# PROCEEDINGS










# *Second* Tri-Service Environmental Technology Workshop

*"Enhancing Readiness Through Environmental Quality Technology"*

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**10-12 JUNE 1997 • ST. LOUIS, MISSOURI**

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# PROCEEDINGS

# TRI-SERVICE
# ENVIRONMENTAL TECHNOLOGY WORKSHOP

**10–12 June 1997**
St. Louis, Missouri

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# ESH Director
# Texas Instruments
# Systems Group & Electronics


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## Second Tri-Service Environmental Technology Workshop

## "Enhancing Readiness Through Environmental Quality Technology"

## 10-12 June 1997

## St. Louis, Missouri

# Texas Instruments
# Environment, Safety & Health

## *A Competitive Advantage*

- **Leadership**
- **Integration**
- **Teaming**

# *Excellence in ESH recognized as being part of a Leadership Corporation*

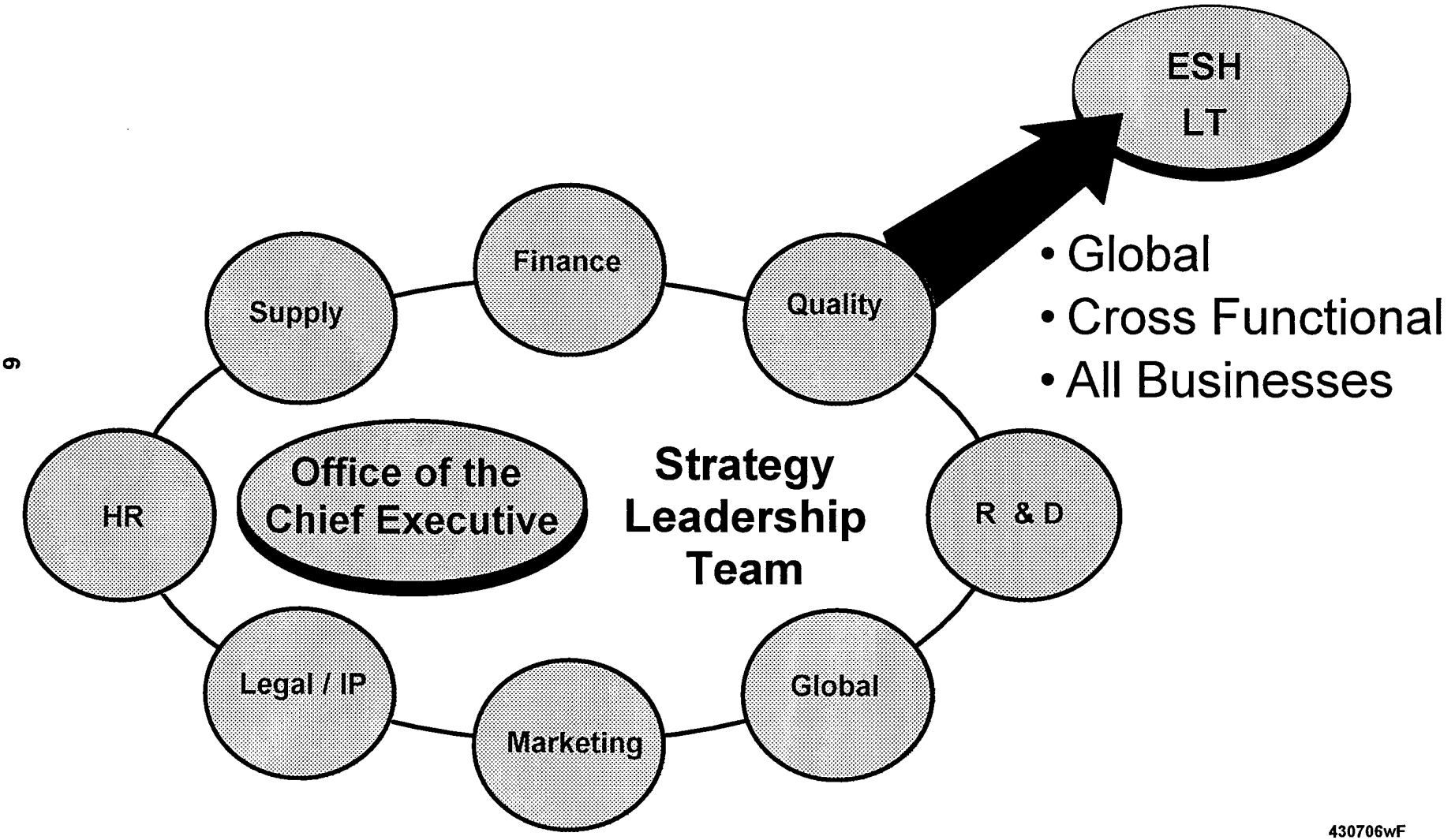





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# Corporate Leadership Team






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# *ESH Vision*

**"Business excellence and leadership in the environment, health and safety are core values of our Texas Instruments' people. These values are integrated into our processes, products, and services and are key ingredients for sustained competitive advantage."**

# Stretch Goals

## 100% Productivity

***Target: Zero Preventable Illnesses, Injuries***

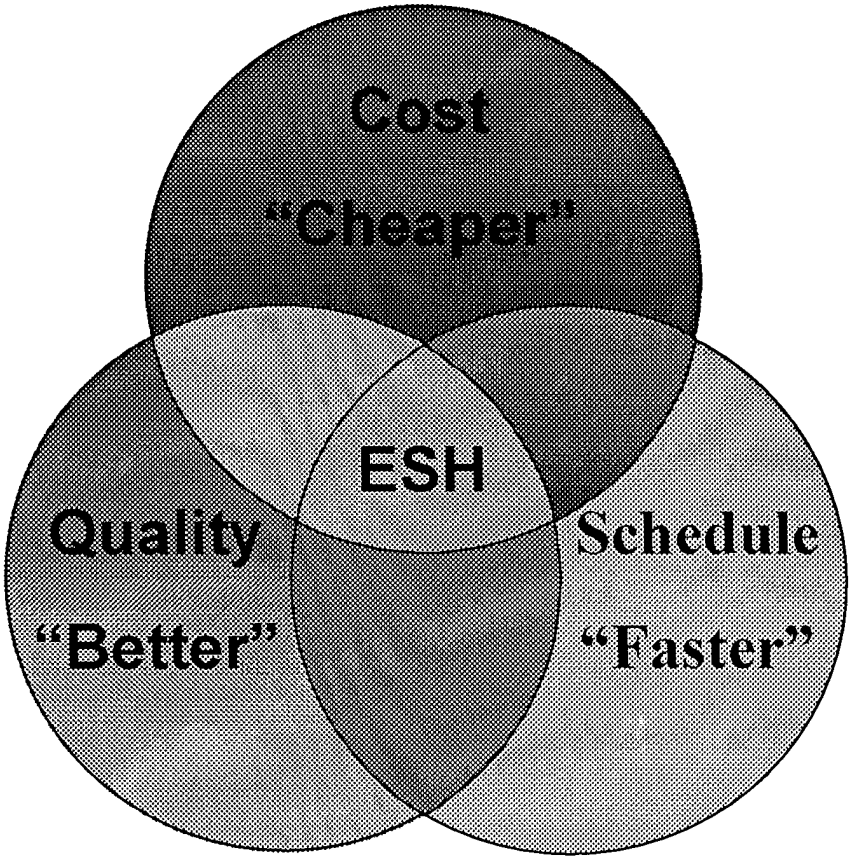
- Occupational illnesses, injuries
- Non-occupational (preventable) illnesses, injuries

## 100% Process Efficiency

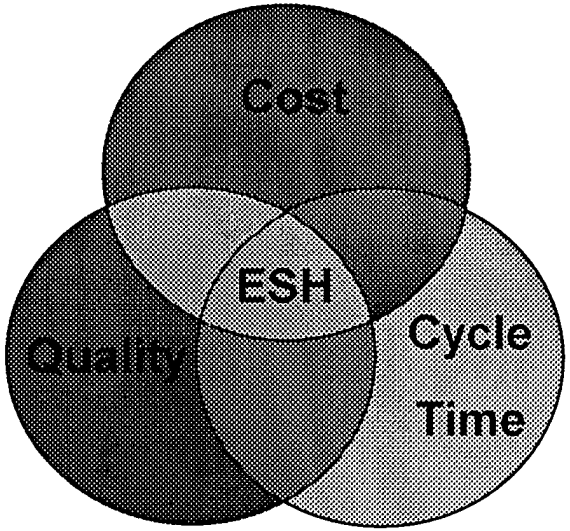
***Target: Zero Wasted Resources***

- Reuse, regenerate, recycle, resell
- No contamination of land, incoming air, water
- Best available energy efficiency

# Environment, Safety & Health Business Integration



# *DFE Process Business Results*



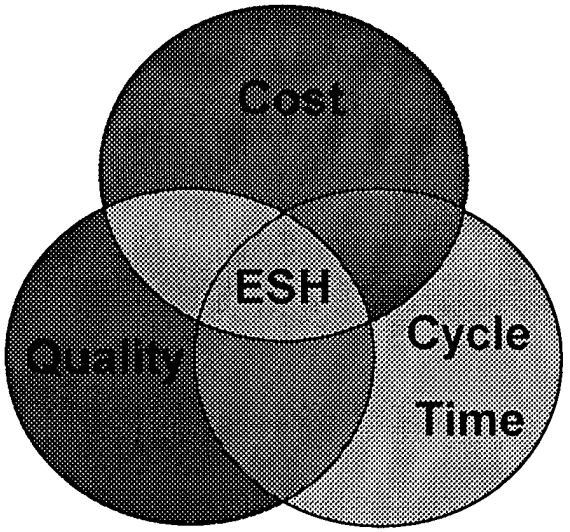

**ACTION:**

- **Implemented Controlled Atmosphere Soldering**

**RESULTS:**

- **$336K annual material savings**
  - **Reduced:**
    - **95% reduction of VOC emissions**
    - **40% reduction in lead consumption**
    - **Reduction in cycle time (no clean)**

# *DFE Process Business Results*



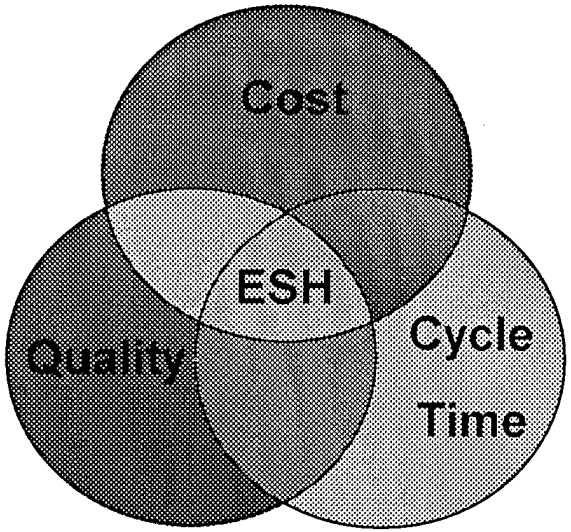

## ACTION:

- **Modified designs to use powder paint**

## RESULTS:

- **Payback: > $500K in first year**
  - **Reduced:**
    - **VOC emissions 40 tons/year**
    - **Waste water disposal 40 tons/year**
    - **Paint sludge disposal 20 tons/year**
    - **Waste solvent treatment 20 tons/year**
    - **Three coating operations to one**
    - **More durable coating**
  - **Implemented on several programs**

# *DFE Process Business Results*

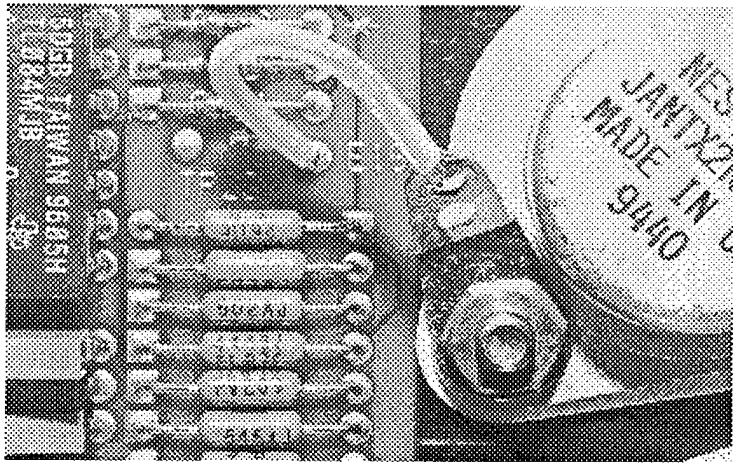


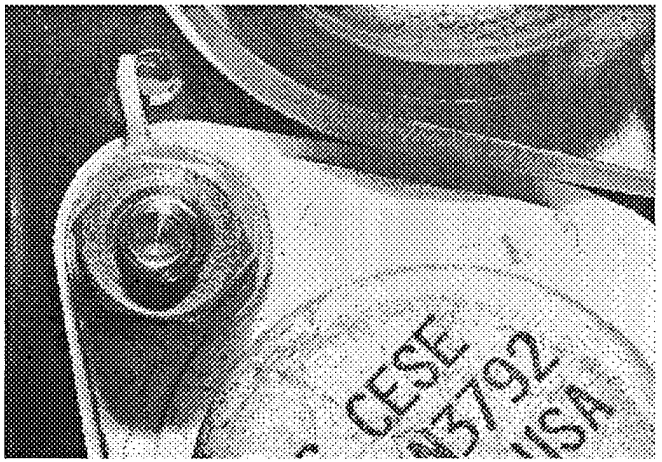

## ACTION:

- Replaced "Spike Lug" Hand Assembly Process

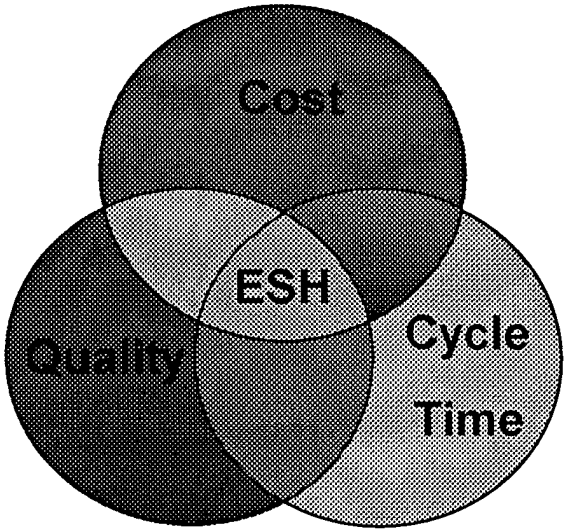
## RESULTS:

- $180K Annual cost savings
- Eliminated very high Repetitive Motion Operation
- Eliminated exposure to hand solder
- Reduced Total Process Cycle Time (.89 hrs/System)
- Solder Defect Improvement





# *DFE Process Business Results*



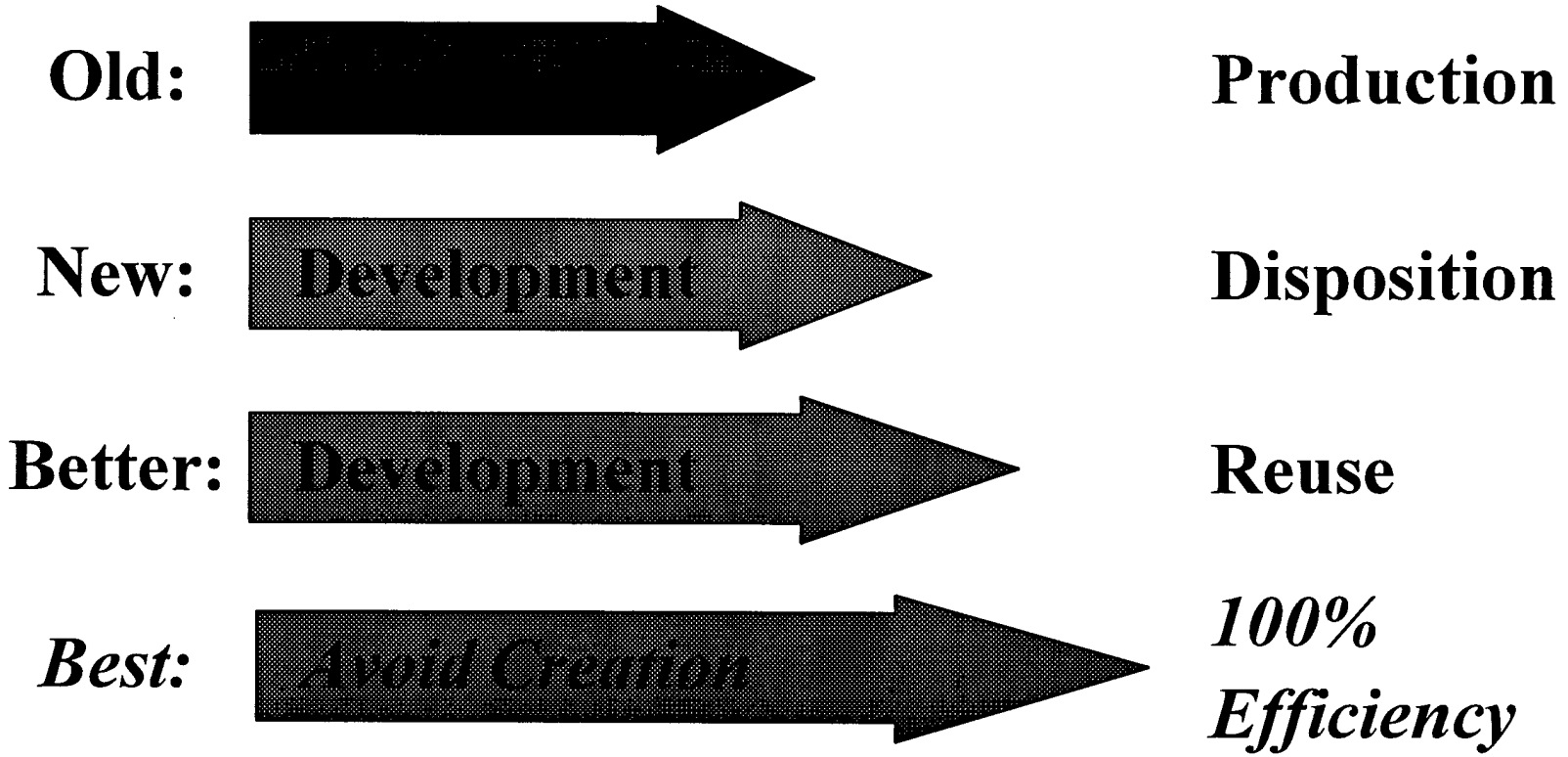

**Action:**

- **Substitute laser ablation for photolithography process on two programs**

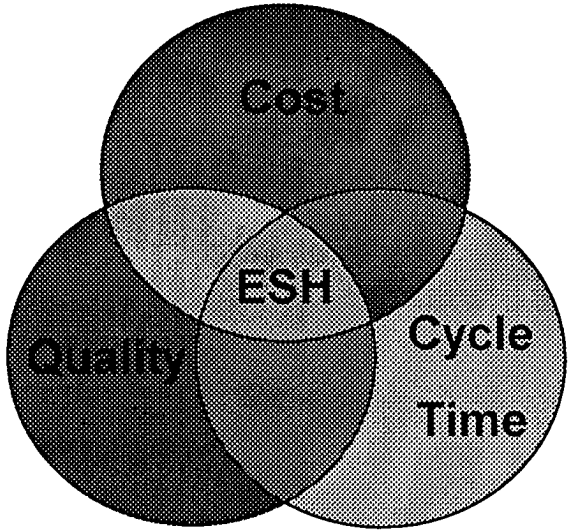
**Results:**

- **Reduced chemical use and waste via elimination of plating baths, developers, strippers, and scrubbers**
- **Reduced process floor space and process steps**
- **9x cycle time reduction**
- **Elimination of HAZMAT releases**
- **Two-thirds cost reduction**

# *Life Cycle Thinking Evolution*



# *DFE Process Business Results*



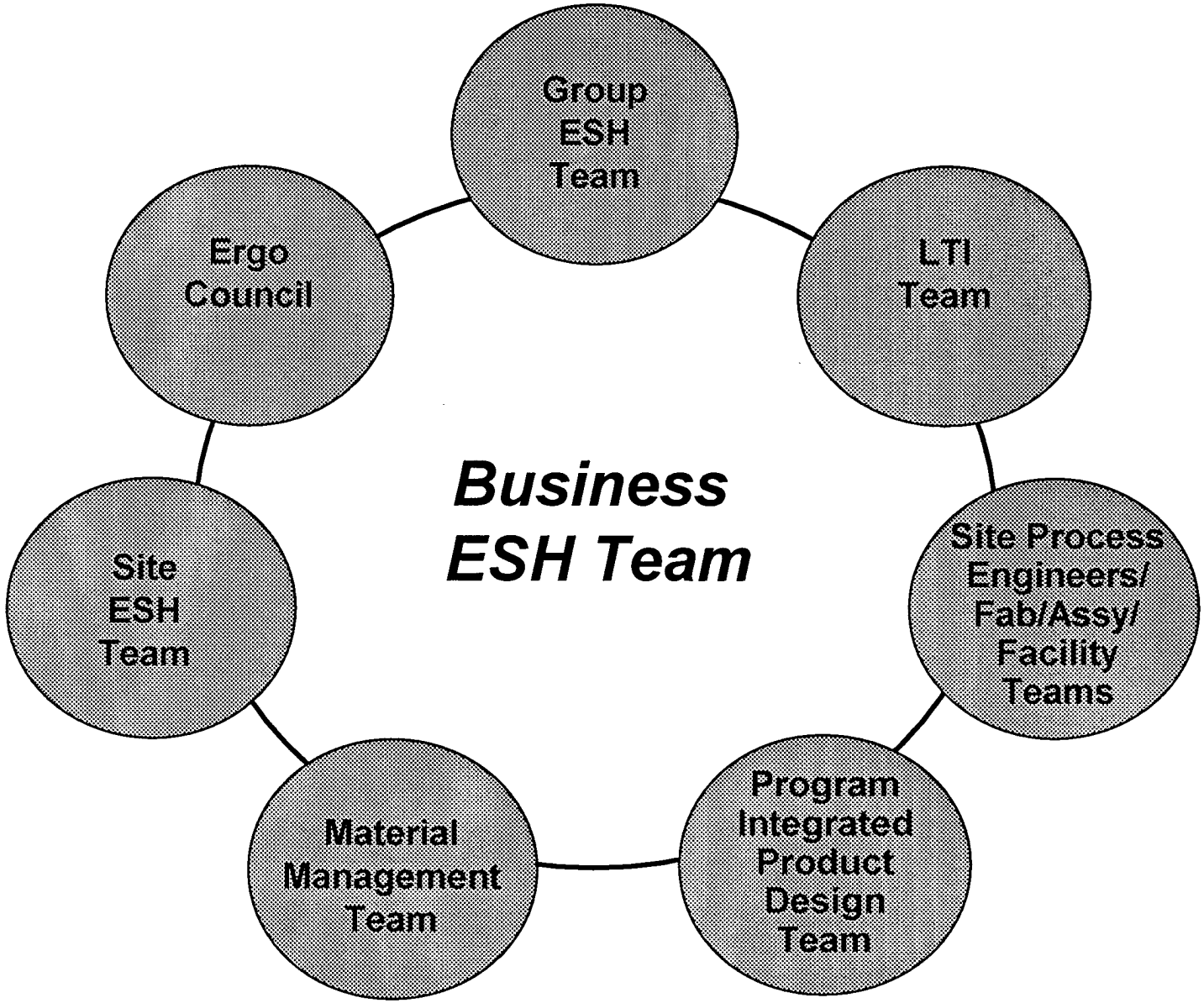

## Action:

- **Eliminate painting of airframe interior & shipping container**

## Results:

- **$4K savings/system, $48M across contracts**
- **Reduced operations steps and cycle time**
- **Reduced paint/chemical usage and waste**
- **Reduced Defect Opportunities**

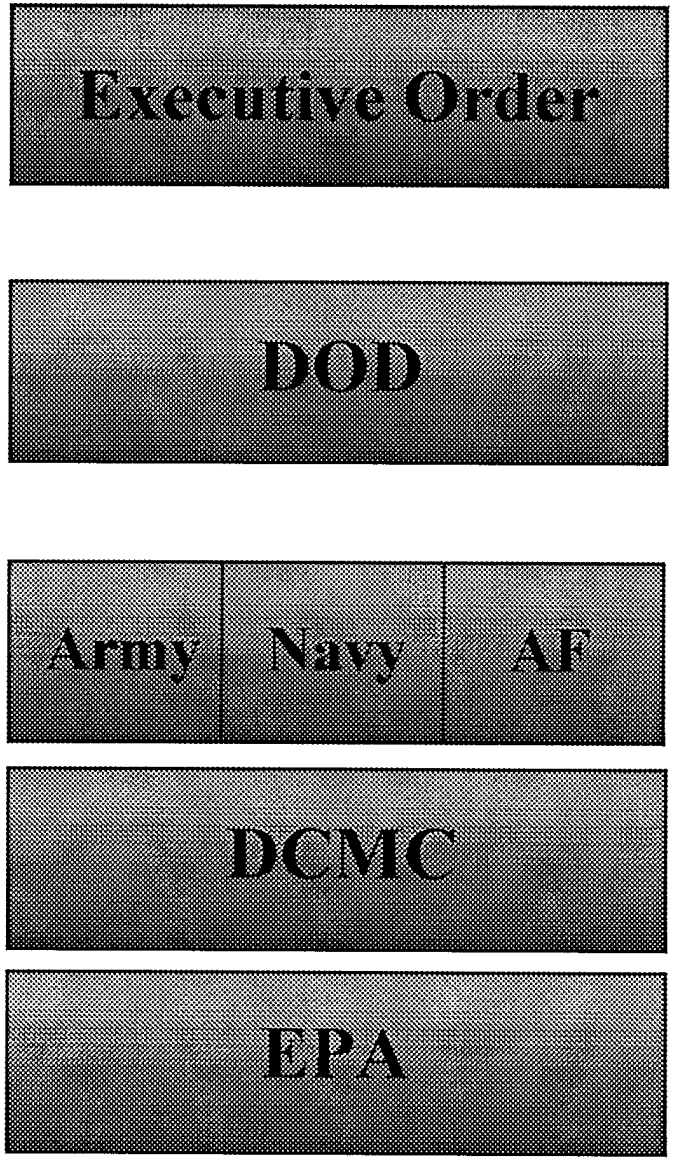
# Environment, Safety & Health
## *Organizational Structure*



# ESH External Teaming

# For Success

- National Center for Manufacturing Sciences (NCMS) Steering Committee for Environmentally Conscious Manufacturing
- National Defense Center for Environmental Excellence (NDCEE) - Executive Advisory Board
- United Nations Environmental Programme (UNEP)
- American Electronics Association (AEA)
- Aerospace Industries Association (AIA)
- EPA/DoD/Industry Ad Hoc Solvents Working Group (IPC)
- Representative to U.S. TC 207 subcommittee (5) on Life Cycle Assessment for ISO 14000 Standards
- Consolidated Uniform Report for the Environment (CURE) with TNRCC
- Joint Group on Acquisition Pollution Prevention (JG-APP)




**Government Vision is embraced by aerospace community**

**Implementation is an issue**

**Lack of "timely" single plan causing a vacuum**

**Services moving to support Vision...not moving in same direction to same drummer**

**Oversight community moving toward operations and other agency activities**

**Inconsistency in the implementation process is dissipating contractors focus from achieving the Government Vision.**

# Joint Group Acquisition Pollution Prevention (JG-APP) Initiative

- Joint Group on Acquisition Pollution Prevention
- Mission Statement
  - Design out/change manufacturing processes
  - Common acquisition pollution prevention interface
  - Lower alternative development and implementation costs
  - Avoid duplication of effort in reduction/elimination of HazMats
- JG-APP objectives compliment the Single Process Initiative (SPI)

# Joint Group Acquisition Pollution Prevention (JG-APP)

- Principals:
  - Brigadier General Bolton, US Air Force, JG-APP Chairman
  - Rear Admiral John B. Totushek, US Navy
  - Major General Roy E. Beauchamp - U.S. Army
  - Major General Williams, US Marine Corps
  - Major General Drewes, Defense Contract Management Command
- Invited Participants:
  - Ms. Dominguez, HQ National Aeronautics and Space Administration
  - Lieutenant Colonel Salomon, Office of Deputy Under Secretary of Defense (Environmental Security)

# Joint Group on Acquisition Pollution Prevention Pilot Program

## Background

- Pilot started in February 1995
- TI chose Paint Alternatives
  - Air Permit (Voc Limits not Emissions)
  - Corporate Goal of Pollution Prevention
- Four Paint Systems Targeted
  - Mil-C-83286
  - Mil-P-23377
  - Mil-C-22750
  - Mil-C-46168 Type II

# Joint Group on Acquisition Pollution Prevention Pilot Program

## Activities To Date

- Identified Top Twenty Programs
  - Obtained Commitment from DoD Program Offices
  - Involved Technical Community
    - Paint Experts (Program and Mil custodians)
    - Depots
    - Environmental Activities
    - National Defense Centers for Environmental Excellence
- Researched Alternatives
- Documented Findings in Joint Test Report

# Joint Group on Acquisition Pollution Prevention Pilot Program

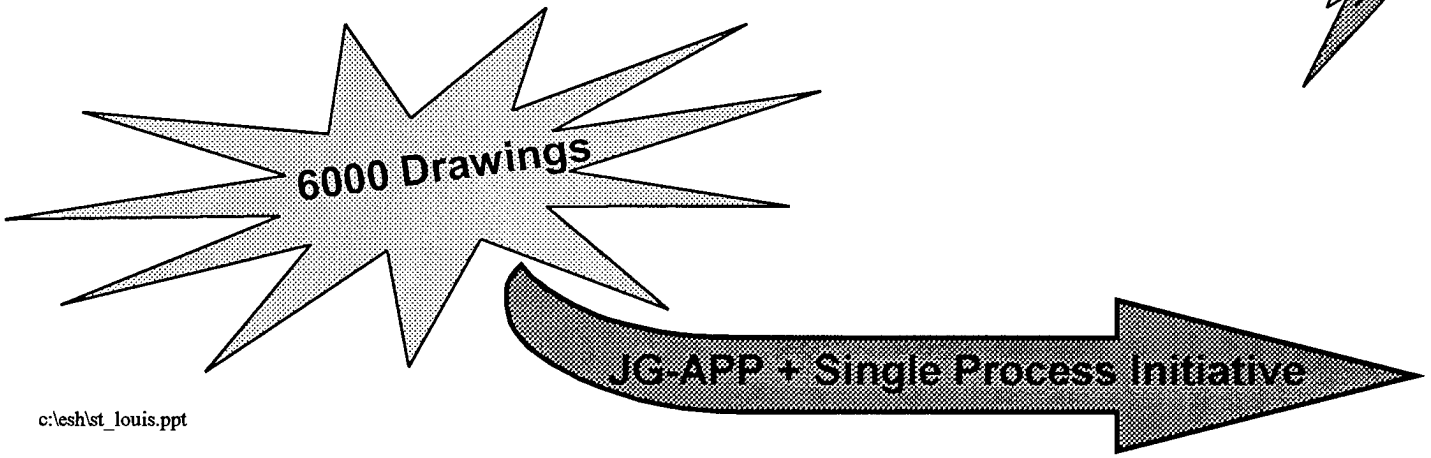
## 1st Block Change

- Signed on April 4, 1996
- ...contractor's single process initiative for alternate coatings is incorporated via a block change modification.
- The military specifications...shall be substituted with the corresponding TI F-specifications...as they apply to the metal fabrication process.
- Covers all contracts where DCMC-TI has been delegated authority.

# Government/Texas Instruments "Success"

- Completed 300 Contract Changes
- Up to 80% reduction of VOC emissions
- Current Status--Celebrated First Technical Block Change




**$$**

**Cost Avoidance**

**$9M**

# Joint Group on Acquisition Pollution Prevention Pilot Program

## 2nd Block Change

- Signed on March 12, 1997
- Contractor is authorized to substitute a performance based standard in place of military specifications for topcoats.
  - Airborne and Marine Interior
  - Airborne and Marine Exterior
  - Ground Based Interior
  - CARC and Low Observable Exterior

# Joint Group on Acquisition Pollution Prevention Pilot Program

## Current Status

- Joint Test Protocol Approved
  - Performance Specification
  - Non Chemistry Specific
- Cost Sharing from programs at ~ $250K for 1997
- Target material is 100% solids and powder coats

# Joint Group on Acquisition Pollution Prevention Pilot Program

## Next Block Changes

- Circuit Card Assembly and Materials Task Force (CCAMTF)
  - 19 members representing Military and Private Sector
  - CTC (NDCEE) to direct execution in increments of $600K and $650K
    - Conformal Coating
    - Alternative Surface Finishes
- Leverage Lockheed Martin JTP/Block Change
  - Ink Stenciling

# Joint Group Acquisition Pollution Prevention (JG-APP) Participating Organizations (CCAMTF)

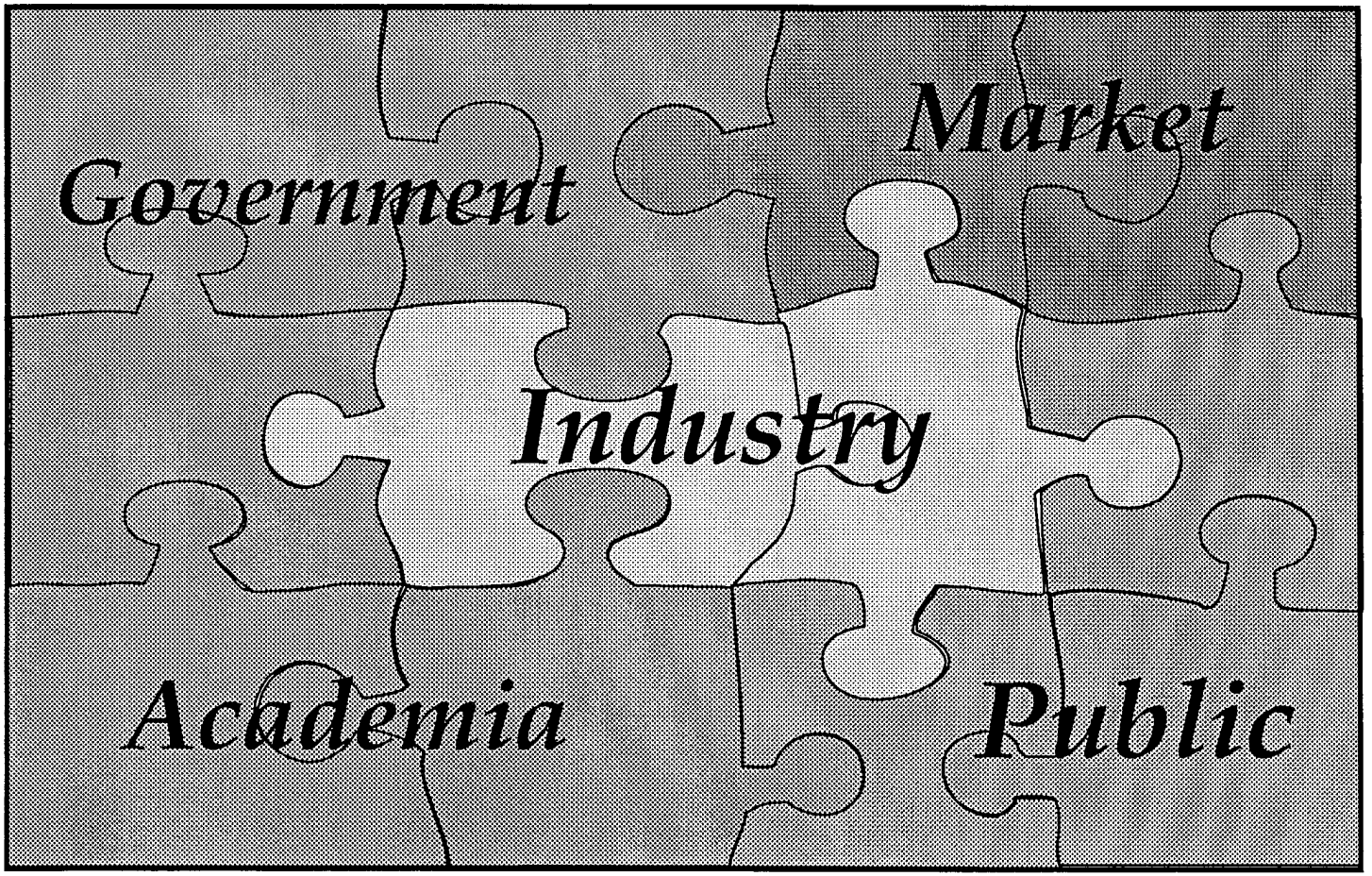
- Southwest Technology Consultants
- Motorola
- AlliedSignal / FM&T
- Lucent Technologies
- Alliant Techsystems
- SEHO USA, Inc.

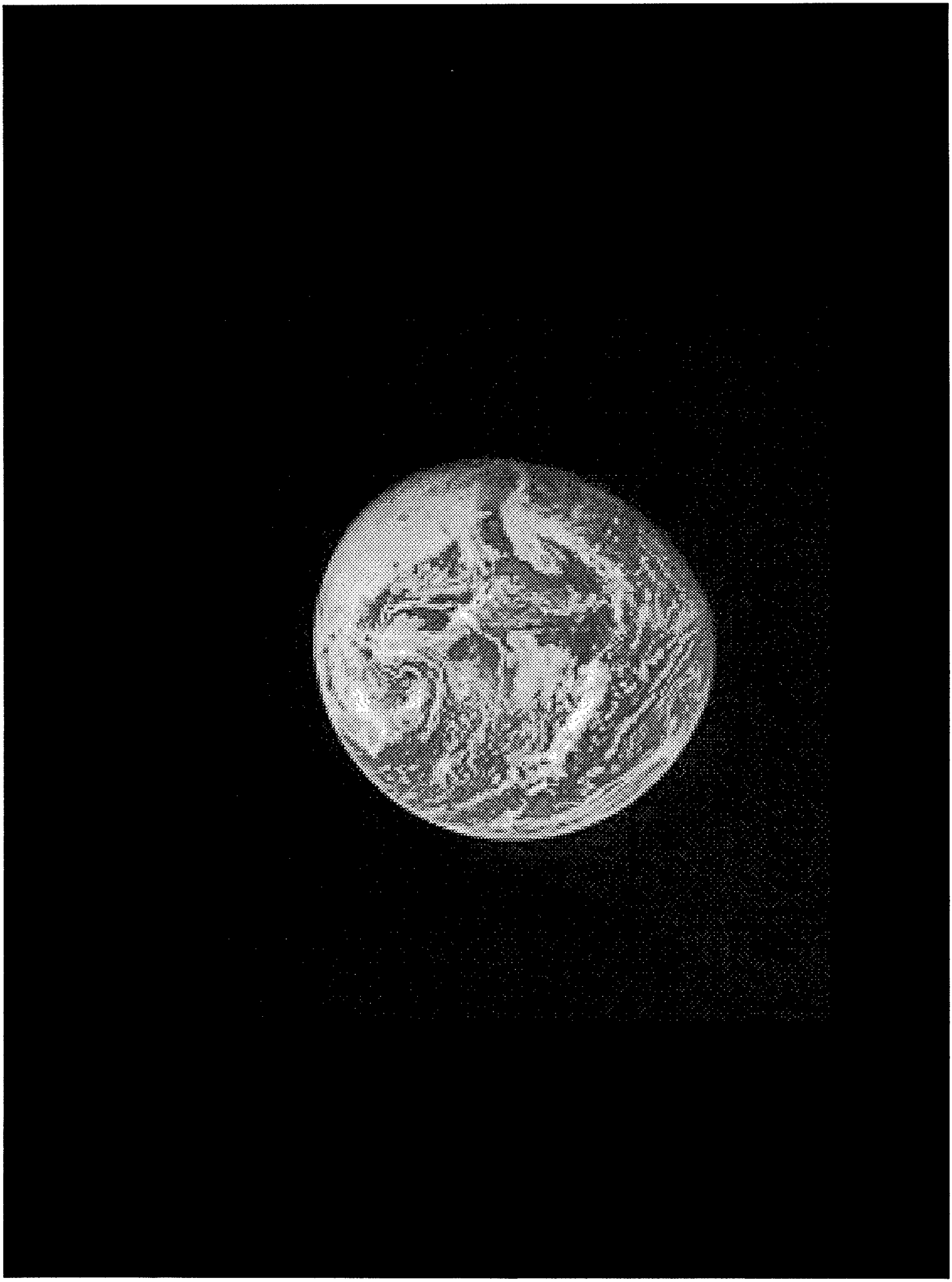
- Texas Instruments
- Hughes Electronics
- Honeywell
- CSL
- GTE
- Les Hymes Associates
- NCMS

- EMPF Indianapolis
- USAF - Wright-Patterson AFB
- US Army - Picatinny

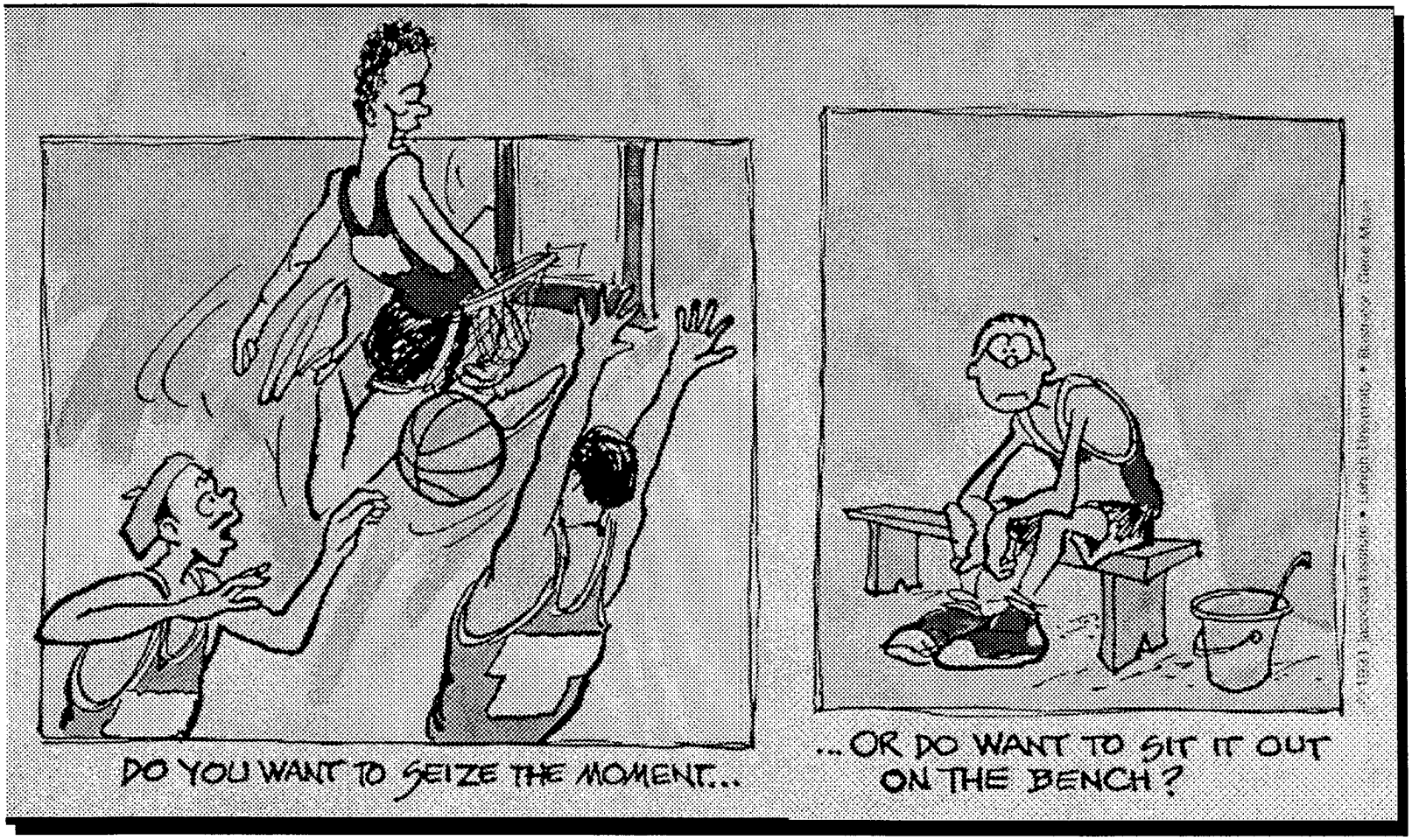
- NAWC - Indianapolis
- USAF - Hanscom AFB
- US Army - MICOM

