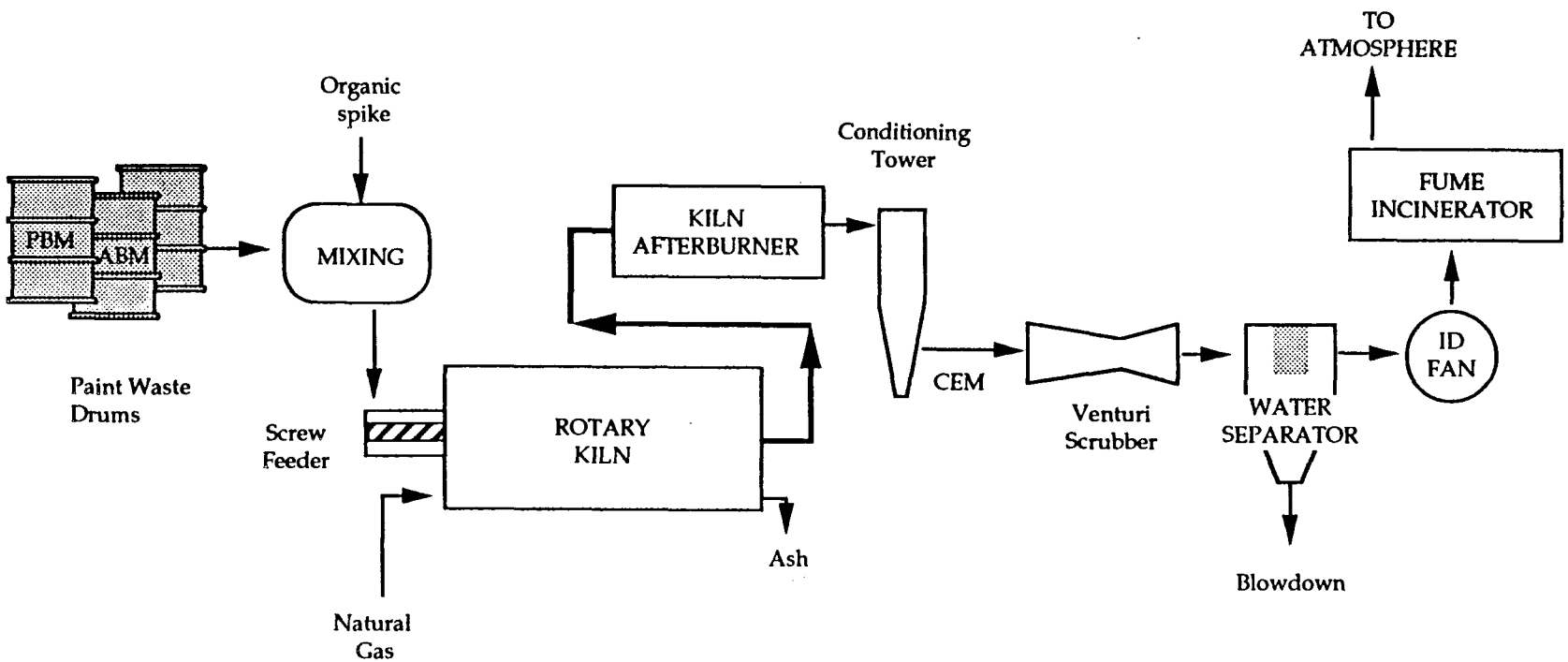


Figure 1. Diagram of the John Zink Co. Rotary Kiln System

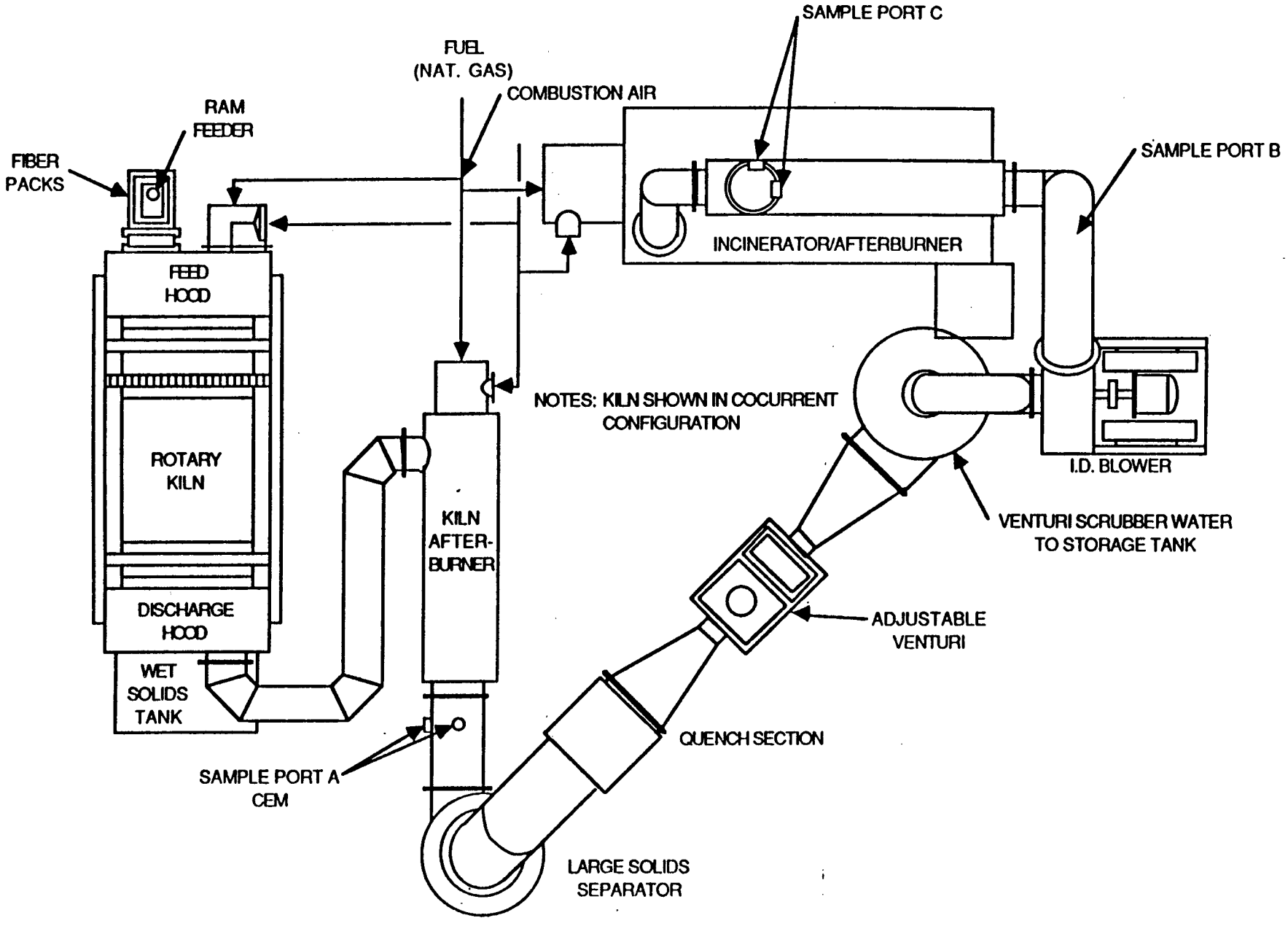


Figure 2. Rotary kiln incinerator configuration for solids.

FIGURE 3. UNCONTROLLED PARTICULATE LOADING

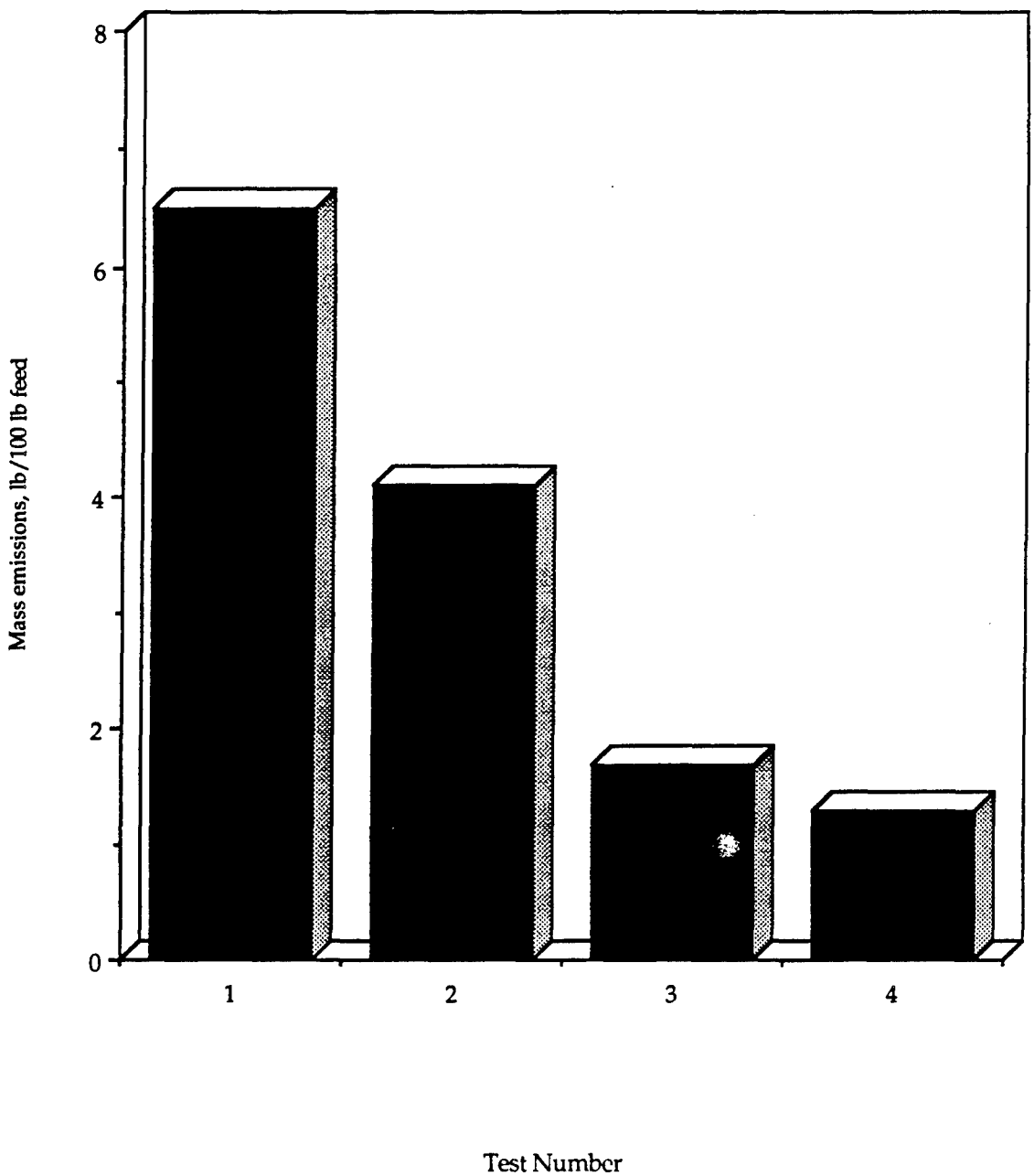


FIGURE 4. SUMMARY OF PARTICLE SIZE DATA

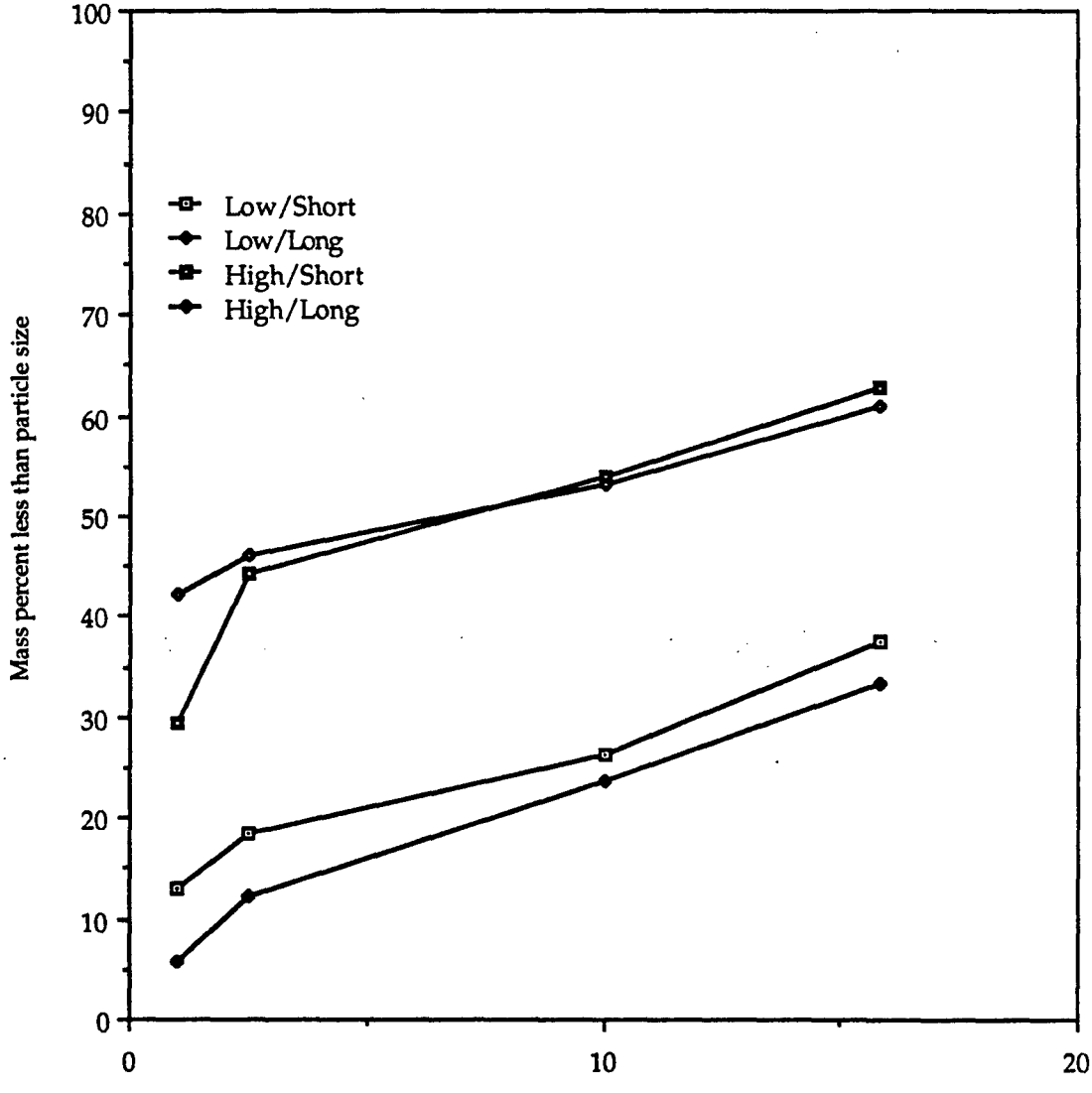
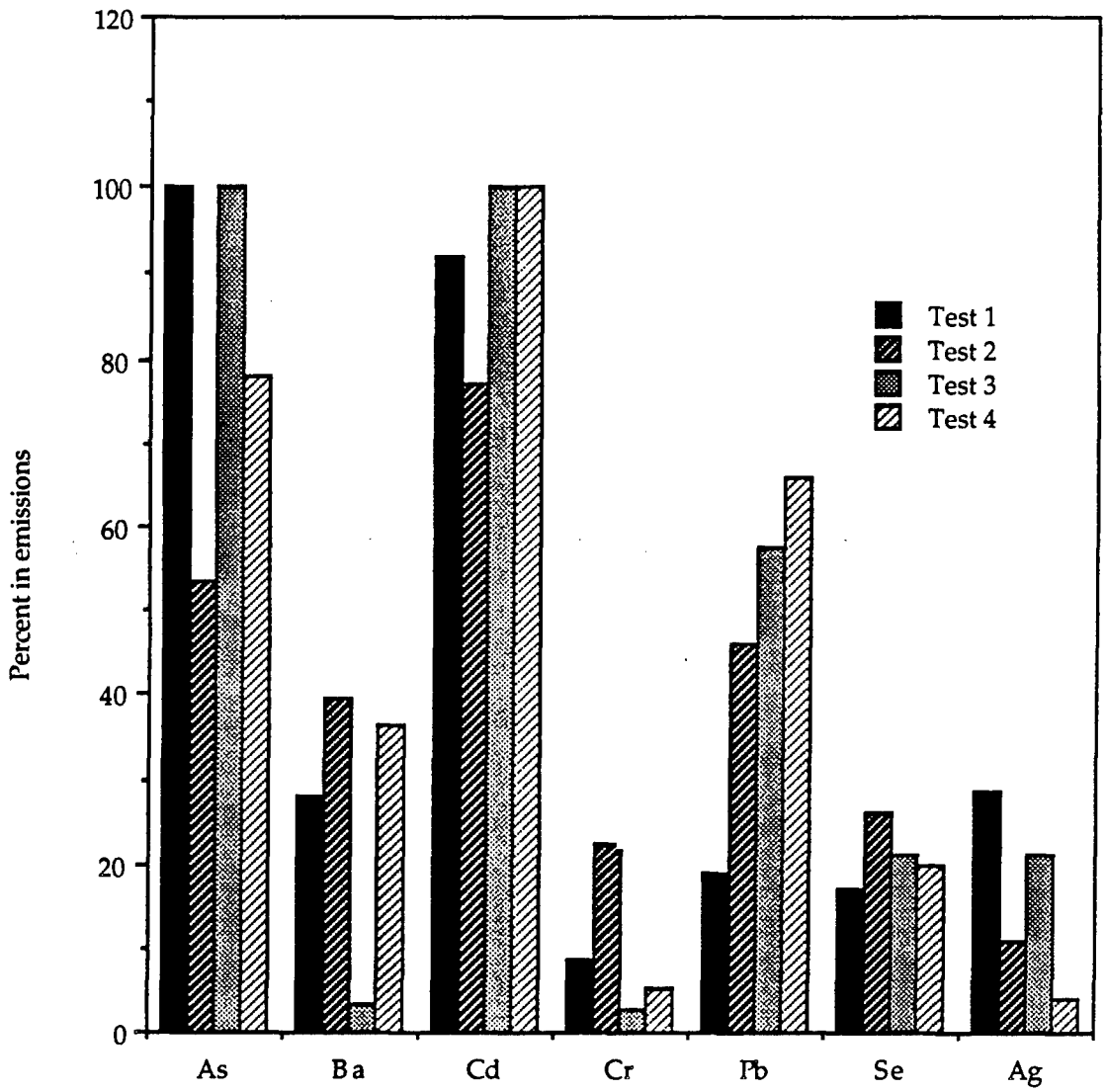


FIGURE 5. PERCENT OF METALS IN FEED EMITTED IN STACK GAS



PILOT-SCALE DEMONSTRATION OF LABORATORY DEVELOPED OPERATING CONDITIONS FOR ALKALINE HYDROLYSIS (CAUSTIC DIGESTION) OF NITROCELLULOSE FINES

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Introduction

The production of nitrocellulose (NC) at the Radford Army Ammunition Plant (RAAP) has resulted in the accumulation of approximately 1.8 million pounds of waste NC fines in the NC/acid flow equalization basin. The primary source of the fines is from NC production wastewater which discharges approximately 2,000 pounds of NC fines per production line per day. Various removal/disposal methods were evaluated by Arthur D. Little, Inc., for the United States Army Toxic and Hazardous Materials Agency. Alkaline hydrolysis (caustic digestion) was among one of the disposal methods found to be favorable. Laboratory-scale studies were performed at RAAP to test the feasibility of caustic digestion and to develop optimum operating parameters (temperature, caustic concentration, and digestion time). The pilot-scale studies were performed to prove out operating parameters developed during the laboratory study and also to prove out a mixing system for keeping the waste NC fines in suspension.

Process Description

The pilot-scale study was conducted utilizing two different equipment setups and two different methods of conducting the experiment. Studies were performed in a 6,000 gal. open-top, flat-bottom carbon steel tank (16.5-ft. diameter, 3.5 ft height). Waste NC fines from the NC/acid flow equalization basin at RAAP were obtained for use in conducting both test runs on the pilot plant. In both cases the NC was added from waste propellant containers positioned on a platform adjacent to the tank. The initial test (run No. 1) made use of two Lightnin™ mixers with blade type impellers to continuously mix the solution of waste NC fines and sodium hydroxide (NaOH) solution (caustic). The caustic solution was prepared from 100% caustic soda beads prior to addition of the waste NC fines. The temperature of the solution of the NC/caustic solution during run No. 1 was taken at discrete intervals with a standard mercury thermometer.

The second test (run No. 2) used an air sparger system for continuously mixing the waste NC fines and caustic solution. The air sparger consisted of six 10-ft sections of 1-in. PVC pipe attached to a main header at 2-ft intervals (fig. 1). Holes (1/8-in. diameter) were drilled on the bottom side of each leg at 3 in. intervals. The system was hooked into a portable air compressor which supplied a regulated 30-psig flow of air. The waste NC fines were added to the tank prior to addition of the caustic to simulate the method that may be used in a full-scale operation. The caustic was added in a concentrated solution form (approximately 18% by weight NaOH) that had been prepared by Chemical Grind personnel at RAAP. The solution temperature was also measured at discrete intervals with a standard mercury thermometer.

Results and Discussion

The laboratory-scale digestion operating conditions developed previously were incorporated into the pilot-scale study. Caustic concentrations of 4% and 5% by weight (corresponding to a 6/1 and 7/1 mole ratio of NaOH to NC nitrogen) were utilized at ambient temperatures in each of the pilot runs. The 4% by weight caustic solution at ambient temperature was chosen because it produced the lowest combination of biological oxygen demand (BOD), chemical oxygen

demand (COD), and total cyanide levels in the laboratory studies. The 5% by weight caustic solution at ambient temperature was initially tried to determine if digestion would occur to some extent on a large scale at ambient temperature.

Run No. 1

Run No. 1 of the pilot study was performed with an actual NaOH solution concentration of 5.3% by weight (approximately a 7/1 mole ratio of NaOH to NC nitrogen). During this pilot run, 500 lbs of NC fines was added to 3,000 gal. of NaOH solution (5.3% by weight). The temperature could not be regulated because the operation was conducted outdoors in a non-temperature controlled tank. The temperature of the solution varied from a low of 58°F to a high of 78°F and averaged approximately 69°F for the complete digestion period. Digestion solution pH for the length of the run averaged 12.37 as illustrated in figure 2. The run was allowed to continue until digestion was determined to have reached completion by analysis of the samples in the Technical Analytical laboratory at RAAP. Completion of digestion of the NC fines was determined from results obtained on the analysis of the digestion solution. Digestion was determined to have been completed after approximately 300 hours. Trends in COD, BOD, nitrites, nitrates, percent undissolved solids, total cyanide, and true color were plotted over digestion time and compared with results obtained during the laboratory-scale study. Nitrogen content of the waste NC fines could not be measured due to safety associated with the method of analysis.

The COD's obtained during pilot run No. 1 varied from 5865 to 9091 mg/L as illustrated in figure 3. The COD averaged approximately 7000 mg/L throughout the entire digestion time; deviations in the COD trend are believed to be due to errors stemming from dilution that was necessary to conduct the analysis within the range of the spectrophotometer as well as the variability associated with discrete sampling. The COD's obtained during the pilot study were approximately 5000 mg/L lower than that extrapolated from the laboratory-scale data. The difference in COD may be explained by two dissimilarities in the experiments. The largest contributor to the difference may be due to the estimated amount and composition of the waste NC fines utilized in the pilot-scale experiment. The actual percentage of solids to water present in the waste NC fines was assumed to be 50%. The actual measured value could not be obtained due to safety considerations and thus could have been less. Additionally, the assumed solids were estimated to be 100% NC (cellulose and other material making up a very small total percentage compared to NC). If these two estimates were high the COD difference may be explained since COD will report virtually all organic compounds present, many of which are non-biodegradable or partially degradable. The other dissimilarity was that the pilot study conducted at a caustic concentration of 5.3% was being compared to data at a 4% concentration.

Figure 4 graphically illustrated that the BOD obtained during run No. 1 varied from 58.2 mg/L to 730 mg/L; the trend in the BOD follows a time versus concentration trend similar to that obtained for the COD. Initially, both decreased in value and then sharply increased between 150 and 200 digestion hours. The dip that occurs is likely due to a sample of the digestion solution that was not representative of the tank's contents. The average BOD obtained during run No. 1 was also approximately 5000 mg/L lower than that

extrapolated from the laboratory-scale data. The difference in BOD may be explained by the two factors discussed previously for COD. The presence of less NC than estimated could have resulted in less decomposition productions which were biodegradable. Figure 5 illustrates that the nitrite and nitrate results obtained during run No. 1 increased in concentration over digestion time. The nitrites appeared to level off at approximately 1700 mg/L, and the nitrates at approximately 1600 mg/L. The increase in nitrites and nitrates was expected to occur as the NC was further digested, thereby releasing some fraction of the three nitrogens per NC chain link.

Figure 6 illustrates that the percent undissolved suspended solids dropped from an initial concentration of 0.02 to 0.002% for run No. 1. Percent undissolved solids were calculated by using the following equation:

$$\% \text{ U.S.S.} = \frac{\text{total solids in solution (dry)}}{\text{total mass of sample of solution}} \times 100\%$$

The final percent undissolved solids for the pilot run was much less than that obtained during the laboratory study (approximately 0.1%). The difference in final percent undissolved solids obtained in the laboratory-scale and pilot-scale experiments can be explained by two possible reasons. The most probable cause for the difference stems from the difference in method of analysis. In the laboratory-scale study the entire solution was filtered thus obtaining all the remaining solids. This method was not feasible for the entire contents of the digestion tank utilized in the pilot-scale study. The pilot-scale samples analyzed may not have been representative of the suspended solids remaining in the digestion tank. The other less likely reason for the difference is that the reaction proceeded to a further extent, leaving less NC and cellulose type material remaining.

The percent of acetone solubles and insolubles present in the undissolved suspended solids obtained during run No. 1 were determined and are illustrated graphically in figure 7. Acetone solubles account for any NC that was not digested; acetone solubles did not exceed 25% of the total mass of undissolved suspended solids.

The concentration of sulfates produced or present in the digestion solution was analyzed throughout the run and is presented graphically in figure 8. The sulfates remained fairly stable at a concentration of approximately 120 mg/L. Sulfates most likely originated from impurities present in the caustic or as contaminants present in the waste NC fines.

Figure 9 illustrates that the total cyanide concentration for pilot run No. 1 was somewhat uniform throughout the test span. The anomaly in the data that occurs around 200 hours is attributed to a sample that was not representative of the entire digestion solution. Overall, the cyanide levels are much lower than those experienced in the laboratory study (0.62 mg/L) for a 4% by weight caustic solution at 85°F. The cyanide concentrations for pilot run No. 1 were abnormally low because the samples were not immediately neutralized to preserve cyanide present in the digested solution. The digestion solution samples for pilot run No. 2 were immediately neutralized and do accurately represent cyanide levels of the entire digestion solution.

The Lightnin™ mixers utilized during run No. 1 were somewhat inadequate for keeping the waste NC fines in suspension. The mixer impellers proved to be undersized for the given dimensions of the tank and an adequate number of mixers were not used. Additional mixers were not incorporated due to the availability of funds in the project and suspected scale-up difficulties that may be encountered in utilizing a conventional mixing method. Occasionally, additional manual agitation was required to circulate material that accumulated at the center of the tank.

Run No. 2

Run No. 2 of the pilot study was performed with an actual NaOH solution concentration of 4.1% by weight (a 6/1 mole ratio of NaOH to NC nitrogen). As in run No. 1, the temperature during this run could not be regulated. The temperature varied from a low of 70°F to a high of 89°F and averaged approximately 79°F for the length of digestion. Digestion solution pH averaged 12.09 for the digestion time period (fig. 2). Equilibrium digestion of the NC required approximately 300 hours to complete.

The COD's obtained during run No. 2 varied from 5517 to 7597 mg/L as illustrated in figure 3. The variation in the COD during the entire digestion period was due to non-uniform composition of the grab samples. The COD's obtained for this run were in the same range of values as those obtained for the first run performed with a 5.3% by weight caustic solution. The laboratory results obtained were, again, 5000 mg/L higher than that experienced in the pilot study.

The BOD's for run No. 2 varied from a low of 531 to a high of 1390 mg/L as illustrated in figure 4. The BOD's increased in magnitude over the digestion time span; this trend does not follow the trend seen in run No. 1. Apparently, a compound or compounds are being formed that supports biological growth. BOD's obtained in the pilot run correspond favorably with those obtained during the laboratory study performed with a 4% by weight caustic solution at 85°F. Apparently, more degradation compounds that were biodegradable were formed during this run than in run No. 4.

The nitrite and nitrate results obtained for run No. 2 (illustrated in fig. 5) of the pilot study increased in concentration over the entire digestion time span. The initial digestion that occurred immediately following addition of the caustic apparently produced large pockets of concentrated nitrites and nitrates, yielding high false readings for the sample taken at time zero.

The percent of undissolved suspended solids present in the digestion solution for run No. 2 dropped from an initial percentage of 0.1 to approximately 0.02 (fig. 6). The percent undissolved solids present in the pilot run was a factor of ten less than that obtained in the laboratory study. The difference is again due to the infeasibility of taking all of the solids out of the entire pilot-scale solution as could be done in the laboratory-scale study. The percent acetone solubles (illustrated in fig. 7) present in the remaining undissolved suspended solids decreased as digestion time progressed.

Figure 8 illustrates that the concentration of sulfates present in the digestion solution averaged around 70 mg/L. The sulfate concentration was

less than that experienced during the first pilot digestion run. Overall, sulfate concentrations were acceptably low for both pilot runs.

Total cyanide concentration for pilot run No. 2 increased throughout the digestion time span as illustrated in figure 10. The concentration of cyanides was much higher than that experienced during run No. 1, however, the cyanide concentrations for run No. 2 were in better agreement with the concentrations obtained during the laboratory-scale study.

The air sparger system utilized in pilot run No. 2 proved to be adequate for keeping the waste NC fines in suspension. The system provided better mixing in the tank which had a depth (L) that was much less than the diameter (D) of the tank (small L/D ratio). The system was calculated to consume air at a rate of 22 cfm. The total open surface area of all the holes drilled in for the pilot air sparger was 2.95 square inches. The actual flow rate of the system was not measured due to the availability of a suitably sized flowmeter. Calculations and actual measurements obtained for a similar system installed in nitroglycerin manufacturing area 2 at RAAP have illustrated that actual air consumption is approximately double the calculated flow.

Errors in Sample Analysis

During the course of the laboratory analysis performed on the pilot digestion samples, two errors in methods of analysis were discovered. The least significant of the errors discovered was the effect that chlorine, from hydrochloric acid (HCl) utilized to neutralize the samples, had on the COD readings. Chlorine apparently causes a false high reading of COD in the technique that was used to determine COD's. Reanalysis of several samples that were not neutralized with HCl did not show a significant drop in the COD readings. Reanalysis of all samples from the laboratory-scale work and both pilot runs was not possible or deemed necessary. The difference in COD's that may have been measured is well within the error of the measuring instrument and analytical method.

The other laboratory analysis found to be in error was the measurement for true color of the solution. The representative for Hach® chemicals stated that the upper limit of the color unit scale was 500 and that the method for determining color on the Hach DR/3000 spectrophotometer was not linear. The dilution of the digestion solution samples (and subsequent multiplication of the spectrophotometer reading by this factor) necessary to obtain on-scale readings with the spectrophotometer does not give a valid true color reading. The numbers obtained for true color in the laboratory and pilot-scale tests are only valid for comparisons against those readings obtained within this work and cannot be compared to other color readings outside of this data.

Mixing and Digestion of NC

The time necessary to accomplish complete digestion of NC is highly dependent upon temperature and caustic concentration. Mixing or maintaining a suspension of the NC, is critical towards achieving complete digestion. Effective contact between particles of NC and the caustic solution must occur in order to accomplish digestion within a reasonable time frame.

Recommendations and Conclusions

1. Caustic digestion can be utilized as a method for degrading waste NC.

2. Laboratory-scale data and pilot-scale data follow similar trends in measured values.

3. Mixing via an air sparger system is better suited for operations where the diameter is much larger than the depth of the holding container (small L/D ratio).

4. Keeping NC in suspension (and in constant contact with the caustic) is critical to attain complete digestion.

5. No less than a 4% NaOH solution (6/1 mole ratio of NaOH to NC nitrogen) and temperatures less than 70°F should be used to achieve digestion within a reasonable time frame.

6. Caustic digestion is best performed in basin 2052 at RAAP after removal of as much NC as possible (or provide adequate agitation) to achieve the best possible contact of NC with the caustic solution.

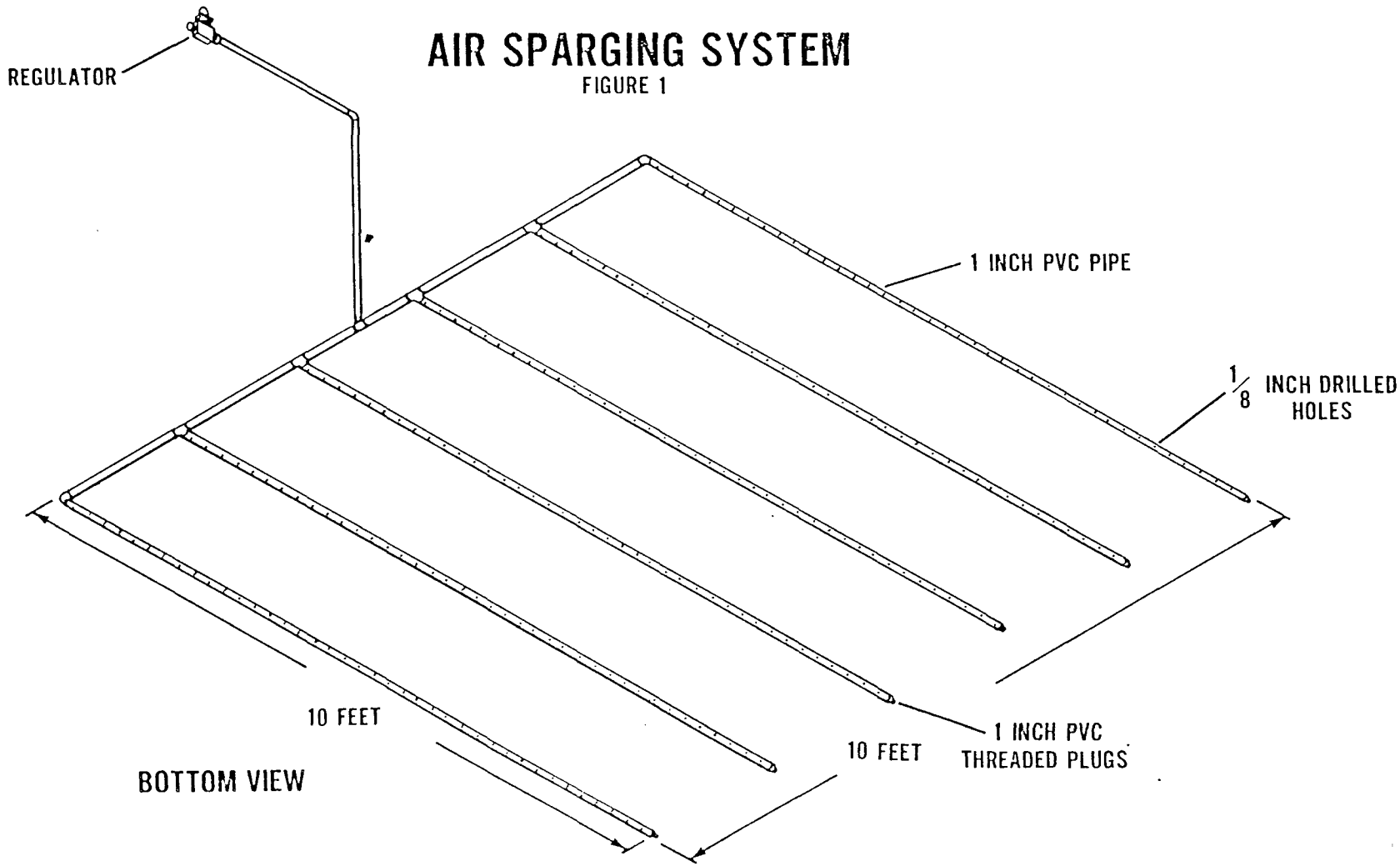

AIR SPARGING SYSTEM
FIGURE 1
REGULATOR
1 INCH PVC PIPE
1/8 INCH DRILLED HOLES
10 FEET
10 FEET
1 INCH PVC THREADED PLUGS
BOTTOM VIEW

Figure 2. Digestion Time versus
pH of Solution

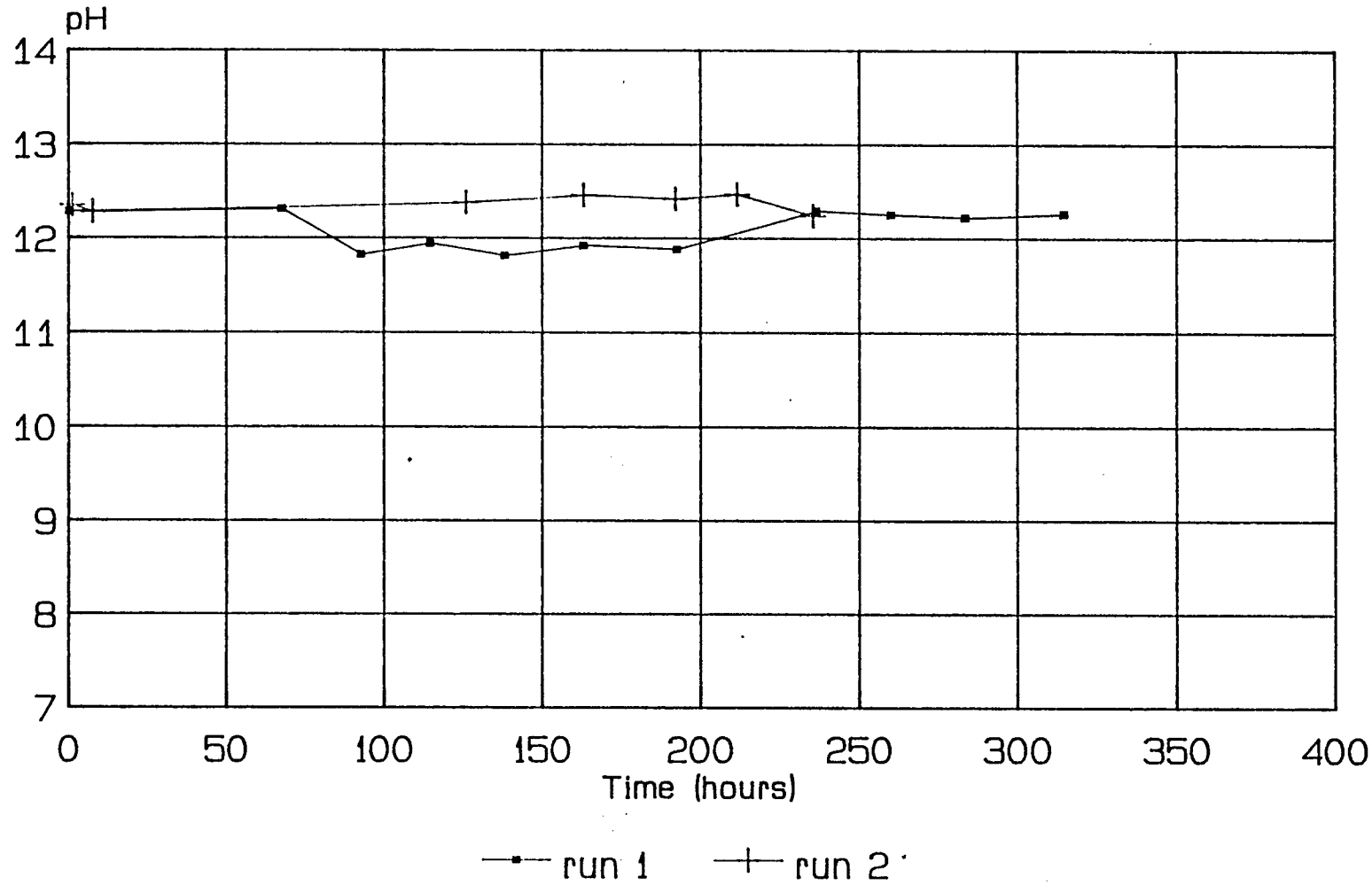


Figure 3. Digestion Time versus
Chemical Oxygen Demand (COD)

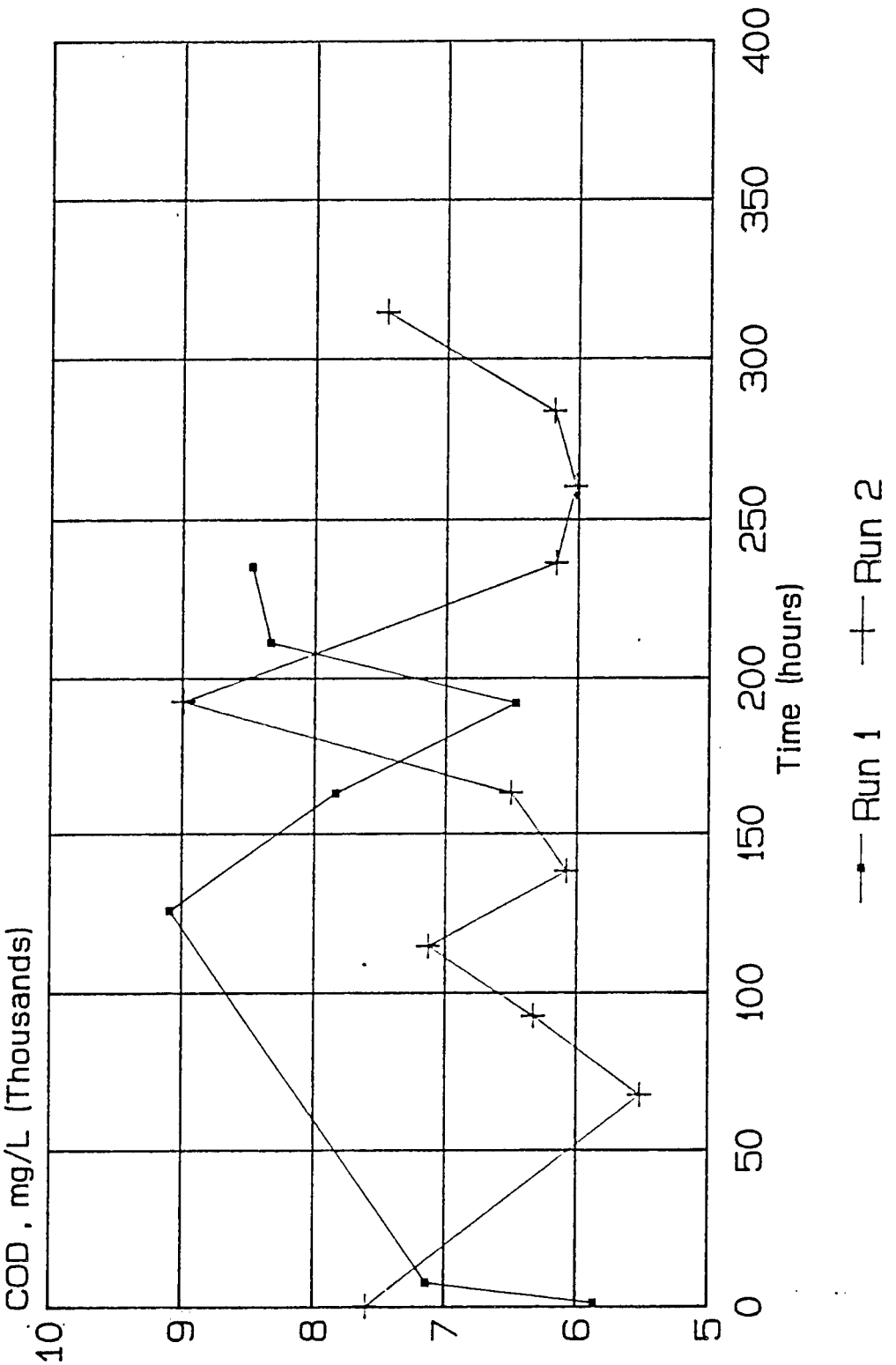


Figure 4. Digestion Time versus
Biological Oxygen Demand (BOD)

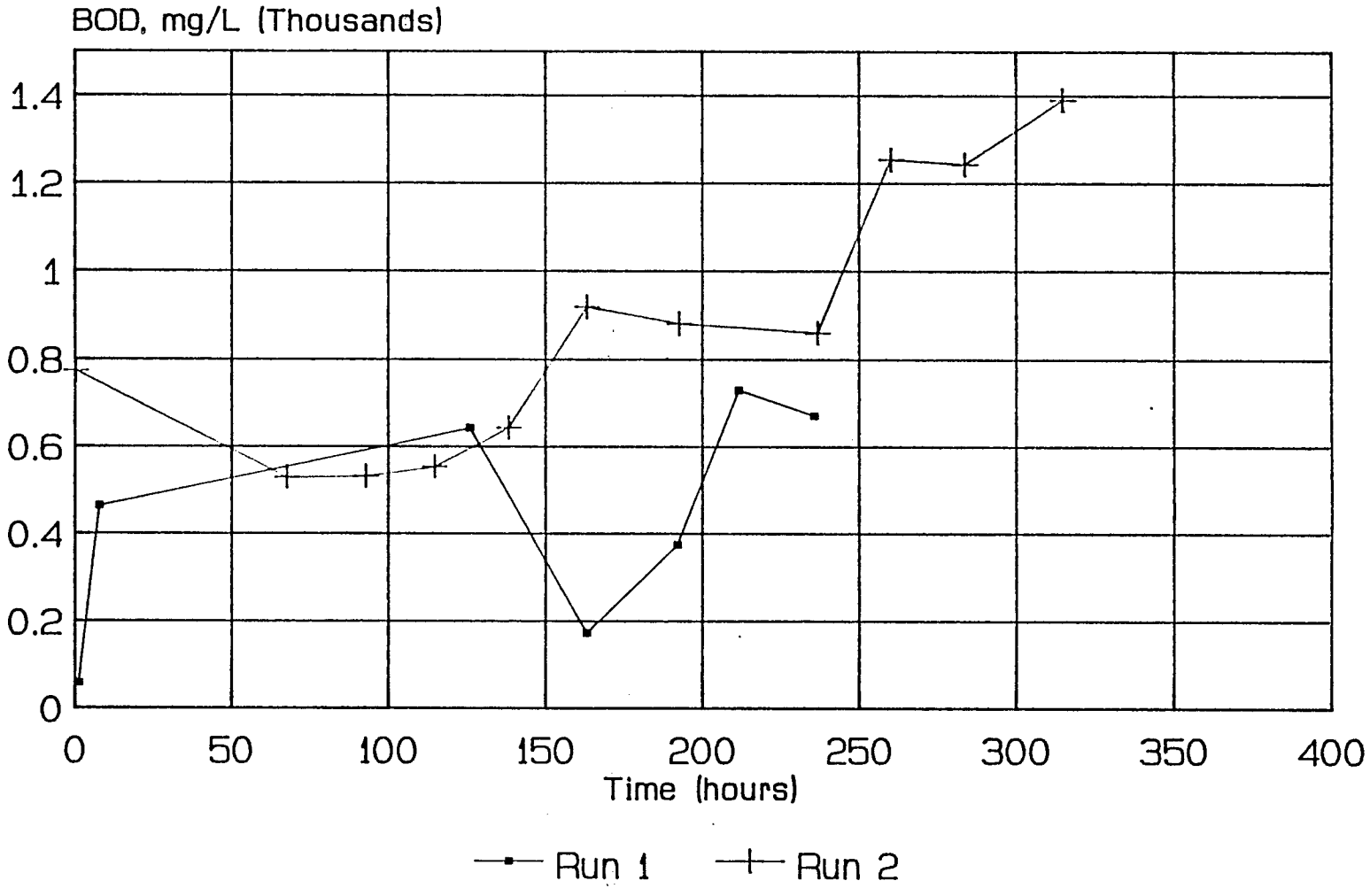


Figure 5. Digestion Time versus
Nitrite/Nitrate Concentration

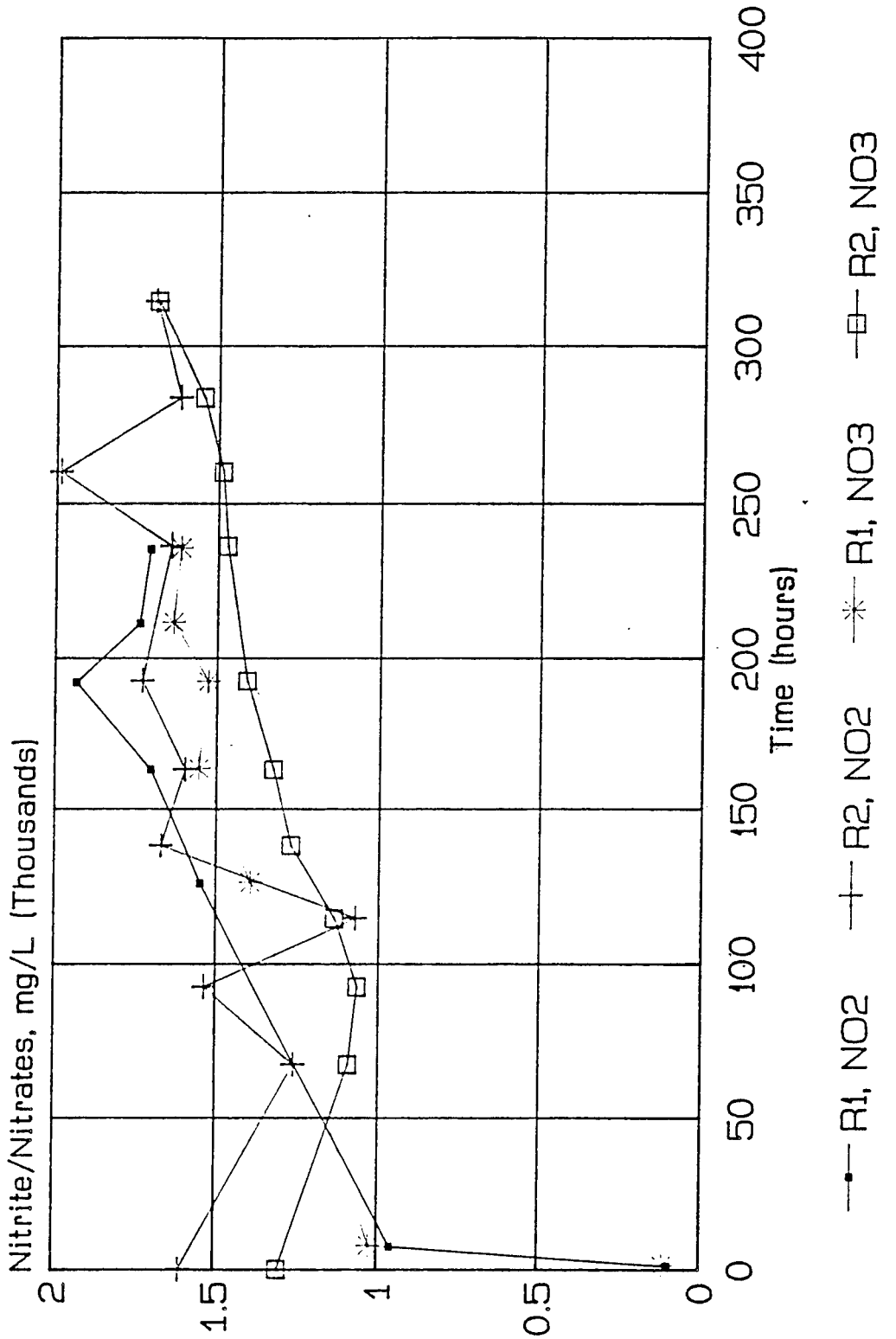


Figure 6. Digestion Time versus
Percent Undissolved Suspended Solids

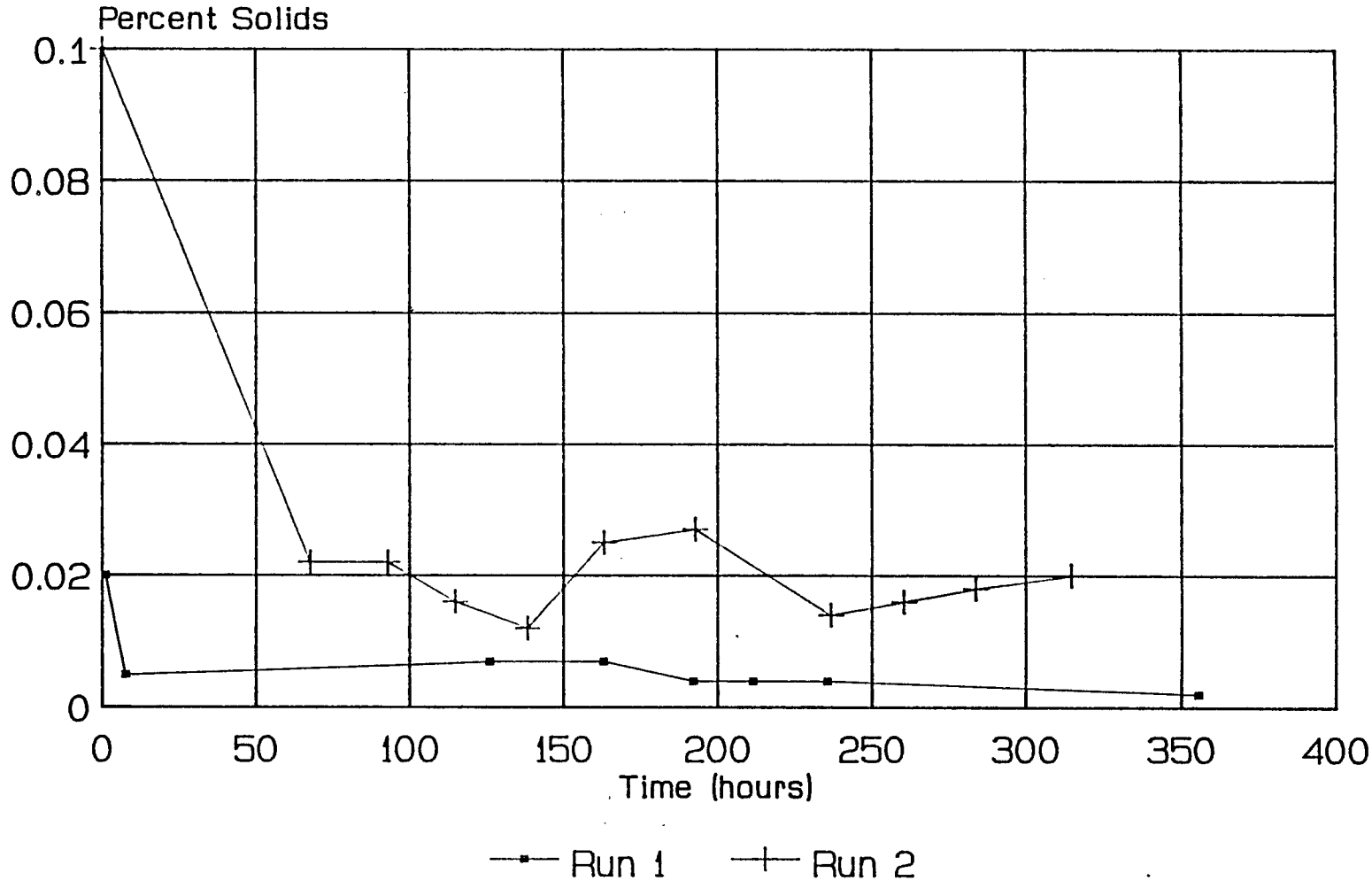


Figure 7. Digestion Time versus
Acetone Solubles and Insolubles

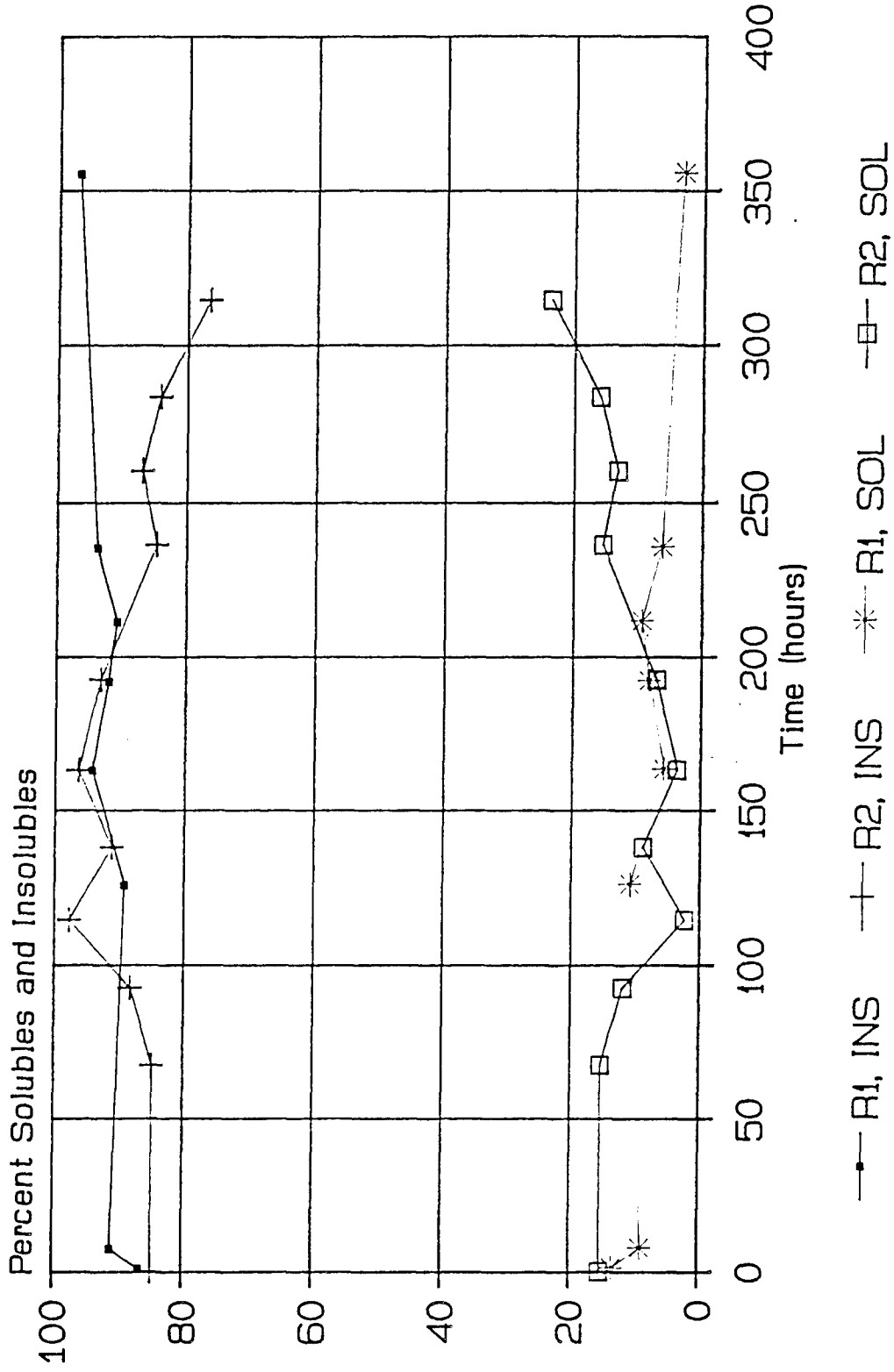


Figure 8. Digestion Time
versus Sulfates

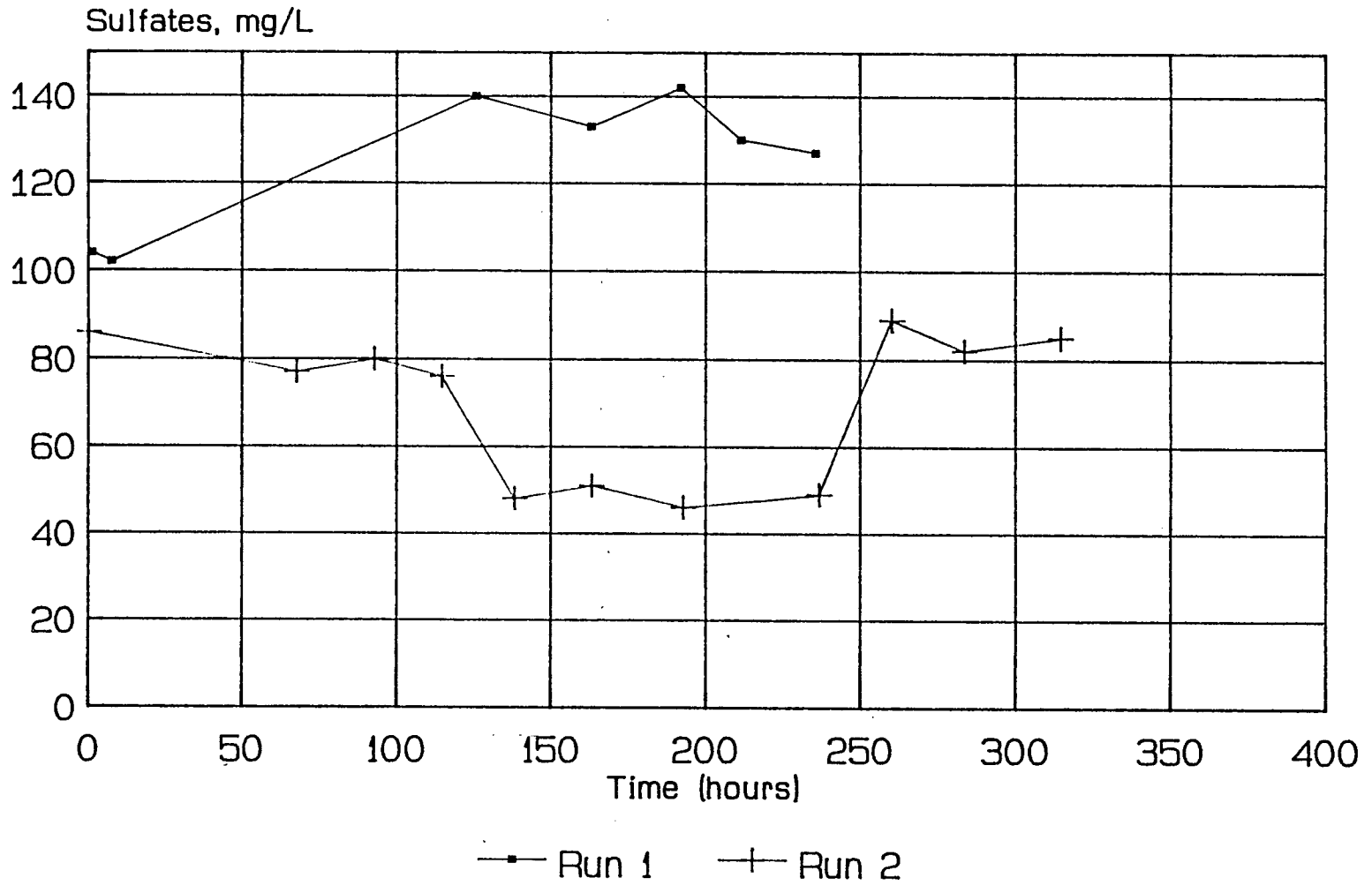


Figure 9. Digestion Time versus
Total Cyanide Concentration

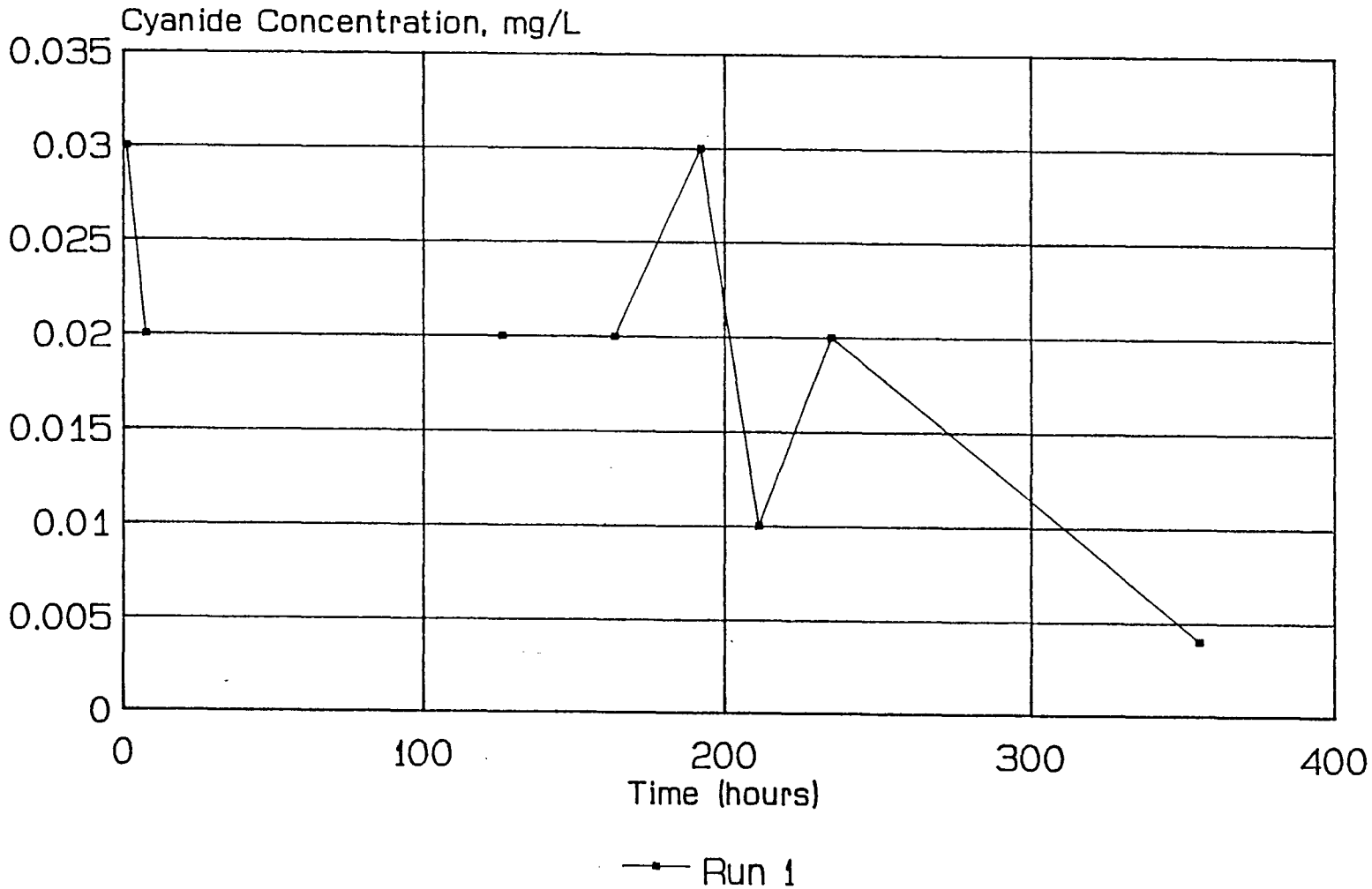
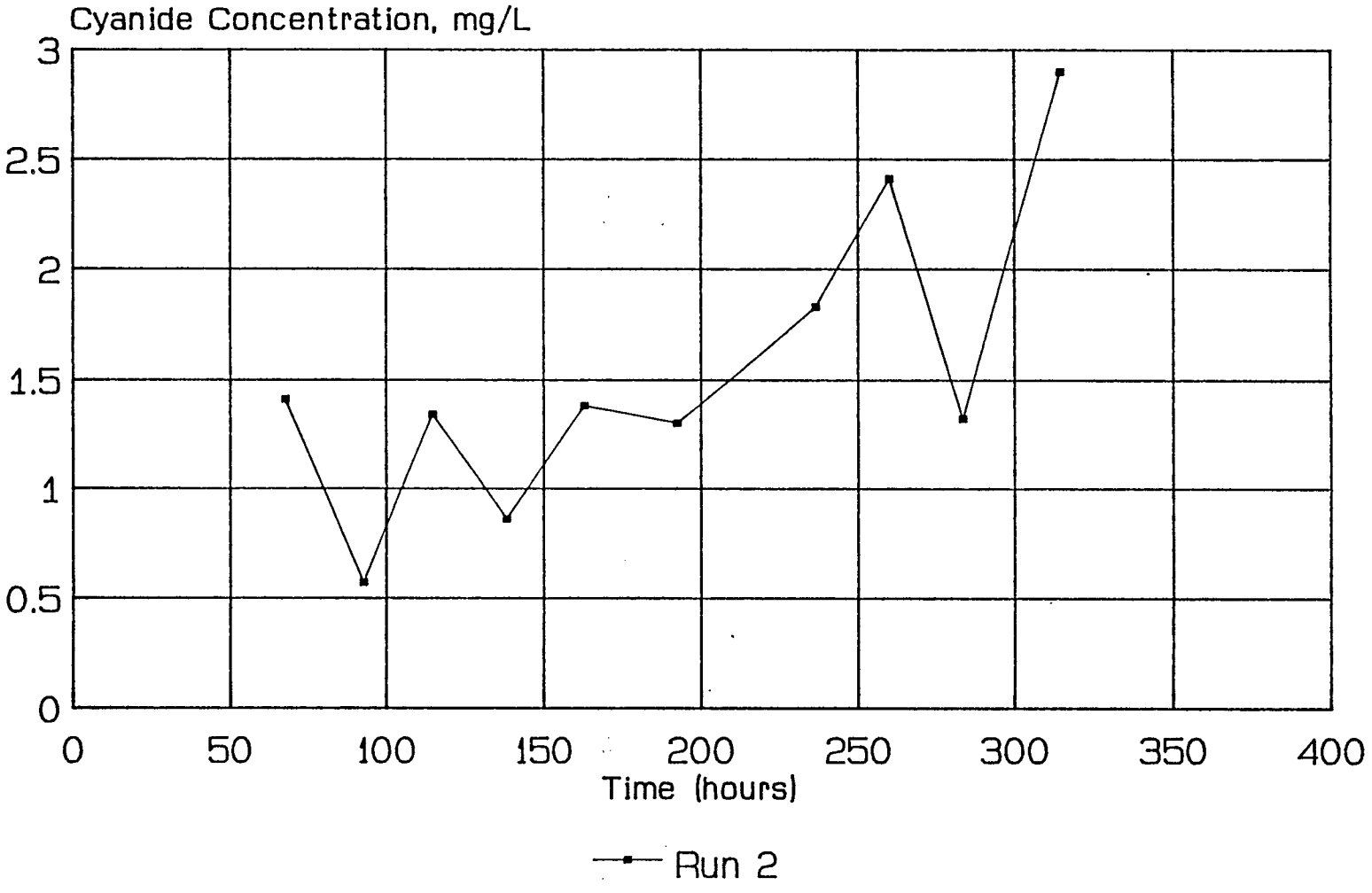


Figure 10. Digestion Time versus
Total Cyanide Concentration



BIOLOGICAL TREATMENT PLANT EFFICIENCY STUDY

BY

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NOVEMBER 1988

BIOLOGICAL TREATMENT PLANT EFFICIENCY STUDY

In 1980, a biological wastewater treatment plant employing rotating biological contactors (RBCs) began operations at Radford Army Ammunition Plant (RAAP). The use of biological degradation, particularly RBCs, in the treatment of munitions wastewater is unique to RAAP. The plant had not received an overall evaluation since the initial start-up and proveout period. As a result, this study was initiated in August 1987 to quantitate the performance of the plant and identify areas for improvement.