# Success = Teamwork = *Industry Leadership*





# It's Your Choice

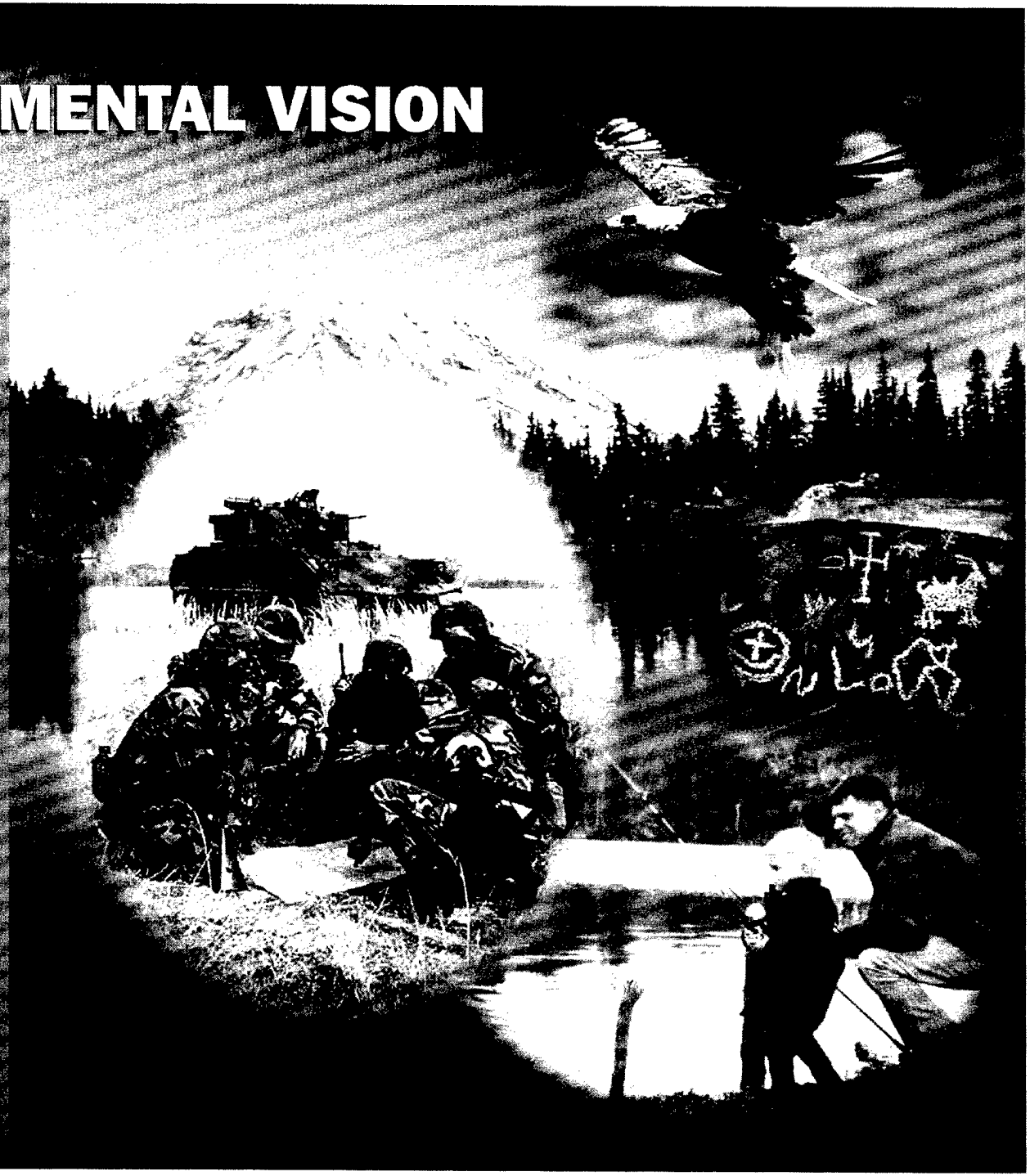


# ARMY PERSPECTIVE

# ARMY ENVIRONMENTAL VISION

The Army will integrate environmental values into its mission in order to:

- **SUSTAIN READINESS**
- **IMPROVE SOLDIERS' QUALITY OF LIFE**
- **STRENGTHEN COMMUNITY RELATIONSHIPS**
- **PROVIDE SOUND STEWARDSHIP**



# NAVY PERSPECTIVE

# Navy Environmental Quality Technology Transfer

**Stephen E. Eikenberry, R.G.**

**NFESC**

**Port Hueneme, CA**

**10-12 June 1997**

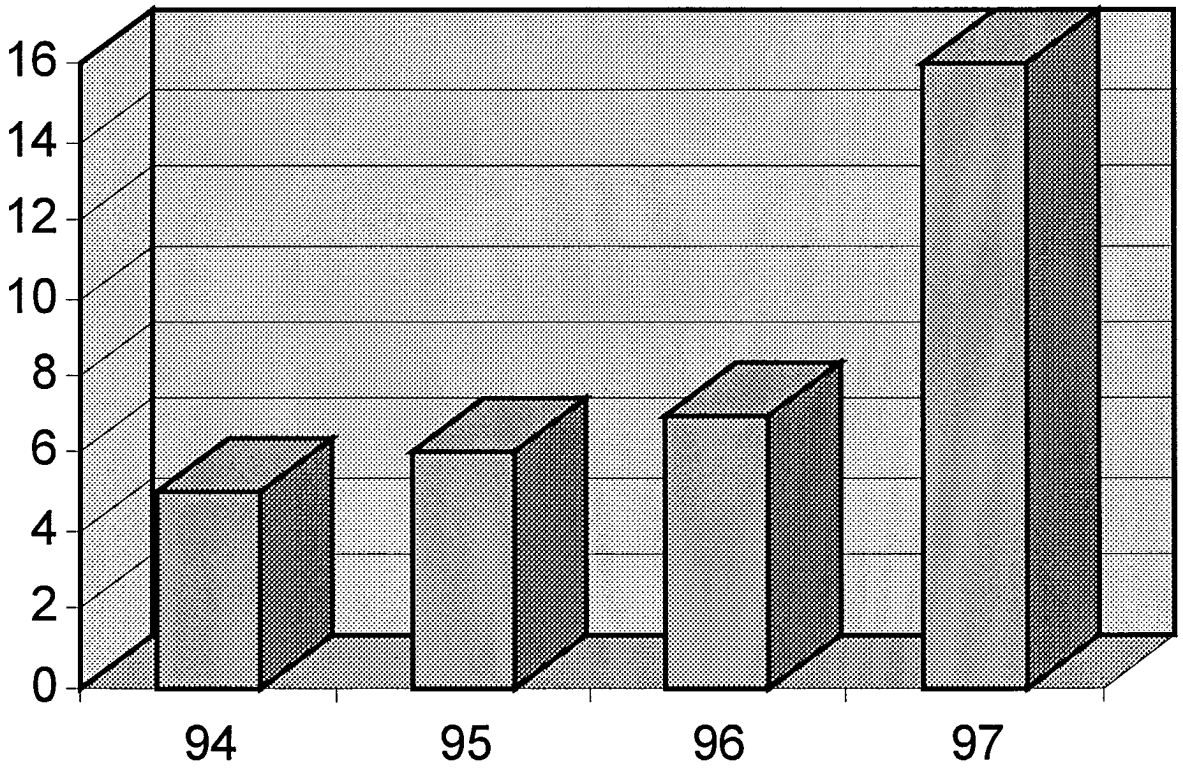
# Technology Transfer Efforts

- Tiger Team
- Hydrocarbon National Test Site
- NELP
- RPM Newsletter
- Environmental Restoration Conference Call
- ARTT
- BADCAT
- Tri-Service Working Groups
- RCI Demonstration

# Technology Transfer Efforts (Cont.)

- P2 Procurement Program
- Tri-Service P2 Opportunity Handbook
- Minimizer Newsletter
- Product Brochures/Videos
- Conference/Seminar Presentation
- Technical Papers/Articles, and Exhibits
- Training Courses
- Web Pages

# Environmental Technologies Implemented by FY



# Technologies and Methodologies FY97

- Small Arms Ranges Remediation
- Hot Air Vapor Extraction
- Biocell (Army)
- ICON Direct Push Site Assessment Technology (NELP)
- Commodore Solvated Electron Process (RCI)
- Klohn-Crippen Chemtech System (BADCAT)
- On-Site Env. Lab Field Screen for Metal (BADCAT)
- Enhanced Cost-To-Complete (CTC) Decision Tree
- General Broad Agency Announcement

# Technologies and Methodologies FY97 (Cont.)

- NOx Reduction Technology
- Sludge Reduction Technology for IWTP
- Sodium Nitrite Wastewater Treatment System
- AFFF Operational Waste Control Technology
- Emission Capture from Arc Welding
- Plating Shop Wastewater Evaporator
- Dry Silver Recovery from Photo/X-Ray Lab
- In-Vessel Composting of Solid Waste

# *Examples of Technologies & Methodologies Implemented*

| Technology | Sites | Dev. $ Invested | $M Saved |
|---|---|---|---|
| • RACs | 162 DOs | $0.4M | $156 Awarded |
| • SCAPS | 118 | $4M | $ 1.9 Cost Avoid. |
| • Biopiles | 11 | $1.3M | $ 1.4 |
| • Bioventing | 14 | $3.2M | $ 27 |
| • Bioslurping | 10 | $2.7M | $ 13 |
| • BCDP | 1 | $3.3M | $ 15 |
| • CTC | All | $0.1M | Part of Decision Pro |
| • Geostatistics | 3 | $0.1M | Reduced by 87% |
| • DQOs | 5 | $0.1M | Part of Decision Pro<br>New ASN Policy |

# Examples of Technologies & Methodologies Implemented (cont.)

| Technology | Sites | Dev. $ Invested | $M Saved |
|---|---|---|---|
| • Hydroblast Wastewater Recycle | 54 | $440K | 35 |
| • BOWTS | 8 | $200K | 11 |
| • Metal Preparation and Plating | 14 | $1,093K | 3 |
| • Shelflife and HAZMAT Recycle | 7 | $1,613K | 4 |
| • DeNOx Ashore | 4 | $1,375K | Compliance |
| • MILCON Consulting | 6 | $300K | 10 (Estimated) |
| • Improved Degreasers | 8 | $350K | Compliance |
| • Sodium Nitrite Wastewater | 4 | $886K | >2 |
| • CFR Truck AFFF Waste Control | * | $193K | Compliance |

* Navy-wide, and possibly DoD-wide

# Summary

- **Savings/Investment Ratio**
  - **Cleanup: 3.8 + No Long Term Liability**
  - **P2/Compliance: 10.1 + Compliance**
- **Technology pays**

# REMEDIATION I

# PHYTOREMEDIATION OF EXPLOSIVES IN GROUNDWATER USING INNOVATIVE WETLANDS-BASED TREATMENT TECHNOLOGIES

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## ABSTRACT

Many army ammunition plants across the country have problems with groundwater contaminated with explosives. A field demonstration was initiated at the Milan Army Ammunition Plant near Milan, Tennessee early in 1996 to demonstrate the feasibility of treating contaminated groundwater with constructed wetlands. Two different systems were designed and installed. A lagoon system consisted of two cells in series with each cell having dimensions of 24 x 9.4 x 0.6 m (L x W x H). A gravel-bed system consisted of three gravel-beds operated in series with a primary anaerobic cell having dimensions of 32 x 11 x 1.4 m (L x W x H), followed by a pair of secondary cells each with dimensions of 5.5 x 11 x 1.4 m (L x W x H). The primary cell is maintained anaerobic by adding powdered milk to the water every two weeks. The secondary cells are maintained aerobic via reciprocation, whereby water is pumped back and forth from one cell to another to cause a recurrent fill and drain action. The lagoons were planted with sago pond weed, water stargrass, elodea, and parrot feather. The gravel-bed wetlands were planted with canary grass, wool grass, sweet flag, and parrot feather. Water began flowing to each of the wetland treatment systems at 19 L $min^{-1}$ starting in June, 1996. The design hydraulic retention time through each treatment system was approximately 10 days. Influent and effluent water samples were collected every 2 weeks. Intensive sampling of water interior to the wetlands occurred every 2 months. Influent concentrations of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrobenzene (TNB), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were respectively 1.2, 1.8, 0.1 and 0.1 mg $L^{-1}$ before November 21, 1996 and respectively 4.6, 4.4, 0.35, and 0.1 mg/L after November 21, 1996. The gravel-bed wetland is reducing TNT and TNB concentrations below 0.002 mg $L^{-1}$. The gravel-bed wetland is removing RDX and HMX in the groundwater, whereas the lagoon wetland is not as effective. Differences in explosive removal in groundwater were observed during the demonstration period with lower removal efficiencies in the winter months compared to summer months.

## INTRODUCTION

Constructed wetlands have been successfully used to treat a wide variety of wastewaters. Municipal wastewater and acid mine drainage encompasse most of the water treated by constructed wetlands (Hedin and Narin, 1993; Kadlec and Knight, 1996). Other wastewaters treated with wetlands include petroleum industrial effluents, pulp and paper wastewater, and landfill leachates (Litchfield, 1993; Marten et al., 1993; Thut, 1993). The main advantage of constructed wetlands is that the technology is inexpensive compared to conventional treatment options. There are capital costs associated with building the wetland, but the minor operation and maintenance costs makes constructed wetlands a cheaper alternative to conventional treatments that include yearly labor and chemical costs.

Many army ammunition plants across the country have problems with groundwater contaminated with explosives. A demonstration was initiated at the Milan Army Ammunition Plant near Milan, Tennessee early in 1996 to test the feasibility of treating contaminated groundwater with constructed wetlands.

## MATERIALS AND METHODS

The design for the demonstration was developed from information obtained from two preliminary microcosm studies conducted in 38 L aquaria and are reported in Sikora et al. (1995) and Behrends et al. (1995).

The demonstration involves a comparison of two wetland types including a lagoon system with submergent plants and a subsurface flow gravel-bed wetland with emergent plants. A lagoon system consists of two cells in series with each cell having dimensions of 24 x 9.4 x 0.6 m (L x W x H) containing 137 $m^3$ water. A gravel-bed system has a first cell with dimensions of 32 x 11 x 1.4 m (L x W x H) containing 205 $m^3$ water and is kept anaerobic by adding 114 kg of powdered milk to the water every two weeks. The second cell in the gravel-bed treatment system has dimensions of 11 x 11 x 1.4 m (L x W x H) containing 43 $m^3$ water and is kept aerobic by reciprocating water back and forth from one interior partition to another (patent application filed). Gravel used in the gravel-based wetlands had 42% porosity. For the purpose of the demonstration, effluent from both wetland treatments goes through granular activated carbon bed canisters before being discharged to the sewer system. The lagoons were planted with sago pond weed (*Potamogeton pectinatus*), water stargrass (*Heteranthera dubia*), elodea (*Elodea canadensis*), and parrot feather (*Myriophyllum aquaticum*). The gravel-bed wetlands were planted with canarygrass (*Phalaris arundinacea*), woolgrass (*Scirpus cyperinus*), sweetflag (*Acorus calamus*), and parrot feather. Water began flowing to each of the wetland treatment systems at 19 L $min^{-1}$ starting on June 17, 1996. On November 21, 1996, the source of the contaminated groundwater was changed to a new well which contained the explosive contaminants at higher concentrations. The design hydraulic retention time was 10 days through the lagoon system and 9.1 days through the gravel-bed system. The retention time in each of the lagoon cells was 5 days. The retention time in the first anaerobic gravel-bed wetland was 7.5 days. The retention time in the reciprocating gravel-bed wetland was 1.6 days.

Influent and effluent water samples were collected every 2 weeks. Intensive sampling of water at interior locations in the wetlands occurred every 2 months. Interior water samples were collected at equal distances between the inlet and outlet at 4 locations in the lagoon cells and first gravel-bed wetland cell and 2 locations in the reciprocating gravel-bed wetland. The demonstration and the scheduled sampling is planned to continue until August, 1997. Data will be presented for biweeklywater samples collected from July 1, 1996 to April 30, 1997 and intensive water sampling that occurred on August 13, 1996, October 8, 1996, December 3, 1996, February 11, 1997, and April 8, 1997.

Water samples were analyzed for explosives via HPLC. A photodiode array detector with a range of 190 to 367 nm was used for analyte qualification and confirmation. A fixed wavelength detector at 254 nm was used for analyte quanitification. Total organic C (TOC) was analyzed via Dohrmann DC 190 TOC analyzer. Total Kjehdahl N (TKN) and ammonium N ($NH_4$-N) were analyzed with LACHAT flow-injection analysis. Biological oxygen demand (BOD) was analyzed via standard methods (Greenberg et al., 1992). Chemical oxygen demand (COD) was determined via HACH digestion and colorimetric analysis. Dissolved oxygen (DO), temperature, and pH were determined with hand-held YSI probe at time of sampling.

Disappearance rate of TNT, RDX, and HMX was analyzed using first-order kinetics (Kadlec and Knight, 1996). Assuming plug-flow hydraulics, the first-order equation for the reduction of a pollutant in a wetland is:

$$\ln (C/Ci) = -y (k/q) \quad (1)$$

where k is the first-order rate constant with units of m/yr, q is the hydraulic loading rate with units of m/yr, y is the fractional distance from inlet to outlet (ranging from 0 to 1), Ci is the influent concentration of pollutant, and C is the concentration at y. The k value for removal of TNT, RDX, and HMX in the lagoon and gravel-bed systems was determined via linear regression of ln (C/Ci) versus -y/q where the intercept was maintained at zero. The slope from the regression was the rate constant, k.

## RESULTS AND DISCUSSION

The temperature of the water leaving the two wetland systems and the temperature of the groundwater entering the wetlands are shown in Fig. 1. The temperature of the groundwater remained relatively stable due to the insulation of the water in the ground. The temperature of the water leaving the wetlands varied considerably as a reflection of the seasonal air temperatures. The first samples collected in July reflect a high water temperature during the summer months of approximately 30° C. During the colder winter months of January and February (days 198 to 256) the effluent water temperature decreased to approximately 5° C.

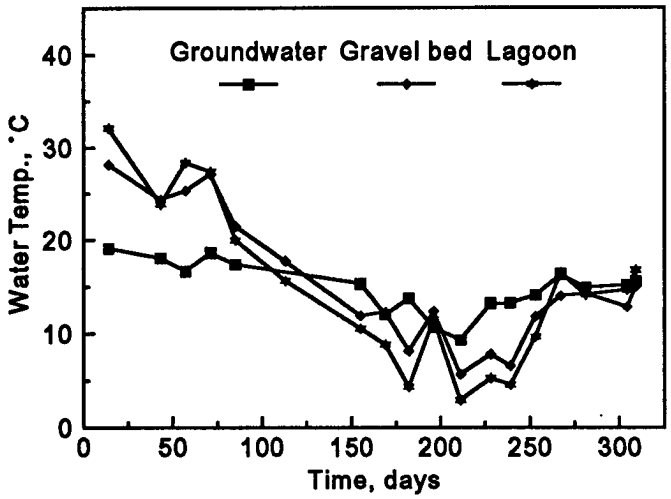



Figure 1. Temperature changes in the influent groundwater entering the wetlands and water leaving the Gravel-bed and Lagoon wetland systems.

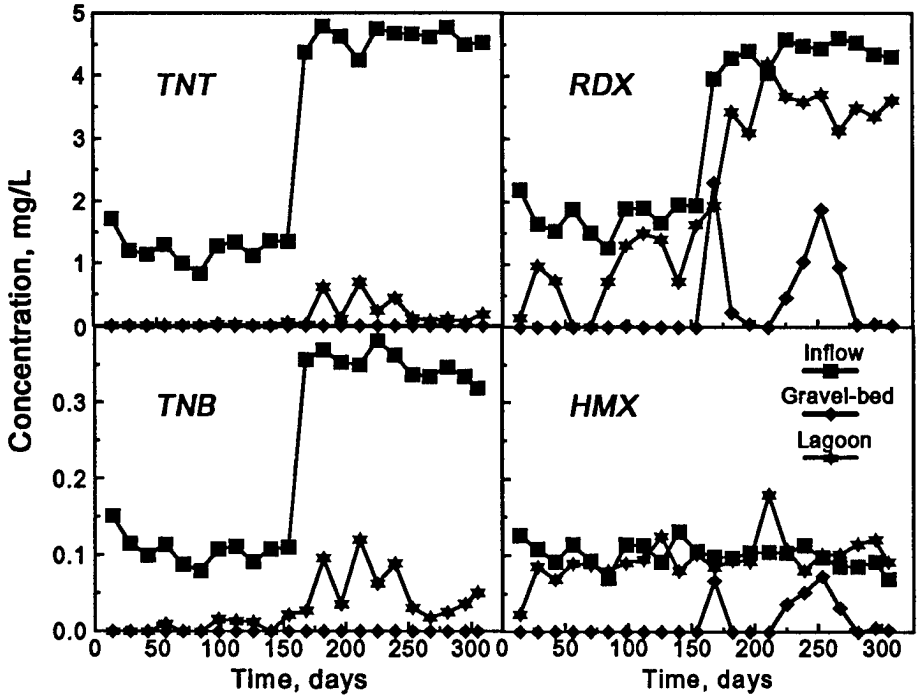



Figure 2. Concentration of four explosives, TNT, RDX, TNB, and HMX, in the inflow groundwater entering the cells and the effluent water leaving the Gravel-bed and Lagoon wetland systems.

Approximate influent concentrations into the wetland systems were 1.2, 1.8, 0.1, and 0.1 mg/L for TNT, RDX, TNB, and HMX, respectively, during the earlier period of the demonstration (Fig. 2). After 155 days, the average influent concentrations were 4.6, 4.4, 0.35, and 0.1 mg/L for TNT, RDX, TNB, and HMX, respectively. The gravel-bed wetland did a good job reducing TNT and TNB effluent concentrations below the detection level of 0.002 mg/L. The gravel-bed removed RDX and HMX below detection levels of 0.005 mg/L during the warmer periods of the year, but some release of RDX and HMX occurred during the winter. The decreased removal efficiencies for RDX and HMX could have been due to colder temperatures decreasing microbial activity. The lagoon system did nearly as well at removing TNT and TNB in the water as the gravel-bed systems but did a poorer job at reducing RDX and HMX. A seasonal effect was observed for TNT and TNB removal in the lagoons where higher concentrations of the explosives were observed in the effluent during winter.

The rate of explosives removal in the wetlands was determined by first-order kinetic analysis (Table 1). The rate of TNT removal in the anaerobic gravel-bed was rapid with k values ranging from 300 to 960 m/yr. The rate of RDX removal in the gravel-bed wetland was not as rapid as TNT but was still high with k values ranging from 41 to 347 m/yr. Removal rate constants for TNT and RDX in the lagoon cells were less than those observed in the gravel-bed wetland (Table 1). Lower rate constants were observed during February in both the gravel-bed and lagoon wetlands which was a reflection of a decrease in the removal efficiency during colder temperatures.

Table 1. First-order rate constants (k values in units of m/yr) for removal of TNT, RDX, and HMX in wetland treatment systems sampled throughout the demonstration period.

| | 1st Gravel-bed | | 1st Lagoon cell | | 2nd Lagoon cell | |
|---|---|---|---|---|---|---|
| | TNT | RDX | TNT | RDX | TNT | RDX |
| Aug | 790 | 273 | 151 | 13 | 198 | 20 |
| Oct | 790 | 347 | 109 | 6.2 | 164 | 8.1 |
| Dec | 960 | 87 | 197 | 22 | 169 | 22 |
| Feb | 300 | 41 | 48 | 3.5 | 93 | 4.8 |
| Apr | 410 | 73 | 114 | 6.9 | 133 | 8.4 |

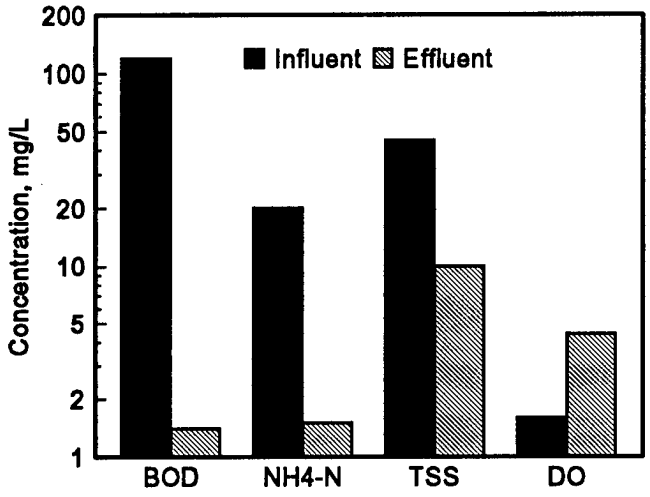



Figure 3. Concentrations of primary pollutants and dissolved oxygen entering and leaving the reciprocating gravel-bed wetland. Data are averaged over entire demonstration period from July 1, 1996 through April 30, 1997.

The reciprocating gravel-bed wetland follows the anaerobic gravel-bed wetland in order to remove nutrients and carbon that is released in the first wetland from continual feeding with powdered milk. Reciprocating water in a gravel-bed wetland allows for aeration of microbial biofilms on the gravel which hastens ammonium and BOD removal via aerobic microbial activity. The average dissolved oxygen concentration increased from 1.6 mg/L going into the reciprocating wetland to 4.5 mg/L exiting the wetland indicating improved aeration of the water (Fig. 3). Ammonium and BOD removal efficiencies were greater than 90 % in the reciprocating wetland and was fairly rapid since the retention time in the reciprocating wetland was only 1.6 days.

In addition to the primary explosives, TNT byproducts analyzed in the water samples were 2-amino-4,6-dinitrotoluene (2A), 4-amino-2,6-dinitrotoluene (4A), and 2,4-diamino-6-nitrotoluene (2,4-A), and 2,6-diamino-4-nitrotoluene (2,6-A). 2,6-A was below the detection limit of 0.006 mg/L in all samples. The byproducts of TNT were observed in the gravel-bed wetlands at the retention time of 1.5 days at concentrations approximately 10% of the influent TNT concentration (Fig. 4). The degradation of TNT in the anaerobic gravel-bed wetland is believed to have occurred via reduction of the molecule to amino derivatives to ultimately form 2,4,6-triaminotoluene (TAT) which may be further polymerized to harmless humic-like substances (Rieger and Knackmuss, 1995). The increased concentration of all the amino derivatives was about 20% of the initial TNT concentration and is comparable to results from a batch study with microcosm wetlands in aquaria where 25% of the initial TNT concentration was observed to form 4-A (Sikora et al., 1996). Both TNT degradation products, 2-A and 4-A, were observed to increase in the lagoon to approximately 2% of the initial TNT concentration in April (Fig. 4). No increase in degradation products was observed with a decrease in TNT concentration in August. The slight or non-existent increase in TNT degradation products in the lagoon system was puzzling. TNT is believed to be degraded by submergent plant species via production of nitroreductase enzymes (Wolfe et al., 1994) which should have yielded amino derivatives in the aqueous phase with a decrease in TNT concentrations as observed with parrot feather in microcosm wetlands (Sikora et al, 1996).

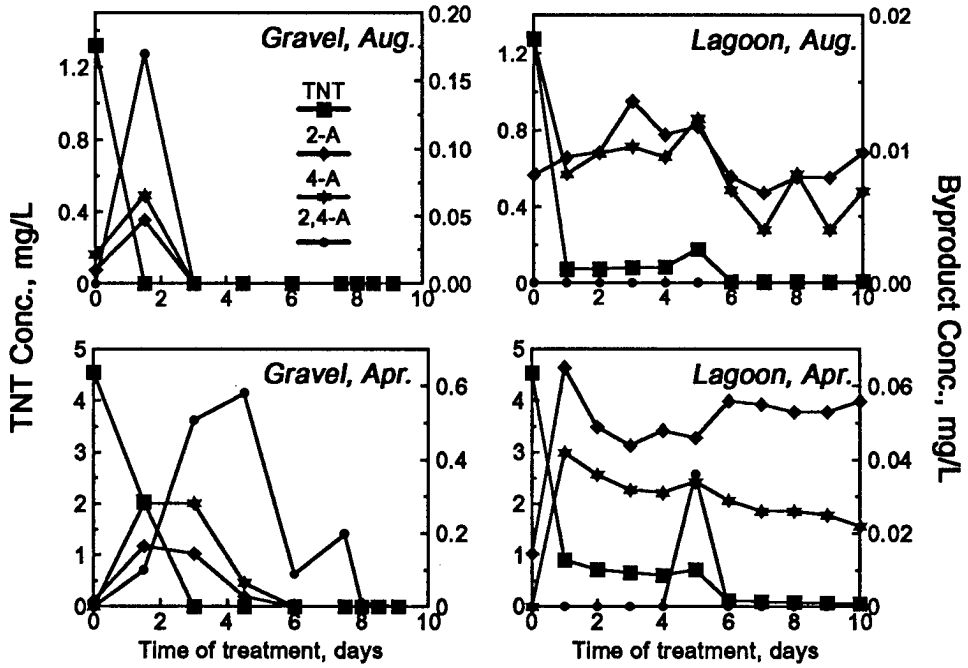



Figure 4. TNT and TNT byproducts (2-A = 2-amino dinitrotoluene, 4-A = 4-amino dinitrotoluene, 2,4-A = 2,4-diamino nitrotoluene) observed in water samples taken from gravel-bed and lagoon wetlands during sampling events in August, 1996 and April, 1997. Left y-axis is for TNT concentrations and right y-axis is for concentration of byproducts.

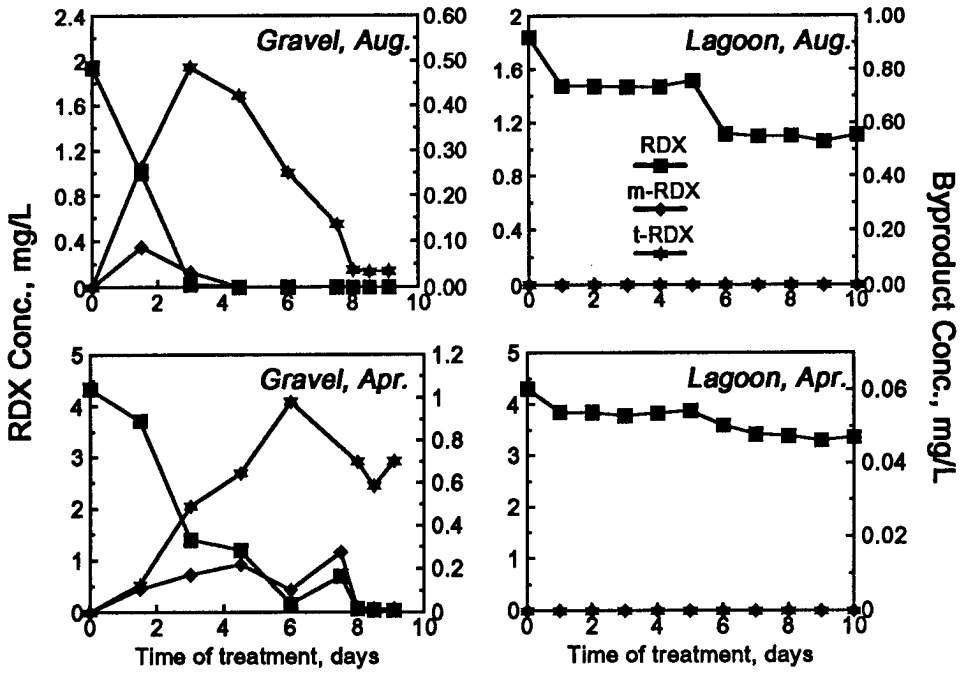



Figure 5. RDX and RDX byproducts (m-RDX = mononitroso RDX, t-RDX = trinitroso RDX) observed in water samples taken from gravel-bed and lagoon wetlands during sampling events in August, 1996 and April, 1997. Left y-axis is for RDX concentrations and right y-axis is for concentration of byproducts.

Byproducts of RDX analyzed were mononitroso-RDX (m-RDX) and trinitroso-RDX (t-RDX). Both m-RDX and t-RDX concentrations were found to increase with concurrent decrease in RDX concentration in the gravel-bed wetlands (Fig. 5). t-RDX was more persistent in the wetland water with 0.06 and 0.7 mg/L t-RDX remaining in the effluent in August and April, respectively. The RDX byproducts were not observed in the lagoon system (Fig. 5). The lack of RDX byproducts was not surprising since there was only a slight decrease in RDX concentrations.

The data presented for explosives removal using wetland systems is preliminary data describing removal in newly constructed wetlands in operation for 10 months. The project is continuing for at least one full year. Longer term observation of these systems is also desirable to determine removal of explosives in matured constructed wetlands. In addition to sampling water, sediment, gravel, and plant samples are being taken and analyzed for explosives to determine if explosives and byproducts are sorbing onto or into various components of the wetlands.

## CONCLUSIONS

Influent concentrations of TNT, RDX, TNB, and HMX were respectively 1.2, 1.8, 0.1, and 0.1 mg/L before November 21, 1996 and respectively 4.6, 4.4, 0.35, and 0.1 mg/L after November 21, 1996. The gravel-bed wetland reduced TNT and TNB concentrations below 0.002 mg/L during the entire demonstration period. Removal of TNT and TNB was complete in the lagoons during the warmer temperatures but less complete during colder winter months. The gravel-bed wetland removed RDX and HMX during warmer temperatures with less removal efficiency during colder winter months. The lagoon was very ineffective at removing RDX and HMX in the contaminated groundwater.

## ACKNOWLEDGEMENTS

The study was funded through the U.S. Department of Defense Environmental Security Technology Certification Program administered through the U.S. Army Environmental Center in Aberdeen Proving Ground, Maryland. The project manager was Darlene F. Bader with the U.S. Army Environmental Center. In addition to the authors, many people were responsible for the success of this demonstration project. Contributors to sample collection and analyses included Cathy McDonald, Earl Bailey, Jerry Clayton, and Keith Bozeman. Contributors to wetland maintenance included Jerry Berry, Danny Williams, and Eddie White. Contributors to conceptual ideas and project direction included Richard Almond and Joseph Hoagland. Contributor to engineering design of the wetlands was Randy Summers.

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# USING PHYTOREMEDIATION TO CLEAN UP CONTAMINATION AT MILITARY INSTALLATIONS

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## ABSTRACT

During and following World War II, wastes from the production of munitions and other military materials were disposed of using the best available practices acceptable at that time. However, these disposal methods often contaminated soil and groundwater with organic compounds and metals that require cleanup under current regulations. An emerging technology for cleaning contaminated soils and shallow groundwater is phytoremediation, an environmentally friendly, low-cost, and low-tech process. Phytoremediation encompasses all plant-influenced biological, chemical, and physical processes that aid in the uptake, degradation, and metabolism of contaminants by either plants or free-living organisms in the plant's rhizosphere. A phytoremediation system can be viewed as a biological, solar-driven, pump-and-treat system with an extensive, self-extending uptake network (the root system) that enhances the soil and below-ground ecosystem for subsequent productive use. Argonne National Laboratory (ANL) has been conducting basic and applied research in phytoremediation since 1990. Initial greenhouse studies evaluated salt-tolerant wetland plants to clean up and reduce the volume of salty "produced water" from petroleum wells. Results of these studies were used to design a bioreactor for processing produced water that is being demonstrated at a natural gas well in Oklahoma; this system can reduce produced water volume by about 75% in less than eight days, representing substantial savings in waste disposal cost. During 1994, ANL conducted a TNT plant uptake and *in situ* remediation study in a ridge-and-furrow area used for the disposal of pink water at the Joliet Army Ammunition Plant. Replicated plots with three levels of TNT-contaminated soil were treated with three levels of chopped hay incorporated into the surface soil and planted with two common crops to enhance *in situ* remediation. Analytical results showed no TNT uptake by crops, and TNT concentrations in the soil of all treatments were substantially reduced, indicating these low-cost treatments can be used to clean up TNT-contaminated surface soil. During 1995, greenhouse studies were initiated on zinc uptake by plants. These experiments were conducted to confirm field data from Applied Natural Sciences, Inc., indicating high levels of zinc in leaves of hybrid poplar trees growing on a zinc-contaminated site. Analytical data from the greenhouse studies show zinc was totally sequestered by the plants with concentrations of >38,000 μg/g (3.8%) zinc in the dry root tissue. Results from recent greenhouse studies show that the pattern of zinc uptake by Eastern gamagrass is similar to that of hybrid poplars. Additional studies are now being conducted to document the uptake and sequestration of other metals by plants. Because the roots sequester most of the metal taken up in many plants, the feasibility of root harvesting is being

investigated as a method to maximize metal removal from soils. Currently, studies also are being conducted to develop analytical methods for determining concentrations of these compounds and their degradation products in plant materials and to document the uptake and detoxification of organohalogens by plants. Phytoremediation systems preserve and often improve soil productivity, minimize environmental disruption, produce few or no wastes, use a natural energy source, require minimal maintenance, and cost about one-tenth as much as traditional cleanup methods.

## 1. INTRODUCTION

Wastes from the production and use of munitions and other military materials in the past were disposed of using the best available and acceptable practices for the time. Wastes were frequently discharged into lagoons or land application areas and solid waste was commonly burned. These disposal practices often resulted in an accumulation of organics and/or metals in the soil and shallow groundwater of the disposal site. Because of current concerns for the environment and human health, many of these sites are classified as hazardous waste sites that now require cleanup. The cleanup of organic and metal contaminants by means of conventional methods (thermal treatment, stabilization, soil washing) is expensive and often destroys or alters the soil, limiting the future use of the site.

Phytoremediation is an emerging cleanup technology. It is defined as the engineered use of selected green plant species to degrade, accumulate, or remove such contaminants as metals, organics, and radionuclides from soil, water, or waste streams. This definition includes all the biological, chemical, and physical processes caused by the plant, by its enzymes, or by free-living organisms in the rhizosphere. Phytoremediation takes advantage of the unique and selective uptake capabilities of plant root systems, together with the metabolism, accumulation, and translocation ability of the entire plant. Plant-based remediation systems can be viewed as biological, solar-driven, pump-and-treat systems with an extensive and self-extending uptake network, the root system.

Phytoremediation has a number of advantages when compared with conventional clean-up technologies, such as incineration or soil washing. Phytoremediation is environmentally friendly because the soil is not damaged or destroyed and secondary wastes are small in volume or can be recycled. Installation and maintenance costs of a phytoremediation system are usually a fraction of the cost of most conventional clean-up methods because it is an *in situ* process that does not require soil excavation or transport. Phytoremediation can be used for a wide range of contaminants, including organics and metals and can often be used to treat several contaminants at the same time. It is a low-tech technology that requires little or no hardware. Phytoremediation is socially acceptable because the public does not object to plants growing in its backyards.

Phytoremediation systems have been used for a number of years. An example of a simple phytoremediation system is a constructed wetland with cattails to increase pH and remove iron from acid mine drainage or remove nitrates from livestock waste lagoons and municipal sewage water[1]. Research at ANL is designed to extend phytoremediation to more complex situations. For example, phytoremediation of a site contaminated with metals and/or radionuclides involves "farming" with selected plant species or crops to "biomine" the soil and concentrate contaminants in the plant biomass[2,3]. The volume of the contaminant(s), sequestered in plant biomass, is reduced for easier disposal. For soil contaminated with organics, the approach is similar, but the plant may metabolize or assist in the degradation of the organic[4]. The potential exists for degrading hazardous organics mixed with radionuclides, thus reducing the waste to a more manageable radioactive one. Sequential cropping with phytoremediation species can reduce contaminant levels to concentrations that are environmentally acceptable, so that the site would no longer considered hazardous. The objectives of

the phytoremediation research program at ANL are to (i) identify plant species best adapted for the metabolism and accumulation of metals and organic contaminants, (ii) evaluate the most promising species under controlled greenhouse conditions, (iii) investigate the use of various soil amendments to enhance phytoremediation, and (iv) demonstrate low-cost, low-tech, environmentally friendly phytoremediation systems under field conditions.

## 2. BIOTREATMENT OF PRODUCED WATERS

Initial research in the area of phytoremediation at ANL began in 1990 with the investigation of the biotreatment of produced waters. Water that is brought to the surface from wells during oil and natural gas production is referred to as "produced water" and includes the water stripped from the oil or gas during cleanup before transport by pipeline. Produced water originates from the same geologic formation as the gas, and its most common characteristic is the elevated concentration of dissolved salt, often greater than that of sea water. Other constituents can include bicarbonates, carbonates, sulfates, hydrocarbons and other organics, and metals. Produced waters are a waste product; their constituents are considered contaminants and are subject to EPA regulations[5]. The current accepted method of disposal is by injection into deep wells, with disposal costs based on volume.

The goal of the this investigation is to develop and evaluate a biological approach to reduce the volume of produced water by using a cost-effective engineered ecosystem, called a contained plant bioreactor system. This plant bioreactor would use natural saltmarsh ecosystems as a model and incorporate salt-tolerant wetland plant species with innovative hydroponic plant growth techniques. Specific objectives to accomplish this goal include (i) identification of candidate halophyte species having attributes appropriate for use in a plant bioreactor system, (ii) conducting greenhouse evaluations to determine salt tolerance and evapotranspiration rates of the most promising species, (iii) use of the data generated in the greenhouse evaluation to develop a plant bioreactor model, and (iv) demonstration of the plant bioreactor under typical field conditions.

To develop biological treatment systems for produced waters, it was logical to look at the halophytes that have already developed a natural ability to grow and be highly productive at high external salinity levels. The plants that occupy the highly saline habitats along sea coasts, in salt and brackish marshes, in estuaries, and in dry, saline interior habitats have already undergone strong selection for their ability to tolerate salt. This large pool of plants provided candidates for evaluation and potential use in an engineered, plant-based bioreactor designed to reduce the volume of produced waters.

Because of the large number of halophytes that potentially could be evaluated, additional selection criteria were used to reduce the number of candidate halophyte species to be evaluated. Besides being tolerant to saline waters, the species should be able to tolerate metals, organics, and low fertility. Species should be easily propagated or available at low cost from commercial sources. Perennials were preferred over annuals for quick startup, a generally longer growing season, and reduced re-establishment time and cost. Because a high transpiration rate was a major consideration, fast-growing plants with extensive root systems were needed. A data base containing the attributes over 65 candidate species was assembled and the five species, one with two varieties, with the highest rating were selected for greenhouse evaluation. The plants tested were saltwater cordgrass (*Spartina alterniflora)*, dropseed (*Sporobolus virginicus*), perennial glasswort (*Salicornia virginica*), sawgrass (*Cladium jamaicense*), Vermillion saltwater cordgrass (*Spartina alterniflora* var. Vermillion), and great bulrush (*Scirpus validus*).