A schematic of the RAAP bioplant is presented in figure 1. The treatment system consists of an aerated equalization basin (1 million gallon capacity) which contains eight floating aerators for mixing and aeration followed by twelve RBCs. The biomass in the wastewater stream is removed in two clarifiers before the treated water is discharged to the New River. The biomass (or sludge) is pumped from the clarifiers to three aerobic digesters. After digestion, the sludge is thickened and then dewatered on a belt filter press. The sludge cake is landfilled on-site.

For the study period of August 17, 1987, to August 31, 1988, the plant achieved average removals of 6,310 lb/day of chemical oxygen demand (COD). The twelve RBC units removed an average of 4,170 lb/day COD based on an average flow rate of 1.33 MGD. An additional 2,180 lb/day COD is removed in the aeration basin. Approximately 40 lb/day COD is returned to the wastewater stream from sludge processing. These results have been broken down into three time periods and presented in table 1.

The discharge limitations for the study period are presented in table 2. The sharp drop in the allowable COD discharge (from 4,280 lb/day to 1,300 lb/day) on July 1, 1988, is due to the expiration of an exemption provided to RAAP in 1986. The necessity of meeting the lower discharge limits has made optimization of treatment capacity essential. Before optimization efforts could take place, baseline performance had to be established.

Although on a daily and weekly basis wastewater received at the bioplant is highly variable, the data presented in table 1 show that the average removal capacity of the plant is suprisingly constant. An average of 6,360 lb/day COD was removed August-December 1987 and an average of 6,090 lb/day COD was removed January-June 1988. This removal continued through July-August 1988 with an average of 6,470 lb/day COD even though the average influent COD to the plant decreased from 10,410 lb/day to 7,800 lb/day. This drop in influent COD was accomplished by the alternate disposal (incineration) of low volume/high organic content waste, i.e., diethylene glycol and triethylene glycol.

Removal in the RBCs was less constant with 3,290 lb/day in 1987 and 4,530 lb/day in the first six months of 1988. However, this level of removal again continued into July and August 1988 with 4,680 lb/day removed. The removal efficiency of the RBCs was calculated by dividing the COD removed by the COD applied. It can be noted in table 1 that removal efficiency increases from 52% for the spring of 1988 to 79% for July and August. It can be seen from these results that for this system total COD removal is a better predictor of RBC performance than removal efficiency.

Aside from the RBCs, the equalization basin and clarifiers affect effluent COD. An average of 2,180 lb/day COD is removed in the aeration/equalization basin due to biological activity and solvent stripping by the floating aerators. This removal is influenced by wastewater temperature and solvent concentration. Since stripping is virtually eliminated in winter months, the six-month averages presented in table 1 cannot be used for predicting performance for shorter time periods.

At times the clarifiers actually add COD to the waste stream, as evidenced by the results for 1988. This increase in COD is from the recycle of the filtrate from the sludge filter press due to the anaerobic condition of the aerobic digesters. The reduction in total effluent COD beginning July 1, 1988, increases the significance of the septic condition of the digesters. Approximately 9% of the effluent COD is from sludge processing. As a result, increased emphasis is being placed on attaining adequate aeration in the three digesters. Filtrate from a properly digested aerobic sludge would not increase the effluent COD. The purchase of a submersible aerator sized to provide a 1-2 mg/L dissolved oxygen concentration and complete mixing has been recommended. The currently used surface aerators and a large bubble, dispersed air system will be used, as needed, in addition to the submerged aerator. Also, in order to increase operator control of the sludge digestion system, the installation of magnetic flowmeters has been recommended.

In an effort to optimize removals by the RBCs, several steps have been taken in the area of nutrient addition and equalization of the influent contaminant concentration. The RAAP wastewater influent does not contain sufficient phosphorus and nitrogen for biological degradation of the organic contaminants. Phosphorus continues to be added in the form of phosphoric acid; however, the addition of nitrogen was changed from the valve-metered, gravity flow of a sodium nitrate slurry to an ammonia nitrate/urea solution metered by pump. Proper nitrogen dosage was also aided by allowing the operators to use nitrate test strips for detecting residual nitrate in the RBC effluent. Periods of inadequate nitrogen concentration have been significantly reduced by these steps.

Variability of the bioplant influent content was reduced by increasing communication between the bioplant operators and operators at the two physical/chemical pretreatment plants. These batch pretreatment plants are located in the NG production areas and are used to decompose nitrate esters in the wastewater before discharge to the bioplant for COD removal. Other actions to improve plant and operator efficiency resulting from this study include automated sampling and speedier reporting of daily laboratory results directly to the operators.

As noted previously the RAAP bioplant is a unique application of RBCs; therefore, very little data are available for evaluating plant performance. In the usual application of RBCs, in municipal wastewater treatment, removal is predicted and reported as biological oxygen demand (BOD). COD analyses are used for process control at RAAP.

The only other data available for comparison are design capacities. The plant was designed to remove at least 4.3 lb COD/day/1,000 ft^2 of RBC surface area. Average removals for the time periods studied varied from 3.3 lb/day/1,000 ft^2 to 4.7 lb/day/1,000 ft^2.

The average COD discharged from the plant based on daily grab samples are presented in table 3 for this study period. As can be seen by the average discharge of 1,330 lb/day for July-August 31, 1988, the ability of the plant to meet the lower limits has been borderline even after the implementation of optimization efforts. During normal conditions the plant has operated as expected and met limitations; however, violations have resulted during peak loadings. Efforts to optimize COD removal and eliminate sporatic high loadings are continuing.

Table 1. Results of one-year study of bioplant operation

Time Period	Average COD removal, lb/day				Removal in RBCs		Removal efficiency, %	
	Basin	RBCs	Clarifier	Plant	mg/L	lb/day/1000 ft^2	RBCs	Plant
Aug 17-Dec 1987	2,950	3,290	130	6,360	300	3.3	42	59
Jan-Jun 1988	1,690	4,530	-130	6,090	390	4.6	52	59
Jul-Aug 31, 1988	1,910	4,680	-120	6,470	430	4.7	79	83
Average	2,180	4,170	-43	6,310	380	4.2	58	67

Table 2. RAAP bioplant COD discharge limitations

	Concentration, mg/L		Mass, lb/day	
	Average	Maximum	Average	Maximum
Aug-Sep 1987	700	1,400	4,280	8,560
Oct-Mar 1987	1,060	2,120	6,420	12,840
Apr-Jun 1988	700	1,400	4,280	8,560
Jul-Aug 1988	200	290	1,300	1,900

Table 3. Average COD discharged from bioplant based on daily grab samples

Time period	COD, lb/day
Aug 17- Dec 1987	4,470
Jan-Jun, 1988	4,320
Jul-Aug 31 1988	1,330

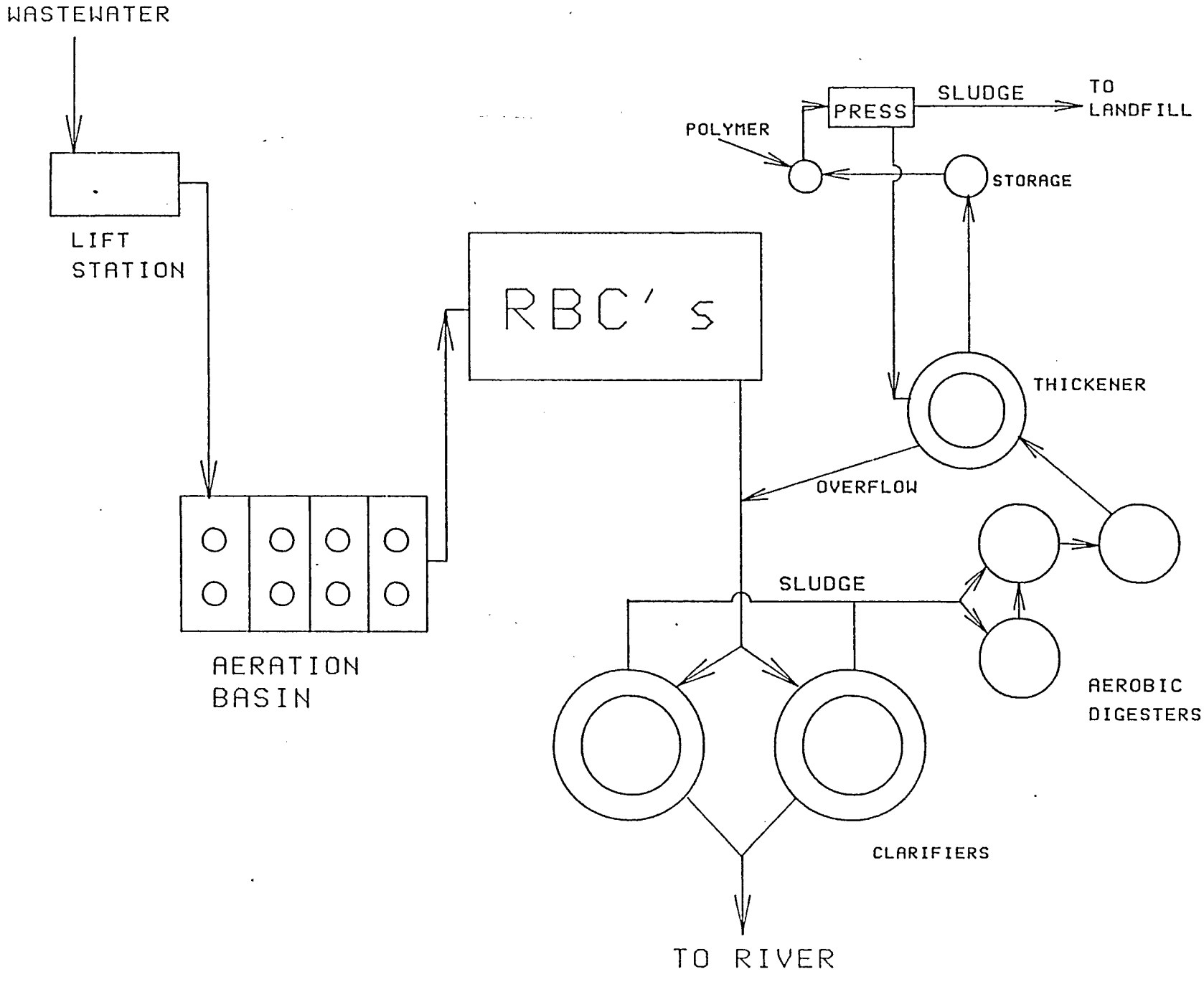


Figure 1. Biological wastewater treatment plant flow diagram

USE OF ALTERNATE CHEMICAL PAINT STRIPPERS TO REDUCE TTO DISCHARGES

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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. In addition to 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 commercially available stripping formulations which are operationally effective and environmentally acceptable replacements for strippers based on methylene chloride. The goal is to alleviate TTO compliance problems and to minimize environmental and health risks and disposal liabilities.

Approach

To test operational effectiveness, alternate stripper formulations were tested first in the laboratory. Following laboratory testing, the most effective strippers were tested 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 Operational Success

Criteria for an operationally successful paint stripper were developed in conjunction 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

Criteria for Environmental, Health, and Safety Acceptability

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 on the basis of 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.

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

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, Terratogenicity, 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

Designation	Specification for: 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

Candidate replacement strippers were solicited from industry and were reviewed for probable success prior to inclusion in the test program. [Organic strippers may contain any or all of the following ingredients: (1) primary solvents, (2) cosolvents, (3) activators, (4) retarders, and (5) surfactants. The primary solvent should rapidly penetrate, swell, and lift the coating.]

MS-111, which conforms to specification 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. One of the alternative strippers, Enthone S-26, contains the same active agents as MS-111, but it also contains an emulsifier which makes the methylene chloride miscible with water. Thus this stripper offers the promise of reduced TTO by the addition of water to the working stripper. No other alternative strippers tested contain methylene chloride. Solvents in the other alternative strippers include diethylene glycol monobutyl ether, n-methyl-2-pyrrolidone, ethanolamine, and aromatic hydrocarbon solvents.

PROCEDURES AND METHODS

Stripper Performance

Steel and aluminum stock panels were cut into 2x3 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 selected strippers, water rinse, and steam cleaning. Eleven (11) alternate stripper formulations, containing no or reduced levels of methylene chloride, have been tested in the laboratory to date. These strippers were tested under controlled conditions with the four coating/substrate combinations on uniform coupons which were previously described. Manufacturer's recommendations were followed. All strippers were stirred during the test at a speed of 200 rpm to help maintain stripper homogeniety with respect to temperature. Some strippers were also tested at a stirring speed of 400 rpm. The other stripping conditions are shown in Table 3. Strippers were evaluated for percentage of coating removed for each paint system at specific time intervals. This percentage was determined by overlaying the coupon with a clear mylar grid subdivided into 20 equal areas. Percentages were determined to the nearest 5 percent. In addition, evaporation, and depletion analyses were performed on selected strippers.

Table 3. Stripping Parameters

Stripper	Stripping Temperature	Stripper Concentration	Hot Caustic Dips
MS-111	Ambient	Neat	Yes
Enthone S-26	Ambient	Neat, 20%, 10%, 5%	Yes
SafeStrip-66	54 C (130 F)	Neat	No
Envirosolv	Ambient	Neat	Yes
Oakite ALM	82 C (180 F)	Neat	No
NonMeth 120	49 C (120 F)	Neat	No
NonMeth 140	49 C (120 F)	Neat	No
Patclin 103B	82 C (180 F)	25%	No
Patclin 104C	82 C (180 F)	50%	No
Key Chemical 570	79 C (175 F)	Neat	No
Pavco Decoater 3321	82 C (180 F)	Neat	No
Fine Organic 606	82 C (180 F)	Neat	No

Alternate 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.

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 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. An overall score for each stripper was determined by summing characteristic scores.

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 procdure 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

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

References:

1. Sax, N. I. Dangerous Properties of Industrial Materials, Sixth Edition, Van Nostrand Reinhold Company, New York. 1984.
2. Weiss, G., ed., Hazardous Chemicals Data Book, Noyes Data Corporation, New Jersey. 1980.
3. Comprehensive Environmental Response, Compensation, and Liability Act.
4. Vector Scoring System for the Prioritization of Environmental Contaminants. Prepared by CanTox Inc. and Senes Consultants Ltd. and Priority List Working Group, Ontario Ministry of the Environment. March 1988.
5. Reinbold, K. A., and G. Barrett. Environmental Hazard Assessment of Chemical Paint Strippers. Draft Report. March 1988.

RESULTS

Stripper Performance

The results of the laboratory stripping tests are shown in Table 5. The line separating elapsed contact times of 2 and 3 hours indicates the point at which production rates would become unacceptable. The strippers are listed in order of descending stripping power.

Table 5. Results of Laboratory Paint Stripping Tests

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%	-

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

Results of laboratory stripper evaporation studies for the more successful strippers are shown in Table 6. Stripping efficiency of the selected strippers after 10 percent evaporation and after depletion by accumulation of free stripped films are shown in Table 7 and 8, respectively.

Table 6. Stripper Evaporation Rate

Stripper	Hours to Deplete by 10%	Relative Rate of Evaporation	Stripper Temperature (F)
Patclin 103B (25%)	2.00	1.500	180
Patclin 104C (50%)	2.50	1.200	180
MS-111	3.00	1.000	70
Oakite ALM	6.00	0.500	180
SafeStrip-66	21.50	0.140	130
Fine Organic 606	52.00	0.058	180
Enthone S-26 (10%)	54.75	0.055	70

Table 7. Stripping Power of 10 percent Evaporated Strippers

Stripper	0.5 hr	1.0 hr	1.5 hr	2.0 hr
Patclin 104C 50%	ACD*	ABCD	-	-
Fine Organic 606	AD B=75%	ABD C not tested	-	-
Enthone S-26 10%	A	A	AC	ABCD B=95%
Oakite ALM	A	AD	AD	AD B=90% C=85%
Patclin 103B 25%	AD	AD	AD	AD
SafeStrip-66	A	A	AD	AD B=20% C=20%

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

Table 8. Stripping Power of Free Film Depleted Strippers

Stripper	0.5 hr	1.0 hr	1.5 hr	2.0 hr
Patclin 104C (50%)	ACD*	ACD	ACD	ACD B=65%
Fine Organic 606	AC B=90% C=50%	ABCD	-	-
Oakite ALM	A	A	ACD	ACD B=60%
Patclin 103B (25%)	AD	AD	AD	AD B=85% C=75%
Safestrip-66	A	A	A	AD
Enthone S-26 (10%)	-	-	-	A=10%

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

Table 9 lists the candidate stripper solutions and MS-111 in declining order of efficiency when used fresh from the container. Of the 11 candidate replacement strippers, four achieved a level of performance equivalent to MS-111 only with increased contact times. The four were Fine Organic 606, Patclin 104C, Oakite ALM, and Patclin 103B. The fifth promising candidate, Enthone S-26, lost virtually all of its stripping power when depleted with free coating films used to simulate accumulated paint residue.

Table 9. Relative Stripping Efficiency of Fresh Strippers in Decreasing Order of Efficiency

MS-111 (MIL-R-46116)
Fine Organic 606
Patclin 104C
Enthone S-26=Enthone S-26 20%=Enthone S-26 10%
Oakite ALM=Patclin 103B
Enthone S-26 5%
SafeStrip-66
Nonmeth 120=Nonmeth 140=Key Chemical 570=Pavco Decoater 3321
Envirosolv L

The four candidate strippers showing the best levels of performance were tested on a pilot scale at SAAD. The relative levels of stripping efficiency under pilot conditions using SAAD depot parts were as follows:

Fine Organic 606 > Oakite ALM = Patclin 104C > Patclin 103B

Patclin 103B did not exhibit adequate stripping properties in this test. Eye irritation from Patclin 104C was reported by the steam clean operator. The addition of a hot caustic dip eliminated this problem.

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 10. The strippers were scored on the basis of 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 scores indicate that any of the four candidate strippers are preferable to MS-111. In addition, hazardous waste concerns and environmental regulations restricting discharges are much more favorable for the candidate strippers compared to MS-111 (Table 11). Based on composition in the stripper tank, the Fine Organic 606 stripper has a less favorable environmental hazard rating than the other candidate strippers, primarily because it is not diluted with water. The Patclin strippers are rated slightly more favorably than the Oakite ALM, primarily because of the increased water content. Scores based on components other than water are relatively comparable for Oakite ALM, Patclin 104C, and Fine Organic 606 but less favorable for Patclin 103B.

Table 10. Stripper Hazard Summary Table

		MS-111	OAKITE ALM	PAT. 103	PAT. 104	F.O. 606
TOXICITY	HUMAN TOXICITY	[2.2] 1 C 1 S 3 M's 2 T's	[1.53] no C's some P's 1-2 M's	[0.55] no C's	[0.96] no C's 1 S	[2.18] no C's 1 M 1 P
	ACUTE ENVIRONMENTAL	[2]	[1]	[1]	[1]	[1]
	CHRONIC ENVIRONMENTAL	[2.1]	[1.41]	[0.56]	[0.74]	[2.18]
ENVIRONMENTAL FATE	BIOACCUM-ULATION	[0.5]	[0]	[0.04]	[0]	[0]
	PERSISTENCE	[2.6]	[0.23]	[0.08]	[0]	[0.70]
	ENVIRONMENTAL TRANSPORT	[2.9]	[1.32]	[0.56]	[1.0]	[2.03]
SAFETY	CORROSIVITY OF STRIPPER	[3]	[1.14]	[0.40]	[0.90]	[2.76]
	REACTIVITY OF THE STRIPPER	[1.2]	[0.55]	[0.37]	[0.62]	[0.06]
	IGNITABILITY OF STRIPPER	[1.2]	[1.01]	[0.46]	[0.58]	[1.12]
TOTALS (WITH H_2O)		no water	[8.19]	[4.02]	[5.8]	no water
TOTALS (W/O H_2O)		[17.7]	[12.41]	[16.08]	[11.6]	[12.03]

C = Carcinogen S = Suspect carcinogen M = Mutagen T = Teratogen
P = Possible carcinogen

Table 11. Regulatory Restrictions

	MS-111	OAKITE ALM	PAT. 103	PAT. 104	F.O. 606
HAZARDOUS WASTE CONCERNS	[3]	[1]	[1]	[1]	[1]
WASTEWATER EFFLUENT CONCERNS	[3]	[1]	[1]	[1]	[1]
HEALTH & SAFETY REGULATIONS	3 TWA VAL 1 500 PPM 2 5 PPM 3 5 PPM	3 TWA VAL 1-3 3 PPM 2 TLV 0.2 & 3 PPM	1 TWA VAL 1 3 PPM	NOT ESTABLISH	1 TWA 3 PPM 1 TLV 3 PPM
DISCHARGE RESTRICTIONS	TTO, RCRA CERCLA CWA	CWA, TSCA FIFRA	CWA, TSCA	NOT ESTABLISH	NOT ESTABLISH

TOTALS FOR EACH STRIPPER

MS - 111 All of the compounds are a hazardous waste, and wastewater effluent concern. They appear in several listing of hazardous compounds that are either now, or will soon be stringently regulated. Note also that some of them are carcinogens. Also contains mutagens.

OAKITE ALM Few of the compounds show up on hazardous waste and wastewater concern listings. There are no carcinogens but there is a slight possibility of one class of compound contained in the stripper. Suspect mutagens.

PATCLIN 103 Few of the compounds show up on hazardous waste and wastewater concern listings. There are no carcinogens. There are some suspect mutagens.

PATCLIN 104 Few of the compounds show up on hazardous waste and wastewater concern listings. There are no carcinogens. There are some suspect mutagens.

F. O. 606 One component shows up on both wastewater and hazardous waste concern listings. There is one possible carcinogen. There is on mutagen.

CONCLUSIONS AND RECOMMENDATIONS

Four candidate strippers demonstrated adequate performance in laboratory tests and were tested on a pilot scale. Of the first three strippers pilot tested, Oakite ALM and Patclin 104C performed comparably well, but Patclin 103B did not perform well enough for continued consideration. Several use factors would appear to favor Oakite ALM over Patclin 104C. Patclin 104C has an evaporation rate nearly 2.5 times higher than Oakite ALM. Life cycle costs are estimated to be about 6% higher for Patclin 104C. Patclin 104C could also be expected to be a higher energy consumer because of its higher evaporation rate and the need for a hot water or hot caustic rinse. Patclin 104C has more odor associated with its use than does Oakite ALM. A full scale field test of Oakite ALM at SAAD was recommended.

In a more recent pilot scale test, Fine Organic 606 slightly exceeded the stripping efficiency of Oakite ALM and Patclin 104C. This stripper has an environmental, health, and safety rating which is less favorable than those of the other three candidate strippers but still better than that for MS-111. Because of the performance of this stripper, Fine Organic 606 may be a candidate for evaluation in a full scale field test.

FIELD TESTING

Oakite ALM was selected for a full scale field test at SAAD. The test began in September and will continue for one year. Stripper performance and evaporation are being monitored. In addition, chemical analyses will determine the relative evaporation rates of stripper components to determine whether bolstering of specific components is required. Composition of rinse water and sludges will be monitored to ensure compliance with discharge and disposal regulations. Environmental hygiene monitoring will also be performed.

KINETICS AND MECHANISM OF METHANE OXIDATION IN SUPERCRITICAL WATER

by

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ABSTRACT

The project, "Supercritical Oxidation of Hazardous Chemical Wastes," is a Hazardous Waste Remedial Actions Program (HAZWRAP) Research and Development task being carried out by the Los Alamos National Laboratory. Its objective is to achieve an understanding of the technology for use in scaling up and applying oxidation in supercritical water as a viable process for treating a variety of Department of Energy Defense Programs (DOE-DP) waste streams. This report presents experimental results for the kinetics of the oxidation of methane and methanol in supercritical water and computer modeling results for the oxidation of carbon monoxide and methane in supercritical water. The experimental and modeling results obtained to date on these one-carbon model compounds indicate that the mechanism of oxidation in supercritical water can be represented by free-radical reactions with appropriate modifications for high pressure and the high water concentration. If these current trends are sustained, a large body of existing literature data on the kinetics of elementary reactions can be utilized to predict the behavior of other compounds and their mixtures.

I. INTRODUCTION

The chemistry of oxidation in supercritical water is being investigated and developed for a usable waste destruction process in "Supercritical Water Oxidation of Hazardous Chemical Waste," a project at Los Alamos National Laboratory funded as a Research and Development task of the Hazardous Waste Remedial Action Program (HAZWRAP) of Department of Energy (DOE) Defense Programs (DP).[1] Relatively low-temperature oxidation in supercritical water has been proposed as a means of destroying hazardous organic wastes, with full control of all effluents. The objective of this Research and Development Task is to gain further understanding of the chemical mechanisms of oxidation in supercritical water, directed toward development of a practical process that can be applied to a variety of hazardous wastes.

At the inception of this project, few chemical reactions had been studied in supercritical water. In order to move toward demonstration of the technology as efficiently as possible, a strategy to develop the maximum amount of practical information on the process was needed. Two general strategies were possible: to conduct a methodical investigation of the destruction kinetics of individual chemical compounds that constitute hazardous wastes, or to develop a basis from which to build upon the existing literature on gas-phase chemical kinetics. The first approach would build a literature comparable to that developed for incineration and combustion and would require substantial resources and time. The second approach relates the reaction mechanisms in the supercritical regime to those associated with low-temperature gas-phase oxidation. By applying a combination of theory and experiment to selected model compounds, chemical kinetics under supercritical conditions can be benchmarked against well-studied oxidation reactions of model compounds. This basic understanding can then be used to extrapolate from the existing literature to a wide variety of hazardous organic materials. In this case, what appears to be a more basic research strategy in fact offers a quick and resource-efficient route to application.

Methane and its partial oxidation products, particularly carbon monoxide and methanol, were selected as model compounds. Methane was chosen for the model compound because it is more difficult to oxidize than other hydrocarbons, and a large data base is available on its reactions. The oxidation mechanisms for the more oxidized one-carbon compounds methanol and CO overlap significantly with the methane oxidation mechanism. In this HAZWRAP task, experimental

data on these compounds are being generated, and a computer model for oxidation of methane in supercritical water is being developed. Large subsets of the methane mechanism are directly transferable to the oxidation mechanisms of other organic compounds, particularly hydrocarbons and oxygenates.

II. BACKGROUND

Above its critical point (374°C and 22.13 MPa), water becomes a fluid that is neither a liquid nor a gas but has some of the characteristics of both. The solvent properties of water in the supercritical state reverse so that non-polar, oily compounds become soluble and salts become insoluble. Under these conditions, oxidation of hazardous organic chemicals such as PCBs and solvents takes place rapidly and completely.

Although this oxidation is similar to combustion, it takes place at a much lower temperature than incineration (about 800 K in contrast to about 2000 K) and in a completely contained system. Almost no nitrogen oxides are produced at these low temperatures, and the effluent can be completely controlled because the system is contained. Because the supercritical state can be produced by pressure or temperature increases without a phase change, less energy input must be added in the reaction zone than in processes in which a phase change takes place, such as incineration of aqueous wastes. In addition, because complete mixing can be achieved in a single-phase supercritical region, reactions are driven to completion, unlike the situation in two-phase systems where concentration gradients across phase boundaries limit the extent to which compounds can be destroyed. This process has the promise of destroying low concentrations of hazardous chemicals in water, such as groundwater contaminated with chlorinated hydrocarbons, at reasonable cost. The reactions are exothermic, and, depending on the nature and concentration of the hazardous chemicals and the design of the process, the excess heat might be used for process heat or to cogenerate electricity.

Many hazardous compounds can be destroyed by oxidation in supercritical water. In principle, any organic compound, that is, any compound composed of carbon and other elements such as hydrogen, nitrogen, phosphorus, sulfur, and the halogens, can be completely oxidized to relatively innocuous compounds. Oxidation of carbon gives carbon dioxide, hydrogen gives water, nitrogen is reported to give ammonia and dinitrogen, phosphorus gives phosphoric acid,

sulfur gives sulfuric acid, and the halogens give the corresponding halogen acids. The mineral acids can be neutralized to salts by use of caustics.

Because water is the solvent and may be a reactant, the process can be used for a variety of organic wastes containing water or water contaminated with organics. There appear to be no upper or lower limits to the concentration of organic in water that can be destroyed by the process. An economic constraint, however, on the organic concentration is the amount of heat generated by oxidation of the organic. For autogenous (heat supplied by the process without added fuel) operation of a supercritical water oxidation plant, the optimum concentration of organic in water* is about 10%. This optimum value will vary with the heat of oxidation of the particular organic compounds present and the engineering design of the apparatus. An engineering tradeoff to be considered in the design of a plant is the organic concentration that generates enough heat to maintain the reaction, but not more than can readily be removed from the processing vessel. Pure or highly concentrated organic wastes can be diluted with water, whereas wastes in low concentrations can have fuel or other organic wastes added. Other factors that influence the engineering design include the residence time in the reactor, which is determined by the oxidation kinetics of the waste, the physical state of the waste and its oxidation products, and the amounts of waste to be processed.

The process appears to be applicable to the destruction of most organic chemicals. Some of the many waste streams that might be treated by supercritical water oxidation include

- liquid aqueous and organic streams as they are originated, including machining wastes, paint wastes, automobile grease and lubricant wastes, PCB-contaminated oil, and waste solvents;
- groundwater contaminated with organics;
- stored wastes, including those that contain sludges or other solids;
- soil contaminated by spills or burial of organics;
- vermiculite and other mineral absorbers used to clean up spills of organics;

* This is an approximate number that has been presented as such by two of the industrial firms in private communications.

- mixed wastes containing both organics and radioisotopes, including uranium machining wastes;
- organometallic compounds, including stream and lake sediments containing organomercury compounds.

A great range of sizes appears to be possible for supercritical water oxidation plants. Standard pressure-vessel technology can be used to provide small- to medium-sized surface installations, which could be permanently installed to process laboratory or manufacturing wastes. In addition, plants with very large capacities have been proposed, in which a cylindrical heat exchanger and reaction vessel is emplaced in the ground by use of oil field drilling and well-completion technology. The depth of the cylinder provides pressure by hydrostatic head, and the emplacement in the earth provides structural strength for containment of the pressure. A waste treatment plant based on oxidation in supercritical water would not require a large land area. Modular plants processing tens of gallons per minute could be skid-mounted and carried on one or two semitrailers. An in-ground unit processing wastewater from a medium-sized city would require about an acre of land. Both the surface and the in-ground plant can be engineered to produce hot, pressurized water, which can be converted to electrical energy, shaft power, or process steam by means of proven power plant technology. A preliminary engineering study discusses some of the issues associated with plant design.[2]

Because this technique may have wide applicability, and because the objective of the HAZWRAP R&D Task is to bring the technique to application as rapidly as possible, the strategy followed has been to obtain a fundamental understanding of oxidation in supercritical water that can be applied as widely as possible to various wastes and conditions. Relatively little information is available in the literature on reactions in supercritical water. The available literature is oriented toward destruction efficiencies,[3] which are applicable only to the compound for which they are determined. To establish a basis for extrapolation of kinetic measurements to a wide variety of compounds, the first objective in this task has been to show that oxidation of a model compound (methane) can be represented by a free-radical mechanism with appropriate modifications for high pressure and high concentration of water. From this basis and with data available in the literature on the kinetics of elementary gas-phase reactions,[4] extrapolations of oxidation kinetics can be made for most hazardous organic chemicals and their mixtures.

III. EXPERIMENTAL

A. Plug Flow Reactor

A tubular reactor system allows isothermal operation with radially well-mixed, one-dimensional plug flow. A schematic diagram of the system used in this study is shown in Fig. 1. The reactor is 4.24 m of 0.635-cm o.d. x 0.211-cm i.d. (0.25 in. x 0.83 in.) Inconel 625 tubing immersed in a fluidized-bed sand bath for temperature control. Dilute concentrations of reactants in water are prepared by dissolution in room temperature water in one-liter agitated tanks. The feed solutions are preheated separately to reaction conditions in less than 10 s in 0.108-cm i.d. Hastelloy C276 tubing and are mixed at the reactor inlet.

The reactor effluent is cooled quickly in a heat exchanger, depressurized, and separated into measured gas and liquid flows. The composition of the gas phase is determined by gas chromatography.

B. Batch Reactor

The schematic of a batch kinetics reactor that can be sampled at several regular intervals is given in Fig. 2. Water or other input liquid is stored in liquid reactant tanks 1 and 2. It is then introduced into one-liter injectors by evacuating the injectors and feed lines. Gaseous reactants or oxidants can be added from reactant gas supplies 1 and 2. Pressure is increased at the injectors by a large-diameter piston driving a smaller-diameter piston. Fluids in the injectors can be pressurized to 5000 psi by applying low-pressure air to the large piston. This pressurization causes gases to dissolve in the water, forming a single phase. Solenoid-operated valves allow the pressurized fluid from one or both injectors to be introduced rapidly into the preheated pressure vessel. The amounts of fluids injected are precisely measured by a magnetic sensing system that provides readout of the position of the piston in the injector. Multiple small samples can be removed and cooled rapidly from two locations in the autoclave by means of solenoid-operated high-temperature valves and subsequently routed to sample bottles.

The reaction vessel (autoclave) has a capacity of one liter and is made from A-286 steel. It is externally heated and rated to withstand 5000 psi at the maximum operating temperature of 700°C. All other components, including valves and tubing, are 300 grade stainless steel. Valves, tubing, and fittings that are subjected to high temperature are rated to 60,000 psi.

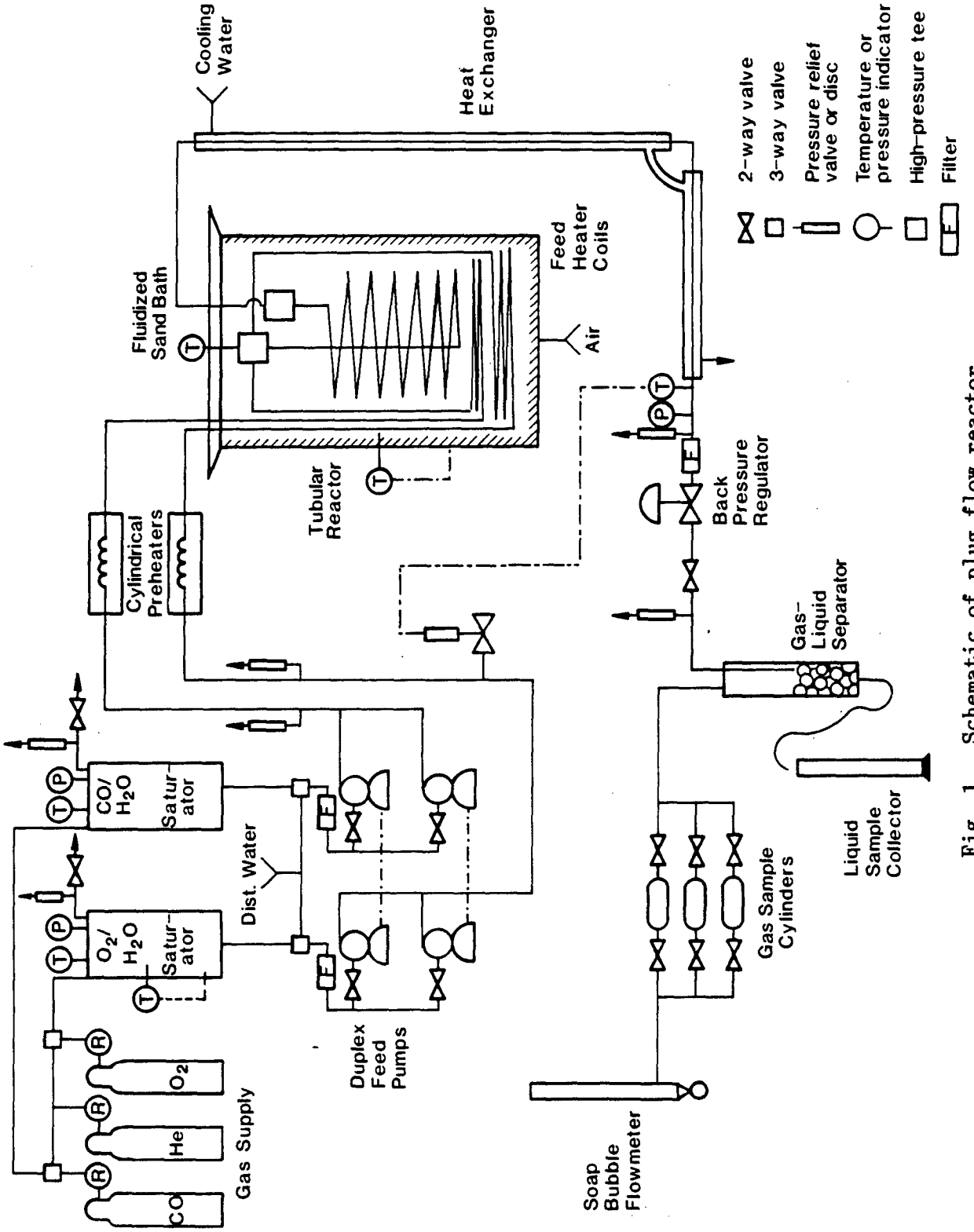


Fig. 1. Schematic of plug flow reactor.

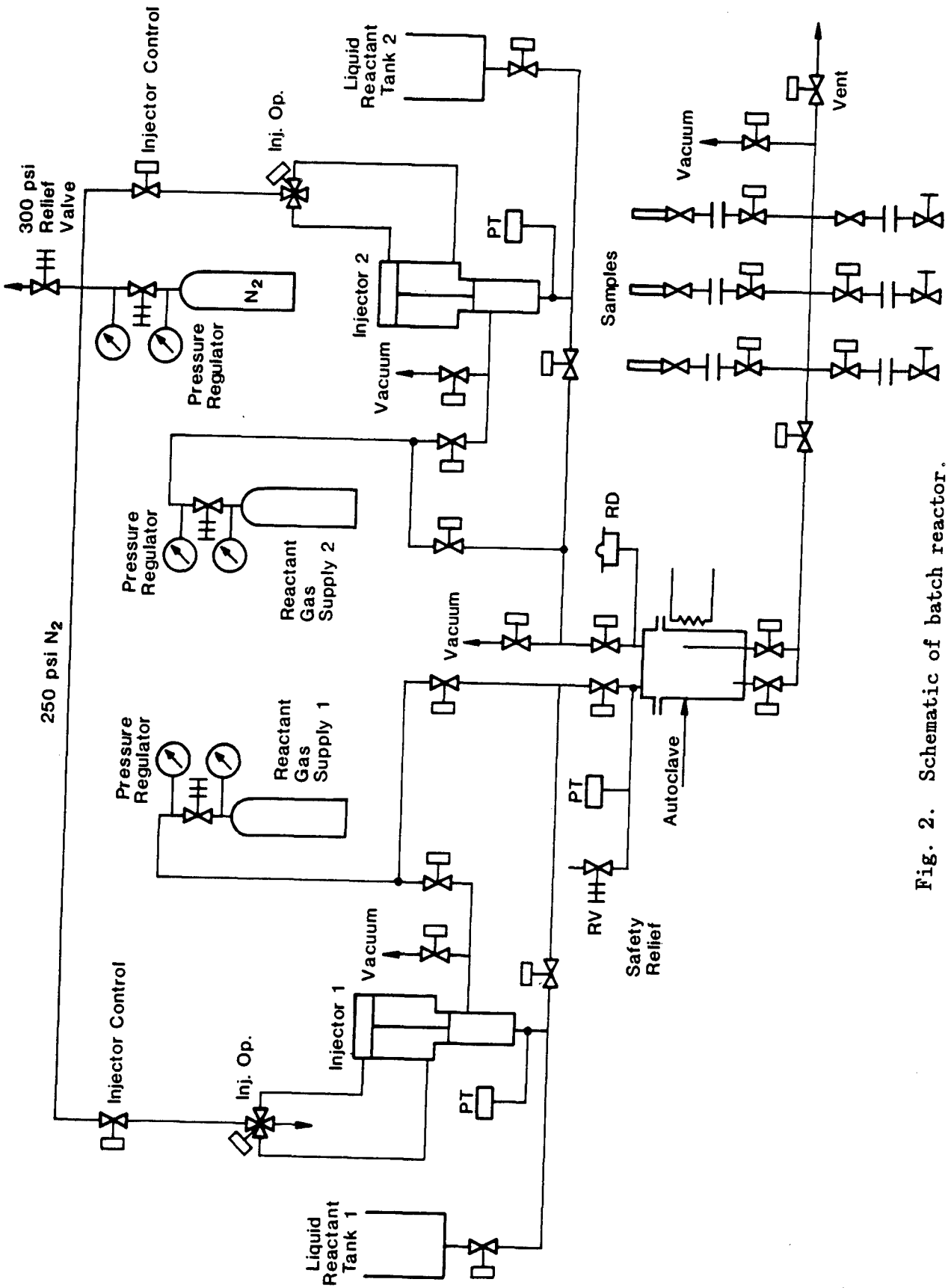


Fig. 2. Schematic of batch reactor.

Instrumentation consists of thermocouples with continuously recording readouts to measure temperature at several locations within the reaction vessel. Pressures for both the injectors and the reaction vessel are measured with strain-gage-type pressure transducers with continuous recording capability. System control and data acquisition are through an HP 3497A data acquisition and control unit and an HP 9845A computer with an HP 82902M disk drive. Analysis of samples is by gas chromatography.

IV. MODEL DEVELOPMENT

At the inception of this HAZWRAP R&D Task, almost no data or analyses were available to suggest the mechanism by which oxidation in supercritical water occurs. The few reported destruction efficiencies[3] do not provide sufficiently detailed kinetic information for evaluation of a mechanism. Rates for overall conversion of reactants, the data from which they were derived, and early modeling results for CO were the only available data relating to a mechanism.[5] The mechanism used for modeling by Helling and Tester[5] was taken directly from the literature on gas-phase reactions.[6] Observed rates of oxidation were reproduced by the model within a factor of two, but the product distribution was not reproduced well.

Because transport properties in supercritical water are gas-like and oxidation is observed to result in conventional oxidation products, a reasonable hypothesis is that oxidation proceeds by a free-radical mechanism, as do both combustion and low-temperature oxidation at atmospheric pressure. If this hypothesis can be shown to be true, mechanisms can be extended from simpler model compounds like methane and its one-carbon partial oxidation products (such as methanol and CO) to other compounds, such as higher hydrocarbons, oxygenates, and chlorinated hydrocarbons, by use of elementary reactions and their kinetic constants available in the literature.

Modeling of chemical kinetics with large sets of elementary reactions is an important and extremely valuable tool in the analysis of the complex chemical systems that underlie such phenomena as combustion and air pollution. The increasing availability of fundamental rate-constant data, the development of computational methods for solving large systems of "stiff" equations, and the extraordinary growth in both power and availability of computing have simultaneously spurred and allowed the increased application of detailed kinetic modeling. By far the most common applications have been in the fields

of combustion and atmospheric chemistry. A model of this sort, validated by experiment, can be a valuable predictive tool for exploration of means to control these complex processes.

Detailed kinetic modeling is accomplished by assembling a multistep mechanism of elementary reactions with the thermochemical data and fundamental rate constants that describe the elementary reactions. No adjustable parameters are included. This information is then translated into a set of differential equations that describes the time variance of species concentrations and of temperature. With starting conditions and concentrations specified, this initial value problem is readily solved by any one of a number of "stiff" equation packages. "Stiff" sets of differential equations contain equations with widely differing time constants. Sets of differential equations describing chemical kinetics are usually stiff.

An elementary reaction is one that describes a single molecular event. For the mechanisms being developed in this HAZWRAP R&D Task, transient free-radical species are usually involved. An example is the well known and very important reaction of hydroxyl radical with methane:

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad . \tag{1}$$

This free-radical reaction is but one step of several hundred in the complex mechanism that describes the oxidation of methane. Elementary reactions can be contrasted to global reactions of the type

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad . \tag{2}$$

This reaction is a proper chemical description of an overall process, but it provides no insight into such questions as the role of CO or the effect of pressure in the oxidation of methane. Such expressions of reaction rates describing overall chemical reactions are termed "global" rate expressions. Global rate expressions are specific to the overall reaction, whereas a single elementary reaction or group of elementary reactions may appear in numerous very different overall reactions. Global rate expressions are valid only for the temperature, pressure, and concentration ranges covered in the experiments used to determine the expression. They cannot be used for extrapolating beyond the range for which they were measured. They also cannot be extrapolated to

mixtures of compounds. The many elementary steps of a mechanism represent the global process described by reaction (2) in a very detailed way, giving insight into the roles of intermediates and a basis for quantitative prediction of the behavior of the process under a wide variety of conditions.

If all the elementary reactions and their kinetic constants for methane oxidation were perfectly known, then the oxidation behavior of methane could be predicted for any reactor, any initial conditions, any diluent, any pressure, or any combination of variables. Unfortunately, this is not the case. However, several mechanisms have been compiled that model methane oxidation very closely for limited ranges of conditions. It is this work that forms a basis for model development for supercritical water oxidation.

When an elementary reaction model is used to model a process that is known to be beyond the original scope of the model, as is being done in extending a combustion mechanism to oxidation in supercritical water, an iterative process takes place in which new chemical steps appropriate to the process conditions are postulated and new fundamental rate constant data are estimated or calculated in order to reproduce the experimental results observed. Eventually, the model is developed to a point of predictive capability. This type of interaction leads to new understanding and chemical insight that cannot be obtained from the use of a global model.

Development of a mechanism to describe oxidation in the supercritical water regime requires that at least three contributing factors be accounted for in addition to the factors affecting the gas phase reactions. These factors are high pressure, the role of water as reactant, and other effects of the presence of water not considered in conventional oxidation or combustion mechanisms.

Reactions in which an otherwise nonreactive colliding molecule is required to supply or remove energy, that is, association or dissociation reactions, always show a linear pressure dependence over some pressure range. At higher pressures (the fall-off region), the pressure dependence decreases, and at still higher pressures, there is no pressure dependence. Relatively few elementary rate coefficients have been measured at pressures higher than one atmosphere, but the theory describing these processes is well developed, and good estimates can be made for most of the rate constants that need to be adjusted for pressure.

Water is a stable product under most combustion conditions and has little effect on the mechanism of oxidation. However, in supercritical water oxidation, water is present at all times in high enough concentration to overcome its stability and hence its usually slow reactions. Thus the reactions of free radicals with water and unimolecular decomposition of water have been added to the basic oxidation mechanism to describe the processes in supercritical water oxidation. Rate constants for processes such as O and H atom attack on water and the collision-induced decomposition of water are available[4b] and have been included in the mechanism.

Two other effects of water upon some of the elementary reactions of the mechanism have been identified, and others are possible. In some reactions, high concentrations of water may cause it to become a collision partner in a reaction normally considered to be a two-body reaction. An example of this is the reaction of H atom with water to produce H_2 and hydroxyl radical,

$$H + H_2O \rightarrow H_2 + OH \quad . \tag{3}$$

If the initial collision of H with H_2O produces a complex with a long enough lifetime that another H_2O can collide with it, the second water molecule may contribute enough energy to the complex to effectively lower the activation energy of the overall reaction, thereby increasing its rate and, in this case, the rate of H_2 production. The modified reaction can be represented as

$$H + 2\ H_2O \rightarrow H_2 + OH + H_2O \quad , \tag{4}$$

with a set of kinetic constants different from those for reaction (3).

In other reactions, water may influence the kinetics by molecular interaction, particularly hydrogen bonding. The extent of hydrogen bonding under supercritical conditions has not been determined. High temperature steam at low pressures does not exhibit significant hydrogen bonding, but under supercritical pressures and at a density nearly 0.1 that of liquid water, hydrogen bonding may occur. Since hydrogen bonds have an energy in liquid water of approximately 5 kcal/mole, such bonding would alter the thermodynamics of affected reactions. Since nonpolar hydrocarbons become soluble in supercritical water, some changes in molecular interactions must take place. If molecular clustering is a factor in this solubility, collision rates within the

clusters will be altered from simple gas-phase values. If this solubility arises because of induced polarity, the dynamics of interaction with other molecules will be altered.

For the basis from which development of a supercritical water oxidation mechanism was started, a mechanism for medium-pressure gas-phase oxidation of methane was chosen. The subset of reactions in that mechanism representing CO oxidation was taken as the basis for development of a CO supercritical water mechanism.[1] Changes to it have included updating of the kinetics constants to the best values available and addition of reaction (4). The CO mechanism now contains 68 elementary reactions, in which the primary cycle consists of the direct oxidation of CO by the hydroxyl radical and production of hydroxyl radicals by reaction of hydrogen atoms with water:

$$CO + OH \rightarrow CO_2 + H \quad . \qquad (5)$$

$$H + H_2O \rightarrow H_2 + OH \quad . \qquad (6)$$

The methane oxidation mechanism, now 156 reactions, contains the modified CO oxidation mechanism. At the high temperatures of conventional combustion, hydroxyl radicals are the primary oxidizing agents for methane. At the temperatures of supercritical water oxidation, the reactions of hydroperoxy (HO_2), methoxy (CH_3O), and methylperoxy (CH_3O_2) radicals also become important.

V. RESULTS AND DISCUSSION

Experimental data have been obtained for the rates of oxidation of methane and methanol with oxygen in supercritical water. Global rate expressions have been derived from these data, and the data have also been used to verify the mechanisms. Detailed reaction mechanisms have been developed for CO and CH_4. The mechanism for CO oxidation has been benchmarked against data from the literature.

A. CO Oxidation

Early oxidation mechanism development[1] focused on CO. The CO mechanism is a subset of the methane oxidation mechanism and of oxidation mechanisms for many other compounds, including hydrocarbons and oxygenates. Thus, it is a simpler mechanism than the methane oxidation mechanism, thereby allowing for more direct evaluation of the effect of changes in the mechanism. Table I

TABLE I

CO OXIDATION AND PRODUCTS: EXPERIMENT AND MODEL

	Experiment Number					
	1		2		3	
Identifier	% CO Oxidized	$[H_2]/[CO_2]$	% CO Oxidized	$[H_2]/[CO_2]$	% CO Oxidized	$[H_2]/[CO_2]$
Experiment (Ref. 5)	11.6	0.73	36.5	0.32	81.3	0.22
Model A-1	3.68	0.0016	70.5	0.0026	99.7	2.4×10^{-5}
Model C-1	≃0	0.021	2.70	0.055	54.1	0.033
Model H	≃0	0.053	1.82	0.156	61.0	0.069

shows the progress toward matching the experimental results as changes reflecting the conditions of supercritical water oxidation are added to a gas-phase free-radical oxidation mechanism. The three experiments were conducted at 400°C, 484°C, and 543°C, respectively. Model A-1 is the mechanism used in the literature.[6] Model C-1 is the subset of CO oxidation reactions from the medium-pressure methane oxidation mechanism. It is a more complete mechanism than Model A-1 and contains some pressure effects and reaction (4). Model H is the current expansion of Model C-1. It contains the best currently accepted rate constants, strong collision limits where appropriate, and some rate constants calculated from equilibrium constants and reverse rates.

In validating the model against experiment, two measures are being used: the amount of reaction, indicated by the percent CO oxidized, and the product distribution, indicated by the ratio of hydrogen to carbon dioxide concentrations. Model A-1 reproduces the product distribution poorly and the amount of reaction only slightly better. Model C-1 accounts for more of the hydrogen production, but reproduces the amount of reaction poorly. Model H shows significant progress in accounting for hydrogen production, but the amount of reaction is not yet satisfactory. A low-temperature process that depletes CO and produces hydrogen, perhaps a catalyzed water gas shift, may be occurring.

B. Methane Oxidation

Oxidation kinetics were determined for methane in supercritical water in the temperature range 640°-700°C and at a pressure of 245 atm (24.5 MPa). A summary of the experimental conditions and results is given in Table II. An

TABLE II

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS FOR OXIDATION OF METHANE IN SUPERCRITICAL WATER

Temperature (°C)	CH_4/O_2 Feed	Residence Time (s)	Conversion (%)	Reaction Rate (10^6 gmole/cm^3-min)	ln(k) (1/s)	$[CO_2]/[CO]$
640	1:2.0	6.1	6.6	1.21	-4.49	2.3
642	1:2.0	11.1	12.7	1.26	-4.40	3.6
650	1:1.0	5.6	11.6	1.35	-3.81	5.6
651	1:2.0	6.0	11.5	2.12	-3.89	12.8
660	1:2.0	5.9	13.0	2.44	-3.74	14.8
660	1:1.2	9.6	15.5	1.89	-4.04	3.3
670	1:2.1	5.8	11.6	2.15	-3.85	12.6
670	1:1.8	9.3	26.2	3.23	-3.42	11.8
675	1:2.2	6.3	19.8	3.91	-3.35	2.9
680	1:2.8	6.0	19.1	2.93	-3.35	2.5
680	1:1.2	9.0	22.1	2.67	-3.58	5.4
683	1:2.0	5.7	12.3	2.29	-3.77	14.2
690	1:2.0	8.9	30.7	3.64	-3.18	12.5
700	1:2.1	6.1	25.9	5.33	-3.01	24.1
703	1:2.1	5.6	26.5	4.82	-2.90	34.8

Arrhenius plot for which first-order oxidation of methane is assumed is shown in Fig. 3. Also shown is the weighted least-squares regression line[7] of the data, where the weights were taken as proportional to k_i^2/σ_i^2. The variances (σ_i^2) for each data point were generated by Monte Carlo error analysis together with estimates of errors in the measured data. The global first-order rate expression for the oxidation of methane was determined to be

$$-\frac{d[CH_4]}{dt} = 10^{7.1\pm1.9}\exp(-37.5\pm8.3/RT)[CH_4] \quad ,$$

where the activation energy is in kcal/mole.

The 98% confidence interval for the data was calculated with the full covariance matrix for the data. The variance of six data points lying outside this interval cannot be accounted for by experimental error alone. A variable not appearing in the regressed equation yet still affecting the reaction rate may be responsible for these deviations. The rate may depend on oxygen concentration, or the methane concentration may need to be raised to a power different from unity. Further experiments are necessary to determine the source of these deviations.

The improved CO oxidation mechanism (Model H) was inserted into the Los Alamos high-pressure methane oxidation mechanism. A simulation with this

mechanism underpredicts the rate of methane oxidation (amount of reaction) and overpredicts the production of CO relative to CO_2 (product distribution). Nonetheless, the results were closer to the experimental data than the methane mechanism containing the unmodified CO oxidation module (Model C-1). Improvements to the CO oxidation mechanism that improve the agreement of the calculated results with the experimental results should also improve the methane modeling. In addition, modifications may need to be made to reactions in the methane mechanism that are not a part of the CO mechanism.

C. Methanol Oxidation

The oxidation kinetics of methanol in supercritical water was determined for the temperature range 450°-550°C at a pressure of 243 atm (24.6 MPa). A summary of the experimental conditions and results is given in Table III. An Arrhenius plot for which first-order oxidation of methanol is assumed is shown in Fig. 4. Also shown is the weighted least-squares regression line[7] of the data, where the weights were taken as proportional to k_i^2/σ_i^2. The variances (σ_i^2) for each data point were generated by a propagation of errors method using estimates of errors in the measured data. The global first-order rate expression for the oxidation of methane was determined to be

$$-\frac{d[MeOH]}{dt} = 10^{24.4\pm2.2}\exp(-94.5\pm7.9/RT)\,[MeOH] \quad ,$$

where the activation energy is in kcal/mole. Dependence on oxygen concentration is being determined.

VI. CONCLUSIONS AND RECOMMENDATIONS

The chemistry of oxidation in supercritical water is being investigated and developed for a usable waste destruction process. Relatively low temperature oxidation in supercritical water has been proposed as a means of destroying hazardous organic wastes, with full control of all effluents. The objective of this HAZWRAP R&D task is to gain further understanding of the chemical mechanisms of oxidation in supercritical water, directed toward development of a practical process that can be applied to a variety of hazardous wastes.

In order to move toward demonstration of the technology as efficiently and rapidly as possible, a strategy of developing the maximum amount of practical information on the process was adopted. Instead of conducting a methodical

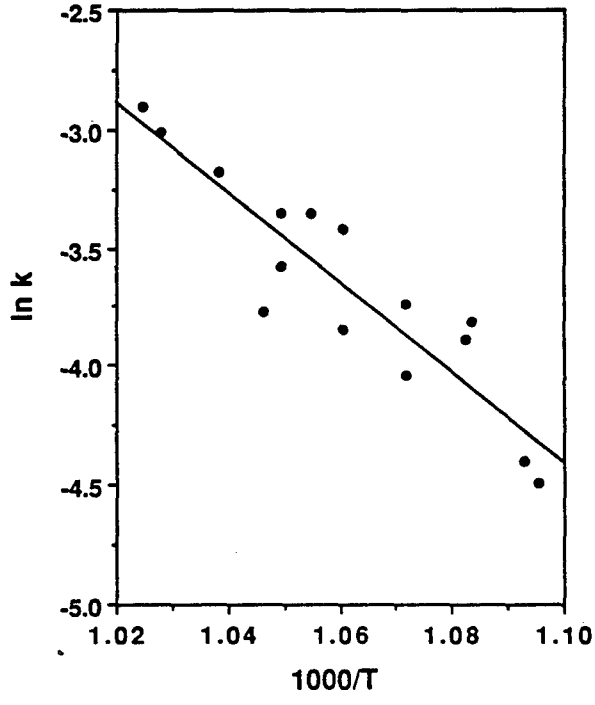


Fig. 3. Arrhenius plot for the first-order oxidation of methane in supercritical water.

TABLE III

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS FOR OXIDATION OF METHANOL IN SUPERCRITICAL WATER

Temperature (°)	MeOH/O_2 Feed	Residence Time, τ (s)	Conversion (%)	Reaction Rate (10^6 gmole/cm^3-min)	ln(k)* (1/s)	$[CO_2]/[CO]$
500	1:5.0	12.1	6.9	0.84	-5.13	4.8
450	1:1.4	11.4	<1.0	<0.1	--	no CO
480	1:1.3	10.3	1.0	0.215	-6.89	no CO
500	1:1.2	9.7	4.2	0.88	-5.42	3.1
550	1:1.3	8.5	94.2	17.4	-1.09	0.7
530	1:1.7	8.9	20.7	2.94	-3.65	2.5
520	1:1.7	9.1	15.7	2.28	-3.98	4.8
520	1:3.2	9.1	15.9	1.24	-3.96	3.7
520	1:0.5	8.9	14.7	5.17	-4.03	0.6
520	1:1.1	9.0	15.1	4.89	-4.00	3.5

*Assumed first-order rate constant $k = \frac{1}{\tau} \ln \left(\frac{[MeOH]_{in}}{[MeOH]_{out}} \right)$.

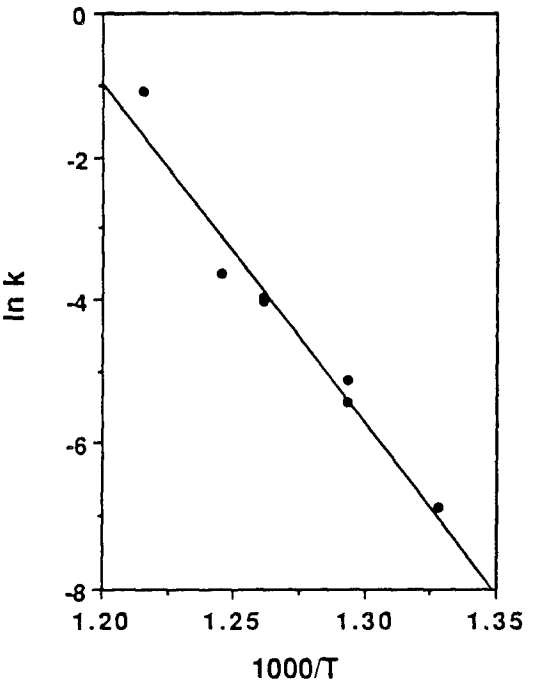


Fig. 4. Arrhenius plot for the first-order oxidation of methanol in supercritical water.

step-by-step investigation of the destruction kinetics of individual chemical compounds that constitute hazardous wastes, a basis is being developed from which to build upon the existing literature on gas-phase chemical kinetics. By applying a combination of theory and experiment to selected model compounds, chemical kinetics under supercritical conditions is being benchmarked against well-studied oxidation reactions of model compounds. This basic understanding will then be used to extrapolate from the existing literature to a wide variety of hazardous organic materials. Methane and its partial oxidation products, particularly carbon monoxide and methanol, were selected as model compounds.

The data from oxidation of methane and other one-carbon compounds in supercritical water and associated modeling, although not yet complete, tend to support the hypothesis that oxidation in supercritical water can be represented by a free-radical mechanism appropriately modified to include the effects of pressure and the high concentration of water. If this hypothesis can be confirmed, it forms a powerful basis for extrapolation of kinetic data to other compounds, and significantly less experimental work will be needed than would

be required for determinations of the destruction kinetics for every compound to be addressed with this technology. In addition, the particular data obtained and the mechanisms developed in this study are part of this basis for extrapolation to other compounds.

In addition to developing a predictive basis for supercritical water oxidation technology, global rate expressions have been experimentally determined for the oxidation of methane and methanol in supercritical water. Additional work is needed to complete the determination of the dependence of the global rate expression on oxygen concentration.

The current mechanism is derived from the gas-phase mechanism by additions and modifications that are well supported and are of the type expected for the conditions of supercritical water oxidation. Further modifications are needed and will be made to the mechanism as more experimental results become available. The mechanism of the water-gas shift reaction should be examined to determine whether steps not currently included in the CO mechanism would provide a higher rate of oxidation at low temperatures. The methane mechanism must be adjusted, insofar as our understanding allows, for the reactivity of H_2O, and sensitivity analysis should be used to ascertain the key steps in the oxidation process. The mechanism of steam reformation of methane should be examined to determine elementary reactions that might not be currently included in the oxidation mechanism.

Methanol oxidation in supercritical water should also be modeled to provide insight into the destruction of oxygenates, for which methanol is a model. Methanol oxidation can be represented by a subset of the methane mechanism, expanded to provide a stand-alone mechanism. The mechanisms for oxidation of CO, methane, and methanol in supercritical water will provide, along with the combustion literature for higher hydrocarbons, a solid base for extrapolation to new compounds.

The modeling work and engineering correlations will both be used for extrapolation of kinetics to additional organic compounds as needed for demonstrations. For example, extrapolation of the modeling to higher hydrocarbons requires that reactions be added in which oxygen attacks that hydrocarbon and the hydrocarbon is subsequently degraded to one-carbon fragments, while reactions in which methane appears as a reactant will be removed. Further experimental data on selected compounds will be necessary to verify the agreement of the modeling. Rates calculated from the global expressions will be

compared with modeling of oxidation in the gas-phase and in supercritical water to derive engineering correlations. Appropriate ratios of these rates will be used to develop data needed for the engineering of the demonstration experiments.

In summary, future work in this R&D task will be in four areas:

1. Experimental and modeling work on the model compounds methane and methanol will be completed. This item is nearing completion.
2. The experimental and modeling results from the model compounds will be put into appropriate form for engineering design of demonstration experiments.
3. Experimental and modeling work on selected higher hydrocarbons and oxygenates will further verify the model and serve as additional input for engineering design. This aspect should be carried out in parallel with item 2.
4. Experimental and modeling work will be extended to other classes of compounds, such as chlorinated hydrocarbons.

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REAL-TIME, *IN SITU* POINT MONITORING BY ION TRAP MASS SPECTROMETRY

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Instrumentation based on the Finnigan Ion Trap Detector is being developed at Los Alamos National Laboratory for real-time, *in situ* point monitoring of organics in soil. The first application of this instrument is the characterization of the vapor phase subsurface transport of volatile organics at chemical waste sites. Three compounds have been targeted for initial demonstrations--trichloroethylene, benzene, and phenol. This paper will describe (1) the operating principles of the ion trap and its advantages over conventional quadrupole mass analyzers; (2) modification of the instrument and sampling systems for the detection of organics in air, soil, and water; and (3) the development of an intelligent, turn-key operating system. The potential of this instrumentation for air-quality monitoring and the analysis of volatile organics in water will also be discussed.

The sensitivity of the ion trap detector has been determined for a variety of compounds to assess its suitability for environmental monitoring applications. An exponential dilution method was used to determine the detection limits for trace organic vapors in air. This is a dynamic calibration where a known concentration of organic vapor in a calibrated volume is continuously diluted by a constant flow of air to the vessel. Detection limits have also been determined with standards prepared using calibrated permeation tubes.

Two gas-sampling systems for the ion trap detector have been evaluated. The first is the direct sampling of gases at atmospheric pressure through a leak valve. Using this method, the limits of detection for most organic compounds approach 1 part-per-million. For environmental monitoring, lower detection limits are achieved by replacing the leak valve with a silicon membrane to provide an enrichment of the organic vapors over permanent atmospheric gases with a concomitant lowering in detection limits. Detection limits with membrane sampling are typically in the low part-per-billion range. Sampling modules for soil and water analyses have been developed and can be used with a small Tenax pre-concentration device. These sampling modules are readily interchangeable and provide versatility without sacrificing performance.

The instrument is fully computer controlled and has been designed to automate instrument calibration, data acquisition, and data analysis and to produce a hard-copy analytical report at the time of analysis. The turn-key operating system allows the instrument to be set-up by minimally trained personnel and to continuously operate in an unattended mode.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF GAS MIXTURES USING FOURIER TRANSFORM INFRARED SPECTROSCOPY*

Jack C. Demirgian and Mitchell D. Erickson

The capability to qualitatively and quantitatively characterize vapor mixtures rapidly is essential in limiting health and environmental damage in the event of leaks or spills by toxic substances. This capability is also useful in site assessment or monitoring. This presentation describes a monitoring method, Fourier transform infrared spectroscopy (FTIR), which is both transportable and can provide qualitative and quantitative analysis of target components in vapor phase mixtures in less than two minutes. Current methods used for vapor phase analysis require application of a sampling train followed by instrumental analysis, such as gas chromatography or mass spectroscopy. Although accurate, most of these methods require extensive sample preparation and analysis that is both expensive and time consuming.

Because of advances in instrumentation, cell design, and software, it is now possible to use FTIR for the characterization of vapor phase components. Although infrared spectroscopy was first used over 20 years ago to identify vapor phase components, it is only now, based upon these advances, that vapor samples for multiple components can be qualitatively and quantitatively characterized at parts per billion levels.

At Argonne National Laboratory, we have demonstrated that, through the combination of a variable pathlength cell, FTIR, and analytical software, target organic components can be quantitatively and qualitatively measured in gas mixtures. The entire method can be automated and results obtained within two minutes. The instrumentation and method will be discussed.

The advantage of the method is real-time results at low cost. Measurement sensitivity can be adjusted to the concentrations encountered by varying the cell pathlength. We have demonstrated a linear range of 125 to 290,000 ppb for carbon tetrachloride using a 1.2- to 7.2-m variable pathlength cell. Enhanced sensitivity is possible with longer pathlength cells. Calibration is straightforward, with only a single calibration point required.

The methodology described is applicable to a broad range of assessment and monitoring problems. Potential applications include monitoring incinerator stack gas, detecting underground leaks, determining the location of spills, characterizing hazardous waste sites, and monitoring munitions disposal.

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Development of Analytical Methods for Military-Unique Compounds

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INTRODUCTION

One of the Army's major environmental problems is the contamination of soil and water with residues of explosives and propellants at many military facilities. This contamination occurred during the disposal of wastewater from production and load-and-pack operations, burning or detonation of off-specification material, and demilitarization of out-of-date explosives. To monitor these sites, analytical methods are required to detect and quantify these military-unique compounds in environmental matrices. Under the auspices of the U.S. Army Toxic and Hazardous Materials Agency (THAMA), the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) has been charged with developing methods for the determination of explosives and propellants in environmental samples. These methods are to be used in two major Army environmental programs: the Installation Restoration Program (IRP) and the Defense Environmental Restoration Account (DERA).

For an analytical method to be acceptable, certain requirements must be met:

1. It must have detection limits sufficiently low to satisfy current and future monitoring requirements.

2. It must be rapid to enable quick remedial action if levels are in violation of discharge permits.

3. It should be precise and accurate so that the extent of contamination can be characterized using a minimum number of replicates.

4. It should be free of interferences from common contaminants in AAP (Army ammunition plant) waste streams, including decomposition products and impurities commonly found in the munitions.

5. It should allow the simultaneous analysis of analytes that often occur together due to the types of formulations typically used in explosives production.