After a period of one to several weeks of acclimatization and growth in the nursery trays, a set of plants was selected for a greenhouse experiment to determine salt tolerance and evapotranspiration rates. Candidate plant species were tested at three salt concentrations (0%, 1.5% and 3%) in

modified Hoagland's solution[6]. Each treatment was replicated three or four times, with replicates consisting of several plants growing in a plastic bucket with the root system submerged in the appropriate salt solution. The plants in each bucket were supported by a styrofoam float, with each plant placed in a hole in the float that was just large enough to support the plant at the transition between stem and roots. The float fit snugly inside the bucket and maintained root immersion in the nutrient solution regardless of the depth. The styrofoam float also inhibited direct evaporation of water from the surface of the solution in the buckets. Thus, most water loss from the buckets with plants was from plant transpiration. In the experiment with bulrush plants, styrofoam pellets floating on the surface of the nutrient solution were used instead of the floats and had the same effect. The stems of the bulrush are rather soft and subject to bending and collapse if manipulated to any extent, as when threading the stems through the holes in the float. Another set of replicated buckets containing test solutions, but without floats or plants, was used to measure direct evaporation from the open liquid surface.

Evapotranspiration is the total amount of water evaporated from an area of plants and substrate. In the greenhouse experiments, direct evaporation from the test solution surface in the buckets containing plants was minimized by the styrofoam floats or pellets, and the principal route of water loss was by plant transpiration. Direct evaporation from the buckets was determined from the open water buckets with no plants. The water depth was measured in each bucket, using a float gauge. The observed depth, subtracted from the previous depth measurement and converted to a volume, represented the amount of water evapotranspired or evaporated during the time interval between measurements. Observed volume changes were mathematically adjusted to standardize all volumes to 24-hour intervals.

Salt concentrations in the buckets were determined by measuring the electrical conductivity of the solution at 24- or 48-hour intervals. The conductivity meter was calibrated against a set of NaCl solutions in nutrient of known concentration. Conductivity readings were converted to a value for salt concentration. When a bucket reached a predetermined minimum solution depth, nutrient solution at the same salt concentration as the starting concentration was added to the bucket to bring it to the original volume. The new salt concentration was higher than the original because all the salt added to the bucket remained and only water was lost, but the concentration was not as high as before the addition. Thus, the experimental plants experienced a fluctuating, but generally increasing, salt concentration over the course of the experiment. Such fluctuations are similar to those found in natural systems caused by tidal fluctuations. This procedure was used to measure evapotranspiration over an essentially continuous range of salt concentrations, up to the salt tolerance limit of the species. As the salt tolerance limit was approached, the plants usually went through stages characterized by a slowing or cessation of growth, severe wilting, drying up of the leaves, and eventually death of the plant.

Data from the greenhouse studies were used to design a plant bioreactor model and select the species used in the bioreactor. Because volume reduction of produced water was the primary objective, it was decided that a batch system would be the most effective. The bioreactor also would be designed in modular units so it could be adapted to the different volumes of produced water from individual wells or groups of gas wells. The bioreactor consisted of two compartments or tanks filled with an inert material to support the plants, with the second compartment about one-half the size of the first compartment. Bulrush was selected as the species for the first compartment and the more salt-tolerant saltwater cordgrass for the second compartment. Pipes connect the compartments and valves are installed at the inlet and outlet and between the compartments. A final or second storage tank is required at the well head for storage of the concentrated produced water for disposal.

The bioreactor is operated using the following procedure. The bioreactor (with all valves closed) is filled with produced water from the well head storage tank with low levels of nutrients added. When

the level of produced water in the compartments reaches about one-half the original volume, the valve on the outlet of the second compartment is opened, the concentrated produced water is drained into the second or final storage tank, and the outlet valve is closed. The valve between the compartments is opened, produced water from the first compartment is drained into the second compartment, and the valve is closed. The last step in the operation is to refill the first compartment with produced water from the well head storage and add nutrients. On the bases of data generated by the greenhouse studies, the total time required for one cycle of the bioreactor would be about 7.5 days, and the volume of produced water would be reduced by about 75%.

In 1995, a full-scale field demonstration of the plant bioreactor was installed at an active gas well in Beaver County, Oklahoma. The plant bioreactor installed is a low-cost, low-tech system. Cattle watering troughs, used as the compartments, are filled with pea gravel to support the bulrush and saltwater cordgrass. The piping, valves, and second storage tank are plastic. The system is gravity-operated and no external power is required. Produced water levels in the cattle troughs are checked daily when the well operation is checked. The only maintenance cost is the small amount of soluble fertilizer added to the produced water to maintain the plants. During operation in the summer, the bioreactor reduces the volume of produced water to about one quarter the original volume in about eight days.

The field demonstration of the plant bioreactor shows that a low-cost, low-tech system can be used to reduce the volume of produced water. The 75% reduction in volume in about eight days results in a similar reduction in produced water disposal cost. The major disadvantage of the system is the reduction in efficiency during cold weather and plant dormancy in the winter. The well operator has constructed a plastic shelter over the unit to keep it in operation during cold weather. For a more detailed description of the development and demonstration of the plant bioreactor, see Negri and Hinchman[7].

## 3. FATE OF TNT IN CROPS AND SOILS

In the past, wastes from the production of 2,4,6-trinitrotoluene (TNT) were disposed of by using the best available and acceptable practices for the time. Waste streams were frequently discharged into lagoons or land application areas and solid waste was often burned, resulting in an accumulation of TNT residues in the soil. A major environmental and human health concern is that TNT, its by-products, and degradation products could enter animal and human food chains through plant uptake by crops growing on explosives-contaminated soils.

Published information on the uptake of TNT by plants is limited to results from hydroponic and greenhouse investigations. Palazzo and Leggett[8] reported uptake of TNT by yellow nutsedge (*Cyperus esculentus* L.) from hydroponic solutions and also reported that TNT and its metabolites, 4-amino-2,6-dinitrotoluene (4A-DNT) and 2-amino-4,6-dinitrotoluene (2A-DNT) were found throughout the plants. Folsom et al.[9] and Pennington[10] also studied TNT uptake by yellow nutsedge from soil amended with TNT, and they reported minimal uptake of TNT by plants. Banwart and Hassett[11] studied the effect of organic residue additions on plant tolerance and extractable TNT from TNT-contaminated soil. Initial TNT levels in the soil were 1,000 and 2,000 mg $kg^{-1}$, and species tested were perennial ryegrass (*Lolium multiflorum* Lam.), sorghum x sudangrass (*Sorghum bicolor* x *S. sudanense* (L.) Moench.), and alfalfa (*Medicago sativa* L.). Little or no growth occurred on unamended soil, but growth and dry matter production were dramatically improved with an addition of 5% (by weight) ground wheat straw (*Triticum aestivum* L.). TNT in soil originally containing 2,000 mg $kg^{-1}$ TNT amended with wheat straw was less than 2% of the initial value after 90 days of crop growth. Cataldo et al.[12] also studied the fate and degradation products of explosives in soils and three plant species: wheat, "Blando" brome (*Bromus mollis* L.), and bush beans. Plants were grown for 60 days in explosives-amended soil. They reported about 70% of the TNT underwent

transformation to A-DNT isomers and unknown chemical species. Explosive uptake by plants appeared to be dependent on soil properties and plant species. TNT uptake in its original form was low, with TNT residues primarily accumulated in plant roots. The majority of contaminants found in plants grown in TNT-amended soils was in the form of 2A- and 4A-DNT. Both of these compounds were also found primarily in root tissues. The highest TNT uptake was observed in plants grown in the soil with the lowest organic matter content. The nonextractable fraction of TNT increased more rapidly and to higher levels in soil with higher organic content compared with a soil with lower organic content. Results from these investigations indicate uptake of TNT and/or its degradation products by plants grown under greenhouse and hydroponic conditions, but data are not available on plants grown under field conditions. Objectives of this field investigation were to determine: (i) explosive uptake by crops grown on TNT-contaminated soils, (ii) the influence of organic material additions to TNT-contaminated soils on TNT uptake by crops, and (iii) the effect of organic material additions on levels of TNT in contaminated soils.

This investigation of the fate of TNT in crops and soils was conducted at government-owned, contractor-operated Joliet Army Ammunition Plant (JAAP). This facility was constructed in the early 1940s for the production of munitions during World War II. The site selected at JAAP for sampling the crop uptake experiment was Group 61. Group 61 facilities were originally constructed in 1941 for crystallizing ammonium nitrate, but were expensively modified in 1945 to reclaim TNT from high-explosive shells. Shell reclamation operations involved the removal and recovery of explosives and a shell-washout operation. Process water (pink water) from the washout operation was disposed of by evaporation and infiltration in a 1.6-ha ridge-and-furrow area (R&FA). All operations at Group 61 ceased in the mid-1950s; in the 40 years following the closure of the Group 61 facilities, erosion has partially leveled the ridges and filled the furrows. After 40 years, the presence of TNT in the furrow surface soil is still evident by a reddish color and lack of vegetation.

Design of the crop uptake experiment involved three levels of soil TNT contamination (high, intermediate, and zero), three levels of organic material additions (high, intermediate, and zero), two crops (forage and small grain), and four replications of each treatment (soil TNT level, organic material addition, crop). Crop establishment and growth were observed and roots, forage, straw, and grain analyzed to determine the influence of TNT level, organic material addition, and crop type on TNT uptake. Soil samples were periodically collected and analyzed to determine the influence of hay additions on concentration of TNT in the soil.

During the fall of 1993 information from a previous investigation[13] and results from soil analyses from samples collected in the R&FA were used to select locations for three 16 m by 24 m areas in the Group 61 at JAAP. High and intermediate TNT-contaminated areas were within the R&FA, while the zero TNT area was in an uncontaminated area next to the R&FA. Arrangements were made with a local contractor to perform soil mixing in the areas during October 1993, and mixing was done by using the following method. Along one edge of the area, parallel with the original furrows, a road grader was used to excavate a trench to a depth about 15 to 20 cm below the original furrow bottom. Soil from the trench was rolled along the length of the blade to mix the surface soil with soil from the lower depths. A second trench was excavated parallel and next to the original trench, with the soil rolled along the blade into the first trench. This operation was repeated across the width of the area. The area was then disked to further mix the soil and smooth the surface. Following disking, the soil was mixed again, using the road grader, but the operation started at the opposite edge of the area. The sequence of excavating with the grader and disking was repeated several times in an attempt to uniformly distribute TNT-contaminated soil throughout the upper 15 to 20 cm of the area soil. After each session of grading and disking, five soil samples were taken from random locations near each of the corners and the center of the area. Each sample was analyzed for TNT concentration, using the field method developed by Jenkins[14]. If the results of the five samples were not within 20% of each other, the area was graded and disked again.

Following the soil mixing operation, each area was divided into 4 m by 4 m plots. Level of organic material addition, crop, and replicate number for each plot for each TNT level area were randomly assigned. Application and incorporation of ground smooth bromegrass hay, purchased from a local farmer, was the next step in plot preparation. Ground hay at rates of 1 and 2% (46 and 92 kg per plot) was weighed for each plot, spread on the soil surface, and incorporated into the soil by using the tractor-mounted rototiller. On 28 October 1994, fertilizer was applied to all plots at a rate equivalent to 224 kg $ha^{-1}$ nitrogen and 112 kg $ha^{-1}$ $P_2O_5$. Following the application of fertilizer, all plots were rototilled and seeded. The small grain crop was soft red winter wheat (*Triticum aestivum* L.) seeded at 135 kg $ha^{-1}$, and the forage was common perennial ryegrass seeded at 13.5 kg $ha^{-1}$. Both wheat and ryegrass seed were hand-broadcast and the plots lightly raked after seeding to cover the seed. A composite soil sample was collected from each plot immediately following seeding. The late planting date and below-normal rainfall after seeding resulted in a complete failure of both the ryegrass and winter wheat on all plots, including the control plots. As a result, all plots were tilled using the tractor-mounted rototiller and replanted on 22 March 1994. Procedures were the same as those used during the October planting, with one exception: oat broadcast at 125 kg $ha^{-1}$ was planted in place of the winter wheat. Rainfall received at the site remained well below normal through June, resulting in poor stand establishment of both oat and ryegrass on all plots, including control plots. On 7 June 1994, barren areas in all the plots were raked, reseeded with oat or ryegrass, and the seed covered by lightly raking.

Oat harvest and initial ryegrass samples were collected on 19 July 1994. Plants were clipped about 2.5 cm above the soil surface within the center square meter of each plot. Care was taken not to include plant material that had been in direct contact with the soil and to prevent contact of the plants sampled with the soil. Plant tops from each plot were bagged as a single sample, but oat grain was separated from the straw in the laboratory for separate analysis. Soil in the root zone was loosened, the root mass of the sampled plants extracted, excess soil removed, and roots bagged for transport to the analytical laboratory. A second sampling from the ryegrass plots was conducted on 21 September 1994, using the procedure described above. Soil and plant analyses were performed in a U.S. Army Environmental Center (USAEC) certified laboratory at the University of Illinois at Urbana, Illinois. U.S. EPA SW-846 method 8330 was used to determine concentrations of TNT and its derivatives in soil samples. A method developed by Banwart and Hassett[11] was used to analyze plant materials for TNT and its derivatives.

The crop uptake experiment at JAAP was compromised by a number of problems sometimes encountered in field studies. One problem was the heterogeneity of TNT in the soil within plots and areas. Regulations require that any contaminated soil that is picked up must be decontaminated before being put down. This presented a soil mixing problem, because the TNT was concentrated in the surface soil of the furrow bottoms and furrows were on about 2.1-m centers. Although soil in the areas was repeatedly mixed by using the road grader, disk, and rototiller, TNT-contaminated soil was not evenly distributed throughout the areas of plots. Composite soil samples were collected from plots after application of the ground hay and analyzed. Mean TNT concentration in the high TNT area was 1120 mg $kg,^{-1}$, but plots ranged from 72 to 2690 mg $kg^{-1}$, with a coefficient of variation (CV) of 72%. In the intermediate area, the mean TNT concentration was 119 mg $kg^{-1}$ and plots ranged from 1 to 525 mg $kg^{-1}$ with a CV of 123%. Other problems encountered in this field study were related to incorporation of the ground hay, project schedule, and weather. Amounts of ground hay incorporated into the soil had to be reduced because it was impractical to incorporate the designed amount of 5 and 10% into the soil with equipment available. The late planting date and below-normal rainfall resulted in a complete crop failure of the fall seeding. All plots were tilled and seeded again during March, resulting in dramatic change, and often increase, in soil TNT concentration on many plots. Immediately after tilling, mean TNT concentration in the high TNT area was 2021 mg $kg^{-1}$, and plots ranged from 76 to 5780 mg $kg^{-1}$ with a CV of 76%. The new mean for the intermediate area was 108 mg $kg^{-1}$, and plots ranged from 1 to 871 mg $kg^{-1}$, with a CV of 179%. These data indicated that instead of replicates with about equal TNT concentrations in plots,

there was a continuum of TNT concentrations ranging from 1 to almost 5900 mg $kg^{-1}$ of TNT in soil. Below-normal rainfall continued throughout the spring and early summer, resulting in a poor stand of the ryegrass and oats. Spot reseeding of crops during June resulted in an uneven stand of both crops. These factors affected the original design and potentially the results of the experiment.

Stands of both ryegrass and oat on most plots, including control plots, were less than normal, probably due to low germination rates caused by dry seedbed conditions following seeding on 22 March. Following spot reseeding of all plots on 7 June, it became apparent that ryegrass was not becoming established on most of the plots in the high TNT area. Only scattered plants became established on several plots in the high TNT plot. The soil surface in these plots had a reddish color, indicating the presence of TNT. Comparison of TNT concentrations from barren plots with that on plots having crop growth showed TNT levels were generally higher on barren plots. The level of hay addition did not influence the establishment of ryegrass in the high TNT plot because all but one ryegrass plot remained barren. This would indicate there is some difference in TNT tolerance between ryegrass and oat. During the summer, there also appeared to be some differences in plant growth among plots in the intermediate TNT area and control area. Establishment and growth of ryegrass and oat were better on plots with hay added, with some apparent difference between levels of hay additions.

Data on the uptake of explosives by crops are not reported because neither TNT nor any of its degradation products were found in the ryegrass tops, oat straw, or oat grain from any of the plots. TNT was not detected in any root samples, but 4A-DNT, and 2A-DNT were found in some of the root samples of both crops. There was no apparent relationship between soil TNT concentrations and presence of 4A-DNT and 2A-DNT in root samples. Ryegrass and oat have fibrous root systems, and the presence of these compounds may be due to contamination by soil not removed during root washing.

Results from greenhouse investigations[11,12] indicate levels of TNT are reduced in soils with higher organic content or by the addition of organic material to soils. This portion of the study was intended to determine if this relationship (observed under greenhouse conditions) also existed in the field. The original experimental design for this study was intended to duplicate some of the variables tested by Banwart and Hassett[11] in their greenhouse investigation. Two levels of soil TNT contamination with replicate plots of known and uniform soil contamination were required to statistically analyze data. A major complicating factor in this field study was the heterogeneity of TNT contamination in plot soils. A part of the original experimental design was also intended to duplicate the 5% and 10% (by weight) organic material additions used in the greenhouse study. However, incorporation of these large volumes of bromegrass hay into the upper 15 cm of plot soil in the field was impractical with equipment available. These factors compromised the field investigation with respect to determining changes in extractable TNT from soil due to level organic material additions.

Table 1 shows concentrations of extractable TNT in soil in plot 20 (high TNT area, 1% hay addition, ryegrass, replicate 4) during the study. Initial sample collection was on 28 October 1993 and the final sample collection was on 21 September 1994. The concentration of extractable TNT decreased by more than 82% by 10 December and continued to decrease to only about 1.6% of the original concentration by 19 July. This decrease in TNT concentration is similar to results reported by Banwart and Hassett[11]. However, the concentration increased slightly, to about 3.4% of the original concentration, on 21 September. Of the 48 plots in this study, this plot is the best example of the expected decrease of TNT in soil. Unfortunately, results from this plot are not typical of the general response observed.

TABLE 1. TNT CONCENTRATION IN PLOT 20† SOIL ON EIGHT COLLECTION DATES (mg $kg^{-1}$)

| 28 Oct | 10 Dec | 17 Feb | 22 Mar | 26 Apr | 7 Jun | 19 Jul | 21 Sep |
|---|---|---|---|---|---|---|---|
| 2220 | 388 | 357 | 259 | 249 | 85 | 35 | 74 |

† High TNT area, 1% hay addition, ryegrass, replicate 4.

Table 2 shows the mean concentration of TNT in plot soils with three levels of hay additions in the intermediate and high TNT areas on eight collection dates. Each mean represents eight observations: four replications of each of the oat and ryegrass plots. Mean concentrations of TNT in the intermediate TNT area with 2% hay added generally decreased during the study, with the exception of increases on 22 March and 19 July. The increase on 22 March was about 65% more than the original mean concentration, and the increase on 19 July was twice the mean concentration on 7 June. All plots were tilled and reseeded on 22 March, and soil samples were collected after plots were tilled. Values from plots varied widely following tillage. Mean concentrations of TNT in the intermediate TNT area that did not receive hay also generally decreased during the study, again with two notable exceptions. The first, on 26 April, was probably related to the spring tilling on 22 March, and the second, on 21 September, was due to very high values from two of the eight plots. Without these two high values, the mean would have been 15.1 mg $kg^{-1}$. Means of TNT concentration from the intermediate TNT area plots with 1% hay added show no trend, only wide variability. Extractable TNT values of individual plots often indicate that one or more values for each sampling date were one or two orders of magnitude higher than other plot values. Mean TNT concentrations in the high TNT area for plots of all three hay additions decreased following the initial sampling, but means for later sample collections indicate this trend did not continue. Values for individual plots varied widely from one sample collection to the next.

TABLE 2. MEAN TNT CONCENTRATIONS IN SOIL ON EIGHT COLLECTION DATES

| TNT Area | Hay Addition (%) | Concentration (mg $kg^{-1}$) by Collection Day and Month | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 28 Oct | 10 Dec | 17 Feb | 22 Mar | 26 Apr | 7 Jun | 19 Jul | 21 Sep |
| Int† | 0 | 170‡ | 151 | 133 | 111 | 201 | 87.7 | 47.9 | 203 |
| Int | 1 | 150 | 573 | 89.1 | 159 | 1230 | 244 | 427 | 447 |
| Int | 2 | 37.0 | 29.9 | 21.1 | 61.5 | 4.9 | 8.1 | 16.1 | 3.1 |
| High | 0 | 1260 | 891 | 1090 | 2590 | 902 | 1140 | 2700 | 726 |
| High | 1 | 1290 | 937 | 1170 | 2310 | 2090 | 2410 | 2540 | 2450 |
| High | 2 | 808 | 742 | 688 | 1170 | 922 | 3580 | 567 | 651 |

† Intermediate.

‡ Each mean represents eight observations, four replications of each for oat and ryegrass plots.

Trends of means shown in Table 1 and of 0 and 2% hay additions for the intermediate TNT area in Table 2 confirm results reported by Banwart and Hassett[11] and Cataldo et al.[12]. The most probable explanation for the decrease in TNT concentration in the soil is that TNT is degraded by microorganisms and enzymes in the soil and/or rhizosphere. Adding organic material to a soil increases nutrient levels, with corresponding increases in microorganism activities and populations. Concentrations of TNT degradation products 4A-DNT and 2A-DNT were determined for plot soil samples. A trend was noted in concentrations of these degradation products in the intermediate TNT plot. Generally, if the concentration of extractable TNT was high, concentrations of 4A-DNT and 2A-DNT were often below detection limits. As TNT levels decreased, concentrations of 4A-DNT and 2A-DNT increased to a maximum of about 15 mg $kg^{-1}$. As the concentration of TNT approached the detection limit, concentrations of these degradation products also decreased. The

presence of 4A-DNT and 2A-DNT indicates microorganisms and enzymes in the soil and/or rhizosphere are degrading TNT if conditions for their survival are favorable.

Results from this study indicate TNT and its degradation products are not translocated to plant tops in crops growing on explosives-contaminated soils. 4A-DNT and 2A-DNT were sometimes found to be associated with plant root samples growing in TNT-contaminated soils. Because TNT, 4A-DNT, and 2A-DNT were not detected in the aboveground portions of plants, vegetation growing on TNT-contaminated soils is not considered a health hazard. However, soil and plant roots may contain TNT degradation products that may be toxic, and their consumption is not advised. Crop uptake of TNT was not changed by the level of hay addition because neither TNT nor its degradation products were detected in any aboveground crop tissues. Data from this investigation show that phytoremediation, the addition of organic material (chopped hay) combined with the growing of green plants, is a viable option for the remediation of surface soils contaminated with low levels of TNT. For a complete description of this study, see Zellmer et al.[15] For an additional investigation of explosives uptake by plants at the Iowa Army Ammunition Plant, see Schneider et al.[16]

## 4. METAL UPTAKE AND ACCUMULATION

Much of the current research on the uptake and accumulation of metals by plants involves "traditional" hyperaccumulators, many of which are small, shallow-rooted plants in the Cruciferae (mustard) family. Phytoremediation research at ANL is expanding the definition of hyperaccumulators to include large, robust woody and herbaceous species that have high evapotranspiration rates. These plants process more soil solution containing dissolved metals, and this higher rate of water use draws more soil solution to the plant root system, sequestering metals in the plant.

Interest in using woody species with high evapotranspiration rates was initially generated when elevated levels of zinc were observed in the leaves of hybrid poplar (*Populus* sp.) trees at a field site. Applied Natural Sciences, Inc. (ANS), had planted and was monitoring hybrid poplars to remediate nitrate and ammonia contamination at a site. The site contained a buried galvanized piping system that is believed to be the source of zinc in the soil solution. ANS uses trees as phytoremediation plants to remove contaminants from soil and groundwater to depths as great as to 12 m (40 ft) in a trademarked process called "Treemediation"[17]

The observed elevated zinc concentration in the poplar leaves and a mutual interest in phytoremediation led to the development of a Cooperative Research and Development Agreement (CRADA) between ANS and ANL. The CRADA partnership provides an effective way to bring observations from the field into the controlled environment of a greenhouse for detailed investigation and a method to transfer laboratory research results back to the field. Objectives of CRADA partnership research with ANS are to (i) identify plant species best adapted for the uptake, accumulation, and degradation of specific contaminants; (ii) evaluate these species in controlled greenhouse experiments; (iii) explain the physical, chemical, physiological, and metabolic mechanisms of contaminant uptake, translocation, sequestration/detoxification, partitioning, and bioaccumulation in phytoremediation plants; and (iv) demonstrate low-cost, low-tech, environmentally friendly phytoremediation systems for remediating metal, radionuclide, and organic contaminants economically at contaminated sites.

During late March 1995, greenhouse experiments were initiated to confirm and extend field data from ANS observations of high levels of zinc in leaf tissue of hybrid poplars. After the poplar cutting had developed a normal root system in June, three groups of cuttings, with three replicates each, were given five increasing doses of zinc during a period of about two months. Cuttings were grown in lysimeters filled with quartz sand to prevent the zinc from binding on the growth substrate.

Analysis of leachate from control lysimeters with quartz sand, but no plants, showed zinc concentration in nutrient solution remained unchanged. The zinc was given in five doses in nutrient solution spiked with $ZnSO_4$, with concentrations ranging from 50 to 2,000 mg $L^{-1}$ Zn. On each zinc addition date, two groups received increasing doses up to 1,500 and 2,000 mg $L^{-1}$ Zn, respectively, while a control group received only nutrient solution containing a low concentration of zinc as an essential nutrient. Available zinc analyses of the nutrient solution showed the levels of zinc were equivalent to many times the levels of available zinc in "normal" soils. Before each zinc addition, sand samples and plant tissues (roots, leaves, and branches) were collected to determine how much zinc remained in the sand, and to track zinc translocation and partitioning of bioaccumulation in poplar aboveground tissues.

The poplars were watered daily, and leachate that passed over the poplar roots and through the lysimeters was collected after each watering. Leachate volume, conductivity, and pH were measured daily to determine the evapotranspiration rates, nutrient use, and biomass increase of the rapidly growing poplar cuttings. Fresh nutrient solution and/or water was added to the leachate before it was recycled to replace water lost by evapotranspiration. Measurement of the transpiration rate was considered to be a critical factor because it determines the rate at which contaminated soil solution is drawn into the plant to be processed.

Leachate analyses showed that in all cases with zinc additions up to 800 mg $L^{-1}$, the zinc was totally absorbed and sequestered by the plants in about four hours during a single pass through the lysimeters. At zinc additions above 1,000 mg $L^{-1}$, leachate levels were always below 100 mg $L^{-1}$ in samples taken on the same day as the zinc addition after only one pass through the lysimeter. Zinc levels in the leachate increased the following day, to concentrations up to about 550 mg $L^{-1}$ in the lysimeters that received 2,000 mg $L^{-1}$ Zn, and then decreased sharply during second the day, to concentrations less than 100 mg $L^{-1}$. After that, zinc concentrations steadily decreased as the plants reabsorbed the zinc as the nutrient solution was cycled through the lysimeters on subsequent days.

Even at the highest zinc application, there were only subtle visual toxicity symptoms: slight leaf chlorosis and some leaf "drooping" in the poplar cuttings compared with the control plants. However, in plants that received more than 800 mg $L^{-1}$ Zn, the evapotranspiration rate decreased significantly as zinc concentration in the roots increased, indicating this physiological effect could have complex causes.

The hybrid poplar plants in the lysimeter pots were harvested in early September 1995. Aboveground tissue was divided into four categories; mature leaves, expanding leaves, old wood, and new wood. The sand was removed from the lysimeters as a "cylinder," without disturbing the roots, sand samples were collected, and the sand was washed from the root system with deionized water. Roots were divided into four types based on appearance, morphology, and color. Type A roots were the clumps of new white or light-colored roots, and type B roots originated at the ends of large, woody roots. Type C roots were very fine, hairlike, dark-colored roots that densely covered the surfaces of the woody roots, and type D roots were the large-diameter, non-woody, fine roots, grayish to brownish, in the bottom of the lysimeter, which was saturated most of the time.

Several leaf harvests were made during the experiment (zinc concentrations in tissues are on a dry-weight basis). Initial leaf samples from plants that received a single dose of 50 mg $kg^{-1}$ Zn showed 528 mg $kg^{-1}$ Zn in the large mature leaves, 300 mg $kg^{-1}$ in medium-sized leaves, and 140 mg $kg^{-1}$ in small leaves. In the leaves and branches harvested at the end of the experiment, zinc concentrations did not exceed 2,250 mg $kg^{-1}$ in the dry leaf tissue and 900 mg $kg^{-1}$ in the woody branches. Roots harvested at the end of the experiment showed much higher concentrations of accumulated and sequestered metal than did any of the aboveground tissues. In the lysimeters receiving the highest dose, 2,000 mg $L^{-1}$, type D roots contained a mean concentration of 38,055 mg $kg^{-1}$ (3.8%) Zn, type C had 15,470 mg $kg^{-1}$, type A had 12,225 mg $kg^{-1}$, and type B had 2,814 mg $kg^{-1}$. The lysimeters

receiving the lower zinc doses with a maximum of 1500 mg $L^{-1}$ had a similar pattern of distribution of zinc among root types, with the type D roots containing a mean concentration of 17,053 mg $kg^{-1}$ (1.7%) Zn. The control lysimeters also showed the same zinc uptake pattern among root types, with the mean concentration for the D roots being 232 mg $kg^{-1}$. This zinc was from the nutrient solution that contained zinc as an essential nutrient.

The hybrid poplar greenhouse experiments complement field studies and data collection on zinc uptake by hybrid poplars that are growing under field conditions, using the Treemediation® system installed by ANS. The implications for engineered soil and wastewater clean-up systems that use hybrid poplar growing either directly in the soil or in special hydroponic systems are very encouraging.

During April 1996, an experiment was started to determine the uptake and accumulation of zinc by Eastern gamagrass (*Tripsacum dactyloides*). Methods used were nearly the same as those described for the hybrid poplar experiment. Three groups of gamagrass plants, each group consisting of five replicates, were continuously given zinc in nutrient solution over a period of about two months at concentrations of 160 mg $L^{-1}$, 600 mg $L^{-1}$, and a control with only the zinc present in the nutrient solution.

Leachate analyses for zinc indicate that initially plants subjected to both levels of zinc were removing up to 70% of the zinc from the leachate. After two months, the plants receiving 160 mg $L^{-1}$ Zn had grown considerably and were almost the same size as the control plants, but some of the mature leaf blades were rolled. The mean zinc removal rate for these plants had dropped to 50% of the zinc in the leachate. At this time, the plants receiving 600 mg $L^{-1}$ Zn were smaller than the controls, their color was a darker green, most of the mature leaf blades were rolled, and the mean zinc removal rate was only about 30% of the zinc in the leachate.

In mid-June 1996, the gamagrass was harvested, using the same procedure described in the poplar experiment. The plants were divided into shoots (leaves and crowns) and roots. The root systems of all the plants had the typical structure of large primary roots and smaller, lateral, secondary roots. In the controls, most of the roots were light in color, with the newest roots being white. The plants receiving the 160 mg $L^{-1}$ Zn had root systems almost as large as the controls, but some of the secondary roots were dark colored or black. The plants that received 600 mg $L^{-1}$ Zn had small root systems with many black roots.

As observed in the hybrid poplar experiment, the Eastern gamagrass roots showed much higher concentrations of zinc than did the shoots. In the lysimeters receiving 600 mg $L^{-1}$ Zn, the roots contained a mean concentration of about 10,000 mg $kg^{-1}$ (1.0%) Zn on a dry-weight basis, while the tops contained about 1,000 mg $kg^{-1}$ (0.1%) Zn. In the plants receiving 160 mg $L^{-1}$ Zn, the roots contained about 4,000 mg $kg^{-1}$ Zn, and the tops about 400 mg $kg^{-1}$ Zn. The roots of the control plants contained about 75 mg $kg^{-1}$, and the tops about 50 mg $kg^{-1}$ Zn. Again, the small amount of zinc in the controls is from the zinc present in the nutrient solution as an essential nutrient.

The levels of sequestered zinc observed in both the gamagrass and hybrid poplar roots exceed the levels found in either roots or tops of many of the known hyperaccumulator species. It is hypothesized that the greater portion of the zinc is sequestered in the cell wall tissue of the root cortex through internal complexation and detoxification, with translocation of a relatively small amount of the zinc to the leaves and branches. The evapotranspiration rate of the hybrid poplar decreased significantly as zinc concentration in the roots increased. Both top growth and evapotranspiration rate of the gamagrass decreased at the higher zinc level as a constant dose. For a more detailed description of zinc uptake and accumulation studies, see Negri et al.[18]

Results from these greenhouse studies and the field experience of ANS indicate that a number of species can be used for the uptake and accumulation of metals, in addition to the traditional hyperaccumulator species. Another major factor influencing metal uptake and accumulation is the evapotranspiration rate of the plant species. The higher the evapotranspiration rate, the larger the volume of water that is pumped through the phytoremediation system. A high rate of water consumption draws more soil solution to the plant roots, resulting in a higher exposure of soluble metals to the root system. A high evapotranspiration rate requires a large, robust plant with an extensive root system. For the phytoremediation of many sites, perennial woody plants are preferred because woody plants generally have deeper root systems and perennials have a longer growing season. Results from the greenhouse studies show the highest proportion of metals is accumulated in the roots. Plans are now being formulated to evaluate root harvesting methods to remove the highest concentration of metals from a site with metal contamination in surface soils.

Several other greenhouse investigations are being conducted to evaluate other aspects of phytoremediation. A key factor controlling the rate at which metals are removed from the soil by plant-based clean-up systems is the availability of the metal to the plant. Metals are bound to soil components in varying degrees, depending on such soil conditions as pH, clay content, organic matter, and redox potential. Only the readily soluble or exchangeable metals are available to plants. One way to increase metal availability is to selectively increase their concentration in the soil solution by using chelating agents. Chelating agents increase metal diffusion in the soil solution and keep the metals in plant-available forms. Natural chelating agents (organic acids, such as citric and acetic) are released by plant roots, making the ions of both nutrients and contaminants more mobile in the soil. Plants can usually break the chelation bond, take up the metal, and release the chelant back into the soil solution.

Current greenhouse experiments are investigating the feasibility of utilizing various chelating agents to induce the release of metals and increase the rate and extent of metal accumulation in plant tissues. These experiments are measuring changes in concentration of metals (Zn, Cd, Pb, Cu) and radionuclides (U and Th) in soil/sediment from the Miami-Erie Canal, near Miamisburg, Ohio. This soil, although considered "clean," has concentrations of these contaminants sufficient to provide information on the relative changes in plant accumulation induced by the addition of chelating agents. Willow plants are being grown in soil-filled lysimeters that are periodically irrigated with constant doses of dilute chelating agents in aqueous solution. Periodically, soil and plant tissue samples are collected and analyzed for metals and radionuclides. The soil samples have been analyzed by sequential extraction techniques to provide empirical information on the probable contaminant species present and the relative percentage of the total contaminant content. Plant concentration is considered as an additional sequential extraction step that represents the sum of metal species that are effectively taken up by the plant.

For many organic contaminants, such as trichloroethylene (TCE) and tetrachloroethylene (PCE), there is evidence that plants can degrade the organohalide to form less volatile compounds, such as trichloroacetic acid (TCAA). The less volatile compounds are sequestered in the plant tissue, while the remainder, passes out of the leaf tissue with the transpiration stream. In hybrid poplar and several other species, there is evidence for an enzyme that breaks down TCE and PCE to TCAA in the plant. A study at ANL is developing rapid, easy, gas chromatographic analytical methods for the detection of TCAA in woody plant tissue. Samples of plant tissue have been analyzed using this new method, and results are being correlated with the presence and concentration of TCAA in plants and the contamination "history" of the site where the samples were collected. This method has the potential for monitoring phytoremediation systems used to cleanup groundwater and soil contaminated with organohalides. The analytical method also can provide a very quick and easy way to determine organohalide contamination by using plant tissue samples, rather than obtaining soil and groundwater samples by coring or drilling operations.

## 5. CONCLUSIONS

As with any remediation method, phytoremediation is not a panacea and it has limitations. Phytoremediation is only effective while the plants are actively growing; it slows down or stops during plant dormancy. Some contaminants are toxic at low concentrations to plants, and some sites may have contaminant concentrations that are too high and toxic for the phytoremediation plants to survive and grow. At other sites, the contaminant may be too deep in the soil for the root system to reach, even using special planting techniques. Phytoremediation can be a slow process and site cleanup may require years, but often the additional time required for remediation can be offset by the much lower cost.

Phytoremediation has a number of advantages compared with such remediation methods as soil incineration. It is an *in situ* process and doesn't require excavation or transport of contaminated soil. Phytoremediation is low-tech, requiring little if any hardware or operational facilities. Installation and maintenance costs are normally a fraction of those of other remediation methods. Phytoremediation does not damage the physical, chemical, or biological properties of the soil, and often the process improves soil fertility and conditions. It can be used for a number of contaminants and can often be used to remediate several contaminants at the same time. A major advantage of phytoremediation is that it generates little or no secondary waste. Finally, it is socially acceptable, because the public does not object to plants growing in its back yards, as it sometimes does to a soil incinerator or other remediation facilities.

## 6. ACKNOWLEDGMENTS

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# The Role of Groundwater Modeling and Simulation in Support of Military Installation Cleanup

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## ABSTRACT

Activities at Department of Defense (DoD) installations have produced contamination of groundwater resources which may pose problems for human health and the aquatic environments adjacent to or on these posts. The U.S. Army Engineer Waterways Experiment Station (WES), in concert with the U.S. Army Environmental Center (AEC) and Headquarters, U.S. Army Corps of Engineers, is leading a consortium of Army, Air Force, Department of Energy, Environmental Protection Agency, and academic researchers in the development of a new state-of-the-art in subsurface modeling: the Groundwater Modeling System (GMS). The GMS has been developed as an aid for site characterization, and for simulating groundwater and unsaturated zone flows, the transport/fate of subsurface contaminants, and the efficacy of remedial actions associated with contaminated groundwater resources at DoD installations and other federal sites. The system is modular in design for operation across a variety of computing platforms. The system has been fielded and is in use for a number of site-specific project applications. The present capabilities of the GMS to support remedial design, and those planned over the next few years, are discussed below.

## 1. INTRODUCTION

The productive use of subsurface flow and transport modeling is a prime concern within the Department of Defense (DoD). The U.S. Army Engineer Waterways Experiment Station (WES) leads a consortium of U.S. Army, Air Force, Department of Energy (DOE), Environmental Protection Agency (EPA), and academic researchers in the development of a new state-of-the-practice in subsurface modeling: the Groundwater Modeling System (GMS). The GMS is an aid for site characterization, for assessing the risk of contaminant exposure to ecological and human populations, and for evaluation of the efficacy of remedial and wellhead protection actions associated with contaminated groundwater resources at DoD installations and other federal sites. The system is modular and operates across a variety of computing platforms. Version 2.0 of the GMS provides full connectivity to six subsurface flow and transport models, visualization, animation, geographic information systems, and parameter estimation under a single consistent user environment. A number of research initiatives related to characterization of the impacts of subsurface heterogeneities on

remedial effectiveness, mathematical description of flow and transport processes for military-unique contaminants, optimization of remedial alternatives, and computational efficiency on multiple computing platforms, are ongoing that are producing new modeling tools. These new system components will continue to be implemented in the GMS through 1999.

## 1.1 PROGRAMMATIC OBJECTIVES

The Groundwater Modeling Program (GMP), particularly the development of the GMS, is being conducted to meet the needs of DoD cleanup specialists (and others) for integrated engineering tools which aid in the evaluation of the efficacy of various remediation alternatives in a straightforward and scientifically defensible manner. This is the central objective of the GMP. This objective is accomplished through use of numerous multi-dimensional numerical models applicable to the wide variety of conditions found within different geologic media involving the physical, chemical and biological processes (and the uncertainties thereof) associated with contaminants of concern to DoD. These models are being enhanced and/or developed to operate efficiently on multiple computing platforms including scalable parallel systems (under the auspices of the DoD Common High Performance Computing Software Support Initiative). The modeling tools are integrated into a singular computational environment from which users can access multiple resident subsurface analysis tools, subsurface numerical models, site conceptualization tools, visualization/animation, and parameter estimation routines. This computational environment operates seamlessly on both UNIX and personal computer architectures. It is expected that the above development will result in modeling tools whose use will reduce the costs of characterization and remediation by from 10 to 20%. This could result in savings DoD-wide of hundreds of millions to billions of dollars.

## 1.2 PROGRAM TECHNICAL INVESTIGATIONS

Presented below are tables listing each GMP major milestone and investigation funded or proposed for the period 1994 - 1999. Discussion of each of the products and/or investigations presented in the tables, which group into seven highly integrated task areas, is beyond the length available for this paper. Note, however, that there is a significant amount of extramural research, an indication of the high level of synergism and leveraging between academia and government researchers, within the GMP. Also note that there are additional studies being conducted by the partnering agencies that will be leveraged by the GMP in the future. The partnering agencies include: DOE's Lawrence Livermore National Lab (LLNL), Argonne National Lab (ANL), Pacific Northwest National Lab (PNNL), and Los Alamos National Lab (LANL); Air Force Armstrong Lab/EQ (AL/EQ); Air Force Office of Scientific Research (AFOSR); Army Research Office (ARO); Army Cold Regions Research and Engineering Lab (CRREL); Army High Performance Computing Research Center (AHPCRC); Army Environmental Center (AEC); EPA's Athens Environmental Research Lab (AERL; now a part of the National Exposure Research Lab), and R.S. Kerr Environmental Research Lab (RSKERL; now part of the National Risk Management Research Lab); and, Cray Research. In addition, collaboration is maintained with the U.S. Geological Survey, the Air Force Center for Environmental Excellence, and the Naval Facilities Engineering Service Center. This partnering and collaboration includes technology exchanges, joint conduct/funding of research investigations, and (in several cases) nearly weekly technical contact, particularly for new model implementation into the GMS.

The proposed major products from GMP research, with their respective delivery dates, are provided in Table 1. All of the computational products within this table will be fielded within the DoD GMS and its various versions. The driving force behind the development of the GMS is to vastly improve the cost-effective design and operation of remediation methods for site-specific military cleanups. To initiate remedial module development, WES has developed a multi-year, phased approach that will provide the ability to simulate and evaluate differing remedial alternatives within the GMS. These technologies were chosen because of their interest to DoD. The maturity of a given remedial technology was also factored into this selection. By the

end of FY97, modules which to simulate the following remediation technologies or actions will be developed and incorporated into the GMS:

* Physical Barriers
* Hydraulic Barriers
* Pump-and-Treat, Steady
* Pump-and-Treat, Pulsed
* Sorption Barrier (equilibrium)
* Natural Bioattenuation (1st-order decay)

Multiple additional remedial simulators, along with enhanced versions of those listed above, will be implemented in the GMS as shown in Table 1. These simulator modules will go into the GMS in as either independent codes or as modifications to models already in the GMS. The target flow and transport models for implementation of these features includes the GMS codes, the NUFT3D multiphase code from LLNL, and other codes such as SEAM3D, ADH, PARFLOW, UTCHEM, etc.

TABLE 1. LISTING OF MAJOR PROGRAM MILESTONES AND PRODUCTS

| No. | Product | Year |
|---|---|---|
| 1 | Documentation of DoD subsurface modeling requirements | FY94 |
| 2 | Initial visualization and user environment | FY94 |
| 3 | Guidance on use of existing multi-dimensional models | FY95 |
| 4 | Implementation of GMS v 1.0 with three existing models | FY95 |
| 5 | Couple GIS, DoD EQ databases w/GMS | FY95-96 |
| 6 | Add NUFT3D, UTCHEM, PARFLOW and ADH to the GMS | FY97-98 |
| 7 | Initial pump and treat optimization capabilities to GMS | FY96-97 |
| 8 | Add physical and hydraulic containment modules to GMS | FY96-97 |
| 9 | Subsurface conceptualization tools with uncertainty | FY96-98 |
| 10 | Add pulsed pump and treat modules to GMS | FY97-98 |
| 11 | Improved multiphase and cold regions algorithms in GMS | FY97-98 |
| 12 | Implementation of GMS v 2.0 w/Map Module | FY96-97 |
| 13 | Steam injection / vapor extraction modules into the GMS | FY97-98 |
| 14 | Initial soil heating modules integrated into GMS | FY97 |
| 15 | Add natural attenuation modules to GMS | FY97-99 |
| 16 | Initial in-situ bioremediation design modules in GMS | FY97-99 |
| 17 | Surface water - groundwater interaction modules in GMS | FY98 |
| 18 | Addition of bioventing and air sparging routines to GMS | FY98-99 |
| 19 | Addition of electrokinetics modules to GMS | FY98-99 |
| 20 | Add metals bioremediation design modules to GMS v3.0 | FY99 |
| 21 | Facilitated transport and fracture flow capabilities in GMS | FY99 |
| 22 | Demonstration of GMS components for specific sites | FY94-98 |
| 23 | Training in use of GMS products | Ongoing |

A synopsis of the technical investigations being integrated in the development of the DoD Groundwater Modeling System is presented in Table 2. As indicated, many of these investigations have been or will shortly be completed. Further, each of these investigations, most of them multi-agency by their very nature, have been designed to insure that the products therefrom, following rigorous verification, plug directly into the GMS. This will, in turn, allow highly accelerated fielding of new modeling and simulation technologies in support of site cleanup beyond that often experienced in traditional "research to field" scenarios.

TABLE 2. OVERVIEW OF GMP TECHNICAL INVESTIGATIONS

| Technical Area/Investigation Title | Investigator(s) | Study Period |
|---|---|---|
| *(A) EVALUATION / ENHANCEMENT OF EXISTING TECHNOLOGY* | | |
| Evaluation of Existing Models | WES | 1994-1995 |
| Evaluation of GMS Features and Enhancement of Existing Models | WES | 1994-1998 |
| Development of Scalable Parallel Version of the GMS Models | WES, University of Texas-Austin, University of Colorado-Denver, AL/EQ, Cray Research, LLNL, PNNL, AHPCRC | 1996-1998 |
| *(B) SUBSURFACE FLOW AND TRANSPORT PROCESS INVESTIGATION* | | |
| Investigation of Scaling Phenomena | WES | 1994-1996 |
| Impacts of Heterogeneity on Remedial Effectiveness | WES, LLNL, AL/EQ, RSKERL, LANL, Jackson State University, University of Minnesota | 1994-1998 |
| Investigation of Fluid Flow and Cont. Transport in Heterogeneous Multiphase Systems | University of North Carolina, ARO | 1994-1998 |
| Molecular-Scale Understanding of Chemical Adsorption | Purdue University, ARO | 1994-1996 |
| Chemical Transport in Multiscale Heterogeneous Porous Media | Purdue University | 1995-1998 |
| Pore-Scale Modeling of Multiphase Contaminant Transport in Freezing/ Thawing Soils | City College of New York, CRREL | 1995-1997 |
| Multiphase Flow in Polluted Soils | Stanford University | 1995-1998 |
| Investigation of Explosives Fate / Transport (multiple, integrated studies) | WES | 1994-1998 |
| *(C) SUBSURFACE CONCEPTUALIZATION AND UNCERTAINTY ESTIMATION* | | |
| Development of Subsurface Conceptualization Tools | WES, Colorado School Mines, University of CA-Davis , ANL | 1994-1998 |
| Design of Optimal Sampling Networks | University of Vermont | 1995-1997 |

| | | |
|---|---|---|
| Decision-Making Enhancements to the DoD GMS Under Conditions of Uncertainty | Duke University | 1995-1997 (joint with Task Area E below) |
| *(D) FLOW AND TRANSPORT MODEL DEVELOPMENT* | | |
| Weighted-Residual, Adaptive Flow and Transport Model | WES, Mississippi State University, Vanderbilt University, North Carolina State University, University of Texas-Austin | 1994-1998 |
| Improvements to FEMWATER / LEWASTE | Penn State University., WES, AERL, Cray Research | 1994-1997 |
| Simulating Flow and Transport Phenomena in Heterogeneous Multi-Phase Systems | University of North Carolina, WES | 1995-1998 (joint with Task Area E) |
| Surface Water / Groundwater Interactions | WES, Penn State University, University of Texas-Austin | 1995-1998 |
| *(E) REMEDIAL ALTERNATIVE SIMULATION AND OPTIMIZATION* | | |
| Development of SEAM3D | WES, University of Virginia | 1995-1998 |
| Investigation of Fluid Flow and Contaminant Transport in Heterogeneous Multiphase Systems | University of North Carolina | 1994 - 1998 |
| Simulation of Electrokinetics | Louisiana State University, WES | 1995-1999 |
| Investigation of Steam Inj., Vapor Extraction, Electrical Heating via NUFT3D | LLNL, WES | 1996-1999 |
| Pump & Treat Optimization | Cornell University | 1995-1997 |
| Implementation of PARFLOW Model | LLNL, WES | 1996-1998 |
| *(F) SYSTEMS INTEGRATION AND VERIFICATION* | | |
| GMS Design, Integration, and Verification | WES, Brigham Young University (BYU) | 1994-1999 |
| GIS and DoD Environmental Database Linkages to GMS (including ArcInfo, GRASS, IRDIMIS,IRPMS) | University of Texas - Austin, AEC | 1994-1996 |
| GMS Module Acceptance Testing, Quality Assurance, and Quality Control | WES, BYU | Ongoing |

| *(G) TECHNICAL ASSISTANCE, DEMONSTRATION, AND IMPLEMENTATION* | | |
|---|---|---|
| Schofield Barracks Demonstration | WES, AEC | 1994-1996 |
| CRREL TCE Containment | WES, CRREL | 1995-1997 |
| C-111 Pumping Investigation | WES | 1996-1998 |
| Fort Dix, NJ Site Cleanup | WES | 1997-1998 |
| Army Modeling Technical Support | WES, AEC, Corps of Engineers Offices, HQ | Ongoing |
| Memphis Army Depot Cleanup | WES | 1996-1997 |
| Aberdeen Proving Grounds | WES | 1995-1999 |

## 2. GMS STATUS

GMS v2.0 is currently being applied by over 325 Tri-Service users (well over half of whom are outside the U.S. Army Corps of Engineers) as well as 70 Environmental Protection Agency users and 65 Department of Energy users. The system is also in use through technical partnerships with the State of North Carolina, the South Florida Water Management District, and over 15 universities. Over 300 copies of the system have been sold through commercial vendors. These groups are using the system for civilian, military, and industrial cleanup design and operation activities on an international basis.

The GMS is designed for directly analogous execution on both personal computers running Windows (3.1, 95, and NT), and for UNIX workstations running X-Windows. Version 2.0 of the system supports multiple analysis tools (the reader is directed to the GMS website at http://hlnet.wes.army.mil/ for module-by-module information on the GMS's components). There are currently six flow and transport models within the system: MODFLOW, MT3D, FEMWATER, MODPATH, LEWASTE, and SEEP2D. Several additional codes (UTCHEM, NUFT3D, PARFLOW, RT3D, ADH) are being added to the system presently, along with enhanced versions of FEMWATER and MT3D.

A key feature to the GMS is its ability to greatly enhance productivity throughout the modeling process. Resource requirements for site characterization and conceptualization, subsurface stratigraphic realization, and initial and boundary condition designation have been reduced by an order of magnitude or more through the use of the system. Much of this productivity enhancement is the result of the development of a new conceptual approach to modeling as discussed below. This approach takes full advantage of the GMS's on-board conceptualization, geostatistical, visualization, and animation capabilities.

### 2.1 CONCEPTUAL MODEL APPROACH

With the current state of the art in groundwater modeling, simulations are typically performed according to the following steps:

1. Develop conceptual model
2. Create numerical grid
3. Assign model parameters and boundary conditions to grid

4. Calibrate model
5. Make predictions

The first step, the development of a conceptual model, is often the most important step in the modeling process. A conceptual model is a simplified representation of the site to be modeled. As a conceptual model is developed, the modeler must make numerous assumptions and simplifications to obtain a workable model. Highly heterogeneous regions are often divided into discrete zones representing areas with similar physical properties. Average or representative property values such as hydraulic conductivity or porosity must be determined. Many physical features at the site are deemed insignificant while others are carefully measured and included in the model. Throughout this process, the modeler attempts to achieve parsimony: a balance between eliminating enough detail to make the model workable while retaining enough detail to make the model accurate and useful. If the conceptual model is not developed properly, steps 2&3 result in wasted effort since it will be impossible to calibrate the model in step 4. In many cases, the user must develop several conceptual models before proper calibration is achieved. This is particularly true in groundwater modeling where appropriate boundary conditions and stratigraphic representations are often difficult to determine.

Most groundwater modeling pre-processing software is designed to automate and enhance the work involved in steps 2-5. The conceptual model is developed independently of the modeling software. A new approach to model development has been incorporated into GMS which not only includes the conceptual model as part of the computer-assisted modeling process, but features the conceptual model as the primary focus of model generation and the data entry process. Rather than focusing the model generation and data entry on a numerical grid or mesh, the user creates a conceptual model on the computer and assigns boundary conditions and model properties to the conceptual model. The conceptual model is defined in a general purpose fashion that is independent of grid type (finite element, finite difference, etc.) and to some degree, independent of the analysis code to be used. Once the conceptual model is defined at this higher level, the numerical model is automatically generated from the conceptual model. The grid or mesh is constructed in a manner that fits or adapts the grid to the conceptual model and the boundary conditions and material properties are extracted and assigned to the appropriate cells or elements.

In order to facilitate the new conceptual model approach to model design, a new module called the "Map Module" has been added to GMS. Four types of objects are supported in the Map Module: DXF objects, image objects, drawing objects, and feature objects. The first three objects: DXF objects, image objects, and drawing objects are primarily used as graphical tools to enhance the development and presentation of the conceptual model. DXF objects consist of drawings imported from standard CAD packages such as AutoCAD or MicroStation. Externally produced site drawings can often provide a useful backdrop or supplement to the graphical desktop during model construction. Drawing objects are essentially a simple set of tools that allow the user to draw text, lines, polylines, arrows, rectangles, etc., to add annotation to the graphical representation of a model. Image objects are digital images representing aerial photos or scanned maps in the form of TIFF files. TIFF files can be imported and registered to real world coordinates. Construction of the conceptual model can then be accomplished using a high resolution image in the background of the graphical desktop.

The fourth type of object, feature objects, is used to construct the actual conceptual model. Feature objects are patterned after the data model used by geographic information systems (GIS) such as ARC/INFO. The GIS data model utilizes points, arcs (polylines), and polygons to represent spatial information. For example, points represent data such as wells or point sources for contaminants, arcs represent rivers or model boundaries, and polygons represent areal data such as lakes or zones defining different recharge zones or hydraulic conductivities. Sets of points, arcs, and polygons can be grouped into layers or coverages. A set of coverages provides a complete description of the conceptual model. Since a GIS approach is used, the

conceptual model can be exported to or imported from a GIS. However, the GIS is not necessary since the entire model can be constructed within GMS.

## 2.2 EXAMPLE APPLICATIONS OF MAP MODULE CONCEPTUAL APPROACH

A sample application of the new conceptual model approach to model development in GMS is shown in Figures 1 - 4. A TIFF image used to guide the construction of the model is shown in Figure 1. This image represents a portion of a USGS quad sheet that was scanned using a standard desktop scanner. Upon import to GMS, three points on the image are identified by the user and the real-world coordinates of the points are used to register or map the image from image coordinates to model coordinates.

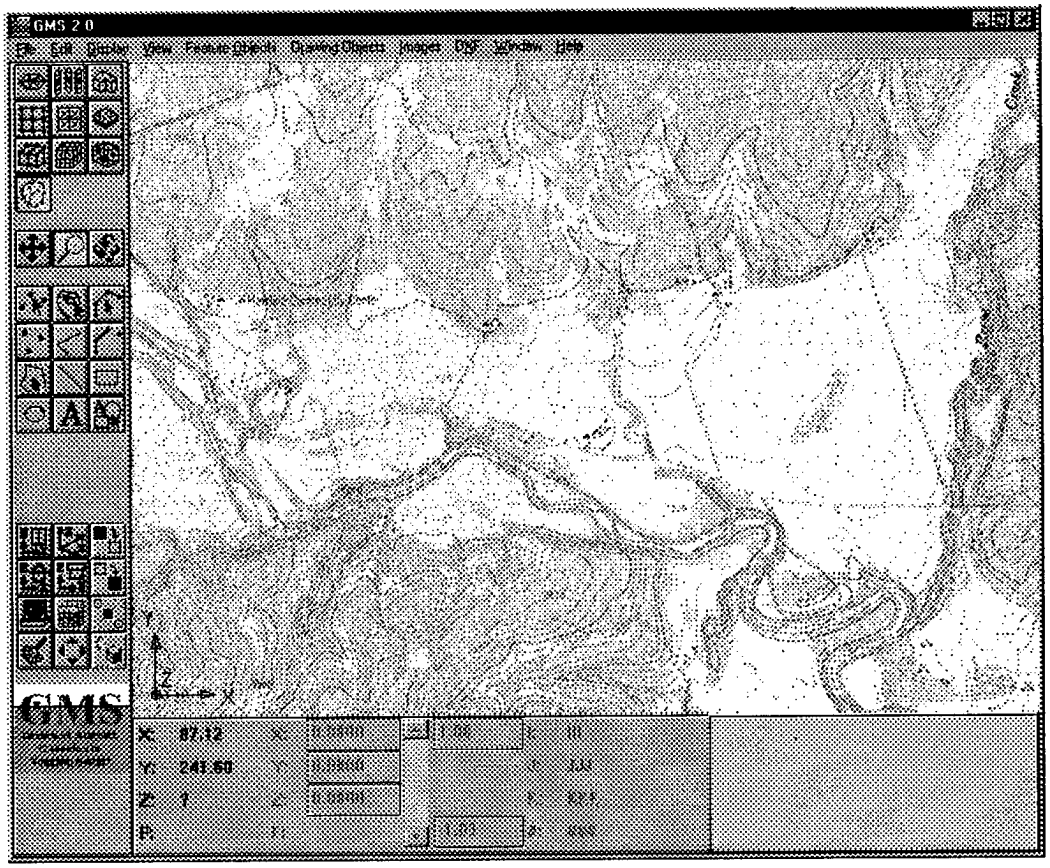



Figure 1. Desktop of the GMS with a Scanned USGS Quad Sheet Used for Developing a Conceptual Model

With a map of the site in the background, the next step is to construct the conceptual model using feature objects (Figure 2). The model consists of points, arcs, and polygons. Once the geometry of the objects is entered, attributes are assigned to the objects. For the case shown, the outer boundary of the model is represented by a combination of no flow boundaries and specified head boundaries. For the specified head boundaries, the head is assigned to the end points of the arcs (the nodes) and is assumed to vary linearly along the arc. The boundary arcs define a polygon representing the region to be modeled. Arcs were also used to represent several drains in the interior of the model. The drain elevations are assigned to the nodes of the arc and the conductance is assigned to the arc (the segments). Three wells with user-specified pumping rates are defined using points. The rectangle shown with dashed lines (Figure 2) is called a grid frame. It is placed graphically by the user to surround the conceptual model and it represents the boundary of the computational grid. The text and arrows in the figure were added using the drawing tools in the Map Module.

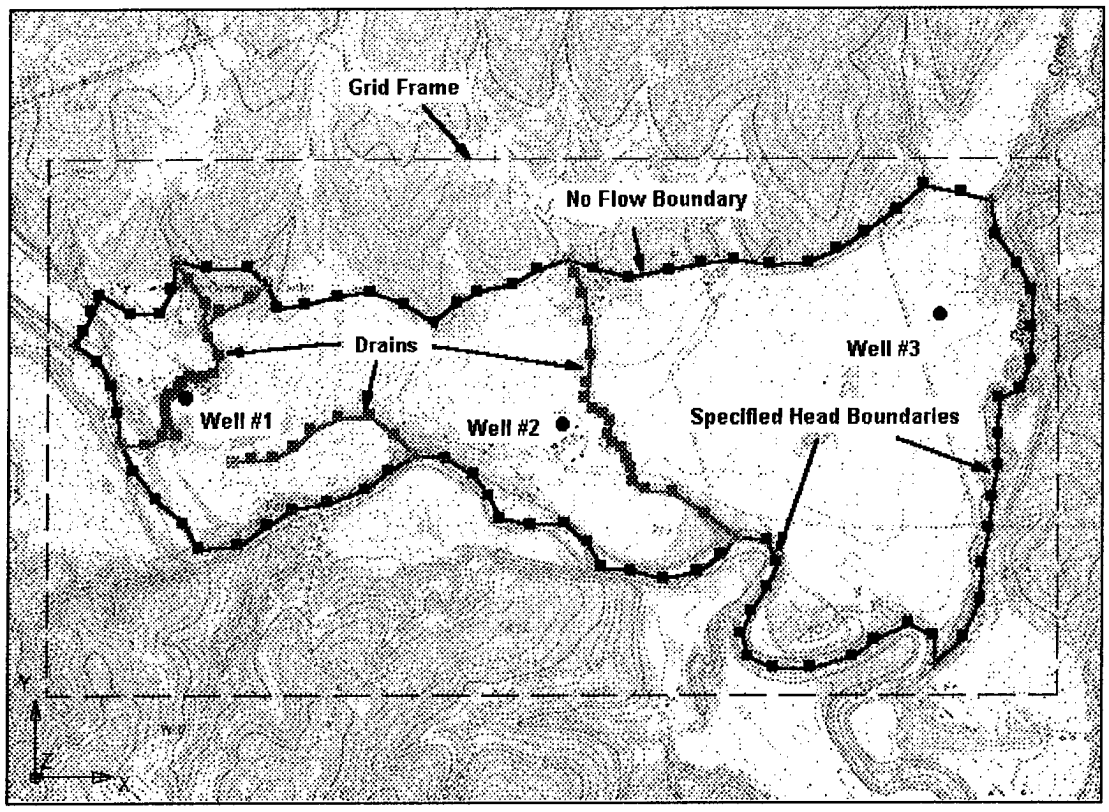



Figure 2. Conceptual Representation of a Groundwater Model Developed with GIS Objects.

Once the conceptual model is defined, the next step is to convert the conceptual model to a numerical model. Using the grid frame, the feature objects, and some cell size and refinement parameters defined at the wells, GMS automatically constructs a grid adapted to the conceptual model (Figure 3). The grid is refined around the wells and the cells outside the model boundary are inactivated. Each of the feature objects is then superimposed on the grid and the appropriate parameters are set up to activate the specified head cells, the drain cells, wells, etc. Conductances for linear objects such as drains and rivers are automatically computed by GMS according to the length of the arc segments within each of the cells. At this point, the model is completely defined and no cell editing is required. If the user decides to change the conceptual model (move a boundary, add some wells, etc.) the changes can be made to the feature objects and the numerical model can be regenerated in seconds. The conceptual model approach can be utilized for finite element models as well. Once the conceptual model is generated, the feature objects can be used to drive an automatic mesh generator included in GMS. The resulting mesh is refined around the wells and honors all interior and exterior boundaries defined by the conceptual model (Figure 4).

## CONCLUSIONS

The Department of Defense is continuing research and development whose primary goal is development of a comprehensive groundwater modeling system for use in the cleanup of contaminated groundwater resources at military installations. The multi-year research effort strongly leverages ongoing and near-future research through partnering with several federal agencies and universities. The integrating product from this research, the Groundwater Modeling System, represents a standardized methodology for the application and analysis of subsurface flow and transport modeling in support of site characterization, risk assessment, and remedial design. Substantial improvements in the effectiveness and defensibility of remedial actions are achievable through implementation of this system, thereby resulting in significant savings in remediation costs.

ACKNOWLEDGEMENT

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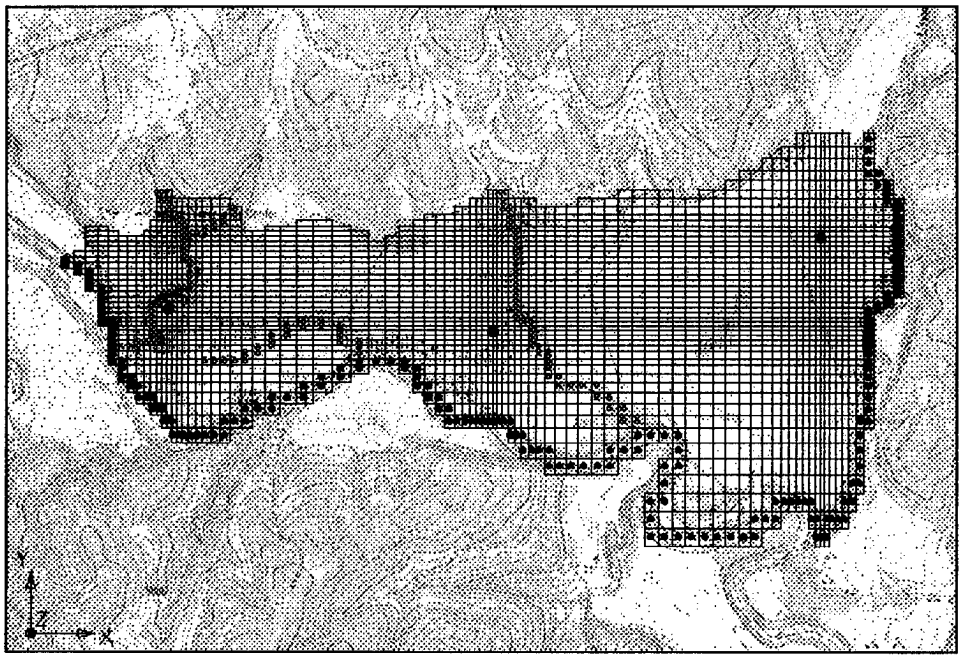


Figure 3. A MODFLOW Finite Difference Model Automatically Constructed from the Conceptual Model.

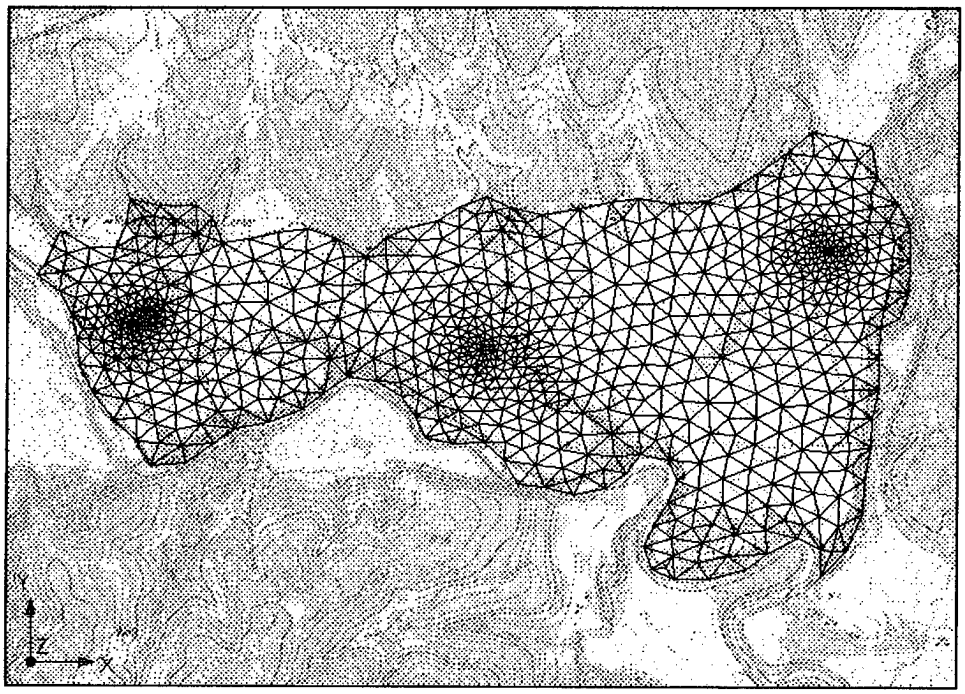


Figure 4. A Finite Element Mesh Automatically Constructed from the Conceptual Model.

# NATURAL ATTENUATION AND BIOSLURPING AT DIEGO GARCIA

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## ABSTRACT

The Indian Ocean island of Diego Garcia served as a base for B 52 bombers during the Persian Gulf War. In 1991 a leak was discovered in a section of an 18 inch diameter JP 5 fuel pipeline. The fuel spill exceeded 160,000 gallons. The site hydrogeology is a fragmented coral matrix with fresh water overlying more dense salt water. Depth to water is less than 10 feet. Tidal action results in twice daily water table oscillations of about two feet. Remediation studies have identified natural attenuation processes that are containing and destroying the fuel contamination. Evidence of natural attenuation processes includes historical records of contaminant concentrations, geochemical data, and direct microbiological evidence. Microbial oxidation of fuel is proceeding naturally in ground water by oxygen consumption, methanogenesis, and sulfate reduction. There is a large area of free phase fuel. This fuel is being recovered using "Bioslurper" vacuum enhanced product recovery technology. The first bioslurper system was installed in March 1996 and recovered 2000 gallons of JP 5 fuel during the first month of operation. Six extraction wells were used. Fuel recovery continued at a rate of about 1000 gallons per month. A second Bioslurper and 10 additional extraction wells was installed in Jan 97. Fuel recovery increased to 8000 gallons for January 1997 and has remained at about 5000 gallons per month since January 1997. Bioslurper is also aerating "bioventing" the vadose zone soils with resulting aerobic degradation of fuel contamination. Additional fuel degradation is occurring as a result of the tidal driven natural bioventing process. Vadose zone soil gas measurements determined that oxygen increased as the tide dropped and methane, along with carbon dioxide, increased as the tide rose. The remediation plan is to use biolsurper to remove the recoverable free phase fuel and allow the natural bioventing process and other natural attenuation processes complete the remediation.

### Site Background.

Diego Garcia is a horseshoe shaped island centrally located in the Indian Ocean at latitude 7 deg south and longitude 72 deg east. Diego Garcia is part of the British Indian Ocean Territory. The climate is tropical. Temperature averages 27 deg C and humidity averages 80%. Annual rainfall averages 107 inches. A wet season occurs from about September through February. A dry season occurs from about March through August. The surface elevation is typically less than 10 feet above sea level. Currently, all personnel residing on the island are supporting US and British military activities. There is no native population. The shallow

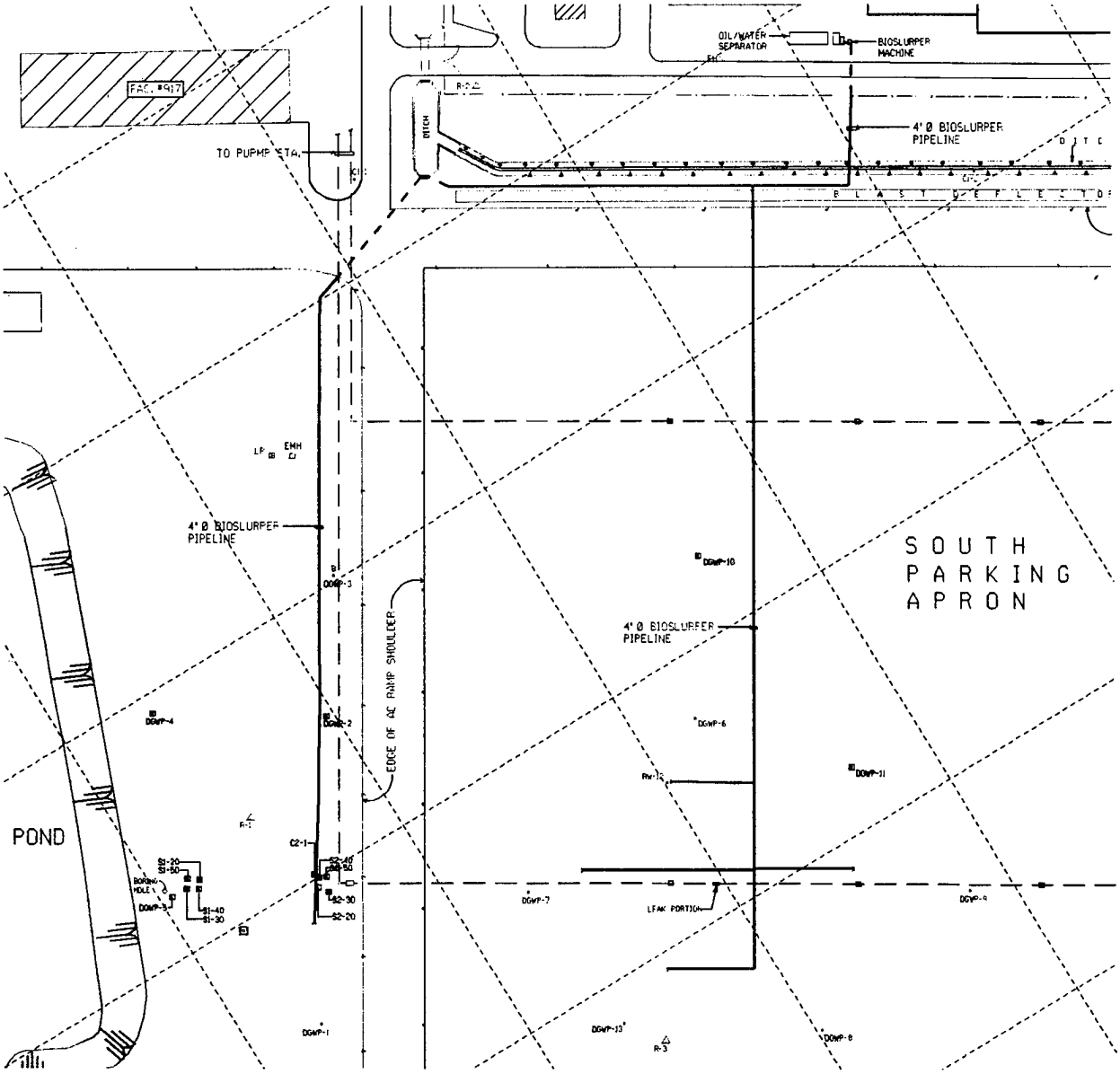



**Figure 1. Diego Garcia South Ramp, Layout of Bioslurper System** (1 inch equals approximately 140 feet)

fresh groundwater serves as the islands source of potable water. Aquifer material on Diego Garcia is formed from carbonate rock and sand. Depth to water is less than 10 feet.

During the Persian Gulf War, Diego Garcia served as a base for US Air Force B-52 bombers. Fuel usage peaked during February 1991 with a monthly total usage of 22 million gallons of JP-5 fuel. The B-52 operations centered on the South Ramp. The South Ramp has a fuel hydrant system with an 18 inch diameter pipeline circling the ramp. In May 1991 inventory records revealed a possible loss of 60,000 gallons of fuel. Pipeline testing led to discovery of a longitudinal split in a section of the pipeline.

**Site Characterization - Monitoring Well Installation**

Following discovery of the JP-5 fuel spill, various site characterization activities were conducted. Starting in June 1991, the U.S. Geological Survey (USGS) installed seventeen shallow monitoring wells for the purpose of surveying the extent of the contamination. In October 1992 a series of nested wells were installed at five locations in grass areas along the edge of the South Ramp. These nested wells were installed by the USGS in sets of four wells. Each of the four wells has five feet of well screen. The four wells were drilled to various depths. These nested wells permit monitoring dissolved contamination at various depths into the aquifer. In September-October 1992, the USGS installed 10 water-level monitoring stations. Each water-level monitoring station was equipped with electronic data loggers to record water-level measurements at 10 minute intervals. These water-level monitoring stations were used to determine the fluctuation of the water-levels due to twice daily tidal effects and to determine general groundwater flow directions.

Starting in September 1995, the Technology Transfer Division of the Air Force Center for Environmental Excellence (AFCEE/ERT) and USEPA National Risk Management Research Laboratory installed additional monitoring locations. In September 1995 nine monitoring points were installed using hand driven probe rods. One inch diameter rods were hand driven into the ground and pulled out using a forklift. A ½ inch inside diameter PVC well was then placed into the open hole. These water monitoring points were installed to total depths of 10-12 feet below ground surface with five foot screen lengths. Five water monitoring points were installed in the grass area between the South Ramp and the retention pond. This area is the leading edge of the free product area. Four water monitoring points were installed through the 18 inch thick concrete ramp in a circle around the location of the pipe split. In March 1996 an additional four water monitoring points were installed in the concrete ramp area. During March 1996 ten Bioslurper recovery wells were installed in the grass area between the South Ramp and the retention pond. These wells were installed using an on island auger truck. Twelve inch diameter holes were augered to depths of 11 feet. A 2 inch diameter well with 5 foot of well screen length was installed in each augured hole. Additionally, four holes were augured to 8 feet in depth for use in placing soil gas monitoring points are various depths. In January 1997, 10 Bioslurper recovery wells were installed in the concrete ramp in the vicinity of the pipe split. For these wells, a eight inch diameter hole was cored through the concrete. The on island drill rig with 6 inch diameter augers was used to drill the recovery wells. These recovery wells are 2 inch PVC wells with 10 to 15 feet of screen and total depths from 17 to 20 feet. A general layout of the site is shown on figure 1.

**Evidence of Natural Attenuation**

Three lines of evidence [1] are used to evaluate the effectiveness of natural attenuation:

a. Historical loss of contaminants
b. Geochemical evidence of attenuation processes
c. Direct microbiological evidence

Historical loss of contaminants: Groundwater samples have been analyzed for dissolved hydrocarbon contamination. The available data dates back to 1993. Additionally, several free product samples have been analyzed by the USEPA. None of the free product samples had measurable levels of benzene or toluene. Concentrations of fuel components dissolved in groundwater have consistently remained at relatively low levels (see Table 1). This can be attributed to the low concentrations of soluble constituents present in the fuel and to active degradation processes in the subsurface.

| Table 1. Total BTEX (ug/L) | | | | | |
|---|---|---|---|---|---|
| | Well | | | | |
| Date | S1-20 | S1-30 | S2-20 | S2-30 | WP-4 |
| Aug 93 | 45.5 | 40.5 | 54.3 | 47.2 | - |
| May 94 | 47.0 | 44.7 | 85.0 | 87.3 | - |
| Oct 95 | 55.5 | 36.4 | 64.2 | 58.9 | - |
| Mar 96 | 61.3 | 55.1 | 65.6 | 76.5 | 16.5 |
| Jan 97 | 60.0 | 57.3 | 63.9 | 60.6 | 9.5 |

note: benzene, toluene, ethylbenzene, xylenes (BTEX)

Geochemical evidence: This line of evidence includes evaluation of natural degradation processes to include: utilization of electron acceptors, production of indicators of electron acceptor usage, and production of products of the degradation processes. The USGS investigations determined that soil gas at locations near the leak had elevated levels of carbon dioxide and methane. Carbon dioxide and methane in soil gas are products of degradation. This finding has been confirmed during soil gas sampling by the USEPA. Additionally, USGS data indicate by the presence of H2S that sulfate reduction was occurring. The recent 3 sampling events (1995, 1996, 1997) by the USEPA determined that sulfate reduction and methanogenisis are active processes degrading dissolved hydrocarbons (see Table 2). There is no indication of iron reduction of nitrate reduction. Background levels of dissolved oxygen vary considerably. However, at locations where dissolved contamination is present, dissolved oxygen was not present. Aerobic degradation is occurring, but the rate is difficult to determine. For dissolved fuel contaminants, sulfate reduction and methanogenisis are the primary degradation processes that are active at Diego Garcia.

| Table 2. Water Quality Analysis. | | | | | | | |
|---|---|---|---|---|---|---|---|
| Back-ground wells | Dissolved Oxygen mg/l | Fuel Carbon ug/l | Methane mg/l | Sulfate mg/l | Nitrate mg/l | Sulfide mg/l | Redox Potential mV |
| C3-4 | 5.2 | <1 | <0.01 | 20.5 | 0.1 | <0.1 | +23 |
| C3-1 | 4.5 | <1 | 0.8 | 5.1 | <0.05 | 0.1 | +3 |
| Plume of Contaminated Wells | | | | | | | |
| S1-20 | 0.0 | 781 | 11.6 | 9.7 | <0.05 | 2.0 | -108 |
| S1-30 | 0.0 | 528 | 11.0 | 18.6 | <0.05 | 5.0 | -137 |
| S2-20 | 0.1 | 725 | 10.7 | 11.5 | <0.05 | 2.0 | -135 |

Direct Microbiological Evidence. A number of samples of contaminated groundwater have been analyzed by the USEPA for the presence of volatile fatty acids. These acids (56) are intermediate byproducts and indicate if current active microbial degradation is occurring. Significant levels of these acids are present at the site, indicating significant microbial degradation is occurring.

**Tidal Mediated Bioventing**

The island of Diego Garcia experiences twice daily tidal variations of up to 5 feet. The magnitudes of these tidal variations vary from day to day. The tidal variations are reflected in variations in the observed depths to water in the monitoring wells. The water levels in the wells varies 60-80% of the tidal variations. These variations in the water table appear to be pumping atmospheric air into and soil gas out of the unsaturated soils. This process is resulting in increased aerobic degradation of fuel components that are smeared into the unsaturated soils. Soil gas measurements taken at various depths in the unsaturated soil indicate that as the water level drops, oxygen levels in the soil gas increase. When the water level rises, oxygen levels drop and methane and carbon dioxide levels rise. These measurements as shown in Table 3 indicate that oxygen is being consumed by microbial activity and carbon dioxide and methane are being produced by the microbial activity.

| Table 3. Soil Gas Components as Related To Water Table Fluctuations. | | | | |
|---|---|---|---|---|
| Water Level (bgs, ft) | Time | Oxygen (%) | Carbon Dioxide (%) | Methane (%) |
| 2.0 | 0800 | 3.1 | 10.1 | 10.0 |
| 0.9 | 1000 | 6.2 | 1.9 | 2.0 |
| 0.7 | 1200 | 8.6 | 1.0 | 1.0 |
| 1.1 | 1400 | 1.7 | 8.8 | 8.9 |
| 2.1 | 1600 | 1.6 | 11.5 | 12.2 |
| 2.4 | 1800 | 1.8 | 11.0 | 11.4 |
| 1.9 | 2000 | 3.9 | 9.0 | 8.9 |

**Bioslurping**

Bioslurping is a form of vacuum enhanced skimming of fuel floating on the water table. A typical bioslurper system [2] consists of a vacuum pump that is piped to fuel recovery wells. The recovery wells are standard wells with the well screen area placed across the water table. A dip tube or "straw" is placed on the inside of the well with the inlet of the "straw" placed at or into the water/floating fuel. The well is sealed at the top so that no atmospheric air can be directly drawn into the well. The top of the "straw" is connected to the piping going to the vacuum pump. The vacuum pump draws fuel and soil gas up through the "straw" and to the vacuum pump. Soil gas enters the well through the well screen that is exposed above the water table. This has the effect of drawing oxygen rich atmospheric air from the ground surface into the unsaturated soils. This "biovents" any contaminated unsaturated soils resulting in aerobic degradation of fuel contaminants. At the vacuum pump, the fuel /water mixture is piped to an oil-water separator where the fuel is removed and collected for recycling. The vapors are discharged directly to the atmosphere or treated if needed and then discharged. Overall the Bioslurper technology is simple and easy to maintain. These characteristics make bioslurping an attractive technology for a location as remote as Diego Garcia.

The first bioslurper system was installed in March 1996. The vacuum pump is a 10 hp liquid ring pump that is located adjacent to an existing oil-water separator in the fuel yard. The piping from the vacuum pump to the recovery wells is 1100 feet of 4 inch diameter PVC. The recovery wells are located in the downgradiant portion of the free product area. Six wells are connected to the first Bioslurper. The "straws" were placed about 1 foot into the water/fuel at low tide. For April 1996, 2000 gallons of fuel were recovered. Fuel recovery rates have averaged about 1000 gallons per month for May 1996 until January 1997. The recovered fuel is being used as fuel at the Diego Garcia diesel powered electric generating plant.

The second Bioslurper system was installed in January 1997. The second vacuum pump is identical to the first and is manifolded together with the first Bioslurper vacuum pump . Ten additional recovery wells were installed in the concrete ramp in the vicinity of the pipe split. Four inch diameter PVC piping was laid on the concrete ramp from the recovery wells towards the vacuum pump. The piping to the additional recovery wells was connected into the existing 4 inch PVC piping system. The PVC piping on the ramp is connected with hose clamps and elastic couplers. This was done so the piping can be quickly removed if the ramp area is needed for military operations. The two Bioslurper systems are connected together into a common piping system. For the month of January 1997, 8000 gallons of fuel was recovered. The recovery rate since then has averaged 5000 gallons per month.

Bioventing effects from Bioslurper operation can result in considerable degradation of fuel hydrocarbons that are in the unsaturated soil. Introduction of atmospheric air into contaminated soils can result in degradation of hydrocarbons [3]. Degradation usually occurs at a rate of 1 pound of hydrocarbon degraded from 13 pounds of air introduced into the soil. Each Bioslurper system has a vapor flow rate averaging 50 cubic feet per minute. This flow is composed of two sources. One is volatile fuel vapors. The second is soil gas that is replenished by atmospheric air. If volatile vapors are neglected, fuel degradation could amount to over 100,000 pounds of fuel degraded per year for each Bioslurper system. During the next field visit, measurements will be made of volatile fuel components, oxygen, carbon dioxide, and methane present in

the Bioslurper vapor discharge streams. This data will be used to attempt to quantify the amount of fuel being removed by Bioventing and vapor extraction.

**Costs**

Bioslurper components are not a major cost item. The most expensive component is the liquid ring pump skid which costs about $9,000 each. Total cost for both Bioslurpers, piping, connectors, well installation material, on island support, travel to Diego Garcia to supervise installation and gather water samples, etc has totaled $133,000. Cost to operate and maintain the Bioslurper system is less than $20,000 per year. In a little over one year over 35,000 gallons of useable fuel has been recovered.

**Future Activities**

The current array of recovery wells covers about 60 % of the extent of the fuel floating on the water. In August 1997, it is planned to install an additional 12 recovery wells to complete the coverage. These new wells will be connected to the existing Bioslurper system. All recovery wells are equipped with valves on the dip tube ("straw"). Various wells will be valved off as levels of fuel in the well drops. Wells with the most fuel will be valved on. The wells will be cycled on and off as the fuel levels recover and drop and as the Bioslurper system capacity allows. Monthly measurements of fuel in wells will be taken as the wells are cycled off. The groundwater will continue to be monitored at six month intervals. Monitoring will include analysis for dissolved fuel contaminants and indicators of natural degradation processes. Soil gas will be field tested at some locations to track degradation of contamination smeared in the unsaturated soils.

Bioslurper will continue to operate until fuel recovery has become nonproductive. At that time the bioslurper system will continue to operate in the Bioventing mode to aerobically degrade fuel that remains in the unsaturated soil. Bioventing operation will continue until soil gas tests indicate that aerobic degradation has been completed. This is expected to take about two years after fuel recovery has stopped. Natural attenuation processes will be monitored as the dissolved fuel components degrade. Natural tidal mediated Bioventing will be relied on to degrade fuel smeared in soils that are outside the influence of Bioslurping/Bioventing.