6. It should be as inexpensive as possible to implement, on both an initial capital cost and a per sample basis.

An analytical approach that has allowed us to meet the above criteria for a number of applications is reversed-phase high-performance liquid chromatography (RP-HPLC) (Figure 1). Through the proper choice of a column and eluent combination, interferences can be minimized and simultaneous analysis of several compounds is possible. RP-

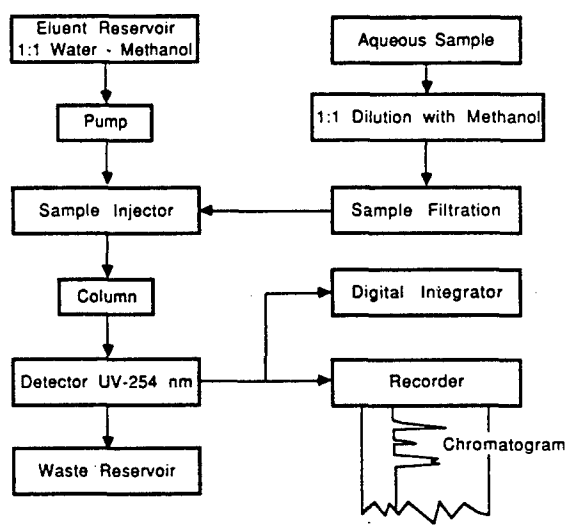


Figure 1. Diagram of RP-HPLC protocol.

HPLC equipment is standard in most analytical laboratories, thereby eliminating a large initial capital cost in order to implement the method. In addition, thermally unstable compounds, such as explosives and propellants, may be accurately measured since separations are achieved in solution at ambient temperature. Using UV detection, detection limits at the low µg/L level for water samples and below 1 µg/g for soil samples have been achieved.

To date CRREL has developed methods for a number of explosives and propellants including nitroaromatics, nitramines, tetrazene, and nitroguanidine in soil and water. This report will summarize the highlights of the method development for these analytes. Figure 2 shows the chemical structures of these compounds and Tables 1–6 outline the steps for each method. Methods are being developed for other analytes such as nitroglycerin (NG), pentaerythritol tetranitrate (PETN), and nitrocellulose (NC). In addition, a method for nitroaromatics and nitramines in plant tissue is currently under development.

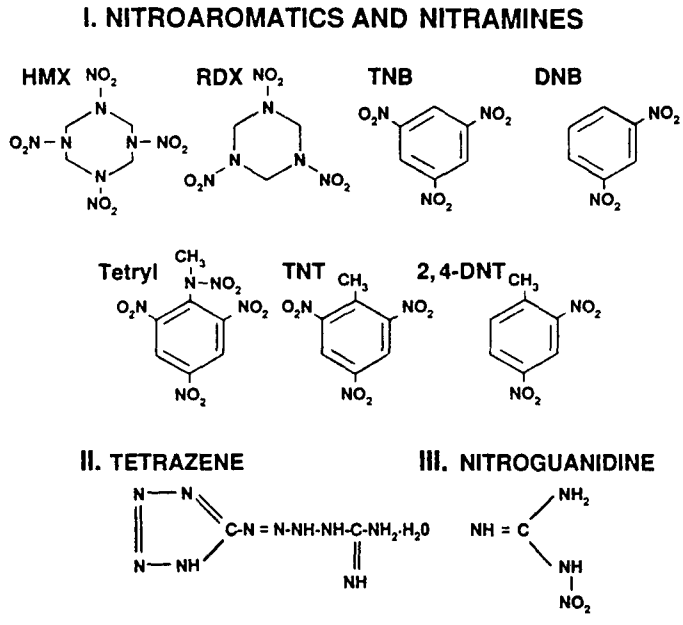


Figure 2. Chemical structures.

NITROAROMATICS AND NITRAMINES

Available Methods

The first step in the development of an analytical method for nitroaromatics (TNT, DNT, TNB, DNB) and nitramines (HMX, RDX, tetryl) was to search the literature for methods that had been reported. In addition, site visits were made to five AAPs and several government laboratories that had extensive experience with these types of analytes. The following types of methods have been used for trace analysis: direct colorimetric analysis; thin-layer chromatography; gas chromatography using various detectors (ECD, PID, FID); and high-performance liquid chromatography, both normal and reversed phase, with electrochemical or UV detection. Jenkins et al. (1984) discuss the advantages and disadvantages of these various methods. As stated above, RP-HPLC was found to be most suited to the analysis of explosives in environmental samples. Methods similar to the one described here for determination in soil have been developed at the U.S. Army Environmental Hygiene Agency (Bongiovanni et al. 1984) and at the U.S. Army Medical Bioengineering Research and Development Laboratory (Brueggemann 1986).

Extraction

To analyze for an organic chemical residue in soil by liquid chromatography, the analyte of interest must first be solvent extracted. As reported by Jenkins and Grant (1987), two solvents, acetonitrile and methanol, and four extraction procedures, Soxhlet, ultrasonic bath, mechanical shaker, and homogenizer-sonicator were compared. Acetonitrile was found to be a superior extracting solvent, particularly for RDX and HMX. The ultrasonic bath recovered more analyte than the homogenizer-sonicator or shaker, and allowed far greater sample throughput than the Soxhlet. Kinetic studies with field-contaminated soils (Jenkins and Walsh 1987) showed that a minimum of 18 hr was required to achieve complete extraction of these analytes using acetonitrile and the sonic bath approach.

An extraction step is not required for water samples analyzed by RP-HPLC. However, the method (Table 1) requires that water samples be mixed with methanol to prevent analyte loss during filtration (Jenkins et al. 1987, Walsh et al. 1988).

Testing RP Columns and Eluents

Once the explosive residue is dissolved in a suitable solvent, the identity and concentration of the individual analytes can be determined. Several RP columns were tested with a variety of eluents (Jenkins et al. 1984, Jenkins and Walsh 1987). Ideally, the principal analytes (HMX, RDX, TNB, DNB, tetryl, TNT and DNT) are resolved from each other and from potential interferences such as SEX, TAX, cyclohexanone, the aminodinitrotoluenes and diaminonitrotoluene, and nitrobenzene.

Two analytical columns were chosen. The primary analytical column is an LC-18 for quantitative analysis, and the confirmatory column is an LC-CN. Both columns are eluted with 1/1 v/v methanol–water (Tables 1 and 2). Figure 3 shows the separations achieved by these analytical columns.

Table 1: Method steps for the determination of nitroaromatics and nitramines in water.

1. Dilute 1:1 with methanol.
2. Filter through 0.5 µm Millex SR membrane.
3. RP-HPLC determination
   - Column: LC-18 (LC-CN)
   - Eluent: 1:1 methanol:water
   - Detector: UV-254 nm

Table 2: Method steps for the determination of nitroaromatics and nitramines in soil.

1. Air dry soil, grind with mortar and pestle.
2. Extract 2-g portion with 10 mL of acetonitrile in sonic bath for 18 hr.
3. Dilute 1:1 with aqueous (5 g/L) $CaCl^2$ solution.
4. Filter through 0.5 µm Millex SR membrane.
5. RP-HPLC determination
   - Column: LC-18 (LC-CN)
   - Eluent: 1:1 methanol:water
   - Detector: UV-254 nm

Table 3. Method steps for the determination of tetrazene in water.

1. Filter chilled samples through 0.45 µm Millex HV membrane.
2. Ion-pairing RP-HPLC determination
   - Column: LC-18
   - Eluent: 2:3 methanol:water
     0.01 M concentration of 1-decanesulfonic acid, sodium salt
     pH 3 (glacial acetic acid)
   - Detector: UV-280 nm

Table 4. Method steps for the determination of tetrazene in soil.

1. Extract 2-g portions with 50 mL of 55:45 methanol:water, and 0.01 M concentration of 1-decanesulfonic acid, sodium salt on a platform shaker for 5 hr.
2. Filter samples through 0.5 µm Millex SR membrane.
3. Ion-pairing RP-HPLC determination
   - Column: LC-18
   - Eluent: 2:3 methanol:water
     0.01 M 1-decanesulfonic acid, sodium salt
     pH 3 (glacial acetic acid)

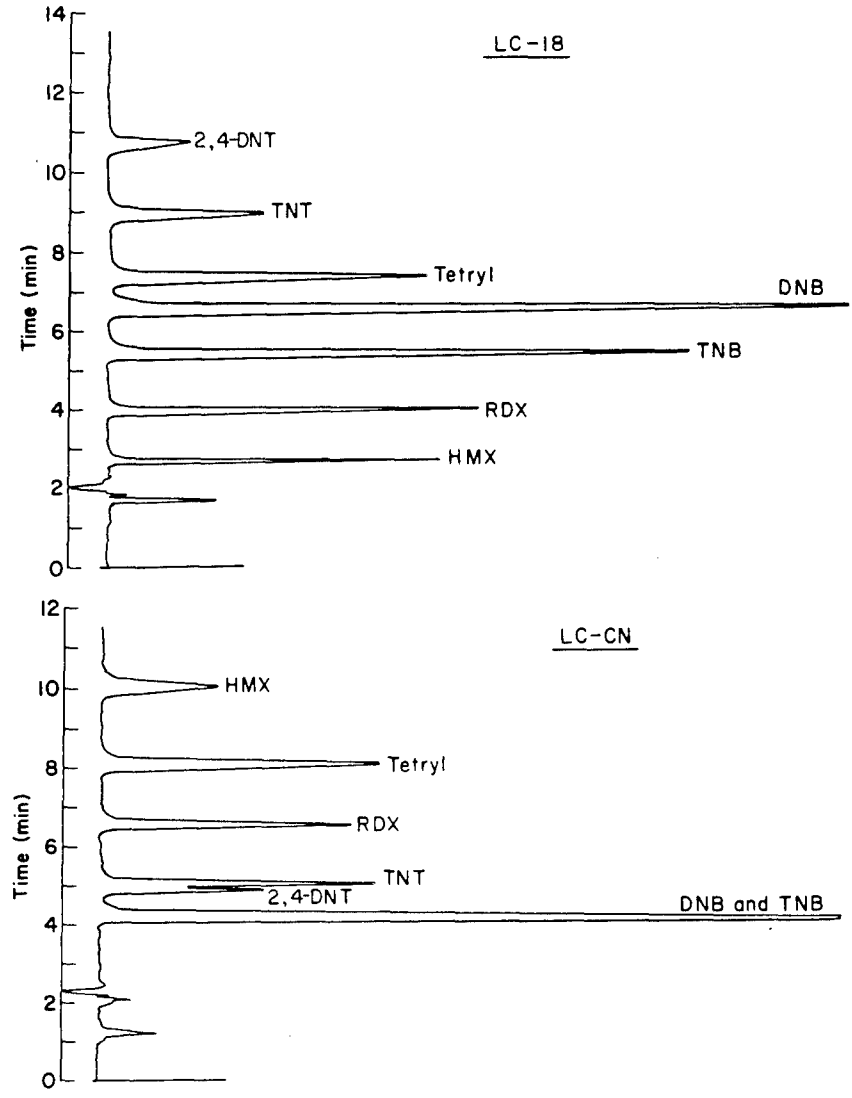


Figure 3. Chromatograms of standards.

Table 5. Method steps for the determination of nitroguanidine in water.

1. Filter through 0.45 µm Millex HV membrane.

2. RP-HPLC determination
   Column: Mixed-Mode RP18/cation exchange
   Eluent: Water
   Detector: UV-263 nm

Table 6. Method steps for the determination of nitroguanidine in soil.

1. Air dry soil, grind with mortar and pestle.

2. Extract 2-g portion with 50-mL of water in sonic bath for 2 hr.

3. Filter through 0.45 µm Millex HV membrane.

4. RP-HPLC determination
   Column: Mixed-Mode RP18/cation exchange
   Eluent: Water
   Detector: UV-263 nm

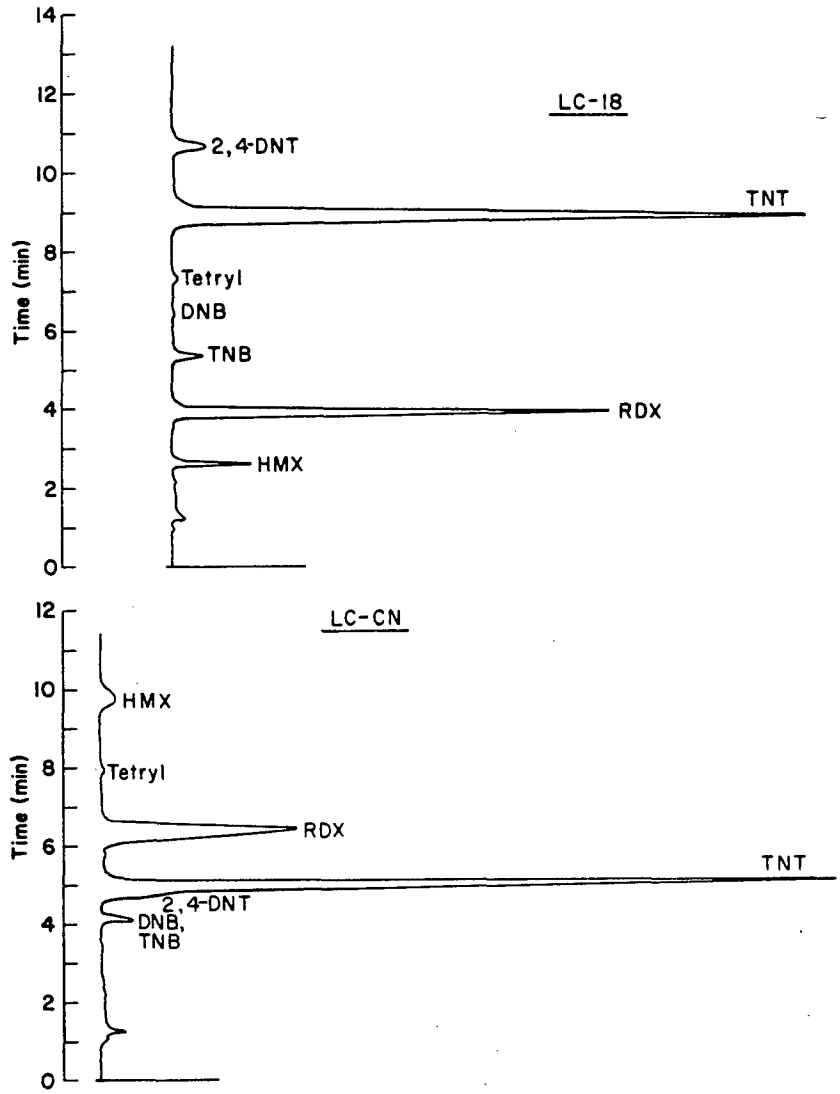


Figure 4. Chromatograms of soil extract.

Method Testing Using Field Contaminated Soils

To see if the soil method performed satisfactorily with a wide variety of soils, samples collected at Army sites from over 10 states have been extracted and analyzed. Figure 4 shows typical chromatograms obtained with real samples. No major interferences have been found.

Two soils, one from Louisiana and the other from Iowa, were used to study the photodegradation of munitions associated with soil (Jenkins et al. 1988). Loss of TNT was demonstrated for both soils and averaged about 10% over a period of 7 days when the soils were exposed to direct sunlight and the surface was refreshed frequently to maximize exposure.

Field-contaminated soils from Louisiana and Iowa AAPs were also used to test if the extraction efficiency was affected by soil to solvent ratio. Three volumes of solvent (10, 25, and 50 mL) were used to extract individual 2-g soil subsamples (Jenkins et al. 1988). Provided that solubility was not exceeded, a 2-g soil sample and a 10-mL aliquot of solvent were recommended to minimize detection limits.

The stability of soil extracts was measured to determine how long extracts could be held prior to analysis. Soils from Milan AAP, Louisiana AAP, Iowa AAP, and Nebraska AAP were used for the study. Extracts were stored at 4°C in the dark for 3, 6, 18, 27, and 71 days. HMX, RDX, DNB and TNT were found to be stable over the entire 71-day testing period (Jenkins et al. 1988).

Establishment of Performance Criteria Using Fortified Water and Soils

Spiked water and soil samples were analyzed to establish certified reporting limits, analytical precision, and method accuracy (Jenkins et al. 1984, 1988, in press). Results are presented in Tables 7 and 8.

Table 7. Performance criteria for water methods.

Analyte	Reporting Limit (µg/L)	Precision (µg/L)	Accuracy (% Recovery)
HMX	13	4.7	98.1
RDX	14	4.7	99.4
TNB	7.3	2.1	95.3
DNB	4.0	1.6	97.7
Tetryl	44	19	96.7
TNT	6.9	2.0	99.7
2,4-DNT	5.7	1.7	100
Tetrazene	3.0	0.87	98.3
Nitroguanidine	4.6	1.9	106

Table 8. Performance criteria for soil methods.

Analyte	Reporting Limit (µg/g)	Precision (µg/g)	Accuracy (% Recovery)
HMX	2.15	0.57	96.4
RDX	1.03	0.19	95.9
TNB	0.24	0.089	96.9
DNB	0.12	0.043	96.6
Tetryl	0.65	0.032	97.1
TNT	0.24	0.13	98.2
2,4-DNT	0.07	0.012	98.3
Tetrazene	1.1	0.22	68-88
Nitroguanidine	0.46	0.14	97.9

Stability of Standard Solutions

Stock solutions prepared in either methanol or acetonitrile were found to be stable over a period of 19 months. These standards were stored in glass at 4°C in the dark with the stoppered joints wrapped in Parafilm to reduce solvent evaporation. The stability of diluted working standards was also studied over an 8-day period and found to be stable over this period (Jenkins et al. 1988).

Ruggedness Testing for Soil Method

Four factors that could potentially affect method performance and might be varied by individual analysts were identified and tested. These four factors were particle size, vortex mixing prior to extraction, concentration of aqueous $CaCl_2$ added for flocculation of acetonitrile extracts, and settling time allowed for flocculation. Two field contaminated soils were used, one from Iowa

and the second from Nebraska. Detailed results are discussed in Jenkins et al. (1988). The method was found to be quite rugged with respect to minor changes in these procedural steps.

Collaborative Test

A full-scale collaborative test was conducted to obtain estimates of accuracy and intra- and interlaboratory precision (Tables 9 and 10) (Bauer et al. in press). Duplicates of four real contaminated soils and four spiked soils were blindly analyzed by eight participating laboratories. Overall, the method appeared to give quite reproducible results over the concentration ranges tested. The results of the test are being submitted to the Association of Official Analytical Chemists (AOAC) for consideration as the standard method for this determination.

Table 9. Results of collaborative test. Accuracy.

Analyte	Accuracy (% Recovery)
HMX	95.7
RDX	95.0
TNB	92.4
DNB	93.6
Tetryl	69.6
TNT	90.4
2,4-DNT	95.7

Table 10. Results of collaborative test. Intra- and interlaboratory precison.

	Precision (%RSD)			
	Repeatability*		Reproducibility#	
Analyte	Spiked	Field	Spiked	Field
HMX	7.4	22.1	20.8	34.5
RDX	4.2	8.2	16.6	16.4
TNB	6.4	20.0	9.4	28.6
DNB	5.4	42.0	7.7	45.2
Tetryl	18.7	13.4	47.3	37.4
TNT	4.4	16.0	16.8	18.4
2,4-DNT	3.7	47.0	4.6	73.0

*Intralaboratory Precision
#Interlaboratory Precision

TETRAZENE

Available Methods

Most of the published analytical methods for tetrazene were developed for monitoring product quality of primer mixes or caps since these mixtures must contain 2–8% tetrazene by weight to be activated by friction or impact. Published quantitative methods for the determination of tetrazene in primer mixes are outlined in Walsh and Jenkins (1988) and include polarographic, spectrophotometric, and thermoanalytical protocols. These techniques are prone to interferences and are therefore inappropriate for environmental determinations. CRREL developed the first chromatographic method for the analysis of tetrazene in environmental samples (Walsh and Jenkins 1987, 1988a, 1988b). The steps involved in these methods for soil and water samples are listed in Tables 3 and 4.

Extraction

Two characteristics of tetrazene make analysis difficult: it is thermally unstable in solution, even at room temperature, and it has limited solubility in water and most common organic solvents. Preliminary tests indicated that tetrazene is practically insoluble in acetonitrile and tetrahydrofuran and it is insoluble in acetone. Solubility in methanol was estimated to be 240 mg/L.

Extraction kinetic studies using spiked soils showed that maximum analyte recovery was acheived with a mixed extracting solvent (Walsh and Jenkins 1988b). This solvent was 55/45 v/v methanol–water with 1-decanesulfonic acid sodium salt at a 0.01 M concentration. During extraction the soils were dispersed by 15 s of vortex mixing and 5 hr of shaking on a platform orbital shaker.

Testing RP Columns and Eluents

Several RP columns were tested. However, when the mobile phase consisted of a combination of water and an organic solvent such as methanol, tetrazene eluted too rapidly to effect adequate separation from common components of water and soil. An LC-18 column eluted with 100% water produced a tetrazene retention time of 6.3 minutes. However, peak shape was poor and HMX and RDX had retention times of 31.5 and 47 minutes, respectively. The very long run times for samples where these components were present would be unacceptable. Ideally, the column/eluent combination should elute tetrazene without interference and elute other potential contaminants within a reasonable run time. While gradient elution could minimize this problem, equilibration time between runs would significantly decrease daily sample throughput, and not all HPLC systems are equipped to do gradient elution.

Thus, an ion-pairing technique was tested to determine if the retention time of tetrazene could be increased while still using a methanol–water eluent that would shorten overall run times. The ion-pairing reagent selected was 1-decanesulfonic acid sodium salt at an eluent concentration of 0.01 M. The pH of the mobile phase was adjusted with glacial acetic acid to ensure complete ionization of tetrazene. Retention time for tetrazene was 2.8 minutes using an eluent composed of 2/3 v/v methanol–water, 0.01 molar ion-pairing reagent at pH 3. Retention times for HMX, RDX and TNT were 3.6, 6.0, and 12.9 minutes, respectively. Figure 5 shows a typical chromatogram under these analytical conditions.

Establishment of Performance Criteria Using Fortified Water and Soils

Certified reporting limits, analytical precision, and method accuracy were established using spiked water and soil samples (Walsh and Jenkins 1987, 1988). Results are presented in Tables 7 and 8.

Stability of Standard Solutions

In the initial phase of this study, we observed that solutions of tetrazene in water or methanol were unstable over time. Before quantitative analyses could be performed, calibration standards and aqueous samples had to be stabilized. Degradation was minimized by keeping solutions at 4°C. Concentrations over 24 hr decreased by only 3% for chilled aqueous samples as opposed to 96–100% for room-temperature samples. Degradation of tetrazene was slower in methanol than in aqueous solutions. Response declined by 1% and 55% for chilled and room-temperature methanol samples, respectively, in a 24-hr period.

Because of this thermal instability, samples must be kept refrigerated prior to analysis, and analyzed as soon as possible after collection.

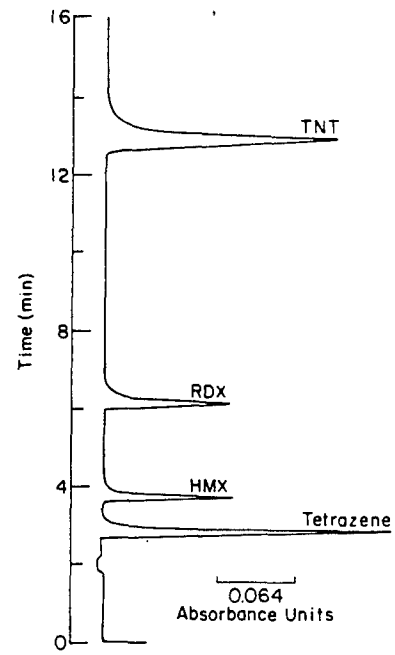


Figure 5. Typical chromatogram showing separation of tetrazene from other explosives.

NITROGUANIDINE

Available Methods

Nitroguanidine ($HN=C(NH_2)NHNO_2$) is a component, along with nitroglycerin and nitrocellulose, of triple base propellant. Its relatively high solubility in water (4.4 g/L) increases the likelihood of groundwater contamination when water is used to clean cutting blades and wash out buildings where triple base propellant is produced.

Nitroguanidine's physical and chemical characteristics preclude analysis by gas chromatography, but several liquid chromatographic methods have been developed using both UV and electrochemical detection. Most of these methods use a reversed-phase C8 or C18 column (Walsh in prep.) eluted with a mobile phase that is predominantly water. Nitroguanidine is not well retained on these columns and elutes early, making interferences likely when environmental samples are analyzed. One method (THAMA) used a cation exchange column eluted with a borate solution following extraction of soils with warm ethanol/water. CRREL developed HPLC methods for the analysis of nitroguandine in soil and water samples (Tables 5 and 6). Separation is achieved by using a mixed mode RP18/cation exchange column. A typical chromatogram is shown in Figure 6.

Extraction

Because nitroguanidine (NQ) is far more soluble in water than in methanol or acetonitrile, water was used to extract soil samples. To determine the length of time required to extract nitroguanidine from soil, a kinetic study was performed. Field-contaminated soils were not available for analysis. Therefore, some samples of USATHAMA Standard Soil were contaminated in the laboratory by adding 1.0 mL of a 2.0-mg/L aqueous NQ solution to 2-g subsamples of soil. The NQ concentration in the soil was thus 1 µg/g. Then, to thoroughly dry the soil and to hasten any interaction between the nitroguanidine and the soil constituents, the soil samples were baked at 50°C for 30 hr and then air-dried for 56 hr. An unspiked soil was treated in the same manner. The soil samples were extracted with 50.0 mL of water by vortexing for 30 s and sonicating. Results indicated that 2 hr of sonication was required for complete recovery. Sonication longer than 4 hr resulted in the extraction of compounds that interfered with nitroguanidine determination.

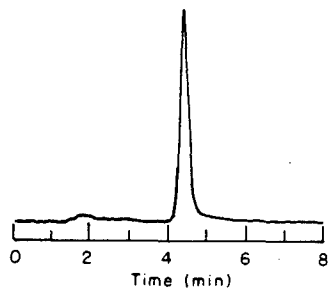


Figure 6. Chromotogram of nitroguanidine standard.

Testing RP Columns and Eluents

Three analytical columns were tested during the method development. These columns included a reversed phase LC-18 (Supelco), a cation exchange LC-SCX (Supelco), and a Mixed Mode RP18/Cation (Alltech Associates). Since the Mixed Mode column resulted in the longest retention time, it was chosen as the analytical column for this study. A longer retention time is desirable to avoid interferences from the early eluting compounds that are commonly found in environmental samples.

Establishment of Performance Criteria Using Fortified Water and Soils

Certified reporting limits, analytical precision, and method accuracy were established using spiked water and soil samples (Walsh in prep). Results are presented in Tables 7 and 8.

Stability of Standard Solutions

Standard solutions were prepared in water and were found to be stable for at least 6 months when stored at 4°C in the dark.

CONCLUSIONS

RP-HPLC analytical methods were developed to determine trace levels of nitroaromatics, nitramines, tetrazene, and nitroguanidine in soil and water. The method to determine nitroaromatics and nitramines in soil has been thoroughly tested with soils from a wide variety of sites, and it has been found to be reliable and inexpensive to implement. A full-scale collaborative test proved that acceptable performance criteria were attainable in everyday use. Methods for tetrazene and nitroguanidine have not been evaluated by a full-scale collaborative test because few areas need to be tested for contamination by these compounds.

Methods will continue to be developed at CRREL as the need arises for other military-unique compounds.

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On-Site Biological Monitoring and Hazard Assessment at Army Sites

By

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Clean-Up Costs and Toxicity

- Higher toxicity estimates lead to higher clean-up costs
- Toxicity estimates based on chemical analyses alone can be overly conservative
- Direct toxicity measurements can provide better indications of potential toxic effects
- There is precedence for regulatory acceptance of on-site toxicity tests

Toxicity Estimation Approach

- Use non-mammalian models to estimate human health and environmental effects
- Use a tiered testing approach - screening, then definitive
- Conduct on-site assessments

On-Site Biomonitoring

- Test systems contained in a mobile biomonitoring facility
- Water or wastewater supplied continuously
- Use aquatic organisms to monitor:
  - ★ Acute toxicity
  - ★ Carcinogenicity
  - ★ Developmental toxicity
  - ★ Aquatic ecosystem effects

Study Objectives

- Establish biomonitoring facility at an Army wastewater treatment plant
- Monitor effluent for carcinogenicity; also determine chemical composition and mutagenicity using standard procedures
- Test response and sensitivity of an automated acute toxicity monitoring system using a simulated spill of 1,3,5-trinitrobenzene (TNB)

Standard On-Site Evaluations

- Aquatic toxicity
  - ★ Effluent - fathead minnow and Ceriodaphnia 7 day tests
  - ★ TNB - bluegill 96 hour acute test
- Effluent mutagenicity - Ames tests
  - ★ Two strains
  - ★ With/without XAD-2 resin concentration
  - ★ With/without metabolic activiation
- Chemical analyses

Results - Effluent Analyses

- Chemical evaluation: Chloroform- 10 ug/l, Bromodichloromethane- 9.5 ug/l
- Ceriodaphnia and fathead minnow 7 day tests: no toxicity
- Ames mutagenicity tests

SAMPLE	STRAIN	METABOLIC ACTIVATION	MUTAGENICITY
Whole Effluent	TA-98	no	-
	TA-100	no	-
	TA-98	yes	-
	TA-100	yes	-
Effluent Extract	TA-98	no	+/-
	TA-100	no	-
	TA-98	yes	+
	TA-100	yes	-

Acute Toxicity Monitoring System

- Ventilatory and movement patterns of 27 bluegills monitored continuously by computer
- Test protocol:
  - ★ TNB concentrations: 0, 0.05, 0.17, 0.56 mg/L
  - ★ Number of fish: 6 or 7 per concentration
  - ★ Test periods: acclimation (3 day)
    baseline (4 day)
    test period (6 day)
  - ★ Data from each fish printed every 15 minutes

Results - TNB Acute Toxicity Tests

- TNB 96 hour LC50: 1.27 mg/L (0.87-1.85)
- Automated monitoring system results:

ENDPOINT	ABNORMAL 15 MINUTE RESPONSES (%) 0 MG/L	0.05	0.17	0.56
Ventilatory Rate	0.3	0	0	98.6
Ventilatory Depth	0	0	0	62.3
Cough Rate	0	0	0	98.6
Movement	0	0	0	0

Carcinogenicity Tests

- Test species - Medaka (Oryzias latipes); 21 days old, 50 fish per tank
- Treatments:
  - ★ Controls (two tanks, one pre-exposed to DEN)
  - ★ 100% effluent (two tanks, one pre-exposed to DEN)
  - ★ Tested on-site 13 weeks, held at lab 13 weeks

Survival and Growth of Medaka After 13 Weeks of Effluent Exposure

TREATMENT	CARCINOGEN-INITIATED	SURVIVAL (%)	MEAN (STD. DEV.) WEIGHT (G)	MEAN (STD. DEV.) LENGTH (MM)
Control	no	94	0.083 (0.047)	16.3 (3.25)
Control	yes	100	0.181 (0.050)	20.5 (5.35)
Effluent	no	74	0.049 (0.046)	12.9 (5.03)
Effluent	yes	94	0.138 (0.030)	19.4 (1.41)

Pathologic Findings in Medaka Livers After 13 Weeks of Effluent Exposure

TREATMENT	CARCINOGEN-INITIATED	DIFFUSE HEPATOCELLULAR VACUOLATION	FOCI OF CELLULAR ALTERATION	HEPATO-CELLULAR ADENOMA
Control	no	0/20	0/20	0/20
Control	yes	0/22	0/22	0/22
Effluent	no	3/15	0/15	1/15
Effluent	yes	17/23	2/23	2/23

Conclusions

- Two novel toxicity assessment techniques were incorporated into a mobile biomonitoring facility and tested at an Army wastewater treatment plant.
- An automated toxicity monitoring system rapidly detected a simulated spill of 0.56 mg/L TNB.
- A carcinogenicity assay using fish evaluated the potential of the effluent to act either as a complete carcinogen or as a carcinogen promoter.
- On-site assessment techniques can provide direct and useful evaluations of the toxicity of potentially contaminated water and wastewater at Army facilities.

Future Research

- Additional tests: developmental toxicity, aquatic microcosm, immunotoxicity, neurotoxicity.
- Further validation of the acute toxicity and carcinogenicity tests.
- On-site testing of effluent and groundwater at a second Army site.

DECREASING SAMPLING COSTS BY INCREASING STATISTICAL EFFICIENCY THROUGH GEOSTATISTICS: A CASE STUDY[a]

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ABSTRACT

The INEL (Idaho National Engineering Laboratory) conducted a post-mortem examination of a dioxin cleanup study having a data base of over 2,000 sampling points. The result of the post-mortem study was that approximately 60% of the sampling and analysis budget could have been saved, had geostatistics been used in the sampling design. Additionally, the final product of the sampling plan would have had greater utility at the site closure negotiations because of the reliability map uniquely generated through a technique known as "kriging." We feel that kriging is an important cost saving tool which should be utilized more often in Installation Restoration Program (IRP) work. Directional variograms showing data anisotropy and sample planning information are shown. Maps delineating the dioxin isopleths and areal variances are also presented.

INTRODUCTION

At the beginning of the 1988 fiscal year the Department of Energy, Idaho Operations Office (DOE-ID) provided its prime contractor (EG&G Idaho, Inc.) at the Idaho National Engineering Laboratory (INEL) funds to bring a new type of data analysis capability to INEL. The geostatistical technique of creating isopleths, "kriging," is of interest to the INEL because of the current extent of INEL's involvement in RCRA/CERCLA remedial investigation studies.

Geostatistics refers to a set of statistical procedures for describing the correlation of spatially distributed random variables and for performing interpolation and areal estimation for these variables. The fundamentals of geostatistics were developed by Krige, Sichel, and de Wijs in the 1950s to estimate ore reserves in the gold fields of South Africa (Cooper and Istok, 1988). Matheron in 1963 gave this empirical tool its theoretical basis through the theory of regionalized variables (Matheron, 1963).

Geostatistics is a potentially powerful tool for the analysis of environmental data. Barnes (1978) used the estimation technique known as kriging to map the distribution of four radioactive isotopes deposited on the Enewatak Atoll during nuclear weapons tests conducted there. Dioxin

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contamination has been studied in the past by Zirschky and Harris (1986). They used kriging to map a dioxin spill along a highway and to identify areas requiring remediation. Zirschky et al. (1985) also used kriging to analyze the distribution of dioxin-contaminated sediments in a stream. In those cases where kriging has been used in pollution control work, it has met with considerable favor (Mason, 1983).

THE GEOSTATISTIC PROCESS

A geostatistical analysis of data gathered at a study site can be divided into the following four steps:

1. Determine if the measured contaminant concentrations are additive and normally distributed. If the data are not additive and normally distributed, then massaging of the data either by transformations and/or outlier analysis may be called for. In environmental data, a log transformation will generally change the fit of the data distribution to a normal distribution (Figures 1 and 2).

2. Estimate the spatial correlation of pairs of measured concentrations as a function of distance (lag) and the direction of their separation (Figure 3). This step is known as the calculation of the experimental semivariogram.

3. In the structural analysis, a theoretical model is fitted to the experimental semivariogram. During this procedure (Delhomme, 1976) real sampling point data are deleted from the data set one at a time, while kriging is performed with the remaining sample values to estimate the deleted data point. Statistical analysis of the kriging errors (i.e., the differences between the kriging estimated values and the respective actual sample values for all sampled points) and the standardized mean-squared errors (i.e., the average of the kriging errors divided by their respective kriging variances) determine if there is a bias in the estimates, and if the estimation errors are consistent with the kriging variances. To be unbiased, the average kriging error must be close to zero (Table 1).

4. The fitted model is used in an interpolation procedure known as kriging (Figure 4). During this step, the kriging algorithm is used to generate expected values for nonmeasured data points and a map of variance at a study site.

GEOSTATISTIC ADVANTAGES

There are three distinct advantages associated with geostatistics:

1. Estimation techniques based on the theory of regionalized variables can be used to obtain the best (estimation error is minimized), linear (i.e., estimated concentrations are given by linear combinations of measured concentrations), unbiased estimates of concentrations at nonmeasured points within a data network. These kriged estimates can be used to generate an improved map of concentrations by providing more nodes, which would be used by a contouring program.

2. It is possible to evaluate the potential error of a data value at any one point because a map showing estimation error is also generated. Statistical confidence can be expressed for remedial action site cleanup and closure activities on an areal basis.

3. The estimation errors are useful in developing an optimized sampling design for future sampling and monitoring at the site. The semivariogram can be used to establish a representative autocorrelation distance (lag) for the contaminant of interest at a site (Flatman et al., 1988). Additionally, insight based on the estimation errors, is gained as to the optimum location of additional sampling points, or the removal of statistically inefficient sampling points.

It is the third advantage of geostatistics, sample planning, which this paper will focus on.

METHODS

To test the utility of geostatistics, we used data generated by an ongoing work-for-others project as a case study. The dioxin cleanup project was designed with a classical statistical grid approach (Crockett, A. B., 1988). The grid had been set on 20 x 20 foot spacing using a common method of determining a grid based on previous projects' coefficient of variances, factored with cost constraints (Mason, B., 1983).

The dioxin data set that was used contained just over 2,000 sampling points. The first step was to remove the negative, zeros and other ancillary data from the set. The trimmed data set contained 1,056 points. Normally, a data set must have 30 to 50 data points to be considered a viable candidate for kriging analysis (Grundy, 1988).

Once the data were evaluated for outliers and transcription errors, a test for normality using histograms and chi-square analysis was completed. The normality test showed the dioxin data were not normally distributed and the histogram suggested a log transformation should be attempted (Figure 1). The results of the log transformation (Figure 2) and the resulting chi-square test showed that the log transformed dioxin data set could be treated as a normally distributed data set.

In sample planning, the experimental semivariogram is used to describe the pattern of spatial correlation (autocorrelation) displayed by the data. Experimental semivariograms were established (Figure 3) after several iterations for the northeast-southwest direction, the southeast-northwest, the north-south, the east-west, and the all directions. All of the semivariograms were spherical with a nugget except for the north-south semivariogram, which was linear. The range of autocorrelation among the five semivariograms showed anisotropy to the N-S. Ranges varied from 65 feet in the E-W direction, to 110 feet in the NE-SW direction, to 130 feet in the SE-NW direction, to 120 feet to linearity in the N-S direction, to 90 feet in the all directions semivariogram.

The all directions semivariogram was cross-validated using the criteria given in Table 1. This established the validity of the semivariogram allowing the next step, kriging estimation, to take place.

The mapped results of the kriging are shown in Figure 4. The log isopleths show the preference for correlation in the north-south direction. This can be explained by the fact that there was a drainage ditch running down the center of the agent orange storage area in an east-west direction. The data are correlated because as leaks occurred in the barrels, the contents flowed either north or south to the drainage ditch. The variance isopleths map shows a low variance. This is the result of an intensive 20 x 20 foot grid, except in the northwest corner where the variance increases because a large portion of the data grid was removed as they represented analytical scatter (i.e., the data were zeros, and less than zero numbers).

SUMMARY

In the past, field sampling plans have been based on the assumption that the measured variable is random and independent throughout its range. At a spill site, however, data are usually correlated to the point source of the spill, and thereby autocorrelated. Ignoring this autocorrelation can invalidate basic statistics, statistical tests, and sampling procedures formulated for a variable with a random and independent distribution. If data are positively correlated, less statistical information per measurement is acquired than by data that are not correlated (Flatman, G. T., et al., 1988). More measurements are required, therefore, where data are spatially correlated to estimate a mean within a given accuracy and confidence using conventional, independent, random based statistics.

The use of geostatistics (kriging) via the semivariogram allows the sampling project leader to identify the extent of spatial autocorrelation (i.e., the range), and thereby establish a sampling grid interval, which is truly independent and therefore statistically efficient. Using the semivariograms obtained from the data, we were able to determine that the autocorrelation of the data would approach a minimum (sill) at 60-foot spacings in the E-W direction and at 180-foot spacings in the N-S direction. If a pilot study had been initiated at the site, it is conceivable that 60% of the sampling and analysis costs (approximately 3 million dollars) could have been saved by simply extending the grid spacing to 60 feet, with no loss in data quality.

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Table 1. CRITERIA TO JUDGE ACCEPTABILITY OF VARIOGRAM/DRIFT MODEL
(In no particular order of importance--USGS, 1988)

1. Average kriging error should be close to zero.

2. Root-mean-square error (standard deviation of the kriging errors) should be lower than the standard deviation of the regionalized variable.

3. Kriged reduced root-mean-square error (standard deviation of the standardized errors) should be close to unit [i.e., in interval 1 plus or minus 2*sqrt(2/N) (Delhomme, 1978, p. 258)]

4. The standardized errors should be independent of the kriged (estimated) values.

5. The standardized errors should be independent of their location as expressed by their X- and Y-coordinates.

6. The kriged value should be positively correlated with the observed value of the regionalized variable. The higher the correlation, the better, so long as the preceding criteria are met.

7. It is important for the final theoretical variogram model to closely approximate the overall appearance of the final observed variogram (after deletion of outlier values). Clark (1986) describes some of the pitfalls and problems in cross-validation. Pay special heed to her final paragraph on page 220. Also see Journel and Huijbregts, 1978, p. 167; p. 246.

Kriged Dioxin Data

VAR	COLUMN	MINIMUM	MAXIMUM	MEAN	DEVIATION	VALID	B	L	N	G	OTHER
1	X-COORD.	0.00E+00	1.560E+03	8.793E+02	3.9044E	+021056	0	0	0	0	0
2	Y-COORD.	0.00E+00	4.000E+02	1.762E+02	1.2206E	+021056	0	0	0	0	0
3	log t237	-1.000E+00	2.813E+00	4.044E-01	7.9338E	-011056	0	0	0	0	0
4	KRIG VAL	-9.221E-01	1.909E+00	4.253E-01	5.9840E	-011056	0	0	0	0	0
5	KRIG ERR	-1.528E+00	1.545E+00	-2.097E-02	4.6171E	-011056	0	0	0	0	0
6	KRGSTDEV	4.423E-01	6.860E-01	4.536E-01	1.8729E	-021056	0	0	0	0	0
7	ERR/STDV	-3.237E+00	3.272E+00	-3.979E-02	1.0100E	+001056	0	0	0	0	0

CORRELATIONS-COMPUTED USING ORIGINAL DATA

	1	2	3	4	5	6	7
1	1.00	.21	-.05	.08	.03	-.04	.03
2	.21	1.00	-.04	-.05	-.01	-.02	-.01
3	-.05	-.04	1.00	.82	.66	-.32	.66
4	-.08	-.05	.82	1.00	.11	-.30	.11
5	.03	-.01	.66	.11	1.00	-.16	1.00
6	-.04	-.02	-.32	-.30	-.16	1.00	-.15
7	.03	-.01	.66	.11	1.00	-.15	1.00

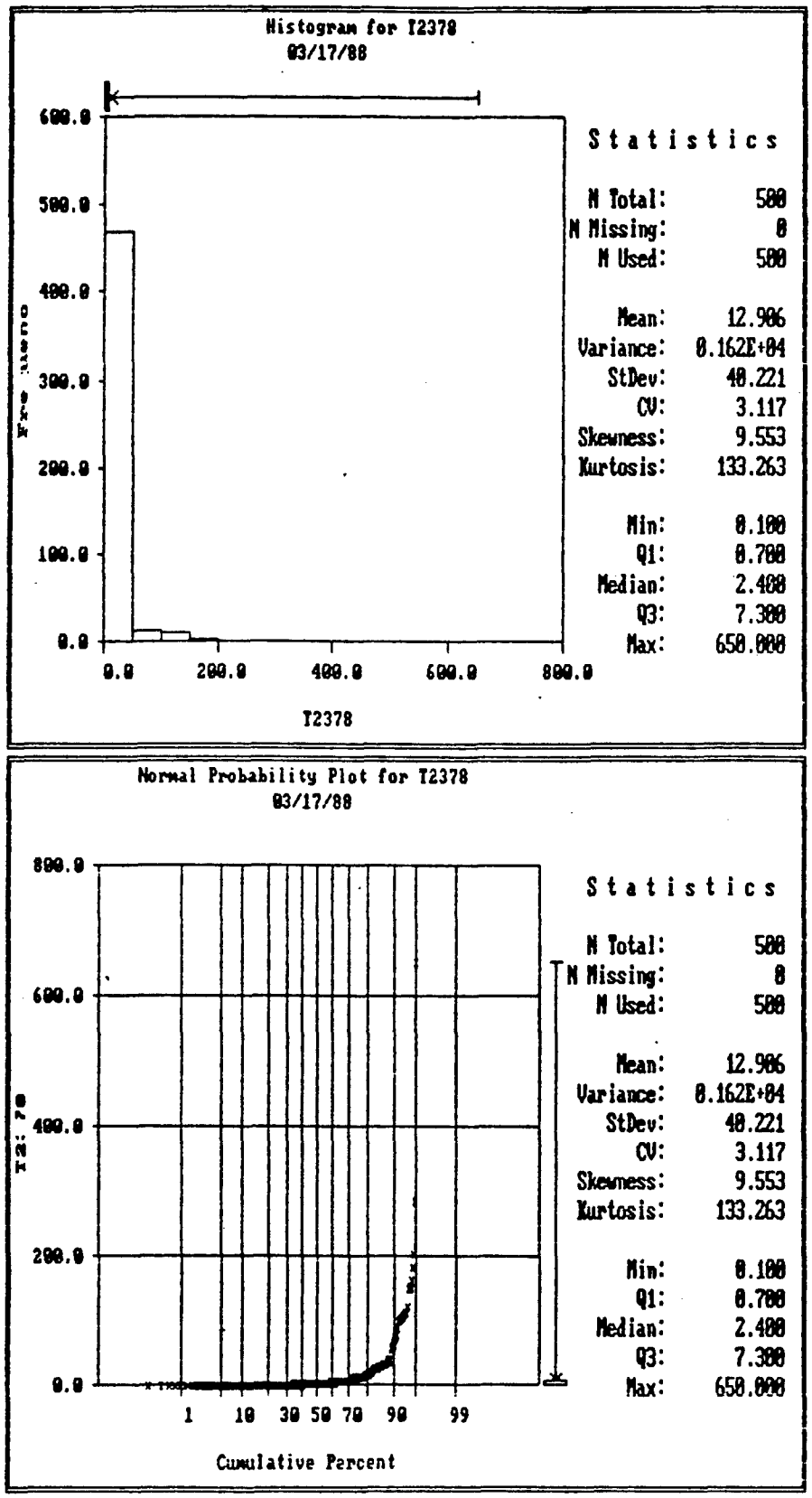


Figure 1. Normal dioxin datagraphs.

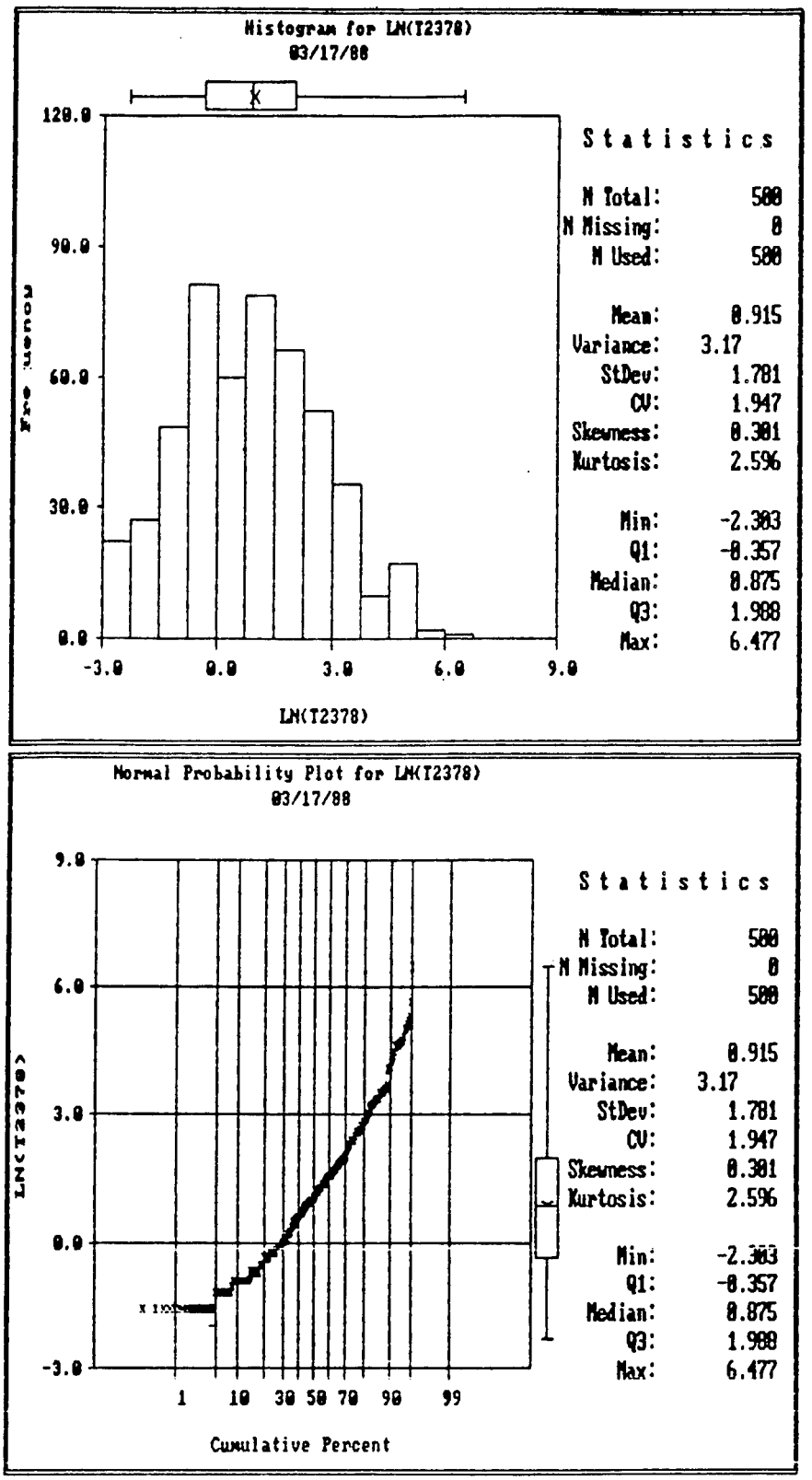


Figure 2. Log normal dioxin datagraphs.

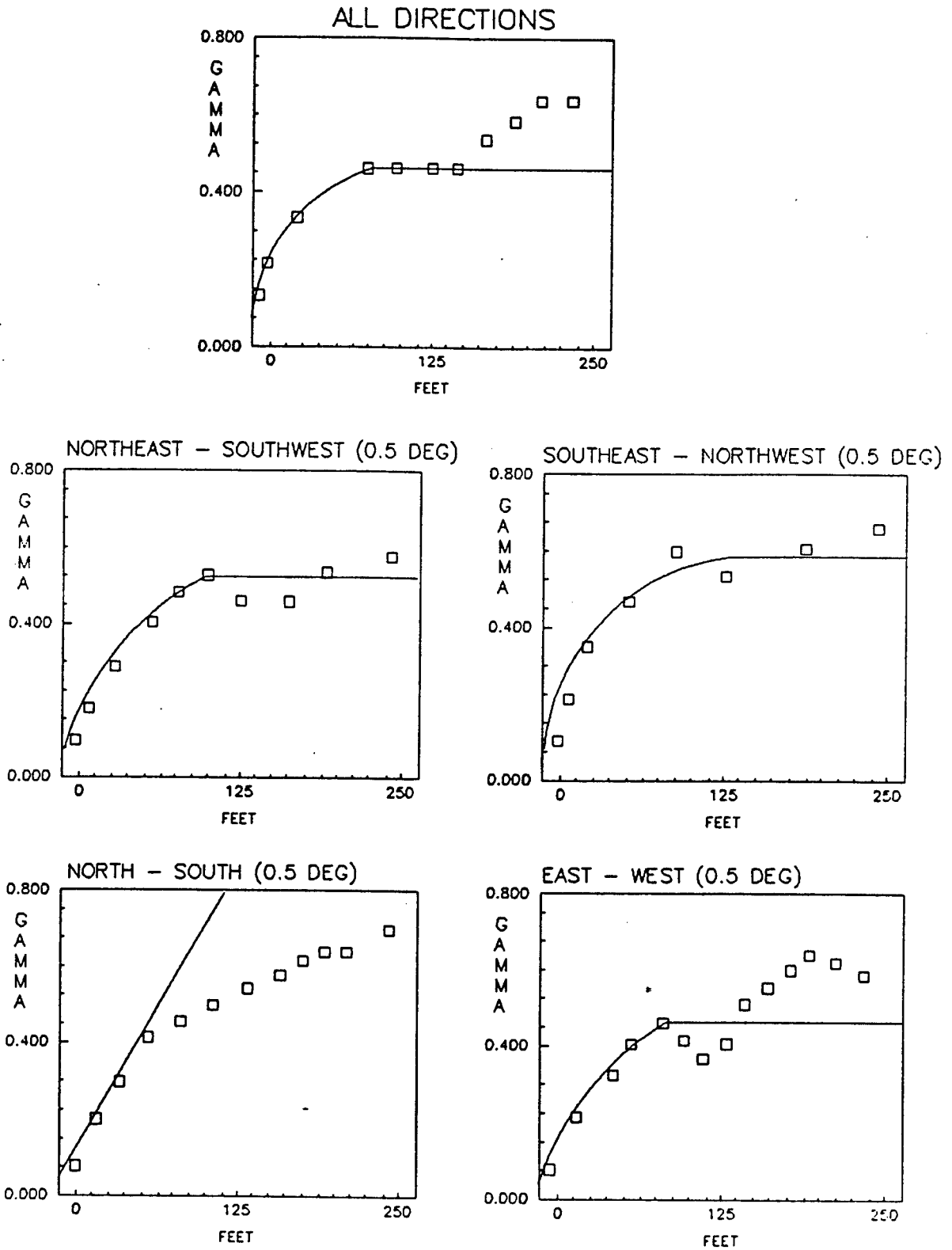


Figure 3. Semivariograms.

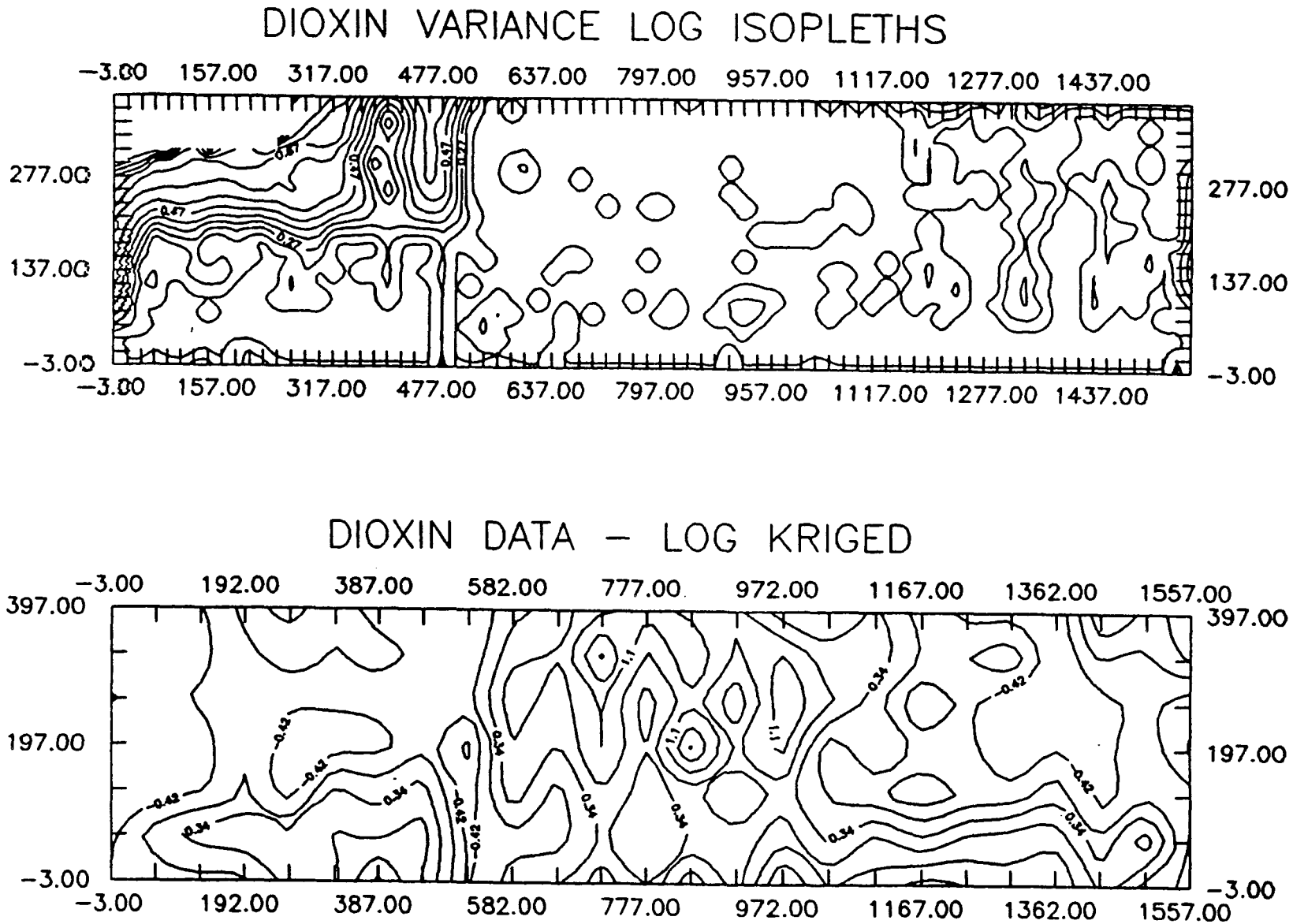


Figure 4. Kriging examples.

COMPARISON OF EPA AND USATHAMA DETECTION CAPABILITY ESTIMATORS

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INTRODUCTION

Reliable estimation of very low analyte concentrations in various sample types has commanded the attention of analytical chemists for many years. Terms such as detection limit, method detection limit, lower limit of reliable assay measurement, limit of quantitation, certified reporting limit, and many others have been introduced to describe this characteristic of analytical procedures. A recently published book (Currie 1988) contains an extensive literature review, historical information and descriptions of fundamentals and applications.

Achieving low concentration measurement capability is clearly required in many situations. However, specific requirements can vary widely and, therefore, a single experimental strategy is unlikely to meet all needs. An environmental survey of a potential toxic waste site usually dictates the need to quantitate over a wide concentration range. To plan an effective remedial program, high concentrations must be determined with reasonable accuracy. Simultaneously, concentrations at the regulatory or action level must be measured in order to define the geographic boundaries of contamination. Because calibration for many analyses is costly in both time and money, most laboratories attempt to satisfy both requirements with a single protocol. Not surprisingly, this requires some degree of compromise. The alternative would be to optimize each analysis by carefully matching with calibration data and consequently reducing the number of samples analyzed to keep costs manageable. Since sampling usually contributes the largest amount of uncertainty in environmental surveys, reducing sample numbers is an unattractive option.

The major point of the above discussion is to emphasize that detection capability is not a fundamental property of procedures, nor is it a constant. Instead it can be managed to a significant extent based on the experimental protocol (number of standards and blanks analyzed, distribution of standards, time span covered by standards measurements, number of repli-

cations of standards and unknowns, etc.). The risks chosen for statistical decisions also play a major role. While most detection limit definitions have provided protection only against false positives (Type I or α risks), there is increased recent emphasis on the need to protect against false negatives (Type II or β risks) (Currie 1988 and 1968, Hubaux and Vos 1970, Kirchmer 1983, Wernimont 1985, Clayton et al. 1987). Also receiving more attention of late is the difference between detection (qualitative) and quantitation (Crummett et al. 1980). Clearly, the levels of assurance chosen for specifying detection criteria will have a substantial impact on their magnitude.

Analytical precision is another major contributor to the size of these estimates; better precision means better low concentration measurement capability, other things being equal. Here again there is a complex relationship between precision estimates and the specific methodology, the experience and attitude of the analyst, the condition of the apparatus, and the laboratory cleanliness. In view of all this, it should not be surprising that reported estimates of detection and quantitation limits vary widely both between and within laboratories.

Two common estimates of low concentration measurement capability for environmental studies are 1) the method detection limit (MDL) specified by the U.S. Environmental Protection Agency (Glaser et al. 1981, Fed. Reg. 1984), and 2) the certified reporting limit (CRL) specified by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA 1987). At recent conferences (Maskarinec and Holladay 1987) and elsewhere, it has been suggested that these two procedures yield widely divergent estimates for the same analyses.

The purpose of this study is to examine this question by extracting such estimates from two extensive data sets. The first was the determination of 1,3-dinitrobenzene (DNB) by reversed-phase high performance liquid chromatography (RP-HPLC) (Jenkins et al. 1988) and the second was the determination of copper concentration by graphite furnace atomic absorption (GFAA). These methods were chosen because prior data showed that the precision of the DNB measurements was relatively constant in the concentration range used whereas that for Cu showed a regular dependence on concentration. Besides comparing MDL with CRL under identical experimental conditions, the program was designed to demonstrate the effects of variations in α and β risks and changes in experimental protocols.

THEORY

Method Detection Limit (MDL). The MDL is defined as the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte" (Fed. Reg. 1984). After estimating the MDL from instrumental responses and prior experience of the analyst, either reagent water or another sample matrix is spiked (if necessary) to give an analyte concentration that is 1 to 5 times the estimated MDL. A minimum of seven replicate aliquots are processed through the entire analytical procedure. If a blank is required, a separate blank measurement is obtained for each sample and the average blank measurement is subtracted from each sample measurement.

Computation of the estimated MDL is accomplished by multiplying the standard deviation of the replicate measurements by the appropriate one-sided t-value corresponding to n-1 degrees of freedom and a 99% confidence level. It is assumed that variances are reasonably homogeneous and that error distributions approximate a normal distribution in the region from the blank to five times the MDL. Although both of these assumptions are frequently violated to a small extent, the error produced is usually acceptable when compared to overall uncertainties. No allowance is made in the MDL estimate for any error contribution by the blank. It is also important to note that while the risk of false positives is only 1% ($\alpha = 0.01$), the risk of false negatives is 50% ($\beta = 0.50$) for a sample with a true concentration equal to the MDL (Fig. 1). Kirchmer (1983, 1988) has chosen to call this quantity the criterion of detection.

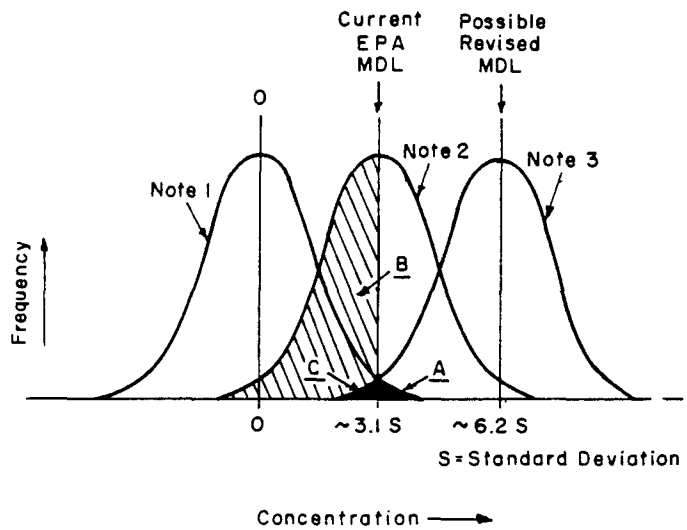


Figure 1. Graphical Illustration of Method Detection Limits (MDL).

NOTE-1 - Distribution of Blank Measurements

NOTE-2 - Distribution of Measurements with a Mean Concentration Equal to the current MDL with $\alpha = 0.01$ (A), i.e., risk of claiming detection when true conc. is zero, and $\beta = 0.50$ (B), i.e., risk of claiming absence when true conc. is = MDL.

NOTE-3 - Distribution of measurements with a mean conc. with $\beta = 0.01$ (C). The α-risk for this possible revised MDL is approximately zero. Risks other than 0.01 could be used for both α and β.

To reduce the risk of false negatives requires incorporation of a realistic β risk factor in setting detection or reporting limits (Fig. 1). The size of α and β risks can be varied to fit the requirements of the problem at hand (Wernimont 1985, Dixon and Massey 1969). For example, the possible revised MDL shown in Figure 1 has a β risk equal to the initially chosen α risk (1%) but there is nothing to prevent choosing other values for these risks. We believe that an experimental value below the criterion of detection should be reported as "not detected, less than the revised MDL" in order to obtain protection against false negatives. Values between the criterion of detection and the revised MDL could be reported in parentheses with a notation to explain that these estimates are less reliable than those above the revised MDL. Unfortunately this system is slightly cumbersome in terms of data processing, which explains why most detection limit estimates are used as a cutoff for numerical values with everything below this value reported as "not detected." When used in this manner, the effective β risk is always 50%.

In the Results and Discussion section of this report we will demonstrate the effects on MDL estimates as these risks are varied. The effect of variance inhomogeneity will also be examined.

Certified Reporting Limit (CRL). The CRL specified by USATHAMA (1987) is extracted using confidence bands as described by Hubaux and Vos (1970). A target reporting limit (TRL) is chosen based on data requirements, and spike additions of the analyte are made at concentrations ranging from 0.5 TRL to 10 TRL. A linear least-squares regression model of the form $F = b_0 + b_1T$ is obtained from a plot of found concentrations (F) versus taken concentrations (T). The data for the plot is obtained on four separate days and then it is pooled. Thus, day-to-day calibration error is included in the pooled standard deviation estimate. This is one distinct difference between MDL and CRL estimates.

The least-squares linear model is then tested against the theoretically expected linear model through the origin. When lack-of-fit tests indicate departure from a linear model, the highest concentration values may be sequentially truncated until linearity is achieved, except that a minimum of three concentration values must remain. A CRL estimate is extracted using 90% confidence bands ($\alpha = \beta = 0.10$) as shown in Figure 2. The standard USATHAMA protocol requires that at least one of the tested concentrations must be below the CRL; otherwise the lowest tested concentration is the CRL. In practice, however, when the CRL is used as a cutoff point and all values below the CRL are reported as "not detected," the β risk becomes 50% just as it is for an MDL used in this fashion. One way to approach this problem would be through the inclusion of a limit of decision (LOD) concentration similar to that suggested for the MDL (Fig. 2). Thus, the "limit of decision" would be estimated from the intersection of the horizontal line corresponding to F at T=0 on the upper confidence band with the best fitting model (Fig. 2). Values below this concentration of T would be reported as "not detected, less than CRL." Values between the LOD and CRL would be reported in parentheses as described for MDL.

Even when the original data set is adequately described by a linear model, the CRL may be higher than required for the intended use of the data. This situation could arise as a consequence of a large pooled standard

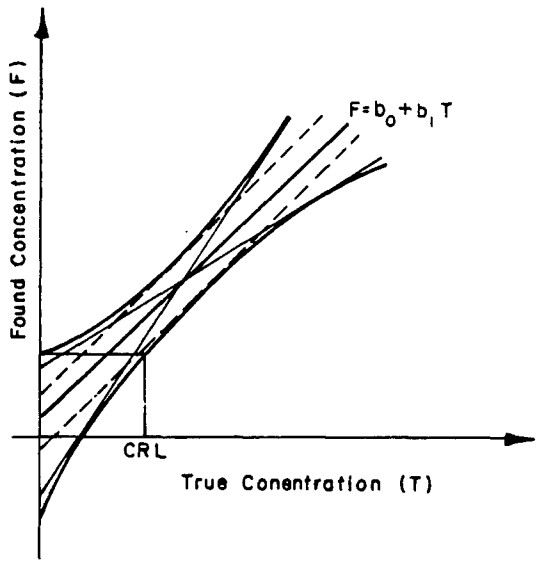


Figure 2. Graphical Illustration of the Certified Reporting Limit (CRL).

The CRL is the value of T corresponding to a point on the lower confidence band where the value of F equals the value of F at T=0 on the upper confidence band.

The curved confidence bands represent the joint uncertainties in the SLOPE (b_1) and intercept (b_0). Current USATHAMA requirements specify $\alpha = \beta = 0.10$ but other values could be used.

deviation where the major uncertainty is produced at the higher concentrations. Hubaux and Vos (1970) note that homogeneity of variance is assumed and that assumption may not hold for some analyses. The most common departure is when the variance increases with concentration. This situation can be dealt with in several ways. One way is to confine all measurements to a very low concentration range but this defeats the objective of reliable quantitation over a wide concentration range. This problem could also be addressed by adding at least one more standard to the calibration at 0.25 TRL or perhaps an even lower concentration. Another possibility is to perform many replicate measurements at low concentration and very few at high concentration, but this also fails to satisfy the requirement of accurate calibration over an extended range. Oppenheimer et al. (1983), recommend weighting to solve this problem. Although this seems like an attractive option, it has not yet been widely employed. The USATHAMA protocol deals with this problem by truncation of the data set but this procedure suffers the disadvantage of being somewhat arbitrary.

Hubaux and Vos (1970) also suggest that ideally, the mean concentration of all standards should be as close to the detection limit as possible. Since the point $\bar{F}$, $\bar{T}$ is the centroid of rotation for uncertainty in the slope, a low value for this point reduces the extent of extrapolation required and thereby reduces the CRL (Fig. 2). The options for reducing the size of $\bar{F}$, $\bar{T}$ are similar to those for reducing the pooled standard deviation. When truncating according to USATHAMA requirements, the slope of the least-squares linear regression line after each truncation must not differ by more than 10% from the slope for the total data set if the original linear model was an adequate fit to the data.

In the Results and Discussion section of this report we will examine the effects of truncation on CRL estimates for two data sets where one exhibits relatively constant variance and the other shows dependence of variance on concentration. The effect of choosing different TRL's will also be considered along with variations in α and β risks (Wernimont 1985). Differences and similarities in CRL and MDL estimates obtained from the same data sets will be related to variations in underlying assumptions.

EXPERIMENTAL

This section contains only an overview of the experimental design; details are available in Grant et al. (in press). Two analytical methods were used: a reversed-phase high performance liquid chromatographic determination of DNB (Jenkins et al. 1988) and a graphite furnace atomic absorption determination of Cu. Solution concentrations relative to target reporting limits (TRL) were prepared at 0.125, 0.25, 0.50, 1.0, 2.0, 2.5, 5.0 and 10 TRL. For the lowest 5 concentrations, 10 replicate measurements of each were obtained in random order on each of 4 days. The higher cocentrations were measured in duplicate on each of 4 days. These two large data sets were used for all estimates of MDL and CRL.

RESULTS AND DISCUSSION

MDL estimates for DNB data set

In accordance with EPA recommendations (Fed. Reg. 1984) MDL's have been calculated using the standard deviations for each set of daily replicates. Appropriate one-sided t-values giving an α-risk of 1% and a β-risk of 50% (Fig. 1) were multiplied times the corresponding estimates of s (Table 1). Although the specifications require s to be derived using analyte concentrations within 1-5 times the estimated MDL, we have included one higher concentration estimate (82.2 μg/L) because there was no evidence that s had increased above these for the lower concentration values. The MDL's ranged from 2.7 to 12.1 μg/L. In contrast, comparable estimates for integrator-derived data ranged from 5.5 to 28.8 μg/L. MDL's for pooled standard deviations from manual peak height estimates (Table 1) range only from 4.7 to 8.0 μg/L. These values are lower than the daily estimates due to smaller values of "t" corresponding to the large degrees of freedom in pooled estimates of s.

Table 1. Method Detection Limits (MDL)* Estimates for Manual Peak Height Measurements of DNB Concentrations. Estimates are based on t-values with α = 1% and β = 50%.

Concentration Taken (μg/L)	MDL Estimates (μg/L)				
	Day 1	Day 2	Day 3	Day 4	Pooled
5.1	8.5	5.1	9.7	12.1	8.0
10.3	4.3	4.8	6.3	6.0	4.7
20.5	4.0	5.9	2.7	10.5	5.7
41.1	4.7	8.7	7.8	8.2	6.4
82.2	5.2	8.9	7.0	6.4	5.5

* $MDL = t_{.99}(S)$

It is interesting to compare the observed scatter of MDL values with the scatter we would predict from confidence limits around the day 1 estimate (MDL = 8.5 μg/L) for the 5.1-μg/L concentration. The chi-squared distribution at the 95% confidence level yielded a range of 5.8 to 15.5 μg/L. Inspection of Table 1 shows no daily estimates above 15.5 μg/L but seven of the twenty values were below the lower boundary of 5.5 μg/L. However, if the mean MDL for all of the day 1 data is used, the confidence limits become 3.7 to 9.7 μg/L. Now, one of the values is below the lower boundary and two exceed the upper boundary. The point here is to reinforce the notion that detection capability estimates are highly uncertain and that this uncertainty is greater when the amount of data collected is small.

Let us now examine the influence of risk assumptions on the size of MDL estimates. For this comparison we will use the pooled standard deviation estimate for the five lowest concentrations (s = 2.42 μg/L) but we will assume only 9 degrees of freedom to correspond with a single set of 10 measurements on one day at one concentration. A composite t value representing the sum of the t values for the chosen α- and β-risks was computed from the equation in Dixon and Massey (1969, p. 273):

$$2t = [z_{(1-\alpha)} + z_{(1-\beta)}] \left[1 + \frac{1.21\ (z_{(1-\alpha)} - 1.06)}{df}\right] \qquad (1)$$

where z is the standard normal variable and df is the number of degrees of freedom. It is claimed that the equation yields values accurate to within 0.5% when df $\geq$ 9. As expected, MDL estimates for DNB increased considerably when β-risks were reduced to sizes comparable to the α-risks (Table 2). If the recommendations given in the Theory section were adopted, the values for $\alpha = \beta$ = 5% would be 4.43 μg/L for the limit of decision and 8.59 μg/L for the MDL. Values between these limits would be reported in parentheses and values below 4.43 μg/L would be reported as "not detected < 8.59 μg/L." We will also refer to this tabulation when we compare MDL to CRL estimates.

Before leaving this topic we should note that no provision has been made for uncertainty associated with a blank correction. For these DNB measurements, no blank corrections were necessary (blank not significantly

Table 2. Variation of MDL Estimates for DNB Changes in α- and β-Risks. Assume 9 degrees of freedom and s = 2.42 μg/L throughout.

α-Risk (%)	β-Risk (%)	MDL (μg/L)
1	50	6.84
1	10	10.2
1	5	11.3
1	1	13.2
5	50	4.43
5	10	7.65
5	5	8.59
10	50	3.34
10	10	6.39

different from zero). However, when blank corrections are required, the MDL estimates would increase by $\sqrt{2}$ to account for the added uncertainty attached to a difference calculation.

CRL Estimates for DNB Data Set

CRL estimates for manual peak height measurements of DNB are summarized in Table 3. The estimates for integrator data exhibit similar trends but they are numerically much larger. Consequently, only the estimates from manual measurements are tabulated. These values, which are based on $\alpha = \beta =$ 10%, show some important systematic trends:

a) As TRL increased, CRL estimates increased. This trend was independent of whether full or truncated data sets were used. Specifically, CRL ranged from 5.9 to 10.0 μg/L for TRL = 10.3 μg/L, from 7.0 to 16.2 μg/L for TRL = 20.5 μg/L, and from 6.6 to 17.9 μg/L for TRL = 41.1 μg/L. The corresponding means were 8.3, 11.2, and 13.0 μg/L, respectively.

This behavior is thought to be caused primarily by the longer extrapolation required for slope confidence bands, as the centroid of rotation ($\overline{F}$, $\overline{T}$) for these bands is farther from zero (Fig. 2). A secondary cause may be the small increase in standard deviation at higher concentrations. Although such a trend was not statistically significant for these data, it could be a major causative factor where variances increase greatly with concentration increases. In any case, none of the CRL estimates for TRL = 41.1 μg/L are acceptable because they all fall below the concentration of the lowest standard, 20.5 μg/L (USATHAMA 1987). When TRL was 20.5 μg/L, four of the 15 estimates were slightly below the lowest standard, 10.3 μg/L. For TRL = 10.3 μg/L all estimates were acceptable.

b) The first truncation produced a reduction in CRL only for the highest TRL, but the second truncation reduced CRL estimates for all three TRL's. This effect was not very pronounced despite reduced extrapolation associated with lowering the value of ($\overline{F}$, $\overline{T}$) because calibration error was

Table 3. Certified Reporting Limit (CRL)* Estimates for Manual Peak Height Measurements of DNB Concentrations.

Target Reporting Limit (μg/L)	CRRL Estimates (μg/L) Full Data Set	Highest Conc. Deleted	Two Highest Concs. Deleted
10.3	8.2	8.5	8.3
10.3	9.2	10.0	9.9
10.3	8.5	7.6	6.0
10.3	8.3	9.4	9.9
10.3	8.0	7.2	5.9
	$\bar{X}$ = 8.4	$\bar{X}$ = 8.5	$\bar{X}$ = 8.0
	R** = 1.2	R = 2.8	R = 4.0
20.5	11.0	10.9	9.8
20.5	12.0	12.2	11.9
20.5	10.4	10.1	7.0
20.5	14.1	14.9	16.2
20.5	10.2	9.8	7.5
	$\bar{X}$ = 11.5	$\bar{X}$ = 11.6	$\bar{X}$ = 10.5
	R = 3.7	R = 5.1	R = 9.2
41.1	14.2	10.5	10.4
41.1	12.9	8.3	6.6
41.1	13.8	10.0	9.6
41.1	17.2	15.3	15.4
41.1	17.5	15.9	17.9
	$\bar{X}$ = 15.1	$\bar{X}$ = 12.0	$\bar{X}$ = 12.0
	R = 4.6	R = 7.6	R = 11.3

* Based on $\alpha = \beta$=10% using USATHAMA (1987) computational protocol (Fig.2).
** Range between high and low CRL estimate.

small compared to sample analysis error. Consequently, prediction bands did not exhibit much curvature.

c) The ranges of CRL estimates increased as TRL increased, presumably due to the greater effect of slight slope changes when long extrapolation was required. However, truncation, which reduces the concentration range, also produced an increase in the variability of CRL estimates. Here, the dominant influence is that the values for the second truncation are derived entirely from randomly varying data whereas the full data sets use the same response values for the highest standards in each iteration. Consequently, the variability in CRL estimates is more fairly represented by the values for the second truncation than for the full data sets.

The results are now at hand for a meaningful comparison of MDL and CRL estimates for manual peak height measurements of DNB concentrations. In Table 1 an MDL value of 6.84 μg/L was reported using the current EPA guidelines of α = 1% and β = 50%. This estimate was based on a pooled standard

deviation, but it assumed only 9 degrees of freedom since it was to represent a typical value for one set of 10 replicate measurements. The current USATHAMA protocol, based on duplicate measurements at each of five concentrations on four separate days and $\alpha = \beta = 10\%$, gave an average CRL of 8.4 μg/L when TRL was 10.3 μg/L (Table 3). If the MDL estimate was also based on $\alpha = \beta = 10\%$, then the value was 6.39 μg/L (Table 2). Clearly, these MDL and CRL estimates compare very favorably, especially considering that the CRL estimates include day-to-day variability and lack-of-fit of regression models whereas the MDL estimates exclude these sources of uncertainty. However, CRL estimates increased significantly as TRL increased. In contrast, MDL estimates were quite insensitive to the concentration used for data generation in this particular analysis. It is concluded that the selection of an acceptably small TRL will yield CRL estimates that are very similar to MDL estimates. But, when a low TRL is not required, we should expect, using currently specified procedures, CRL to be larger than MDL

It is also worth noting that there is no a priori requirement that $\alpha = \beta$ when generating CRL estimates. The required equations for computations with $\alpha \neq \beta$ are given in Wernimont (1985, p. 76). Similarly, the estimated limits of decision and the CRL could be specified as suggested in the Theory section.

MDL Estimates for Cu Data Set

As with DNB results, MDL's were calculated according to EPA recommendations (Fed. Reg. 1984) using the s values from sets of daily replicates. Since variance homogeneity was demonstrated for copper concentrations of 0.150, 0.300 and 0.600 μg/L, MDL estimates were obtained for each of these concentrations (Table 4). Once again, the highest concentration (0.600 μg/L) is slightly above the specified 1-5 times the estimated MDL but we chose to retain the values. The MDL's ranged from 0.052 to 0.172 μg/L, or omitting the 0.600 μg/L results, 0.052 to 0.145 μg/L. For the pooled standard deviations, the estimates only ranged from 0.070 to 0.107 μg/L. The mean MDL estimate for the day 1 data was 0.074 μg/L and the 95% confidence limits around this value, assuming 6 degrees of freedom, were 0.048 to 0.163 μg/L. Only one of the 12 MDL estimates for individual data sets is outside of this range. Of course, changes in risk assumptions will produce a pattern of variation in MDL estimates similar to that shown for DNB in Table 2.

Table 4. Method Detection Limits (MDL)* Estimates for Copper Concentrations. Estimates are based on t-values with $\alpha = 1\%$ and $\beta = 50\%$.

Concentration	MDL Estimates (μg/L)				
Taken (μg/L)	Day 1	Day 2	Day 3	Day 4	Pooled
0.150	0.052	0.085	0.090	0.145	0.077
0.300	0.088	0.099	0.065	0.093	0.070
0.600	0.081	0.133	0.132	0.172	0.107

* MDL = $t_{.99}(S)$

We must also note that the copper MDL's should actually be increased by $\sqrt{2}$ to account for the "furnace blank" corrections that were applied to all of these responses. However, since the current EPA procedure does not require this adjustment, it has been omitted here. Fortunately this omission does not invalidate MDL and CRL comparisons because the latter estimates were also obtained using blank corrected data.

CRL Estimates for Cu Data Set

CRL estimates were obtained as described in the discussion of DNB results except that all Cu responses were corrected for the "furnace blank" (Table 5). Trends in these values are as follows:

a) As TRL increased, CRL estimates also increased for both full and truncated data sets. Specifically, CRL ranged from 0.113 to 0.237 μg/L for TRL = 0.300 μg/L, from 0.238 to 0.523 μg/L for TRL = 0.600 μg/L, and from 0.365 to 1.32 for TRL = 1.20 μg/L. Corresponding means were 0.182, 0.350, and 0.768 μg/L.

Table 5. Certified Reporting Limit (CRL)* Estimates for Graphite Furnace Atomic Absorption Copper Determinations.

Target Reporting Limit (μg/L)	Full Data Set	Highest Conc. Deleted	Two Highest Concs. Deleted
0.300	0.237	0.230	0.187
0.300	0.222	0.195	0.113
0.300	0.190	0.155	0.145
0.300	0.200	0.179	0.139
0.300	0.197	0.173	0.171
	$\bar{X}$ = 0.209	$\bar{X}$ = 0.186	$\bar{X}$ = 0.151
	R** = 0.047	R = 0.075	R = 0.074
0.600	0.496	0.274	0.268
0.600	0.485	0.246	0.238
0.600	0.497	0.279	0.264
0.600	0.485	0.244	0.238
0.600	0.523	0.339	0.377
	$\bar{X}$ = 0.497	$\bar{X}$ = 0.276	$\bar{X}$ = 0.277
	R = 0.038	R = 0.095	R = 0.139
1.20	1.30	0.571	0.421
1.20	1.32	0.597	0.365
1.20	1.31	0.604	0.444
1.20	1.30	5.557	0.398
1.20	1.30	0.583	0.449
	$\bar{X}$ = 1.31	$\bar{X}$ = 0.582	$\bar{X}$ = 0.415
	R = 0.03	R = 0.047	R = 0.084

* Based on $\alpha = \beta$=10% using USATHAMA (1987) computational protocol (Fig.2).
** Range between high and low CRL estimate.

The proportionate increase in Cu CRL is much greater than that observed for DNB with the same relative increase in TRL. With Cu, the increase is not primarily due to greater extrapolation from the centroid as TRL increases, but because the standard deviation is much larger for high than for low Cu concentration. As noted in the discussion of DNB results, heterogeneous variances can cause this to be a dominant effect. Hence, the influence of the choice of TRL is much greater for Cu than for DNB.

b) The impact of variance heterogeneity is also strongly evident when truncation is employed. In contrast to DNB results where truncation produced only minor reductions in CRL estimates, the CRL's for Cu are dramatically reduced with successive truncation, especially for large TRL. Clearly the reduction of s associated with deletion of high concentration data accounts for most of this decrease in CRL estimates.

It is also worth noting that the choice of TRL is extremely important because of the USAHTAMA requirement that 0.5 TRL becomes the CRL when the CRL estimate is below 0.5 TRL. For Cu, that restriction has only a minor effect for full data sets after one truncation (although all five CRL's for one truncation and TRL = 0.600 μg/L are slightly below 0.300 μg/L). However, after the second truncation, 12 of 15 CRL's are below 0.5 TRL. Since truncation is routinely used, the CRL is effectively determined by the choice of TRL unless an iterative procedure involving lower TRL's is employed. Alternatively, the USATHAMA (1987) protocol could be altered to include standard concentrations of 0.25 TRL or 0.1 TRL. The same problem was evident with DNB but it was somewhat less serious than for Cu.

c) As noted for DNB, only the twice truncated data represent random results since the high concentration responses were the same in each iteration. Consequently, the variability of CRL estimates is best reflected by the values for the second truncation (Table 5). There was no apparent systematic dependence of this variability on the size of TRL.

Let us now compare MDL with CRL for the Cu determinations. Based on a pooled standard deviation of 0.034 μg/L from the three lowest Cu concentrations and assuming 6 degrees of freedom in the estimate, the MDL = 0.107 μg/L according to current EPA guidelines (α = 1%, β = 50%). For $\alpha = \beta$ = 10% the corresponding MDL = 0.098 μg/L. The CRL estimate, also based on $\alpha = \beta$ = 10%, was 0.151 μg/L when TRL = 0.300 μg/L and the two highest concentrations were omitted by truncation. With no truncation the CRL was 0.209 μg/L for TRL = 0.300 μg/L. As TRL increased, the CRL estimates rapidly escalated to produce values which were much larger (3-13 times) than MDL. In contrast, the CRL estimates for DNB only exceeded the MDL estimates by a factor of a little more than 2 in the worst case. This difference in behavior is a clear reflection of the effect of variance heterogeneity. When variances increase even in the low concentration region as they do for Cu, CRL estimates can only approximate MDL if very low TRL's are chosen. Otherwise, CRL's will be much larger than MDL's.

CONCLUSIONS AND RECOMMENDATIONS

1. The magnitude of variability of repeat Method Detection Limit (MDL) estimates and Certified Reporting Limit (CRL) estimates is emphasized to defuse the notion that such descriptors are fundamental parameters.

2. The influence of risk assumptions on MDL and CRL estimates has been demonstrated. It is recommended that proper attention must be given to Type II errors (β risk or false negatives) because current procedures set this risk at 50%. To overcome this problem, it is suggested that the limit of decision be used in conjunction with MDL or CRL (see Theory Section). The choice of both α and β risks should be properly married to the problem at hand.

3. As Target Reporting Limits (TRL) increase, CRL estimates also increase. This behavior is most evident when variances increase with concentration, even in the low concentration range, as exemplified by graphite furnace atomic absorption determinations of copper.

4. Truncation of "found vs. taken" curves lowers CRL estimates although the effect is much more profound in the presence of heterogeneous variances. Even with homogeneous variances, truncation will still produce some decrease in CRL due to the reduction of extrapolation of confidence bands when the centroid values, $\bar{x}$ and $\bar{y}$, are made smaller.

5. For systems with reasonably constant variance in the low concentration region (i.e. RP-HPLC determination of DNB), MDL and CRL estimates according to current risk assumptions show remarkably good agreement. However, when variance increases with concentration (Cu), CRL can be considerably larger than MDL. The magnitude of this discrepancy is directly proportional to the size of TRL.

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PLANT UPTAKE OF 2,4,6-TRINITROTOLUENE

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Introduction

2,4,6-Trinitrotoluene (TNT) is of environmental concern at manufacturing facilities and on many army installations where TNT is loaded and packed. The concern is due primarily to toxicity of the parent compound and of certain of its degradation products to fish and other aquatic fauna (Osmon and Klausmeir 1972; Liu, Spanggord, and Bailey 1976; Nay, Randal, and King 1974; Won, DiSalvo, and Ng 1976). Operations in which TNT is handled often generate large volumes of waste waters high in TNT and other potentially hazardous compounds. Historically, these waste effluents were discharged directly into local streams or into settling lagoons (Nay et al. 1974, Liebel et al. 1978). However, since passage of the Clean Water Act (1970), environmental consciousness has mandated more appropriate disposal practices, e. g., filtration of effluents and incineration. Nevertheless, contamination of soils and groundwater resulting from past practices has been detected (Leibel et al. 1978).

Only a few factors affecting the environmental fate of TNT have been well defined. For example, photodecomposition (Burlinson 1980) and microbial degradation (Kaplan and Kaplan 1982) are known to occur in the environment, and a soil leaching study has been reported (Greene, Kaplan, and Kaplan 1984). Only limited data is available concerning effects of TNT on plants. Schott and Worthley (1974) demonstrated that

TNT is toxic to the floating aquatic plant duckweed (*Lemna perpusilla*), and Palazzo and Leggett (1983) reported depression in yields of ryegrass by TNT. Palazzo and Leggett (1986) have also demonstrated uptake of TNT and two of its principal degradation products, 4-amino-2,6-dinitrotoluene (4ADNT) and 2-amino-4,6-dinitrotoluene (2ADNT), by yellow nutsedge (*Cyperus esculentus*) in hydroponic cultures. However, no data were found concerning plant uptake from TNT-contaminated soils. Plant uptake is potentially important in TNT-contaminated soils that have become naturally vegetated, especially in areas foraged by wildlife or cattle.

In 1984 the U. S. Army Engineer Waterways Experiment Station (WES) initiated experiments to study plant uptake of TNT from soils using a standard plant bioassay procedure that had been developed to assess mobilization of contaminants into plants from dredged material. These studies were funded by the U. S. Army Biomedical Research and Development Laboratory, Ft. Detrick, Frederick, MD, as a part of their Environmental Quality Technology research effort. A summary of these plant bioassay studies is the subject of this report.

Plant Uptake Using ^{14}C-Labeled Compounds

Plant uptake of TNT, 4ADNT, and 2ADNT from two soils, Tunica silt and Sharkey clay, was investigated. The treatment rate was 80 ug of the respective treatment compound per gram of soil on an oven-dry weight (ODW) basis. TNT- and 4ADNT-treated soils received both ^{14}C-labeled and unlabeled compounds. 2ADNT-treated soils received only unlabeled 2ADNT. Treated and control soil batches were potted in the standard WES plant

bioassay. After a 45-day growth period, plants were harvested. Soils were sampled at the time of planting and at the time of harvesting. Both plants and soils were extracted and analyzed by gas liquid chromatography (GLC). Extracts of plants and soils treated with ^{14}C were analyzed by liquid scintillation. Extracts of soils treated with ^{14}C-labeled compounds were also analyzed by a complete combustion technique for more efficient recovery of ^{14}C.

Results indicated that little TNT and 4ADNT, and no 2ADNT was absorbed by leafy portions of the test plant, yellow nutsedge. Plant uptake was greatest from 4ADNT-treated silt, an indication that 4ADNT is more readily mobilized into the plant than TNT or 2ADNT. Greater plant uptake from silt than from clay indicated that bioavailability is reduced in the clay. The reduction in bioavailability may be due to an increase in soil sorption of TNT and its degradation products to clay over time. Results of the study suggest that plant uptake from soils contaminated with 80 ug of the respective treatment compound per g will not be environmentally significant.

A comparison of percent recoveries of ^{14}C from soils by extraction and by complete combustion indicated significant differences. Recoveries were consistently greater by combustion which indicated that extraction did not remove all of the ^{14}C that was present in the soils. Recoveries from TNT-treated silt were also consistently greater than those from TNT-treated clay, an indication that TNT adsorption to clay reduced extractability. The same was not true for 4ADNT-treated silt and clay. Little difference existed between recoveries of ^{14}C from 4ADNT-treated silt and clay, an indication that adsorption exerted less

effect on extractability of 4ADNT than of TNT.

A detailed report of this study is cited below:

Pennington, J. C. "Plant Uptake of 2,4,6-Trinitrotoluene, 4-Amino-2,6-Dinitrotoluene, and 2-Amino-4,6-Dinitrotoluene Using ^{14}C-Labeled and Unlabeled Compounds," in review, U. S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Effects of Treatment Levels and pH

The principal objectives of this study were to determine the effects of soil pH and higher TNT treatment levels on plant uptake of TNT. Plants were grown in the standard WES plant bioassay using the same two soils that were used in the ^{14}C study. Soils were adjusted to four pH values (5, 6, 7, and 8) and treated at four levels of TNT (0, 100, 200, and 400 ug TNT per gram ODW). Soils were sampled immediately after treatment, after a 20-day incubation period, and at the time of harvesting. Plants and soils were extracted and analyzed by GLC.

Statistically significant plant uptake of TNT from soils did not occur at any treatment level or pH when compared with controls. Both 4ADNT and 2ADNT were detected in plants, but only 4ADNT at pH 6 in the silt at 200 ug/g treatment level differed from controls. However, soil treatment level and soil type exerted a dramatic effect on plant yields. Yields were virtually unaffected by treatment levels in clay (Figure 1). However, in the silt yields were significantly reduced in the 200 ug TNT/g treatment, and only plants from one of four replicates survived in the 400 ug TNT/g treatment (Figure 2). Plant yields tended to decrease as the pH of TNT treated soils increased.

When results of this study are compared with results of the ^{14}C study, it is surprising that significant levels of neither TNT, 4ADNT,

nor 2ADNT were found in the plants at the higher treatment levels. However, the ^{14}C analysis used in the first study was much more sensitive than GLC analysis, and GLC analyses for neither study showed significant levels of treatment compounds.

Results of soil analysis indicated a decrease in the concentration of TNT in the silt, and to a lesser extent, in the clay during the study. The decrease was greatest from the time of treatment to the first sampling (20 days), and was limited after 20 days (statistically significant in the highest TNT treatments only). Some of the decrease is attributable to the production of 4ADNT and 2ADNT, but volatilization loss as an artifact of treatment with the organic solvent, methanol, is also possible. Miller, Hebert, and Zepp (1988) have indicated that migration and subsequent volatilization of low-volatility organic compounds in soil is enhanced by the presence of organic solvents. Soil concentrations of 4ADNT and 2ADNT rarely exceeded 20 ug/g of soil.

A detailed report of this study is cited below:

Folsom, B. L., Jr., Pennington, J. C., Teeter, C. L., Barton, M. R., and Bright, J. A. "Effects of Soil pH and Treatment Level on Persistence and Plant Uptake of 2,4,6-Trinitrotoluene," in review, U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Conclusions

Results of these studies indicated that high soil levels of TNT exerted a significant effect on the yields of the ubiquitous yellow nutsedge. However, only a limited amount of TNT, 4ADNT, and 2ADNT were mobilized into leafy portions of the plant. Furthermore, pH of TNT-treated soils exerted no effect on plant uptake and little effect on plant yields.

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THE FATE OF CHEMICAL AGENTS ON STRUCTURAL SURFACES SUBJECTED TO THERMAL DECONTAMINATION

by

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INTRODUCTION

As part of their responsibilities in DOD real property disposal, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) must develop and demonstrate technology to identify, contain, and eliminate toxic and hazardous materials and related contamination. In support of this mission, Battelle's Columbus Division (BCD) has recently completed two projects that identified promising decontamination systems on a bench scale in the laboratory. The objective of the current project is to further define the fate of chemical agents (HD, VX, and GB) adsorbed on structural components such as concrete. This current program is seeking to elucidate the chemistry and kinetics of such interactions through (a) development of a transient heat and mass flow model for desorption and transport of agents from porous substrates; (b) conduct of experiments with agent simulants to verify the kinetic model; and (c) conduct of experiments with agents to demonstrate the utility of the model and to identify specific chemical species desorbed and residual in structural materials during hot gas decontamination.

METHODS

Modeling

The purpose of the model development portion of this program is to provide USATHAMA with a flexible, convenient, and simple-to-use means for exploring the consequences of changes in process, building structure, and contamination type and level parameters for the hotgas desorption process (HDP). The model is based on transient heat and mass flow considerations with inclusion of both desorption and pyrolysis of the agents and uses the Crank-Nicholson of solution. The code is written in C for use on 80286/80287 based microcomputers. It is menu driven with user selected (1) gas properties, (2) structural materials and dimensions, (3) boundary conditions, (4) contaminant type, (5) contaminant distribution and level, and (6) output modes. As examples, the user can select any of four boundary conditions (both sides of wall heated, one side air cooled, one side insulated, or one side in contact with moist soil); and output can be tabular or in the form of either time or depth profiles of temperature, adsorbed phase concentration, or gas phase concentration. The code supports hard copy output to plotters using HPGL or bit-image graphics to either IBM or Epson compatible printers. While a default set of recommended materials properties is included in the code, virtually every parameter can be changed to simulate special cases.

Experimental

While many of the materials properties needed for the modeling effort are either readily available from standard sources or easily obtainable by simple laboratory measurements, relatively little is known about either the chemical nature of residual contamination of concrete structures or the products and rates of release of residues under HDP conditions. The purpose of the experimental phase of this program is, therefore, to determine the possible nature of agent residues and provide key information on their rates of release. This work was divided into three segments:

(1) Preliminary method development using half-mustard (HM) and di-isopropylmethylphosphanate (DIMP) as agent simulants.

(2) Extraction and analysis of concrete core samples (certified XXX) obtained from Newport Arsenal.

(3) Experiments with concrete samples spiked with HD, GB, and VX to determine degradation products, thermal degradation products, and thermal release rates.

Apparatus used in the preliminary experiments with simulants and in the determination of thermal release rates of agents from spiked samples of concrete is shown in Figure 1. This apparatus consisted of a heated sample holder (mounted in a closed stainless steel container) that is interfaced to a time-of-flight mass spectrometer (TOFMS) through a molecular beam sampling head. This arrangement permits continuous real-time monitoring of off-gas products from a concrete sample under controlled temperature conditions. The temperature of the sample can be programmed at fixed rates or can be stepped from one setpoint to the next.

In the simulant experiments, concrete slabs (0.5 x 1 x 1 cm) were spiked with a stock solution of simulant be either injection on the top surface using a syringe or immersion in stock solution overnight. The stock solutions consisted of 5.5 percent of either HM or DIMP in hexane, and spike loadings to the concrete were nominally 600 μg or simple multiples of this amount. Samples were placed in sealed vials and stored overnight to allow the hexane to evaporate. The dry samples were placed in the sample holder which was then attached to the molecular beam sampler. After a few initial mass scans at room temperature, the sample temperature was programmed to 200-250 C at rates of 5 to 10 C/min while mass scans were continuously repeated. Initial runs with this procedure showed no evidence for residual simulants. Subsequent runs were therefore made using only freshly prepared samples or samples that had been soaked in the stock solution overnight.

Samples for the agent experiments (still in progress) were prepared using concrete derived from the Newport cores and were spiked at a level of 10 mg/g for each agent. Thermal desorption runs were made as above.

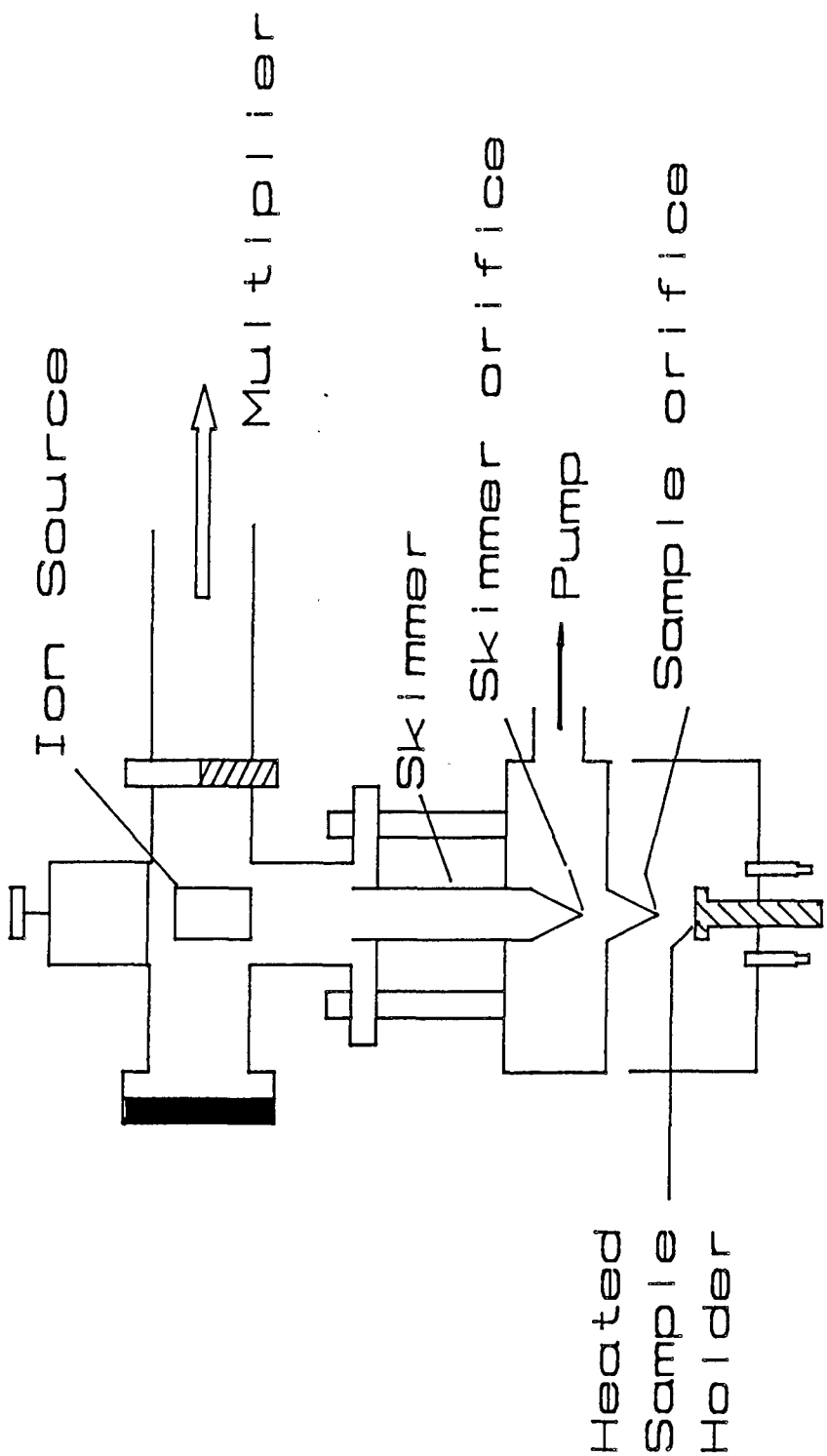


Figure 1. Molecular Beam Sampling Interface.

RESULTS

HDP Model

In its current stage of development, only the heat transfer portion of the HDP model is functional. Provisions have been made for the mass transfer modules and peripheral I/O segments related to the mass transfer have been incorporated, but key data needed from the laboratory work is still being accumulated. The accuracy of the heat transfer module (temporarily de-coupled from mass transfer) has been checked extensively with each boundary condition and a variety of changes in input parameters. In the case of both sides of the wall being heated, the model results were compared with the explicit solution that is available. In the cases of the other boundary conditions, calculations were compared with other machine solutions that were available for specific sets of conditions. Extensive evaluations also were made by both Battelle and USATHAMA personnel for ease of use and general utility of the code, and recommendations for improvement of useability have been incorporated into the overall code design. The code also has been optimized for speed with the most complex case (determined by the 64K per data segment limitation of the 80286 processor) being completed in about 40 sec (Compaq 286).

Figure 2 shows the main menu of the HDP code; several sub-menus are used depending on selections made from the main menu. Figure 3 shows typical hard-copy output of temperature as a function of time at several different depths in a concrete wall.

Laboratory Experiments

Typical results obtained for the initial laboratory experiments with HD and DIMP are illustrated in Figures 4 and 5 respectively. In both cases, the simulants were found to evaporate from the concrete relatively rapidly, with measurable rates of evaporation at room temperature. Analysis of the low temperature side of the curve shown in Figure 5 yields an apparent energy of 16.5 kcal/mole compared with an enthalpy of vaporization of 17.8 kcal/mole as derived from vapor pressure data. A similar analysis of the HD data yields an apparent energy of 7.9 kcal/mole as compared with an enthalpy of vaporization

HOT GAS PROPERTIES

Gas (F)low Rate = 5000 cfm (G)as Temperature = 1000.0 F

WALL PROPERTIES

(C)onductivity = 0.70 Btu/ft-hr-F (S)pecific Heat = 0.21 Btu/lb-F
(D)ensity = 144 lb/ft^3 (T)hickness = 8.0 in
(H)eight, Width = 12.0 x 12.0 ft (I)nitial Temperature = 70.0 F

BOUNDARY CONDITIONS

(1) Both sides heated (2) Air cooled side
(2) Moist soil side (4) Insulated side

OUTPUT CHOICES

(5) IBM Printer (6) Plotter (7) Disk

CHEMICAL AGENT

(8) HD (9) GB (0) VX

Set up problem by pressing letter or number key for each variable you wish to change or set.

Figure 2. Main Menu for HDP Model.

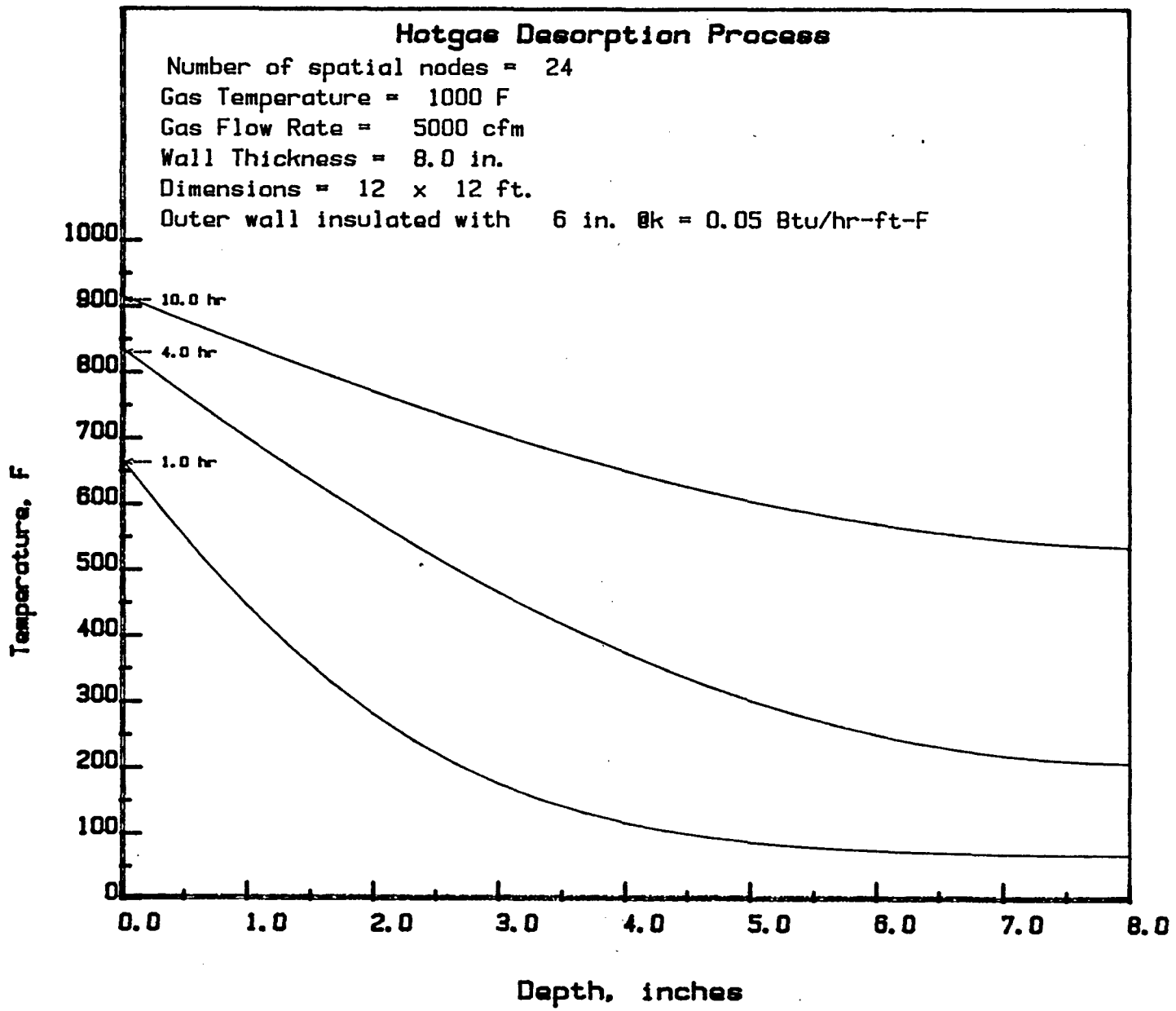


Figure 3. Sample Temperature Profile Produced by HDP Model.

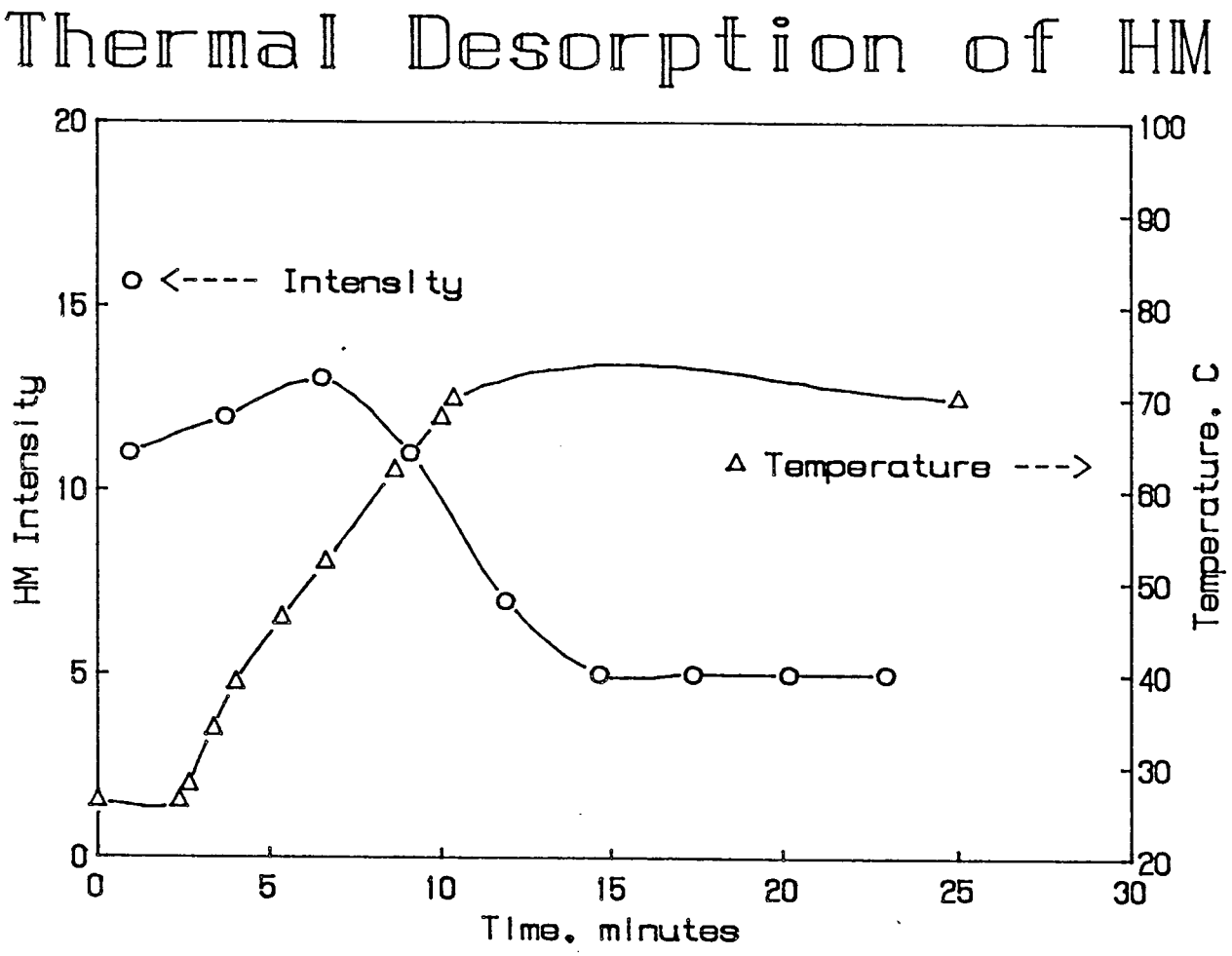


Figure 4. Typical Response Curve for Desorption of HM from Concrete.

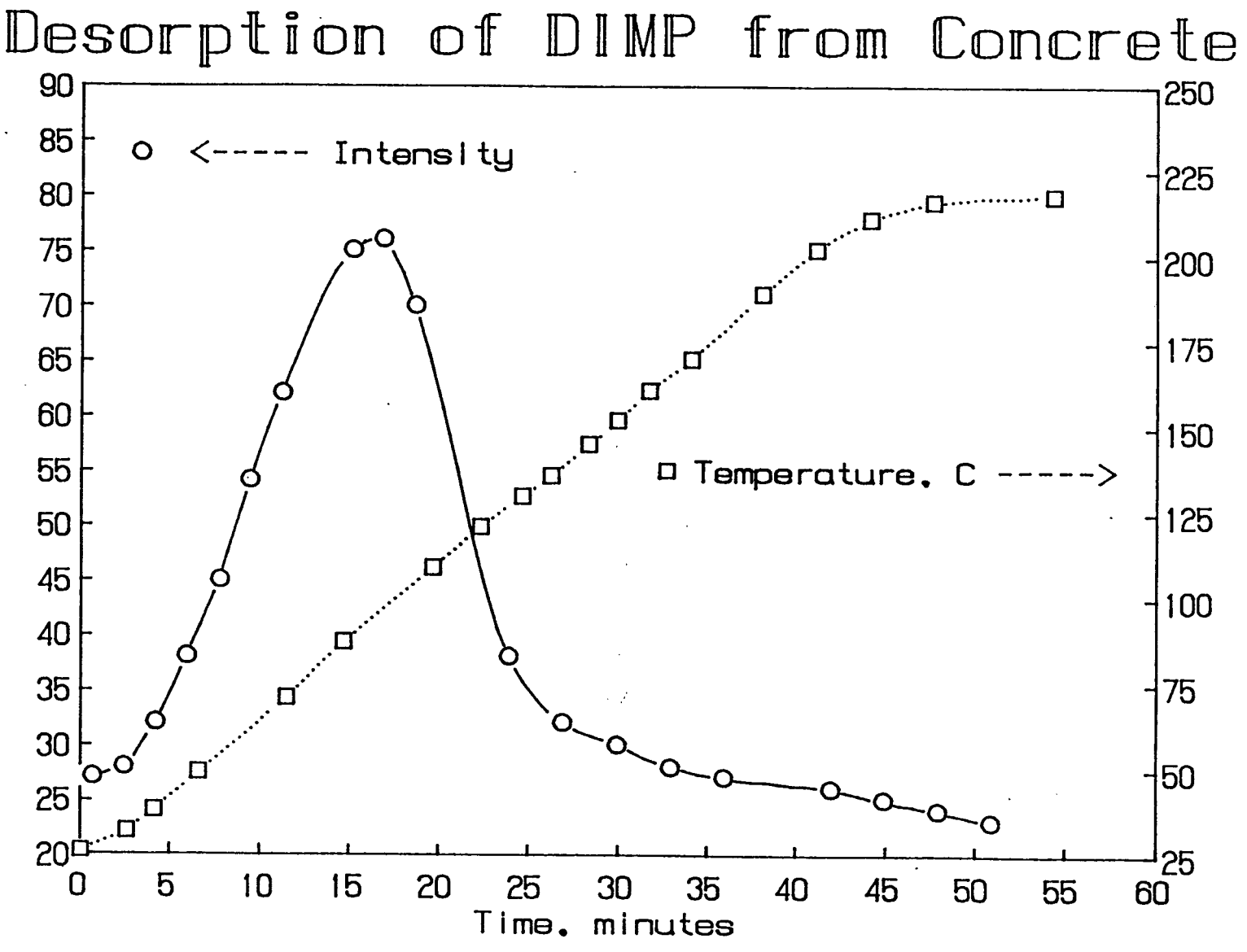


Figure 5. Typical Response Curve for Desorption of DIMP from Concrete.

of 8.7 kcal/mole. These experimental values are within experimental error of the values derived from vapor pressure data and suggest free vaporization of the simulants (i.e., little or no interaction with the substrate). However, because of the appreciable evaporation even at room temperature, balance between the amounts of simulant added to the concrete and the amounts recovered by thermal desorption was not possible.

Initial examinations of the Newport core samples showed no evidence for chromatographable organic residues when the samples were extracted with either chloroform or dimethylsulfoxide. Evaluation of samples of the Newport cores that have been spiked with HD, GB, and VX is still in progress. With the GB sample, all of the initial 10 mg of agent was consumed by the concrete in about 2 weeks, but solvent extractable products were not present in sufficient quantities for mass spec identification. Additional agent has, therefore, been added to the GB sample in an attempt to generate higher concentrations of products. The HD also is being consumed by the concrete but, as with the GB, product formation is not yet sufficient for identification. A sample of neat VX stored in contact with crushed concrete began to show signs of degradation (color change and increased viscosity) after about one week. No chromatographable products were observed in the early examinations of the residual VX, but this test also is continuing.

SUMMARY

A flexible user-oriented computer model has been developed to facilitate evaluation of potential effects of parameter changes on the Hotgas Desorption Process. This software development activity is being coordinated with laboratory evaluations of the residues and thermal desorption products obtained by HDP treatment of concrete that has been contaminated with HD, GB, or VX.

MAMMALIAN TOXICITY STUDIES WITH NITROGUANIDINE

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Nitroguanidine (NQ), a primary component of U.S. Army triple-base propellants mixtures, is produced at the Sunflower Army Ammunition Plant, DeSoto, Kansas. Wastewaters discharged from the plant contain NQ and its degradation products/intermediates, such as nitrosoguanidine (NSQ), guanidine (G), and guanidine nitrate (GN). The U.S. Army is concerned that discharge waters from the plant comply with U.S. Environmental Protection Agency (USEPA) regulations, however, the toxicity data on these compounds are limited. Therefore, acute, subchronic, toxicokinetic, developmental (teratogenic), and genotoxic experiments were conducted. This work was carried out at Letterman Army Research Institute, Presidio of San Francisco, California, under an Intra-Army Work Agreement, to develop environmental and health effects criteria.

Materials and Methods

Test chemicals

Nitroguanidine (99.6-99.9%) (Sunflower Army Ammunition Plant, DeSoto, Kansas), guanidine hydrochloride (98%) (Sigma Chemical Co.) and guanidine nitrate (99.99%) (Chemical Dynamic Corp., South Plainfield, NJ.) were used in testing. Nitrosoguanidine (97.5%) (2.5% nitroguanidine) was prepared at the U.S. Army Biomedical Research and Development Laboratory.

Animals

Rats (Sprague-Dawley), mice (ICR), rabbits (New Zealand, white) and guinea pigs (Hartley strain) were used in testing. They were maintained at 14-20C and R.H 40-70%, and provided food and water ad libitum.

Tests

Primary eye, skin irritation, and dermal toxicity tests in rabbits, dermal sensitization tests in guinea pigs, acute oral toxicity tests in rats and mice, subchronic tests in rats, developmental toxicity test in rats and rabbits, and genotoxicity tests (Ames Salmonella/mammalian microsome mutagenicity assay, mouse lymphoma forward mutation assay, sister chromatid exchange

and Drosophila melanogaster sex-linked recessive lethal test) were conducted according to standard EPA health effects testing guidelines (40 CFR 798).

Results

Acute toxicity tests

The results of dermal and ocular irritation, dermal sensitization, and dermal toxicity studies for NQ, NSQ, G, and GN are presented in Table 1.

Eye irritation

No significant signs of irritation were observed in the eyes of rabbits receiving NQ or NSQ (0.1 g/eye). Slight conjuctival vasodilation at 1 and 4 hr following dosing with NQ or NSQ were observed but did not meet test criteria for positive response. G or GN produced a positive response (score 1-2). Corneal opacities and slight inflammation in the iris and conjuctiva were observed in the eyes of rabbits treated with G or GN. The score of 1-2 was considered a mild irritation potential in rabbits according to test criteria. The chemical nature of G and GN suggest that the severity of the corneal erosions observed in this study could have been ameliorated significantly by irrigating the eye promptly after exposure.

Skin irritation

NQ or NSQ was applied (0.5g/site) to both intact and abraded skin under semi-occlusive patches for 4 hr. No evidence of dermal irritation (erythema, edema and inflammation) was observed in rabbits during 14 days observation. G or GN, when tested under similar conditions, produced severe skin irritation. Erythema, edema, and eschar formation were detected at 24, 48, and 72 hr. after dosing. Irreversible skin damage was apparent at the time of sacrifice, 14 days after dosing (GN).

Dermal toxicity

Test chemicals (NQ, NSQ, G, or GN) when applied for 24 hr under a semi-occlusive patch to the shaved backs of male and female rabbits at a "limit" dose of 2 g/kg showed no signs of toxicity for 14 days observation. None of the animals exhibited any reactions at the site of exposure during the 72 hr after dosing with NQ or NSQ, but G or GN showed dermal inflammation after 24 hr. In one animal, necrosis and eschar formation were observed. These results are consistent with those obtained in skin irritation tests.

Dermal sensitization

No evidence of dermal sensitization was produced in guinea pigs by dermal exposure to NQ, NSQ, G, or GN. Animals were exposed 3 times at weekly intervals to these chemicals under a semi-occlusive wrap for 6 hr. After a 2-week latent period for development of immunological reactivity, a challenge dose was similarly applied (Buehlers method). None of the animals exhibited dermal sensitization reactions to these chemicals at their highest nonirritating dose (10%).

Acute oral toxicity

Results of the acute oral toxicity studies are presented in Table 2. Single dose oral toxicity studies were performed with NQ, NSQ, G, and GN in rats and mice. Compounds were suspended in corn oil and administered by oral gavage. Dose response relationships were obtained for mortality and systemic toxicity in both species with G and GN. Because of low toxicity dose responses were not obtained for NQ and NSQ. The results of acute oral toxicity tests were MLDs > 5g/kg for NQ and NSQ in rats and mice of both sexes, while oral MLDs 50 values for G in rats were 556 mg/kg in males and 475 mg/kg in females. Similar values were obtained in male and female mice. The GN was comparatively less toxic than G. The MLD 50 values were 989 mg/kg for male and 730 mg/kg for female rats and 1105 mg/kg in male and 1025 mg/kg in female mice. Females were found to be more susceptible than males of both species to G or GN. The clinical signs observed in rats and mice were associated with gastrointestinal tract, urinogenital system and central nervous system disorders. On the basis of oral MLD50 values in rats and mice, NQ and NSQ may be considered slightly toxic compounds, while G and GN may be considered as moderately toxic.

Subchronic toxicity tests

A 14-day subchronic toxicity study was conducted in male and female rats by administering NQ in the diet at dose levels of 0, 100, 316, and 1000 mg/kg. The results indicate that NQ did not affect food consumption, or body weight gain, but produced a significant dose related increase in water consumption. Clinical signs attributable to the test compound were not observed during the study. Serum chemistry analyses revealed decreased potassium and calcium values, which may have been due to the increased water consumption. These findings indicate that NQ is not toxic in rats when administered in diet at doses as high as 1000/mg/kg/day for 14 days.

A 90-day subchronic toxicity study was conducted in male and female rats by administering NQ in the diet at 0, 100, 316, and 1000 mg/kg/day. Clinical signs were observed daily; food and water consumption and body weight measurements were recorded

weekly. Hematology, clinical chemistries, and gross and microscopic observations of tissues were evaluated at 6 and 13 weeks. The results indicate that NQ caused a decrease in body weight gain and food consumption in both sexes in the high dose group (1000 mg/kg). There was also a dose-related increase in water consumption in male and female rats. No other clinical signs were observed during NQ feeding. There were no changes in hematology and clinical chemistries attributable to NQ exposure, although isolated changes were observed that could not be correlated with NQ treatment. Microscopic examination of tissues from the control and 1000 mg/kg dose groups revealed no lesions attributable to administration of NQ. These results indicate that NQ is relatively nontoxic when administered at doses as high as 1000 mg/kg/day for 90 days except for a reduction in body weight gain at 1000 mg/kg/day. Similarly, NQ was found to be nontoxic to mice when administered in the diet at doses as high as 1000 mg/kg/day for 90 days.

Developmental toxicity

The potential of NQ to produce developmental toxicity was evaluated in pregnant rats. NQ in 1% carboxymethylcellulose was administered at doses of 0, 100, 316, and 1000 mg/kg by oral gavage on day 6 through day 15 of gestation. Fetuses were delivered by Cesarean section on day 20, weighed, and examined. The results demonstrate 1000 mg/kg NQ produced decreased food consumption and weight loss in the dams. Fetuses from the 1000 mg/kg/day group were significantly smaller than control. NQ did not produce effects on pregnancy and survival of fetuses (Table 3). The effect of NQ on the incidence of fetal malformations is presented in Table 4. There was no significant difference in the incidence of malformations among dose groups. Fetuses from the 1000 mg/kg/day group were significantly smaller than controls with an increased ossification of the sternebrae, caudal vertebrae, and pubis. There was no evidence of developmental toxicity of NQ in rats under conditions of this study. However NQ produced maternal and fetal toxicity at the 1000 mg/kg/day dose level. On the basis of the subchronic and developmental toxicity studies, 316 mg/kg/day may be considered as a No-Observed-Effect Level in rats.

The developmental toxicity of NQ was also evaluated in pregnant New Zealand white rabbits at doses of 0, 100, 316 and 1000 mg/kg in a suspension of 1% carboxymethylcellulose administered by oral gavage on days 6-18 of gestation. Fetuses were delivered by Cesarian section on day 29, weighed, and examined. The results show that NQ produced maternal toxicity (45% mortality), weight loss, and decreased food consumption in the 1000 mg/kg group. All dose groups exhibited developmental toxicity as an increased incidence of resorptions. There were no dose-related malformations. Based on these findings, NQ has no teratogenic potential but has the potential to cause

developmental toxicity. The No-Observed-Effect-Level was 316 mg/kg/day in rabbits.

Metabolism studies

The absorption, distribution, and elimination of 14C NQ were studied in rats following oral and intravenous administration. Rats were dosed orally with 14C NQ (20 mg or 200 mg/kg, 5-10μ Ci) in 1% gum tragacanth and intravenously via the tail vein (20 mg/kg) in sterile saline and placed in metabolism cages. Urine samples at 4, 8, 24, 32 and 48 hr and feces samples at 24 and 48 hr after dosing were collected, and radioactivity was determined in samples by liquid scintillation counting. After 48 hr of dosing rats were sacrificed, and blood and major organs (liver, heart, lung, kidney, testes, ovary, spleen, brain, muscle) were removed. Tissue samples of 200-500 mg were used to determine radioactivity.

The cumulative recovery of radioactivity in the urine after administration of 14C NQ is given in Table 5 and 6. Approximately 95% of the administered dose was recovered in the urine of all dose groups in 48 hr. The majority of the dose (60-80%) of the dose was excreted in the first 8 hr after dosing. The amount of radioactivity excreted in the feces was 0.4-1.6%, 48 hr after dosing. There was no significant radioactivity in the tissues (less than 0.02% of the dose) detected 48 hr after dosing. These results indicate that NQ is rapidly absorbed following oral administration and eliminated in urine in 48 hr. The half-life in the rat was 1.8 to 2.9 hr. NQ is essentially eliminated in urine unchanged, as there were no detectable metabolites observed in urine samples when analyzed by TLC and HPLC methods.

Genotoxicity tests

NQ and NSQ were evaluated for their ability to produce genotoxicity in the Ames Salmonella/ mammalian microsome mutagenicity assay, the Chinese hamster ovary cell (CHO) sister chromatid exchange (SCE) assay, the mouse lymphoma forward mutation assay, and Drosophila melanogaster sex-linked recessive lethal (SLRL) test. The results indicate that NQ was not mutagenic or clastogenic in these assays while NSQ produced a positive response in the mouse lymphoma and SCE systems (not dose-related), which suggests that it may be a weak mutagen. Compounds G and GN when tested in Ames assay also exhibited a negative response (Table 7).

Summary

1. The health effects of nitroguanidine, a primary component of U.S. Army triple-based propellant mixture, and of its degradation product/manufacturing intermediates (NSQ, G, GN) were studied for compliance with EPA regulations.

2. Nitroguanidine and nitrosoguanidine were slightly toxic to rats and mice (oral MLD50 values >5000 mg/kg), while guanidine and guanidine nitrate were moderately toxic (oral MLD50 values 475-1100 mg/kg).

3. Nitroguanidine and nitrosoguanidine were nonirritating to eyes and skin of rabbits, while guanidine and guanidine nitrate showed mild (eye) and severe (skin) irritational potentials in rabbits.

4. All compounds were found to be non-toxic to rabbits, when applied dermally (2 g/kg) and did not produce dermal sensitization in guinea pigs.

5. Nitroguanidine was not toxic to rats when administered in the diet at doses as high as 1000 mg/kg/day for 14 days.

6. In a 90-day feeding study at doses of 0, 100, 316, and 1000 mg/kg/day, nitroguanidine caused a decrease in body weight gain and food consumption, and an increase in water consumption at the high dose (1000 mg/kg/day). No other clinical signs and no changes in clinical chemistry and hematology measurements attributable to nitroguanidine were observed in rats.

7. There was no evidence of developmental (teratogenic) toxicity of nitroguanidine in rats and rabbits under conditions of the study (100, 316 and 1000 mg/kg/day); however, nitroguanidine produced maternal and fetal toxicity at the 1000 mg/kg/day dose level.

8. Nitroguanidine was rapidly absorbed following oral administration, and 95% of the administered dose was eliminated in the urine by 48 hr. No significant radioactivity in tissues (liver, heart, lung, kidney, testes, ovary, spleen, brain and muscle) was detected at 48 hr. of dosing. Nitroguanidine was essentially eliminated in the urine unchanged as no metabolites were detected when the urine was analyzed by TLC and HPLC.

9. All compounds (NQ, NSQ, G, GN) were negative in Ames *Salmonella* mutagenicity assay. Nitroguanidine was also found to be negative in the mouse lymphoma, sister chromatid exchange assay, and *Drosophila* SLRL test systems, while nitrosoguanidine produced positive response in the mouse lymphoma and sister chromatid assay systems, which suggests that it may be a weak mutagen.

10. These studies indicate that nitroguanidine may be considered as a slightly toxic compound and that 316 mg/kg may be considered as a No-Observed-Effect-Levels in rats.

TABLE 1

ACUTE TOXICITY TESTS

TESTS	NITRO-GUANIDINE	NITROSO-GUANIDINE	GUANIDINE-HCl	GUANIDINE NITRATE
EYE IRRITATION	NEGATIVE	NEGATIVE	POSITIVE (MILD)	POSITIVE (MILD)
SKIN IRRITATION	NEGATIVE	NEGATIVE	POSITIVE (SEVERE)	POSITIVE (SEVERE)
ACUTE DERMAL TOXICITY [1]	NONTOXIC	NONTOXIC	NONTOXIC	NONTOXIC
SKIN SENSITIZATION [2]	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE

1 RABBITS, 2g/kg

2 GUINEA PIGS-BUEHLERS METHOD 1965

TABLE 2

ACUTE ORAL TOXICITY RESULTS

ANIMALS *		ORAL MLD_{50} VALUES, mg/kg			
		NITRO-GUANIDINE	NITROSO-GUANIDINE	GUNIDINE-HCl	GUANIDINE NITRATE
RATS	MALE	>5000	>5000	556	989
	FEMALE	>5000	>5000	475	730
MICE	MALE	>5000	>5000	579	1105
	FEMALE	>5000	>5000	475	1028

* CHEMICALS WERE ADMINSTERED IN CORN OIL TO SPRAGUE-DAWLEY RATS AND ICR MICE

TABLE 3

EFFECT OF NITROGUANIDINE ON PREGNANCY AND SURVIVAL OF FETUSES OF RATS

TREATMENT * (mg/kg/day)	PERCENT	
	GRAVID	LIVE FETUSES[1]
0	85	100
100	77	95
316	82	100
1000	90	95

* DOSED 6-15 DAY OF GESTATION BY ORAL GAVAGE OF NITROGUANIDINE IN CARBOXYMETHYLCELLULOSE (1%)

1 EXAMINED ON DAY 20

TABLE 4

EFFECT OF NITROGUANIDINE ON THE INCIDENCE OF FETAL MALFORMATIONS AND VARIATIONS IN RATS

	NITROGUANIDINE (mg/kg/day)			
	0	100	316	1000
NUMBER FETUSES/LITTERS	282/23	245/19	224/18	212/18
ANY (EXTERNAL/VISCERAL/SKELETAL)				
MALFORMATIONS	1/1	0/0	3/3	1/1
VARIATIONS	49/18	35/18	32/15	67/14

TABLE 5

CUMULATIVE RECOVERY OF RADIOACTIVITY IN URINE FOLLOWING ADMINISTRATION OF [^{14}C]NITROGUANIDINE TO RATS

	Percentage of administered radioactivity[a]		
	Time after administration		
	8 hr	24 hr	48 hr
Dose group A (20 mg/kg, iv)			
Male	71.4 ± 9.2	89.7 ± 5.5	93.4 ± 4.3
Female	73.1 ± 11.1	93.2 ± 4.8	96.1 ± 4.2
Dose group B (20 mg/kg, oral)			
Male	67.3 ± 10.5	95.7 ± 6.8	99.5 ± 6.9
Female	76.3 ± 4.5	96.3 ± 4.8	103.9 ± 3.2
Dose group C (200 mg/kg, oral)			
Male	65.8 ± 9.3	95.3 ± 2.5	98.3 ± 2.8
Female	61.8 ± 5.8	94.9 ± 6.6	97.8 ± 6.1

[a] Mean ± SD, $N = 6$.

TABLE 6

DISTRIBUTION AND EXCRETION OF RADIOACTIVITY 48 hr AFTER ADMINISTRATION OF [^{14}C]NITROGUANIDINE TO RATS

	Percentage of administered radioactivity[a,b]					
	Group A (iv, 20 mg/kg)		Group B (oral, 20 mg/kg)		Group C (oral, 200 mg/kg)	
	Male	Female	Male	Female	Male	Female
Major Organs[c]	0	0	0	0	0	0
Whole blood	0	0	0	0	0	0
Expired air[d]	—	—	—	—	—	—
Feces						
(urine contaminated)	0.7 ± 0.4	0.6 ± 0.4	1.6 ± 1.3	1.2 ± 0.7	0.7 ± 0.2	0.4 ± 0.1
Urine	93.4 ± 4.3	96.1 ± 4.2	99.5 ± 6.9	103.9 ± 3.2	98.3 ± 2.8	97.8 ± 6.1
Total recovery	94.1	96.7	101.1	105.1	99.0	98.2

[a] Mean ± SD, $N = 6$.

[b] Zero values indicate levels less than 0.02% of administered radioactivity.

[c] Liver, lung, kidney, spleen, brain, skeletal muscle, testes, ovaries.

[d] No radiolabel was found in expired CO_2 of pilot study animals ($N = 8$); subsequent studies did not include expired air measurements.

TABLE 7

GENOTOXICITY TESTS

TESTS	NITRO-GUANIDINE	NITROSO-GUANIDINE	GUANIDINE-HCl	GUANIDINE NITRATE
AMES ASSAY	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE
MOUSE LYMPHOMA ASSAY	NEGATIVE	POSITIVE	–	–
SISTER CHROMATID EXCHANGE ASSAY	NEGATIVE	POSITIVE [1]	–	–
DROSOPHILA SEX LINKED RECESSIVE LETHAL TEST	NEGATIVE	NEGATIVE	–	–

1 NOT DOSE RELATED

INFLUENCE OF WELL CASING MATERIALS ON CHEMICAL SPECIES IN GROUND WATER

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INTRODUCTION

Prior to 1985 polyvinyl chloride (PVC) well casings were the most commonly used casing material for ground water monitoring. In 1985 the EPA published the initial draft of the Resource Conservation and Recovery Act (RCRA) "Ground Water Monitoring Technical Enforcement Guidance Document." This document required that only Teflon (polytetrafluoroethylene, PTFE) or stainless steel 316 (SS 316) be used in constructing wells. The EPA was concerned that the materials commonly used in ground water monitoring might affect the quality of the samples. Specifically, these materials might adsorb or leach constituents, thereby affecting the quality of the ground water samples, or the casings might not have the long-term structural characteristics required for RCRA monitoring wells. While the requirements are less rigorous in the final draft of this document, fluorocarbon resin or stainless steel (SS) is required for monitoring volatile organics in the saturated zone. However, a careful review of the literature published prior to 1985 did not reveal much evidence to support this position.

Few studies have examined the interaction of well casing materials and metal species. There is considerable evidence, however, that sorption of metals by plastic and glass containers can be significant (Eicholz et al. 1965, Robertson 1968, Batley and Gardner 1977, and Masse et al. 1981). Miller (1982) found negligble loss of Cr by PVC well casings but large losses of Pb. These results were similiar to other studies with Pyrex glass and polyethylene where Pb was the most rapidly lost analyte (Shrendrikar et al. 1976).

One in-situ study compared the sorption/leaching of metal species by PVC, PTFE, and SS wells (Barcelona and Helfrich 1986). (The wells were located at upgradient and downgradient locations at two sites.) They found increased levels of Fe in water samples taken from the non-purged SS well, but did not find any other statistically significant differences between samples taken from wells constructed with the three casing materials. A previous, in-situ study (Houghton and Berger 1984) found that a steel-cased well appeared to leach a number of metal species, including Fe, Cd, Cr, Cu, Mn, Mo, Se, and Zn, when compared with a PVC well and another well constructed of acrylonitrile-butadiene-styrene (ABS). (The wells were sampled twice.)

Several recent publications have studied sorption of organic species by well casing materials. Miller (1982) tested PVC for sorption of trace levels (2-14 ppb) of six halogenated organic compounds including bromoform, trichlorofluoromethane, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and tetrachloroethylene. He found slow loss of tetrachloroethylene in samples containing PVC; he estimated that loss was 25 to 50% after 6 weeks.

Reynolds and Gillham (1986) tested both PVC and PTFE for sorption of trace levels (ppb) of five halogenated organics: 1,1,1-trichloroethane (TRI), 1,1,2,2-terachloroethane (TET), bromoform (BRO), tetrachoroethylene (TEY), and hexachloroethane (HEX). After 5 weeks, they found slow sorption of all the analytes except BRO by PVC. They also found that the PTFE slowly

absorbed TRI, TET, and HEX and rapidly sorbed TEY. In comparison 50% of the TEY was sorbed by the PVC in 5 weeks, while the same amount was sorbed by PTFE casings in only 8 hours.

Sykes et al. (1986) compared the sorptive properties of PVC, SS, and PTFE well casings. The casing materials were equilibrated for 7 days (5°C) in analyte solution, placed in fresh analyte solution, and then tested for losses due to sorption after 1 and 24 hours. After 24 hours they did not find any significant losses for any of the casing materials.

While these studies indicate that sorption may be a significant problem for the plastic casings over the long term, only one study, Miller (1982), examined desorption. In that study he observed some desorption of tetrachloroethylene during the first 2 weeks.

Organic substances may also leach from casing materials. There is not much literature on the leaching of organics from SS casings. One would not expect to find much in the way of organics leaching from metal casings, although one possible exception is lubricants. Components of PVC that could leach include vinyl chloride monomer (VCM), plasticizers (phthalate esters), thermal stabilizers, pigments, lubricants, fillers, impurities, and transformation products. We do not expect that leaching plasticizers would be a problem since rigid PVC products are essentially free of these substances (Barcelona et al. 1984). Previous problems with the leaching of residual vinyl chloride monomer (RCVM) have been greatly reduced by lowering the RVCM content in the resin and final product (Barcelona et al. 1984). Also the amount of leaching stabilizers can be reduced if stabilizers with relatively large organic moieties are used or by pretreating the casing with dilute acid, or by precleaning and/or prerinsing it (Dietz et al. 1977, Packham 1971).