**Conclusions**

Site characterization and remediation activities of bioslurping and natural attenuation are being accomplished in a timely and cost effective manner. Understanding the natural processes occurring at a site can greatly simplify the long term cleanup plan.

ACKNOWLEDGEMENTS

The authors are grateful to TSgt James Medeiros for his assistance in installing the bioslurper wells and equipment and monitoring the remediation equipment. The research described has not been subjected to a U. S. Environmental Protection Agency review process. Therefore, an official endorsement should not be inferred.

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# CASE STUDY USING THE AIR FORCE TECHNICAL PROTOCOL TO EVALUATE NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER

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## ABSTRACT

Parsons Engineering Science, Inc. (Parsons ES) was retained by the Air Force Center for Environmental Excellence (AFCEE) to conduct a treatability study (TS) to evaluate using remediation by natural attenuation (RNA) for groundwater contaminated with chlorinated aliphatic hydrocarbons (CAHs) at Hill Air Force Base (AFB), Utah. The field investigation and subsequent data analysis followed procedures and techniques described in AFCEE's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater.*[1] Groundwater samples were analyzed for water quality parameters plus a suite of geochemical indicator parameters designed to document the occurrence and significance of natural attenuation. The analytical results were used to complete a preliminary screening exercise wherein points are assigned based on the presence of biodegradation daughter products and the distribution and concentrations of geochemical indicator parameters. The screening exercise allows the investigator to determine if natural attenuation is likely to be a viable remedial alternative before additional time and money are expended. Several lines of chemical and geochemical evidence for the Hill AFB site (and consequently, the results of the screening exercise) consistently indicate that, although dissolved CAHs are undergoing biologically facilitated reductive dehalogenation, this process is limited and localized. Site-specific contaminant decay rates computed using groundwater quality data were low, further indicating the limited nature of RNA. The analysis results were used to support fate and transport modeling of the dissolved CAH plume. The research described has not been subjected to a U.S. Environmental Protection Agency (USEPA) review process. Therefore, an official endorsement should not be inferred.

## 1. INTRODUCTION

Hill AFB is located 25 miles north of Salt Lake City, Utah. The TS focused on the dissolved CAH plume emanating from the Tooele Army Rail Shop (TARS), located along the western boundary of the Base. The TARS was constructed in 1942 and was used to service and repair railroad engines. Trichloroethene (TCE) was reportedly used at the rail shop from 1949 to 1964, and was discharged to a gravel leachfield, resulting in groundwater contamination. A remedial investigation performed by Radian Corporation (Radian) detected a TCE plume extending approximately 1 mile west of the rail shop (Figure 1).[2] The study area has been designated as Operable Unit (OU) 5.

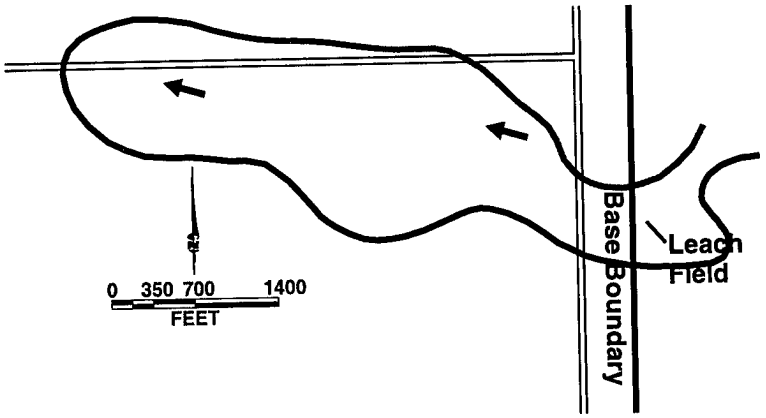



Figure 1. Outline of TCE plume.

The TS was performed according to procedures outlined in the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*.[1] This document describes the processes that contribute to natural attenuation, the site characterization activities that can be performed to evaluate the occurrence of natural attenuation, fate and transport modeling activities that can be performed to predict the future impact of natural attenuation on dissolved CAH contamination, and the post-modeling activities that should be completed to ensure successful support and verification of remediation by RNA.

The protocol document outlines recommended steps for documenting the impact of natural attenuation at a site. One of the first steps is to perform preliminary screening to assess the potential for RNA at a site. If the screening indicates that RNA is a potential remedial alternative, then available site characterization data can be used to document the degree to which RNA is occurring. This paper describes how site characterization data were used to characterize the occurrence of RNA at OU5, and how the screening results supported the conclusions drawn from the characterization.

## 2. FIELD PROGRAM AND ANALYTICAL PROTOCOL

The review of available data indicated that some TCE was being transformed to dichloroethene (DCE), but additional site characterization was required to fully evaluate the occurrence and mechanisms of RNA. A Geoprobe® was used to install temporary, small-diameter monitoring points, which were sampled together with preexisting monitoring wells. Many time-sensitive chemical analyses [e.g., dissolved oxygen, oxidation reduction potential (ORP)] were performed either at the wellhead or in a U.S. Environmental Protection Agency (USEPA) field laboratory; analyses that could not be performed in the field were performed at the USEPA National Risk Management Research Laboratory (NRMRL) in Ada, Oklahoma (Table 1).

TABLE 1. ANALYTICAL PROTOCOL

| Matrix/Parameter | Method | Matrix/Parameter | Method |
|---|---|---|---|
| **Groundwater** | | **Groundwater (continued)** | |
| Volatile Fatty Acids (N)[a/] | RSKSOP-177 | Hydrogen Sulfide (F) | Hach Method 8131 |
| Phenols (F) | CHEMetrics Method 4AAP | Carbon Dioxide (F) | CHEMetrics Method 4500 |
| Dissolved Hydrogen (F) | Reduction Gas Analyzer | Chloride (N) | N-601 [b/] |
| Ferrous Iron (Fe+2) (F) | Hach Method 8146 | Ammonia (N) | E350.1 |
| Manganese (F) | Hach Method 8034 | Methane (N) | RSKSOP-175/RSKSOP-147 |
| Sulfate (N) | N-601 [b/] | Ethene (N) | RSKSOP-175/RSKSOP-147 |
| Nitrate + Nitrite (N) | E353.1 | Total Organic Carbon (N) | RSKSOP-102 |
| Redox Potential (F) | Direct-reading meter | Aromatic Hydrocarbons (N) | RSKSOP-133 |
| Dissolved Oxygen (F) | Direct-reading meter | Total Fuel Carbon (N) | RSKSOP-133 |
| pH (F) | Direct-reading meter | Metals (N) | ICP, GFAA (lead only) [c/] |
| Conductivity (F) | Direct-reading meter | Chlorinated VOCs (N) | RSKSOP-146 |
| Temperature (F) | Direct-reading meter | **Soil** | |
| Alkalinity (F) | Hach Method 8221 | Total Organic Carbon (N) | RSKSOP-102 & 120 |

a/ (N) = Performed at USEPA National Risk Management Research Laboratory in Ada, Oklahoma; (F) = field analysis.

b/ Waters capillary electrophoresis Method N-601.

c/ ICP = Inductively coupled plasma spectrometry; GFAA = graphite furnace atomic absorption.

Microorganisms obtain energy to carry out life processes by oxidizing organic matter. This is accomplished by transferring electrons from electron donors (e.g., BTEX, landfill leachate, native organic carbon, or CAHs) to electron acceptors. Electron acceptors are elements or compounds that occur in relatively oxidized states and can participate in reduction oxidation (redox) reactions with electron donors (e.g., oxygen, nitrate, ferric iron hydroxide, sulfate, carbon dioxide, or CAHs). CAHs may undergo biodegradation through three different pathways: use as an electron acceptor, use as an electron donor, or through cometabolism, where degradation of the CAH is fortuitous, and there is no benefit to the microorganism. At a given site, one or all of these processes may be operating, although at many sites the use of CAHs as electron acceptors appears to be predominant (especially the more chlorinated CAHs such as tetrachloroethene [PCE] and TCE). Use of electron acceptors other than CAHs may be energetically favorable; therefore, if alternate electron acceptors are abundant in the groundwater, the biodegradation of CAHs may be inhibited.

On the basis of the above discussion, the analyte list for OU5 groundwater samples included potential electron donors and electron acceptors in addition to volatile organic compounds (VOCs) (Table 1). Biodegradation products and other physical and geochemical parameters that indicate whether the phreatic environment is favorable for biodegradation also were targeted for analysis. Biodegradation products include volatile organic daughter products produced when the parent VOC is degraded (e.g., dichloroethene [DCE] produced when TCE is reductively dechlorinated), methane (produced when carbon dioxide [$CO_2$] is reduced by microbially mediated processes), ethene (produced when chloride is stripped from vinyl chloride [VC]), ferrous iron (produced when ferric iron is reduced), and volatile fatty acids (VFAs). VFAs are produced as a result of microbial metabolism of a carbon source. Because they volatilize fairly rapidly, they are indicators of recent microbial activity.

Other geochemical indicators that allow assessment of whether subsurface conditions are favorable for biodegradation to occur include ORP, dissolved hydrogen ($H_2$), temperature, and pH. ORP is a measure of the relative tendency of a solution or chemical reaction to accept or transfer electrons, and can be used as a crude indicator of which redox reactions may be operating at a site. Reductive dechlorination, which is the most frequently occurring process for the natural biodegradation of the more highly chlorinated solvents (PCE and TCE), occurs most rapidly under low ORP (e.g., sulfate reducing and methanogenic) conditions.[3]

Concentrations of dissolved $H_2$ also can be used to evaluate redox processes in groundwater systems. $H_2$ is continuously produced in anaerobic groundwater systems by fermentive microorganisms that decompose organic matter. This $H_2$ is then consumed by respiratory microorganisms that use nitrate, ferric iron, sulfate, or $CO_2$ as electron acceptors. Significantly, nitrate-, ferric iron-, sulfate- and $CO_2$-reducing microorganisms exhibit different efficiencies in utilizing the $H_2$ that is continually being produced. Because each electron accepting process has a characteristic $H_2$ concentration associated with it, $H_2$ concentrations can be an indicator of predominant redox processes.[4] These characteristic ranges are shown in Table 2.

TABLE 2. RANGE OF HYDROGEN CONCENTRATIONS FOR A GIVEN ELECTRON ACCEPTING PROCESS

| Terminal Electron-Accepting Process | Dissolved Hydrogen Concentration (nanomoles per liter) |
|---|---|
| Denitrification | <0.1 |
| Ferric Iron Reduction | 0.2 to 0.8 |
| Sulfate Reduction | 1 to 4 |
| Methanogenesis | 5 to 20 |

## 3. DATA ASSESSMENT

Analytical data were plotted on site maps to allow assessment of the geochemical environment within the plume. These maps helped answer the following questions: Is the soil and groundwater geochemistry conducive to the occurrence of CAH biodegradation? Is biodegradation occurring? If so, to what degree and what are the dominant biodegradation mechanisms?

All of the OU5 data indicate that, although biodegradation of dissolved CAHs is occurring, it is very limited and localized. For example:

- Daughter products produced when TCE is reductively dechlorinated (DCE, VC, ethene) were scarce to nonexistent along the plume flowpath. Therefore, only a small fraction of the parent CAH (TCE) is being transformed to DCE, and the process is not sufficient to transform the parent CAH and chlorinated daughter products to nonchlorinated end products such as ethene.

- The molar fraction of TCE does not decrease with distance from the source area, and remains significantly elevated above the molar fraction of DCE (Figure 2).

- ORP data indicate that groundwater is sufficiently reducing to support the occurrence of reductive dechlorination, but redox conditions do not appear to be optimal for this process. (Figure 3). It should be noted that ORP data alone cannot be used to reliably predict the electron acceptors that may be operating at a site, because the platinum electrode probes of the measurement instrument are not sensitive to some redox couples (e.g., sulfate/sulfide).[5]

- Dissolved $H_2$ data indicate that redox conditions are not optimal for reductive dechlorination; $H_2$ concentrations detected within the TCE plume ranged from $<0.1$ to 0.4 nanomoles per liter (nM/L), indicating that denitrification or ferric iron reduction should be the dominant electron accepting process in the plume area (Table 2).

- The groundwater throughout the plume area is aerobic and relatively oxidizing; therefore, conditions are not optimal for the occurrence of reductive dechlorination, which is an anaerobic process that occurs most readily under highly reducing conditions.

- Nitrate and sulfate concentrations within much of the plume area are sufficiently high that use of CAHs as electron acceptors may be inhibited due to preferential use of these anions as alternate electron acceptors.

- Methane was infrequently detected and, where present, occurred at low concentrations. The scarcity of evidence of methanogenic conditions also suggests the lack of optimal conditions for reductive dechlorination.

- The scarcity of VFAs in groundwater further supports the observation that microbial biodegradation of CAHs is very limited in OU5 groundwater.

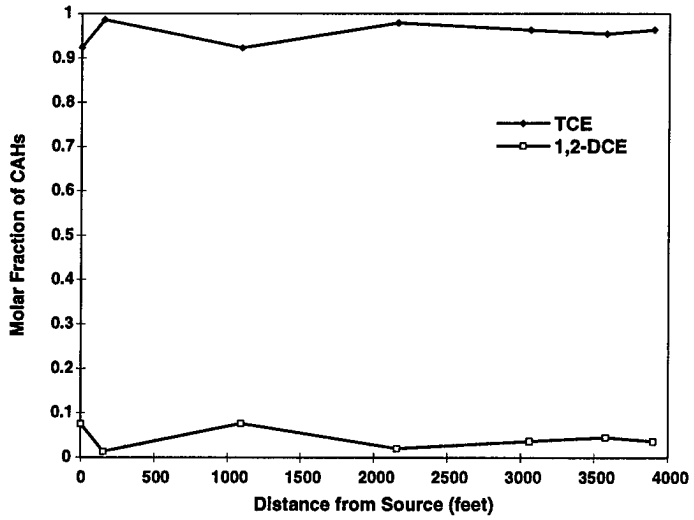



Figure 2. Molar fractions of TCE and 1,2-DCE along plume axis.

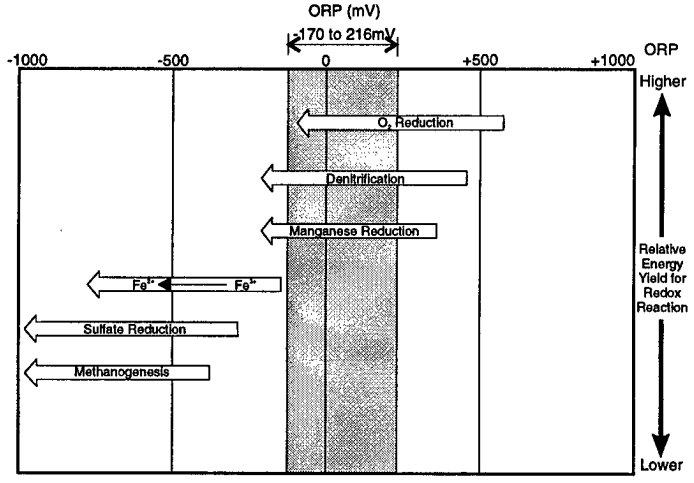



Figure 3. Range of ORPs measured in OU5 groundwater.

## 4. SCREENING PROCESS

Experience at CAH-contaminated sites to date indicates that RNA alone can bring concentrations of CAHs to below regulatory levels for approximately 20 percent of spills.[1] Therefore, an accurate assessment of the potential for natural biodegradation of CAHs should be made before investing in a detailed study of natural attenuation. However, RNA in combination with engineered remedial actions may reduce remediation costs at a greater percentage of sites. The screening process presented in the AFCEE protocol consists of the following steps:[1]

1. Determine if biodegradation is occurring using geochemical data;
2. Determine groundwater flow and solute transport parameters;
3. Locate source(s) and receptor exposure points;
4. Estimate the CAH biodegradation rate constant using site-specific data or, if necessary, literature values for the contaminant(s) of interest;
5. Compare the rate of solute transport to the rate of attenuation using a simple analytical model to determine if the residence time along the flow path is adequate to be protective of human health and the environment at receptor exposure points; and
6. Determine if screening criteria are met.

The application of the screening process to OU5 at Hill AFB is described in the following paragraphs.

### 4.1 SCREENING STEP 1--Determination if Biodegradation is Occurring using Geochemical Data

A worksheet was developed for the chlorinated protocol document to allow the investigator to determine if RNA is likely to be a viable remedial alternative before additional time and money are expended.[1] It is recommended that the chemical and geochemical data for a minimum of six locations be available to complete the screening process; the six data collection points are shown on Figure 4. For the OU5 site, the worksheet was completed at the end of the TS process to summarize the numerous lines of evidence supporting the limited and localized occurrence of biodegradation and to quantify the degree to which biodegradation is occurring. However, if sufficient data exist, it is advisable to complete the worksheet prior to collection of additional data to determine the need for additional site characterization and to identify any key data gaps.

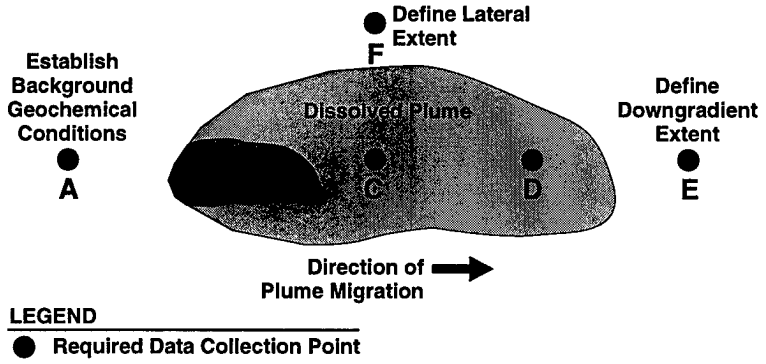



Figure 4. Data collection points required for screening.

The screening worksheet for OU5 and the interpretation of points awarded are shown in Tables 3 and 4, respectively. For scores less than 15 the investigator can infer that biodegradation is either not occurring or is occurring too slowly to constitute an effective remediation alternative. The score computed for OU5 is 11.5, indicating that the evidence for biodegradation of chlorinated organics is present, but limited. Therefore, there is a need for engineered remedial action to meet remediation objectives at OU5.

TABLE 3. ANALYTICAL PARAMETERS AND WEIGHTING FOR PRELIMINARY SCREENING OF OU5 CAH PLUME

| Analysis | Concentration in Most Contaminated Zone | Interpretation | Value | OU5 Score |
|---|---|---|---|---|
| Oxygen | <0.5 mg/L<br>>1 mg/L | Tolerated, suppresses the reductive pathway at higher concentrations | 3<br>-3 | 3<br>-- |
| Nitrate | <1 mg/L | At higher concentrations may compete with reductive pathway | 2 | 2 |
| Iron II | >1 mg/L | Reductive pathway possible | 3 | 0 |
| Sulfate | <20 mg/L | At higher concentrations may compete with reductive pathway | 2 | 0 |
| Sulfide | >1 mg/L | Reductive pathway possible | 3 | -- |
| Methane | <0.5 mg/L<br>>0.5 mg/L | Redox conditions not optimal<br>Redox Conditions optimal | 0<br>3 | 0<br>0 |
| Redox Potential | <50 millivolts<br><-100mV | Reductive pathway possible<br>Reductive pathway likely | 1<br>2 | --<br>1[a/] |
| pH | 5 < pH < 9<br>5 > pH >9 | Optimal range for reductive pathway<br>Outside optimal range for reductive pathway | 0<br>-2 | 0<br>0 |
| TOC | > 20 mg/L | Carbon and energy source; drives dechlorination; can be natural or anthropogenic | 2 | 0 |
| Temperature | > 20°C | At T >20°C biochemical process is accelerated | 1 | 0 |
| Carbon Dioxide | >2x background | Ultimate oxidative daughter product | 1 | 0.5[b/] |
| Alkalinity | >2x background | Results from interaction of carbon dioxide with aquifer minerals | 1 | 0 |
| Chloride | >2x background | Daughter product of organic chlorine | 2 | 1[c/] |
| Hydrogen | >1 nM/L<br><1 nM/L | Reductive pathway possible, VC may accumulate<br>Reductive pathway unlikely, VC oxidized | 3<br>0 | 0<br>0 |
| Volatile Fatty Acids | > 0.1 mg/L | Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source | 2 | 0 |
| BTEX | > 0.1 mg/L | Carbon and energy source; drives dechlorination | 2 | 0 |
| PCE | | Material released | 0 | 0 |
| TCE | | Material released<br>Daughter product of PCE | 0<br>2[d/] | 0<br>0 |
| 1,2-DCE | | Material released<br>Daughter product of TCE. (If *cis* is greater than 80% of total DCE it is likely a daughter product of TCE) | 0<br>2[d/] | 0<br>2 |
| VC | | Material released<br>Daughter product of DCE | 0<br>2[d/] | 0<br>0 |
| Ethene/Ethane | >0.01mg/L<br>>0.1 mg/L | Daughter product of VC/ethene | 2<br>3 | 0<br>0 |
| Chloroethane | | Daughter product of VC under reducing conditions | 2 | 0 |
| 1,1-DCE | | Daughter product of TCE or chemical reaction of 1,1,1-TCA | 2[d/] | 2 |

a/ Partial points awarded because the occurrence of ORPs along the plume flowpath that are less than -100 mV is limited to one well, indicating that conditions favorable to reductive dechlorination are very localized.

b/ Partial points awarded because elevated carbon dioxide concentrations were detected, but are not widespread.

c/ Partial points awarded because the chloride concentration in one well, while greater than 2X the average background chloride concentration, is not greater than the maximum background chloride concentration.

d/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the parent compound).

TABLE 4. INTERPRETATION OF POINTS AWARDED DURING NATURAL ATTENUATION SCREENING

| Score | Interpretation |
|---|---|
| 0 to 5 | Inadequate evidence for biodegradation of chlorinated organics |
| 6 to 14 | Limited evidence for biodegradation of chlorinated organics |
| 15 to 20 | Adequate evidence for biodegradation of chlorinated organics |
| >20 | Strong evidence for biodegradation of chlorinated organics |

4.2. SCREENING STEPS 2 THROUGH 4--Determine Solute Fate and Transport Parameters, Biodegradation Rates, and Potential Receptor Exposure Points

For scores equal to or greater than 15, the investigator can proceed to step two of the screening process and determine groundwater flow and solute transport parameters. These parameters include the hydraulic gradient, hydraulic conductivity, effective porosity, dispersivity, and the retardation coefficient (using total organic carbon data for soil). Site-specific data should be used where possible, but accepted literature values can be used if site-specific data are not available. Available data also can be used to estimate biodegradation rate constants and the distance between the contamination and any potential downgradient receptor exposure points (steps 3 and 4 of the screening process). Calculation of site-specific biodegradation rates is discussed in the AFCEE protocol document.[1] The first-order TCE decay rates computed for OU5 using site-specific data ranged from $1 \times 10^{-7}$ $day^{-1}$ to $2 \times 10^{-5}$ $day^{-1}$, which equate to TCE half-lives of 95 to 19,000 years. The low magnitude of these decay rates are consistent with the low score presented in Table 3. At OU5, the most likely downgradient receptor exposure point consists of wetlands located approximately 10,000 feet downgradient from the current toe of the TCE plume. The wetlands are a potential groundwater discharge area, and the potential for the plume to migrate to this area is of interest.

4.3 SCREENING STEP 5--Assess the Migration and Fate of the Contaminant(s) using Modeling

The primary purpose of step 5 of the screening process is to determine if the contaminant is attenuating rapidly enough to allow degradation to acceptable concentrations before receptors are exposed. If conservative model input parameters are used, the solute fate and transport model should give conservative estimates of contaminant plume migration. If the modeling shows that receptors will not be exposed to contaminants at concentrations above risk-based corrective action criteria, then the screening criteria are met and the investigator can proceed with the natural attenuation demonstration. In most cases, use of a simple analytical model that simulates retardation, dispersion, and first-order decay will be adequate for the screening process. The analytical model BIOCHLOR, under development by the Technology Transfer Division of AFCEE, will be geared toward evaluating groundwater transport of chlorinated compounds under the influence of biodegradation.

A numerical model was constructed for OU5, in part to allow accurate simulation of the effects of engineered remedial actions that have been implemented or will potentially be implemented in the future. The OU5 modeling indicated that, unless adequate engineered remedial actions are implemented, the plume has the potential to migrate nearly 2 miles beyond the current plume toe over the next 100 years, and to persist at concentrations substantially in excess of the 5-µg/L state groundwater quality standard for more than 100 years (Figure 5).

If the receptor exposure pathways analysis suggests that one or more pathways may be completed before natural attenuation can reduce chemical concentrations below applicable regulatory or risk-based levels of concern, then the fate and transport model can be used to evaluate the effects of source removal/reduction on plume migration. This can be accomplished by modifying the contaminant source term, and will allow a reevaluation of the exposure pathways analysis.

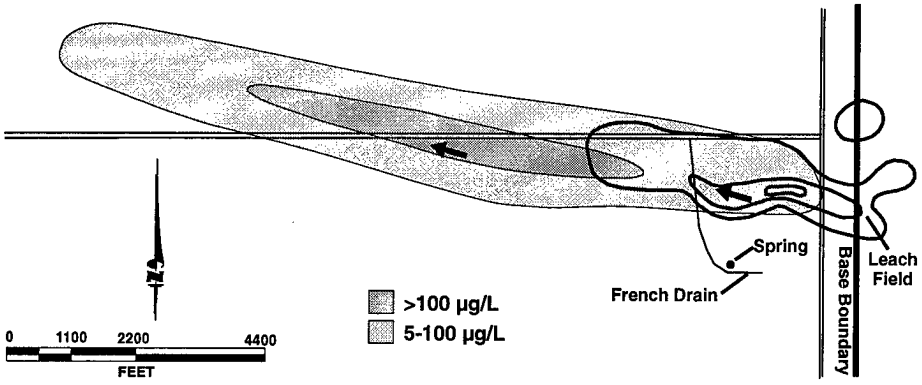



Figure 5. Simulated TCE plume (year 2097) assuming no engineered remediation.

4.4 SCREENING STEP 6--Determine if Screening Criteria are Met

Before proceeding with the full-scale RNA evaluation, the investigator should ensure that the answers to both of the following questions are yes:

- Has the plume moved a shorter distance than expected based on the known (or estimated) time since contaminant release and the contaminant velocity, as calculated from site-specific measurements of hydraulic conductivity and hydraulic gradient, and estimates of effective porosity and contaminant retardation?

- Is it likely that the contaminant is attenuating at rates sufficient to be protective of human health and the environment at potential receptor exposure points, based on modeling results?

- If the answer to these questions is yes, then the investigator is encouraged to proceed with the full-scale RNA demonstration. For OU5, the screening process results indicate that the answer to both questions is no.

## 5. CONCLUSIONS

Extensive site characterization data indicate that TCE biodegradation in OU5 groundwater is limited and localized, and RNA is probably not an effective remedial alternative by itself. During the course of the RNA TS, the steps of the preliminary screening process presented by Wiedemeier *et al.* (1996) were completed. The conclusions regarding the significance of RNA at OU5 drawn from the various screening steps are internally consistent, and support the conclusions drawn independently from the site characterization data, indicating that the screening process is a useful tool that can indicate the importance of RNA at a site prior to investing in a detailed study of natural attenuation. If completion

of the screening process is desired, the required site characterization data should be collected early in the investigation before a significant amount of effort is expended.

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# EFFECTIVE TOOLS

# RANGE EVALUATION SOFTWARE TOOL (REST) AND ARMY SAMPLING AND ANALYSIS PLAN (ASAP) FOR SMALL ARMS RANGES

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## ABSTRACT

The Range Evaluation Software Tool (REST) and the Army Sampling and Analysis Plan (ASAP) represent a qualitative and a quantitative tool, respectively, developed to quickly and inexpensively evaluate the potential for lead to migrate off of small arms ranges. The demonstration of ASAP at two installations provided a preliminary verification of REST.

## INTRODUCTION

This paper describes the results of a demonstration of two tools for small arms ranges: the Range Evaluation Software Tool (REST) and the Army Sampling and Analysis Plan (ASAP). The purpose of the demonstration was to test the efficiency and user friendliness of REST and to apply the methodologies of ASAP (one portion) to confirm the lead transport potential indicated by REST. The software, REST, was tested at Fort Wolters, TX, Camp Swift, TX and the Auburn Training Site, ME, while the ASAP was tested at only the two Texas sites.

The sponsors of this effort (the U.S. Army Environmental Center, the Army Training and Support Center, and the Defense Evaluation Support Activity) recognize that the three military services have thousands of small arms ranges, and therefore, need a cost and time efficient mechanism to evaluate which ranges require modification to mitigate lead migration. Military range managers may obtain REST and ASAP by contacting the Army Environmental Center, located at Aberdeen Proving Grounds.

## REST and ASAP PURPOSE AND DESIGN

Both REST and ASAP are designed to help military range personnel evaluate whether range related contaminants migrate away from small arms firing ranges. REST, a Windows-based software application, works on IBM compatible Personal Computers (386 or higher) with a minimum of a Windows 3.1 Operating System. It estimates the potential for heavy metals migration for user defined "Areas of Concern," based on site characteristics. It displays a series of input screens which request information related to the range usage, its physical and geological characteristics, its geographic

location, and its climatic conditions. The REST output provides a four level relative ranking associated with a numeric score indicating overall migration potential:

- high potential = 8-10;
- medium potential = 6-7;
- low potential = 4-5;
- very low potential = 1-3.

REST also provides a numeric score (0-10) to five parameters contributing to the Overall Score:

- Ammunition Mass,
- Corrosion,
- Aerial Transport,
- Surface Water Transport,.
- Groundwater Transport.

These individual parameter scores indicate for the user which parameters contribute to the overall score. The scoring system used by REST represents a qualitative evaluation of lead transport. High scores assigned to the three transport pathways indicate a potential transport problem even if no ammunition has been fired on a range. In other words, a range may have a score of 10 for surface water transport, indicating a potential to transport Pb in streams, but have a score of 1 for Mass (MassScore). Therefore, the overall score would equal 1 or very low potential migration. This tells the range manager that if he changes the range usage in the future to increase the mass of Pb fired into that particular range, he may have a Pb transport issue.

REST calculates these scores according to the following equations (numeric scores for any individual parameter calculation greater than 10 defaults to a value of 10):

$$\text{Overall Score} = \text{MassScore}\,[1-(15-\text{MigrationSum})/30]$$

Where:

$$\text{MigrationSum} = \text{Subsurface} + \text{Surface Air} + \text{Surface water}$$

$$\text{MassScore}=\text{MassFactor}[1-(5-\text{CorrosionFactor}/10)]$$

Where:

Subsurface is a function of (distance to water table, soil type, rainfall, soil pH, etc.)

Surface Air is a function of (Windspeeds, ground cover, soil type etc.)

Surface Water is a function of (soil type, distance to surface water, slope angle, rainfall etc.)

Mass Factor is a function of (Pb mass, soil volume)

Corrosion Factor is a function of (soil type, salt water, water table depth, precipitation, soil pH etc.).

The design for the Army Sampling and Analysis Plan, ASAP, follows the same conceptual model as REST: dictating the physical sampling of each of the three transport pathways (Air, Surface Water, and Subsurface or Groundwater). Physical sampling is advised for any site which receives an overall

score of 5 or higher or an individual pathway score of 5 or higher. This approach saves time and money by focusing site characterization toward areas and pathways needing analysis and possibly range modifications.

## DEMONSTRATION METHODS

Software demonstration methods: Given that these tools must be usable by installation personnel, the demonstration of the software (REST) used installation personnel. Personnel were asked to fill in screens with their site data. Any difficulties encountered using the software or interpreting the output were noted by TRW personnel. User feedback TRW received from the three installations (Ft. Wolters and Camp Swift, TX, and the Maine National Guard Headquarters, Camp Keyes, regarding a 25 meter range at the Auburn Training Site, ME) was translated into software changes. Output scores for Ft. Wolters and Camp Swift were used to compare with ASAP physical sampling results (preliminary software verification).

Sampling demonstration methods: TRW personnel acted as the "ASAP user" or "sampler" at both Camp Swift and Fort Wolters. Two individuals (one PhD geologist and one Ms chemist) spent approximately 8 hours at each of the installations (one range each) implementing ASAP, Section 4.0, "Sample for Surface Water Transport," as well as one portion of Section 5.0, "Sample for Groundwater Transport" (the vertical soil sampling at the source area). GP Environmental conducted the chemical and geotechnical analyses on the samples.

TRW's Work Plan, "Demonstration of the Range Evaluation Software Tool (REST) and the Army Sampling and Analysis Plan (ASAP) at Three Army National Guard Sites: Auburn Training Site, Auburn Maine; Fort Wolters, Texas; and Camp Swift, Texas" dated November 26, 1996, describes the detailed testing methodology for these sites. This work plan contains a "Technical and Sampling Plan" specifically for these three sites based on maps and previous site visits, a "Quality Assurance Plan," and a "Health and Safety Plan." The "Technical and Sampling Plan" dictated taking surface-soil-composite samples in a grid fashion near the source areas (berm) and including the surface stream for both installations. Fort Wolters had two parallel berms which were separated by approximately 20 meters. Both berms were sampled. Camp Swift had a series of pop-up target mounds across an M 60 range. Two mounds adjacent to a stream were sampled at Camp Swift as part of the up-stream sampling grid. We took another grid of surface soil composite samples further down stream, including several stream bottom samples. The sampling plan indicated taking two water samples, if possible at both the upstream grid location and the down stream grid location. Up stream locations had dry stream beds for both Fort Wolters and Camp Swift. Therefore, we took two down stream water samples at each installation.

GP Environmental used TRW's Work Plan as guidance for QA/QC procedures and to determine numbers and types of sample vessels TRW needed in the field. GP personnel sent sample containers inside transport coolers directly to Fort Wolters the day before TRW personnel arrived. TRW personnel also sent sampling equipment (soil probe and acetate liners) to Fort Wolters ahead of their arrival. Both the coolers and the equipment were shipped back to their point of origination by Federal Express. Chain of custody forms accompanied coolers.

In addition to filling out chain of custody forms, field personnel took copious notes logged into a field notebook regarding sample locations, sample descriptions, and field conditions. Of particular importance, were the soil and sediment size descriptions (e.g. sand, silt, clay, loam).

## RESULTS

Software Usability: The three sets of REST users found that the input and output screens were easy to read and interpret, the references necessary for data entry were easily acquired, the time for data entry was acceptable (30 minutes), and the output data would be useful in terms of focusing installation pollution prevention and maintenance efforts.

Comparability of REST predictions with ASAP results: Analytical results compare well, indicating a very preliminary software verification.

Fort Wolters had a "Low" overall REST score (3.6) due to a low Ammunition Mass score of 1.0 despite a score of 9.0 for Surface Water transport. Analytical results from the surface sediments indicate low but persistent above background concentrations for surface water sediments at Fort Wolters. Sedimentary lead concentrations within the stream leading away from the two berms at Fort Wolters remain at values approximately twice the average background value (2x=27.6 mg/kg). Outside of the stream bottom itself, soil Pb concentrations fall close to background (27.6 mg/kg) within 20 meters of the berms. Water samples showed very low Pb concentrations below detection and 1.23 μg/L at Fort Wolters (compared to the Maximum Contaminant Level of 15 μg/L for drinking water per 40 CFR 141). Samples described as having high clay contents had higher Pb concentrations (see Figure 1).

Camp Swift had a "Very Low" REST score (1.3) due to a low Ammunition Mass score of 1.0 despite a score of 6.0 for Surface Water transport. Camp Swift water samples showed very low Pb concentrations of 1.51 and 2.73 μg/L (compared to the Maximum Contaminant Level of 15 μg/L for drinking water per 40 CFR 141). Soil and sediment Pb concentrations generally fell close to background concentrations (5mg/kg) within approximately 10 meters of the pop-up target mounds where spent rounds could be visually identified. The exception to these general results were a few clay rich samples which had approximately twice the background concentrations.

ASAP ease of use and cost: The surface water portion of ASAP tested was easily implemented by TRW personnel (one day per site) at a cost of $7000 in analytical services (for two sites). Individuals with a bachelors degree or more in environmental science are good candidates for implementing this tool.

## DISCUSSION AND CONCLUSIONS

The persistently high lead concentrations in the Fort Wolters downstream sediment samples indicate the potential for off range migration. Sedimentary lead concentrations within the stream remain at values approximately twice the average background value (2x=27.6 mg/kg). This level is below the threshold of regulatory concern (3 times background). The distribution of soil lead concentrations did not separate the 25 meter from the 1000 meter berm source area as the primary contributor to higher than background downstream lead concentrations. Alternatively, Camp Swift downstream sedimentary lead concentrations were not consistently elevated above background, which corroborates the REST score of Very Low. Both sites require additional sampling for verification.

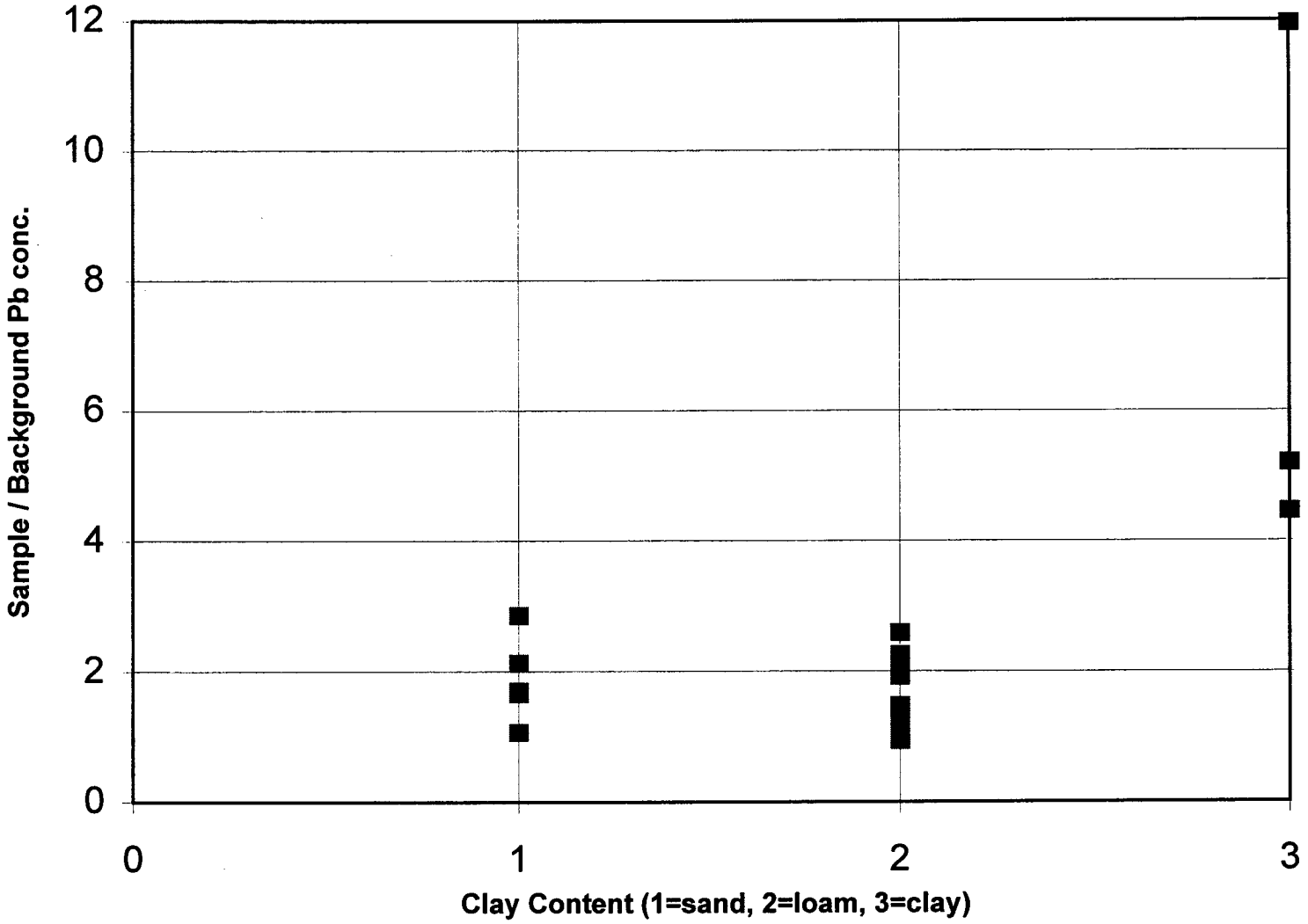
We found above background Pb concentrations only in stream bottom sediments and even then, preferentially in clay rich samples (Figure 1). Sampling schemes that do not focus on the transport pathways and soils likely to contain high Pb concentrations may not reveal actual Pb migration.

Given that clays are smaller than sand particles, they are often transported in streams as suspended load and their transition from a stationary position in the stream bottom to suspension is a function of stream velocity. Thus, the demonstration data (Figure 1) which shows a close association between high lead concentrations and high clay content supports Merrington and Alloway's (1994) conclusion that suspended load carries the greatest portion of lead for surface water transport. This implies that high stream velocities generated by storm events may carry the greatest volume of lead bearing suspended sediments.

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Merrington, G. and B.J. Alloway, 1994, The Transfer and Fate of Cd, Cu, Pb, and Zn from two historic metalliferous mine sites in the U.K., Applied Geochemistry, Vol. 9, pp. 677-687.

**Figure 1**
**Ratio Lead Concentration (sample/background) Versus Clay Content for Soil and Sediment Samples, Fort Wolters, Texas**



# OPERATIONS & READINESS I

# BALANCING NATURE AND CULTURE ON HISTORIC MILITARY LANDSCAPES

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## ABSTRACT

The U. S. Army has recently recognized the evaluation and management of historic military landscapes as an integral component of cultural resource management. The process of properly assessing and managing military landscapes, however, can be problematic due to several broad and necessary requirements. These requirements include the need to preserve the historic character of the landscape, the need to enhance the military image and improve quality of life, and the growing need to implement environmentally and economically beneficial landscape practices on Federal properties, as set forth in a signed memorandum from President Clinton in April, 1994.

This paper presents work, sponsored by the U. S. Army Environmental Center (USAEC), currently underway at the U.S. Army Construction Engineering Research Laboratories (USACERL) to conduct landscape inventories and management plans for installations in two geographic regions of the country: the Desert Southwest (Forts Bliss, Texas and Huachuca, Arizona) and the Mid-Atlantic region (Fort Myer, Virginia). The landscape inventories follow the process set forth in the Army's **Draft** *Guidelines for Documenting and Evaluating Historic Military Landscapes* (1996). Each management plan will become a prototype for other Army installations within that region by providing historically and ecologically sensitive designs, appropriate plant lists, guidelines for enhancing the image of the base and improving quality of life for residents and installation personnel. Of particular concern in the Desert Southwest installations is the overuse of water in historic areas, and the need to replace ecologically inappropriate plants with more drought tolerant species. Plan implementation in these areas is expected to reduce both water usage and associated costs.

Much of this work is being done in collaboration with the Department of Landscape Architecture at the University of Illinois.

## 1. INTRODUCTION

Increased attention has been focused on the evaluation and management of historic landscapes in military and non-military settings alike. The most significant challenge to be faced is preserving and enhancing a landscape's historic character while providing ecologically sensitive landscape treatment recommendations--two important objectives that are not always compatible. Recently, the Army recognized the need for historic landscape management plans to be an integral part of cultural resource management. Since 1994, a multi-disciplinary team of landscape architects, historians, architects, and

geographers at U.S. Army Construction Engineering Research Laboratories (USACERL), has been studying and adapting relevant planning models toward developing a holistic approach for creating landscape management plans that respond to the unique needs and distinctive settings of military installations.