Two studies have looked for analytical interferences in leachates from PVC. In one study the leachate was solvent extracted, concentrated 1000-fold, and then analyzed by flame ionization gas chromatography (Miller 1982). In the other study the leachate was analyzed directly by reversed-phase high performance liquid chromatography (Parker and Jenkins 1986). No interferences were found in either study. Curran and Tomson (1983) compared five plastics for leaching of contaminants (analysis was by capillary gas chromatography). They found that Teflon was the best, although they also found that one PVC pipe that had been washed with detergent also did not leach any contaminants.

Based on our literature review, we found it difficult to make a recommendation regarding the selection of a well casing material for ground water monitoring of metals and organics. Most of these studies examined only one or two casing materials. Also, most of the literature was subjective; either the data presented were not very quantitative or else the studies lacked adequate replication. The purpose of our study was to examine whether PTFE and SS well casings were superior to PVC casings (as claimed by the EPA) for monitoring trace levels of both metal and organic species in ground water. For these studies we used four types of well casings manufactured specifically for ground water monitoring: PVC, PTFE, and SS 304 and 316.

INORGANIC STUDY

Experimental

Four metal analytes were studied; they were arsenic, cadmium, chromium and lead. This study used a complete factorial design to test the effect of concentration level of metals, pH and total organic carbon on sorption.

Two concentrations were used (50 and 10 μg/L for As, Cr, and Pb; 10 and 2 μg/L for Cd). The higher concentrations were the maximum levels set by the EPA for primary drinking water. The two pHs used were 7.8 (the natural pH of the well water) and 5.8 (acidified natural sample). Humic acid was added to half the samples (5 mg/L) to raise the total organic content of the water. Duplicate samples were run for each set of conditions. Two-centimeter sections of 5-cm (2 in.) diameter (rinsed) well casing were then placed in 125-mL polypropylene jars containing 100 mL of the test solution. The samples were kept at room temperature for 72 hours. (For further information regarding the experimental design please see Hewitt, in press.) Sample aliquots were taken from each container after 30 minutes and after 4, 8, 24, and 72 hours. The aliquots were placed in clean 7.5-mL polyethylene vials and were acidified to a pH <1 with nitric acid, to prevent losses due to sorption by the container. Concentrations of each metal were based on two or more injections, and analysis was by graphite furnace atomic absorption spectroscopy.

Results and Discussion

During this experiment, surface rust developed on approximately 45% of the stainless steel casings. In several cases (SS 316 at a low pH), sufficient oxidation occurred to form a hydrous iron oxide precipitate. In this study we found that the SS 316 was more susceptible to rusting than the SS 304; 69% of the SS 316 rusted compared with 19% of the SS 304. We noticed that for the SS 304 casings rusting occurred on or near the cut surface, while for the SS 316 casings rusting occurred primarily near the weld on the outer wall.

In general there was no change in the arsenic concentration for either of the samples containing PVC or PTFE during the 72-hour test period (Fig. 1). This may be because the preferred state of this metal in aqueous solution is in the anionic form as arsenates ($H_3AsO_4^-$, $H_2AsO_4^-$, and $HAsO_4^{2-}$) under oxidizing conditions and arsenites ($H_3AsO_3^-$, $H_2AsO_3^-$, $HAsO_3^{2-}$) under

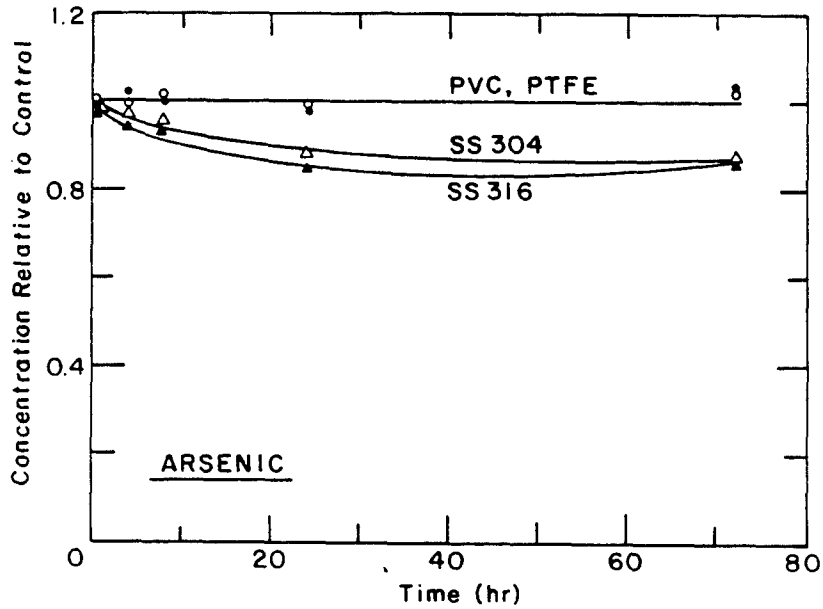


Figure 1. Arsenic Concentration Trends for Four Well Casing Materials.

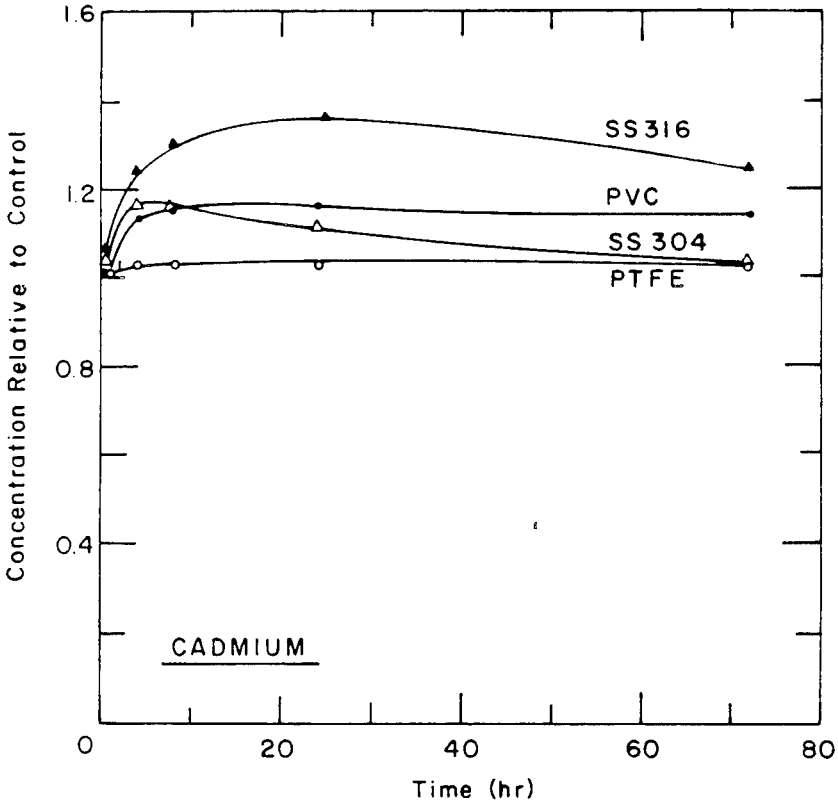


Figure 2. Cadmium Concentration Trends for Four Well Casing Materials.

reducing conditions. These partially dissociated oxy acids are negatively charged and not likely to interact with surfaces such as plastics, which are known for their cation exchange capacity (Masse et al. 1981). Both SS casings showed a net loss for As of 10-15% over the 72-hour period studied.

Within the first 4 hours, the cadmium concentration increased by 10% or more for all the casing materials except for PTFE (Fig. 2). After the first 4 hours the concentrations in the samples with the PVC casings did not increase. We also found that pH had a significant effect; more Cd was leached in the low pH samples. The concentration in the samples with the SS 304 casings increased by 15% after 4 hours. After that there did not appear to be any further enrichment, and after 72 hours the concentration of Cd returned to the same level as that of the controls. Once again, more Cd was leached in the low pH samples. The SS 316 casings leached the most Cd and continued to leach Cd for 24 hours; then there was some loss during the following 48 hours. We observed a large standard deviation for replicate treatments with both stainless steel casings; following the initial samples, the relative standard deviations ranged from 12 to 15% for the SS 304 and from 47 to 68% for the SS 316. Because of the variability in the measured concentrations of the samples with SS 316, there was no significant effect of pH. When comparing sample duplicates where large differences were observed, we noticed that one of the samples had visible surface oxidation. The relative standard deviations for the replicate solutions exposed to plastic materials were lower than 6%.

There was no measurable sorption of chromium by the PTFE, PVC and SS 304 casings (Fig. 3). This may be because the stable form of chromium is dichromate and chromate ($Cr_2O_7^{2-}$, CrO_4^{2-}). As stated previously for As, negatively charged species are not as likely to interact with plastics.

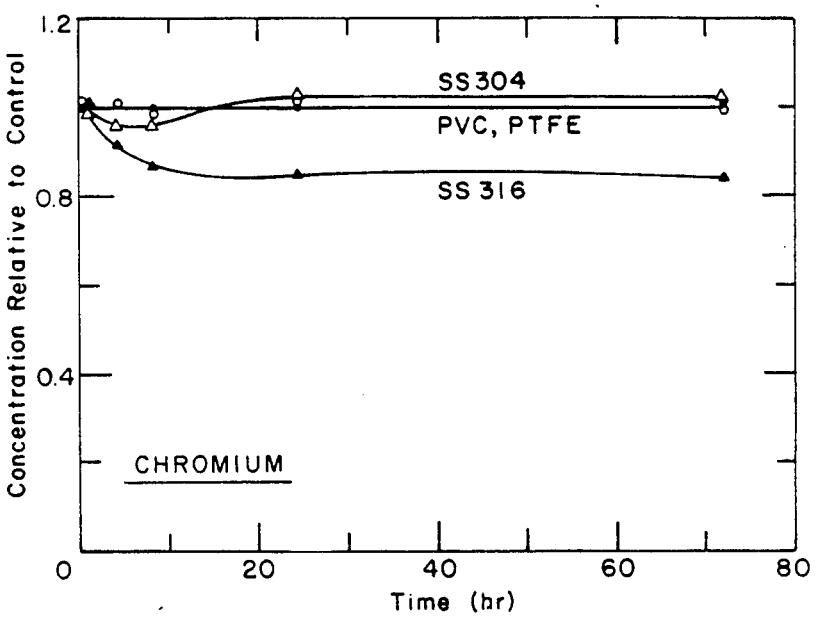


Figure 3. Chromium Concentration Trends for Four Well Casing Materials.

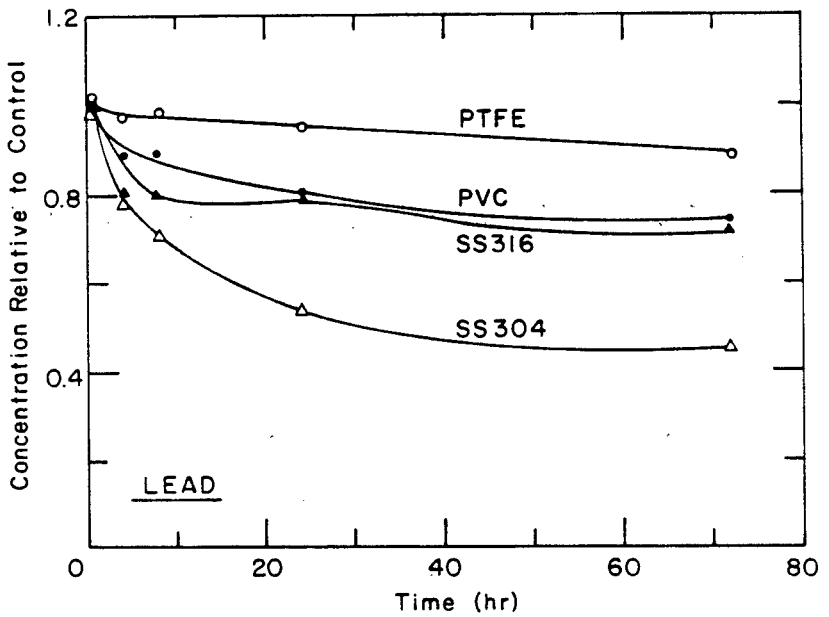


Figure 4. Lead Concentration Trends for Four Well Casing Materials.

Samples containing the SS 316 casings lost 8% of the analyte after 4 hours and 13% after 8 hours. There was little subsequent loss; final loss after 72 hours was 16%. Once again the standard deviation was large for these samples. After 8 hours the relative standard deviation was already 10%. It appeared that surface oxidation was greater at lower pHs and these differences from sample to sample contributed to the large variability. The standard deviation was also large for the SS 304 samples; after 8 hours the relative standard deviation was 16% and after 72 hours it was 42%. Again the paired samples with the largest differences in their measured concentrations had one member with visible surface oxidation.

All the solutions exposed to the 4 casings materials showed some loss of lead with time (Fig. 4). Loss was the least for the PTFE casings; loss

was only 5% after 24 hours and 10% after 72 hours. PVC was the next least active surface with 10% loss after only 4 hours and 20% loss after 24 hours. Losses of Pb for the solutions exposed to SS 316 were initially greater than for PVC; however, the loss after 72 hours was also about 20%. Losses were the greatest for samples containing SS 304; 22% was lost after 4 hours and 47% was lost after 24 hours. With this analyte, we saw a large increase in the standard deviation with time only for the samples containing the SS 316 casings. For both SS casings, loss of Pb was reduced at the lower pH. At the lower pH the hydrogen ions may have competed for sorption sites, thereby reducing Pb sorption. Added humic material apparently acted as a complexing agent in solution making lead less prone to sorption.

ORGANIC STUDY

Experimental

The four types of well casings were also tested for sorption/desorption of low levels of 10 organic substances. The substances tested were hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5-trinitrobenzene (TNB), cis- and trans-1,2-dichloroethylene (CDCE and TDCE), m-nitrotoluene (MNT), trichloroethylene (TCE), chlorobenzene (CLB), and o-, p- and m-dichlorobenzene (ODCB, PDCB, MDCB). We used pairs of isomers to test the effect of molecular structure on sorption. A combined analyte test solution was prepared using well water. The concentration of each analyte in this solution was approximately 2 mg/L.

For this experiment, sections of casing were cut 11-14 mm in length; because the wall thicknesses were different for the different casings, the length was varied so that the surface area for each type of casing would be the same. These sections were then cut into quarters and two of these pieces were placed in 40-mL glass vials. The vials were then filled with the aqueous organic solution so that there was no head space and then capped with Teflon-lined plastic caps. Vials with no well casing material served as controls. Mercuric chloride was added to the organic solution to prevent biodegradation of the organics. Three aliquots were taken from the orginal container for time 0 samples. Three samples for each material were sacrificed for each sample time. Sample times were 1 hour, 8 hours, 24 hours, 72 hours (3 days), 168 hours (7 days), and approximately 1000 hours (6 weeks).

After removing an aliquot from each of the 1000-hour samples for analysis, we emptied the vials and rinsed the well casings with fresh well water. The samples were placed in clean vials that were then filled with fresh well water with no head space, capped, and allowed to stand for 3 days. The well water was then analyzed to determine if desorption occurred.

All analytical determinations were made by reversed-phase high performance liquid chromatography (Parker and Jenkins in press). Our analytical precision was extremely good; the relative standard deviation ranged from 0.4 to 3.9%, as determined by the pooled standard deviation of triplicate initial measurements. For each analyte and sample time, a one-way analysis of variance (ANOVA) was performed to determine if the well casing material had a significant effect on the analyte concentration. A multiple range test was also performed to determine which materials were significantly different from each other. (For further information please see Parker and Jenkins, in press.)

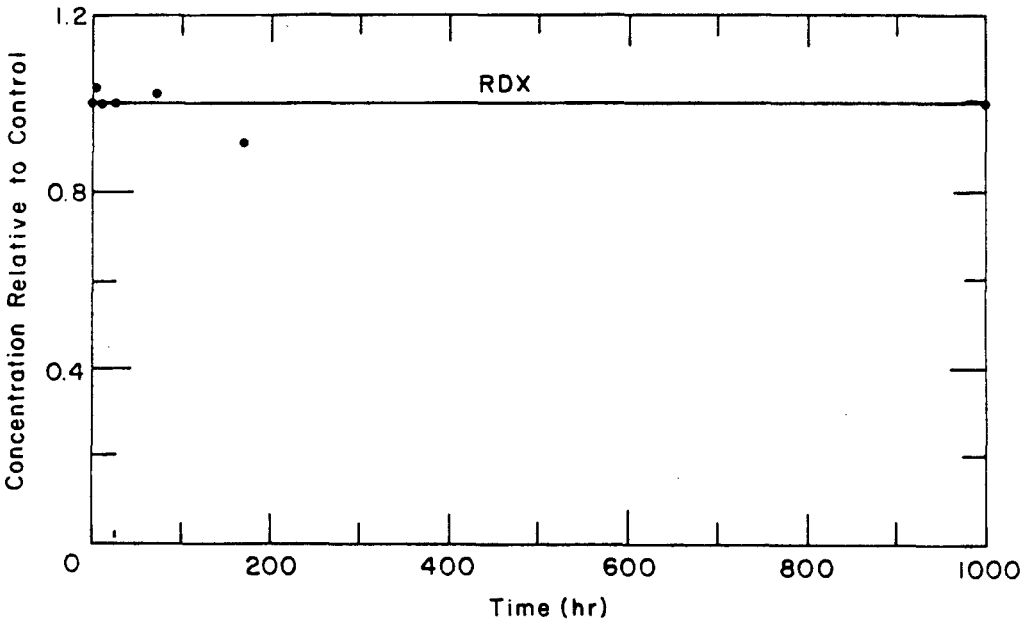


Figure 5. Concentration of RDX in Samples Exposed to PTFE Well Casings.

Results and Discussion

Neither type of SS casing affected the concentrations of any of the ten analytes in solution. However, we did notice that both types of casings were prone to rusting. For the plastics, the results differed from analyte to analyte.

For RDX and TNB there was also no statistically significant effect of the well casing material on the concentration, even after 1000 hours. Figure 5 shows the concentration of RDX with time for the samples containing the PTFE well casing.

After RDX and TNB, the substance that was next least sorbed was MNT. Loss was significant only after 1000 hours and then only for samples containing the PTFE casings (10% loss).

There was significant loss for the remainder of the substances in the samples containing the PTFE casings and for many of the samples containing the PVC casings as well. With CDCE there was a statistically significant loss with the PTFE casings after only 8 hours (4% loss). After 1000 hours 21% of this analyte was lost. There were no significant losses of CDCE in the samples containing PVC at any time. Figure 6 shows the losses of CDCE and TDCE with time for PTFE. TDCE was lost much more rapidly and to a greater extent than CDCE. Once again, after only 8 hours there was a statistically significant loss (8%) of TDCE in the samples containing PTFE. After 24 hours the samples with the PVC casing were also significantly lower than the the control samples, with 7% loss; loss for the PTFE samples was 12%. After 1000 hours, 44% of the TDCE was lost in the samples containing PTFE, and 17% was lost in the solutions containing PVC.

For TCE there was a statistically significant loss in the samples with PTFE after only 8 hours (Fig. 7). After 24 hours there was also a statistically significant loss in the samples with PVC casings as well; loss was 5% for the PVC samples and 15% for the PTFE samples. After 1000 hours significantly more TCE was lost in the PTFE samples, with 60% loss, than in the PVC samples with 12% loss.

We saw a similiar pattern of loss with CLB, ODCB, MDCB, and PDCB. Figure 8 shows the losses for the four well casing materials for MDCB . In

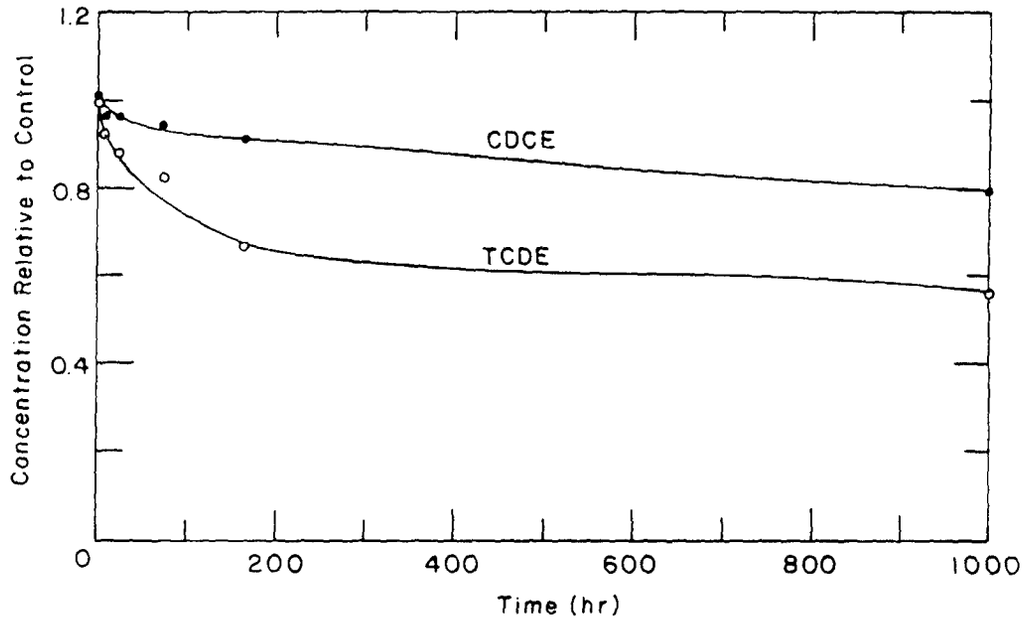


Figure 6. Comparison of Loss of CDCE and TDCE in Samples Exposed to PTFE Well Casings.

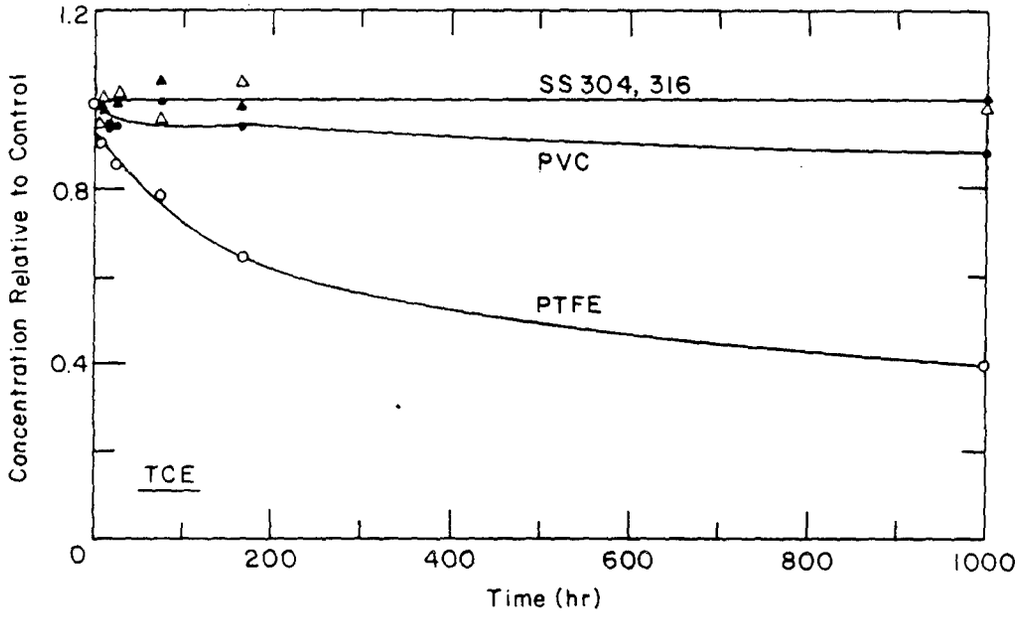


Figure 7. TCE Concentrations in Samples Exposed to Four Well Casing Materials.

all cases losses were greater for PTFE than for PVC. Figure 9 shows the loss of CLB, ODCB, MDCB and PDCB for the samples containing PTFE. (PDCB is in parentheses since the loss was essentially identical to that of MDCB.) The order of loss was PDCE and MDCB > ODCB > CLB.

We also placed the casings from the 1000-hour samples in fresh water and allowed them to sit for 3 days. This was done to determine if the analytes lost during the previous part of this experiment could be recovered. If the analytes could be recovered, this would indicate that the losses were due to sorption. As expected, we did not recover any of the

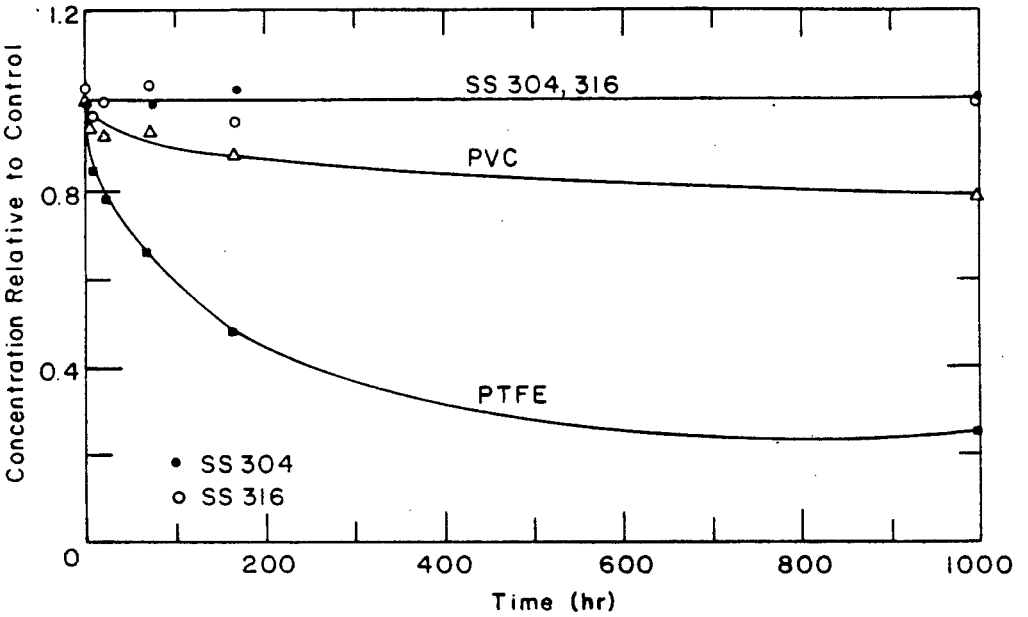


Figure 8. MDCB Concentrations in Samples Exposed to Four Well Casing

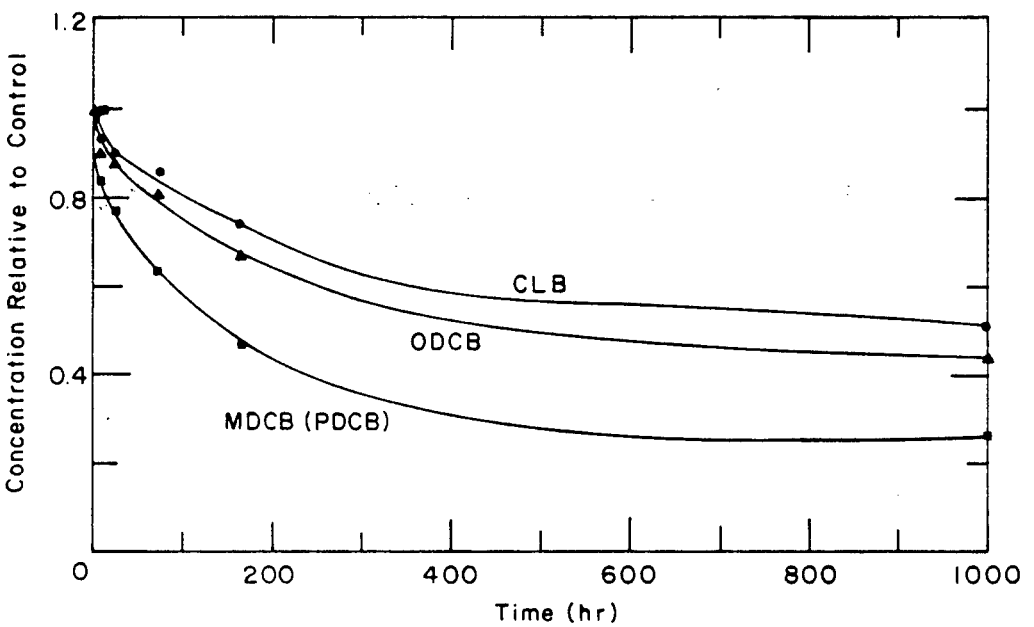


Figure 9. Comparison of Losses of CLB, ODCB, MDCB and PDCB by Samples Exposed to PTFE Well Casings.

organics from the SS casings. We did recover measurable amounts of all the organics that had been lost by exposure to the plastic casings. Thus some type of sorption mechanism is responsible for the loss of organic analytes observed with the plastic casings. The amount of analyte recovered closely paralleled the amount that was sorbed (Table 1). Therefore, desorption of sorbed analytes could result in falsely high values if analyte concentrations in the well were to decrease.

We did not find any simple correlation between the rate of loss (sorption) of the organic constituents with either molecular weight,

Table 1. Results of Desorption Study.

Casing Material	Concentration in mg/L RDX	TNB	CDCE	TDCE	MNT	TCE	CLB	ODCB	PDCB	MDCB
PTFE	ND	ND	0.20	0.44	0.08	0.48	0.28	0.36	0.32	0.36
PVC	ND	ND	0.08	0.15	0.04	0.13	0.10	0.15	0.16	0.20

ND = None detected

solubility (polarity), or the Octanol/Water Partition Coefficient. However, we noticed that where pairs of isomers were tested, the more linear (less polar) isomers were sorbed the most rapidly and to the greatest extent. While we do not know for certain whether sorption was due to adsorption on the surface or absorption within the bulk plastic, the larger losses of the more linear molecules may indicate that diffusion into the polymer network occurred. Berens and Hopfenberg (1982) studied the diffusion of organic vapors in PVC and found that elongated or flattened molecules had distinctly greater mobility than nearly spherical molecules of the same mean molecular diameter.

In the desorption study we noticed that the more linear, smaller TDCE and TCE molecules were desorbed to a greater extent from the PTFE casings than the larger DCB molecules.

SUMMARY AND CONCLUSIONS

In summary, our inorganic studies indicated that both SS 304 and 316 casings were subject to oxidation, creating sites for sorption and a mechanism for release of impurities and major constituents. The sporadic occurrence of oxidation made concentrations of trace metals exposed to SS casings prone to large variations. SS casings sorbed both cations and anions at rates faster than PVC or PTFE. PVC casings were a source of low levels of Cd. Most of the leaching occurred during the first 4 hours. PVC was also a moderately active surface for sorption of Pb. PTFE showed no interaction with As, Cd, or Cr and was the least sorptive of the four casings for Pb. Clearly this material is the best choice when samples must be collected for analyses of trace levels of metals. PVC is the best second choice; especially if it is pretreated by either washing or soaking in dilute mineral acid (to reduce or eliminate problems with leaching, Packham 1971) .

In contrast, our organic sorption study indicated that PTFE was clearly the poorest choice of the four well casing materials tested. Significant losses of all the chlorinated compounds and one nitroaromatic compound occurred within 1-8 hours. While PVC did sorb several of the organics, sorption was always less and much slower than for PTFE; usually 24 hours lapsed before significant losses occurred. There was no sorption observed for any of the organics studied by either SS casing, although again rusting was observed. At this time we can not predict which classes of compounds are the most susceptible to sorption by the plastic casings.

The follow-up desorption study showed that those substances that are sorbed can be released at a later date, thereby giving falsely high values.

Choosing one casing material for samples that will be analyzed for both trace metals and organics is a compromise. However, PVC appears to be the best choice of the four casing materials, based on the results of the tests we have performed to date.

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INTRODUCTION

U.S. ARMY BIOMEDICAL RESEARCH AND DEVELOPMENT LABORATORY ENVIRONMENTAL QUALITY/HEALTH EFFECTS

The USABRDL environmental research program has as its goal the development of a sufficient knowledge base to define the environmental fate of Army-unique pollutants, smokes, obscurants, conventional munitions, and other hazardous and toxic materials and their toxicity to terrestrial and aquatic life forms and humans exposed to them. The environmental data base is not only required by regulation and statute, but also serves to conserve resources, to assist in maintaining readiness and avoiding or succeeding in costly litigations.

The research program is divided into three areas. These are: (1) Assessment, Characterization, and Fate; (2) Environmental Hazard Assessment; and (3) Environmental Criteria Documentation. Each area builds on the preceding, culminating in the publication of criteria documents.

The Assessment, Characterization, and Fate area serves to define, confirm the need for, and prioritize research. The efforts begin with critical assessments of scientific literature to establish a preliminary literature based data set and hazard assessment. Almost parallel to the literature activities, techniques are developed to analyze and sample for the materials and wastes discovered in the literature assessment. The mechanisms and rates of environmental processes affecting the persistence (fate) of military relevant chemicals in water and soil systems are determined as the last activity in this area.

Within the Environmental Hazard Assessment process, studies are conducted to determine the level of adverse effects from exposure to military wastes and materials on economically and ecologically important terrestrial plants and animals. Studies are also conducted to determine the mammalian and aquatic toxicity of the materials of interest.

Environmental Criteria Documentation activities provide the final product of the research. Both criteria and health advisories are then calculated and published. These documents define the concentration levels that will protect the environment and human health from emissions from the production, use, and disposal of military relevant materials.

THE PHOTOCHEMISTRY OF NITROGUANIDINE IN WATER AND OTHER TREATMENT CONSIDERATIONS

W. Dickinson Burrows

Production of nitroguanidine at Sunflower Army Ammunition Plant (SFAAP), DeSoto, KS, is associated with a number of waste streams with quite different characteristics. Initial studies by the US Army Biomedical Research and Development Laboratory have been directed toward physical chemical treatment of wastewater containing relatively low levels (less than 100 mg/L) of guanidine and nitroguanidine. Ultraviolet photolysis was investigated as an alternative to granular activated carbon adsorption for removal of nitroguanidine.

For an initial nitroguanidine concentration of 50 mg/L, photolysis exhibits zero-order kinetics through complete disappearance, regardless of pH, and the rate is somewhat faster than for other nitramine explosives and propellants, such as RDX, for example. The products of photolysis became a matter of concern when it was discovered that photo-nitroguanidine is toxic to aquatic organisms by approximately two orders of magnitude more than the parent compound. The principal products from unbuffered nitroguanidine solutions are guanidine, urea and nitrite ion, with lesser quantities of cyanoguanidine, nitrate ion and ammonia, accounting for 80 percent of the carbon and virtually all of the nitrogen. Nitroso-guanidine is a transient intermediate; in separate experiments it was shown to give 90 percent conversion to guanidinium nitrite at a rate slightly faster than for nitroguanidine. Photolysis of nitroguanidine at pH 10 proceeds at nearly the same rate as the unbuffered reaction, but the product mix is different; less than 25 percent of nitroguanidine carbon is accounted for as urea, guanidine and cyanoguanidine. Elemental nitrogen is a significant product.

All the stable products of unbuffered nitroguanidine photolysis except urea and nitrate ion are known to be much more toxic to aquatic organisms than the parent compound. The breakdown of nitroguanidine by sunlight in natural waters has been shown to have an initial half-life of 1 to 2 days, indicating that discharge of wastewaters will present a hazard to aquatic life only if the average nitroguanidine level substantially exceeds the present SFAAP permit limit of 25 mg/L. On the other hand, treatment of nitroguanidine wastewaters with ultraviolet light, which is much more rapid, could result in accumulation of photolysis products at toxic levels.

ENVIRONMENTAL MICROBIOLOGY AND EFFECTS OF NITROGUANIDINE (NQ) ON PHYSIOLOGY OF PLANTS

Elizabeth P. Burrows

Screening studies have shown that NQ is inert to aerobic biotransformation by microorganisms in natural waters and soils, under conditions which resulted in complete biodegradation of 1,3-dinitrobenzene. Even in the presence of soil microorganisms growing on a substrate such as methanol there was no significant cometabolism.

Because disposal of NQ-containing wastewater by land application is practiced at Sunflower Army Ammunition Plant, a laboratory study was undertaken to assess the probable effects and possible impact on the local vegetation. Selected species (soybeans, tall fescue, and smooth bromegrass) were grown both in hydroponic media and in soils in the presence of increasing concentrations of NQ, and the effects on growth and viability of the plants were determined by measurement of various physiological parameters. At higher concentrations (>1mM in soybeans) toxicity was manifested by growth inhibition and leaf damage (chlorosis). Both grass species showed little or no effects over the concentration range studied (2-8 mM).

Experiments with ^{14}C-labeled NQ to determine extents of uptake from both water and soil, distribution in the plant, and metabolic fate have been undertaken and are in progress. A linear relationship between starting NQ concentration and depletion of ^{14}C from the hydroponic medium by soybeans has been observed. Preliminary experiments indicate that less than 20% of the ^{14}C depleted from the medium is recovered from the plant by extraction. The apparent loss of volatile material, presumably CO_2, by metabolism of NQ in the plant is to be verified by trapping experiments in the near future. The results so far are consistent with the hypothesis that NQ is absorbed by the soybean root and translocated to the leaves, where it induces chlorosis and is metabolized.

BIODEGRADATION OF THE GUANIDINE COMPONENT OF NITROGUANIDINE WASTESTREAMS BY ENVIRONMENTAL AEROBES

Wayne Mitchell

Degradation of the guanidine (guanidinium ion) component of nitroguanidine wastewaters by aerobic microorganisms could be demonstrated in a variety of surface water and soil samples. In surface waters, degradation of guanidinium ion was characterized by long and variable periods prior to enhanced microbial activity. Breakdown of the cation was considerable slower than that of the guanidinium containing amino acid arginine. A carbon source could potentiate the degradation of guanidinium ion, in which case its carbon was mineralized and its nitrogen could be used for growth; however, at nutrient levels in surface water, only slight short term mineralization of the cation's carbon was demonstrated and was considerably slower than that of urea carbon. Degradation of guanidinium ion by microorganisms capable of growing on it as a sole carbon source could also be demonstrated, but the process was estimated to be slow when compared to utilization rates for other xenobiotic compounds. The development of such populations in surface water samples was also dependent on the concentration of guanidinium ion.

In some soils at low levels, the biodegradation of guanidinium ion was rapid, extensive, and approached the levels of urea degradation. With increasing concentrations of guanidinium ion, its degradation was much slower than that of urea but was eventually as extensive. Degradation of the cation in soil could be stimulated by carbon supplements and was not significantly inhibited by other components of nitroguanidine waste streams.

Both fermentative and oxidative microorganisms were isolated which used guanidinium's nitrogen for growth in the presence of a carbon source. In one such organism, a Pseudomonad, patterns of urea and guanidinium carbon mineralization were nearly the same. Induction of the enzyme urease was seen to accompany guanidinium ion utilization in this isolate.

LABORATORY ANALYSIS OF THE TOXIC EFFECT OF PURIFIED NITROGUANIDINE AND NITROGUANIDINE PHOTOLYSIS PRODUCTS ON SELECTED FRESHWATER ORGANISMS

Michael Major

The toxicity of nitroguanidine (NQ) in the fresh water aquatic ecosystem is seen to depend very much upon the specific conditions encountered. Under laboratory conditions, pure NQ was not sufficiently toxic, even at maximum saturation, to produce an LD50/EC50 response in any of 9 species tested. However, the solubility of this compound increases by more than 76 percent in the temperature range between 12 and 22°C and compounds found naturally in aquatic systems may also increase its solubility. In addition, a series of photolysis products, when present as a group, increases aquatic toxicity by nearly two orders of magnitude when compared with pure NQ.

The compounds responsible for this increase in toxicity and the existence of possible synergism have yet to be determined. It is known, however, that the toxicity of photolyzed NQ is little diminished by storage. Hence, it is unlikely that either the nitroso or free radical guanidinyl forms are involved. Assay of photolysis products reveals concentrations of guanidine sufficient to produce a low level chronic response in water fleas but not nearly enough to produce the multi-species acute response seen here.

Nitrite ion accumulates in increasing proportion to other components during the photolysis of more concentrated NQ solutions. This tendency is important to these experiments because test water was obtained by dilution of a concentrated stock solution of photolyzed NQ. It is therefore probable that the nitrite component of the photo-NQ mixture contributes at least a portion of the observed toxicity.

ADDITIONAL
PAPERS

LABORATORY IDENTIFICATION OF GLASS COMPOSITIONS SUITABLE FOR DISPOSAL OF WASTE REACTIVE METAL

by

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I. INTRODUCTION

A. *Objective*

A one-step integrated process is being developed for the conversion of waste sodium to a glass form for ultimate disposal. Much of the waste sodium is contaminated with small amounts of radionuclides. The objective of this research was to define glass compositions that contain a relatively high content of sodium, are conveniently formed from readily available materials, and are resistant to leaching of the sodium and the associated radioactive contaminants by environmental waters. The selection of the glass composition is thus affected by the amount of sodium it contains, the processing temperatures and materials required, and the rate at which its constituents are leached by ground or rain water.

B. *Background*

Waste reactive metals, primarily sodium from the effort to develop sodium-cooled fast breeder nuclear reactors, represent a small but significant amount of hazardous waste that needs to be disposed of in a safe and economical manner. The major problem with direct disposal of sodium is, of course, that it is extremely reactive and interacts violently at room temperature with many materials, including air, water, steam, and carbon dioxide. Reaction with air, water, or carbon dioxide results in the release of large amounts of heat, and the reaction with water or steam produces not only heat but significant quantities of hydrogen as well, resulting in a potentially explosive mixture.

In addition to the chemical hazard, much of this sodium also contains small but varying amounts of radioactive contaminants. These radionuclides are generated as a result of nuclear reactor operations (or from the operation of test facilities used for the development of nuclear reactor subsystems). These radioactive contaminants must not be permitted to enter the biological environment in an uncontrolled manner.

The sodium needs to be disposed of in a safe and effective manner. Sodium is not a "listed" waste, but rather a "characteristic" waste. The Resource Conservation and Recovery Act (RCRA) requires that appropriate steps be taken to reduce the rate of generation of wastes through process modifications, that wastes currently in storage be examined to identify the possible recovery of useful materials, and that the wastes that need to be disposed of be suitably packaged to ensure that the biological environment is not affected. Other relevant regulations include 10CFR61, which specifies the characteristics of the waste packaging desired.[1] Based on current knowledge of the waste sodium inventory, compliance with the 10CFR61 requirements should pose no serious problems for the glass produced by the sodium conversion process.[2]

The improved method being developed for the disposal of waste sodium is a one-step integrated process to oxidize sodium and convert it to a glass.[3] Such a process has the advantages that the product is resistant to environmental degradation and requires low cost materials such as sand and limestone; the process energy required to produce the glass can be derived, to a large extent, from the exothermic oxidation of the sodium itself; the process requires no utilities other than electricity; and procedures for working with glass, such as casting and annealing, are well developed and in commercial practice. The glass form is

chemically inert and, at least for the majority of the waste sodium that contains only very small amounts of radioactivity, can be disposed of in an ordinary landfill.

II. EXPERIMENTAL

A. *Sample Glass Preparation*

Twenty- to thirty-gram samples of the glasses to be examined were prepared in the laboratory. These glasses were made from two or more of the following anhydrous reagents (Atomergic Chemicals Corporation): 99.9% SiO_2, 99.9% Na_2CO_3, 99.999% CaO, 99.9% B_2O_3, and 99.8% Al_2O_3. Both Na_2CO_3 and B_2O_3 required extra drying before use because of their hygroscopic nature. For this purpose, the B_2O_3 was heated slowly over a period of five days to a glassy state (1000°C). This glassy B_2O_3 was ground to a powder using a mortar and pestle and then used in the sample glass formulations. The Na_2CO_3 was dried by heating at 200°C for 24 to 48 hours. The constituents for the desired glass sample were then weighed out and placed in a 40 mL crucible made of 90% platinum-10% rhodium.

The ingredients were sintered in a tube furnace according to the temperature program shown in Fig. 1-a. The crucible was heated to 850°C at a rate of 1.05°C/min, held at 850°C for 5 h, heated up to 1600°C at a rate of 3.55°C/min, held at 1600°C for 30 min. The molten glass was then poured into a 32 × 10 × 16 mm boron nitride mold preheated to 350°C. The glass loaf was then allowed to cool to room temperature. The platinum/rhodium crucible was cleaned with 48% hydrofluoric acid after each glass sample was made.

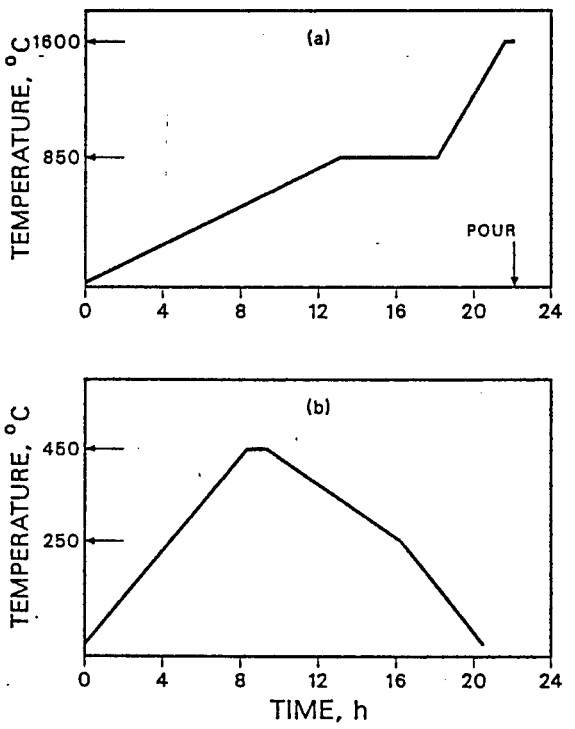


Fig. 1. Temperature Program for
(a) Glass Formation
(b) Annealing

The glass loaves were annealed in a second tube furnace according to the temperature program shown in Fig. 1-b. The loaves were heated from room temperature to 450°C at a

rate of 0.85°C/min, held at 450°C for 1 h, cooled down to 250°C at a rate of 0.5°C/min, and then cooled to room temperature at a rate of 0.9°C/min. Glass compositions containing calcium oxide were annealed at 475 to 500°C. Annealing the glass samples was necessary because the unannealed samples were very friable and difficult to cut into the cubes needed for the leach tests.

B. *Leaching Tests*

The loaves of glass were cut with a wafering saw into cubes approximately 1 cm on edge for testing. The cubes were polished with three successively finer grits of emery paper (240, 400, and 600), cleaned with acetone in an ultrasonic cleaner for 15 min, dried, and then weighed. The initial dimensions of the cubes were then measured with a micrometer, and a surface area for each sample was calculated.

The water leaching tests were conducted according to the protocol specified for the MCC-1 test.[4] The accelerated leach tests were conducted at 60°C using deionized water and Teflon containers with supporting nets for the glass samples. All of the containers were conditioned before use by filling them with deionized water for 2 to 3 days before the leach tests. This preconditioning helped wash off any manufacturing or storage impurities, especially plasticizers. The glass samples were then placed into the preconditioned containers, and the correct amount of deionized water (resistivity = 18.0×10^6 Ω) was added using a burette. The samples and their containers were then placed in an oven set at 60°C. At 5- to 7-day intervals, the cubes were taken out of their containers, dried, weighed, and then returned to the test. All samples were tested in this manner for at least 30 days.

After the sample weights were measured at each interval, a normalized mass per unit surface area was calculated to allow for changes in the surface caused by leaching. For the glasses with a relatively high leaching rate, the surface area of the cube started becoming more and more difficult to measure as grooves started forming in the glass and the corners began to get rounded. In such cases, the following procedure was used to determine the surface area. First, the sample density was calculated using the method of L. I. Demkina.[5] The calculated density (ρ, g/cm^3) and the measured weight (m, g) were then used to obtain a calculated volume for the sample. Finally, assuming that the sample was cubical, a computed surface area (A_s, cm^2) was obtained from

$$A_s = 6 \cdot (m/\rho)^{2/3}$$

The weight change over the elapsed time (Δt, s) could then be normalized per unit surface area as

$$\text{Leach rate} = \frac{\Delta m}{6 \cdot (m/\rho)^{2/3} \cdot \Delta t}$$

where the leach rate is expressed in g/cm^2-s (or in other consistent units). All leaching data were thus analyzed as weight loss normalized to unit surface area of the sample.

III. RESULTS AND DISCUSSION

Compositions of the various glass samples that were prepared in the laboratory are given in Table 1. As mentioned previously, all of these samples were subjected to the

Table 1. Compositions of Sample Glasses Prepared in Laboratory

Molar Composition of Glass	No. of Samples
$20\%Na_2O$-$80\%SiO_2$	2
$25\%Na_2O$-$75\%SiO_2$	1[a]
$30\%Na_2O$-$70\%SiO_2$	2[a,b]
$35\%Na_2O$-$65\%SiO_2$	4[a]
$30\%Na_2O$-$5\%CaO$-$65\%SiO_2$	1
$30\%Na_2O$-$8\%CaO$-$62\%SiO_2$	3
$30\%Na_2O$-$12\%CaO$-$58\%SiO_2$	1[b]
$30\%Na_2O$-$15\%CaO$-$55\%SiO_2$	1[b]
$30\%Na_2O$-$2.5\%B_2O_3$-$67.5\%SiO_2$	1[a]
$30\%Na_2O$-$5\%B_2O_3$-$65\%SiO_2$	2[a,b]
$30\%Na_2O$-$7.5\%B_2O_3$-$62.5\%SiO_2$	2
$30\%Na_2O$-$10\%B_2O_3$-$60\%SiO_2$	1[b]
$30\%Na_2O$-$12.5\%B_2O_3$-$57.5\%SiO_2$	2
$30\%Na_2O$-$15\%B_2O_3$-$55\%\ SiO_2$	1
$30\%Na_2O$-$10\%CaO$-$1\%Al_2O_3$-$59\%SiO_2$	2
$30\%Na_2O$-$10\%CaO$-$3\%Al_2O_3$-$57\%SiO_2$	2[b]
$30\%Na_2O$-$10\%CaO$-$6\%Al_2O_3$-$54\%SiO_2$	2
$20\%Na_2O$-$10\%CaO$-$3\%Al_2O_3$-$67\%SiO_2$	1
$30\%Na_2O$-$10\%B_2O_3$-$1\%Al_2O_3$-$59\%SiO_2$	2
$30\%Na_2O$-$10\%B_2O_3$-$3\%Al_2O_3$-$57\%SiO_2$	3
$30\%Na_2O$-$10\%B_2O_3$-$6\%Al_2O_3$-$54\%SiO_2$	2
$20\%Na_2O$-$10\%B_2O_3$-$3\%Al_2O_3$-$67\%SiO_2$	2
$11\%Na_2O$-$9\%B_2O_3$-$1\%CaO$-$2\%Al_2O_3$-$77\%SiO_2$	1

[a]Samples dissolved within 30 days.

[b]X-ray diffraction test run showed no crystallinity (amorphous).

accelerated leach tests. In addition, pieces from six of the glass samples were examined by X-ray diffraction, as indicated in Table 1. No evidence of crystallinity was apparent in any of these six samples.

In general, as the sodium content in the sample was increased, the workability of the glass improved, but it became more susceptible to leaching by water. It thus became evident

that a compromise must be made among the desired objectives of high sodium content, easy glass workability, and high integrity of the glass against attack by environmental waters. While Na_2O-SiO_2 glasses were the most easily made and worked, they disintegrated almost completely during the leach tests. Addition of other constituents (CaO, Al_2O_3, and B_2O_3) tended to impart much greater resistance to leaching, while at the same time, it tended to make the glass more viscous and more difficult to pour into the molds. Glass formation and leaching behavior for the different families of glasses are discussed separately below.

A. *Soda-Silica Glasses*

All of the samples that had 30 mol % or more of Na_2O were completely dissolved within 5 days from the start of the test. The sample containing 25% Na_2O disintegrated in less than 2 weeks. The two samples containing 20% Na_2O lost almost half their weight in 30 days and disintegrated completely in about 50 days. Thus, glasses containing only Na_2O and SiO_2 are unacceptable for disposing of sodium-containing radionuclides.

These Na_2O-SiO_2 glasses, however, were the easiest to form and pour into molds. Even though they dissolved or disintegrated in water relatively quickly at 60°C, they are chemically inert and would be relatively slow to dissolve in water at ambient temperatures. Thus, these glasses may be used for the disposal of waste sodium containing no radioactive contaminants.

B. *Soda-Silica-Lime Glasses*

Addition of CaO to Na_2O-SiO_2 glasses made the glasses more difficult to prepare and anneal. Several of these samples showed what appeared to be small crystallization spots, particularly for samples containing 15 mol % or higher of CaO. During the leach tests, many of the CaO-glass samples developed cracks or even split into two pieces, indicating that they had not annealed properly; however, the rates of weight loss were considerably lower than those for the Na_2O-SiO_2 glasses. The observed data for the Na_2O-SiO_2-CaO glasses are summarized in Fig. 2 where the curves represent the regression line of the observed data for the normalized leach rate. The resistance to leaching increased as the CaO content of the glass was raised. For Na_2O-SiO_2-CaO glasses containing 30 mol % Na_2O and more than about 10% CaO, the leach rate was in the range $0.5\text{–}2.5 \times 10^{-4}$ mg/(mm^2 · h).

C. *Soda-Silica-Boron Glasses*

Soda-silica glasses made with varying amounts of B_2O_3 were easier to make than the soda-silica-lime glasses. While these glasses were poured into the boron nitride molds, fumes of B_2O_3 were released. These are toxic, and if these glasses are to be made in a scaled-up process, the equipment design would have to incorporate a scrubbing system to avoid such emissions to the atmosphere. Leaching data for the Na_2O-SiO_2-B_2O_3 glasses are given in Fig. 3. The leach rates of these glasses were less than half of those of the Na_2O-SiO_2-CaO glasses, for the most part being less than 0.5×10^{-4} mg/(mm^2 · h); however, no clear trend was evident regarding the effect of the B_2O_3 content of the glass on its leachability.

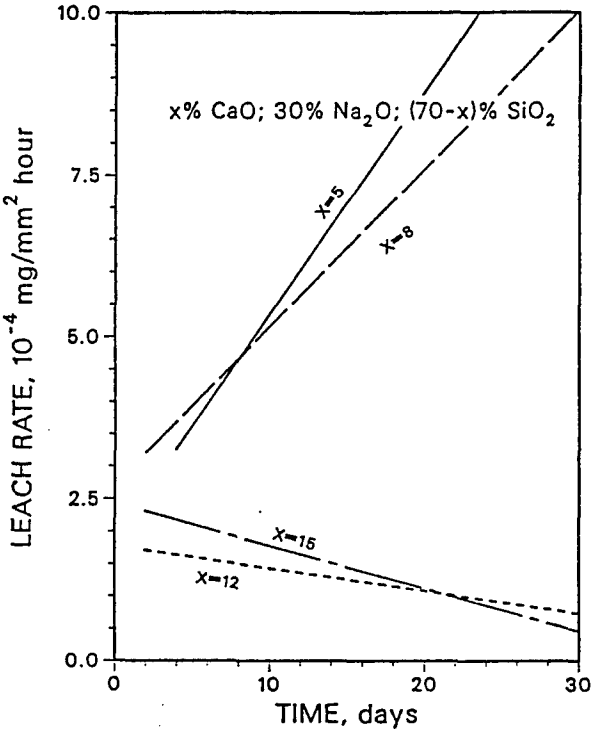


Fig. 2. Leaching Data for Na_2O-SiO_2-CaO Glasses

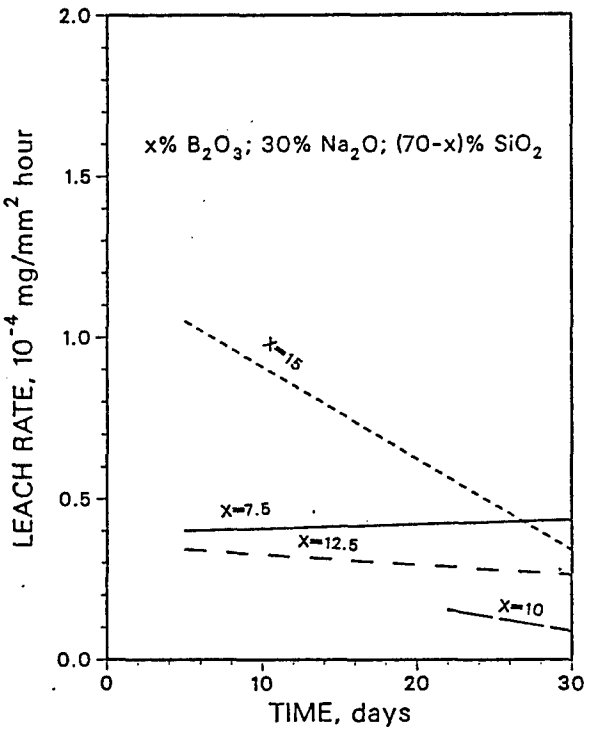


Fig. 3. Leaching Data for Na_2O-SiO_2-B_2O_3 Glasses

D. *Soda-Silica-Lime-Alumina Glasses*

The addition of Al_2O_3 to Na_2O-SiO_2-CaO glasses made the preparation and workability of these glasses comparable with those of the Na_2O-SiO_2-B_2O_3 glasses. The observed leach rates were also comparable, as shown in Fig. 4. Increasing the Al_2O_3 content

decreases the observed leach rate of the glass, with the overall leach rates at or below the 0.5×10^{-4} mg/(mm^2 · h) observed for the Na_2O-SiO_2-B_2O_3 glasses. To examine the effect of annealing on the leach rate, one sample containing 30% Na_2O-3% Al_2O_3-10% CaO-57% SiO_2 was tested without being annealed. The leach rates were somewhat higher for the unannealed sample.

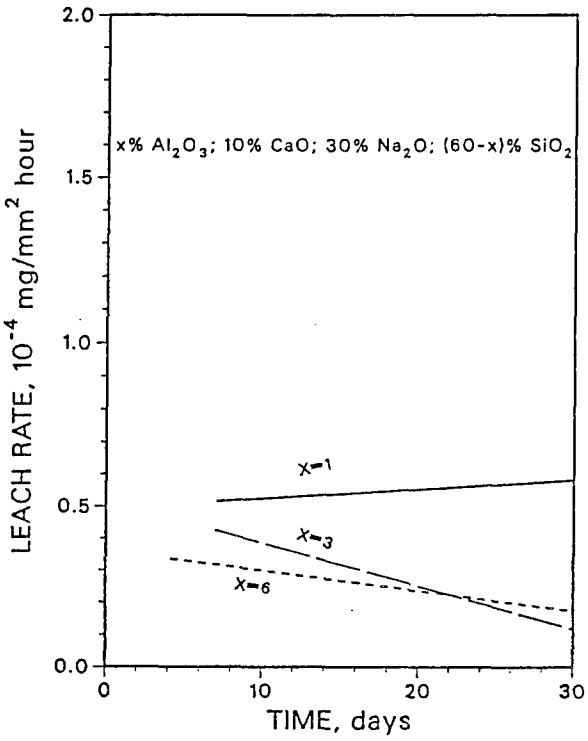


Fig. 4. Leaching Data for Na_2O-SiO_2-CaO-Al_2O_3 Glasses

E. *Soda-Silica-Boron-Alumina Glasses*

Adding Al_2O_3 to the Na_2O-SiO_2-B_2O_3 glasses lowered the leach rates even further, yielding the lowest leach rates for the 30 mol % Na_2O glasses observed in the tests (see Fig. 5). The leach rates decreased as the Al_2O_3 content was increased so that leach rates of 0.3×10^{-4} mg/(mm^2 · h) or less could be achieved by use of Al_2O_3 contents of 3 mol % or higher. One sample containing 3% Al_2O_3 was tested without being annealed; the leach rate for this sample was comparable with the annealed samples of the same composition.

F. *Low Soda Glasses*

All of the glasses discussed previously contained 30 mol % (or higher) of Na_2O. It is desirable to select a glass that contains a high proportion of sodium so that, for a given amount of sodium to be disposed of, a relatively small amount of glass would be formed. To examine the effect of lowering the sodium content on the leachability of the glass, several samples were prepared with 20 mol % Na_2O. Leaching data for these 20% Na_2O samples are shown graphically in Fig. 6. These samples attained much lower leach rates than any of the glasses discussed previously, with values below 0.05×10^{-4} mg/(mm^2 · h).

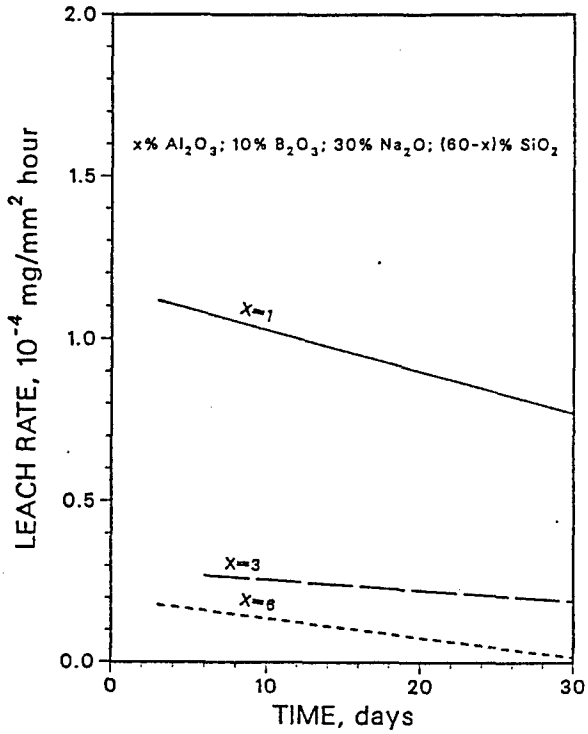


Fig. 5. Leaching Data for Na_2O-SiO_2-B_2O_3-Al_2O_3 Glasses

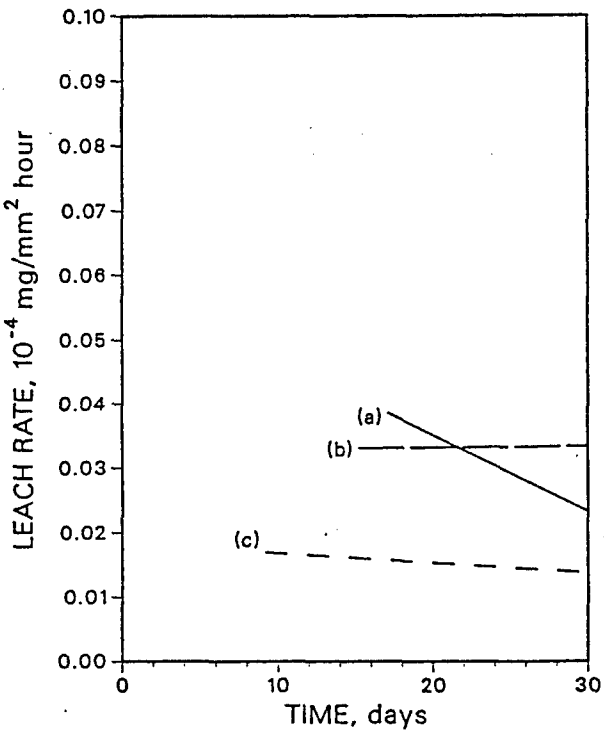


Fig. 6. Leach Rates for Low Na_2O Glasses:
(a) 20% Na_2O, 3% Al_2O_3, 10% CaO, 67% SiO_2 (Table B.30),
(b) 20% Na_2O, 3% Al_2O_3, 10% B_2O_3, 67% SiO_2 (Table B.37), and
(c) 20% Na_2O, 3% Al_2O_3, 10% B_2O_3, 67% SiO_2 (Table B.38).

One glass sample was prepared with 11 mol % Na_2O. It also contained 2% Al_2O_3, 0.7% CaO, and 8.9% B_2O_3, the rest being SiO_2. This glass composition was obtained from reported work in high-level nuclear waste storage.[6] This glass was extremely viscous at the pour temperature but showed *no* observable weight loss after 50 days of leaching.

Table 2. Relative Weights and Volumes of Glass vs. Sodium

Glass	kg Glass/kg Na	L Glass/L Na
$10\%B_2O_3$-$30\%Na_2O$-$60\%SiO_2$	8.90	3.51
$3\%Al_2O_3$-$10\%CaO$-$30\%Na_2O$-$57\%SiO_2$	8.89	3.32
$6\%Al_2O_3$-$10\%B_2O_3$-$30\%Na_2O$-$54\%SiO_2$	9.20	3.62
$3\%Al_2O_3$-$10\%CaO$-$20\%Na_2O$-$67\%SiO_2$	12.51	4.81
$3\%Al_2O_3$-$10\%B_2O_3$-$20\%Na_2O$-$67\%SiO_2$	12.75	5.18
$2\%Al_2O_3$-$1\%CaO$-$9\%B_2O_3$-$11\%Na_2O$-$77\%SiO_2$	21.68	9.02

As mentioned previously, it is desirable to select a glass with as high a sodium content as practical, if the glass is acceptable from other considerations. For a given amount of sodium to be disposed of, the weight and volume of the product glass vary in inverse proportion to the content of sodium in that glass. For six of the more leach-resistant glasses among those prepared for this study, the calculated ratios of the glass weight and volume to the weight and volume of the waste sodium are shown in Table 2. For glasses containing 30 mol % Na_2O, ~9 kg of glass is produced for 1 kg of waste sodium; volumetrically, ~3.5 L of glass is produced from 1 L of sodium. For glasses containing 20 mol % Na_2O, the advantage of a lower leach rate is obtained at a slight increase in the weight ratio to ~13 and an increase in the volume ratio to ~5. If the glass with 11% Na_2O is selected, ~22 kg of glass/kg Na would be produced, representing ~9 L of glass/L of Na.

IV. CONCLUSIONS

Glass preparation and leaching tests with over 40 glass samples showed that a glass becomes easier to prepare and work as the sodium content in the glass increases. A glass with a high sodium content is also easier to dispose of because much less of it is produced from a given amount of waste sodium. On the other hand, glass tends to become more susceptible to attack by water as its sodium content increases. All glasses have very low reactivity with environmental waters and gases at ambient temperatures. We concluded that:

- For the disposal of waste sodium containing no radioactive species, forming a glass with only silica as the added constituent is most desirable. This composition makes it easy to form the glass and cast it into bricks or other shapes suitable for disposal. This composition also results in the smallest amounts of glass for disposal.
- For the disposal of waste sodium that contains short-lived radionuclides that may safely be released to the environment over a prolonged period of time, a glass composition similar to 30% Na_2O-10% CaO-3% Al_2O_3-57% SiO_2 or 30% Na_2O-10% B_2O_3-3% Al_2O_3-57% SiO_2 may be used. These glasses would require somewhat higher processing temperatures than the simple Na_2O-SiO_2 glasses and would produce somewhat higher quantities of glass to be disposed of, but would provide isolation of the radioactive species from the biosphere for a much longer time.

- For waste sodium containing long-lived radioactive species, a low-sodium glass such as 11% Na_2O-1% CaO-2% Al_2O_3-9% B_2O_3-77% SiO_2 would provide an acceptable waste form. Such a glass would, however, require much higher processing temperatures than the glasses mentioned previously and may also be considerably more difficult to cast into molds.

ACKNOWLEDGMENT

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LABORATORY STUDY OF IN SITU VOLATILIZATION TECHNOLOGY APPLIED TO LETTERKENNY ARMY DEPOT SOILS

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ABSTRACT

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) has demonstrated that in situ volatilization (ISV) is a viable treatment for in situ decontamination of soils containing volatile organic compounds (VOCs). ISV treatment involves drawing air through the soil matrix, thereby stripping the VOCs from the soil.

A bench-scale investigation was conducted on three VOC-contaminated soils from the Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania, to define ISV applicability and determine the effect of residual VOCs in the soil following ISV treatment on the receiving groundwater. The investigation involved an ISV extraction test and subsequent column leaching test on the treated soil. A specially designed aeration chamber system capable of testing up to 30 lbs. of contaminated soil, of allowing optimum air/soil interface, of monitoring relevant parameters, and of moisture addition was utilized for testing. The column leaching test was conducted in 4-foot glass columns with deionized water being permeated through the compacted soil.

Soil samples were analyzed before and after the ISV extraction test. The results demonstrated that two of the soils collected (Waste Disposal Trenches and Burning Pit) had non-detectable VOC concentrations. The K Area sample was found to have approximately a 90 percent reduction in VOCs due to the ISV treatment. Although ISV treatment was effective at significantly reducing VOC concentrations in the soil, significant VOC concentrations were detected in the leachate generated from the treated soils indicating additional treatment may be necessary.

INTRODUCTION

Contamination of soils and groundwater with volatile organic compounds (VOCs) has been found at Letterkenny Army Depot (LEAD), Chambersburg, Pennsylvania. The major VOCs found were trans-1,2-dichloroethene, trichloroethene, tetrachloroethene, benzene, toluene, and total xylenes.

A remedial action technology identified for treatment of the contaminated soil is in situ volatilization (ISV) of the VOCs. ISV involves the removal of volatile organics from the contaminated soil by mechanically drawing or venting air through the unsaturated contaminated soil layer. The ISV process provides a pressure gradient (forced air flow) to overcome capillary pressure and a concentration gradient (clean injection air) to enhance the diffusion of the contaminant across phase boundaries into the vapor phase. The major driving force governing VOC removal rates during most of the treatment period is the concentration gradient. However, as time progresses, overcoming the high capillary pressure of the smaller pores and desorption of VOC from soil fines will be the rate limiting transfer mechanism governing the final soil VOC concentration and the total ISV treatment time. The presence of moisture to compete with the contaminant for adsorption sites on fine soils may also affect desorption and removal of VOCs. Pilot- and full-scale studies at the Twin Cities Army Ammunition Plant (TCAAP) utilizing the ISV technology have demonstrated that it is a viable technology for treatment of VOC-contaminated soils. However, the applicability of ISV to different site-specific soil types and specific contaminants has not been fully defined.

After the ISV treatment process has been completed, the residual VOC in the soil may still exist as a potential source of leachate. The VOC concentration trends and migratory pathway of this leachate will depend on the subsurface environment, local water infiltration rates and the soil and VOC physiochemical properties. The ultimate impact of the residual VOC on groundwater can be estimated by conventional methods of groundwater and transport modeling of contaminant plumes.

A bench-scale study was conducted to generate the information necessary to evaluate the applicability of ISV to LEAD soils and to estimate maximum VOC removal in the soils. Also, the ISV system may achieve a high degree of VOC removal, but VOCs at low-level residual concentrations in the soil may not be removed. In order to determine the concentration of VOCs in the leachate that may be generated from the treated soil that may migrate and enter the groundwater aquifer, a specially designed bench-scale aeration chamber and column leaching test were utilized to determine optimum removals and effect of the treated soils on groundwater.

TEST APPARATUS

The bench-scale ISV aeration system used for the test was designed to evaluate the applicability of the ISV treatment to site-specific contaminated soils. The test system operated under optimum extraction conditions. Figure 1 is a schematic of the ISV system used for testing.

The contaminated soil from LEAD was placed into the stainless steel (20-gauge) aeration chamber (12 in. diameter x 12 in. high) of the ISV extraction unit. The cone-shaped bottom or inlet of the ISV extraction unit was fitted with a 12-inch diameter, 200-mesh stainless steel screen. The screen/cone configuration evenly distributed air from the blower across the cross-sectional area of the soil sample. A flow control valve, immediately following the outlet of the blower, vented the pressurized air to provide a predetermined flow rate to the extraction chamber. A port in the inlet pipe was fitted with a fogging spray vector to allow for moisture addition. Ports in the inlet pipe, located adjacent to the extraction unit and off-gas pipe, allowed for monitoring of flow, pressure, temperature, and relative humidity. A separate port in the off-gas pipe was fitted for total VOC monitoring.

The discharge of the off gas from the extraction system was directed through a 55-gallon activated carbon canister to ensure that no elevated VOC concentrations (>1 ppm) were discharged into the atmosphere.

The column leaching test system was designed to simulate long-term leaching of rainwater through the soil. Figure 2 is a schematic of the test apparatus. The ISV treated soil was removed from the ISV aeration chamber and compacted into the column leaching system columns. The soil was compacted to simulate field conditions.

The size of the test column was 4 inches I.D. by 4 feet high. Three feet of the column was filled with soil, and the remaining 1 foot was filled with deionized water. The column was constructed of glass. Glass construction eliminated chemical compatibility problems associated with the use of other materials, such as plexiglass, PVC, etc., due to the presence of VOCs in the contaminated soil. Heavy-walled glass columns were used since the columns were subjected to head pressure during the tests. Porous stones were placed on the top and bottom of the soil column to ensure uniform distribution of the water over the entire cross-sectional area of the soil column. Porous stones were also chemically compatible with the VOCs being investigated.

The leachate collection bottom plate, tubing, fittings, etc., were made of Teflon to eliminate chemical compatibility problems due to the potential presence of the VOCs in the leachate. The leachate samples were collected in septum bottles for analysis. O-rings were provided to eliminate the loss of pressure and leakage of leachate from the column. A leachate trap was placed on top of the collection buret to minimize possible losses of VOCs during leachate collection. Nitrogen gas applied head pressure on the soil column. Nitrogen, an inert gas, was used to preclude potential oxidation reactions of the permeant or organics in the soil.

SOIL AND GAS CHARACTERIZATION

The soil sampling program in this investigation was designed to collect samples that were representative of LEAD contaminated soils for the bench-scale study. Soil samples were collected from the East Patrol Disposal Area locations identified during the remedial investigation at LEAD as having the maximum VOC concentration.

Samples were collected from three distinct areas based on soil boring data. Soil sample collection utilized an organic vapor analyzer (OVA) to screen contaminated soils. The OVA was used to determine the samples with maximum soil VOC contamination. Soil samples were placed in a specially designed bottle, a stopper with sampling ports was inserted, the OVA probe was attached, and the headspace was analyzed for VOC concentration. Based upon these on-site data, soil samples were collected.

The soil sample locations, depths, and OVA-estimated VOC concentrations were as follows:

Location	Waste Boring*	Sample Depth (ft)	Estimated VOC Concentration (OVA) (ppm as methane)
K Area (Lagoon)	WB-31	5-8	700
A Area (Waste Disposal Trenches)	WB-18	4-6	100
B Area (Burning Pit)	WB-25	9-11	50

* Waste Boring - locations identified in LEAD RI/FS report.

The collected soils were physically characterized to determine the proper classification and the physical properties of the soil. The results of the characterization are presented in Table 1. The soils were classified as well-graded sands with silt and/or gravel.

The soil samples were quantified for chemical constituents using EPA Method 601/602 adapted for soils. A continuous FID total VOC analyzer (Foxboro OVA) was used to monitor the extraction off-gas. A strip-chart recorder was utilized to allow for continuous monitoring. Leachate samples were quantified using EPA Method 601/602.

RESULTS

The ISV aeration test was conducted on three distinct soil samples: K Area (WB-31), A Area (WB-18),

and B Area (WB-25). The K Area (WB-31) soil test was conducted in duplicate for quality assurance purposes (Tests 1A and 1B). The aeration tests were terminated when non-detectable concentrations of VOCs were reached in the extraction off-gas. A minimum test time period of 24 hours was incorporated for all testing.

Tests 1A and 1B were conducted on duplicate samples, simultaneously. The extraction off-gases were monitored alternately throughout the test period. Figures 3 and 4 present the VOC concentration over time plots for these tests. The extraction off-gas monitoring results demonstrated an initial peak VOC concentration until non-detectable concentrations were monitored after seven hours of testing. The duplicate run showed consistently reproducible results for both test samples.

Table 2 presents the soil monitoring data for the two tests. The initial soil VOC analysis revealed three VOCs with detectable concentrations: trans-1,2-dichloroethene, trichloroethene, and tetrachloroethene. The total VOC concentrations found in the initial soils were approximately 100 mg/kg in Test 1A and 400 mg/kg in Test 1B. The difference in VOC results for the initial soil samples from the duplicate test runs is due to the heterogeneity of the soil and the inability of the standard grab sampling technique to effectively represent the average soil VOC concentration. Grab sampling is the standard and accepted technique for collection of soil samples for VOC analysis. Composite sampling was not performed because VOC losses occur during partitioning and mixing of the soil. Table 2 also presents the total VOC reductions due to the ISV treatment. Reductions were excellent in both soils, demonstrating the volatility of the compounds in the collected soils. The final soil concentrations were approximately the same indicating that the residual VOCs reached a common equilibrium state at which no further volatilization occurred. These tests were continued for 16 hours beyond reaching non-detected VOC concentrations in the extraction off-gases; therefore, reaching an equilibrium state would be expected.

Soils collected from the WB-18 (A area) and WB-25 (B area) locations were identified in the field as VOC-contaminated; however, on receipt at the laboratory, the initial analyses found no detectable VOC concentrations in the soils. The ISV aeration test was conducted on the samples during the initial analyses, and air flow through the soil was easily attained. The final analysis of both soils resulted in non-detectable VOC concentrations. All soil testing and sampling was performed in a prompt and consistent manner. Samples were preserved at 4°C until analysis and at no time were the 7-day holding times exceeded. A possible reason for the lack of VOCs from A Area (WB-18) and B Area (WB-25) was field error in the selection of contaminated soil. The field OVA monitoring used is only accurate to an order of magnitude. Also, the high volatility and low concentration of the expected VOCs in these areas (benzene, ethylbenzene, and toluene) make it difficult for soil sample selection. Due to the lack of VOC concentrations, these two samples were not incorporated in the column leaching test.

The column leaching test was conducted on the Tests 1A and 1B final ISV treated soils combined. These two soils were combined to provide sufficient soil weight for testing.

The column leaching test involved collection of four leachate samples over an estimated equivalent field leachate volume generation of 100 years. The estimated equivalent field leachate volume is the local percolation rate in inches of water per year applied to the cross-sectional area of laboratory soil column. Additional head pressure was required to force yearly volumes of simulated rainwater through the soil column in a reasonable time period. Applied pressure was controlled to ensure the permeability did not increase more than one order of magnitude. This limit was applied to assure desorption characteristics were not significantly changed. Leachate samples were collected at 10, 20, 50, and 100 years of equivalent field leachate volume. Table 3 presents the leachate VOC analytical results. The three VOCs followed consistent concentration trends throughout the test period. Figure 5 presents the leachate concentrations over the equivalent years of leaching time period. This plot demonstrates increasing leachate VOC concentrations up

to a peak at 50 years, with a gradual decrease until the 100-year volume. All three compounds followed the same peaking pattern at the 50-year mark. The highest VOC concentration detected was trans-1,2-dichloroethene at 290 ug/L after 50 years of equivalent leaching volume. The trichloroethene concentration decreased to 42 ug/L after 100 years of leaching volume. Tetrachloroethene had the sharpest decreasing slope after 50 years, decreasing from 150 to 77 ug/L.

These leachate VOC concentrations demonstrate the trends in leaching that will be evident in the LEAD soil following ISV treatment at the K Area location. The peak VOC concentrations were observed after 50 years of leaching.

SUMMARY OF FINDINGS

The key factors in assessing ISV treatment applicability and efficiency are the physical characteristics of the soil, the amenability of the VOC contaminant to volatilize with applied air, and the residual VOC concentrations in the soil.

Porous granular soils are the most favorable soil types for ISV application. They have higher pore interconnectivity and, therefore, higher pneumatic and hydraulic conductivity. This permits greater convection and diffusion of VOCs through the soil fabric under induced airflow (ISV) at lower pressure drops. The granular soils are neutral in charge and have little affinity to organics; therefore, adsorption is due mainly to capillary tension, which can be overcome by the pressure gradients produced in the ISV process. Fine soils of silts and clays are the least favorable soil types. They have low pore interconnectivity, and higher pressure drops are produced under induced airflow. The negatively charged surfaces of the fine particles have a high affinity to polar and positively charged organics and will resist volatilization. The physical characterization (Table 1) demonstrated that all samples were classified as well-graded sands with silt and/or gravel, which indicates that applied air will be feasible in similar soil types.

The ISV bench-scale study demonstrated that the K Area samples (WB-31) were amenable to volatilization of the identified VOCs in the soil. The VOC reductions of 87 and 95 percent in the duplicate samples showed that excellent VOC reduction should be expected in pilot- or full-scale application. The other two samples collected, A Area and B Area, were found to have non-detectable levels of VOCs, and direct conclusions concerning those soils cannot be made.

The column leaching test conducted on the K Area (WB-31) ISV treated soil showed that the residual VOC contamination will contribute VOC concentrations to the receiving aquifer. Concentrations of trans-1,2-dichloroethene as high as 290 ug/L were evident in the leachate. The leaching characteristics of all compounds demonstrated that leachate VOC concentrations increased to peak levels after 50 years of leaching and then decreased over the next 50 years. This leaching trend demonstrates that the desorption characteristics of the VOC contaminants from the ISV-treated soil gradually increased over the first 50 years following treatment. This indicates that the groundwater aquifer can receive VOC contaminants from leachate of the soil for this 50-year period before the realized effect will decrease. This information can be vital in the determination of the ultimate effect on the receiving aquifer.

The VOCs in the leachate represent the condition at the bottom of the ISV treated soil strata, not those in the immediate vicinity of the aquifer at LEAD. The soil collected from the K Area was at 5- to 8- foot depths. The aquifer of concern is estimated to be at approximately 25 feet below ground level. The ultimate impact of the leachate on aquifer water quality will have to be evaluated considering the following factors:

- Concentrations of VOCs in the aquifer projected dispersion/migration of the leachate through the overburden soil media.
- Health risk assessment of the VOCs considering their projected concentrations in the groundwater and the potential groundwater receptors.

Based on this investigation, it was concluded that ISV treatment will be effective at reducing VOC concentrations in the K Area (WB-31) soil. Although ISV treatment was effective at significantly reducing VOC concentrations in the soil, significant VOC concentrations were detected in the leachate generated from the treated soils indicating additional treatment may be necessary.

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TABLE 1. PHYSICAL CHARACTERISTICS OF SOIL SAMPLES

Parameter	K Area (WB-31)	A Area (WB-18)	B Area (WB-25)
Natural Moisture Content (%)	17.4	21.0	14.3
Gradation:			
Percent passing sieve #5	61.6	82.2	88.5
Percent passing sieve #10	43.4	58.5	66.0
Percent passing sieve #35	14.4	25.1	25.6
Percent passing sieve #60	6.9	15.5	15.0
Percent passing sieve #100	4.2	11.0	10.4
Percent passing sieve #200	2.1	6.7	5.3
Bulk Density (lbs/ft^3)	115	105	102
Unified Classification	Well-graded sand with gravel (SW)	Well-graded sand with silt and gravel (SW-SM)	Well-graded sand with silt (SW-SM)

TABLE 2

LETTERKENNY ARMY DEPOT

BENCH-SCALE ISV SOIL MONITORING DATA

SOIL BORING WB-31 (K AREA)

		Trans 1,2,Dichloroethene		Trichloroethene		Tetrachloroethene		Total VOC		Total VOC
	SOIL WEIGHT lb	CONCENTRATION ug/kg	TOTAL WEIGHT ug	CONCENTRATION ug/kg	TOTAL WEIGHT ug	CONCENTRATION ug/kg	TOTAL WEIGHT ug	CONCENTRATION ug/kg	TOTAL WEIGHT ug	REDUCTION
TEST 1A INITIAL	18	18	116	6.7	56	73	472	99.7	644	
TEST 1A FINAL	17	4	22	2.3	13	9	49	15.3	83	87%
TEST 1B INITIAL	21	19	150	14	111	360	2851	393	3113	
TEST 1B FINAL	19	4.1	32	2.9	23	14	109	21	164	95%

Tests 1A and 1B were duplicate runs on composite soil sample. Concentrations are presented on a dry weight basis.

TABLE 3

LETTERKENNY ARMY DEPOT

COLUMN LEACHING DATA SUMMARY

SOIL BORING WB-31 (K AREA)

EQUIVALENT YEARS	LEACHATE VOC CONCENTRATION		
	Trans 1,2,Dichloroethene ug/L	Trichloroethene ug/L	Tetrachloroethene ug/L
10	200	57	90
20	230	59	92
50	290	110	150
100	250	42	77

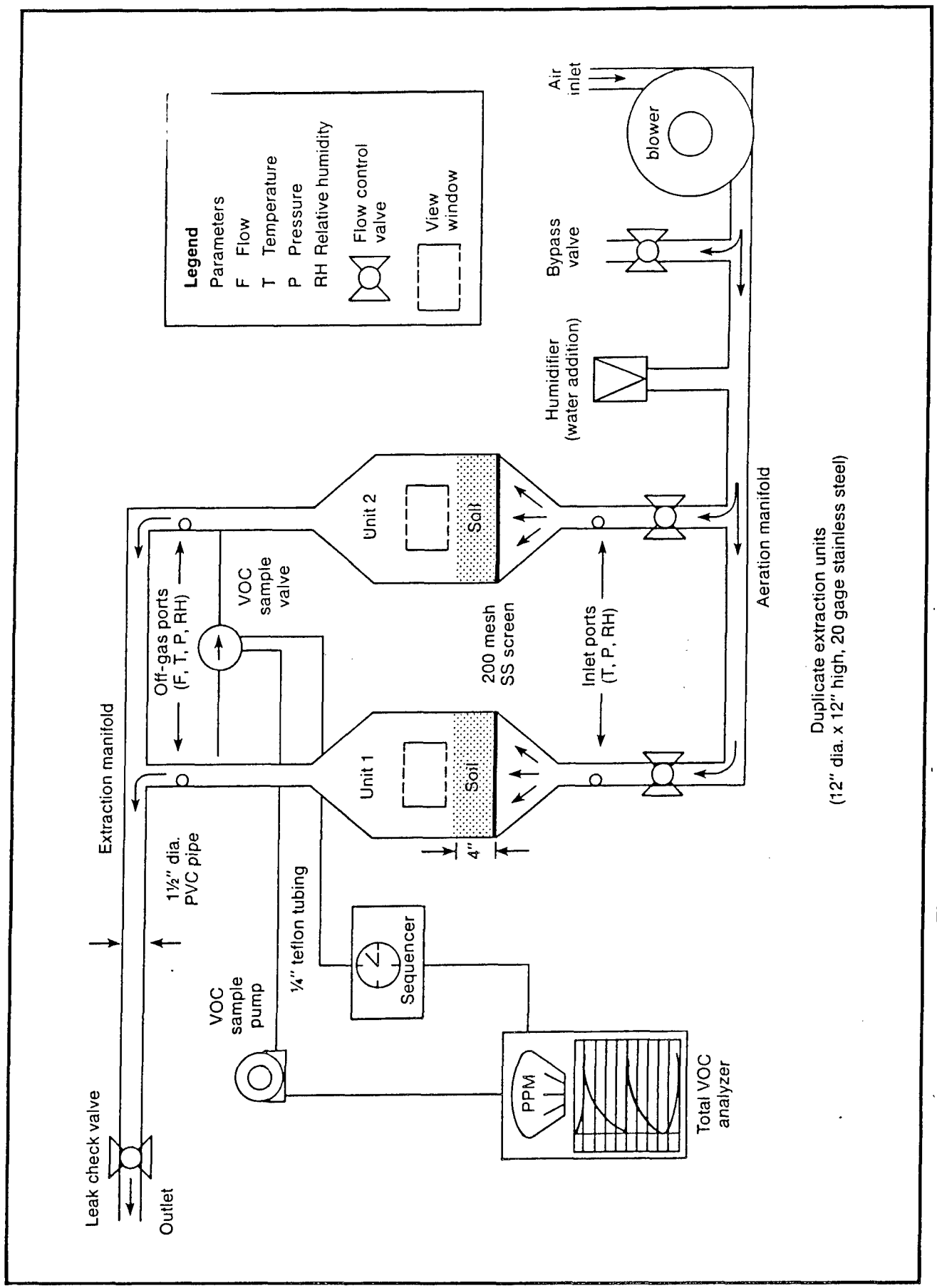


Figure 1. Schematic of the ISV chamber aeration system.

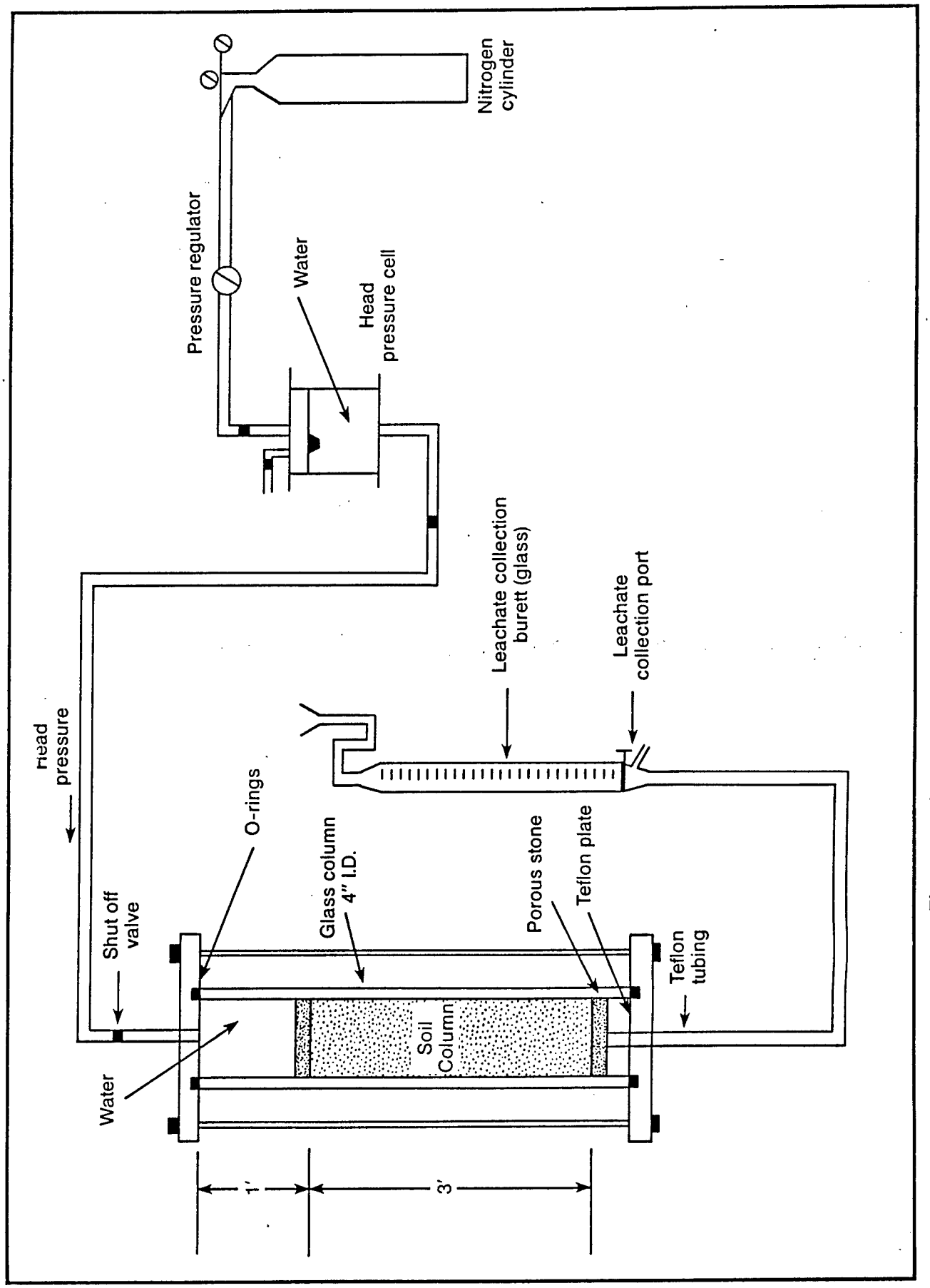


Figure 2. Schematic of the column leaching test apparatus.

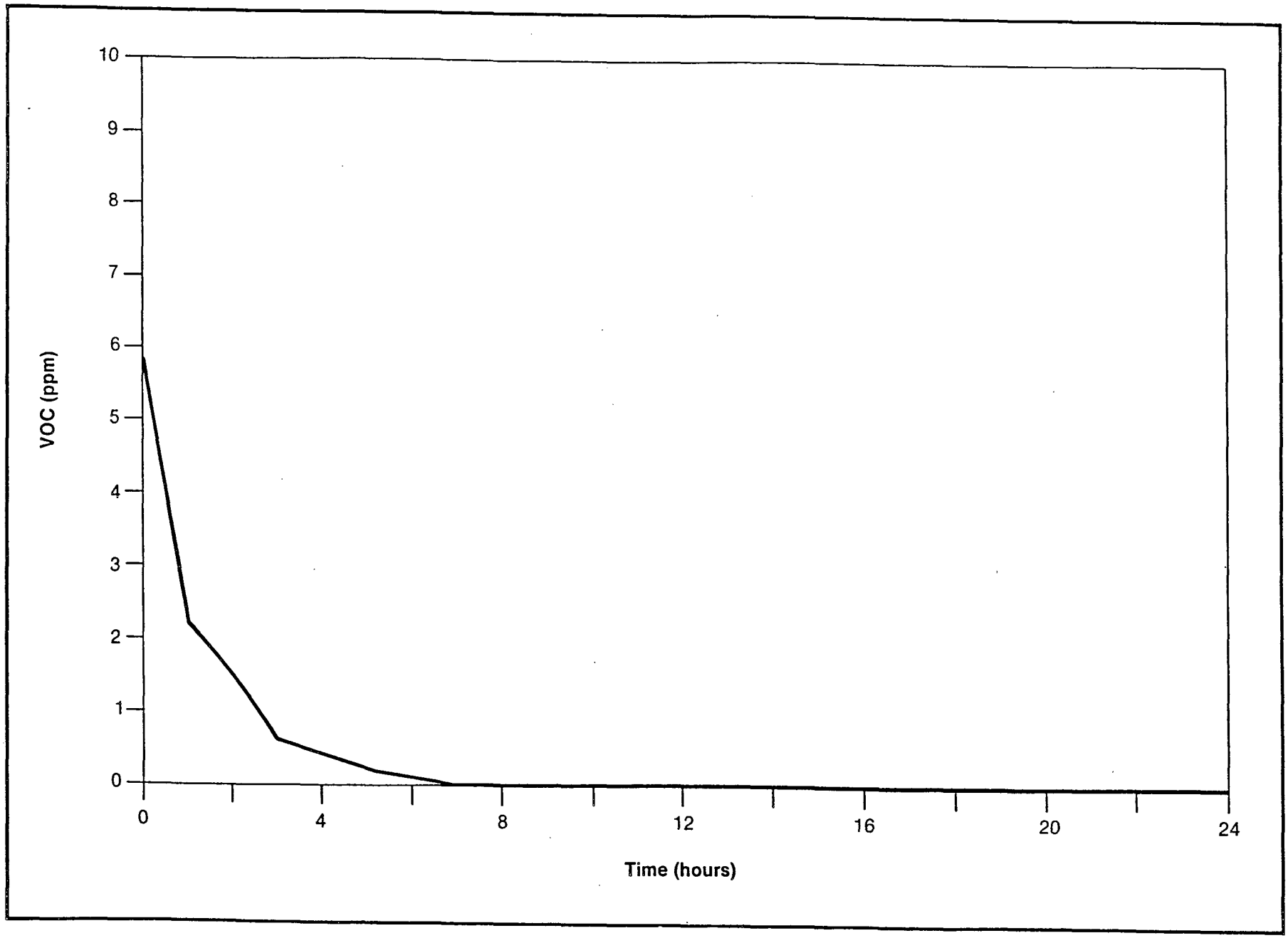


Figure 3. Test 1A K Area (WB-31).

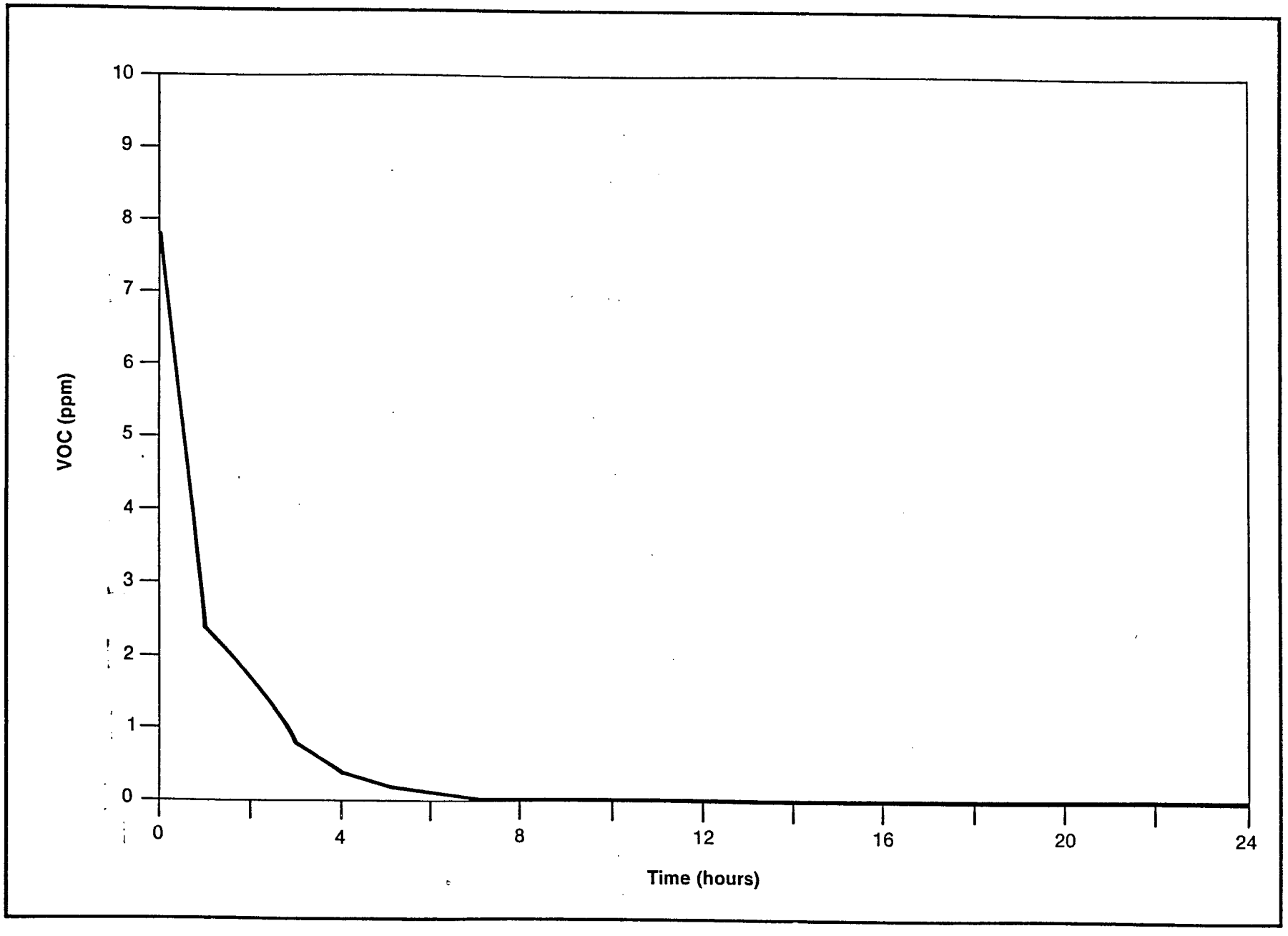


Figure 4. Test 1B K Area (WB-31).

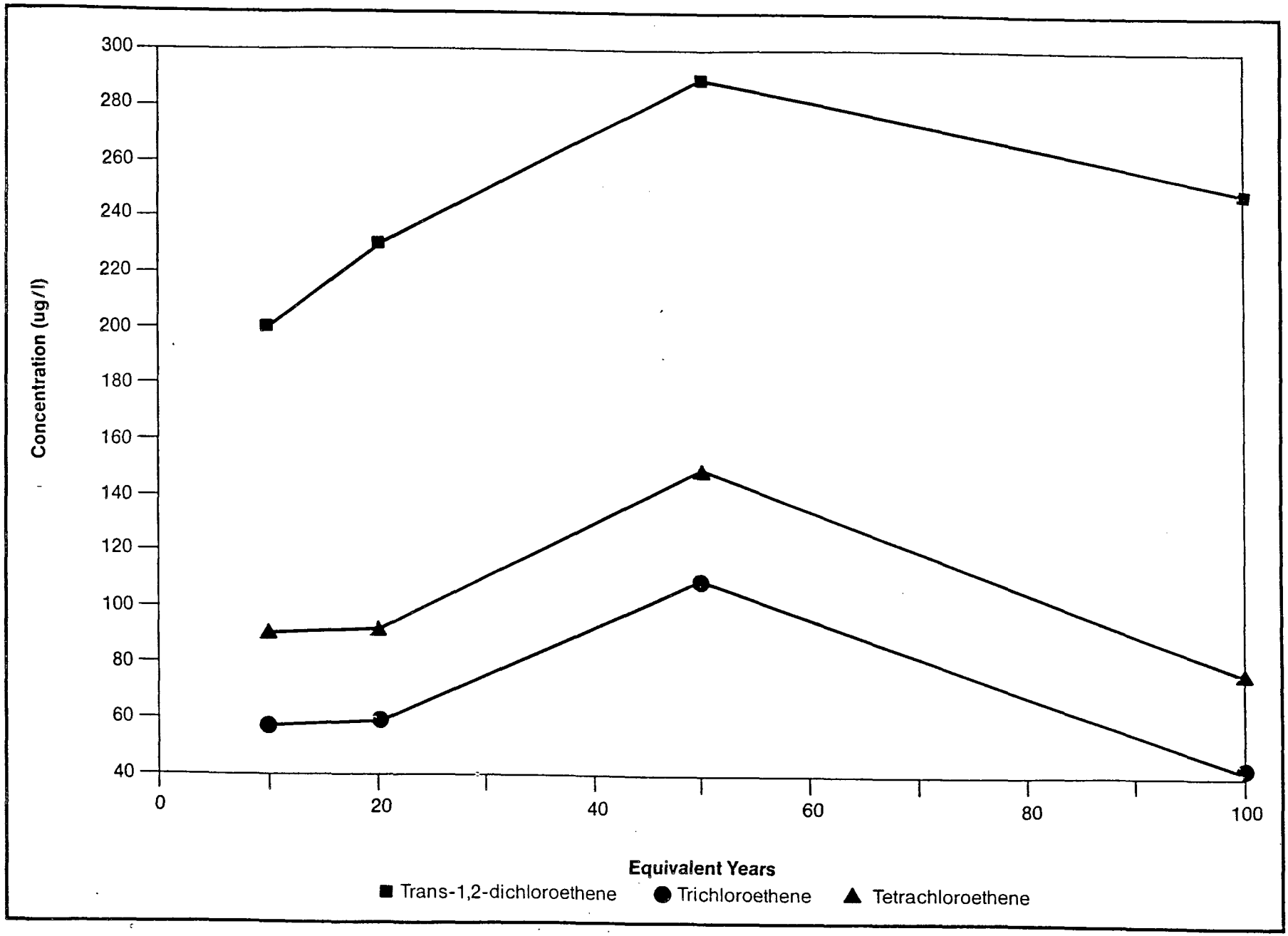


Figure 5. Leachate concentrations.

THE HOT GAS DECONTAMINATION PROCESS FOR CHEMICAL AGENTS IN STRUCTURES AND EQUIPMENT

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ABSTRACT

As part of its Installation Restoration Program, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), is investigating new and innovative ways to decontaminate chemical agent contaminated structures. The objective of this program is to develop decontamination techniques to meet future requirements to decontaminate facilities previously used for the manufacture, testing, storage and disposal of chemical agents. Facilities of concern include building structures, aboveground and underground storage tanks, process equipment, sumps and process conduit and piping. An important aspect of this project is the potential for major cost savings that could result from low temperature decontamination of structures for reuse or disposal.

In Phase I of the program 66 agent decontamination concepts were identified and evaluated. In Phase II, seven concepts were evaluated in the laboratory for their ability to remove controlled amounts of chemical agents from samples of building materials to levels below detection limits. Based on effectiveness, reliability, waste product characteristics, possible hazards and approximate cost, three decontamination concepts (hot gas, steam, and 1-octylpyridium 4-aldoxime bromide, or OPAB) were selected for further engineering evaluation. Both the steam and hot gas processes penetrated porous materials such as concrete and appeared promising for building decontamination. The hot gas decontamination concept was found to be the most effective, and was recommended for further evaluation in a pilot test in the third phase of the program.

A pilot test of the hot gas process was conducted at Dugway Proving Ground (DPG) using a concrete and steel test structure contaminated with controlled quantities of mustard (HD). The test structure and burner were located in a chemical agent test chamber and controlled remotely. Coupons of painted and unpainted concrete and steel were mounted on the inside of

quantities (4 mg/square inch) of HD to simulate conditions in a contaminated building. Pretest blanks and spike samples were collected and analyzed in accordance with methodology verified in the laboratory for extracting HD from pulverized concrete, from soil, and from painted and unpainted concrete and steel surfaces.

This paper summarizes the evaluation of decontamination process concepts, laboratory testing, the analytical verification of decontamination, and the results of the DPG pilot test of the hot gas process.

1.0 INTRODUCTION

The U.S. Army owns many facilities, which may include buildings or large items of equipment, that have been used in the manufacture, processing, loading, storage and destruction of chemical warfare agents. These operations involve permanent facilities and a variety of process and handling equipment. As part of their responsibilities in The Army Installation Restoration Program, USATHAMA must develop procedures to identify, contain and eliminate toxic and hazardous materials at facilities that have been declared excess or are candidates for excessing. USATHAMA must provide the technical basis to implement decontamination and also the standards to ensure that decontamination has been effective.

The only currently approved decontamination method for chemical warfare agents is incineration at a temperature of 1000°F for 15 minutes. Materials exposed to such conditions are described as having attained "5X" status and defined as suitable for unrestricted use (DARCOMR 385-102, 1982). However, the expense required to accomplish such decontamination is excessive. The successful development of an alternative decontamination technique which would not require the dismantling of a facility and which would result in a 5X decontamination (or the equivalent) without incineration represents a potentially large cost savings to the Government. Many facilities that have been contaminated with chemical agents are structurally sound and it would be most desirable to decontaminate them by a process that would not damage structural integrity. Free from chemical agent decontamination, the facility could be reused or excessed with substantial cost savings.

USATHAMA has instituted the multi-phase Novel Process Technologies program to investigate ways to decontaminate buildings and other structures in the field. Phase I and II were concept development and laboratory evaluation studies of methods for decontaminating building materials. The hot gas decontamination concept was chosen as the most effective process for removal of chemical agent from a variety of materials as well as the most cost effective out of 66 concepts evaluated.

This paper presents summaries of the first two phases of the Novel Process Technology programs and the results of a pilot test of the hot gas process.

2.0 Phase I. Identification and Evaluation of Novel Decontamination Process. [1]

The Phase I study identified and evaluated novel methods for the decontamination of facilities (buildings and equipment) contaminated with chemical agent during manufacturing storage or demilitarization. The first step entailed review of literature and an installation survey followed by idea generation and detailed concept development. In the second step, criteria to evaluate the concepts were developed and covered Mass Transfer, Destruction Efficiency, Safety, Damage to Buildings, Penetration Depth, Applicability to Complex Surfaces, Operating Costs, Capital Costs, and Waste Treatment Costs. Thirdly, these criteria were used to select promising concepts for further evaluation in a follow-on laboratory program.

A. Literature and Installation Surveys.

Twenty-seven pesticide manufacturers were contracted to determine their decontamination methods. The pesticide industry was selected because of the similarity between the molecular structure of chemical warfare agents and some pesticides. The results of the survey were that the pesticide industry uses decontamination procedures similar to those currently in use for chemical warfare agents. These include washing with water, soapy water, steam, solvents, caustic, dilute acid, sodium hypochlorite, sodium carbonate, Chlorox^{R}, and calcium hydroxide. The decontamination residues may be further treated, collected on absorbent materials, incinerated, or disposed of in deep wells, landfills, or industrial sewers.

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[1] H.M. Grotta, et al. "Development Of Novel Decontamination Techniques For Chemical Agent Contaminated Facilities. Phase I, Identification and Evaluation Of Concepts." Battelle Columbus Division to U.S. Army Toxic and Hazardous Materials Agency, Report DRXTH-TE-CR-83208, February 1983.

A literature survey was conducted to identify pertinent data for application to novel means of agent decontamination. Both government and non-government publications were searched. The government indices were: Smithsonian Science Information Exchange (SSIE), current research reports; National Technical Information Service (NTIS), unclassified research reports; Defense Technical Information Center (DTIC), defense-related classified and unclassified research reports; and Central Information Reference and Control (CIRC), unclassified foreign defense-related reports.

The non-government indices searched were: Chemical Information System (CIS), a broad, chemical data base; Oil and Hazardous Materials (OHMTADS), part of CIS; Compendex, an engineering index; Comprehensive Dissertation Index (CDI), abstracts on dissertations; Applied Science and Technology Index (AS and TI), applications; Chemical Abstracts (CA), broad, chemical data base; and Environmental Health and Pollution Control (EH and PC), reports on pollution control.

The computer search of the literature resulted in approximately three thousand abstracts on chemical agents and explosives which were reviewed by project team members who selected approximately one thousand as pertinent to the concept development task. These were categorized by subject matter and served as a basic data and information resource for the project team.

Five Army installations were visited by project team members to determine the types and characteristics of surfaces, materials, and structures which might require decontamination. The installations visited were: The Edgewood Area of the Aberdeen Proving Grounds, Joliet Army Ammunition Plant, Sunflower Army Ammunition Plant, Rocky Mountain Arsenal, and Louisiana Army Ammunition Plant. Twenty structures were surveyed ranging from small frame buildings built in 1942 to large concrete and steel complexes built in the late 1970's. Contaminants included a variety of explosives, chemical warfare agents and related chemicals.

Survey activities included inspections, interviews with employees, notetaking, photography (where permitted), contamination measurements, and examination of maps, plans, and engineering drawings. The results of the survey were tabulated according to agent type and structural materials for the five installations and were used by the project team in the development of decontamination concepts and evaluation criteria.

B. Chemical Agent Decontamination Concepts.

A total of 66 chemical agent decontamination concepts were evaluated in the Phase I study. These were grouped into four categories: chemical; physical/extraction; physical/abrasive; and thermal. Generally, the chemical concepts involved application of chemical reactive materials to the contaminated structure with subsequent reactions causing the destruction of the agent contamination. The physical/extraction concepts involved introduction of solvent materials into the structure followed by recovery of the agent/solvent material and separation or destruction of the agent. The physical/abrasive concepts removed the surface layers of structures and collected the contaminated materials for further processing to destroy agents. The thermal concepts raised the temperature of contaminated surfaces or of entire structures to volatilize and/or destroy the chemical agents. In several of these concepts the agents are vaporized but not destroyed and require further process steps to achieve destruction.

Table 1 lists the decontamination concepts that were evaluated. These are described fully in the Phase I report (Ref. 1).

TABLE 1. AGENT DECONTAMINATION CONCEPTS EVALUATED DURING PHASE I

CHEMICAL	PHYSICAL/EXTRACTION	PHYSICAL/ABRASIVE	THERMAL
OCTYL PYRIDINIUM 4-ALDOXIME BROMIDE (OPAB)	SURFACTANTS	HYDROBLASTING	FLASHBLASTING
DS2 (A)	STRIPPABLE COATING	ACID ETCH	HOT PLASMA
CD-1 (B)	VAPOR CIRCULATION	SANDBLASTING	MICROWAVE HEATING
SUPERTROPICAL BLEACH (STB)	SOLVENT CIRCULATION	DEMOLITION	FLAMING
ALL PURPOSE DECONTAMINANT (APD) (C)	SUPERCRITICAL FLUIDS	VACU-BLASTING	HOT GASES
MONOETHANOLAMINE	ULTRASONIC EXTRACTION	CRYOGENICS	SOLVENT SOAK/BURN
GAMMA RADIATION		SCARIFICATION	INFRARED HEATING
NITRIC ACID		ELECTROPOLISHING	CARBON DIOXIDE LASER
AMMONIUM HYDROXIDE		DRILL AND SPALL	ELECTRICAL RESISTANCE CONTACT HEATING
HYPOCHLORITES			
DANC			
GASEOUS AMINES			
CHLORINE			
STEAM			
AMMONIA/STEAM			
PERCHLORYL FLUORIDE			
GERMAN EMULSION			
HYDROXAMIC ACIDS			
SODIUM HYDROXIDE SOLUTION			
DIMETHYLSULFOXIDE			
MACROCYCLIC ETHERS			
PROPIONYL FLUORIDE			
PHENOLS/CATECHOLS			
CARBONATE/BICARBONATE SOLUTIONS			
CHLORITE SOLUTIONS			
CHLORINE DIOXIDE			
NITROGEN TETROXIDE			
BORON TRIFLUORIDE			
OZONE			
SULFUR DICHLORIDE			
UV/OZONE			
ULTRASONIC DECOMPOSITION			
COPPER LIGANDS			
VANADIUM CATALYZED HYDROLYSIS			
ANTHRANILIC ACID-SILVER COMPLEXATION			
MAGNESIUM HYDROXIDE IMPREGNATED ALUMINA			
COMPLEXATION WITH MOLYBDENUM LIGAND			
PERFORATES			
MICROBIAL DEGRADATION			
PERMANGANATE SOLUTIONS			
ENZYME PROTEINS			
SODIUM SULFIDE			

A) Mixture of 70 weight percent diethylenetriamine, 28 weight percent methyl cellosolve and 2 weight percent sodium hydroxide.

B) Mixture of 55 volume percent monoethanolamine, 45 volume percent propylene glycol and 2.5 weight percent lithium hydroxide.

C) Mixture of 54 weight percent monoethanolamine, 44 weight percent isopropanolamine and 2.5 weight percent lithium hydroxide.

C. Decontamination Concept Evaluation Criteria

The concept evaluation criteria used for all concepts in the Phase I study were as follows:

Safety:	Potential for burns, explosion, radiation exposure, poisoning, flying fragments, noise, or flammability.
Damage to Structure:	Thermal cracking, dehydration, warping, fires, surface damage, corrosion, or degradation of ceramics.
Depth of Penetration:	Thermal profiles, surface removal, solvent penetration, reactive chemical penetration.
Applicability to Complex surfaces:	Adaptability of heating equipment, abrasive equipment, solvent applicators, and chemical applicators to complex structures.
Operating cost:	Labor, materials, utilities, setup, and cleanup costs.
Capital cost:	Equipment for heating, surface abrasion, solvent and chemical application, and personnel protection.
Waste Treatment/ Recovery cost:	Hoods, scrubbers, filters, solvent and chemical recovery, incinerators, and collection equipment.

For chemical decontamination concepts, two additional criteria were used, mass transfer, and destruction efficiency.

Mass Transfer:	Effectiveness of contact between the reagents and the toxic materials.
Destruction	Degree of completeness of reaction between the reagents and the toxic materials.

A four unit scoring system was used for each of the criteria and decontamination concepts. The ratings were: Very good, +2; good, +1; poor, -1; and very poor, -2. The ratings for each decontamination concept were totaled for the four categories. Table 2 is a sample of the scoring tabulation, in this case for the thermal decontamination concepts.

Table 2. Thermal Decontamination Concepts Evaluation

CRITERIAN	HOT GASES	IR HEATING	FLAMING	MICRO-WAVE	FLASH BLAST	SOLVENT SOAK	CONTACT HEATING	HOT PLASMA	CO_2 LASER
Safety	+	-	+	-	+	--	--	+	-
Damage to Building	+	+	+	+	++	+	+	+	+
Penetration Depth	+	+	-	++	--	-	+	-	++
Applicability to Complex Surfaces	++	+	-	+	--	-	-	--	--
Operating Costs	++	+	+	-	+	+	--	--	--
Capital Costs	+	+	+	-	+	++	+	+	--
Waste Treatment	+	++	++	++	++	++	++	++	++
TOTAL SCORE	+9	+6	+4	+3	+3	+2	0	0	-2

The most promising concepts recommended for further evaluation in Phase II were the use of:

- o Hot Gases
- o Steam
- o N-Octyl-pyridinium 4-aldoxime bromide (OPAB)
- o Monoethanlolamine (MEA)
- o FREON 113^{R} Vapor Circulation
- o Ammonia Gas or Ammonia/Steam
- o Flashblast

These suggested decontamination methods are briefly described as follows:

Hot Gases. The interior of a building is heated by hot exhaust gases from a combustion device located outside the building. As the material temperature increases, agents will decompose by pyrolysis and/or volatilize from the surface. If agent volatilization occurs, provision to treat the building exhaust gas to remove/destroy the intact agent would be required.

Steam. A boiler is provided outside the building and steam is piped into the structure, decontaminating the entire building at once. The elevated temperature will promote agent hydrolysis reactions and cause volatilization of agents from subsurfaces. The steam itself should penetrate concrete, perhaps more readily than might be expected for liquid reactants. The condensate must be collected, tested, and processed to destroy residual agents if present.

OPAB. OPAB is a dilute aqueous solution of 1-octylpyridinium 4-aldoxime bromide. The reaction of oximes with the nerve agents is well documented, but this reagent appears to be especially effective with VX. Its safety has been validated and, in fact, it is closely related in structure to the nerve agent antidotes, PAM and toxogonin. The products of OPAB reaction with nerve agents are the same as those produced on hydrolysis, but this reagent is especially appealing because of its speed and safety.

MEA. MEA is known to be a very active reagent for HD. It is a good solvent for HD and is rapidly alkylated by HD. Unlike HD, the products of HD decomposition by this reagent are all water soluble (as is MEA), thus facilitating removal of products via a water wash. The reaction with HD should not be reversible.

FREON 113 Vapor Circulation. FREON 113 is heated to its boiling point and the vapors allowed to circulate in a building. The vapors permeate porous building materials where they condense, solubilize the agent, and aid diffusion. The condensed FREON, laden with contaminant, is collected in a sump and treated to permit recycle.

Ammonia Gas. The appeal of gaseous decomposition systems is their ability to permeate throughout a building including subsurfaces. Ammonia should react with HD to produce thiomorpholines. Ammonia alone is not expected to effectively decontaminate nerve agents, but, in the presence of water (perhaps as steam), will raise the pH and promote hydrolytic decomposition. Because ammonia is moderately toxic, it must be introduced into a sealed building and exhausted through an absorber. This approach is thus similar to steam treatment, but provides a reagent specific for HD which will at the same time promote base catalyzed GB and VX hydrolysis in the presence of moisture.

Flashblast. The flashblast device consists of a high intensity Xenon-quartz strobe light which can be focused onto a contaminated surface. The high energy light pulse produces enough heat to remove paint and rust films and to thermally decompose surface contaminants.

3.0 Phase II. Laboratory Evaluation of Novel Agents Decontamination Concepts [2]

A. Evaluation Procedures

The second phase effort was designed to experimentally evaluate the concepts selected from Phase 1 and to recommend one to three of the most promising concepts for field evaluation in Phase III. The ideal case was

development of a single decontamination method which is both cost effective and universally applicable to all types of agent-contaminated materials. However, the development of a single decontamination method specific to one agent would also be considered in the event that a "universal" concept was infeasible. Materials of concern identified from Phase I site surveys for which decontamination methods were to be developed in Phase II included:

- o Stainless steel - painted and unpainted
- o Mild steel - painted and unpainted
- o Concrete - painted and unpainted

The experimental evaluation was conducted in stages with each concept being tested in conditions in which it was progressively more difficult to attain decontamination. At each stage of the process, attempts were made to make the concept work by either altering process parameters or the use of additives.

In the first stage of the evaluation, the decontamination effectiveness of each chemical concept (i.e., MEA, OPAB, Steam, and Ammonia) against HD, GB, and VX was determined in laboratory glassware (i.e., no matrix present). Based on these experiments the most promising concepts were selected for further evaluations.

In the second stage of the evaluation process, the selected chemical concepts as well as the hot gas, flashblast and vapor circulation concepts were evaluated in a test chamber. Unpainted stainless steel spiked with HD, GB, or VX was selected as the substrate for the second screening of the concepts. Unpainted stainless steel allowed the highest recovery of agent and therefore yielded the most accurate measure of decontamination effectiveness. Based on the experimental data, the three most promising concepts were then selected.

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[2] E.R. Zamejc, et al. "Development Of Novel Decontamination Techniques For Chemical Agent (GB, VX, HD) Contaminated Facilities. Phase II, Laboratory Evaluation Of Novel Agent Decontamination Concepts." Battelle Columbus Division to U.S. Army Toxic and Hazardous Materials Agency, Report AMXTH-TE-TR-86012, June, 1985

The third stage of the evaluations focused on the decontamination of painted and unpainted mild steel, painted stainless steel and concrete in the test chamber. The materials provided places into which agent can be absorbed (i.e., paint and concrete pores). Two concepts were then selected for evaluation in the engineering/economic analyses from which a concept applicable to all three agents was recommended.

B. Fate of Agent In Concrete

Suitable analytical methods for the agent decontamination studies were unavailable when laboratory experiments were initiated. Consequently, analytical method development was undertaken for the agents GB, HD, and VX on selected building materials. Building materials examined included painted and unpainted mild steel, stainless steel, and concrete. Attempts to recover agents by solvent extraction from the painted and unpainted steels were successful and produced no unanticipated results. Use of the solvent extraction method proved significantly less successful for agents added to concrete than was observed for agents on metal. Assorted modifications to this basic method were tried but the results were disappointing, in that GB could not be extracted by any technique attempted at levels significantly above the method detection limit. Although HD and VX could be partially recovered from unpainted concrete, the precision (repeatability) observed was extremely poor. These results suggested that all or part of the agent applied to the concrete specimen was not available to be extracted due to interaction with the concrete. Results of the analyses suggest that the interaction of the nerve agents with concrete is a chemical reaction which causes agent hydrolysis. The interaction of concrete with HD appears to be incomplete or reversible in that substantial amounts of HD are extractable even after a 24 hour exposure period.

A detailed discussion of the fate of agent in concrete* and a report on analytical methodology** developed for the laboratory evaluation program were included in the Phase II report (Ref. 2).

The analytical method developments indicated the utility of the extraction/GC-FPD method of analysis for determining residual HD, GB, or VX in or on matrices found in agent contaminated structures. It has been used instead of the air sampling-impinger method accepted by the Army. The extraction procedure proved to be rapid and was reliable enough to demonstrate the effectiveness of various substrate decontamination concepts.

C. Laboratory Evaluation Results

The concept selection results from the Phase II experimental and engineering subtasks are illustrated in Figure 1. The experimental evaluations demonstrated that the hot gas, steam and OPAB concepts were effective decontaminants for each agent/material combination investigated. Each of the other decontaminants (e.g., flashblast, ammonia, etc.) was effective to some extent, but either the effectiveness was limited to specific agent/material combinations or the concept appeared less promising.

The engineering evaluations indicated that it is feasible to apply either the hot gases or the steam decontamination concept to structures representative of Army installations. Because of the limited depth of penetration into porous materials, the use of OPAB as a general decontaminant is not feasible. However, OPAB is recommended for use as a protective coating during application of the hot gas or steam concept and as a non-corrosive decontaminant for specific applications such as decontamination of the inside of pipes, sumps, and other equipment.

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* Ref. 2. Appendix VII. B.C. Garrett and T.L. Hayes, "Fate Of Agent In Concrete."

** Ref. 2. Appendix IX. T.L. Hayes and E.J. Mezey, "Summary Of Analytical Methodology In Support of Task 3, Laboratory Evaluation Of Novel Agent Decontamination Concepts."

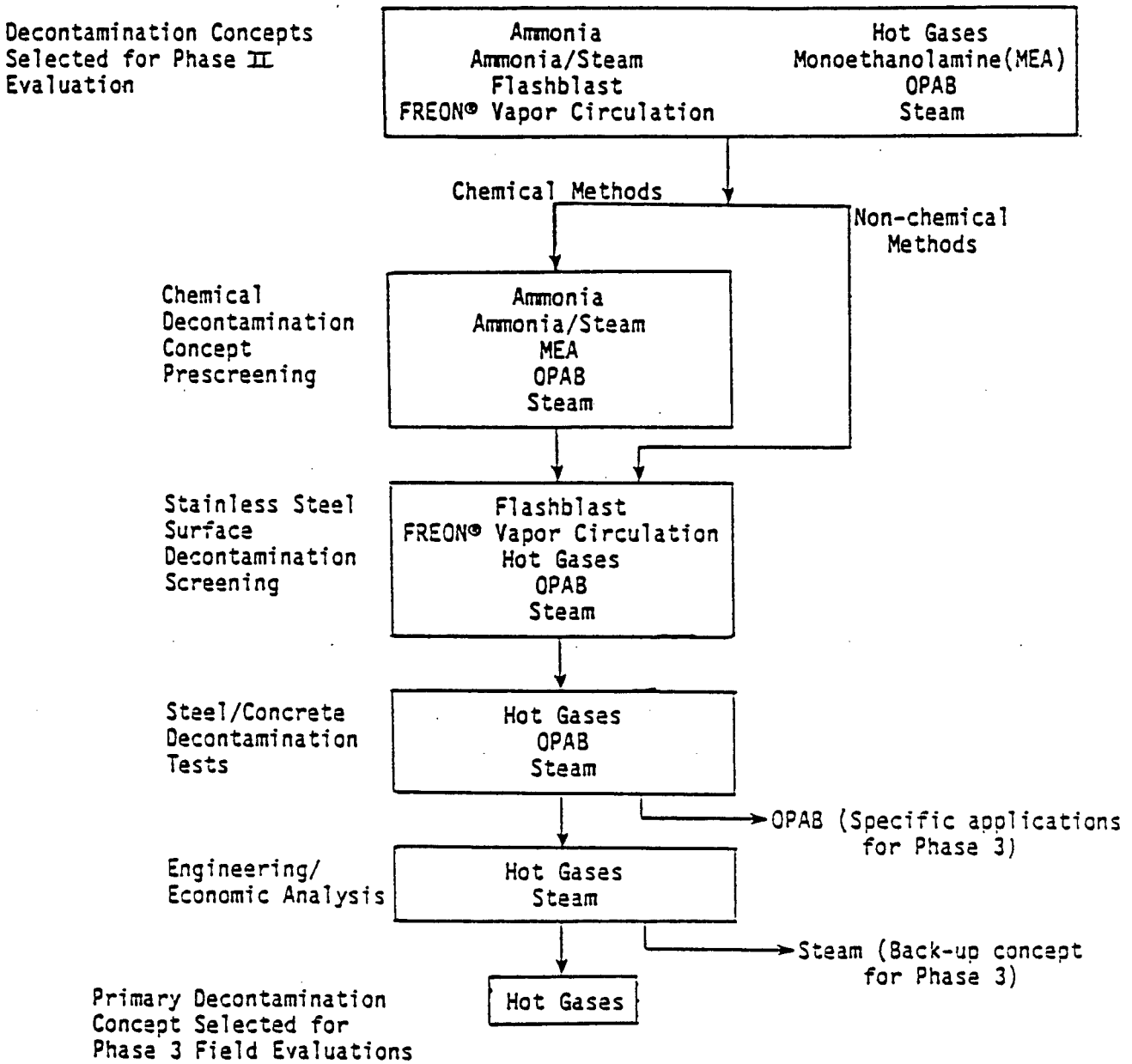


FIGURE 1. CONCEPT SELECTION RESULTS FROM THE PHASE II EXPERIMENTAL AND ENGINEERING EVALUATIONS

Results of the economic analyses indicated that the hot gas concept would be preferred over the steam concept. As such, the hot gas concept was recommended as the primary decontamination concept for field evaluation in Phase III of the program. Steam should be retained as a back-up concept to the hot gas concept.

4.0 Phase III. Pilot Testing of the Hot Gas Building Decontamination Process [3].

A. Pilot Test Program Overview

The hot gas decontamination process was evaluated in a pilot scale study to determine its effectiveness in removing a controlled amount of chemical agent mustard (HD) from a test structure.

The pilot test was conducted in Building 3008, an environmental test chamber at Dugway Proving Grounds (DPG), July 16-23, 1987. The test structure was placed inside Building 3008, which is equipped with a carbon filter system to contain toxic emissions from test operations involving chemical warfare agents.

The test structure was fabricated with walls made of poured concrete, solid and hollow concrete block, and mild steel. Half of each wall was painted. Coupons of painted and unpainted concrete and steel, mounted on the inside of the test structure, and two areas on the floor were spiked with low concentrations (4mg/square inch) of HD to simulate conditions in a building decontaminated to meet 3x criteria (defined in DARCOMR 385-31 and DARCOMR 385-102). Pre-test blanks and spike samples were collected and analyzed in accordance with methodology developed in the laboratory for extracting HD from pulverized concrete, from soil, and from painted and unpainted concrete and steel surfaces.

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3 W. McNeill, et al; "Pilot Plant Testing of the Hot Gas Building Decontamination Process." Report AMXTH-TE-CR-87130, Battelle Columbus Division to U.S. Army Toxic and Hazardous Materials Agency, October 1987.

Test operation and collection of background data were started 18 hours prior to agent spiking and 91 hours prior to the start of heating.

The air temperature inside the test structure was raised in increments to 750°F until all points monitored on the building had reached 300°F for one hour. Attaining this condition required 35 hours. Cooldown to less than 105°F required 38 hours for a total heating and cooling time of 73 hours.

After cooldown, the test structure was opened and photographed, and all samples were collected and analyzed.

B. Test Structure Design

The test structure was a 10 x 8 x 8 foot building with a steel door opening onto an 8 x 8 foot platform as shown in Figure 2. Each wall of the building was made of a different material: one of 12-inch thick concrete, one of standard 16 x 8 inch by 8-inch thick solid concrete block, one of 16 x 8 x 8 inch hollow concrete block, and one of 0.25 inch steel plate. One half of the building floor was 12-inch thick concrete and the other half was 6-inch thick concrete. The platform floor and building ceiling were 0.25 inch steel plate. The entire structure was mounted on a one foot high, 12 x 8 foot base made of I-beams, which was filled with local soil from DPG. The base was supported 13 inches from the floor of the test chamber by four casters. Therefore, the top of the soil base and the test structure floor were 25 inches above the test chamber floor. The steel door frame and penetrations for heating, cooling, and room exhaust ducts were located in the steel wall of the test structure. The entire structure was insulated with high temperature fiberglass insulation (2 inch thick Owens Corning Insul-Quick).

Painted and unpainted concrete and carbon steel coupons were placed in the test structure. The steel coupons were installed on the steel wall; concrete coupons were installed on the test structure floor and concrete walls. The concrete coupons measured 5x5 inches, and were fabricated in two

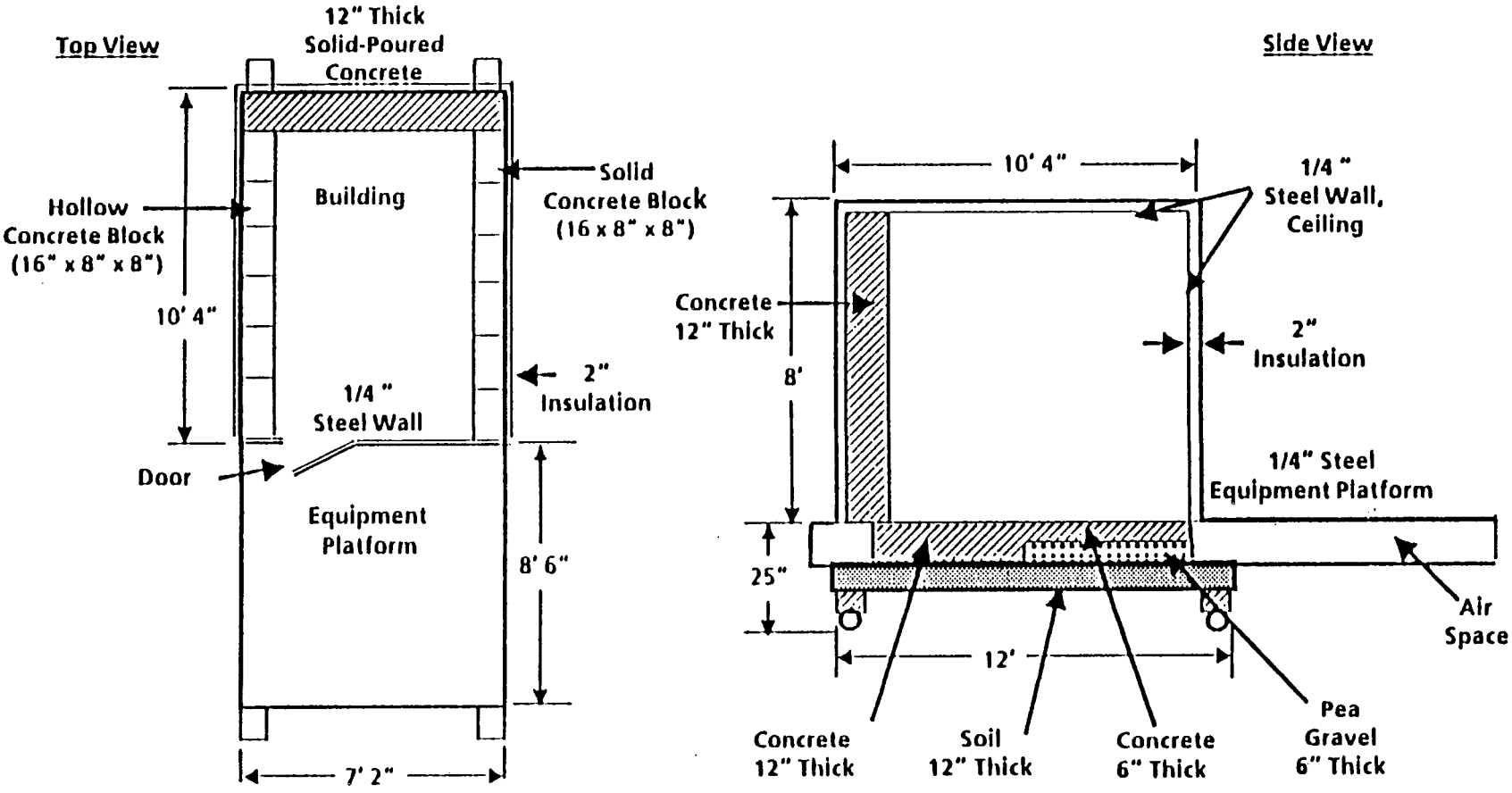


FIGURE 2. SKETCH OF TEST STRUCTURE

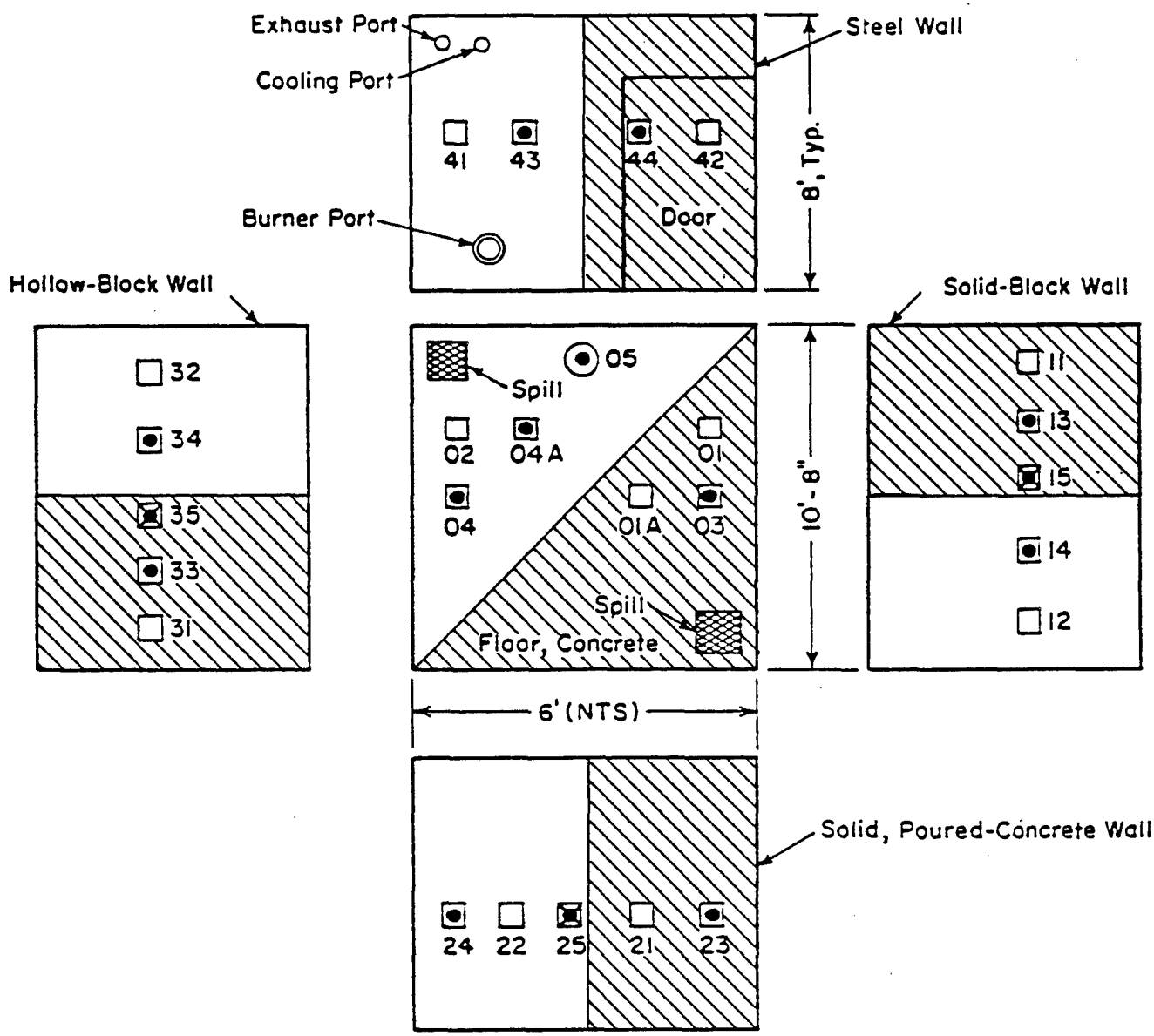
thicknesses: 0.25 and 0.5 inches. Low porosity and high porosity concrete coupons were prepared in order to simulate more closely the variety of concrete which can be found in the field. The steel coupons also measured 5x5 inches, and were made of 0.25 inch carbon steel.

The coupons were mounted within the test structure as shown in Figure 3. Several coupons were mounted with the agent spiked surface facing into the test structure and several were mounted with the spiked surface facing the test structure wall. In addition, a 5 inch diameter circular plug of concrete, was spiked on the bottom and inserted into a 4 inch deep hole cut out of the unpainted concrete floor. This coupon was designed to simulate HD contamination at depth.

To simulate a spill of HD onto concrete, two 20 x 20 inch areas on the painted and unpainted sections of the concrete floor were ridged in concrete caulking. A controlled spike was delivered to each of these two confined areas and allowed to soak into the concrete for about three days prior to the burner startup.

Figure 4 indicates thermocouple placement in the test structure. Standard type K Chromel Alumel thermocouples were used. The flexible type was used to monitor material temperatures (in the solid walls and on the surfaces), and the rigid probe type was used to measure air temperatures in the test structure and in the middle of the hollow block wall.

The structure was heated with a 550,000 BTU/hr burner operating with propane fuel and 90 scfm of air supplied by a combustion blower. Air flow of up to 500 acfm was maintained through the structure prior to and during the test. Negative pressure of -0.1 to -0.2 inches of water was maintained within the structure. Dilution air was supplied to the exhaust duct to provide a flow of 1000 acfm which cooled the air below 400°F, the maximum permitted in the carbon filter environmental containment system. Temperatures, air flows, pressures and burner operation were controlled from a panel in the control room remote from the test structure.