The U. S. Army Environmental Center (USAEC) has provided funds for USACERL to develop *Historic Landscape Inventories* (HLI) and *Historic Landscape Management Plans* (HLMP) for approximately six Army installations in different geographic regions of the country. The intent is to develop a method that is comprehensive in addressing both historical and environmental concerns--a model for historic landscape planning that may find applications in both military and non-military settings. The goal is to integrate ecology and landscape stewardship into cultural resource management.

HLIs identify significant historic landscape areas or features and evaluate their historic integrity in terms of contributing and noncontributing elements. The purpose in identifying contributing features is to guide the development of appropriate preservation and management recommendations which are presented in HLMPs. Noncontributing features are accompanied by treatment recommendations which describe approaches to mitigating negative impacts on a landscape's historic character. Recommendations are reviewed for their appropriateness to the historical context as well as the ecological and environmental parameters of the region.

The primary purpose of these HLIs and HLMPs is to document, evaluate and manage landscapes in compliance with the National Historic Preservation Act (NHPA). Additional benefits to be realized at an installation from applying the proposed treatments include creating ecologically sensitive landscapes, enhancing the image of the military, and improving quality of life for residents and personnel. USAEC in collaboration with USACERL is currently in the process of selecting installations in six distinct ecological regions for purposes of field testing the method and various tools for conducting phases of the work. The focus is on the Desert Southwest and Mid-Atlantic regions in the first of a three year effort. The case studies feature Fort Bliss, Texas and Fort Huachuca, Arizona in the Desert Southwest, and Fort Myer, Virginia in the Mid-Atlantic.

Ecosystem management for installations can be viewed as a continuum embracing at one extreme the natural, undisturbed landscape (the part we should conserve) and the other being the human, built landscape (the part we can control). Just as installations prepare plans to manage threatened and endangered species and other aspects of the natural landscape, historic landscape management plans provide guidance for enhancement of the built environment. This area of research can have a significant impact by anchoring the most highly personalized end of the ecosystem management continuum--the human landscape.

## 2. BACKGROUND

To preserve and protect our cultural heritage, federal agencies are required to comply with federal preservation legislation. The most prominent federal regulation that installation cultural resource managers must address with respect to historic military landscapes is the National Historic Preservation Act (NHPA). Sections 106 and 110 of the NHPA address federally-owned or controlled cultural resources. Cultural resources are defined as buildings, structures, sites, objects, districts, landscapes, archeological sites, traditional cultural properties and archival resources. Section 106 requires federal agencies to take into account the effects of undertakings on any property listed in, eligible or potentially eligible for listing in the National Register of Historic Places (NRHP). The purpose of Section 110 is to ensure that historic preservation is fully integrated into the ongoing programs and missions of Federal Agencies. It requires federal agencies to establish, monitor, review and evaluate their preservation programs. This includes the

identification and management of cultural resources eligible or potentially eligible for listing on the NRHP.

Four years ago USACERL initiated a program to help Army installations comply with the NHPA by developing methods for inventorying and managing historic military landscapes. Traditional methods for determining historic districts involved delineating an area around historic buildings without considering the landscape as a whole. The landscape approach embraces a more holistic view that takes into account the geographical setting, land forms, vegetation, circulation systems and the arrangement of buildings. Because these aspects of the landscape are more complex than individual structures and are harder to define, there was a need for a more comprehensive method of assessing historic military landscapes.

USACERL defined and developed a method for identifying and evaluating the historic significance of military landscapes. This guidance document is being published as Department of the Army's technical guidelines, *Guidelines for Documenting and Evaluating Historic Military Landscapes* (hereafter referred to as the *Draft Guidelines*). The method describes the unique processes and historical context of military installations and emphasizes the importance of the relationships among individual buildings, circulation networks, and landscape features that contribute to a historic military landscape. By applying a holistic landscape approach to a national military context, the *Draft Guidelines* provide a systematic approach to documenting the evolution of a military installation and evaluating the significance of its contributing resources.

The two project types (HLI and HLMP) were originally intended to help Army installations comply with cultural resource legislation. However, the scope of management plans extends far beyond simple compliance. Since the purpose of these plans is to recommend historic landscape treatments for the future, an opportunity exists to balance natural and cultural issues. The recommendations provided by management plans will help to provide a quality living environment for soldiers and their families, one that preserves the historic and embraces the environmental character of the landscape.

Before 1995, there was no guidance for how to manage and maintain historic military landscapes. Non-military examples existed, but these involved intensive, time consuming and expensive research. It was therefore necessary to design a cost effective, time efficient method for completing these plans. Through partnering with the University of Illinois, USACERL organized a team of landscape architects, architects and geographers to develop the Fort Sam Houston Landscape Master Plan. The purpose of the master plan was to provide recommendations for preserving the historic landscape character of this National Historic Landmark. The greatest challenge was to be faithful to the historic record as well as sensitive to the severe water shortage in the San Antonio area. Since people were not always water conservation conscious, it was important to assess what had been done historically and determine if those practices were appropriate for the present and the future. The project's success was a result of a keen understanding of both natural and cultural issues. It was awarded the Texas Historical Commission's Award of Excellence in Historic Architecture. This success led to the initiation of the USAEC sponsored project that is the topic of this paper. The following describes the approach for executing this work.

## 3. APPROACH

The process of creating HLMPs begins with a thorough understanding of the natural and cultural resources of both the regional and local landscape. Extensive archival research is conducted to gain knowledge of the cultural landscape history and to assess regional landscape characteristics. HLIs are prepared for purposes of identifying and assessing military landscapes in terms of their historical significance. HLMPs, which provide guidance on managing natural and cultural features on an installation, are completed using the information provided by the landscape inventory and knowledge of environmental factors that will

influence management guidelines including selection of hardy plant species and identification of appropriate landscape maintenance practices. This approach, which has been applied and adapted to several installations in recent years, provides a comprehensive and systematic process for developing management strategies that are specific to the installation's needs and landscape setting.

## 3.1 HISTORIC LANDSCAPE INVENTORIES

The landscape inventory is conducted using a holistic approach, one that examines the relationship among buildings, roadways, vegetation and land forms within a multidisciplinary research framework involving history, military history, architecture, landscape architecture and planning. A successful HLI accomplishes three objectives which are important to subsequent phases of work. It places the military installation within the larger historic context; determines the significance of the installation landscapes as they relate to the context(s); and assesses historic integrity--the ability of the landscapes to convey their significance.

This landscape inventory process is described in the Department of the Army *Draft Guidelines* prepared by USACERL in 1996. The intent of that document is to provide a general set of guidelines to assist interested persons and agencies with historic landscape documentation, architectural surveys, and archeological studies. The holistic landscape approach espoused in the *Draft Guidelines* should be integrated into basic survey and evaluation activities that document an installation's overall history and significance.

Recently, USACERL developed a HLI for Fort Bliss, Texas. The steps that were followed throughout the formation of that inventory will be discussed as an example, and are indicative of the methods employed by USACERL at other installations, including Fort Riley, KS., Fort Sam Houston, TX., West Point Military Academy, and Fort Myer, VA., where inventories have either been completed or are currently under production.

The initial phase of a HLI involves the placement of the installation into a larger historic context, that being the national military context, or any of the three levels as defined by the National Register: national, state, or local. Primary and secondary archival resources are reviewed and a synopsis of the installation's site history is written and each period and theme of landscape development is established. The National Archives I and II is the single greatest repository for this type of information. Additional resources may be found at the installation, local libraries or historical society archives. In addition, other federal and military sources are contacted including the Library of Congress and the United States Army Military History Institute.

The final stages of the HLI are to assess the historical significance and integrity of the landscape. Quality of significance is evaluated according to NRHP criteria. Specifically, the criteria applied to landscape evaluation include association with events that have made significant contribution to our history, or association with the lives of persons significant in our past, or association with a distinctive style of design or designer. Further, the NRHP recognizes seven aspects that, in various combinations, are applied to define integrity--location, design, setting, materials, workmanship, feeling and association.

Once the historic context, significance, and integrity have been documented, the geographic limits of historic landscape subareas are initially determined and further refined through on-site surveys. During these surveys, photographs are taken, field notes are made, sketches are drawn and landscape characteristics such as land uses, circulation networks and natural features are recorded on maps.

At Fort Bliss, a historic context had previously been written by an associated team at USACERL which focused on architectural development at Fort Bliss. That context had established thematic and

chronological groupings for the buildings at the installation. Using this completed context as a guide, a more specific landscape-related study was conducted. The references cited in the architectural context proved useful, but due to the specific nature of the landscape inventory, additional information was needed, specifically documentation of the natural landscape, climatic conditions, and landscape planning/design styles that influenced the development and evolution of the landscape.

Eleven distinct subareas were identified at Fort Bliss, which, taken as a whole, comprise the entire historic main cantonment. In the description of each subarea, defining features were identified, a statement of significance and period of significance was provided, and a brief statement of integrity was written. Working with architects and historians at USACERL, the conclusions drawn from the HLI and the architectural surveys were combined to establish boundaries for the formal definition of the Historic District.

Although the objectives of the HLI are well established, it may be necessary to modify the method depending on circumstances and the availability of research materials. For example, the installation may already have a Historic District placed on the National Register, so the results of the inventory will be affected by pre-established conclusions. The manner in which a HLI is completed may take different directions, but the *content* of the inventory must fulfill the roles of documenting, identifying and assessing significant landscape areas and features. Subsequent phases of work, including the development of a management plan, are dependent on this foundation.

## 3.2 REGIONAL LANDSCAPE ASSESSMENT

The development of HLMPs requires an understanding of the natural characteristics as well as the cultural history of a military base setting. A description of the natural setting serves to explain influencing factors such as temperature ranges, rainfall patterns, seasonal variations and extremes, topography, soil properties, and endemic plant and animal species. These natural characteristics complement, and sometimes oppose, cultural characteristics. In addition, an understanding of the natural characteristics will assist in the development of a more comprehensive description of an installation. This will also help to develop and implement environmentally and economically beneficial landscape practices. This specifically concerns installations based in the southwestern part of the United States, where water usage is a critical issue.

### 3.2.1 Natural Characteristics and Ecoregions

The natural component of HLMPs can be described from both a regional perspective as well as from a site specific level. Regional descriptions, such as for the dry American Southwest, provide the dominant biological and physical characteristics of an area in a broad context that separates it from other regions in the U.S. All installations in this region share similar natural characteristics and will benefit from one regional management plan. Ecoregions, as defined by Robert G. Bailey (1995) and others, have defined distinct regions of ecosystems for the U.S. and serve as the basis for regional landscape management plans.

For example, the ecoregion description for the desert southwest is defined as the Dry Domain by Bailey and is further broken down into two divisions, the Tropical/Subtropical Steppe Division and the Tropical/Subtropical Desert Division. Further, each Division is subdivided into Provinces. The Tropical/Subtropical Steppe Division contains three Provinces including the Southwest Plateau and Plains Dry Steppe and Shrub Province, within which Fort Sam Houston is located. Fort Bliss and Fort Huachuca are located in the Chihuahuan Desert Province of the Tropical/Subtropical Desert Division.

Installation-specific characteristics are more detailed descriptions of the regional characteristics. These site-specific factors direct the development of the HLMP by demonstrating appropriate planting

techniques, plant species selection, and environmentally-friendly landscape practices. These include water and energy conservation, pollution reduction (pesticide and power plant emissions) and maintenance costs reduction (mowing, pest control, weak unadapted plants).

### 3.2.2 Data Types and Their Sources

Descriptions about natural characteristics are collected from published sources such as Bailey's ecoregions descriptions and horticulture books, and from institutions and local experts. The types of data that are collected at the regional level include ecoregion descriptions, precipitation, temperature, plant species and hardiness zones. At the installation scale, additional data is gathered including site geology, soil descriptions, microclimate and indigenous plant species. Plant palettes are subsequently developed according to plant scale (large trees, large shrubs/small trees, vines, shrubs/cacti, and ground cover), water requirements, and whether a plant is endemic, introduced or exotic to the region.

Also, mapped data from geographic information systems (GIS), computer aided drafting (CAD) systems, soils reports and other sources is assembled and synthesized into a consistent format for presentation and use in preparing the HLMP. On-site photography, surveys and field work is conducted by the research team as necessary to supplement and confirm site data obtained from all external sources.

## 3.3 HISTORIC LANDSCAPE MANAGEMENT PLANS (HLMPs)

The historic landscape management plan is a tool that the installation will use to preserve and maintain significant historic landscape resources. A successful management plan achieves a balance among historic resources, environmental issues and current needs. It incorporates the results of the landscape inventory and the regional landscape assessment with current site information. The following sections describe the methodology and tools used to assess the installation requirements, develop recommendations, and direct the implementation of a landscape management plan.

### 3.3.1 Phase I - Research and Project Preparation

The development of the HLMP begins with the definition of the historic landscape subareas to be reviewed. The subareas are initially defined in the HLI, and further refined through consultation with the installation Cultural Resource Manager (CRM) and on-site surveys. The research team develops a statement of design objectives for each subarea that addresses a combination of historic, mission-related and environmental issues. In addition, a schedule for conducting the work and a set of potential products is prepared. This step accomplishes a transition from the broader landscape perspective provided by the HLI to a site-specific scale for more detailed site analysis and treatment recommendations.

This is also a data gathering phase for the acquisition of site-specific information about each subarea. Useful materials may include historic and current maps, photos, plant lists, and any documentation describing management of the landscape. Current landscape management information is often available from an Installation Design Guide (IDG) or current master plan. Installation personnel such as the Master Planner, Director of Housing, and Natural Resource Manager are important sources for obtaining site information and for learning about current issues that might impact the management plan. These personnel as well as the CRM continue to be involved throughout the process for reviews, feedback, and decision-making about the final recommendations.

In addition, basemaps of the installation and for each of the historic subareas are acquired or developed prior to visiting the site. These maps are used not only as guides to the installation but also for making

field notes and recording existing conditions. Ideally these maps are generated directly from AutoCAD or GIS files, ensuring better accuracy and eventual compatibility with the installation's planning system.

### 3.3.2 Phase II - Site Inventory

In concurrence with an understanding of the cultural and natural history of an installation, detailed site inventories of the historic subareas are prepared during on-site visits. These inventories include information pertaining to existing land use, focusing in particular on the placement and condition of buildings, landscape, roads, pathways, and important markers, and relationships among these landscape components.

The inventory is conducted using a traditional field work approach. The project group is divided into smaller teams with responsibility for specific areas. Field notes and scaled maps are used to record any additional buildings or features (walls, stairs, sidewalks, patios, planting beds, parking or sitting areas, utility structures), vegetation (type and size) and comments about general conditions. Photos are taken to record all important structures and their settings, open areas such as parade fields, and views within and around the historic areas. These photos are reviewed for how well they represent the range of current conditions, and compared against the historic photos to determine whether they capture the changes from the historic setting. Additional surveys are conducted and photos taken to fill any identified gaps in the record.

### 3.3.3 Phase III - Site Assessment

The first stage of site assessment involves identifying and documenting the distinguishing landscape characteristics that compose each historic subarea. This analysis is conducted with reference to the historic period of significance determined in the HLI. Historic landscape or building features which are still evident in the landscape from that period are noted as contributing to the historic character. Landscape or building changes which occurred outside the periods of significance are determined by comparing the current conditions against the findings of the HLI and other detailed historic information. These changes can be evaluated as either sympathetic (not historic but not in conflict with the historic character) or noncontributing (disruptive to the historic character). For example, features that may contribute to historic character include buildings of appropriate architectural style or the consistent use of street tree plantings to line roads or parade grounds. Noncontributory features may include replacement porches, add-on back doorways, or use of inappropriate materials to construct walls, fences or patios.

The second step in site assessment addresses current conditions and issues of quality. Landscape materials are evaluated for their suitability to the setting from both an environmental and a historic character standpoint. Plantings may be judged as inappropriate because of incompatibility with maintenance practices, inability to thrive in a location, or growth characteristics and placement which detract from the historic setting or hide important historic attributes. In addition, building exteriors, garages, walls and fences are evaluated for current condition and any inappropriate modifications that may have resulted from painting or other maintenance operations.

Finally, the research team investigates how an area is currently used. This is important in being able to integrate concerns for maintaining the historic character with meeting the current needs of the installation. It may also highlight previously unconsidered opportunities that could be utilized to improve the quality of life for residents and an installation's public image. At this point, the historic integrity of the subarea described in the HLI is refined, indicating how compatible the appearance and use of the current landscape is with its historic period of significance. Historic integrity may also provide an indication of the type and extent of landscape treatment that may be required to preserve the desired historic character.

### 3.3.4 Phase IV - Recommendations

Landscape treatment recommendations are proposed to address weaknesses in the integrity of historic areas. Recommendations may focus on preserving a specific landscape use or treating landscape components to restore historic character. All proposed recommendations or treatments must be sensitive to current needs and not interfere with the mission of the installation.

Many recommendations involve the use of plants to accent or enhance historic architecture or to mask an obtrusive but permanent noncontributing feature (e.g., parking area, fencing, utility structures). To support planting treatments, lists of recommended plants that integrate historic and environmental concerns are included in the HLMP. Plants are categorized into groups appropriate for the different subareas based on how their form, color or style support the historic character for a particular area. For example, at Fort Bliss, plants were categorized as appropriate for the dominant architecture styles of Victorian era, California bungalow, and Spanish Mission. In addition to planting and other landscape treatments, recommendations may also suggest opportunities to improve underutilized areas or to enhance the public image of the installation. Such opportunities might include the potential for creating demonstration gardens, historic exhibits, walking tours, or common open spaces in residential areas. While these suggestions are not directly in support of historic landscape preservation, they are intended to improve the overall appearance of the installation and enhance the outdoor space in ceremonial, housing and administration areas.

For example, recommendations presented in the HLMP for Fort Bliss included the removal or replacement of intrusive features such as fencing, plantings, and minor structures, re-establishing the historic uniform street tree plantings around the parade ground, installing additional plantings to enhance the historic character of housing areas, and the introduction of a children's play area in a housing area.

Graphic images are used to illustrate current situations that compromise the historic character and to visually represent potential solutions to these situations. A variety of software such as computer aided drafting, photo manipulation and desktop publishing/presentation tools, as well as hand-drawn graphics, are used to express in both words and graphics how the application of the proposed treatments will improve the historic character of the installation. Landscape management plans are organized and presented using tools that will be most efficient in helping the installation with implementation as well as dissemination of the proposed recommendations within and outside the installation.

### 3.3.5 Phase V - Implementation

The recommendations are finalized after detailed review with the CRM and other integral installation personnel. Those aspects specifically directed toward restoring and protecting the historic landscape character are summarized and become part of the Cultural Resource Management Plan.

In addition, all the recommendations of the HLMP should be incorporated into the Installation Master Plan and/or Installation Design Guide. The actual implementation of the recommendations will be phased in over time as either immediate, minimal treatments or long-range, comprehensive solutions. The design component of the recommendations is conceptual only, but may include scaled drawings for demonstration gardens/areas to further illustrate design style and appropriate use of plants. These design concepts are critical records to improve and maintain historic character, and will serve as guides for the installation to initiate improvements with the assistance of the U. S. Army Corps of Engineers district offices or outside consultants.

The use of software tools for preparing the HLMP allows for a better transition of the plan to the installation. Many of the ideas can be immediately integrated with the installation's AutoCAD system, and various presentation materials can be quickly converted into educational and promotional materials for the base. Also, the Internet is being investigated as a way to disseminate information about landscape management planning throughout the DOD. The Internet would be a valuable tool for documenting and disseminating information about regional planning, and opening up a dialogue between installations regarding issues and solutions for historic landscape protection. USACERL will continue to work with the installation to develop explanatory materials to promote better understanding of the need for and approaches to historic landscape management, and to generate interest and support especially from residents and installation personnel.

## CONCLUSION

With the support of the USAEC, this approach to preparing HLIs and HLMPs is to be applied to six installations in different ecoregions of the United States. Each management plan will become a model for other installations within that region, accomplishing a transfer to installation planning personnel of the tools and techniques required for successfully preparing and implementing HLIs and HLMPs. Benefits to be realized at the scale of an installation include protection of historic landscape character (in compliance with NHPA), enhancement of military landscape image, and improvement of quality of life for base residents and personnel. Further, the protection of historic resources and promotion of ecologically sound landscape practices as described in HLMPs is an important and necessary step in responding to Presidents Clinton's 1994 memorandum and enhancing the Army's reputation with respect to landscape stewardship.

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Directorate of Public Works, Facility Engineering Plans & Services, Fort Myer, Virginia.

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# GUIDELINES FOR MAPPING VEGETATION ON MILITARY LANDS

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## Introduction

In the days BC (Before Computers), a vegetation map was usually a representation on paper or Mylar of plant species and communities on a site, along with roads, streams, etc. The graphics were hand-drawn or pasted on with decal symbols. Although serviceable, the scale might be a little inaccurate, the coverage uneven, and uses limited. Users were almost exclusively natural resource managers with direct responsibility for land management.

With the growth of computing techniques and advances in remote sensing, modeling, and sampling theory, a vegetation map can now possess a great deal of sophistication. The quality, information content, and flexibility of vegetation maps have risen dramatically. Information is no longer valuable to a few, but can be shared, manipulated, and presented to serve many different clients. A major benefit is the ability to deal with temporal issues, such as applying predictive models on vegetation changes from the influence of human actions, making relatively easy updates to the maps from monitoring, and running "what-if" scenarios under alternate management options.

The usual intent of a vegetation map is to supply an inventory of plant communities; their location, extent, geographical distribution in the landscape, relationship to other landscape features, and a description of selected characteristics. Therefore, a vegetation map is a spatial representation of plants on the landscape. The expansion of computer technology has transformed this usually cumbersome package, when done on paper only, into a stack of overlapping digital data files that store and display an array of individual vegetation

characteristics. Therefore, as opposed to the days BC, an updated description of a vegetation map is *a geographically registered digital database that will store, manipulate, and display spatially-arranged vegetation information. That information may include data such as species composition, community descriptions, tree diameter, and vegetation height.*

This rise in capabilities is accompanied by a rise in the complexity of the process of developing a vegetation map. Recognizing the importance of a tool to benchmark vegetational changes for many activities at an installation, the Army Environmental Center funded the four Corps of Engineers research laboratories to develop and test guidelines for vegetation mapping on Army lands. Guidelines have been written to support in-house work, contracting, or a combination of mechanisms. This paper describes those guidelines and suggests their applicability to the other Services.

## Approach

The need for guidelines was examined and verified with a survey of 34 Army installations during the spring of 1996. The purpose of the survey was to determine current status and application of existing Army vegetation maps; determine the detail, methods, and uses of these maps; and gain an understanding of lessons learned from these efforts. The survey revealed 81 existing vegetation and related maps on the 34 installations. Twenty one of the 81 maps were still in preparation. Of the 60 that were completed, 15 were not being used and 34 needed updating. Sixty nine of the products are or will be in a Geographic Information System (GIS) format. Methods used to produce the maps differed, but a combination of aerial photography and ground truthing was the favored approach. The average cost of producing 18 maps was $172,000 on 11 installations, where these figures were known. Only 19% of the maps were produced in-house, showing an important role for outside agencies and contractors and the importance of good guidelines for contract work to provide satisfactory products.

Additional input from the installations was received at a workshop in August 1996. Representatives of 14 installations were queried on details such as what attributes should be displayed on maps, how they use maps and their accompanying data, and what their previous mapping experience has been. The list of users of vegetation maps on an installation can be extensive because the condition of vegetation is rich in information. Primary users are natural resource managers and land managers involved with the installation training or testing mission. Resource-specific issues such as forestry and endangered species management require good plant inventories. Other users include personnel involved with cultural resources, safety, the public, and managers at higher command levels.

In addition to the operational requirements for the information contained in vegetation maps and associated files, regulatory drivers exist in numerous Department of Army citations. Department of Defense Instruction 4715.3 section F.1. General Conservation Management includes requirements to assess the military mission and to prepare detailed inventory of resources. The planning level survey described in the Instruction states that the "Biological inventory should include soils, vegetative communities, critical species, and wetlands and water sources."

Recognizing that other agencies also have needs for vegetation maps, researchers examined the mapping programs of the U.S. Forest Service, the Bureau of Land Management, and work by The Nature Conservancy for the National Park Service. The activities of the Federal Geographic Data Committee on vegetation classification were also examined. When appropriate, protocols and products from those entities were included. The remainder of the guidelines were written from experience and the literature.

The Guidelines

From an examination of the divergent group of map users, it may be inferred that goals and objectives for preparing a map are highly varied. This implies a set of choices by the user as to what is to be described and mapped, how information is to be collected and organized, and how the products are to be used. Each of these choices has consequences for the associated time and costs of the process.

The guidelines serve as a reference summarizing the process and best options for mapping vegetation that address the needs of the installations, both for implementation of specific projects and for larger-scope vegetation mapping programs. The guidelines are not intended as a "one size fits all" solution; but rather emphasize and promote the need for mapping flexibility at different levels of detail on a single installation.

The guidelines contain 27 sections organized into five chapters: Introduction and Use, Decision Framework, Reference Library, Case Studies, and Project or Contract Management. The Introduction describes the philosophy behind mapping, such as to plan a mapping program with "independent" components to take advantage of different funding opportunities, and to plan information collection for flexibility to meet future needs and to be compatible with expanded information topics (data types, locational information, recurring and changing needs). The benefits of vegetation information in a GIS environment are emphasized.

The Decision Framework provides recommendations and diagrams for planning information collection, including suggestions on how to set mapping objectives among multiple users, what classification system to select, and specifications and costs of various mapping options. The decision framework is written around six steps in the vegetation mapping process (Figure 1). These are not entirely linear, having several iterations and multiple parallel pathways, but are a starting point for organizing the process.

The chapter called the Reference Library provides a technical back-up and reference for use in planning and conducting the mapping work. Sections in the Library include the status of and Federal standardization of classification systems, capabilities and uses of remote sensing platforms and image analysis, relevant points on GIS technology, field methods, and accuracy assessment. The relationships between multiple users, multiple objectives, and typical attributes collected during the mapping process are described to help the user design a database; an excerpt of that section is shown in Figure 2. Also included in the Reference Library are example Memoranda of Agreements and related mechanisms to help get the work done, references to

other sources of information such as vendors, list servers, and work by other agencies, and a matrix of laws and regulations showing their pertinence to vegetation maps.

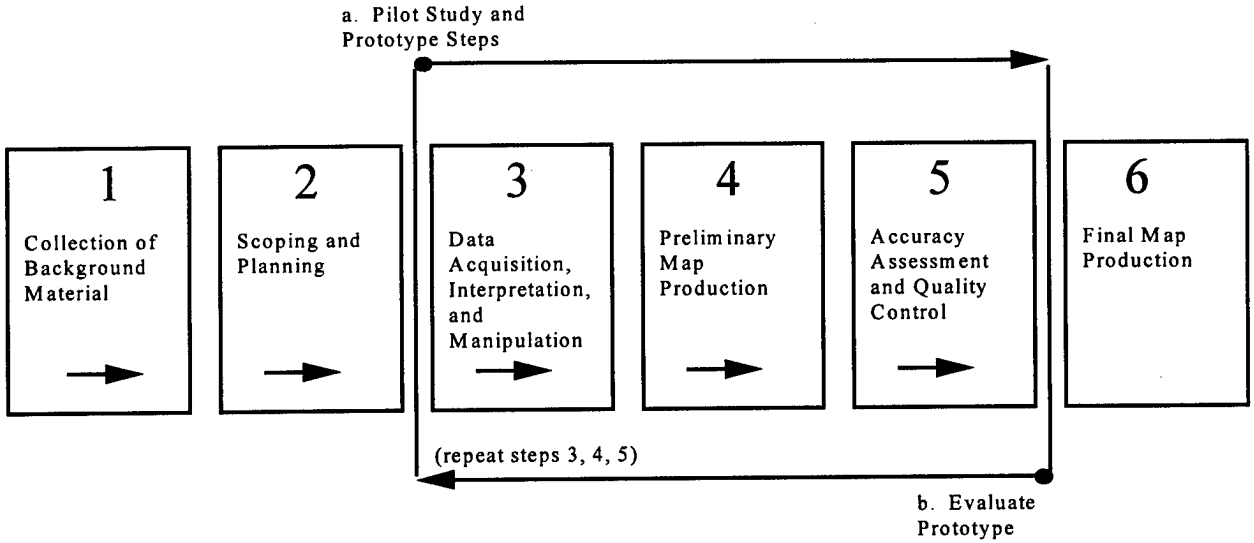



Figure 1. Overview of the vegetation mapping process.

| | User Categories | | | | |
|---|---|---|---|---|---|
| **Attribute** | **Mission Concerns** | **Land Manage.** | **Fish and Wildlife** | **Endangered Species** | **Pest Manage.** |
| Physiognomic group | yes* | no | no | no | no |
| Association | no | yes | yes | yes | yes |
| Species of plant | no | maybe | yes | yes | yes |
| Canopy cover | yes | maybe | yes | maybe | maybe |
| Stand height | yes | maybe | yes | yes | no |
| Stem diameter | yes | maybe | yes | maybe | no |
| Stem spacing, density | yes | no | yes | maybe | maybe |
| Leaf persistence | maybe | no | maybe | maybe | no |
| Fuel load | yes | maybe | yes | maybe | maybe |
| Species diversity | no | maybe | yes | maybe | no |
| * Yes, no, or maybe indicates whether a specific map attribute is useful for a particular application or set of users. | | | | | |

Figure 2. Excerpt from section describing users and vegetation attributes

The Case Study chapter contains a complete template for a Scope of Work with examples and a set of lessons that have been learned on getting good and usable products. Project or Contract Management covers the many details necessary to assure that the user gets the product he or she needs, at acceptable and affordable quality.

These guidelines were developed by the Army for Army installations, and are presently in review by Army installations and representatives of selected Federal agencies and organizations involved in mapping efforts. Revision is expected in the last quarter of this year. The need for vegetation maps extends well beyond that of Army land managers to anyone responsible for land, water, and biotic resources. Other services are encouraged to participate in the field review process to ensure applicability to a wider constituency, namely the Tri-Service community. The Army Environmental Center invites other services to cooperate in advancing the guidelines through review, testing, and revision.

Benefits of the Guidelines

The guidelines resulting from this work are flexible, but allow standardization to the degree that it is beneficial. The decision process outlined is a logical way to approach a complex problem, and builds on a large amount of prior experience. The guidelines include updates on the rapidly growing areas of imagery and computer capabilities, and highlight the difficult and little understood area of accuracy assessment. Sections such as those with cost estimate information and case studies provide practical assistance. In articulating the broadened audience that currently exists for vegetation maps, the guidelines provide new insights on the use of vegetation in training, change detection related to impacts, and improved conservation practices. Using maps prepared with these guidelines, the installations should see improved capabilities and reduced costs for collecting compliance data, managing training, managing natural and cultural resources, and restoring impacted lands.

# DESIGN OF MODULAR BULLET-TRAPPING UNITS USING SHOCK-ABSORBING CONCRETE (SACON)

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## ABSTRACT

Shock-absorbing concrete (SACON) is being investigated as a recyclable bullet-trapping material for use on small-arms training ranges. SACON is a foamed concrete material made with the density that is one-half to one-third that of conventional concrete. Barriers made from SACON absorb bullets fired directly into the concrete without producing ricochets. To facilitate the use of SACON in target protectors, target backstops and erosion control structures, it is necessary to design man-portable pre-cast modules or blocks that can be easily moved onto a training range and used to build structures that are safe, structurally stable and easy to maintain. Economical considerations require that the modules or blocks be simple to manufacture using forming techniques that are readily available and inexpensive. Three module designs (chevron-shaped blocks, interlocking I- and T-shaped blocks and simple rectangular blocks) have been investigated. This initial investigation indicates that the simplest shapes provide significant advantages in reduced effort in deployment and reduced cost in manufacture.

## 1. INTRODUCTION

Shock-absorbing concrete is a low-density, foamed concrete similar to light-weight concretes used in many commercial and industrial applications including fire barriers, sound-deadening walls and insulating roof decks[1]. At the USAE Waterways Experiment Station (WES), shock-absorbing concrete (SACON) research and development activities have focused on its use at military firing ranges in making safe (non-ricocheting) bullet barriers[2-4]. The SACON blocks developed for small-arms training ranges typically have densities between 65 and 90 pounds per cubic foot (1040 and 1440 kg per cubic m) and are formed from cement, sand, water, aqueous foam, and fibrous reinforcement materials[5]. No coarse aggregate (particles above sand size) are used in the concrete.

SACON has been used on training ranges in both cast-in-place and precast concrete construction. The precast modules are generally more practical than cast-in-place structures because of the requirement that the cast-in-place concrete not be fired on until it cures for approximately 28 days. Cast-in-place construction requires the training range be closed during curing. Using precast blocks or modules minimizes the "down-time" for the range and makes it possible to make repairs without disrupting training schedules. Precast units can be made in all sizes, shapes and colors. The larger blocks and panels may require heavy construction equipment (cranes or loaders) be taken out on the range. Smaller blocks or modules can be moved without heavy equipment. For most purposes a block can be considered "man-portable" if it weighs 200 pounds or less (91 kg or less). The engineering challenge is to design safe, stable, durable, bullet barriers that use only blocks or modules that are man-portable.

## 2. FUNCTIONAL CONSIDERATIONS

Modular SACON units that are made from man-portable blocks are being installed at firing ranges to demonstrate the functional capability of this type of design and to evaluate the service life in a typical training range environment.. SACON has been used primarily for target backstops, target lifter protection (coffin protectors) and soil erosion control structures to protect the ground in front of and behind "pop-up" targets.

The SACON modular units installed at military firing ranges must display specified physical characteristics in order to comply with functional and safety requirements. The modular unit density must be matched to the types of weapons used at a given firing range. Weapon type, bullet type, and firing distance must be considered when selecting a SACON mixture design that has an appropriate density. Firing angles incident to the SACON exposed surfaces must be greater than 11 degrees to prevent bullet ricochets from occurring. Modular unit thickness also needs to be sufficient to allow for an economical service life before blocks require replacement. In general, a barrier completed from modular units requires a thickness greater than 22 inches (0.56 m) especially when placed into service on a high-use firing range. All cracks, openings, or potential passage-ways for bullet "shoot-through" must be blocked. This can be done by orienting the blocks at angles so that none of the cracks between blocks are continuous through the thickness of the wall. In multi-layer walls, the blocks in the rear of the wall cover the cracks between blocks in the front of the wall. It is desirable that the units interlock to minimize shifting of blocks within a stack when bullets impact the blocks..

Modular units also must be designed to facilitate manual lifting and handling without special slings or lifters. Each unit must be designed to weigh less than 200 lbs (91 kg), and to have a shape that will allow several persons to lift and carry it with an even load distribution. Mass considerations are important since the units are handled on more than one occasion. Initial installation requires lifting and handling each unit, and the units may need to be re-positioned during service on the range. The units may also be handled at the end of their useful service life when they are removed for recycling or disposal.

## 3. MODULAR UNIT TYPES

Several types of SACON blocks or modules have been designed, constructed, and placed into service on military firing ranges. The modules are shaped as chevrons, I-blocks, T-blocks, rectangular blocks, or cylinders. The cylinders are designed to resemble logs or stumps so that they blend in with existing log piles and stumps that are used as bullet barriers on some ranges.

### 3.1 CHEVRON-SHAPED BLOCKS

he chevron-shaped blocks (Figures 1-2) were the first attempt at making modular units and were designed to produce a wall or vertical barrier that is a made with a single layer of large blocks. Each surface was inclined at an angle of 15 degrees from the vertical or horizontal. The inclined surfaces that formed the joints (or cracks between adjacent blocks) prevented the wall from having any points where a bullet traveling in a straight line would encounter a crack that would continue straight through the full thickness of the wall. All corners were created by non-perpendicular intersecting sides, and a complex mold was required to cast the units. Each modules or block has a mass of approximately 200 lbs (91 kg).

Several problems were encountered when the blocks were placed in service. The sides tapered to a thin edge and the thin portions tended to break when the blocks were moved. Bullets hitting the thin edges produced more damage then bullets striking the thicker portions of the blocks. The thin edges could be easily "shot-away." The bullets that struck the inclined vertical surfaces tended to separate the blocks and open joints between adjacent blocks. There was no good way to built a wall that was more than one block in thickness. It was not possible to connect two vertical walls together to form a wall with double the thickness. The block design employed allowed only a 24 inch-thick (0.6 m-thick) wall to be built.

### 3.2 I-SHAPED AND T-SHAPED BLOCKS

In additional trials the block shape was changed to an I-shaped block or a T- shaped block (Figures 3-4). The T-shaped block was one-half of an I-shaped block. The new shape eliminated the tapering edges that had been a problem on the chevron-shaped blocks. The I-shaped blocks were the same mass as the chevron-shaped blocks, but were easier for two or more persons to lift. The block design allowed the blocks to be interlocked to form a wall several blocks thick. Building a thicker wall increased the service live of the wall. Vertical and horizontal joints were offset to minimize localized bullet penetration patterns or "shoot-through" along joints or cracks. The T-shaped blocks were designed to fill in the gaps at the end of the staggered rows of blocks so that the face of the completed wall could be flat.

The I-shaped blocks were an improvement over the chevron-shaped blocks in that the molds were easier to fabricate and the blocks were easier to demold. The simpler shape also reduced the problem of broken edges and corners. The blocks could be easily stacked in the field to form a wall. The blocks were still a heavy lift and hard to handle without equipment and the use of the molds added to cost of manufacture. This design showed that "shoot-through" could be prevented by the stacking arrangement of the blocks and that a single block did not have to be

made in a complex shape to avoid continuous joints or cracks through the wall.

## 3.3 SIMPLE RECTANGULAR-SHAPED BLOCKS

Evaluation of the performance of the I-shaped blocks led to further simplification of the blocks. A simple block design that had a mass of 94 pounds (43 kg) was developed (Figures 5-6). The simple block had the advantages of the non-tapered shape of the I-shaped block, and could be manufactured by casting a slab that was 6 inches (152 mm) or more in thickness and cutting the slab into blocks. This technique eliminated the need to fabricate a mold and the light-weight concrete can be easily cut using a diamond-tipped concrete saw. The problem of joints or cracks was addressed by staggering the orientation in the stacks of blocks so that no continuous joints were produced in the wall formed from the blocks. The blocks were easier to move and single blocks could be removed without disassembling the stack of blocks as was the case with the interlocked I-shaped blocks.

## 3.4 CYLINDRICAL MODULES

On some ranges, where it is necessary to provide erosion protection to keep gulleys from forming and still preserve the training realism of the range, stacks of logs or rows of stumps were placed on the range in the areas where bullets impacted behind the target positions. SACON modules used on these ranges were molded and pigmented to resemble logs or stumps and placed on the range in the same way the wood had been used. Imitation logs were prepared by casting SACON in commercial fiberboard cylindrical molds (Figures 7-8). The length of the logs was varied so that the mass of the SACON would be low enough to lift and put in place without heavy equipment.

The cylindrical modules worked reasonably well; but the stacked cylinders did have to be anchored to keep the lower layer of cylinders in place. The curved surfaces can produce unusual impact angles and the cylinders are necessarily thinner toward their perimeters.

# CONCLUSIONS

Precast SACON blocks or modules are the most useful approach to developing bullet barriers for use on small-arms training ranges. The major requirements for safety, consistent quality, low cost speed of installation and ease of construction are met by blocks that can have simple shapes and are prepared to sizes that can be handled without heavy lifting equipment. The most practical approach to producing blocks or modules from SACON involves using simple shapes that can be manufactured using cast-and-cut techniques rather than individual molds. A offset or staggered pattern of assembling the blocks rather than a complex block shape is the best method of addressing the problem of joints and cracks producing a potentially weak path that could develop a "shoot-through" type of barrier failure. The advantages of complex interlocking blocks is offset by the problems involved in producing the blocks and in disassembling and reassembling an interlocked stack to replace damaged blocks or straighten blocks that shift. It is possible to develop a modular system that will significantly reduce the problem of bullet dispersal without creating special requirements for extra personnel or heavy equipment for maintenance.

## ACKNOWLEDGMENTS

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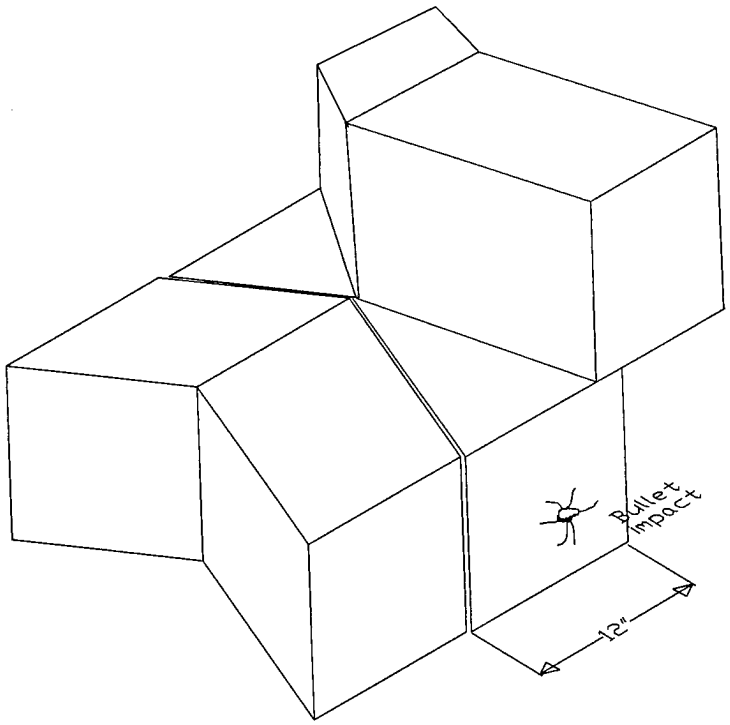



Fig. 1. Drawing of chevron-shaped blocks developed for a SACON bullet barrier. Note the thin edges produced by the angled sides. Dimensions are in inches; one inch equals 25.4 mm.



Fig. 2. Chevron-block wall set up at Camby Hill Range, Ft. Knox, KY. The angled lower surfaces required a specially built wooden pallet be prepared as a base.

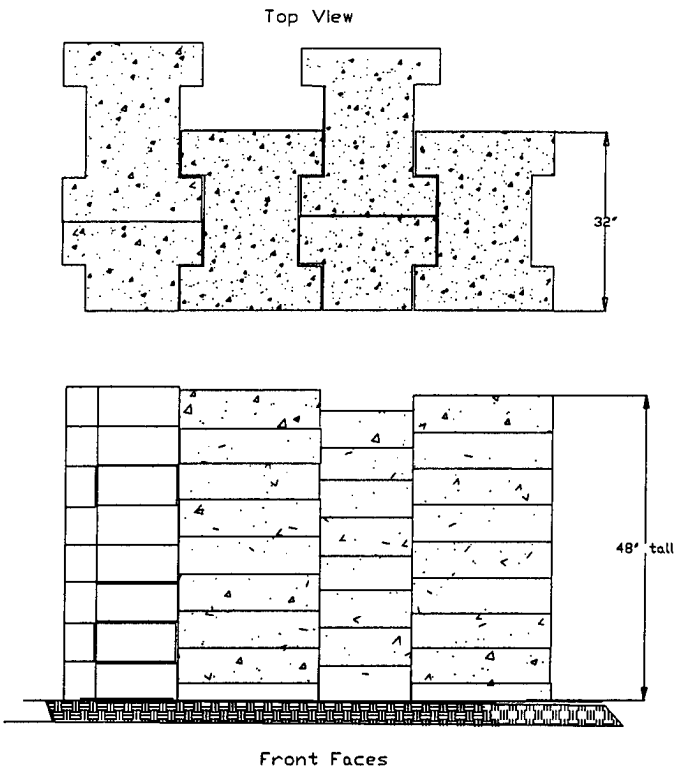



Fig. 3. Drawing of a wall formed from I-shaped and T-shaped blocks of SACON. Thin blocks are inserted in the rear row of blocks to prevent the horizontal joints between blocks from forming a continuous path through the wall. Dimensions are in inches, one inch equals 25.4 mm.