LEGENDS			
Coupon Code			Painted: concrete and steel areas
00	Concrete floor		Unpainted: concrete and steel areas
10	Solid-block wall	◉	Spiked coupon
20	Concrete wall	⊠	Spiked coupon with face to wall
30	Hollow-block wall	◉	Spiked coupon (4" deep in concrete floor)
40	Steel wall	□	Unspiked coupon

FIGURE 3. COUPON PLACEMENT IN TEST STRUCTURE

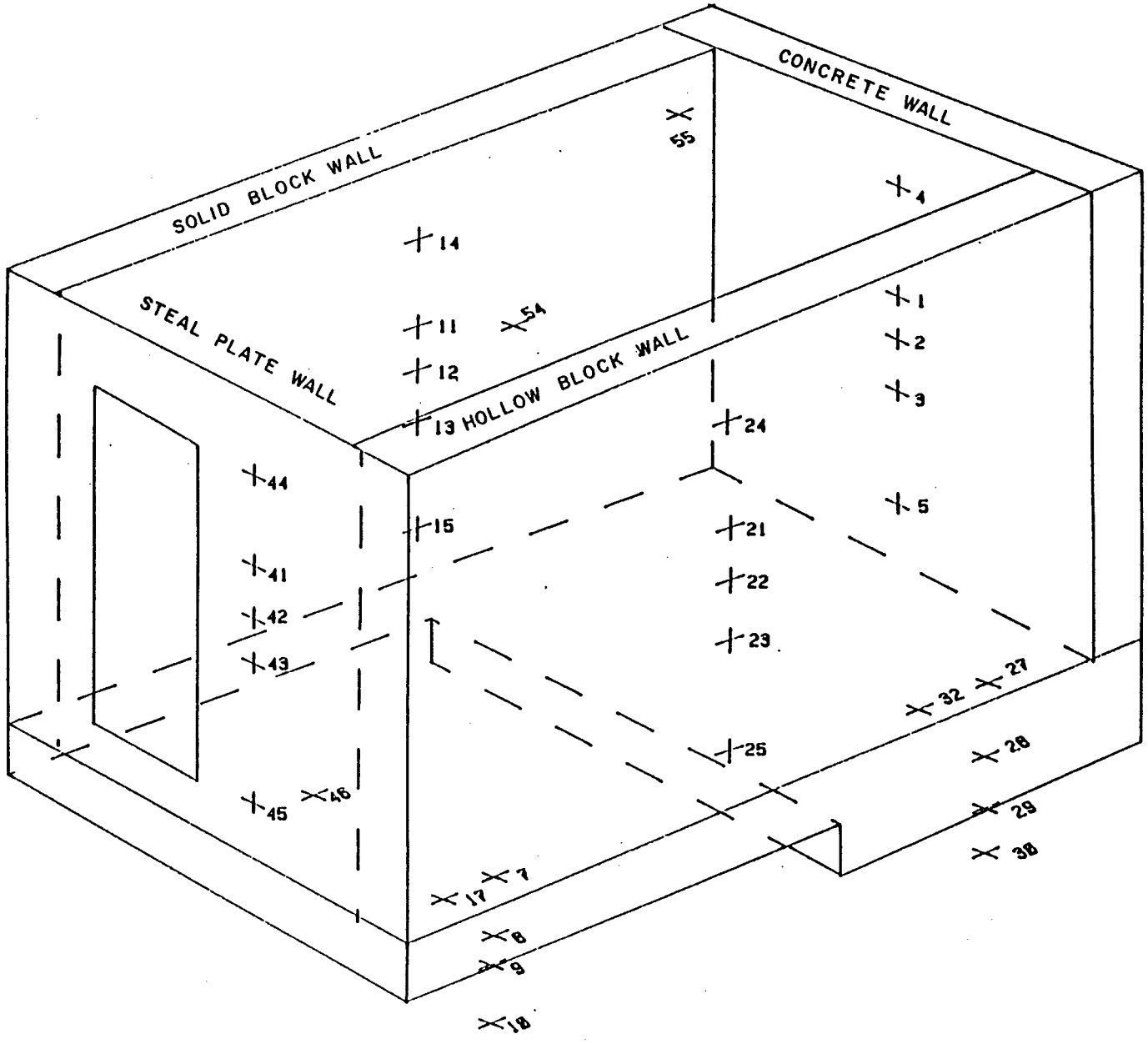


FIGURE 4. THERMOCOUPLE PLACEMENT IN THE TEST STRUCTURE

C. Test Operations

(1) Background Data, Sampling, and Analysis

Before the testing began, the thermocouple and pressure transducers were calibrated and background data such as temperature, pressure, and air flow rates were taken by the data acquisition system. The calibration provided confidence in the readings and the background data provided a point of reference for the balance of the test. Background chemical analysis samples were also collected. These samples included concrete floor samples (powdered concrete from drilling 3/8 inch diameter holes 3/8 inch to 1/2 inch deep) next to the floor spill areas and wipe samples from the floor and wall. Air samples were taken using bubblers and an ACAMS.*

Bubblers were placed to sample three locations within the test structure, four locations in the exhaust ducts, two locations adjacent to the outside walls of the structure and one location in the soil base below one of the floor sections that was spiked with agent. The ACAMS sampled air in the exhaust duct at the point of exit from the test structure.

Air sampling was started approximately 18 hours prior to spiking the structure and coupons with HD and approximately 91 hours prior to the start of heating of the structure.

After the test was completed and the structure had cooled, samples were collected for chemical analyses. These included: 38 wipe samples from steel and concrete structural surfaces and coupons; 4 soil samples from beneath the floor; 7 pulverized concrete samples drilled from floor and concrete blocks; and 2 paint samples from the floor and steel door.

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* The ACAMS (automatic continuous air monitoring system) collects vapor samples in a solid sorbent preconcentrator. The samples are desorbed thermally to a gas chromatograph with a flame photometric detector. Cycle time for adsorption, desorption, and analysis is eight minutes and sensitivity for HD is approximately 0.0001 mg/m^3. The bubblers contained 10 ml of hexylene glycol and were operated at one liter per minute with a six hour sampling time, and a sensitivity of approximately 0.003 mg/m^3.

Analytical methods had been developed for HD in structural materials and were verified for use in the pilot test program [4]. These procedures were used to analyze pre- and post-test samples from the test structure.

(2) Agent Spiking

Eighteen hours after the start of the test, the coupons were spiked with approximately 7.6 ml of a 2.0 weight percent solution of HD in hexane to deliver 4 mg/in^2 of HD to each coupon. After the coupons were placed into their holders in the test structure, the floor spill areas were spiked with 4 mg/in^2 of HD. The test structure was then closed. The ventilation blowers remained on to keep the test structure at negative pressure and pass the exhaust through the 1200 acfm activated carbon filter. Agent spiking was followed by a 73 hour period during which time the HD was partly absorbed by the structure and partly evaporated into the exhaust system.

(3) Heating and Cooling of the Structure

The burner was started 91 hours after the start of the test, at a controller set point temperature setting of 200°F. At 92 hours the burner control set point was raised to 250°F. The test exhaust temperature was 192°F. The burner control set point was raised 50°F every hour until it reached 400°F, after which it was held at this setting for 6 hours. The burner control setting then was raised in 50°F increments every hours until a temperature of 750°F was attained at the hot gas inlet to the structure. The burner was maintained at this temperature until all the structure temperatures exceeded 300°F for a minimum time of 1 hour. This condition was reached at 126 hours, 35 hours after the burner was fired. The burner was then shut off to start the cooldown period which continued for 38 hours when all the test structure internal temperatures dropped to 105°F or less.

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4 T. L. Hayes, "The Development of Analytical Methods for Determination of HD Contamination In or On Building Materials." Contract No. DAAA15-86-D-0001, Task 1, Battelle Columbus Division to U.S. Army Toxic and Hazardous Materials Agency, August 1986, (also included as Appendix B in Ref. 3).

The test structure was then opened 164 hours after the start of the test for inspection, photography, and collection of samples.

D. Pilot Test Results

(1) Temperature-Time Profiles

The temperature heat-up and cool-down profiles of each of the walls and floor sections are shown in Figures 5 to 10. The plots begin at 80 hours and heating started when the burner was turned on 91 hours after the start of the test. The graphs for the poured concrete wall, the solid concrete block wall, and the hollow concrete block wall compare thermocouple readings from the interior surface of each wall, middle of each wall, and three locations on the exterior surface of each wall. The plot for the steel wall displays the temperature profiles for halfway up the wall and near the ceiling. The profiles for the two floor sections contain readings from the interior surface of the floor, the middle of the floor, the exterior surface of the floor, and the soil beneath the floor ("sand box"). Each graph also contains the temperature profile of the thermocouple used for burner control for comparison with the other thermal profiles displayed.

Several of the thermal profiles showed intervals where the signals were noisy, possibly due to moisture or movement in the thermal contact. This was a minor effect, and had no significant impact on the temperature-time data.

The thermal profiles show that for the concrete walls and the floors, the interior surfaces heated faster and attained higher temperatures than did either the middle of the walls or the exterior surfaces. The thermal profiles of the steel wall paralled the burner air temperature profile very closely.

Figures 11 and 12 compare interior and exterior wall surface temperatures. The steel wall reached the highest temperatures during the test. The poured concrete wall interior surface reached the highest

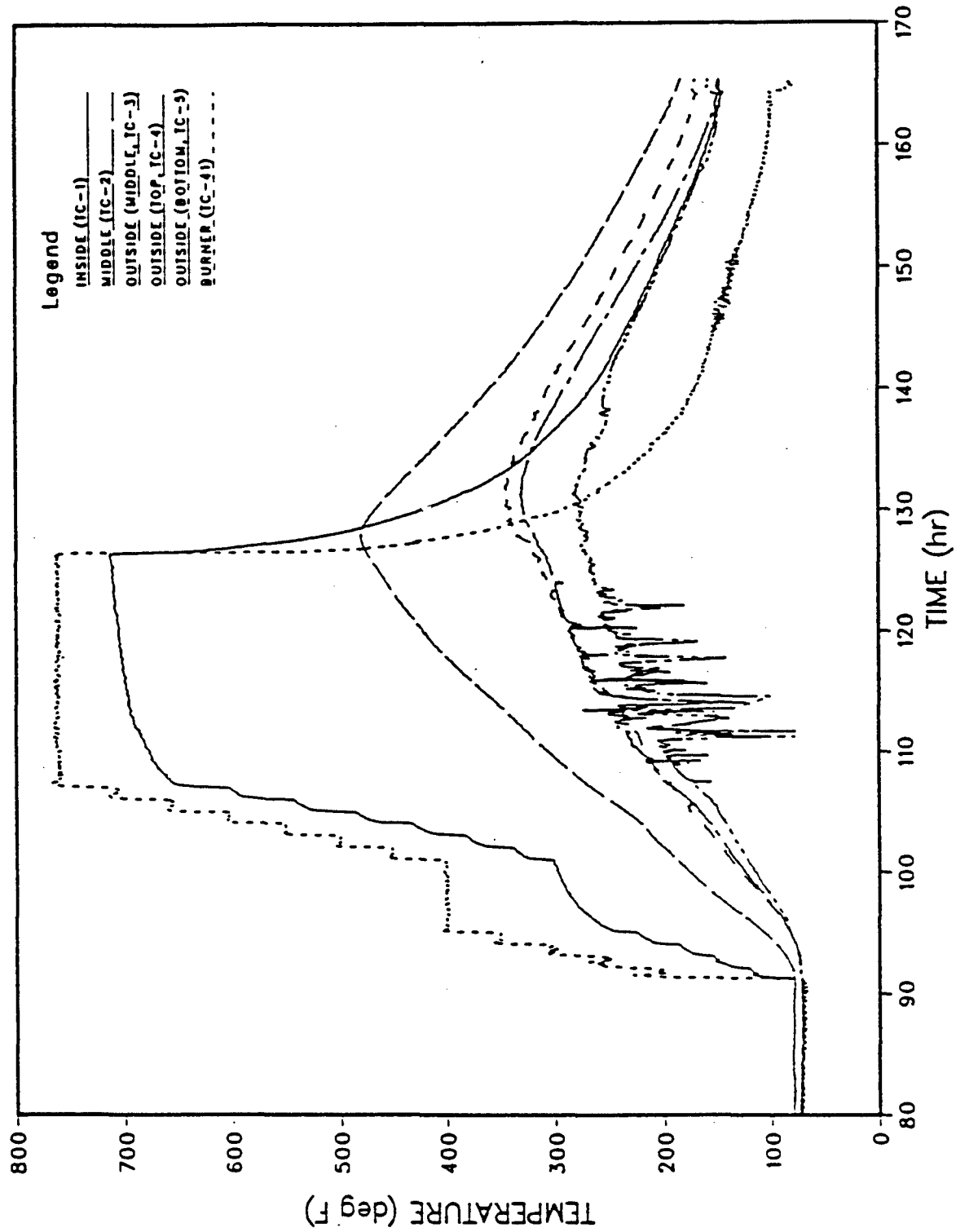


FIGURE 5. TEMPERATURE PROFILES OF THE CONCRETE WALL

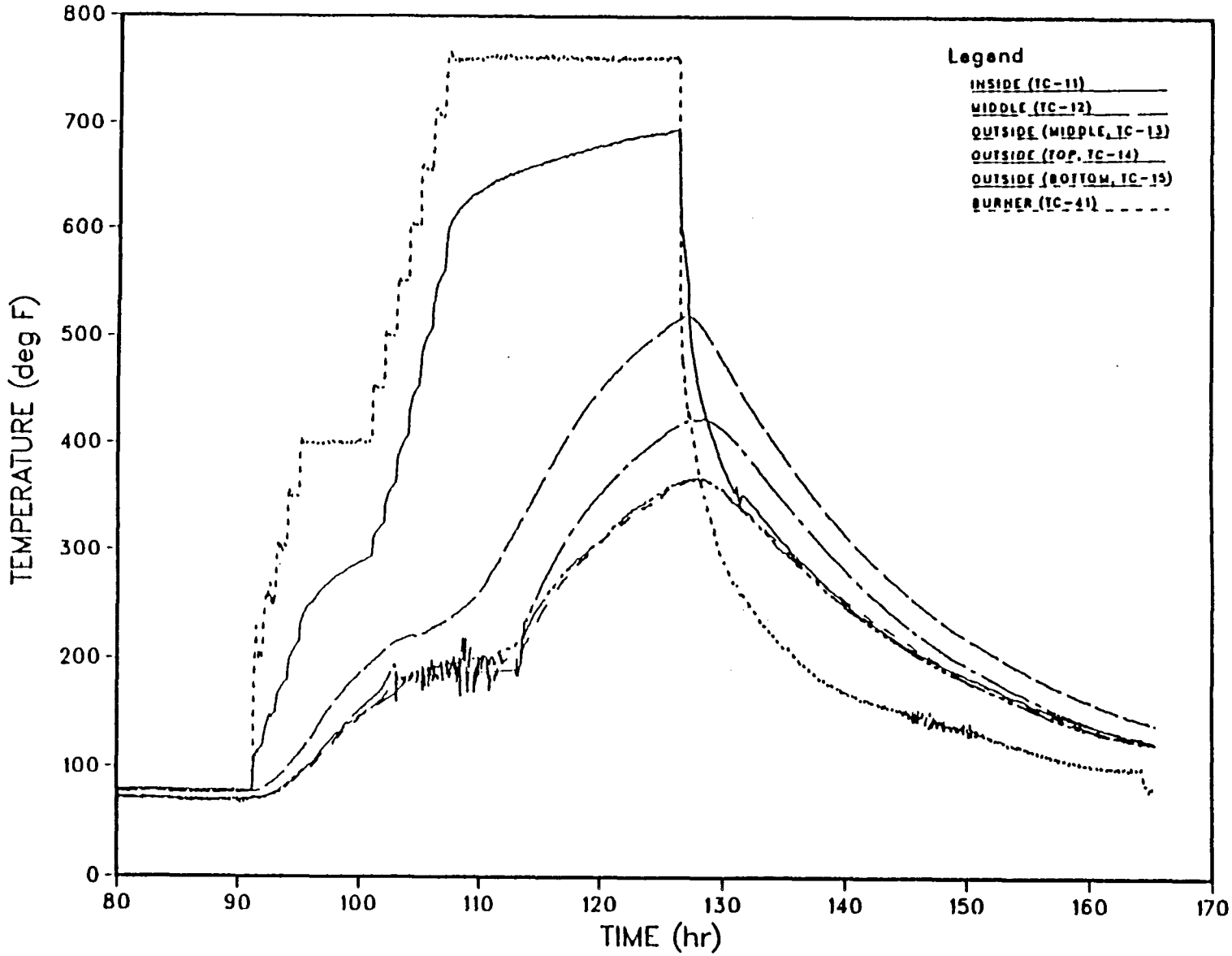


FIGURE 6. TEMPERATURE PROFILES OF SOLID BLOCK WALL

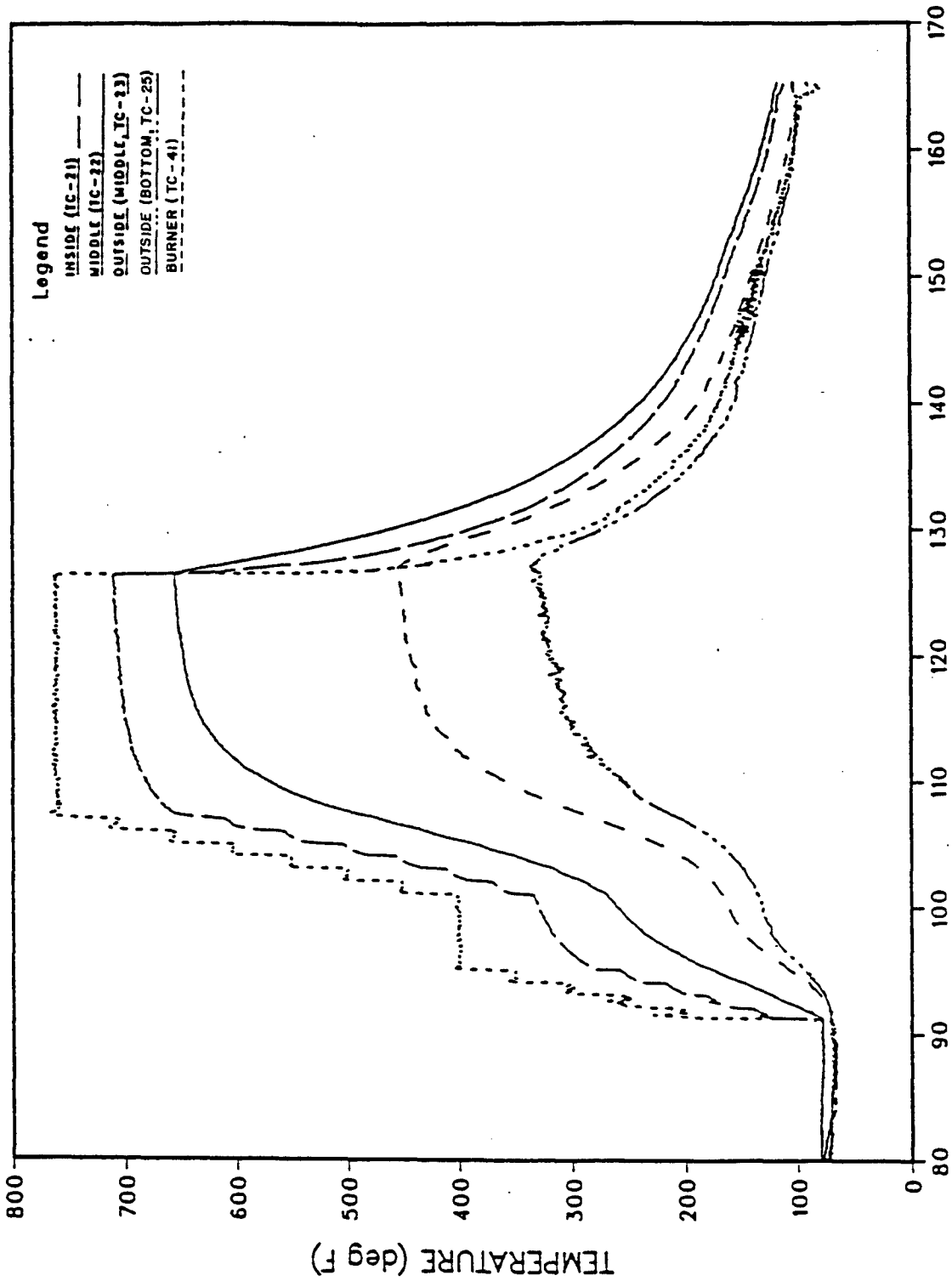


FIGURE 7. TEMPERATURE PROFILES OF HOLLOW BLOCK WALL

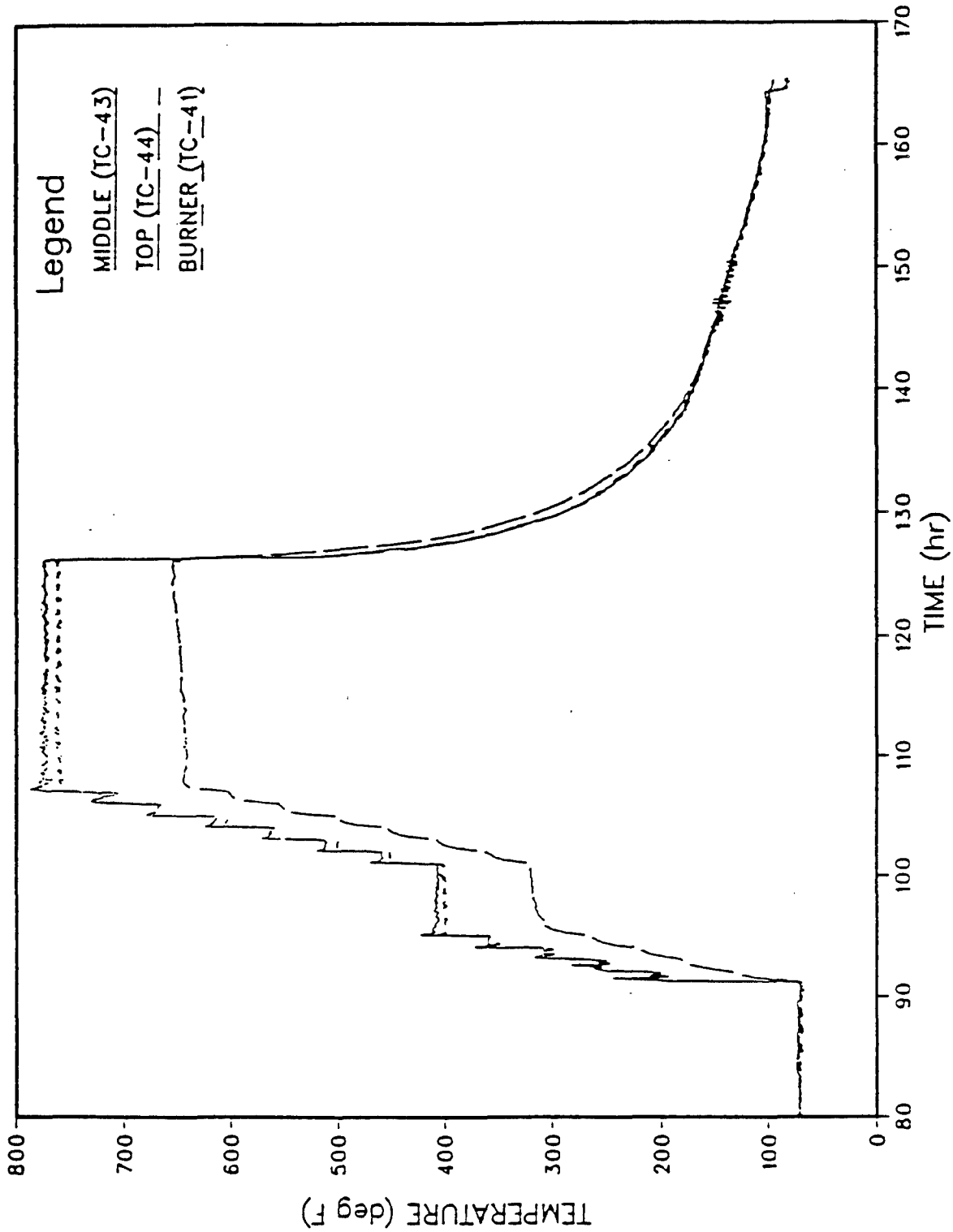


FIGURE 8. TEMPERATURE PROFILES OF STEEL PLATE WALL

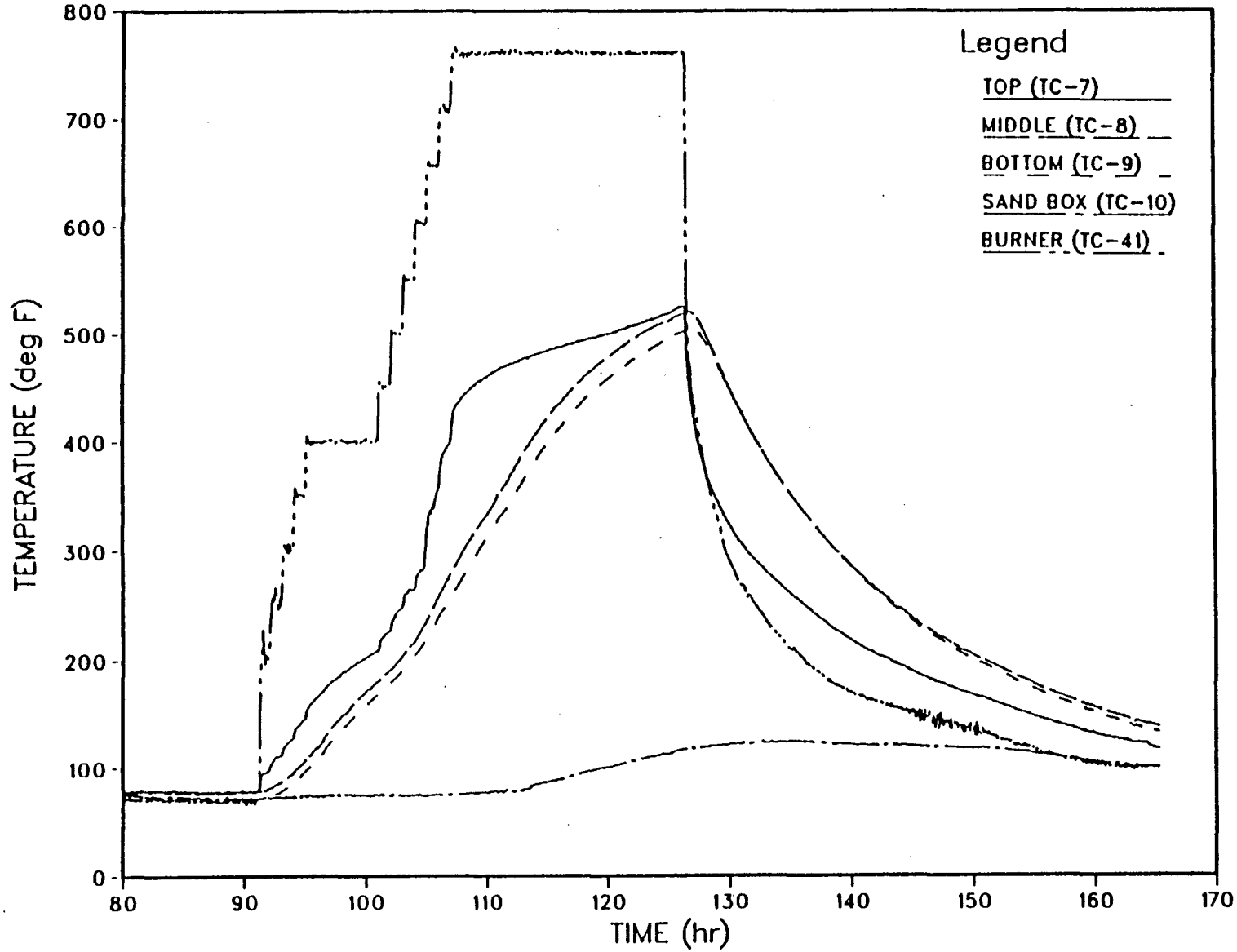


FIGURE 9. TEMPERATURE PROFILES OF 6-INCH THICK FLOOR

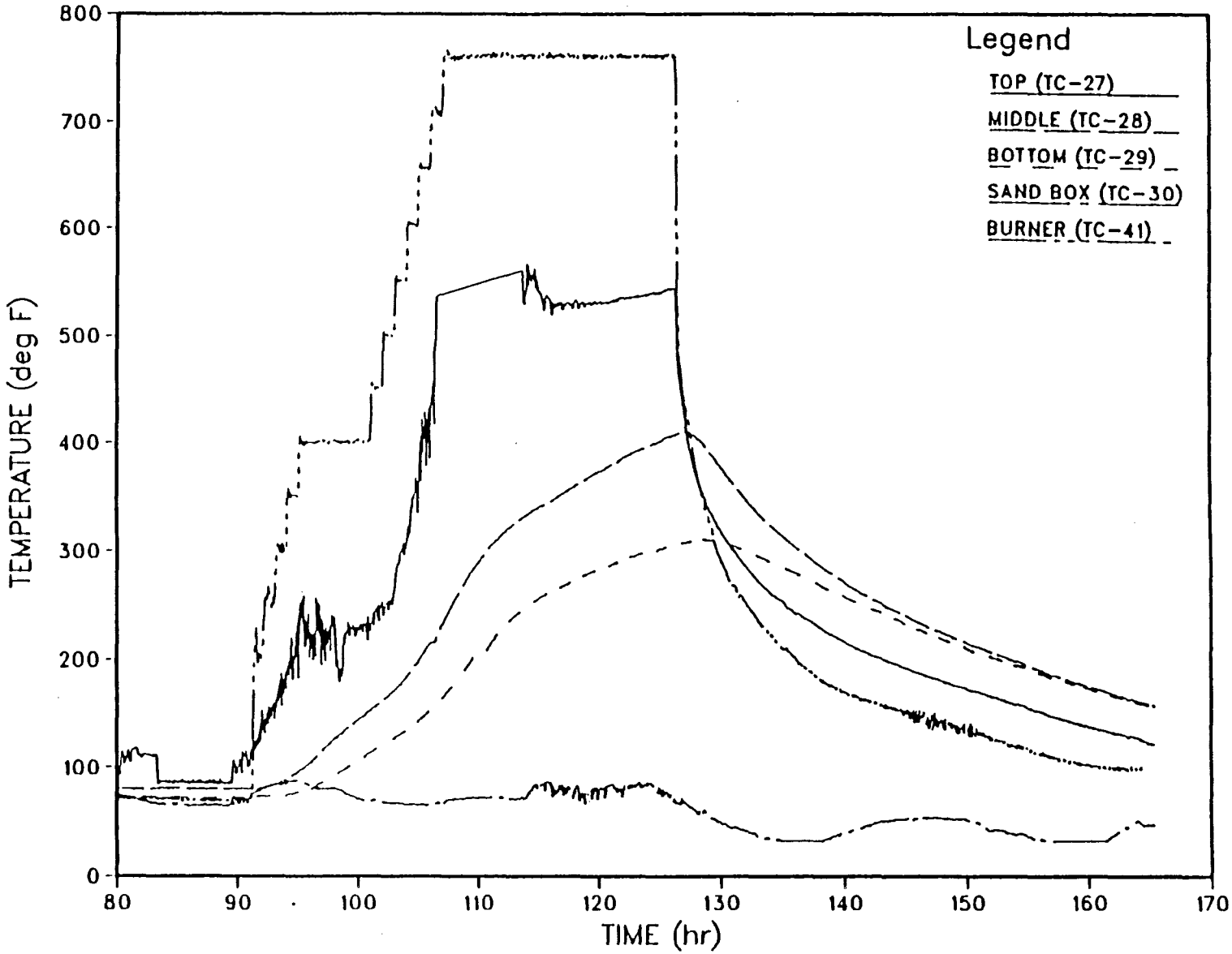


FIGURE 10. TEMPERATURE PROFILES OF 12-INCH THICK FLOOR

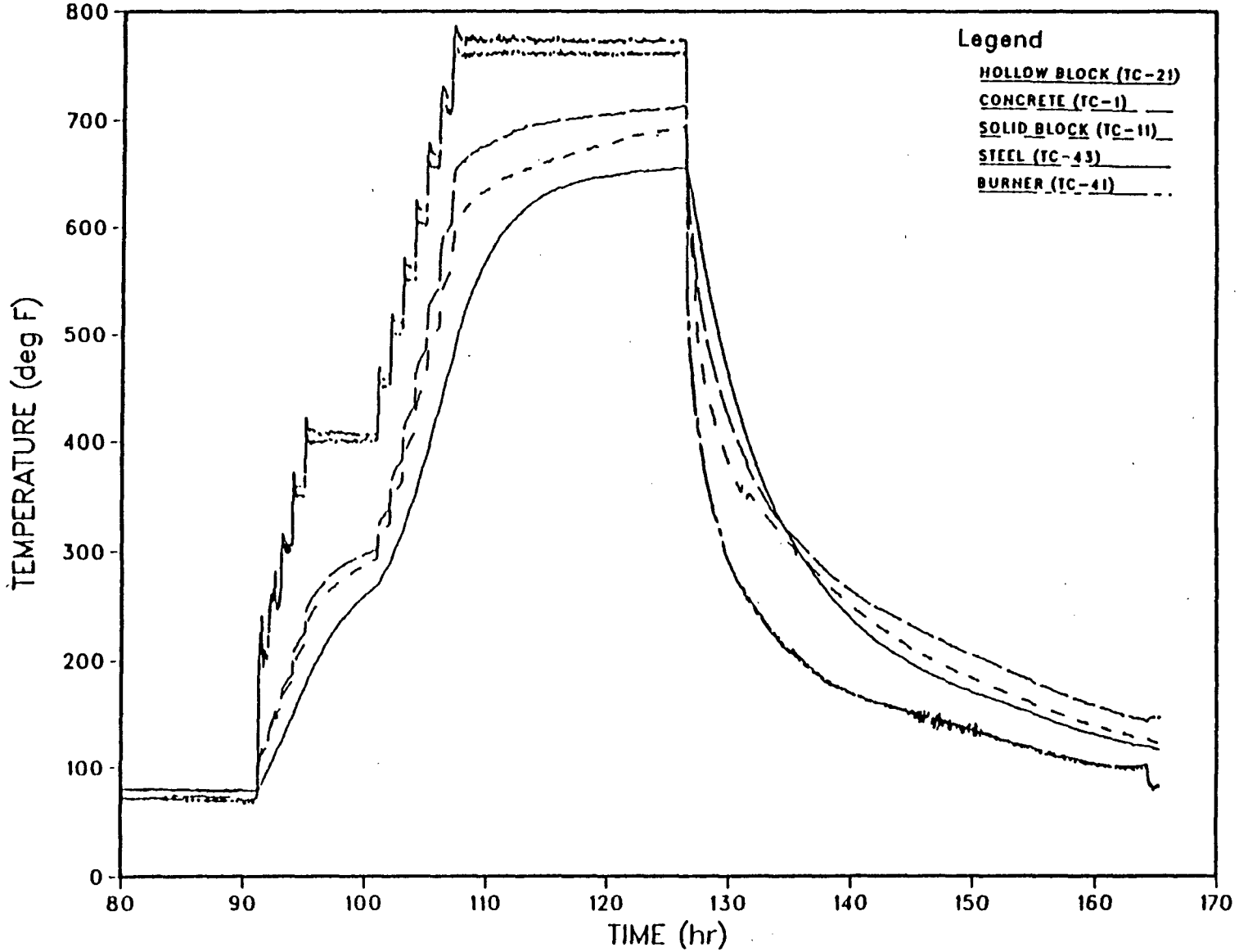


FIGURE 11. TEMPERATURE PROFILES FOR INTERIOR WALL SURFACES

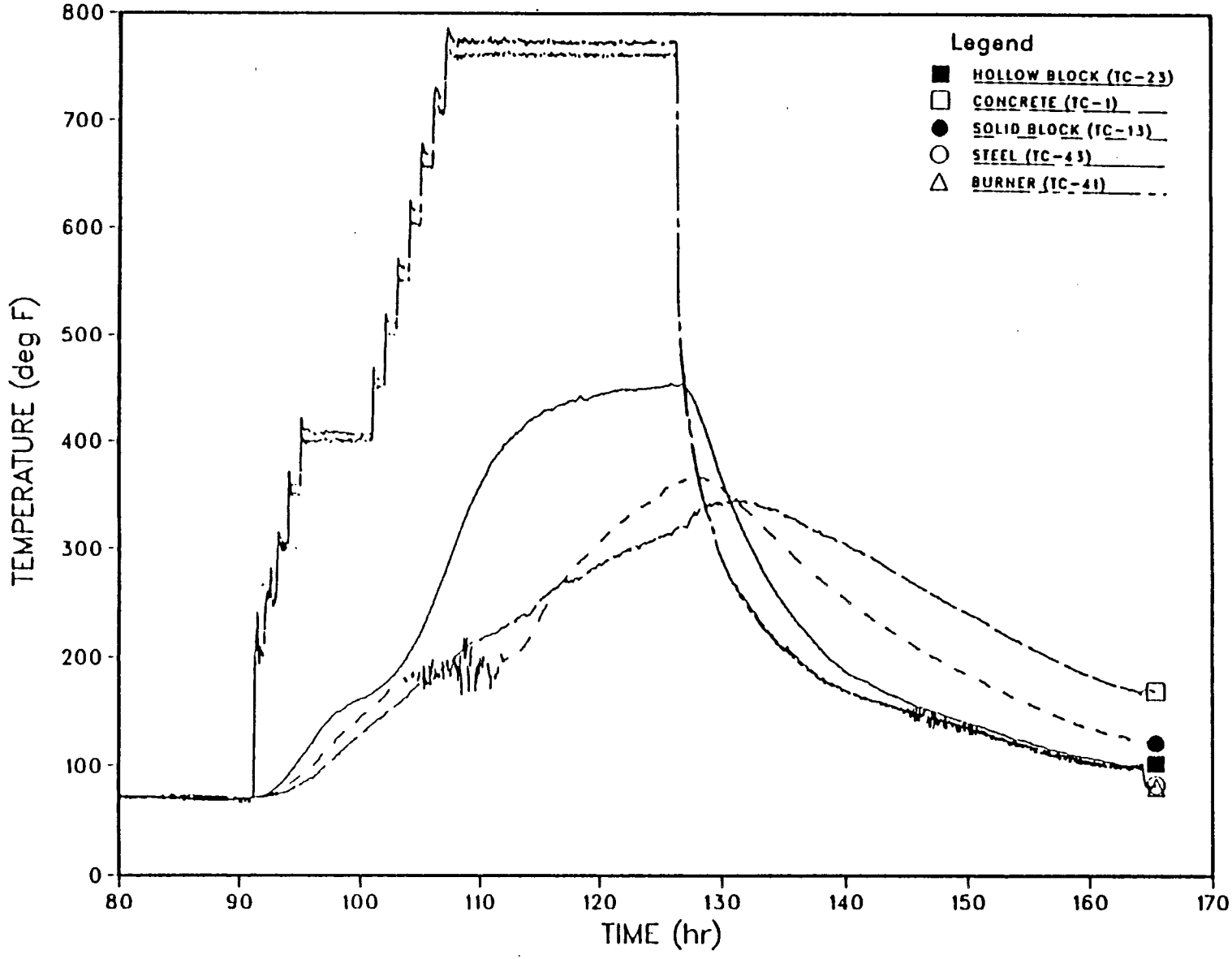


FIGURE 12. TEMPERATURE PROFILES FOR HALFWAY UP EXTERIOR WALLS

temperatures of all the non-steel walls during the heatup phase. The exterior of the hollow block wall heated faster than either the poured concrete wall or the solid block wall. The different thermal characteristics of the building materials heated in this pilot test demonstrate that building construction will be an important factor in the site-specific design of hot gas decontamination system field operations.

(2) Air Monitoring

Of these ten bubbler stations monitored, only five showed any values above the TWA of 0.003 mg/M^3. Four of these were inside the structure or in the exhaust duct, and one in the soil below the spill area on the six inch thick floor.

Figure 13 shows bubbler and ACAMS data during the test. The bubbler data shown is from a monitoring station near the door of the structure. The ACAMS monitored the exhaust duct at the exit from the structure, but upstream from the point where dilution air was injected into the exhaust flow.

The ACAMS and bubbler values both rose to 0.06 mg/M^3 during the first six hour monitoring period after the structure was spiked with agent. During the following 24 hour period the HD values dropped below the TWA and just prior to the start of heating the ACAMS readings had decreased to 0.0007 mg/M^3. It was apparent that most of the HD was removed from the structure by evaporation.

However, there was a residue of HD in the structure that was vaporized when heating started. The release of agent at the start of the heating cycle apparently occurred too quickly to be observed in the bubblers, but was detected by the ACAMS. Figure 14 provides an expanded plot of the ACAMS data during the initial heating of the structure. The HD concentration then decreased to below detectable after eight hours of heating. At this point the ACAMS began to behave erratically due to excessive moisture in the system which exceeded the capacity of the trap on

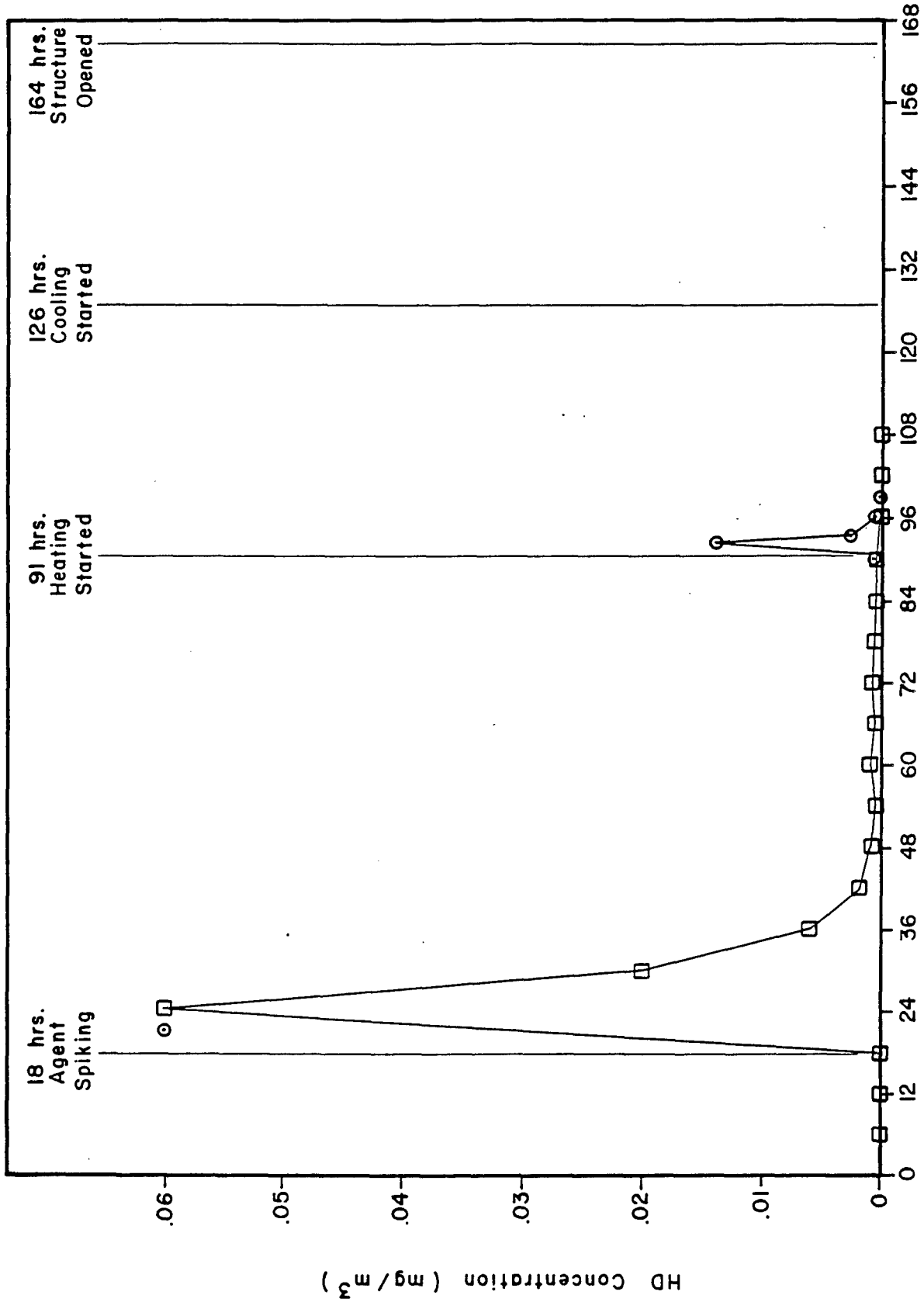


FIGURE 13. HD CONCENTRATION IN TEST STRUCTURE OR EXHAUST DUCT AS MEASURED BY BUBBLER SAMPLES (□), AND ACAMS (⊙).

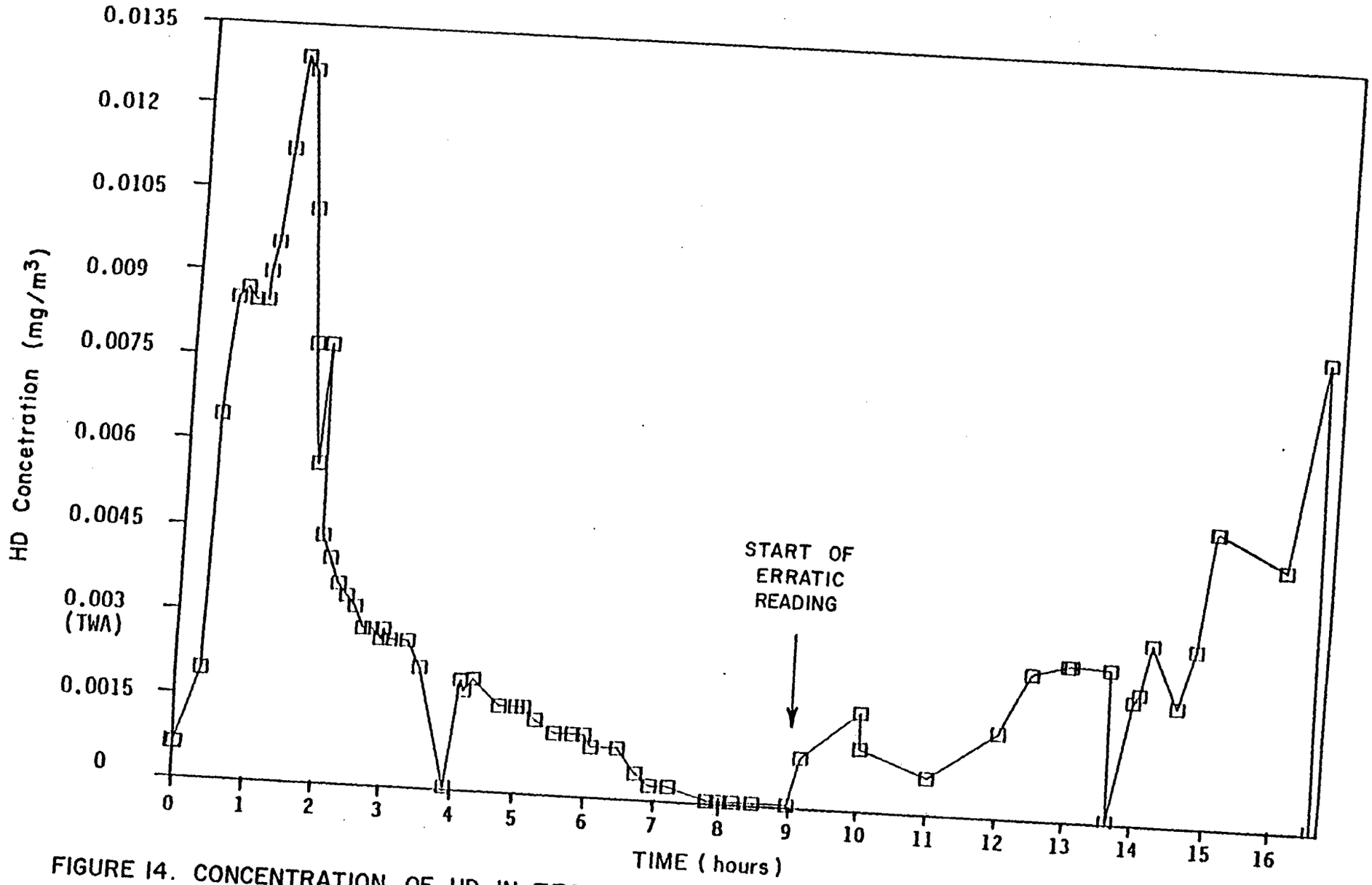


FIGURE 14. CONCENTRATION OF HD IN TEST STRUCTURE AIR AS MEASURED BY ACAMS DURING INITIAL HEATING.

the sampling line. Similar problems occurred with the bubblers and no further air monitoring data could be obtained. However it appeared that the HD had been volatilized from the structure before the erratic behavior of the monitors started.

Bubbler samples monitoring the soil below the spill area on the six-inch floor showed positive at about 0.006 mg/M^3 (two times the TWA) prior to spiking the structure. A slight increase in the bubbler values appeared about 50 hours after spiking the structure. The bubbler values then dropped below background. Whether there were traces of HD in the soil or an unidentified interferent was not determined.

(3) Post-Test Sample Analysis Results

No HD was detected above the theoretical detection limits in any of the more than fifty samples subjected to the hot gas decontamination process.

(4) Test Structure Integrity

The test structure appeared to be sound and in good condition following heating, although no tests for structural soundness were performed. There were no visible signs of structural damage as a result of the thermal decontamination test. There were no cracks in the wall, no separation of the walls at the corners or ceiling. The concrete did not appear to be weakened by the heating based on the time required to drill 3/8 inch diameter holes after the test. The alkyd (Sani-flat) paint used on sections of the floor and walls remained intact on the concrete but chalked and flaked from the metal. This difference in performance may be related to the higher temperatures attained on the metal surfaces compared with those attained on the concrete surfaces.

5.0 Conclusions

1. The hot gas decontamination process effectively removes chemical agent HD from painted and unpainted concrete and painted and unpainted steel. Low concentrations of HD that have been absorbed into concrete decrease when subjected to the hot gas process to levels below the detection limit of the best available analytical technology (see No. 3, below).

2. The engineering aspects of implementing the hot gas system are well defined. Beyond site-specific modifications, no major changes to the hot gas burner system or setup are needed to make the design field-ready.

3. The laboratory methods verification study shows that the methods for extracting HD from pulverized concrete and soils work well and give verifiable, quantitative results. The theoretical detection limit for this method is approximately 0.5 ug of HD/g concrete or soil, or about 500 parts per billion (ppb).

4. Sampling concrete in the field to depths of about two inches from the surface is possible by pulverizing the concrete with an electric drill and collecting the fines for analysis. This method is appropriate for collecting samples of up to 10 grams of concrete.

5. Sampling the surfaces of unpainted and painted steel and concrete is possible by wiping a cotton swab on the surface and extracting the swab with

solvent. However, this method is strictly a screening technique and should not be used for quantitative recovery of HD.

6. The hot gas process did not cause visible structural damage to a concrete and steel building in which the gas temperature was held at 750°F, and the wall temperatures exceeded 300°F for one hour. However, no structural testing was conducted. Paint remains intact on concrete surfaces, but chalks and flakes from the steel surfaces.

7. In order for the hot gas decontamination technology to be accepted for use in military structures, a sampling protocol will be required that will reliably demonstrate complete removal of agent and be effective in the presence of interferents. Since existing 5x decontamination criteria do not provide for any residual agent, it will likely be necessary to demonstrate agent removal below detection limits of the sampling and analysis protocols developed for use with the hot gas decontamination process.

MODELING TRANSPORT AND DISPERSION OF SPILLS OF CONTAMINANTS IN TVA WATERWAYS

by

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The potential for accidental spills of hazardous material into surface waters is always a possibility near any industrial complex. These spills can affect water supplies, aquatic resources, recreation, and all other water uses. Advanced planning will permit responsible agencies to respond to such emergencies promptly and appropriately. The Tennessee Valley Authority (TVA) has developed procedures for responding to waterborne accidental releases of contaminants from its nuclear plants and several other key industrial facilities in the Tennessee Valley. The emergency response procedure includes an established chain of communication for processing and disseminating information concerning spill characteristics.

In support of its nuclear program, TVA has developed a plan with specific instructions to be implemented by affected TVA organizations during a radiological emergency at any of its three nuclear plants. In the event of an emergency, the nuclear plant shift operator receives initial notification of an accident (Figure 1). The operator then notifies the Central Emergency Control Center (CECC) and the State Emergency Management Agency (SEMA) if there is a leakage of radioactive material. The CECC subsequently alerts the TVA radiological monitoring team, including the Engineering Laboratory in case of a waterborne spill, and notifies appropriate States and the Environmental Protection Agency.

A key and unique aspect of this plan involves the use of computer models for predicting plume movement and spreading. The models provide timely information on expected exposure concentrations, leading and trailing edges of the plume and travel times along the spill path. These results are used to notify downstream water users of expected plume arrival times and contaminant concentrations at their intakes. The results are also used to guide field sampling to track the actual movement of the plume and to suggest possible dam operations for containment of the spill or mitigation of its impact.

The mechanisms included in the models for mixing and transport of contaminants are advection and dispersion. The models provide contaminant concentrations in time and space after a spill. The predictions depend on the characteristics of the spill (time, location, initial concentration, rate, and duration) flow conditions (spatial and temporal), and geometry of the water body.

Advection is estimated by a flow routing model for unsteady flow (Figure 2). If only time and location of a spill is known, advection can be used to predict the travel time of the center of mass of the contaminant. Dispersion is based on an analytical solution to the mass transport equation and uses an average velocity generated by the flow model. The rate of contaminant release is assumed constant and the spill is assumed to begin from a line or plane source (Figure 3).

A more advanced transport model has also been developed, based on the streamtube concept. This model allows for varying geometry and temporal and spatial variability (Figure 4). The model can predict irregular positioning of vertical line sources or plane spills of any spatial origin and temporally-varying input.

A team of engineers at the Engineering Laboratory in Norris, Tennessee, is responsible for calibrating, verifying, maintaining, and periodically updating the models. The Spill Team is also responsible for maintaining a public and industrial water supply intake inventory within a 50-mile radius of each industrial site included in the spill plan. Spill Team members have been trained in the basic assumptions, capabilities, limitations, and application of the operational models. Periodic training and testing is conducted to ensure that the members remain proficient. Computer programs and operational procedures are consistent with quality assurance procedures and Nuclear Regulatory Commission standards. Periodic drills are also conducted to ensure efficient operation during emergency situations.

TVA is also currently developing models to respond to releases of nonnuclear hazardous materials into Tennessee waterways. These sites include the Clinch River near Oak Ridge, Tennessee; the Ocoee River near Copperhill, Tennessee; and the Holston River Basin.

FIGURE 1

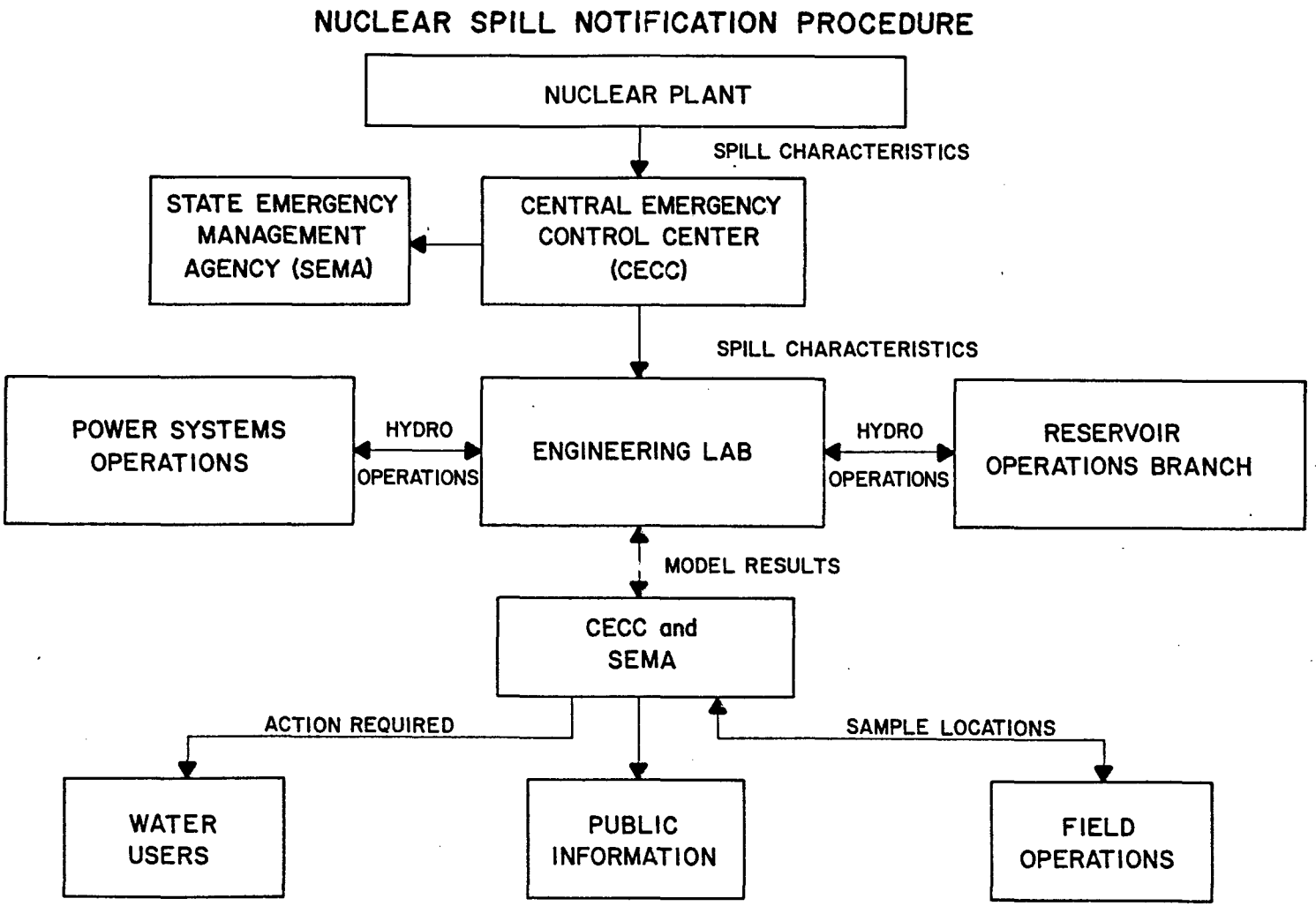

NUCLEAR SPILL NOTIFICATION PROCEDURE
NUCLEAR PLANT
SPILL CHARACTERISTICS
STATE EMERGENCY MANAGEMENT AGENCY (SEMA)
CENTRAL EMERGENCY CONTROL CENTER (CECC)
SPILL CHARACTERISTICS
POWER SYSTEMS OPERATIONS
HYDRO OPERATIONS
ENGINEERING LAB
HYDRO OPERATIONS
RESERVOIR OPERATIONS BRANCH
MODEL RESULTS
CECC and SEMA
ACTION REQUIRED
SAMPLE LOCATIONS
WATER USERS
PUBLIC INFORMATION
FIELD OPERATIONS

FIGURE 2

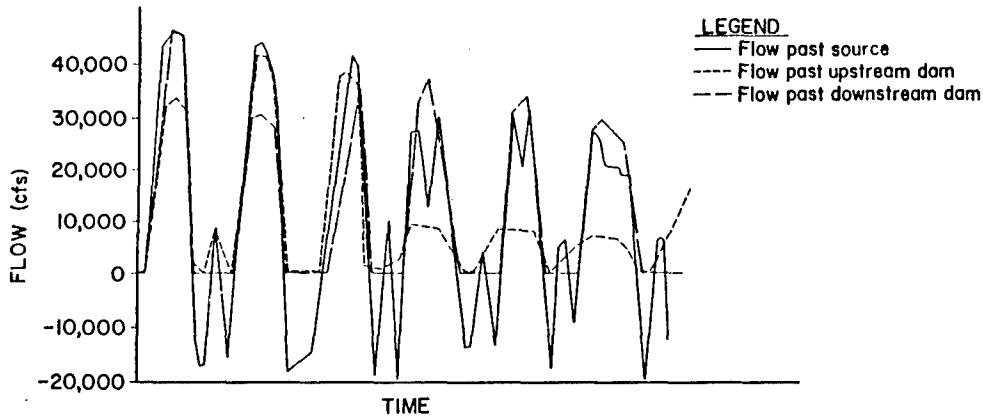


FIGURE 3

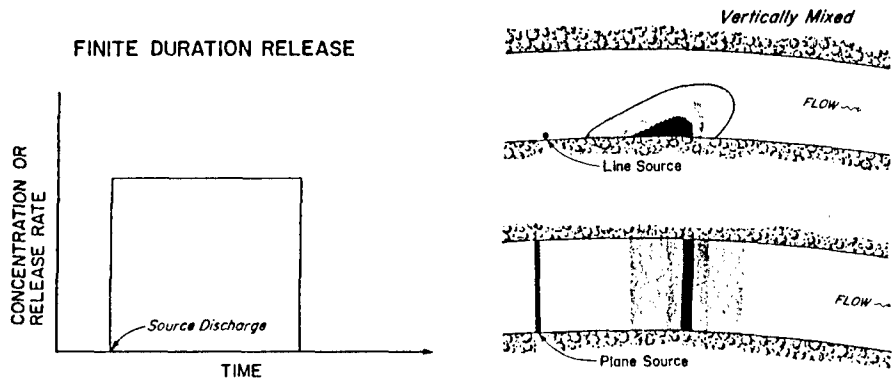
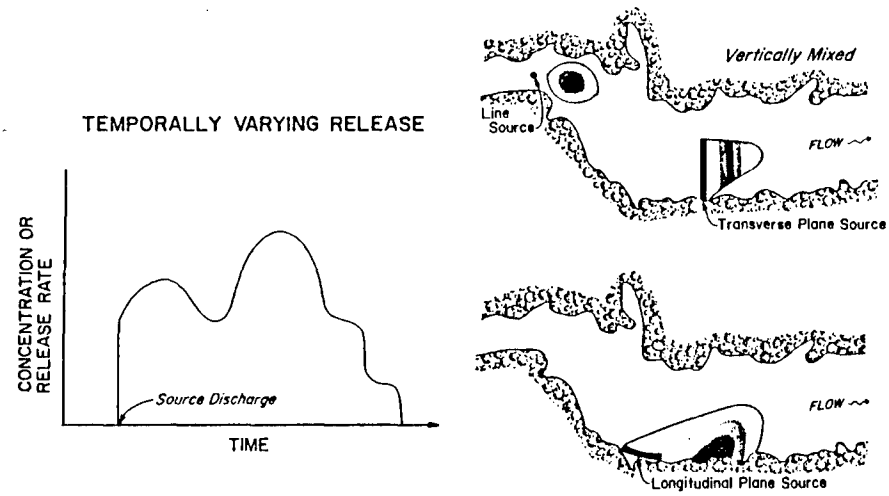


FIGURE 4



Interim Response Actions at Rocky Mountain Arsenal

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ABSTRACT

The Rocky Mountain Arsenal (RMA), a site known historically for the production of chemical agents and pesticides, has been undergoing an intensive environmental program.

The office of the Program Manager for RMA Contamination Cleanup has been established to centrally manage all activities associated with the contamination cleanup strategy of RMA. The Army is in the process of conducting a comprehensive Remedial Investigation/Feasibility Study (RI/FS) for which a Record of Decision (ROD) is projected to be completed in January 1993.

The Army in cooperation with the Environmental Protection Agency (EPA), Region VIII, the State of Colorado Department of Health, and Shell Oil Company, has identified thirteen specific Interim Response Actions (IRA's) that are considered necessary and appropriate to commence in advance of issuance of the ROD.

The IRA's are "removal" actions as provided under CERCLA and are to be consistent with the contribute to the efficient performance of the Final Response Actions. The IRA's include the assessment and implementation, as appropriate, of three new groundwater intercept and treatment systems, two on the RMA and one offpost; the evaluation and improvement, as necessary, of existing groundwater intercept and treatment systems at the RMA boundary; the identification, examination, and proper closure of old or unused wells on RMA; the removal and temporary containment of liquids, sludges, and soils from a 93 acre lined surface

impoundment; the remediation of contaminated liquid in a former process area wastewater collection sump; the remediation of the above ground structures and contaminated wastewater in a former Hydrazine Blending and Storage Facility; the application of dust suppressants in areas subject to release of windblown contaminated dust; the remediation of sections of the sanitary sewer system which are potential conducts for contaminant flow; the remediation of friable asbestos; the remediation of selected potential active sources of groundwater contamination; and the implementation of a program to treat wastewaters resulting from CERCLA Response Actions at RMA.

INTRODUCTION

The Rocky Mountain Arsenal (RMA) is located adjacent to Adams County, Colorado, approximately 10 miles northeast of downtown Denver and encompasses over 17,000 acres (Figures 1 and 2). Since its establishment in 1942, RMA has been the site for the manufacture of chemical and incendiary munitions, and the demilitarization of chemical ordnance. Industrial chemicals (pesticides) were also manufactured by private industry from 1947 to 1982.

Disposal practices at RMA have included discharge of industrial effluents to unlined and lined surface impoundments and burial of solid wastes, practices that were commonplace and widely accepted by industry at the time. In addition, unintentional spills of raw material, and intermediate and end products have occurred within the manufacturing complexes and adjacent areas of the arsenal.

The disposal practices and unintentional spills resulted in soil and surface water contamination. Eventually, the surface and near surface contamination migrated into the shallow alluvial groundwater. (Figure 3 represents the generalized alluvial groundwater flow across RMA).

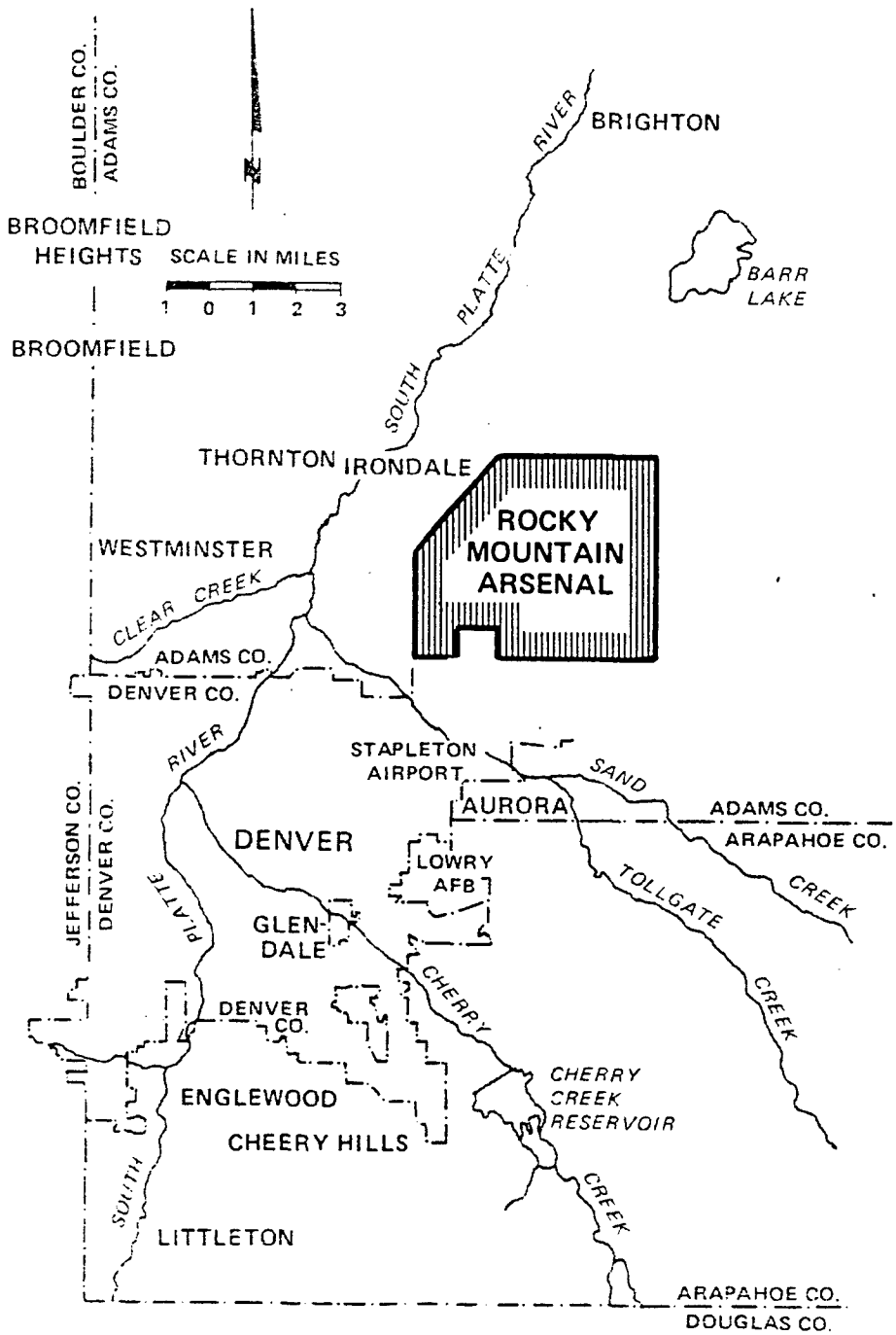


FIGURE 1
MAP OF RMA
DENVER VICINITY

Source: (Rocky Mountain Arsenal Contamination Control Program Management Team, 1983)

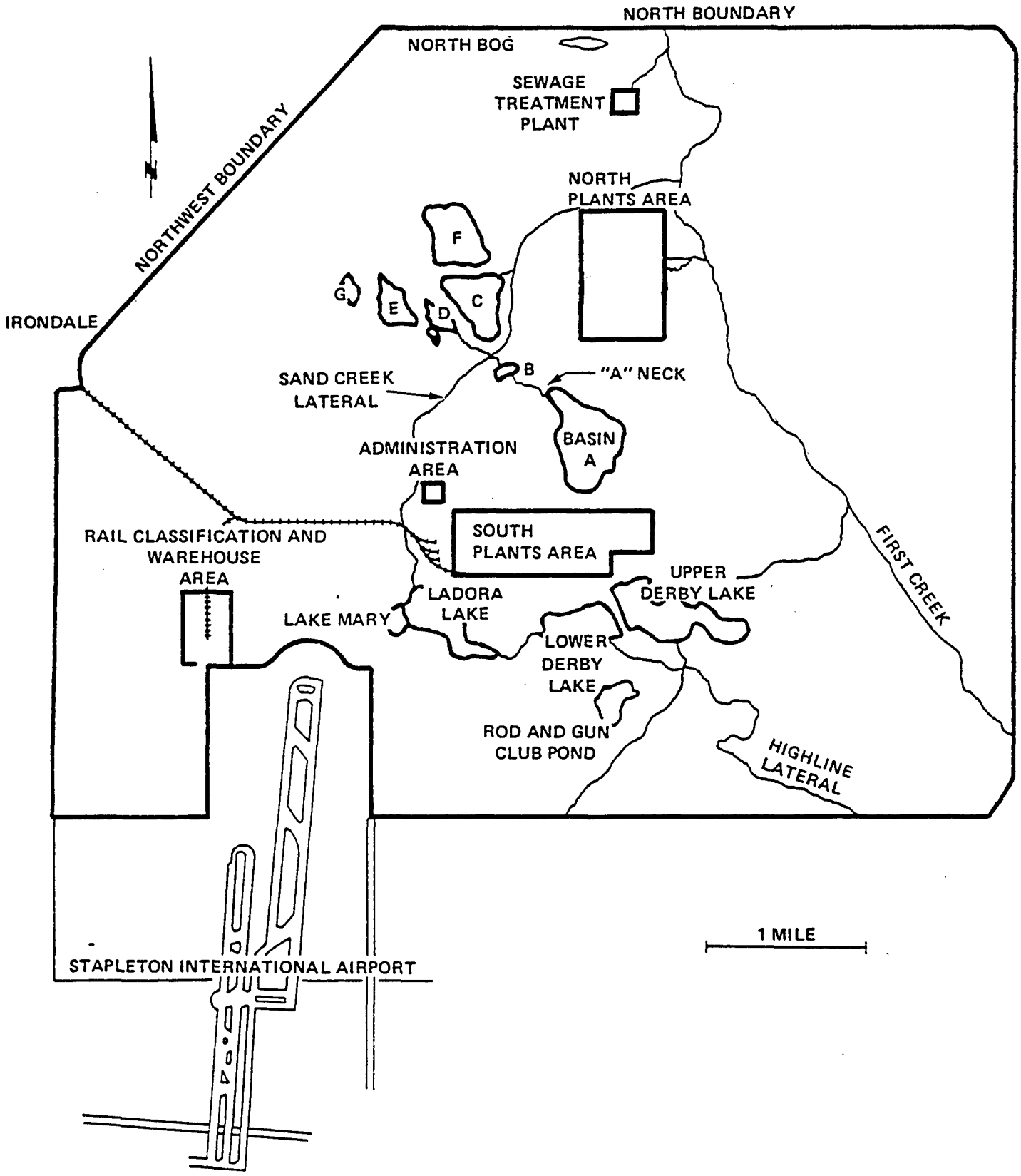


FIGURE 2-
GENERAL MAP OF RMA

Source: (Rocky Mountain Arsenal Contamination Control Program Management Team, 1983)

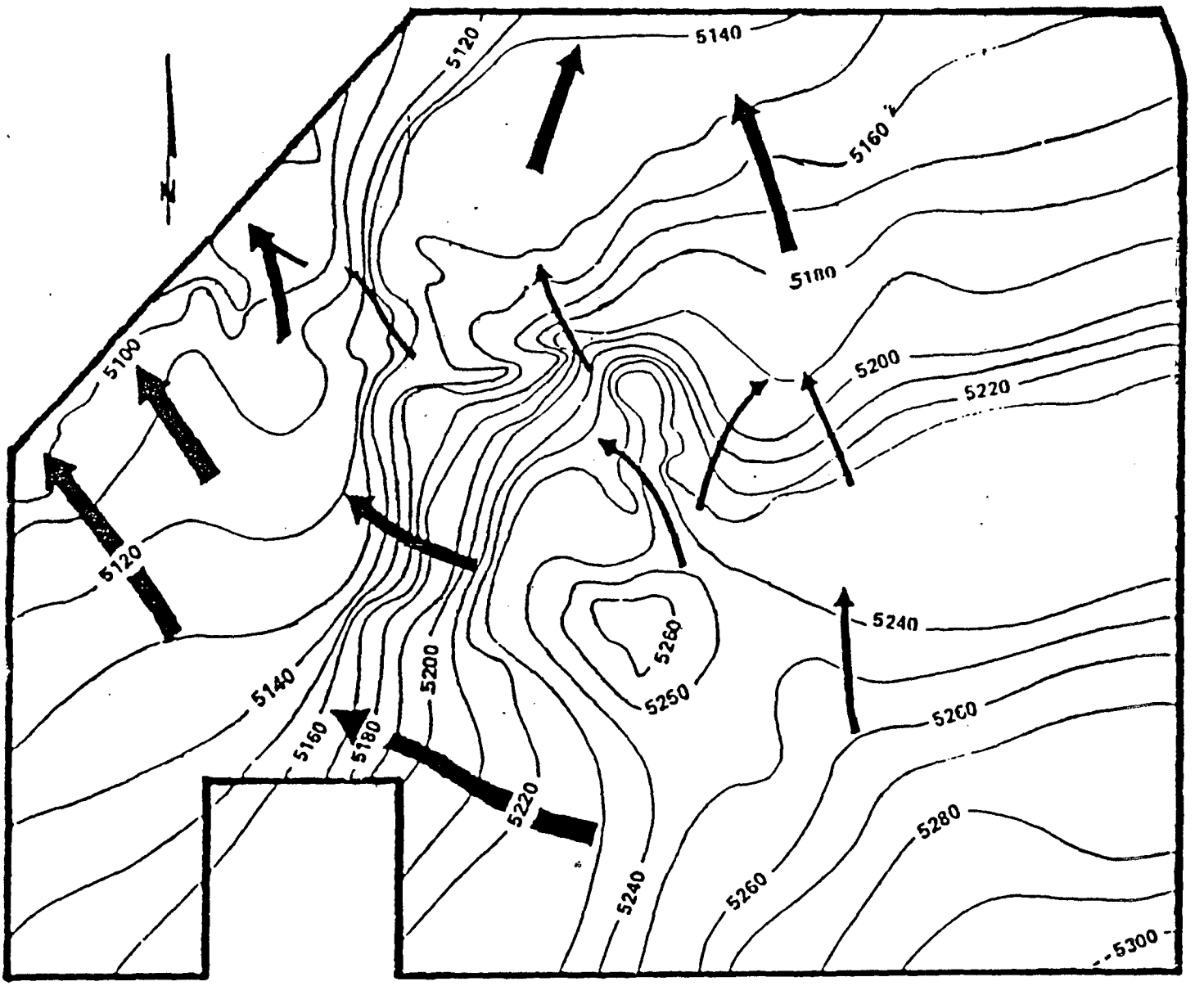


Figure 3. Generalized Alluvial Groundwater Flow Across RMA
Source: (Rocky Mountain Arsenal Contamination Control Program Management Team, 1983)

Offsite groundwater contamination was first discovered in the mid 1950's when minor crop damage was observed on land north of the installation. This discovery of contaminants led to the construction of 93 acre asphalt lined surface impoundment known as Basin F.

In the mid 1970's two organic compounds were identified in groundwater off the Arsenal. Subsequently the Army established a contamination control program to systematically investigate and remediate the contamination problems. One significant action under this program was the start of construction in late 1977 on a pilot groundwater contaminant/treatment system at the north boundary of RMA. The success of the pilot system led to the expansion of the system which was completed in 1982.

On 9 December 1983, the Department of Justice (DOJ) on behalf of the Department of the Army (DA) filed a $1.8 Billion lawsuit against Shell Oil Company (lease of Arsenal facilities) for reimbursement of environmental response costs and for damages of natural resources at RMA. The lawsuit was filed under the provisions of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA). The State of Colorado on behalf of the Colorado Department of Health has also sued Shell Oil Company and the Army for environmental damages both on and off RMA.

In October 1984, the Department of the Army commenced its Comprehensive Remedial Investigation/Feasibility Study (RI/FS) with respect to onpost and offpost contamination associated with RMA.

The Program Manager for Rocky Mountain Arsenal Contamination Cleanup (PMRMA) was formed in July 1985 to centrally manage and conduct the environmental program at RMA and is responsible for:

a. Conducting an RI/FS program consistent with CERCLA and SARA legislation to support the Army in the previously mentioned lawsuits,

b. Implementing the eventual cleanup which will be specified in a Record of Decision (ROD), the end product of the RI/FS.

In 1987, a significant delay was acknowledged in completing the RI/FS process and issuing the ROD for the final remediation of RMA contamination. The Army, Shell Oil Company, EPA Region VIII, and the State of Colorado recognized the need for initiating response actions during the interim period to mitigate the release or threat of release of hazardous substances, pollutants or contaminants on or from the Arsenal. A process was drafted for the planning and implementation of interim response actions (IRA) at and adjacent to the Arsenal and was reported on June 5, 1987 to the U.S. District Court for the District of Colorado. These IRA's encompass any action determined to be necessary for implementation prior to the final remediation of the Arsenal. The interim response action process includes an assessment of alternative technologies, followed by a decision document supported by a publicly available record. A consensus list, provided below, was developed by the parties for thirteen interim response actions that are considered necessary and appropriate.

- Ground Water Intercept and Treatment System(s) North of RMA;
- North Boundary System--Recharge Trench Construction and Boundary System Evaluations and Improvements;
- Ground Water Intercept and Treatment System North of Basin F;
- Abandoned Well Closure;
- Ground Water Intercept and Treatment System in the Basin A Neck Area;

- o Basin F--Liquids, Sludges, and Soil Removal and Liquids Treatment;
- o Building 1727 Sump Liquid Remediation;
- o Hydrazine Facility Remediation;
- o Fugitive Dust Control;
- o Sanitary Sewer Remediation;
- o Asbestos Removal
- o Other "Hot Spot" Contamination Source Remediation; and
- o Pretreatment of CERCLA Liquid Wastes.

The IRA's are "removal" actions as provided in the CERCLA Section 101(23), 42 U.S.C. Section 9601(23), and are to be carried out in accordance with CERCLA Section 104, 42 U.S.C. Section 9604. The IRA's themselves are to be, to the maximum extent practicable, consistent with and contribute to the efficient performance of the Final Response Actions for the Onpost and Offpost Operable Units at RMA. If an IRA will not fully address the threat posed by a release and a further response is required, the IRA will be transitioned into the Final Response Actions. The IRAs are governed by a process set forth in a proposed Consent Decree, and will generally proceed in the following manner:

- o Army's Initial Evaluation of IRA;
- o Army's Preparation of Draft Applicable or Relevant and Appropriate Regulation (ARAR) Selection Document;
- o Army's Preparation of Draft IRA Assessment;
- o Army's Issuance of Draft IRA Assessment & ARARs to the EPA, Shell Oil Company, and the State;
- o Comment Period on Draft IRA Assessment/ARARs by the EPA, Shell Oil Company, and the State;

- o Army's Issuance of Proposed IRA Decision Document;
- o 30-Day Public Comment Period on Proposed IRA Decision Document;
- o Army's Issuance of Draft Final IRA Decision Document;
- o Dispute Resolution May Be Invoked within 20 days of Issuance of Draft Final IRA Decision Document;
- o Army's Issuance of Final IRA Decision Document;
- o Within 30 days of Issuance of Final IRA Decision Document, Judicial Review May Be Sought;
- o Performance by Lead Party (Shell or Army) of Design Work Specified in IRA Decision Document;
- o Issuance by Lead Party of IRA Implementation Document, including IRA Deadlines; and
- o Implementation by Lead Party of IRA.

The basic IRA process is shown diagrammatically in Figure 4. The purpose of this process is twofold; (1) to ensure the development and implementation of a technically sound IRA as quickly as possible; and (2) to provide an opportunity for meaningful input from the public as well as the other involved parties.

The following paragraphs briefly described each of the IRA's as they currently stand.

Groundwater Intercept and Treatment System North of RMA

This IRA consists of the assessment and, as necessary, the selection, and implementation of one or more groundwater intercept and treatment systems north of RMA. The objective is to eliminate much of the potential for any future exposure from contaminated groundwater plumes and mitigate groundwater contaminant migration north of RMA. Contaminants of concern include organic (e.g.,

Interim Response Action Process

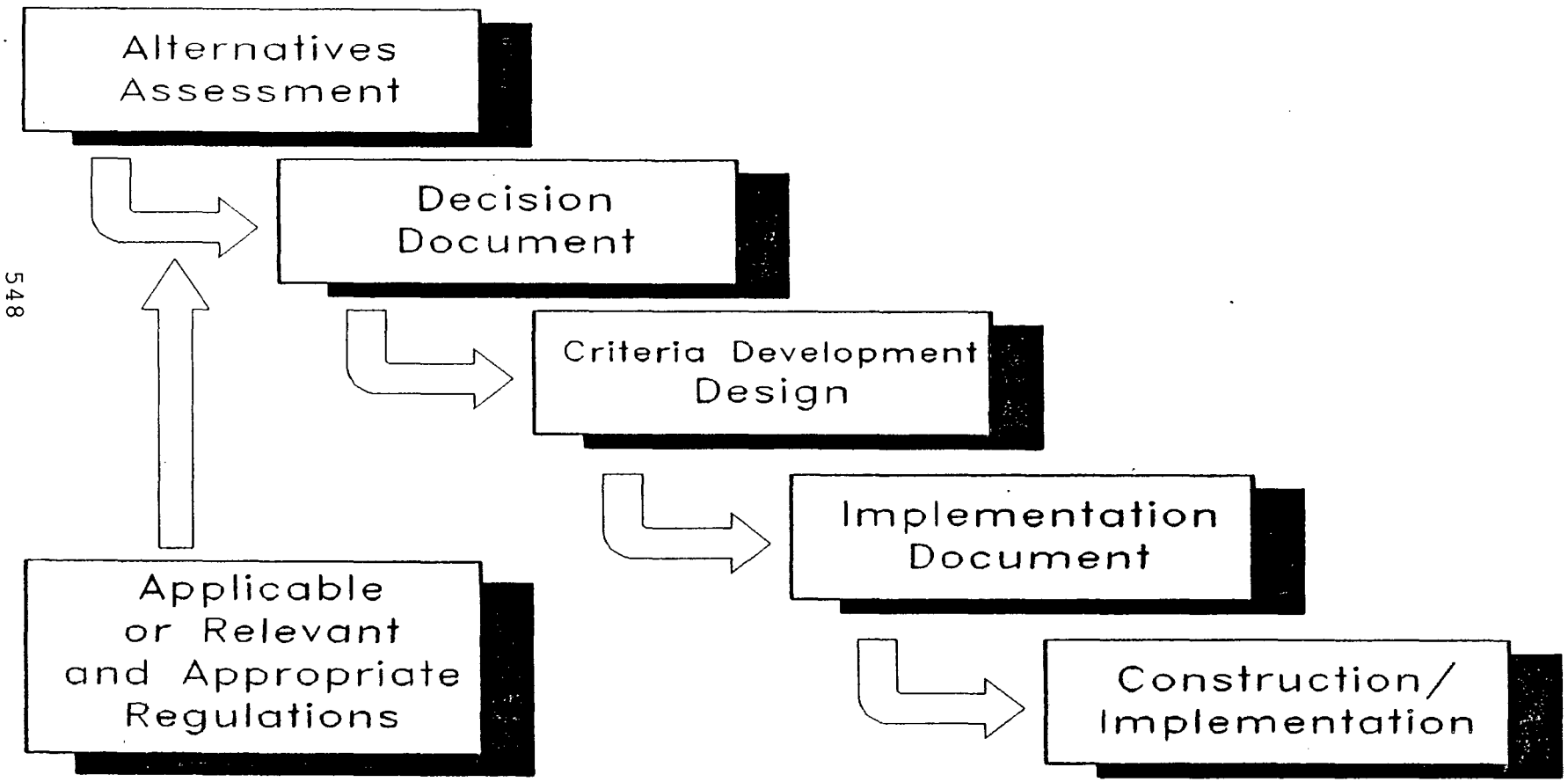


FIGURE 4

Interim Response Action Process

Trichloroethylene (TCE), benzene, aldrin, and endrin) as well as some inorganic (e.g., cadmium, chromium, and fluoride) compounds. Preliminary concepts include a system for a single pathway north of the RMA boundary consisting of a pump and treat system using activated carbon, with the possible addition of air stripping, for organics, and ion exchange for inorganics. The final alternative will not be known until the assessment phase is completed in December 1988.

Improvement of the North Boundary System

This IRA involves the improvement of the North Boundary Containment/Treatment System by the construction of groundwater recharge trenches and the assessment, selection and implementation of any other system improvements to the North Boundary System. To prevent any further flow of contaminated groundwater off the north boundary of the Arsenal, construction on a pilot containment/treatment system 250 feet south of the northernmost Arsenal boundary was started in 1977. By 1982 an expanded system was completed. The system consists of (1) a 6,470 foot long, 3 foot wide, bentonite slurry wall with an average depth of 30 feet; (2) Fifty-four withdrawal wells and 38 reinjection wells; and (3) a carbon adsorption water treatment plant. A previous Army study recommended the construction of recharge trenches to correct a hydraulic imbalance along the western half of the system. The first phase of this IRA involved the construction of ten gravel filled recharge trenches, approximately 160 feet long X 12-20 feet deep, and 3 feet wide, along the downgradient side of the slurry wall. Construction of the trenches was completed in October 1988 and operation of the trenches will be evaluated and factored into the second phase of improvements. The assessment for other system improvements is ongoing and will identify any other potential actions in the December 1988 timeframe.

Groundwater Intercept and Treatment System North of Basin F

This IRA consists of the assessment and selection of a groundwater intercept and treatment system north of Basin F and the implementation of such a system, as necessary. The purpose of the IRA is to initiate capture, as soon as possible, of the contaminated alluvial (upper) aquifer waters suspected to be emanating from below Basin F and at the same time, collect operational data that will aid in the selection and design of a final response action. The current concept is for a hydrogeologic system consisting of approximately 8 to 10 extraction wells spaced at approximately 100 foot intervals with recharge wells mirroring the extraction wells approximately 200 feet downgradient. Treatment for the organic contaminants of concern will be carbon adsorption. The addition of air stripping will be evaluated during the preliminary design. No inorganic treatment is being considered initially, based on water quality data, other than pretreatment to prevent precipitation of calcium and magnesium. The final design may vary based on any additional information collected during design activities.

Closure of Abandoned Wells on the Arsenal

This IRA consists of identifying, locating, examining, and properly closing old or unused wells on RMA to prevent the migration or potential migration of contamination through them. Prior to the construction of RMA in 1942, as many as 250 water wells for agricultural and residential use were constructed on what is now RMA. In addition, since RMA was established, hundreds of monitoring wells have been installed on the Arsenal. Approximately 150 to 200 of these wells have been determined as no longer usable. A plan was developed to prioritize the closure of wells based on such criteria as location in known groundwater contamination plumes and depth or penetration of two or more aquifers.

Additionally, generic approaches to closure of different types of wells (e.g., large diameter dug wells vs. typical monitoring wells) were developed. Closure actions for approximately 400 wells were initiated in April 1988 and are scheduled to continue through February 1990.

Basin A-Neck Ground Water Intercept and Treatment System

The purpose of this IRA is to prevent the spread of contaminants now migrating via the alluvial groundwater northwest of Basin A, and at the same time, collect operational data that will aid in the selection and design of a final response action. Alluvial groundwater below Basin A flows primarily to the northwest through a narrow alluvial valley located between two bedrock highs. The alluvial valley is known as the Basin A Neck. Extraction, treatment, and recharge technologies for Basin A Neck system have been reviewed for two locations based on technical feasibility, time to implement, and cost in order to select the most appropriate alternative to meet the objectives of the IRA. The current concept is for a hydrageologic system located at the narrowest portion of the Basin A Neck area. Extraction and recharge methods include wells or subsurface drains (The specific method will be finalized during the forthcoming design phase). Treatment alternatives focused on organic contaminants of concern. (e.g., chloroform, chlorophenylmethyl sulfone, dithiane, TCE) with mean projected influent values less than one part per million. Treatment for organics will be by carbon adsorption with the possible addition of air stripping. No treatment of inorganics is being considered initially, based on existing water quality data, other than possible pretreatment to prevent precipitation of hardness related compounds. The final design may vary based on any additional information collected during design activities.

Basin F Liquids, Sludges, and Soils Removal and Basin F Liquids Treatment

The Basin F Liquids, Sludges and Soil Removal consists of the remediation of contaminated liquids, sludges, and soils from and under Basin F, a 93 acre surface impoundment that was first in 1956 to provide environmentally safe solar evaporation disposal of contaminated liquid wastes from Army and lessee chemical manufacturing operations at RMA. The objective of the IRA is to abate any potential for infiltration of contaminants to the ground water, preclude potential for volatile emissions, and eliminate any potential impact of Basin F on wildlife from liquids which remained in the basin after termination of Basin F as an active facility in 1982.

The project consists of; (1) transferring approximately 8 million gallons of liquids to storage facilities; (2) construction of a 600,000 cubic yard temporary storage pile within a 10 acre area of the basin; and (3) grading, capping, and revegetating, the remaining basin area. To date, the liquids have been removed and are stored in a combination of tanks and double lined surface impoundment. Waste pile material is being stabilized in preparation for placement into the waste pile configuration. The double lined waste pile bottom with leachate detection and collection system has already been finished. Completion of this action is scheduled for summer of 1989.

Building 1727 Sump Liquid Remediation

This action consists of remediating contaminated liquid in what is known as the Building 1727 Sump and to control any remaining threat of releases. The 1727 Sump, with a capacity of 80,000 gallons, was designed to handle the liquid waste (e.g., floor wash-downs, spills, neutralization activities, and storm water run-off) generated with the North Plants area (Chemical weapons production and

demilitarization) of RMA. Even though the North Plants operations ceased several years ago, water has continued to collect in the sump, most likely from water line leakage, possible groundwater infiltration within the North Plants area, and stormwater runoff. The contaminants of concern are arsenic, fluoride, and the organic compound, Isopropylmethylphosphonate (IMPA). The selected IRA alternative consists of treating existing wastewaters with activated alumina to remove the arsenic and fluoride, followed by granular activate carbon to remove the IMPA. The standing liquid has been removed and treated and several feet of sediment in the bottom of the sump (thought to be a major source of contaminants) was removed. The sump will be cleaned and inspected verify its integrity, and any water that continues to collect in the future will be sampled, analyzed and treated by the existing wastewater treatment system before being discharged to the RMA sanitary sewer. Since the sump still continues to provide a central collection point now and possibly in the future during final remediation, other more permanent solutions were considered more appropriate for actions taken in concert with the final remedial actions at RMA.

Hydrazine Blending and Storage Facility Remediation

The objective of this IRA is to mitigate any threat of release of wastewater stored at the HBSF and remediate the aboveground structures. The HBSF which is owned by the Air Force and was operated by the Arsenal from 1962 to 1982 was used as a depot to receive, blend, store and distribute Hydrazine fuels. Currently, approximately 270,000 gallons of wastewater resulting from the decontamination of tanks and lines after the last of the Hydrazine was removed is being stored at the facility. Contaminants of concern include Hydrazine, monomethyl Hydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), and n-nitrosodimethylamine (NDMA), a

suspected carcinogen, methylene chloride, and chloroform, all in the low parts per billion range. A thorough alternatives assessment identified a UV/oxidation treatment approach for the wastewater followed by discharge to the Arsenal sanitary sewer system. In addition, all above ground structures will be dismantled and removed to an approved off-site disposal facility. Test runs for wastewater treatment are scheduled to begin in the summer of 1989.

Fugitive Dust Control

The objective of the IRA is to mitigate, as expeditiously as possible, any threat of the release of windblown contaminated dust from RMA. The primary sources of contaminated windblown dust are the unvegetated areas located in Section 36, a one square mile area at the center of the Arsenal, where the unlined Basin A is located. A natural, humate organic binder dust suppressant that had been previously used at RMA was selected for application. The dust suppressant was applied in three phases, starting with the drier, more accessible areas of Basin A in the February 1988 timeframe and finishing in August 1988 when the final candidate areas had reached a trafficable stage. Approximately 140 acres were covered at an application rate of 1,200 gallons of suppressant per acre. The rated effective life of the undisturbed suppressant is approximately five years. The treated areas will be routinely inspected during the life expectancy of the material and reapplication will be performed as necessary. Any additional candidate areas will be treated in a similar manner as they are identified.

Sanitary Sewer Remediation

This IRA involves eliminating the RMA sanitary sewer as a potential conduit for contaminant flow by assessing and identifying candidate segments of the sewer system for remediation. Portions of the RMA sanitary sewer system, especially

those sections which may be located below the ground water table, may be subject to infiltration of contaminants, and in turn allow the contaminants to flow through and exfiltrate at other areas of the system. Once the candidate sections are identified, the type of remediation (e.g., removal, plugging, etc.) will be coordinated with the Arsenal operations to ensure that the IRA is consistent with long range plans for sewer service to activities at the Arsenal.

Asbestos Removal

The IRA for asbestos removal focuses on the immediate remediation of friable asbestos where any potential for human exposure exists. Through the information from an active Army Asbestos Abatement program at the Arsenal and a comprehensive Buildings Remedial Investigation study, new or previously unidentified candidate locations for the remediation of friable asbestos were selected for confirmatory testing. The confirmatory testing consists of visual inspection, bulk analysis, and air monitoring in and around selected buildings. This assessment will screen, identify, confirm the final locations for friable asbestos remediation, which will occur promptly following the assessment determinations. Thirty two buildings and associated structures are included in the current asbestos IRA program.

Remediation of Other Contamination Sources

This IRA consists of the assessment, selection, and implementation, as necessary, of remedial actions at selected areas where limited existing information suggests the possibility that there may be active sources or "hot spots" for continuing groundwater contamination. The objective of the IRA is to mitigate any releases or threat of releases from these "hot spots" sources of contamination. Initially five areas were identified for consideration under this action: (1) Disposal trenches for numerous items, as identified through

historical records (e.g., drums, military hardware, asbestos, etc.) located within approximately a 107 acre area of Section 36; (2) Lime settling pits used to precipitate arsenic from production liquid wastes, also located in Section 36; (3) Three settling ponds measuring 75 ft. x 100 ft. x 5 ft. which may be contaminated with inorganic forms of arsenic and mercury; (4) A TCE spill in the RMA motor pool area; and (5) A dibromochloropropane spill the RMA Railroad holding yard. Since the assessment is scheduled to start in October 1988 the nature and extent of the response actions have not yet been determined. The baseline concept for confirmed, discrete "hot spots" would be removal and placement of such material in a properly constructed temporary storage area or areas at RMA until the final remedial actions are selected in the Record of Decision. This IRA may be expanded to add other source areas as warranted.

Pretreatment of CERCLA Liquid Waste

The objective of this IRA is to develop and implement a program to ensure the proper treatment of all wastewater resulting from CERCLA response actions at RMA. The wastewater streams include those from the ongoing RI/FS activities, IRA activities, and RMA activities in direct support of the CERCLA response actions. Examples of wastewater sources are monitoring well purge water, decontamination facilities, pump test water, onsite laboratory facilities, IRA treatment facilities, and any future pilot test facilities. The assessment, which is scheduled to start in October 1988, will (1) evaluate requirements related to wastewater quantity and quality resulting from existing and planned CERCLA activities; (2) conduct laboratory and field testing of relevant treatment technologies; and (3) investigate the additional requirements for continued use of an existing treatment system consisting of granular activated carbon and air stripping and the possibility of additional or satellite facilities.

CONCLUSION

The RMA IRA Program and the current list of thirteen IRAs represent a concerted effort toward the eventual cleanup of the Arsenal. Since the inception of the IRA Program in mid 1987, one action has been completed, four projects are ongoing, four are in the decision document stage, and four are in the assessment phase. The program includes actions that are, without a doubt, beneficial, but just as important is the establishment of a process which allows for speed in implementation while also affording the other organizations (i.e., EPA, Shell, and the State) and the public an opportunity for meaningful input.

KEY WORD INDEX

INTERIM RESPONSE ACTIONS

REMEDIAL ACTIONS

INTERIM ACTIONS

REMEDIATION

CLEANUP

MOVAL ACTIONS

Hot Gas Decontamination of Explosives-Contaminated Equipment

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INTRODUCTION

The manufacture, handling, and loading of explosives at Army industrial facilities have resulted in the contamination of process equipment, sewer systems, and buildings. Because of this residual contamination, many process items cannot be reused or be disposed of as scrap. Contaminated sewer lines are also a disposal problem after they are excavated.

Previous pilot studies[1] have shown that decontamination of structural components is possible using a heated gas to thermally decompose or volatilize explosives with subsequent incineration in an afterburner.

BACKGROUND

A pilot study will be conducted to evaluate the feasibility of hot gas decontamination of explosives-contaminated process equipment. The pilot test will be conducted at the Hawthorne Army Ammunition Plant (HWAAP) in Hawthorne, Nevada. The pilot test is scheduled to be conducted during the period from 3 January 1989 through 28 March 1989.

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[1]Arthur D. Little, Inc., Pilot Plant Testing of Caustic Spray/ Hot Gas Building Decontamination Process. Prepared for USATHAMA (Task Order Number 5). USATHAMA Reference AMXTH-TE-CR-87112. August 1987.

OBJECTIVES OF THE PILOT TEST

The objectives of the pilot test are to evaluate the hot treatment process to determine:

- The effectiveness of the treatment on various items of process equipment and process equipment materials.
- The effectiveness of the treatment on vitrified clay pipe.
- The effects, if any, that the treatment has on the reuse of process equipment.
- The time-temperature dependencies for the decontamination of explosives on metal and clay surfaces.
- The operation parameters for future production decontamination systems.

CRITERIA FOR A SUCCESSFUL DEMONSTRATION

The pilot demonstration will be considered successful if the analytical results from some of the test runs indicate that the explosive compounds shown in Table 1 are not present above detection limits (as specified in the appropriate analytical method) on the surface or within the internals of the equipment being evaluated.

It is preferable that the operating conditions that result in a successful analytical demonstration (i.e., explosives concentration below detection limits) do not destroy the structural or operable components of the equipment to be evaluated. Treated equipment will be visually inspected for cracks, warping, blisters, etc. However, the primary goal of the pilot study is to determine operating conditions that effectively decontaminate the equipment for safe disposal, not for potential reuse.

PROCESS DESCRIPTION

The process equipment will be supplied by the government and consists of the following major items:

- Air preheater.
- Flash chamber.
- Afterburner.
- Control system.

TABLE 1

EXPLOSIVES TO BE EVALUATED DURING THE PILOT STUDY

- 2,4,6-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-Dinitrobenzene (DNB)
- 1,3,5-Trinitrobenzene (TNB)
- 2,4-Dinitrotoluene (2,4-DNT)
- 2,6-Dinitrotoluene (2,6-DNT)
- 2,4,6-Trinitrophenylmethylnitramine (tetryl)
- Smokeless powder (Nitrocellulose/Nitroglycerin)
- Ammonium picrate (Yellow D)

A process flow diagram of the process equipment is shown in Figure 1. Explosives-contaminated test equipment is placed inside the flash chamber and the chamber is securely closed. Ambient air is blown into the air preheater by means of the combustion air blower. The ambient air is heated to the appropriate target temperature in the air preheater. The hot gas is ducted into the flash chamber and distributed through gas diffusers. The hot gas thermally decomposes or volatilizes the explosives from the test equipment. The contaminated vapor stream is withdrawn from the flash chamber by way of the vent fan. Gases are directed to the afterburner, which incinerates the contaminants. Treated gases are then discharged to the atmosphere. The treated equipment is removed from the flash chamber and is sampled.

The air preheater, afterburner, and control system were used previously in a pilot-scale demonstration of hot gas decontamination of process buildings at Cornhusker Army Ammunition Plan (CAAP). These items were transported from CAAP to HWAAP by the government.

The flash chamber (Building 117-15) is an existing facility at HWAAP. The facility was originally designed for flash powder decontamination of explosives-contaminated equipment.

EQUIPMENT TO BE TESTED

To demonstrate the technology, the following types and quantities of process equipment slated for disposal will be used in observation equipment:

- Power boxes (12).
- Steam-heated risers (12).
- Support racks for shells (12).
- Vitrified clay pipe sections (12).
- Ship mines (8) (contaminated with smokeless powder).
- Steel pipe (2).
- Steam-heated discharge valves (2).
- Aluminum pipe (2).
- Motors with gear reducers (2).

Process equipment will be prescreened for existing levels of explosives. If not present, spiking with known concentrations of TNT or ammonium picrate will be conducted to verify removal efficiency.

OPERATING CONDITIONS

The primary goal of the pilot study is to evaluate the time/temperature relationships for decontamination of TNT. However, a limited number of test runs will also be conducted to evaluate decontamination of ammonium picrate and the effect of varying the heat-up rate. A maximum of 12 test runs will be conducted.

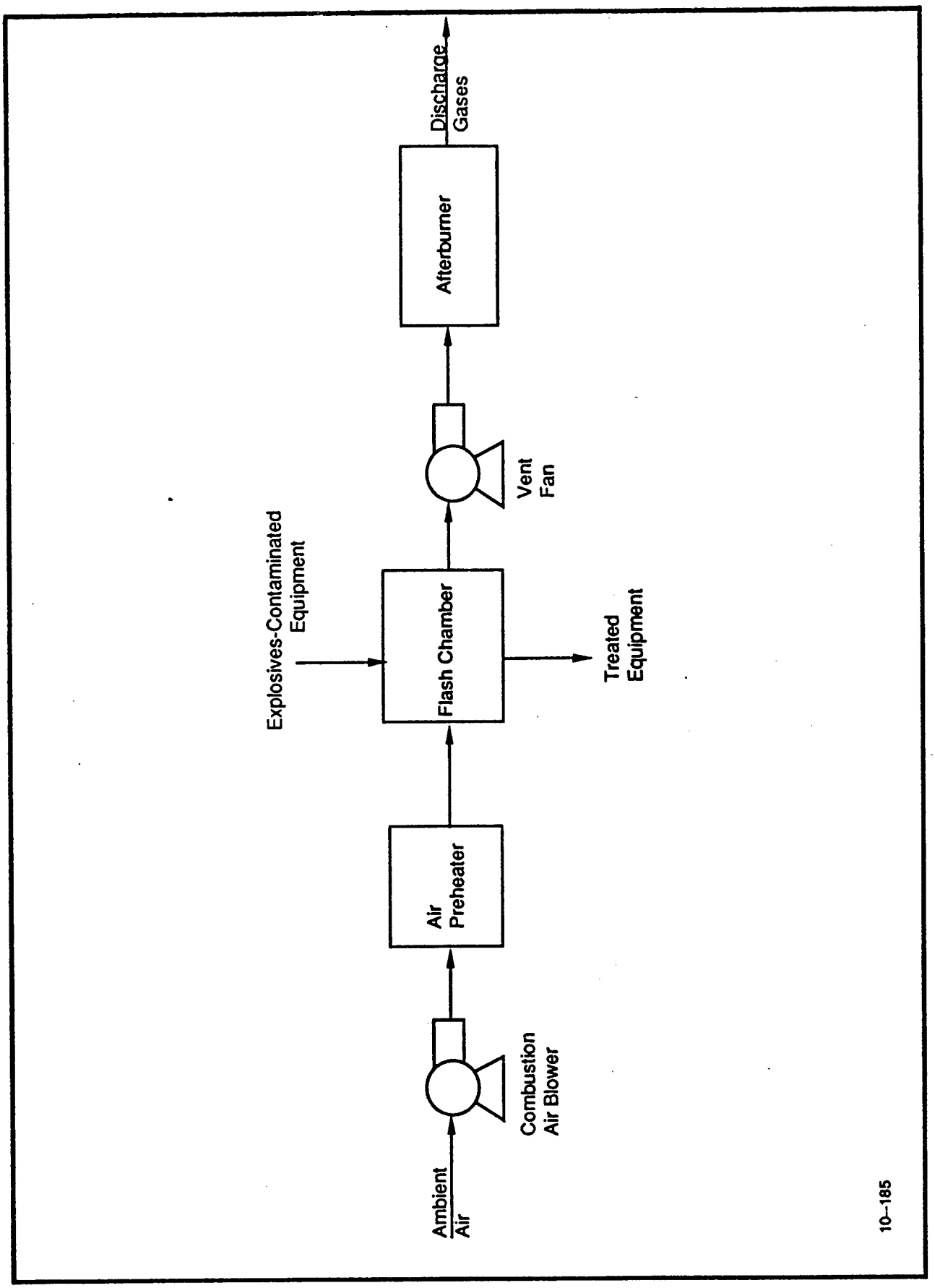


Figure 1 Process flow diagram for hot gas decontamination of explosives-contaminated equipment.

Nine test runs will be conducted to evaluate the time/temperature relationships for decontamination of TNT. A three-by-three matrix has been developed and is shown in Table 2. Three temperatures (400°F, 500°F and 600°F) and three residence times (24, 36, and 48 hours) will be evaluated at a heat-up rate of 50°F/hour. Operating times, temperatures, and heat-up rates were selected based on review of the final report for the pilot study of hot gas decontamination of process buildings.

A maximum of two test runs will be conducted to evaluate the feasibility of hot gas decontamination for equipment contaminated with ammonium picrate. In addition, two test runs will be conducted to evaluate the effects associated with a heat-up rate of 100°F per hour. The heat-up rate is potentially a problem with reuse of nonmetallic materials, such as vitrified pipe and refractory materials.

STACK TESTING

To demonstrate the destruction and removal efficiency (DRE) of the afterburner, stack testing will be conducted at the afterburner inlet and outlet. Stack tests will be conducted during the first three test runs for explosives (those listed on Table 1) and smokeless powder. Operating conditions during these test runs are expected to represent the entire range of conditions to be evaluated during the pilot test. It is anticipated that the operating conditions and contaminants of concern for these test runs will be as follows:

- 600°F/48 hours - explosives/smokeless powder.
- 400°F/24 hours - explosives/smokeless powder.
- 500°F/36 hours - explosives/smokeless powder.

DATA ANALYSIS

After the pilot test is conducted, a written report will be completed. The report will include test data results and evaluation of equipment performance. The efficiency of the afterburner will be evaluated based on the demonstrated destruction of contaminants. The report will address the effects of varying temperatures and residence time on TNT decontamination, the feasibility of the process on ammonium picrate, and the effects of varying heat-up rates on equipment. A recommendation will be made regarding optimum operating parameters.

TABLE 2

BASIC TEST MATRIX FOR HOT GAS DECONTAMINATION OF TNT-CONTAMINATED EQUIPMENT

Test Duration	Flash Chamber Temperature 400°F	500°F	600°F
24 hours			
36 hours			
48 hours			

ORGANOTIN ANTIFOULING HULL PAINTS AND THE U.S. NAVY
A HISTORICAL PERSPECTIVE

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ABSTRACT

An interim finding of no significant impact for the U.S. Navy's fleetwide implementation of tributyltin (TBT) containing organotin antifouling hull paints appeared in the U.S. Federal Register of 21 June 1985. This finding was based on an environmental assessment and committed the Navy to (1) slow implementation of the painting program, extending over a 10-year period; (2) use of paints with release rates not greater than 0.1 μg TBT/cm^2/day; (3) environmental monitoring at major Navy harbors, ensuring a target average concentration of 50 ng TBT/L or less; and (4) a commitment to update the environmental assessment in 1988. The paints intended for use by the Navy were registered by the U.S. Environmental Protection Agency and were used widely by recreational and commercial vessels. The public announcement by the Navy of its intended action resulted in a nearly unanimous negative response from Federal, state, and private agencies.

This paper describes the U.S. Navy's research effort, which demonstrated the unique operational and economic benefits provided by these paints for its combat ships; the consequences of preparing the environmental assessment for Fleetwide implementation; the importance and complexity of TBT paint release rates; the response of the environmental community to potential risks of TBT use; concerns and action taken by the U.S. Congress and the U.S. Environmental Protection Agency; the role of water column monitoring and laboratory bioassays; the enactment of regulatory legislation by states on both coasts; and the Navy's leadership in establishing a strategy for the environmental management of TBT.

INTRODUCTION

The U.S. Navy's military specification copper-based antifouling paints (Formulas 121 and 129) were developed when our ships were on a 2-year cycle of drydocking and repainting. However, the typical operating cycles have been lengthened to 5 years for some ships and 7 years for others. Even longer cycles may be imposed in the future. Longer operating cycles increase availability and therefore provide for more ship per capital investment. The currently used copper-based antifouling paints lose their effectiveness after 14 months in most waters and after as few as 7 months in tropical waters as shown in Figure 1, which is based on data from 43 Navy ships.[1] As a result, Navy ships do not have effective antifouling protection throughout the 5- to 7-year cycles between overhauls and repainting. Figure 1 also shows why recreational craft using copper paints require repainting every year and perhaps more often in warmer waters.

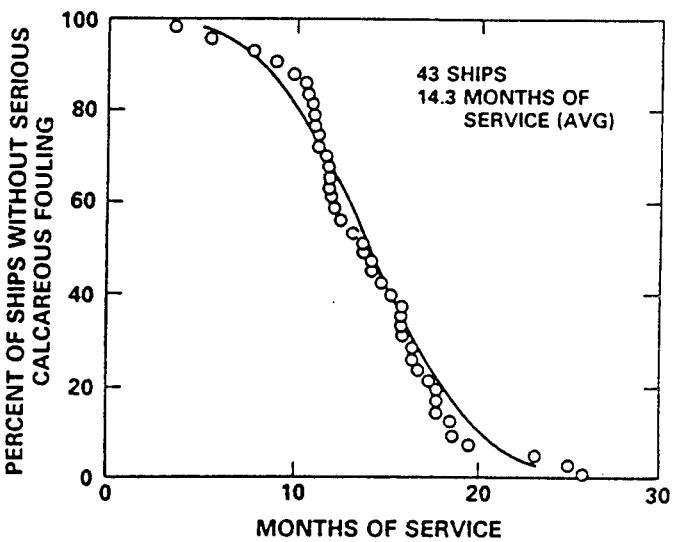


Figure 1. Effective Life of Standard Navy Copper-Based Antifouling Paint on Navy Surface Ships in the Pacific Fleet

Antifouling hull paints play a critical role in Fleet operational readiness. The drag and secondary effects on ship propulsion equipment caused by serious infestations of fouling organisms, such as barnacles and tubeworms, on ship hulls and cooling water intakes seriously degrade performance by:

- Reducing maximum attainable speed by as much as 10 knots
- Increasing total underway fuel consumption up to 16%
- Increasing underway refueling frequency

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- Decreasing maximum cruising ranges
- Increasing self-generated sonar noise and degrading ability to avoid detection and to detect targets
- Increasing maintenance as a result of higher duty of the propulsion system and more frequent dockings and hull cleaning.[2]

Improvements in hull design over the last 80 years have permitted Navy ships to minimize hydrodynamic drag and thereby achieve maximum speed and range. Retaining these benefits from improved hull design depends almost entirely on a clean, smooth hull assured by antifouling paints. Marine fouling growths cause large increases in hydrodynamic drag, degrading performance and increasing fuel consumption. The rise in the cost of fossil fuels over the last 15 years and the uncertainty of continued availability have raised this issue to a new level of importance. Most U.S. Navy ships now spend at least 60% of their time in port and only 40% actively steaming. Since fouling organisms attach themselves to hull surfaces mostly while ships are in port, this has increased exposure to biological accretion. Many U.S. Navy ships operate in tropical waters, where the increased vigor of and longer growing season for marine fouling organisms make even greater demands on antifouling hull paints.

Consequently, the U.S. Navy has been engaged in the formulation and research of antifouling paints, including organotin paints, for many years. We have been formulating organotin paints since 1970, and we have been conducting research into the effects of tributyltin paints since 1976. From the beginning, the Navy has been concerned with the effect these paints may have on the environment, and has taken steps to minimize such effects.

Extensive ship trials have demonstrated that TBT antifouling paints provide fouling-free hull protection for the full 5 to 7 years. Power trials on one ship showed almost no power increase with time. This means that the ship's hull is in almost the same smooth conditions as when freshly painted. Only TBT antifouling hull paints achieve that kind of performance. The U.S. Navy needs the extended service life that TBT paints provide.

In addition to significant operational benefits, the economic fuel savings from the Navy's use of TBT paints would be substantial. The fuel savings resulting from 100% implementation would be approximately 1.8 million barrels per year (at 1984 fuel consumption rates). At the Navy's 1984 delivered fuel price of $60.42 per barrel, this fuel saving equates to a cost avoidance of $110 million per year.[3]

ENVIRONMENTAL ASSESSMENT

Based on these demonstrated potential benefits, the U.S. Navy made the policy decision to begin fleetwide implementation. Before this could begin, however, we prepared an Environmental Assessment of the proposed action in compliance with the National Environmental Policy Act (NEPA) of 1969.[4]

For the preparation of the Environmental Assessment, we developed numerical models of several harbors to dynamically simulate the distribution and fate of TBT released from Navy hulls. A key parameter required for the exercise of such numerical models is the release rate of TBT from the antifouling paint surface. The U.S. Navy can determine precisely the wetted hull area of its ships. Therefore, the release rate times the wetted hull area per ship provides an exact TBT environmental loading rate at a specific berthing location. In anticipation of the importance of TBT release rates, the Navy had developed two measurement methods. A method for conducting measurements in the laboratory was developed at the David Taylor Naval Ship Research and Development Center;[5,6] the other, for conducting such measurements directly on the hull of a ship in the water was developed at the Naval Ocean Systems Center.[7] Both procedures represent flat plates in gently moving water, attempting to simulate ships at rest in a harbor. Both procedures show reasonable agreement. Measurements made on a number of commercially available, registered paints showed results that ranged over two orders of magnitude; that is, acceptable antifouling performance was seen in paints releasing TBT from 0.1 $\mu g/cm^2/day$ to greater than 10 $\mu g/cm^2/day$. The implication of this result is profound, because it means that paints which release 100 times more TBT to the environment than is necessary are in wide use. Furthermore, there is no evidence to show that release rates less than 0.1 $\mu g/cm^2/day$ do not provide adequate antifouling performance. In fact, release rates measured on the hull of a Navy ship, free of hard fouling after 4 1/2 years, showed an average rate significantly less than 0.1 $\mu g/cm^2/day$. This ship continues to be free of hard fouling after 6 years of exposure.

The exercise of the numerical models caused us to recognize that a release rate of 0.1 $\mu g/cm^2/day$ was necessary in order to prevent environmental harm in some harbors where Navy ships would be berthed. Most, but not all, commercially available TBT paints had substantially higher release rates, as previously stated.

Based on our preparation of the Environmental Assessment and over 10 years of research in the laboratory and field, we were convinced that our proposed action of gradual fleetwide implementation with Navy-specified TBT paints would not result in significant environmental harm. Accordingly, on 21 June 1985, the Navy issued an Interim Finding of No Significant Impact for the proposed fleetwide implementation.[8]

The measures the Navy took to ensure that the use of TBT paints would not cause significant environmental harm were:

- Using only those commercially available TBT paints that have the lowest release rate of TBT.
- Implementing TBT paints slowly, by painting no more than 10% of the Fleet annually nationwide until full implementation is achieved, requiring 10 years.
- Monitoring drydock TBT discharges and environmental conditions and effects at major homeports.
- Refining capabilities to predict environmental consequences of full Fleet implementation.
- Updating the Environmental Assessment in 1988 when the results of additional research studies, environmental monitoring, and initial implementation are available.
- Modifying or terminating TBT paint use, if experience shows that to be necessary to avoid significant adverse effects.

The Navy's decision to use only the lowest release rate TBT paints, which arose as a result of the NEPA process in preparing the Environmental Assessment, profoundly influenced the TBT paint industry. Several companies have and are continuing to make substantial efforts to lower the TBT release rates of their paints. In addition, the fact that commercial paints with acceptable performance have TBT release rates ranging over two orders of magnitude demonstrated that as much as 90% of the TBT currently released into the environment from these paints is unnecessary.

RESPONSE

In spite of the U.S. Navy's environmentally conservative approach, the release of the Environmental Assessment and the Interim Finding of No Significant Impact resulted in a nearly unanimous negative response from Federal, state, and private agencies concerned with environmental protection. Only the state of Hawaii found no fault with the Navy's plans. The response of the rest appeared to assume that the Navy's action would introduce a new, highly toxic and persistent substance representing an unknown, unquantified threat to estuaries in general and to economically significant marine organisms in particular. While the responses were made in good faith to a specific action proposed by the Navy, they seemed to ignore the following facts.

- TBT paints are legal, having been registered by the U.S. EPA under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and additionally registered in several states.
- TBT paints are widely used in the private sector on fishing fleets, commercial, and cruise ships; in addition, their use on recreational craft is extensive and growing.
- Restrictions to the use of TBT paints instituted in France and England were limited to small craft and did not apply to ocean-going vessels.
- Restrictions in France and England were primarily the result of TBT-painted recreational craft moored in close proximity to beds of the Pacific oyster, which is especially sensitive to TBT.

It is interesting to note that a study of vessel-related contamination of southern California harbors by copper and other metals including tin was published in 1979.[9] This study included data from harbor mussels collected in 1974 which contained up to 10 times natural levels of copper. In addition, the vessel-related materials, cadmium, chromium, lead, tin, zinc, and PCB were measured at levels 2 to 20 times above background in tissue specimens collected from areas of high vessel activity.[9] While the tin levels in mussel tissue were not measured as TBT at that time, it is likely that it was TBT. More importantly, this study showed that vessel-related contamination of harbors was a problem 10 years before the Navy considered fleet-wide use of TBT paints.

REACTION

A number of events ensued in reaction to the U.S. Navy's implementation plan:

- Water column TBT monitoring was begun by California, Virginia, Maryland, and the U.S. EPA.
- Marine scientists on both coasts made public statements expressing alarm.
- Media reaction to these public statements caused more media reaction, reflecting and magnifying public statements of alarm by marine scientists.
- The U.S. Congress, heeding the alarm expressed by marine scientists, included a statement in the 1986 Department of Defense Appropriations Act which prevented the Navy from painting any of its vessels with TBT paint.[10] Unfortunately, as a result, the Navy could not even paint its aluminum-hulled craft with TBT, a necessary and routine procedure for 20 years. Furthermore, all ocean-going vessels, including foreign navies and recreational craft in the U.S.A. continued to use these high performance hull coatings, while the U.S. Navy could not.

- The U.S. EPA initiated a Special Review of all pesticide products containing TBT as paint antifoulants, under authority of FIFRA.[11] This action was based on a Tributyltin Support Document,[12] which included large amounts of Navy-generated data.

- The U.S. EPA then issued a Data Call-In Notice to all registrants of TBT antifouling paints, requiring them to provide extensive data on their products.[13] This notice included a requirement to provide TBT release rate information on all registered paints.

With the entrance of the EPA, the concern about TBT paints raised by the Navy's intention to use them properly shifted to the widespread and growing use of these materials in the private sector. Of greatest initial interest was the determination of TBT release rates from the paint film.

TBT RELEASE RATES

In anticipation of the EPA's Data Call-In Notice requiring the measurement of TBT release rates, the industry, with over 300 registered products to be measured, found the Navy's procedures too costly. Accordingly, the American Society for Testing and Materials (ASTM) was asked to develop a less expensive procedure. ASTM Subcommittee D01.45, Marine Coatings, formed a special task group that consisted of representatives from industry, the U.S. Navy, the Canadian Navy, the U.S. EPA, and the National Bureau of Standards. After a number of meetings and extensive discussions, a proposed method was devised. It consists of a polycarbonate cylinder painted with the candidate paint. The cylinder rotates at 60 rpm in a baffled, cylindrical container of synthetic seawater. Samples of the seawater are analyzed periodically for tin content by solvent extraction and graphite furnace atomic absorption spectroscopy. This method is designed to provide a laboratory procedure to measure solvent-extractable TBT release rates which occur during a period of immersion under specified conditions of constant temperature, pH, and salinity. This method serves as a comparative guide for organotin release rates in service. Results obtained may not necessarily reflect actual TBT release rates which will occur in service, but they provide comparisons of the release rate characteristics of different antifouling formulations. After several revisions, the Chairman of ASTM Subcommittee D01.45 approved the use of Draft #6 of the proposed method by the EPA with the understanding that this draft is subject to revision prior to issuance of an official ASTM standard. This draft, with some amendments by the EPA, became part of the Data Call-In Notice to TBT paint registrants.[13]

Consternation arose among registrants, users, and regulators as preliminary results from the EPA release rate method became available, because there was a substantial difference in the results of paints measured by the EPA and Navy procedures. For example, two registered, commercially available, field-proven TBT paints for steel-hulled Navy ships gave Navy-measured release rates of 0.1 and 0.2 $\mu g/cm^2/day$; the same paints measured by the EPA method gave release rates of 1.9 and 4.0 $\mu g/cm^2/day$, respectively. Both coatings are ablative paints, providing for a self-smoothing of the hull surface as the ship moves through the water. It appears that these paints, designed to ablate when a ship is underway, released significantly more TBT on the surface of a 7-cm-diameter cylinder rotating at 60 rpm, the EPA method, than in the Navy's flat plate technique. For a nonablative paint such as one approved for use on Navy aluminum hull craft, the difference was not as large, being 1.5 by the Navy method and 1.8 $\mu g/cm^2/day$ for the EPA method. What added to the consternation was that pending state and Federal legislation designed to regulate the use of TBT paints was being based on Navy release rate information, while the largest data base, on the basis of which TBT paints would be regulated, was being accumulated by the EPA.

The U.S. Navy's approach to measuring TBT release rates was to apply such measurements to predicting the environmental fate of TBT, using numerical models. This raises the question of which procedure comes closest to measuring the release rate under actual environmental conditions. The EPA procedure contains a statement disclaiming that results reflect release rates occurring in service. Of the Navy procedures, the measurement made directly on the hull in water, though time-consuming and expensive, comes closest to reproducing conditions of paint age; water salinity, pH, and temperature; and the presence on the paint of a microbial biofilm or slime layer.

RELEASE RATES AND THE BIOFILM

Surfaces exposed to natural waters, even if they are releasing biocides to prevent macrofouling, become coated with a biofilm or slime layer. This layer consists of a complex community of bacteria, protozoa, diatoms, and other microalgae together with their cellular exudates.[14,15] This slime layer can increase ships' frictional resistance to motion by up to 10%.[16,17] Ablative TBT paints, which do not accumulate biofilms under dynamic conditions, become coated with slime under static conditions.[18,19] The role of the biofilm in modifying the release of TBT from painted surfaces was investigated at the Navy Biosciences Laboratory several years ago.[20] This study showed that microbial biofilms formed on painted panels releasing TBT accumulated high concentrations of the biocide. These slime layers were removed from the panels and centrifuged to separate solids from the liquid portion. The TBT content of the centrifugate was measured to be greater than 20 mg/L, which is considered to be above the solubility limit of TBT in seawater, while the biofilm interstitial water contained 1 mg/L, considered to be near the solubility limit. These concentrations of TBT, if biologically active, are four or more orders of magnitude above biocidal levels. In a recent investigation at the David Taylor Naval Ship Research and Development Center, biofilms were formed in the laboratory with either TBT-resistant bacteria or

algae on surfaces painted with a commercially available, controlled, low release rate TBT paint.[21] In both cases, significant short-term changes in the steady-state TBT release rate were observed. These investigations focus attention on the biofilm as a significant factor in understanding the mechanism of antifouling by TBT, and its influence on the release and biodegradation rate of TBT.

As a result of the TBT biofilm investigations conducted so far, the following hypothesis is proposed. The slime layer and its exudates accumulate TBT from controlled release paints. This layer behaves as a biological capacitor, concentrating TBT to several orders of magnitude above concentrations lethal to settling organisms and thereby either preventing their attachment or killing them shortly after attachment. The high concentration of TBT in the interstitial water may also decrease the rate of diffusion of TBT from the paint matrix by decreasing the concentration gradient in accordance with Fisk's First Law of Diffusion. If the foregoing hypothesis is valid, it has two practical consequences.

1. The wide range of TBT release rates as measured by laboratory procedures may not be as significant for environmental impact as previously considered, because the biofilm has the capacity to modify the diffusion of TBT through the paint matrix.

2. Paints having much lower release rates may be as effective as the currently available, field-proven low release rate paints with nominal rates of 0.1 $\mu g/cm^2$/day because the biofilm will accumulate biocidal concentrations of TBT.

A test of this hypothesis is underway at the National Bureau of Standards under Navy sponsorship. The NBS research will:

- Develop techniques to measure TBT concentrations in biofilms using epifluorescence microscopy with appropriate fluorogenic ligands and Fourier transform infrared spectroscopy.
- Measure the rate of TBT accumulation in biofilms.
- Determine the bioavailability of TBT in the biofilm.
- Determine a method to evaluate the potential effectiveness of very low TBT release rate paints.

The foregoing illustrates the complexity of determining the release of TBT from painted surfaces in natural waters; nevertheless, preliminary monitoring data from Navy harbors where TBT test ships are located indicate that observed TBT concentrations are lower than or approximately equal to the concentrations predicted by the numerical models, based on Navy measured release rates. This demonstrates that while release rates can be used to make predictions, it is environmental monitoring of the water column that provides key information concerning potential environmental consequences.

ENVIRONMENTAL MONITORING

Ultratrace analytical procedures to measure TBT and its degradation products in natural waters were not available until recently. An Interagency Workshop on Aquatic Sampling and Analysis for Organotin Compounds was held at the U.S. Naval Academy, Annapolis, MD, 3-5 June 1986.[22] It was clear from the workshop that a number of adequate analytical procedures to determine TBT and other organotin compounds in water had been developed. However, the number of samples that could be analyzed during an average 8-hour day ranged from 3 to 50. Therefore, the proper selection of a procedure for harbor and bioassay samples will affect laboratory costs significantly.

Two analytical procedures for ultratrace speciation of butyltin compounds in natural waters were developed under Navy sponsorship; one at the National Bureau of Standards,[23] and the other at the Naval Ocean Systems Center.[24] An interlaboratory comparison of both methods showed good agreement.[25] Under Navy sponsorship, the National Bureau of Standards has initiated a world-wide interlaboratory comparison of analytical methods for speciation of butyltin compounds in aqueous solution. Progress of this undertaking is being reported at the Oceans 87 Conference.

In preparation for fleetwide implementation of TBT paint, the Navy conducted baseline measurements in 15 U.S. harbors and estuaries.[26] This was the most extensive sampling and analysis effort conducted anywhere in the world. Results showed that the highest concentrations of TBT in water were consistently found in recreational craft marinas, small boat harbors, and adjacent to vessel repair facilities. Sites in open or well-flushed harbor areas often exhibited TBT concentrations less than 5 ng/L (parts per trillion) in water. Of 455 water samples analyzed for TBT content during the course of this baseline survey, 75% measured less than 5 ng/L. The presence of high concentrations of TBT in and near recreational craft marinas has been confirmed by other investigations.[27-29]

A more recent monitoring effort was conducted in northern Chesapeake Bay.[30] This effort found high TBT and dibutyltin concentrations in recreational craft marinas early in June when freshly painted boats were placed in the water. A sharp decline in TBT concentrations occurred during summer and early fall. In addition, TBT values declined two to three orders of magnitude when measured away from marina areas. This monitoring effort demonstrated the following:

- The presence of dibutyltin, the first degradation product of TBT;

- The sharp decline in TBT concentrations away from marina areas; and

- The overall decline of TBT values after the beginning of the boating season.

All of these factors indicate that regulation of the primary source of this biocide in marinas will probably result in its rapid disappearance from the water column of estuaries. Water column monitoring in estuaries previously measured is the best means to determine the effectiveness of regulatory implementation.

Measurement of TBT in the water does not provide information about TBT bioavailability; therefore, the measurement of high concentrations of TBT by itself does not constitute direct evidence of environmental harm. When combined with laboratory toxicity studies, however, high concentrations of TBT in marinas constitute persuasive circumstantial evidence for potential harm and therefore regulatory action.

BIOLOGICAL EFFECTS

Laboratory measurements of the toxic biological effects of TBT are being reported in an increasing number of scientific papers. Most papers have reported acute effects at TBT concentrations orders of magnitude above what is actually measured in the environment, with the exception of the very highest transient values found in some recreational craft marinas. This was partially due to an inability by most laboratories until very recently to measure TBT and distinguish it from its biodegraded products at concentrations less than 1000 ng/L; and the ability to obtain rapid, unquestionable results in terms of mortality and dramatic morphological effects. Toxicity papers presented at the Oceans 86 Conference reflected such unrealistically high values, but also presented results of effects at much lower concentrations. The lower concentrations used were 20 to 45 ng/L[31-34] and the higher ones were 300,000 ng/L and higher for effects on human erythrocytes.[35] Of increasing value and interest are chronic studies, which are more difficult to perform than acute studies, requiring substantially more investment of laboratory skills and time. A model example of such a study was performed by the Naval Ocean Systems Center using mysid shrimp.[33]

As the TBT bioassay data base grows in size, the question of its interpretation concerning ecological significance grows in importance. This issue was addressed by M.H. Salazar at the Oceans 86 Conference.[36] He cited a review by White and Champ[37] which drew the following conclusions about bioassays.

- They are not comparable among laboratories.

- They do not accurately simulate the natural environmnent.

- They are not good predictors of ecological consequences.

- Their use by regulators as a predictive tool is questionable.

For these reasons, Salazar pointed out, the interpretation of laboratory bioassay results and extrapolation from the laboratory to the field is subjective, even for well characterized contaminants. He concluded that the interpretation and environmental significance of organotin bioassays depends upon a complete understanding of bioavailability, and environmental impact cannot be predicted with the data available from organotin bioassays and environmental monitoring. Taking such conclusions seriously creates a problem, because almost the entire data base on TBT consists of monitoring and bioassay data. One step to resolve this problem is to conduct more site specific flow-through bioassays, such as the first one of its kind reported by R.S. Henderson at the Oceans 86 Conference.[34] Results of this study showed that no significant deleterious effects were evident on either the settlement or survival of fouling organisms, or the condition index of American oysters (Crassostrea virginica) in long-term exposures at 40 ng/L.

WATER QUALITY CRITERIA FOR TBT

What the rapidly growing TBT community has been awaiting is a TBT water quality criterion developed by the U.S. EPA under Section 304(a) of the Clean Water Act. In recent testimony before a U.S. Senate committee, it was announced that the EPA will issue a water quality advisory instead of a criterion while awaiting a significant amount of new data which may result from the TBT Special Review.[38] While the advisory is based on less data and therefore more uncertainty, it is intended to be used in the same manner as water quality criteria for the establishment of water quality standards. The testimony announced that criteria for saltwater are on the order of 240 ng/L for the Criterion Maximum Concentration (acute) and 30 ng/L for the Criterion Continuous Concentration (chronic).[38] It was also pointed out that additional chronic data will not be available for another 2 to 4 years.

LEGISLATION

Although the EPA is conducting a Special Review of TBT paints, it is clear that under the statutory requirements of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), implementation of regulatory action might not be forthcoming for several years.[38] Prior to regulatory action, FIFRA requires a careful risk and benefit analysis based on an extensive data base which still needs to be established. State legislatures, and the U.S. Congress, are not under such constraints. Accordingly, with the states of Maryland and Virginia providing leadership, state legislatures and both houses of Congress began preparing legislation to regulate the use of TBT paints. Nearly identical bills have been enacted in Maryland, Virginia, and Oregon; a similar bill is nearing enactment in California. More stringent bills have been enacted in Washington and Alaska. Essentially, these bills ban the sale and use of TBT paints by vessels under

25 meters, with the exception of aluminum hulls, and require the application of these paints for larger vessels in certified boatyards using paints with TBT release rates below a specified limit, generally 5 $\mu g/cm^2/day$, as measured by the EPA method. Also, TBT bills have been prepared in both houses of the U.S. Congress.

The consequences of such legislation, if adequately enforced, can be profound. Not only were paints being used with TBT release rates 100 times higher than necessary for efficacy, as previously pointed out, but now, as a result of legislation, the suspected major sources of TBT entering the environment will be eliminated or severely curtailed. Whether the legislative action by the states of Maryland and Virginia will manifest itself in significantly lower TBT water column concentration in the Chesapeake Bay during the 1988 boating season remains to be determined.

ORGANOTIN ANTIFOULING HULL PAINTS FOR THE U.S. NAVY

Let us return to the Navy's use now that the momentum of environmental concern over TBT, initiated and focused by the Navy's intention to use these high performance antifouling coatings, has resulted in the EPA's Special Review as well as passage of regulating legislation. None of the TBT legislation enacted prevents the Navy from using TBT paints. For 1987, the U.S. Congress authorized the Navy to conduct a two-harbor case study on the application of TBT paints to its ships.[39] Accordingly, an Implementation Plan was prepared jointly by the David Taylor Naval Ship Research and Development Center and the Naval Ocean Systems Center.[40] Implementation of the case study involved development of a mathematical model of Pearl Harbor, documenting the shipyard activities involved in the application of the paint, monitoring the concentration of butyltins in harbor waters following undocking of the ship, and studying the environmental fate and toxicity of TBT in Pearl Harbor waters. The first ship painted as part of this plan was a frigate at the Pearl Harbor Naval Shipyard.

The state of Hawaii, however, filed a preliminary injunction in the U.S. District Court to prevent this frigate from being undocked, causing any form of TBT to be placed in the waters of Pearl Harbor, or painting any other ships with TBT. Hawaii based its motion on the grounds that the Navy had violated the following:

1. The Coastal Zone Management Act
2. The National Environmental Policy Act
3. The Federal Water Pollution Control Act.

After extensive testimony was taken, the Court concluded that Hawaii's arguments were without merit and ordered the motion for preliminary injunction be denied in all respects.[41] The Court concluded that the Navy had not violated any of the Federal acts as charged by Hawaii. The frigate was undocked and the study proceeded. The Federal Court in its ruling also stated the following:[41]

> "The Navy is by far and away the most responsible user of TBT in Hawaiian waters. It uses paint with low release levels, has instituted procedures to minimize discharge from drydocks, has contributed immensely to the available base of scientific data, and is proceeding in a very cautious manner. If some damage is indicated after the program is commenced, the program can be discontinued. If damage occurs, it will not be irreparable and can be eliminated. Given the widespread unregulated use of TBT by others, the harm posed by the Navy is nonexistent."

This citation from the Court's ruling is of particular interest since it restates the Navy's position in its Interim Finding of No Significant Impact.[8]

Another state in which U.S. Navy ships have a significant presence is Virginia. This state has enacted legislation regulating TBT paint use which does not prohibit the Navy from implementing its program. A public hearing on organotin antifouling paints was conducted by the Virginia Department of Agriculture and Consumer Affairs. Testimony presented at that hearing put the Navy's potential contribution of TBT to Virginia waters into perspective.[42] The following vessel statistics and assumptions were used.

- Commercial ship traffic in Virginia waters in 1985 was 3246, according to the Virginia Port Authority. Of these ships, 22% were assumed to use organotin, and the average underwater hull area was assumed to be 20,000 ft^2. (Use of organotin paints on commercial vessels may be much higher than 22%.) A TBT release rate of 1 $\mu g/cm^2/day$ by the Navy method was assumed.

- The Chesapeake Bay fishing fleet numbers 2840 according to the National Marine Fisheries Service; half of that was assumed to operate in Virginia waters, with an average underwater hull area of 300 ft^2, and an estimated 80% use of TBT paint, releasing 1 $\mu g/cm^2/day$.

- Based on U.S. Coast Guard data, 158,000 recreational craft operate in Virginia waters; these craft have an average length of 20 feet and an average underwater hull area of 150 ft^2. Only 10% of these use any antifouling paint and of these 30% use organotin paints with an estimated release rate of 5 $\mu g/cm^2/day$ by the Navy procedure.

Table 1 presents estimated releases of TBT to Virginia waters based on these assumptions and residence times. Estimates for the commercial fleet are very conservative and could easily be four times higher. Based on recently enacted legislation, the contribution from recreational craft, at least those smaller than 25 meters, should be eliminated,

if not entirely during the next boating season, at least during the one thereafter. While this would increase the percent of the potential Navy contribution, Table 1 serves to place it in proper perspective.

Table 1. Estimates of TBT Released to Virginia Waters from Vessels

Vessel Type	Painted Hull Area (ft^2)	Release Rate ($\mu g/cm^2$/day)	Vessel Residence Time (%)	Total Release (lb/yr)
Commercial Ships	14,360,000	1.0	10	1089
Fishing Fleet	340,000	1.0	50	127
Recreational Craft	711,000	5.0	100	2661
U.S. Navy*	4,700,000	0.1	50	176

*Hypothetical 100% implementation in 10 years.

While Table 1 is limited to Virginia, it is illustrative for other states where the U.S. Navy has a significant presence. On a nationwide basis, if the entire Navy were painted with TBT after 10 years, its contribution would represent 2% of the current contribution to the environment.[43]

SUMMARY

The U.S. Navy, in its continuing efforts to maintain operational readiness in fulfilling its military mission as well as minimizing cost, has identified low release rate TBT-based antifouling paints as the best means to keep its water-wetted hulls smooth and efficient worldwide. Although the Navy's contribution of the TBT biocide to the environment is small when compared to private sector use, its announced intention through publication of an Environmental Assessment, stimulated the environmental community into action. While this clearly was not the intent, it was clearly the result. The Navy's research was instrumental in providing the U.S. EPA with data to support its Special Review; in identifying TBT release rate as an intrinsic property of these paints and as a means for their regulation; in developing analytical methods for environmental monitoring; in encouraging the industry to lower the release rate; and in establishing a regulatory strategy by identifying recreational craft marinas as the primary source of TBT entering the environment and therefore as the place where regulation should focus.

The original determination of need for these high performance state-of-the-art antifouling hull paints remains the same. It is anticipated that the U.S. Navy will now be able to proceed with its implementation program to use these paints, as they are being used by most other navies in the world.

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