Fig. 4. Interlocking I-block walls at Camby Hill Range, Ft. Knox, KY. The white stains on the walls are calcium carbonate efflorescence caused by the high lime content of the SACON. This is the same type of stain that is caused by Portland cement-based mortars used in masonry walls.

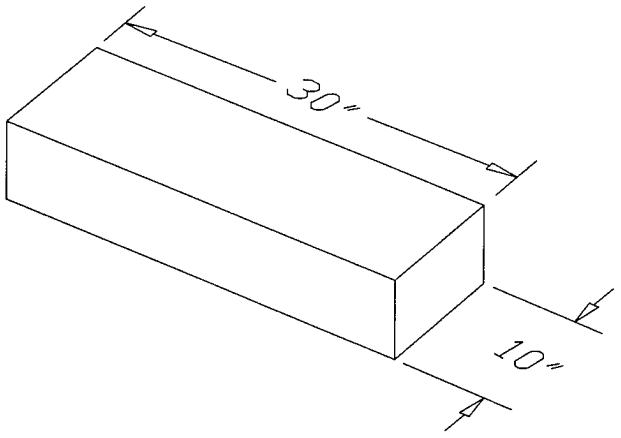



Fig. 5. Drawing of the simple rectangular block developed for use in a SACON bullet barrier. The thickness is typically held to 6 inches (152.4 mm).



Fig. 6. SACON bullet barrier on Ditto Hill Range, Ft. Knox KY. The wall is built from rectangular blocks . Note that the joints in the wall are not aligned during sacking. No continuous openings are produced when the wall is assembled. Paint was applied to the surface of the blocks to blend the wall into the surrounding vegetation.

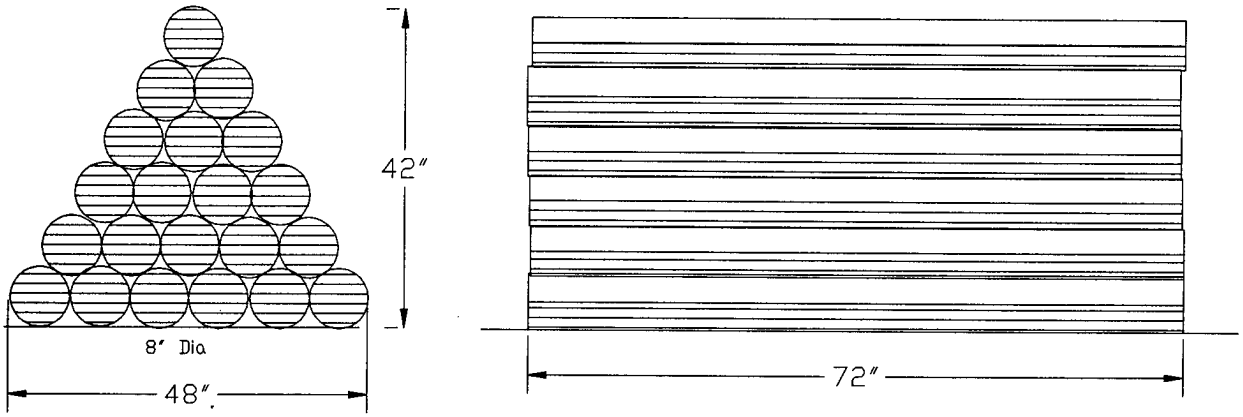



Fig. 7. Drawing of SACON bullet barrier formed from concrete cylinders. The stack shown is made from 8-inch (203 mm) diameter cylinders. Similar stacks were made from 12-inch (304 mm) diameter cylinders. The lengths of the SACON "logs" were varied make it possible to lift each "log" without equipment.

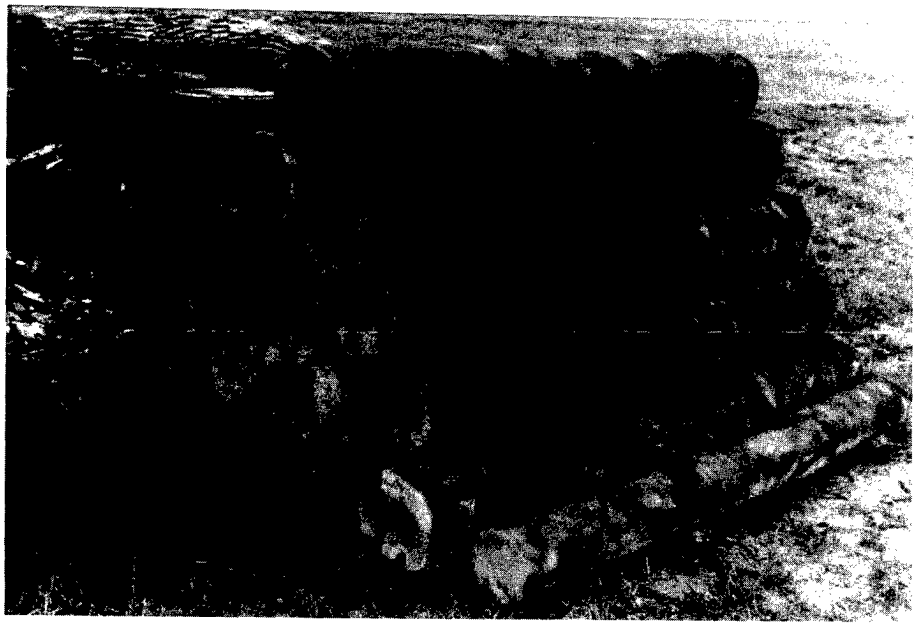


Fig. 8. SACON "log stack" on the Morgan-Dripping Springs Range, Ft. Knox, KY. The cylinders stacked to form the wall are 12 inches (304 mm) in diameter. An 8-inch diameter cylinder is used to protect the wooden stakes anchoring the base of the stack. Paint was applied to better blend the barrier into the background.

# DUST CONTROL MATERIAL PERFORMANCE ON UNSURFACED ROADWAYS AND TANK TRAILS

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## ABSTRACT

Wheeled and tracked vehicle operation on dry, unsurfaced roadways creates tremendous amounts of dust as soil particles are dislodged and carried into the atmosphere through wind action. Numerous products have been developed for controlling dust on unsurfaced roadways but very little data exists from replicated, large scale field experiments designed to evaluate their effectiveness, durability over time, and cost. To assist installation public works, environmental, and natural resources managers in selecting durable and cost effective dust control products, a research/demonstration project on unsurfaced roadways at Fort Hood and Fort Sill was initiated during the spring of 1996. Products evaluated included 38% calcium chloride, calcium lignosulfonate, proprietary polyvinyl acetate and polyvinyl acrylic emulsions, soybean processing by-products, and an untreated control. At Forts Hood and Sill, each dust control product was applied to recently graded 500-yard segments of unsurfaced roadways according to manufacturers recommendations. This arrangement was repeated three times at each installation, allowing for statistical inferences to be drawn from the dust control data. Dust control data were collected at monthly intervals following product application. Levels of dust control associated with each product and the untreated control were evaluated using dust collection pans and photographic images captured immediately preceding and at 5 seconds after controlled vehicle traffic. Data were evaluated using analysis of variance and products ranked in order of effectiveness using mean separation procedures. Cost and performance data suggest that calcium chloride, calcium lignosulfonate, and soybean processing by-products provide good levels of dust control for periods exceeding 60 days.

## INTRODUCTION

Wheeled and tracked vehicle operation on dry, unsurfaced landscapes creates tremendous amounts of fugitive dust as soil particles are dislodged and carried into the atmosphere through wind action. During wet weather, these dislodged soil particles are subject to water erosion which has the potential to carry them into surface waters, thereby reducing water quality and creating sedimentation problems for area streams and wetlands (Cowherd et al. 1990). Fugitive dust generated from helicopter, wheeled, and tracked vehicle

training exercises has the potential to create many different kinds of problems. Most notable of these are associated with safety, air quality, increased military vehicle maintenance requirements, and tactical considerations (Armstrong 1987). Dust clouds generated from helicopter landing pads and tank trails impair the visibility of military vehicle operators, increasing the likelihood of accidents and injury. Excessive dust from tank trails acts as a respiratory irritant to military vehicle operators and is considered a safety and air quality hazard when it drifts into nearby housing and administrative areas or onto adjacent highways and streets. Excessive wear and tear on military vehicles and aircraft results from the intrusion of dust into engine and turbine compartments, air filtering systems, and other sensitive mechanical and electrical components (Hass 1986). Finally, dust generated from helicopter and tank movement provides an unmistakable signature to enemy forces in a tactical scenario.

Although not directly related to mission and training problems mentioned above, dust also has adverse effects on vegetation near helicopter pads, roads, and trails. A covering of dust on leaf surfaces increases leaf temperatures (Eller 1977; Hirano, Kiyota, and Aiga 1995) and water loss (Ricks and Williams 1974; Fluckinger, Oertli, and Fluckinger 1979), while decreasing carbon dioxide uptake ( Fluckinger, Oertli, and Fluckinger 1979; Thompson et al. 1984; Hirano et al. 1990; Hirano, Kiyota, and Aiga 1995). These physiological changes suggest that vegetation around helicopter pads, roads, and trails is susceptible to chronic decreases in photosynthesis and growth which may eventually lead to accelerated erosion problems from lack of adequate roadside vegetative stabilization.

The relative merits of various agents for controlling dust on helicopter landing pads, tank trails, and unsurfaced roadways have long been the subject of heated debate. At one time or another, nearly every conceivable material has been sprayed onto unsurfaced roadways in an attempt to control dust, stabilize the road surface, and reduce vehicle maintenance costs (Kirchner 1988). Manufacturer's claims are abundant, yet Department of Army public works, safety, and environmental managers have very little actual data upon which to base product selection. An aggressive dust control program requires a systematic evaluation of dust control agents, application rates, and maintenance requirements in order to be labor and cost effective. Therefore, large scale, field oriented, comparative product testing under carefully controlled and replicated experimental conditions is a necessary prerequisite for informed decision making. The objective of this study is to evaluate the effectiveness, cost, and maintenance requirements associated with several dust control agents when used on unsurfaced roadways and tank trails at Fort Hood, Texas, and Fort Sill, Oklahoma.

## MATERIALS AND METHODS

Criteria against which potential dust control agents should be evaluated include previous performance, applicability to a wide range of soil and climatic conditions, prewetting requirements, ease of application, soil surface penetrability, environmental friendliness, and curing time. Based on these criteria, 38% calcium chloride (CaCl), two polyvinyl acrylic polymer emulsions (PVA1 and PVA2), calcium lignosulfonate (lignin), and soybean feedstock processing by-products (SBF) were selected for use on roadways and trails at Fort Hood and Fort Sill.

With the assistance of environmental personnel at Fort Hood and Fort Sill, three roadways/trails were selected for treatment with dust control agents. Each roadway/trail was divided into six 0.3 mile segments based on general similarities in surface characteristics, slope, aspect, and underlying soil types. Prior to dust control agent application, roadways/trails were graded to remove excess surface material, potholes, and washboarding. Following grading, each equal length segment received one of the following randomly assigned dust control treatments: CaCl, lignin, PVA1, PVA2, SBF, or no treatment at all. This arrangement resulted in a total of three segments receiving each dust control treatment. For the purpose of statistical analyses, this arrangement was classified as a randomized complete block experimental design with three replications.

In collaboration with Range Control, arrangements were made to apply dust control materials to roadways/trails during the week of 01 June to 05 June 1996. CaCl and lignin were applied at a rate of 0.50 gallons/sq yd using tanker trailers equipped with 12 foot spray bars. PVA2 was diluted with water (1:7

volume ratio of PVA2 to water) and applied at a rate of 1.0 gallons/sq yd using tanker trailers equipped with 12 foot spray bars. SBF was applied at a rate of 0.4 gallons/sq yd using heated (140 degrees Fahrenheit) tanker trailers equipped with 12 foot spray bars. PVA1 was diluted with water (1:7 volume ratio of PVA1 to water) and applied at a rate of 1.0 gallons/sq yd using water spreading trucks. All dust control materials were applied in a manner that prevented surface puddling and provided for six inches of overlap between previously treated areas.

Following application of dust control agents to respective roadways/trails at Fort Hood and Fort Sill, normal traffic was allowed to resume and dust control/traffic test evaluations initiated. Dust control/traffic test evaluations of each treatment in each replicate were conducted at monthly intervals for a period of three months. During each traffic test, dust control was evaluated using two different techniques. On each side of treated tank trails, tared, oil-coated dust collection pans (Vallack and Chadwick 1992; Vallack 1995) were placed about six feet away from roadway/trail edges in positions that avoided possible contamination from adjacent treatments. After 24 to 96 hours, dust collection pans were retrieved, re-weighed, and amount of collected dust determined.

To supplement dust collection pan data, photographic images were also used during every traffic test to evaluate and quantify the degree of dust control afforded by the different agents. On respective sides of each treatment in each replicate, a video camera or black and white 1 sq yd backdrops were set up opposite one another at a height of 3 feet in order to capture video images of the relative dust obscuration levels immediately preceding and at 5 seconds after controlled vehicle traffic travelling at 30 miles per hour. These images were digitized and analyzed for level of obscurance using computer image processing techniques capable of classifying and grouping individual pixels based on relative darkness due to dust. Indices from video images captured during controlled traffic tests on tank trails were used to provide semi-quantitative data concerning the relative effectiveness of each dust control agent. Video image indices and dust collection pan data were analyzed using analysis of variance procedures and treatment means separated using Student-Newman-Keuls test (Steel and Torrie 1980).

## RESULTS

Thirty days following treatment application at Fort Hood, dust deposition data indicated that CaCl, lignin, SBF, and PVA2 were effectively reducing dust levels by at least 50% when compared to the control (Table 1). Similar trends were observed 60 days following treatment application, except that dust levels had more than doubled when compared to data collected at 30 days. Despite this trend, CaCl was still significantly more effective than other treatments (Table 1). The combination of persistent drought conditions, no measurable precipitation, and heavy tracked vehicle traffic volumes are probable reasons for the rapid deterioration in treatment effectiveness observed between 30 and 60 days.

Thirty days following treatment application at Fort Sill, dust deposition data indicated that CaCl, lignin, SBF, and PVA2 were reducing dust levels by at least 66% when compared to the untreated control (Table 2). These levels of dust control were still present 60 days following treatment application except for PVA1 and PVA2 which had deteriorated markedly between 30 and 60 days. Heavy volumes of tracked and wheeled vehicle traffic between 30 and 60 days following treatment have apparently broken the surface sealing films characteristic of these products, resulting in increased levels of dust production.

Imaging analysis of video collected from controlled vehicle passes on each treated roadway section also indicated that CaCl, lignin, and SBF provided the greatest levels of dust control, while PVA1 and PVA2 provided the lowest levels of control (Tables 3 and 4).

Cost data for each dust control agent used in this evaluation are presented in Table 5. With the exception of PVA1, costs associated with each dust control agent include shipping, product application, and associated labor expenses. PVA1, however, was applied by installation personnel using water spreading trucks and the cost associated with its application does not include labor expenses. It should be noted that although SBF costs are relatively high compared to the other agents, significant decreases are expected as product distributors for this new agent are identified and utilized.

**Table 1.** Mean dust deposition (lb/ac/day) from treated tank trails at Fort Hood, TX, on three dates about 30, 60, and 100 days following dust control agent applications.

| | Dates | | |
|---|---|---|---|
| Treatment | 02 July 1996 | 02 August 1996 | 12 September 1996 |
| Control | 16.54a* | 29.03a | 34.27a |
| PVA1 | 12.11b | 26.62a | 32.10a |
| PVA2 | 8.20bc | 20.71b | 30.46a |
| SBF | 7.22bc | 19.25b | 32.92a |
| Lignin | 6.39bc | 16.74b | 31.88a |
| CaCl | 5.05c | 12.63c | 25.41b |

* Treatment means within columns followed by the same letter are not significantly different at the 0.05 level of probability as determined by Student-Newman-Keuls test.

## CONCLUSIONS

All treatments except PVA1 remained effective for 30 days following agent application at both Fort Hood and Fort Sill. At Fort Hood, heavy tracked vehicle traffic volumes combined with persistent drought conditions limited the efficacy of all treatments, especially between 30 and 60 days following treatment applications. Despite these conditions, CaCl and lignin continued to reduce dust levels by at least 50% when compared to untreated areas. Under somewhat lighter tracked and wheeled vehicle traffic volumes encountered at Fort Sill, CaCl, lignin, and SBF continued to effectively reduce dust levels by at least 66% when compared to untreated controls. Cost and performance data suggest that CaCl and lignin provide good dust control under a wide range of conditions for periods exceeding 60 days. Because of differences in traffic type and volume, soil types, roadway/trail surface characteristics, climate, and topography between sites/installations requiring dust control, product performance can and will vary. This variation makes it impossible to provide blanket recommendations concerning one or two products. However, based on data presented here, the performance and durability of dust control agents evaluated in this demonstration can likely be improved using installation specific adjustments in application rates and procedures. Regardless of dust control product used, maintaining a given level of dust control on tank trails will require more frequent applications than for roadways supporting primarily wheeled vehicle traffic.

**Table 2.** Mean dust deposition (lb/acre/day) from treated roadways at Fort Sill, OK, on three dates about 30, 60, and 100 days following dust control agent applications.

| | Dates | | |
|---|---|---|---|
| Treatment | 30 June 1996 | 29 July 1996 | 10 September 1996 |
| Control | 15.78a* | 13.16a | 10.33a |
| PVA1 | 8.14b | 10.87b | 10.94a |
| PVA2 | 5.59c | 10.07b | 7.76b |
| SBF | 5.02c | 5.44c | 5.98b |
| Lignin | 4.98c | 5.55c | 5.70b |
| CaCl | 3.58d | 4.24d | 3.69c |

* Treatment means within columns followed by the same letter are not significantly different at the 0.05 level of probability as determined by Student-Newman-Keuls test.

**Table 3.** Differences in levels of dust obscuration (mean change ratio) from treated tank trails at Fort Hood, TX, on three dates as determined by video image analysis.

| | Date of Video Imaging Measurements | | |
|---|---|---|---|
| Treatment | 02 July 1996 | 02 August 1996 | 12 September 1996 |
| Control | 100.00* | 100.00 | 100.00 |
| PVA1 | 154.26 | 84.66 | 283.13 |
| PVA2 | 50.40 | 82.33 | 164.70 |
| SBF | 74.78 | 93.61 | 225.98 |
| Lignin | -3.69 | 79.09 | 93.50 |
| CaCl | -32.77 | 69.18 | 57.11 |

*Mean change ratios below 100 indicate that levels of dust obscuration were less than those for the untreated control. The lowest mean change ratios are associated with the most effective treatments for reducing levels of dust.

**Table 4.** Differences in levels of dust obscuration (mean change ratio) from treated tank trails at Fort Sill, OK, on two dates as determined by video image analysis.

| | Date of Video Imaging Measurements | |
|---|---|---|
| Treatment | 30 June 1996 | 10 September 1996 |
| Control | 100.00* | 100.00 |
| PVA1 | 121.18 | 120.43 |
| PVA2 | 111.14 | 99.65 |
| SBF | 65.22 | 76.50 |
| Lignin | 81.81 | 26.27 |
| CaCl | 61.03 | -23.74 |

*Mean change ratios below 100 indicate that levels of dust obscuration were less than those for the untreated control. The lowest mean change ratios are associated with the most effective treatments for reducing levels of dust.

**Table 5.** Cost per square yard for dust control materials applied at Fort Hood, TX, and Fort Sill, OK, during June 1996.

| | Sites | |
|---|---|---|
| Treatment | Fort Hood | Fort Sill |
| Control | $0.00 | $0.00 |
| SBF | $0.68 | $0.70 |
| PVA1 | $0.56 | $0.66 |
| PVA2 | $0.40 | $0.47 |
| CaCl | $0.33 | $0.40 |
| Lignin | $0.28 | $0.30 |

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# COMPLIANCE

# WATER REDUCIBLE POLYURETHANE CHEMICAL AGENT RESISTANT COATINGS (CARC)

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## ABSTRACT

Protective coatings with such Army-unique requirements as camouflage and chemical agent resistance generate Volatile Organic Compounds (VOCs) and hazardous wastes during the application process. The basic camouflage topcoat, MIL-C-46168, is a two component, solvent-based polyurethane that has a VOC content of 420 g/L and is used on all Army combat vehicles, aircraft, and tactical equipment. Federal and local regulations resulting from the Clean Air Act and its 1990 amendments restrict the amount of VOCs emitted during the application of surface coatings. Lower limits are anticipated in the future and are currently enforced in areas such as Southern California.

The U.S. Army Research Laboratory (USARL) Coatings Research Team has developed a formulation with a lower VOC content. This formulation consists of a water-reducible Chemical Agent Resistant Coating (CARC) that utilizes hydroxyl-functional polyurethane dispersions and water-dispersible polyisocyanates. This water-reducible CARC has a VOC content of 220 g/L and has enhanced weather resistance, flexibility, and mar resistance. Applying this water-reducible CARC at military painting installations can reduce the VOC emissions by approximately four million pounds per year.

U.S. Army Environmental Center (USAEC) Environmental Technology Division has funded the USARL to develop and optimize the application process for the water-reducible CARC for the United States Army. The water-reducible CARC will be extensively field tested before the final formulation will be made available for DoD use.

## BACKGROUND

Historically, it has been critical to ensure water is not present in non-aqueous, two-component polyurethane formations due to its undesirable reaction with isocyanate. The reaction between water and isocyanate forms an unstable carbamic acid. The carbamic acid quickly decomposes to generate carbon dioxide and amine (Reaction 1) (Woods 1990; Oertel 1985). The amine then reacts with additional isocyanate to yield the substituted urea (Reaction 2). In a solvent-borne, two-component system, this reaction inhibits the development of crosslinking that is crucial in providing the film with the integrity and performance expected from with two-component polyurethanes. However, developments in waterborne polyurethane technology have enabled high-performance functional polyurethane dispersions (Jacobs and Yu 1993). While there is a competing reaction occurring with water, the kinetics and raw materials used in the formulations ensure that sufficient crosslink density is established within the film.

In two-component waterborne polyurethane coatings, the water-dispersible aliphatic polyisocyanate reacts slowly with water. Thus, an excess of polyisocyanate will preferentially react with the hydroxyl groups of the polyurethane dispersion. Jacobs and Yu (1993) have proposed that since the polyisocyanate is dispersed and not dissolved in water, it coalesces with the polyol dispersion particles, enabling the isocyanate group to be close enough to the hydroxyl group for crosslinking to occur.

$$RNCO + H_2O \rightarrow [RNHCOOH] \rightarrow CO_2(g) + RNH_2 \quad (1)$$

$$RNH_2 + RNCO \rightarrow RNHCONHR \quad (2)$$

The initial studies were based on formulations with isocyanate (NCO) to hydroxyl (OH) ratios between 2.0:1 and 3.5:1 to obtain optimum film properties. The data presented in this investigation are formulations based primarily on ratios of 3.5:1 NCO to OH ratios using fully pigmented systems conforming to color number 34094, Green 383, as stated in MIL-C-46168D, U.S. Army specification for two-component polyurethane coatings. Throughout this paper, water-reducible formulations will be designated Formula 1. The water-reducible formulations implement water-dispersible hydroxy-functional polyurethane and water-dispersible polyisocyanates with conventional siliceous-type extenders for flattening purposes, as well as prime pigments used to make the base green camouflage coating.

## RESULTS

### General Testing

The samples were sprayed unless noted otherwise. Color and specular gloss were determined using standard opacity charts (Leneta, Form 2A) as a substrate. All tests were performed with a dry film thickness of 45-55 μm. Table I lists the general coating tests that are specified under MIL-C-46168.

**TABLE I**

| TEST | REQUIREMENT IN MIL-C-46168 | FORMULA I |
|---|---|---|
| Color & Spectral Reflectance | $E_{NBS}$ 2.00[1] | $E_{NBS}$ 1.41 |
| VOC | VOC 420 g/L | VOC 180 g/L |
| Specular Gloss | 60° ≤ 1.0, 85° ≤ 3.5 | 60° ≈ 0.9, 85° ≈ 1.7 |
| Water Resistance (with primer) | 168 hr. immersion | no blistering |
| Hydrocarbon Resistance | 168 hr. immersion | no blistering |
| Polish Resistance<br>Gloss | 100 strokes<br>85° ≤ 12.0 | pass<br>900 strokes<br>85° ≈ 11.5 |

[1] *Hunter's revised National Bureau of Standards (NBS) color difference equation*

### Flexibility Determination

When formulating this material, it has been our attempt to develop a working formulation that will meet current Army specification requirements or exceed them whenever possible. The possibility of exceeding specific requirements is often at the expense of other properties of the coating. Yet in the development of this material significant improvement has been noticed with respect to flexibility without

any compromise to the durability or properties of the film. Flexibility has not been a major or critical element with respect to tactical-type equipment. Subsequently, CARC formulations are satisfactory at ambient temperatures but have difficulty at zero and sub-zero temperatures. Current water-reducible formulations have exceptional flexibility at ambient and sub-zero temperatures (Neale and Ellicks 1995). Testing was conducted using No. 31 gage cold rolled luster finish steel panels prepared in accordance with procedure B, phosphoric acid etched, method 2012.1 of FED-STD-141C. The panels were sprayed to a dried film thickness of 0.0009 to 0.0011 inches and air dried in a horizontal position for 72 hours at ambient temperature and then baked for 96 hours at 105°C. The panels were then conditioned at ambient temperature for 30 minutes. Flexibility was evaluated in accordance with method 6221 of FED-STD-141C. All zero and sub-zero evaluations followed the same procedure except the mandrel and panels were conditioned for four hours at the given temperature and tested within the chamber to ensure the stability of the environmental conditions. Table II summarizes the flexibility data using a 1/8 inch (1 in = 2.54 cm) mandrel.

**TABLE II**
**FLEXIBILITY EVALUATION**

| TEMPERATURE | FORMULA I |
|---|---|
| 75° F | Pass |
| 32° F | Pass |
| -28° F | Pass |
| -65° F | Pass |

Accelerated weathering is another important screening device used to ensure that formulations developed may adequately provide the necessary performance with respect to colorfastness and durability. Formulations were evaluated using both Ultra Violet Condensation (UVCON) and Xenon-type weatherometers. The Xenon testing was conducted using an Atlas Ci-65 chamber with borosilicate inner and outer filters. Xenon conditions were 102 minutes of light and 18 minutes of light and deionized water specimen spray with a black panel setting of 63°C, 50% relative humidity, and irradiance at 0.35 $W/m^2$. The Atlas (UVCON) Screening Device programmed for 4 hours of UV and 4 hours condensate per cycle. Fluorescent UVA-340 bulbs with a 60°C temperature setting during the UV cycle and 50°C temperature setting for the condensation were used. All panels were sprayed to a dry film thickness of 45 to 55 μm and air dried for seven days. The results were tabulated using NBS color difference versus total hours of exposure. Randomly selected commercial batch samples of two-component polyurethanes were evaluated to provide a comparative baseline. Samples were tested until they exceeded the 2.5 NBS color change limit currently used for two-component polyurethanes in MIL-C-46168. Formula I weathered for 1,400 hours while the standard only weathered 600 hours before failure in the Xenon weatherometer. In the UVCON instrument, Formula I weathered 2,200 hours and the standard 1,400 hours before failure. The data in both the UVCON and Xenon exposure suggest exceptional accelerated weathering resistance for Formula I.

Field Testing

Field evaluations will be conducted in two segments, the spraying of test panels and the spraying tactical vehicles. Panel testing will consist of approximately 2700 panels which will include a variety of steel, aluminum, and armor type substrates. These panels will then be pretreated, primed, and topcoated. The coating systems will vary to include combinations of solvent-borne and water-reducible primers and topcoats. The following tests will then be conducted: wet and dry adhesion, salt spray, cyclic corrosion

evaluations (prohesion & GM 9540P/B), accelerated weathering, outdoor exposure, and electrochemical impedance spectroscopy. The test matrix is intended to provide data to assist in comparing the current water-reducible formulation to our solvent-based systems and establish a database for future evaluations and coating systems. Vehicles from various Army commands will also be sprayed with the water-reducible CARC and evaluated for such parameters as dry time, potlife, spaying properties, etc. These vehicles will then be sent out to the field for evaluation under a variety of service conditions. The pass/fail criteria for the evaluations may include durability, adhesion, retention of gloss and color, and flexibility.

## CONCLUSIONS

The most recent formulations developed have passed all Army mission requirements including camouflage properties and chemical agent resistance. Since CARC is used on a wide variety of Department of Defense equipment, users include painting installations across the DoD and original equipment manufacturers. Applying this water-reducible CARC at military installations can reduce the VOC emissions by approximately four millions pounds per year. Finally, the reduction of VOCs and improved performance properties will potentially avoid costly expenditures such as the installation of pollution abatement equipment and emission fines while sustaining all Army mission requirements.

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# DEMONSTRATION OF BIOFILTER TECHNOLOGY TO TREAT VOCs IN AIR EMISSIONS FROM AN AMMUNITION PLANT

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## 1. ABSTRACT

The US Army Construction Engineering Research Laboratory contracted MBI International to perform a study of biofiltration of industrial waste gas streams. Phase I of the study was a laboratory investigation of the treatability of a specific gas stream. The laboratory study was concluded in September, 1995. Phase II was the design, placement and operation of a full-scale biofilter. The project was completed in August, 1996.

The specific gas stream originates from a munitions drying operation at the Olin Chemical Company, Lake City, AAP, Independence, MO. The production line is a blank bullet coating operation. In the production line, slats of blank ammunition are inverted and dipped into a coating material to seal the shell tips. The slats are then righted and moved into a drying box. The major solvent in the coating is ethyl acetate (70%) with about 30% of other solvent, such as, xylene and low molecular weight alcohols. The coating is thinned 50% with ethyl acetate, such that ethyl acetate represents more than 90% of the VOC load. The concentration of VOC's is 400 ug/L at an air flow rate of 1000 $ft^3$/min.

Laboratory results were collected on six test biofilter columns (15L). Steady state operations over a wide range of VOC loads were studied. The biofilters consistently destroyed 90-95% of the VOC's. Square-wave dynamic loading cycles were studied to represent shift changes at the production facility. At high loadings, the biofilter performed well. At low organic loadings at applications of 5 hr/day or the gas stream, the filters required a small supplement of glucose to maintain column efficacy.

A 1000 cubic foot bed volume, engineered media, biofilter was installed at Lake City AAP in January, 1996. The unit consists of a skid mounted, class 1-division-1 explosion resistant design including the blower package, biofilter media, and nutrient addition. The unit was monitored for six months.

## 2. INTRODUCTION

Biofiltration is a process that utilizes biologically active porous media to treat a contaminated gas steam[1]. The first reported usage of biofiltration technology was in Germany for cleaning up gaseous discharge[2]. Since then, this technology has been widely

used to control odors from industrial processes and waste water treatment plants [3]. There are approximately 500 biofilters currently in operation in Europe and 100 in the U. S., with most of these utilized for odor abatement [4]. Biofiltration has a high potential for development as an economical and efficient pollutant destructive control technology [5] However, the process has not been extensively studied for use as a limit based technology as is being required of for MACT status in the 1990 Clean Air Act.

Biofilter media can be classified based on the relationship of water to the media as a) natural bed media, b) trickling bed media, and c) engineered bed filters.

Simple compost and peat biofilter media have been used in Europe for over 30 years [6] The common compost media include natural materials (tree clippings and wood bark) and dewatered municipal sludge. This type of compost is high in organic carbon and nitrogen, and has excellent moisture retaining properties. Therefore, additional nutrient solutions may not need to be added until the second or third year of service[6]. The small particle is considered to have a large surface area, providing sufficient space for organism attachment[7]. However, the small particles generally cause significant pressure drop [8]. The main disadvantage of a natural bed media is the low organic loadings which may be applied due to potential nutrient and plugging limitations stemming from a lack of control over the biological process.

A trickling media biofilter is usually filled with a randomly packed structured material[9] which can be made from propylene, polyurethane, ceramics or granular activated carbon. The large particles provide sufficient space to slow down the column clogging and subsequent increases in headloss. Wittorf[10] recommended that the randomly packed media should have an effective diameter exceeding 16 mm to avoid plugging from excess biomass production. The media is relatively impervious to water and most of the biological growth occurs on the surface of the media. Lack of water retention by the media requires that a nearly continuous trickle of water be applied to the filter. The main advantage of a trickle bed is that very high organic loadings may be achieved because the nutrient and biomass may be controlled. The disadvantage is that the continuous film of water acts to limit the rate of collection of non-soluble organics from the air.

The selection of biofilter media is a critical decision since the best performance is a balance of long and short term goals such as nutrient control, biomass control, kinetic destruction rates, and pressure drop[11]. Desirable biofilter media should combine the natural features of the compost media with sufficient space to provide long service life[12]. In this study we use an engineered media constructed of nutrient and buffer impregnated polyurethane foam. In the lab studies, 3/4 to 1 inch cubes were used, while for the field unit we used a mixture of 3 inch diameter by 4 inch length inch cylinders (1/3 bed volume) and associated cutting scrap (2/3 bed volume). The filter has a high water holding capacity so that the water recycle rate is minimal. Thus, the bed is operated to combine the advantages of the natural bed media with those of a trickling bed filter.

2.1 Interplay of Design Considerations on Laboratory Experiments

In this paper we discuss the results of laboratory and field tests with ethyl acetate, which represents the off-gas from a US Army munitions coating operation. During design and scale-up, test columns were operated in steady state loading conditions and in square-wave step feed mode to simulate daily start-up and shut-down activities at the plant. The experimental phase was implemented to better predict field performance and laboratory tests reflect the changing assessment of the site conditions.

The initial experimental design was driven by the need of the client to maintain full plant capacity while remaining in compliance. Thus, the initial tests were performed, and ultimately, the plant was designed to accommodate a solvent use rate of 22,000 pounds per year. Based on a full year (365 days), this represents a loading of 40 g/$M^3$-hr for around the clock operation (24 hr/day) for a 1000 cubic foot (28 $M^3$) filter. However, for a 1960 hour per year operations basis, the loading could be very significant (180 g/$M^3$-hr). On this basis and the extant fan capacity of 500 cfm., the concentration of consumable organics was initially expected to exceed 5500 ug/L with ethyl acetate representing 85% of the total organic load. The other components expected were ethanol, isobutyl acetate, toluene, 2-methyl-1-propanol, n-butyl acetate, mixed xylenes, and n-butanol.

The biofilter design must also accommodate the present loading conditions. Operational data were not readily available and initial tests showed that the production line was actually operated at 500 cfm and that the process vent was inefficiently designed and used. Three sets of samples were collected in which the average VOC concentration was just over 300 ug/L. Thus, after a significant investment of design time and experimental time, it was discovered that the biofilter would potentially be operated at a yearly loading (1960 hr/yr at 500 cfm) of only 1100 pounds per year.

Based on the poor capture efficiency of VOC's at the vent, the client decided that the biofilter fan capacity should be doubled to 1000 cfm. Furthermore, improvements were made to the production plant hood to improve capture efficiency. Thus, we never knew until after start-up what the loading to the filter would be. After start-up, we measured influent gases in the range of 400 ug/L ethyl acetate and 40 ug/L isobutyl acetate. We were also notified at that time that the production schedule would be four days per week, 20 hours per day. Thus, when the filter actually started-up, the yearly loading was expected to be 6580 LB per year for an average yearly loading of 12 g/$M^3$-hr and an instantaneous loading of 27 g/$M^3$-hr.

## 2.2 Laboratory Methods

Ethyl acetate was obtained from Aldrich Chemical Co., Milwaukee, Wis. Ammonium chloride, potassium phosphate, sodium carbonate and other trace compound were obtained from J. T. Baker Chemical Co., Philipsburg, N. J. All chemicals were reagent grade. An oil free, compressed dry air was supplied to the biofilters.

The laboratory-scale biofiltration reactors used in this study were glass columns with a 10.0 cm diameter and 220 cm height (Figure 1). There were approximately 3.0 L liquid (leachate) capture volume and 15.0 L of media volume. Sample ports were placed at the influent, effluent, and at intervals along the bed depth which separated the columns into three stages of equal volume. The porosity of the bed was approximately 89% as measured by helium dilution. All of the biofilters were operated with the air forced downward through the columns. The ethyl acetate was introduced into the air stream by a Harvard Apparatus syringe pump (model 55-1111, South Natick Mass.) across a wick to assure volatilization. Leachate was recycled to the top of the columns. During start-up, the leachate recycle was continuous. After start-up, the recycle interval was 5-15 minutes per hour. The recycle was used to humidify the column, and provide buffering capacity and nutrient solution. Leachate was removed from the reactors and replaced with fresh nutrient solution once a week. The stock nutrient was formulated to provide essential macro- and micro nutrients such that 700 ml of nutrient would be sufficient for each 50 g/$m^3$-hr of ethyl acetate load applied to the reactor. This ratio was maintained during the step-feed tests such that the nutrient addition was proportional to the average hourly ethyl acetate loading. The recovered leachate was analyzed for alkalinity, total solids, total volatile solids, ammonia and nitrate nitrogen, and phosphate to provide information on the

biomass and nutrient mass balances. Room temperature, column bed height, headloss, leachate pH and buffer capacity were recorded daily. The leachate pH was adjusted to greater than 8 on a daily basis utilizing a stock buffer solution and the leachate volume was adjusted to 1.5L to compensate for humidification losses. To control microbial growth and maintain a low headloss, a periodic back washing was performed. The wash water contained biomass and nutrients, which were included in the overall mass balances. During the planning of the experiments, it was expected that the columns would require back washing about once per month. However, the columns did not appear to need back washing this frequently. Three of the columns did not require any back washing. The other columns required washing on a 40-60 day cycle.

The nutrient solution consisted of two stock solutions, trace nutrients and macro-nutrients. The trace nutrient stock solution contained: 1.50 g nitrilotriacetic acid, 0.10 g $FeSO_4.7H_2O$, 0.10 g MnCl2.4$H_2O$, 0.17 g $CoCl_2$.6H2O, 0.10 g $CaCl_2.2H_2O$, 0.10 g $ZnCl_2$, 0.02 g $CuCl_2.2H_2$), 0.01 g $H_3BO_3$, 0.01 g $Na_2MoO_4$, 1.0 g NaCl, 0.017 g $NaSeO_3$, 0.026 g $NiSO_4.6H_2O$ and 12.8 g NTA made up to1.0 L in deionized water. The macro-nutrient solution contained: 38.5 g $NH_4Cl$, 4 g NaCl, 7.0 g $KH_2PO_4$, 10.0 g $K_2HPO_4$, 10.0 g $NaHCO_3$ and 30 ml of the trace stock solution made up to 1.0 L in deionized water. The pH of the solution was adjusted to 8.0 with NaOH. The nitrogen supplement applied to each column on a weekly basis. The target nutrient addition was based on providing 6 g N per 100 g ethyl acetate. The stock buffer solution for adjusting the leachate pH was made by dissolving 160 g Nikko in 4.0 L of deionized water.

Gas samples were collected directly from the inlet, stage 1, stage 2 and outlet sampling ports of the biofilter in gas tight syringes. The samples were immediately injected into a gas chromatograph (Varian model 3600, Walnut Creek, CA) outfitted with a flame ionization detector. Triplicate samples were analyzed and data were reported as the arithmetic average. Separation was accomplished with a Supelco Inc. (Bellefonte, PA) 30 X 0.32 with 0.25 μm film column (#2694014) at an oven temperature of 40 °C. The detection limit of this method was 2.2 ug/L (0.6 ppmv).

An engineered medium was developed in our laboratory and used in this study. The basic medium is a proprietary, nutrient bearing polyurethane foam either in the form of a 1.5 cm cube, or in a specially designed form of proprietary nature with an effective diameter of about 4 cm. In order to obtain the sorption capacity of the medium and experimental system, a breakthrough study was conducted in a clean biofilter column with dry, fresh medium. Ethyl acetate vapors (1600 ug/L) were applied to the column at a rate of 50 g/m3-hr at a nominal retention time of 1.0 minutes. Influent, effluent and staged samples were taken to watch for breakthrough of ethyl acetate at various times until the concentration in the effluent equaled that of the influent. Breakthrough occurred in less than 30 minutes. From the sorption breakthrough testing, the medium used in this experiment had very little sorption capacity for ethyl acetate.

2.3 Field Methods

The field unit biofilter installed at the Lake City AAP, Independence, MO, was manufactured by Envirex Incorporated, Waukesha, WI. The biofilter plant is a skid mounted system including blower, recycle pump, controls instrumentation and safety devices. The unit is rated explosion resistant Class I Division I. The media box is roughly 7.5 feet by 22.5 feet by 10 feet in height. The 1000 $ft^3$ synthetic media bed is divided in two 3 foot depths by a horizontal screen. The bed is held above a leachate pool with an operating depth of 1.5 feet, representing approximately 1900 gallons. The primary function of the recycle pump is to periodically return the leachate to the biofilter media

(four 15 minute intervals every 24 hours at 50 gpm). The recycle pump is also used to fill the biofilter for backwash and to discharge leachate or backwash water from the filter.

Nutrient and buffer were added on a one per month basis, (approximately 5 gallons per month). The nutrient/buffer is formulated to provide enough nitrogen, phosphorus, and carbonate alkalinity for this length of service. The nutrient solution consisted of 27 gallons of a 14-10-2 fertilizer solution, and 55 pounds of ammonium carbonate made up to a volume of 55 gallons. Trace nutrients were provided by occasional additions of brewer's yeast. Start-up was supported by additions of granulated table sugar.

TABLE I Operations Parameters, Lake City, AAP

| Operation | Parameter |
|---|---|
| Inlet Flow (cfm) | 1000 |
| Operating Temperature | 40-100 ($^0$F) |
| Operating pH Range | 6-8 |
| Inlet Vapor Stream VOC | 400 ug/L ethyl acetate<br>40 ug/L isobutyl acetate |
| Recycle Pump Timer | 4 cycles per day<br>30 minutes per cycle |
| Nutrient Addition | 5 gallons/month |
| Backwash Frequency | 3 per year |
| Backwash Cycle Duration | 60 minutes |

The blower system provides a constant volume of vapor stream to the pilot plant and was used in media regeneration during backwash. The blower facilitates solids control during backwash when the blower discharge is diverted to a set of air headers at the tank floor. The air provides sufficient turbulence to remove excess biomass from the media while the tank was flooded.

Table 1 is a summary of operation parameters for the 1000 cubic foot biofilter.

## 3. LABORATROY RESULTS AND DISCUSSION

### 3.1 Start-up and Operation of the Steady State Reactors

Each column was inoculated with 15 ml of a mixed culture of ethyl acetate degrading microorganisms plus a proportional dose of nutrient solution plus tap water to a total volume of 1.5 L in the leachate pool. The VOC stream was then applied continuously to the biofilter. The leachate was then recycled continuously to the top of the reactor for several days until the microorganism population was established, as indicated by a reproducible removal efficiency of at least 90 % of the applied ethyl acetate. Start-up of the continuously fed biofilters was usually achieved after 14 days. After start-up, the leachate recycle was set for 5 minutes per hour.

After start-up, the steady state columns were operated at organic loading ranges from 15 to 100 g/m$^3$-hr with retention times ranging from 1.0 to 2.0 minutes. The influent ethyl acetate concentration ranged from 220 to 3200 ug/L. Figure 2 shows the overall removed of nearly 99 % for all steady state tests.

### 3.2 Dynamic loading study

Due to the work schedule at the coating operation, the loading to biofilter follows a square wave pattern, rather than constant loading. In the laboratory study, the columns were loaded with organic vapors on a five day work week with five hour shifts. That is, Monday through Friday, the columns were loaded with organic vapor from 9 AM to 2 PM. On the weekends and from 2 PM to 9 AM during the week, the columns were fed house air containing no ethyl acetate. It was felt that this would represent a more deleterious schedule on the biofilter than expected in the field and allow enough time to plan and execute the experiments.

The discontinuously fed reactor was started in a fashion similar to that described for the constantly loaded reactors, except that the organic load was discontinuous. The reactor ethyl acetate at 50 g/m$^3$-hr. five hours per day. Recycling was performed continuously at the beginning of start-up to allow microorganisms to inhabit the media. Air was continuously supplied to the reactor even when the ethyl acetate feed was turned off. Figure 3 is a summary of the operation of the column.

One difference between the performance of the constant loading tests and the discontinuous loaded test was the length of time required for start-up. While the start-up of the constantly loaded reactors usually occurred within fourteen days, i.e., removals of greater that 90% ethyl acetate were consistently observed, a lengthy start-up was required for the discontinuously fed reactors. The reactor was fed only 5 hours per day and 5 days per week, therefore the loading rate was 15% of the start-up loading rate for the continuously loaded reactor (50 g/m3-hr).

Since the reactor was being fed discontinuously, one question was whether the reactor would demonstrate consistently poor results throughout the feed cycle, or whether the biology would become more efficient towards the end of the cycle. A time coarse study was performed on day 16 after start-up. The measured influent closely matched the expected square wave pattern. However, the removal efficiency was slightly higher at the beginning of the cycle (around 60%) and then tended to be low (from 25-35%) throughout the feed cycle. This likely indicates that an initial amount of ethyl acetate was absorbed into the liquid phase, followed by a slower uptake by the biomass. Therefore, we felt the biofilm had not developed fully at this low loading rate.

By day 24 after start-up, we became concerned that the reactor was not starting properly (Figure 3). Microscopic examination of leachate showed a low density of organisms with low motility. In general, we have found that a high density of organisms with high motility in the leachate population is desirable for treating ethyl acetate. We felt that additional carbon was needed to establish and maintain a stable population in the reactor.

By day 24, it was determined that direct intervention would be required to establish the column biology. To establish a healthy biomass, 20 g of glucose was added to the leachate on day 24 and again on day 25. As seen in Figure 3, the performance of the reactor improved dramatically. The removal rate started increasing from 23.3% on day 24 to 97% on day 35. This steady state performance was maintained until day 45. An average removal efficiency of 95.7% was achieved. During this time, five additions of 20 g glucose were made on days 24, 25, 31, 38 and 45 as shown by (*) in Figure 3.

We were curious to determine if the removal of ethyl acetate was constant throughout the feeding cycle, or if there was a lag period at the start of the cycle. A second time course study was performed on day 45. A short lag of about one hour was seen to persist, wherein, the average removal was about 92%. Thereafter, the removal improved to approximately 98% during the remainder of the feed cycle. We did not feel that this short lag phase would be a problem, so no further data were collected on this issue.

In order to study the minimum glucose requirement, glucose addition was stopped after day 45. Without glucose addition, the system maintained a high removal efficiency for more than 30 days. A gradual decrease in removal efficiency was observed between day 74 and 84. During this period, the removal efficiency decreased from 90% to approximately 60% (Figure 3). Another glucose addition schedule was tested from day 84 through day 115. In this feed protocol, glucose was added to the reactor at a rate of 2.0 grams per day, one hour prior to the start of ethyl acetate addition. This glucose addition schedule was maintained until the end of the experiment. The removal efficiency was low

from day 84 until day 95, then increased again to over 90% by day 106. The full capacity of system wasrecovered after 20 days on this feed schedule.

Even when the dynamically loaded biofilter was supplemented with glucose, there was not apparent need to wash the filter even after 115 days of operation. It may be speculated that the biomass decay and sheering loss due to the recycle was able to balance the biomass growth to avoid the column clogging. The media provided good support during 115 days of operation.

## 4. FIELD RESULTS AND DISCUSSION

### 4.1 Removal Efficiency in the field

The field results are based on eleven field trips. Table 2 is a summary of the nutrient additions made from January through August, 1996. The biofilter was inoculated on January 25, 1996.

**TABLE 2. Summary of Additions to the Biofilter at Lake City AAP**

| Date | Sugar (lbs) | Yeast (lbs) | Nutrients (gallons) |
|---|---|---|---|
| 1/25/96 | 50 | 3 | 13.75 |
| 2/13/96 | | | 22 |
| 2/28/96 | Biofilter accidentally flooded | | |
| 3/20/96 | 50 | 2 | 10 |
| 4/10/96 | | | 5 |
| 4/17/96 | | | 10 |
| 5/8/96 | | | 5 |
| 6/4/96 | | | 5 |
| 6/26/96 | | | 5 |
| 7/15/96* | 25 | 1 | 5 |
| 7/16/96 | | | 5 |
| 8/7/96 | | 1 | 5 |

* The biofilter was drained the next day when it was backwashed

During the February 28 trip, a solenoid valve was accidentally tripped and the filter was flooded. The filter was then drained and an unknown quantity of nutrients and biomass were lost from the system. While process air addition continued from the February 28th date, the filter was probably less than fully active due to loss of inoculum and nutrients and continued cold weather. The filter was reseeded on March 20 with the re-addition of table sugar and nutrients. Therefore, the true start-up did not occur until March 20, 1996. In the following analyses, the March 20th date is used as the official start-up. A number of other maintenance issues impacted performance. These issues will be discussed as they relate to the performance of the filter.

Table 3 is a summary of the gas removal efficiency of the biofilter. The data represent the average of ten influent and ten effluent samples. The lower calibration limit is 10 ug/L for ethyl acetate and 40 ug/L for isobutyl acetate. Values presented which are less these limits are presumptive. Other volatile organic gases were not detected at any concentrations.

The low efficiency on March 20th is further evidence that the filter was not fully inoculated by that date as discussed earlier.

A plant wide power failure on or about May 4th caused the blower to be shut down until restarted on May 7. The gas samples taken on May 8th, therefore represent performance within 20 hours of a serious setback.

A second equipment problem arose on or around May 30th and impacted the June 4th sampling. The recycle pump had been down approximately 4 days due to a stuck float switch. The blower had been on during this time so that the media had become dry. The data collected on June 4th represented a period two hours after restarting the recycle

| TABLE 3. Summary of Removal Data Collected at the Lake City AAP Site | | | | | | |
|---|---|---|---|---|---|---|
| | Ethyl Acetate | | | Isobutyl Acetate | | |
| Date | Influent ug/L | Effluent ug/L | % Removal | Influent ug/L | Effluent ug/L | % Removal |
| 1/22/96 | 354 | - | - | 38.6 | - | - |
| 2/13/96 | 308 | 265 | 14 | 47 | 19 | 60 |
| 3/20/96 | 452 | 176 | 61 | 64 | 46 | 29 |
| 4/10/96 | 127 | 14 | 89 | 10 | 6 | 42 |
| 4/17/96 | 305 | 0 | 100 | 33 | 0 | 100 |
| 5/8/96 | 418 | 1 | >99 | 55 | <1 | >99 |
| 6/4/96 | 191 | 8 | 96 | 17 | 2 | 8 |
| 6/26/96 | 373 | 27 | 93 | 66 | 10 | 86 |
| 7/15/96 | 327 | 109 | 67 | 49 | 41 | 16 |
| 8/7/96 | 314 | 42 | 87 | 42 | 12 | 72 |

pump. The high removal efficiency observed (93%) is a positive sign that the filter can withstand desiccation.

The final significant occurrence was a scheduled plant shutdown from July 1- July 14, 1996. The blower was shut off during this time. However, the recycle pump remained operational. These events caused a septic condition to arise, necessitating a backwash to be performed for odor control. The July 15 sample represents a special case in which the filter had been septic for two weeks. Poor removal efficiency is likely due to this condition.

Samples of the leachate recycle water were collected before and after nutrient addition and tested for pH, alkalinity, solids, nitrogen and phosphorus. Nutrient control was based on balancing the nitrogen and phosphorous with the VOC loading. In all cases, the addition of nutrient buffer solution brought up the pH of leachate to between 7.7 and 8.7 from a range of 6.3 to 7.5. The carbonate alkalinity in the leachate ranged from less than 300 to 840 mg/L $CaCO_3$ before nutrient addition to 350 to 2000 mg/L after nutrient addition. Ammonia nitrogen was typically made up to the range of 400 mg/L N after nutrient addtion from less than 100 mg/L before nutrient addtion. Phosphate usage was sporratic, ranging from 32 to 87 mg/L Posphate-as P before nutrient addtion and between 25 and 139 after addition. Volatile solids in the leachate were very low (0.05 to 0.8 mg/L) and represented a wide deviation from laboratory expectations.

| TABLE 4. Nutrients and Buffer Utilization (March 20 - June 26, 1996) | | |
|---|---|---|
| | Grams | Percent of VOCs Feed |
| VOCs | 105,000 | - |
| Nitrogen | 11574 | 11 |
| Phosphorus | 1695 | 1.6 |
| Alkalinity | 25500 | 24 |

Table 4 is a summary of nutrients used between March 20 and June 26, 1996. During this time, approximately 105,000 grams of VOCs were fed to the filter. The nutrient and buffer utilization were slightly higher than predicted from lab data. In extensive steady state tests, we observed that between 2.3 - 7.7 g N , 1.3 - 1.8 g P, and 6.5 g alkalinity as $CaCO_3$ would be used for every 100 g ethyl acetate fed to the filter. Part of the difference between the laboratory and the field data

may be due to the use of table sugar during start-up of the field unit which was not incorporated into the carbon balance. High nitrogen use rates may also be due to inefficient nitrate use in the field. Nitrate-N accounts for about 10% of the nitrogen in the field unit. Nitrate was never used in laboratory tests. While laboratory data showed that between 7.6 - 12 g volatile solids (biomass) would be produced per 100 g ethyl acetate treated, insufficient field data were collected to determine the biomass production rate.

## 5. TECHNICAL SUMMARY

### 5.1 Laboratory study

This study provides information for designing high flow rate biofilters for ethyl acetate treatment. With the continuously loaded condition, the reactors were able to start-up in one week and achieve 99 % removal efficiency for a large range of loading rates (from 15 to 100 g/m3-hr). During the dynamic loading mode, an organic load of 50 g/m3-hr applied for 5 hr. per day on five days per week was not sufficient to form a stable capability during the start-up period. The addition of a second carbon source (glucose) was needed to help the biodegradation capability to establish in the reactor and to maintain a stable population during the operation. With the second carbon source addition, the reactor could achieve a removal efficiency of 95% in the dynamically loaded condition. The growth of biomass was under control during the dynamic loading condition and the reactors did not have a clogging problem even without backwashing. The engineered media used in this study proved sufficient support and good attachment for the microorganisms.

From these data we concluded that the low organic loading expected in the field would not be a problem if the feed were continuous, but that a slow start-up in the field might be expected. We expected that the ammonia nitrogen and buffer addtions would be critical.

### 5.2 Full-Scale Study

We attempted to apply our laboratory experiences to the field, especially in terms of the nutrient addtion and start-up trick of adding sugar to the reactor. The full-scale biofilter operated successfully during the five month period from March 20- August 7, 1996 with treatment efficiency of approximately 91% ethyl acetate and 68% isobutyl acetate. These numbers are representative of the biofilters removal efficiency after true start-up and excluding the sampling point when the biofilter was allowed to become septic during a plant shutdown. A sample data that was of particular interest is June 4th because the recycle pump had failed at least four days previously and the media was dry to the touch. The observed 93% removal efficiency was from a sample set taken two hours after re-establishing the recycle flow.

Nitrogen usage in the field was higher than expected being about 11 g N per 100 g VOC as opposed to the observed rate of 2.3 - 7 g N per 100 g VOC from this and other laboratory studies. The higher rate may have been due to the initial doses of table sugar added to the field reactor which were not taken into consideration in the carbon balance.

We were unable to close a solids balance on the field scale reactor leachate, thus we could not confirm solids production data for this reactor.

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Figure 1: Schematic of the Laboratory (15L) Biofilters

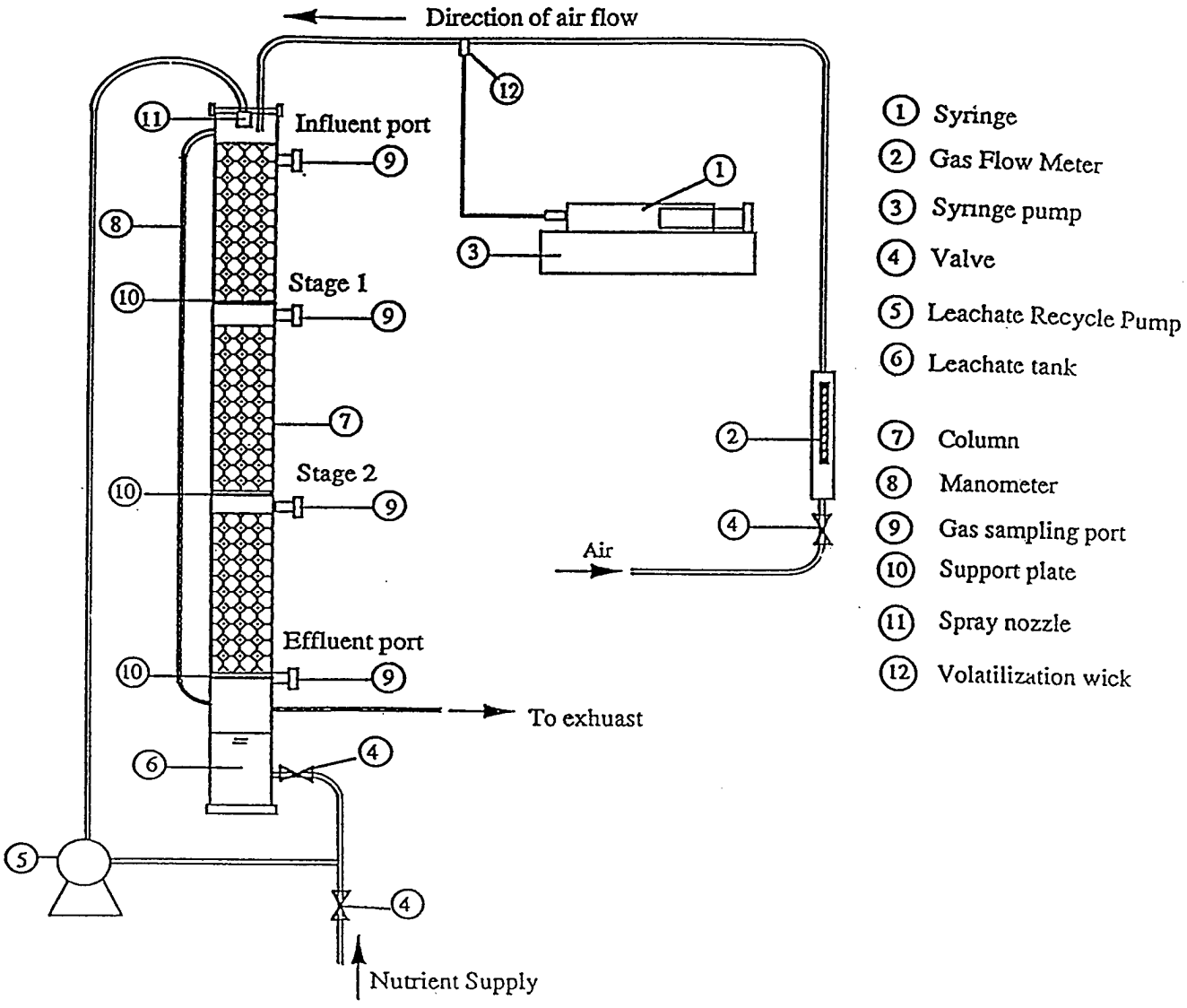


Figure 2: Removal of Ethyl Acetate in Continuoulsy Fed Lab-scale Biofilters

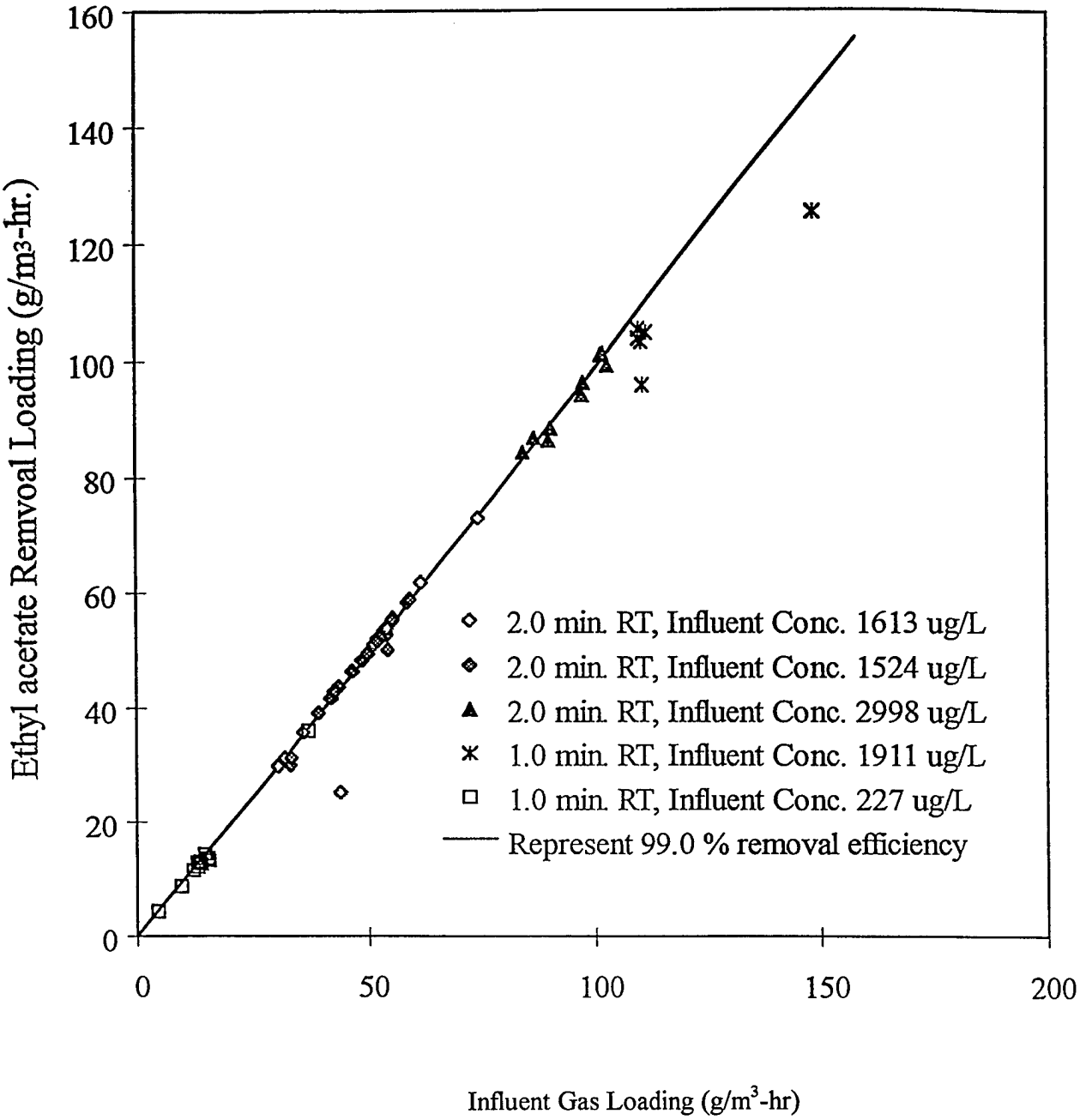
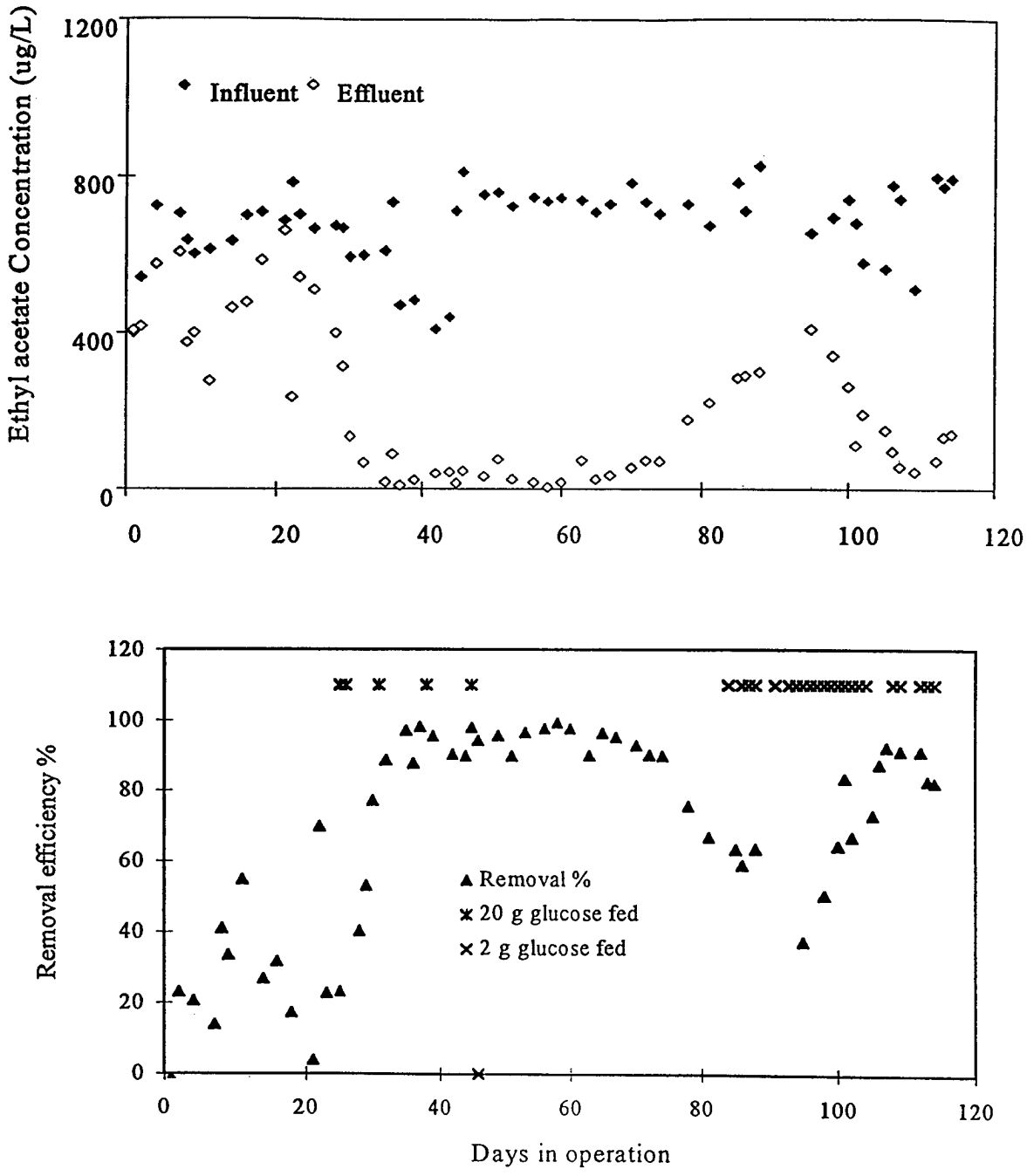


Figure 3: Performance of the Lab-scale Biofilter under Dynamic Loading Conditions



# LESSONS LEARNED: LEAK DETECTION SENSORS FOR WATER, FUEL, AND ENERGY PIPE SYTEMS

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## ABSTRACT

Leak detection and location in piping systems is crucial in that a given leak repair can cost in the range of $2-15K per leak, due in large part to multiple trenching required to locate the source. Moreover, a single gallon of gasoline can render a million gallons of water non-potable. The aspects of leak detection which are and will continue to be the most critical are leak location and magnitude. A highly sensitive system which monitors infrequently does little to protect the user from the costly event of a major discharge. A system which monitors continuously but is only able to detect major discharge events puts the user at the same risk level. The objective of this work is to publish a lessons learned document based on the evaluation of passive leak detection technology applicable to water, fuel and energy pipe systems.

The five main technologies in use for the detection of liquid leaks are chemical concentration detection, acoustic systems, impedance methods, infrared methods, and Supervisory Control and Data Acquisition systems. To achieve sufficient performance from a leak detection system, the piping system should first be verified for integrity, then have a continuous monitoring system installed and tested. The system must also be relatively maintenance free and inexpensive to operate. None of the systems surveyed or researched provide the optimal level of leak detection alone.

In researching the available leak detection technologies, USACERL has performed 8 site surveys. Of the Commercial Off the Shelf (COTS) leak detection systems investigated, the most promising technology for reliable detection of fuel leaks in underground piping systems appears to be the Arizona Instruments (AZI) system. The system cycles clean, dry air from the monitoring station out the length of each segment and then draws a soil gas sample across an electronic gas analyzer which will detect hydrocarbons. AZI claims a lower detection limit for gasoline of 150 ppm and 60 ppm for JP4.

The most promising technology for detecting and locating small (0.1 gallons per hour) leaks is the acoustic leak detection system. The Joint Department of Defense, Department of Energy, and Environmental Protection Agency (EPA) Strategic Environmental Research and Development Program (SERDP) project has documented the capability of acoustic leak detection technology , with full scale field tests at the EPA test facility scheduled to start during late FY 97.

Cost and performance analysis of the available systems indicates the most cost effective system for detecting fuel distribution system leaks is manufactured by Arizona Instruments Inc. followed by the Tracer Research ALD 2000 system (continuous monitoring), and finally the various cable systems with the constraint that they must be installed in double wall piping systems.

## 1. INTRODUCTION

The average clean up cost of a leak is estimated by U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) to be $193K, ranging higher where ground water is contaminated. The cost of effecting leak repairs is approximately proportional to the amount of trenching needed to access the leak. Some passive leak detection systems can provide leak location to within 6 inches of the leak location, saving critical time when locating a leak, and minimize unproductive trenching for repairs.

There are five main technologies in use for the detection of liquid leaks, each associated with the physical phenomena which occurs either at a leak site or in the system due to the leak. Chemical

concentration detection is referred to by the term "sniffing" and requires the leak to provide concentrations which are detectable above normal, naturally occurring concentration levels. Acoustic systems rely on noise produced by turbulent liquid flow to detect leaks in piping systems. Impedance methods involve laying a cable in probable leak sites and monitoring the change in the cable's impedance to determine when it comes in contact with a liquid. Infrared methods rely on the difference in temperature between the piping system and surrounding soil to provide a thermal signature which can be observed by special imaging equipment. Supervisory Control and Data Acquisition (SCADA) systems use process control sensors to detect discrepancies in the performance of a system which can indicate a leak, and require the use of a computer, sensor data acquisition, and an analysis algorithm to evaluate the sensor data and produce a leakage determination.. One subset of the SCADA system category which is often used as a stand-alone leak detection system is Level Monitoring which can be used only in closed systems which allow for an accounting system to detect losses. Another SCADA subsystem which is also used as a stand-alone system is Mass Flow measurement methods which rely on various physical phenomena to obtain accurate measurements of the total mass flow between two points on a pipeline. Each technology mentioned has a detection sensitivity associated with the system it is used with. These five technologies are evaluated here in terms of the phenomena exploited, their system applicability, and their advantages and disadvantages when applied to the detection of leaks in a buried pipe system responsible for carrying liquids.

## 2. LEAK DETECTION TECHNOLOGY DESCRIPTIONS

For simple binary indicators, such as the conductive cable systems, detection of the leak is dependent on the triggering of the sensor, requiring no computational accuracy. A more complex systems, such as the cable impedance systems require not only the sensors be sensitive to the liquid to be detected, but also that computations have sufficient numerical precision to accurately locate the leak source. The type of phenomena the sensors are designed to detect directly affects the computational accuracy required for reliable leak detection and location.

### 2.1 Cable Systems

Impedance Mismatch cable systems usually utilize a coaxial cable with a permeable outer shield which is excited at a known frequency. Because the dry cable has a known impedance and length, when a leak changes the dielectric properties at a particular location within the cable, it creates an impedance which can be located along the length of the cable by signal attenuation and phase measurement. This technology is used to detect leaks of fuels, solvents, electrolytes, acids, bases, and aqueous leaks. The advantages of this system is that it can be sensitive to different types of liquids and can be easily installed. The disadvantages of this system is that after exposure to water or fuel, the cable may need to be replaced.

Conductivity cable systems utilize two conductors, generally stainless steel, which are woven into a specially treated cable or ribbon. When a conductive liquid forms a continuity path between the two wires, a leak condition is indicated and can signal an alarm. The system is generally installed in locations which are accessible during or after installation. The system is used for aqueous leak detection or (with special polymers) detection of petroleum leaks. The advantages of this method is that it can be used in piping systems as well as storage tanks. The disadvantage of this method is that leak location cannot be determined. System design allows for false indications depending on initial designed sensitivity.

### 2.2 Acoustic Methods

Acoustic leak detection methods rely on piezoelectric transducers to translate pressure waves generated by fluid escaping the piping system to an electrical signal. Current systems rely on an operator

listening to the filtered output signal to determine whether a leak exists, without locating the leak. This relies on operator experience and can lead to false leak or no leak indications. Currently a Joint Department of Defense, Department of Energy, and Environmental Protection Agency Strategic Environmental Research and Development Program (SERDP) is developing an acoustic technology which has detected leaks of 0.1 gallons per hour. The passive acoustic leak detection technology is also capable of locating leaks within inches of their source. The acoustic leak detection technology has the potential for providing the most cost effective, reliable, method of leak detection and location for petroleum and aqueous based piping systems.

2.3 Mass Flow Sensors

Magnetic inductive flowmeters rely on the conductive properties of the liquid. The flow passes through a magnetic field and this produces a voltage difference over the cross-section of the flow area. This voltage is proportional to the (average) flow velocity. By knowing the conductivity of the liquid, the strength of the magnetic field, and the cross-sectional area, the flow velocity can then be determined by measuring the potential. A key advantage is that he sensors are relatively inexpensive and are very accurate, but there are velocity restrictions which depend on the liquid being pumped.

Calorimetric flow sensors utilize the calorimetric principal to determine flow velocity at a certain point in the flow field. The flow is locally heated and then the temperature is sensed a short distance downstream. Based on the thermal permitivity (the temperature dependent rate at which thermal energy propagates through a given medium) of the material, the temperature differential indicates the flow velocity. Assumptions on flow field profile are then used to calculate the volumetric flow rate from which the mass flow rate can be determined for a liquid of known density. These sensors have a highly accurate flow detection. The main disadvantage is precisely controlling the temperature at the sensor. Fouling of the sensor can also be a problem depending on the liquid being transported in the piping.

Ultrasonic flowmeters utilize time-of-flight measurements of wavefront propagation or doppler shift of the ultrasonic signal, the flow velocity average can be determined using two piezo-electric transducers, one a "sender" and the other a "receiver". Ultrasonic flowmeters can be used for a wide range of materials from sewage to ammonia, nitrogen, natural gas, air, acids, heavy oils, or desalinated water. The Ultrasonic sensor systems have high measuring accuracy, no pressure loss or flow obstructions, low power consumption, and can be purchased in the intrinsically safe version for explosive environments. A disadvantage is the high initial cost of the signal processing equipment.

2.4 Gas Sniffing

Gas sniffing technology utilizes electro-chemical sensors that are calibrated to background concentration levels of the particular compound of interest. In some situations this compound can be an additive to the liquid to make detection feasible. Sensors are located or transported to a suspected leak location where readings are taken and compared with threshold values to determine either a "leak" or "no leak" condition. These sensors are commonly used with Volatile Organic Compounds (VOCs) which produce highly localized concentrations of vapor when a leak occurs. This system is good for some liquids, such as petroleum products, which produce vapor that can permeate through the soil covering the pipe system and produce an area of concentration sufficient for detection around the leak location. Leaks of liquids with varying ambient concentrations, such as water, can easily be masked by the background noise. It is also not possible to chemically detect the presence of a water leak without adding potentially toxic marker compounds to the water.

2.5 Infrared Imaging

Infrared inspections are performed with a video camera capable of recording infrared radiation. The camera records the temperature differential and the images are processed to show the different temperatures in a color spectrum. Data can be videotaped for future review and processing. These

systems are generally used for systems which can produce significant thermal signatures even through several feet of earth. This limits them to use with piping systems which can transport liquids which will tolerate temperatures significantly above the surrounding ambient air temperature, such as heating water or steam. When conditions permit, the system or suspect locations within the system are scanned for leak indications. The advantages of this system are that it can be used to scan large areas at a time and does not require any excavation. The infrared technique is especially useful for surveying heating and cooling distribution piping systems. The disadvantages of this process are that it cannot be used for any system that doesn't present a temperature differential.

### 2.6 Level Monitoring

Level monitoring uses high precision storage tank liquid level measurements to determine the volume of liquid contained in each tank of the system. In a closed system, the volume should be constant for a given pressure and temperature when there is no leak present in the system. Any variation in the level generates an alarm that something is out of specification ranges for the system. Sensors can be float switches, capacitance, or continuity. Any petroleum distribution system which goes to a static state for suitable length of time would be a candidate for liquid level monitoring for leak detection. The implementation of this system for leak detection is relatively inexpensive, directly related to the accuracy required for the particular system to detect leaks of a particular rate. Liquid level monitoring requires the system to be in a static state for a period of time which is dictated by the resolution of the sensors and the volume of the system. A large volume system would require extremely precise measurement sensors which would be subject to noise, or an excessively lengthy static state holding period to detect small leaks in the system.

### 2.7 SCADA Systems

Supervisory Control and Data Acquisition (SCADA) systems rely on process monitoring sensors to convert physical phenomena such as pressure, temperature, flow rates, and density into electronic signals which can be integrated by the control system. SCADA systems rely on the combination of sensor inputs to determine the state of the system which is then used to modify the control inputs to bring the system (heat distribution, petroleum delivery, etc.) to the desired state. Complete information about the liquid system is precisely determined at sensor locations. The sensor inputs at adjacent measurement locations can be used to determine leak locations as well as rates. The time frame required to detect and locate a leak in the system is only dependent on the frequency with which the system is sampled. The cost of sensors and data communication equipment necessary for implementing a SCADA system on a large piping system is prohibitive.

## 3. FIELD SURVEY RESULTS

Several sites were surveyed for leak detection systems installed on water, fuels, and energy pipe systems. The only systems found were for the detection of fuel leaks. Several technologies discussed above could be adapted for water and energy pipe systems, however the cost of the technology is not easily offset by the cost of possible losses, due to the lack of perceived environmental impact from a large scale loss.

Personnel were queried about the system's utility, system effectiveness, false alarm rates, maintenance requirements, and the overall abilities of their system. The following is a summary of these site visits.

### 3.1 Pensacola NAS, FL

The leak detection system is made by Arizona Instruments Inc. (AZI) and had the sensor tube buried between the pipes during construction of the pipe line, as shown in Figure 1. The line is monitored by 10 remote monitoring stations which cover the entire pipeline. Each monitoring station can be contacted via modem and controlled remotely as well as being controlled by operator input at the monitoring station by means of a touchpad. The monitoring stations are also capable of calling the host computer system and reporting alarms. The system operates by cycling clean, dry air from the monitoring station out the length of each segment (blowdown) and then drawing a soil gas sample across an electronic gas analyzer to detect hydrocarbons. The literature provided by AZI quotes a lower detection limit for commercial gasoline of 150 ppm, and for JP4 Jet Fuel of 60 ppm. The lower detection limit for either JP5 or JP8 is not specified.

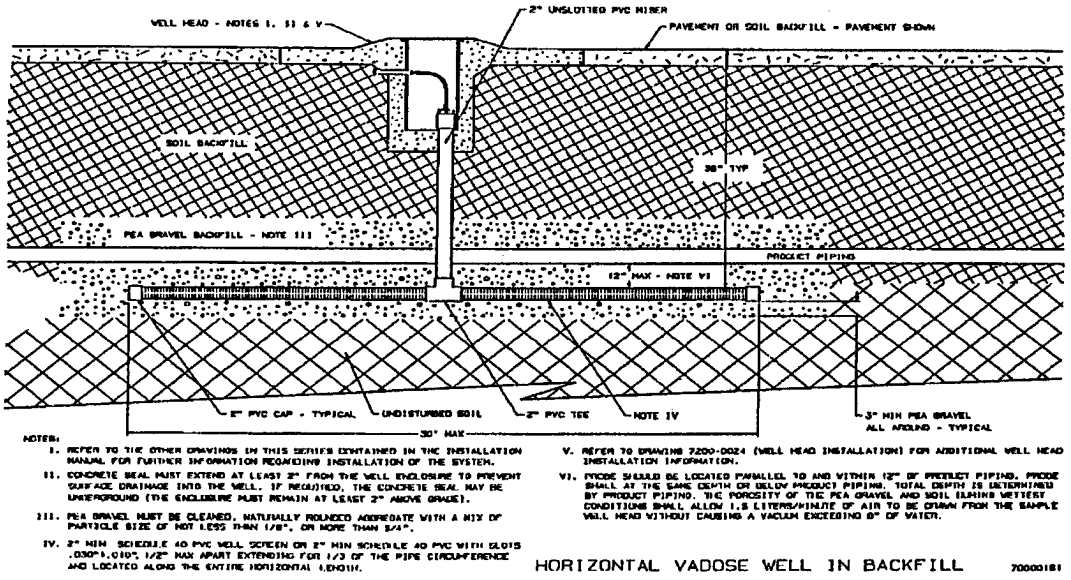



Figure 1. AZI Model Twelve-X installation schematic

Experience showed that the rising and falling water table levels would occasionally drown the system by not allowing it to pull a vapor sample. The sensor pipe was used as a riser to try to mitigate the ground water problem. The major length of the sensor tube was run horizontal and then turned upwards at the sensing location providing a vertical column which could be cleared during the blowdown phase of the test and then used to acquire a vapor sample. Despite the modification, the operator suggests not installing this particular leak detection system in areas of high ground water.

3.2 Anchorage Airport - Anchorage, AK

The leak detection and location system is controlled and tested by the Hansa Consult system. The system was installed in 1988. The leak detection is done by pressurizing the 8 mile pipe line to 16 bar and then holding pressure for about 20 min, as shown in Figure 2. The pressure is measured 75 times then is reduced to 6 bar and held for 20 min. The pressure is measured 75 times and then raised again to 16 bar and measured again 75 times. Testing takes place during the night hours because the system must be taken off-line. The system is reported to have worked very well. System operation can be verified by opening a bleed off valve during testing. However, all the computer programming code is written in German and any problems have to be resolved by staff personnel located in Germany.

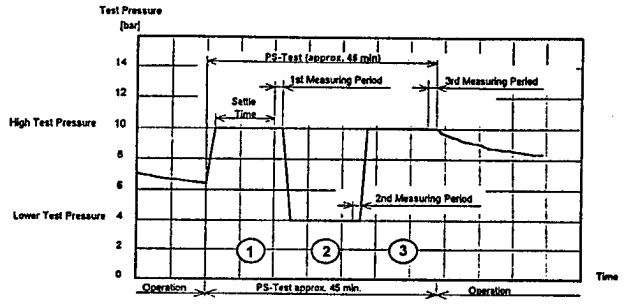



Figure 2. Hansa Consult Sample Pressure Step Test

3.3 Elmendorf AFB, AK

The leak detection system is a Permalert PAL-AT system with four cables, two for the diesel fuel and two for the mogas. One cable on each system detects water and the other detects fuel. The Permalert system relies on the conductivity and impedance of the cable loop to detect liquids. Leak location can realistically be determined to within one or two feet if the leak is immediately detected. The system had no problems until some additional construction was done and water apparently entered the jacket. The cables for detecting water, in both the mogas and diesel pipelines indicate water in the system.

3.4 North Island NAS, CA

The leak detection system is a constant pressure volumetric leak detection system from Vista Research. The system controls line pressure by adding the necessary volume of product to the line to compensate for thermal deviations in the product line, as shown in Figure 3 and Figure 4. The system has been certified by third party blind testing to be capable of detecting leaks of 0.1 gal/hr with 95% confidence level (per EPA standards). A 'Tightness Test' consists of maintaining an equilibrium pressure for approximately one hour and then raising the pressure and maintaining the new equilibrium pressure for a similar length of time, with 25 minutes of stabilization time required prior to test initiation. The system verified pipe integrity with a leakage reading of 0.0001 gallons per hour which was considered measurement noise.



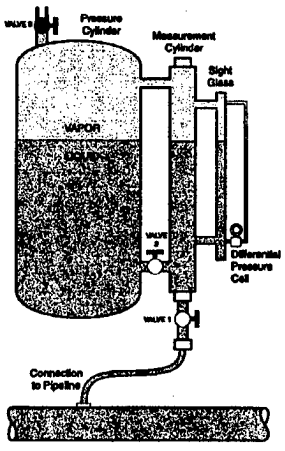



Figure 3. Schematic Diagram of the Vista Research LT100 system
Figure 4. Valving, Graduated Cylinder, and Resevoir Tank for Vista Research System

## 3.5 Travis AFB, CA

The leak detection and location system was manufactured by Argus Technologies and was installed by the contractor 1 ft. above the top of the main line with sand backfill added to cover the sensor tube while the remaining trench depth was filled with native soil. The leak detection system observed at this location consisted of a semi-permeable diffusion tube with air sampling. The system pumps clean, dry air through the system and uses a marker gas to signal the end of the test. In this way, a leak location can be interpolated from the time differential between the arrival of the contaminated air sample and the arrival of the marker gas. Approximate air velocity in the tube during a test is 3 ft./sec.

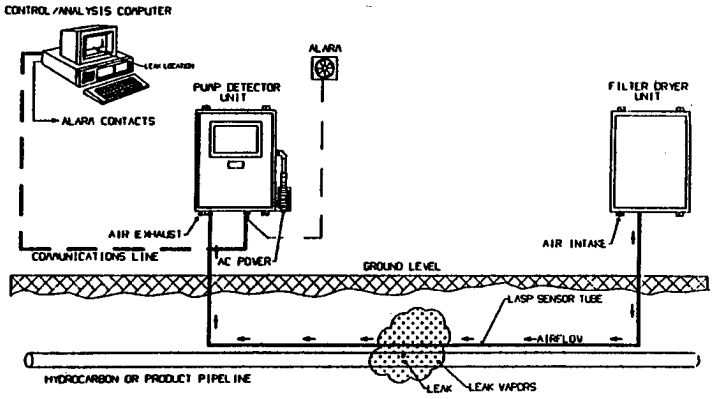



Figure 4. Argus Technologies LASP system functional diagram



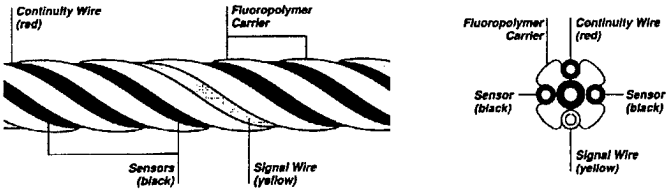
Figure 5. Argus Technologies Air Drying and Filtration Unit

The system remains idle to allow a sufficient concentration of vapors to build up in the sensor tube. The system literature claims leak location resolution of 1 percent of line length. This can be reduced by interspersing the total line length with test points at which marker gas is injected to produce a segmented test flow for the system. Leak rate detection and resolution is a function of system installation and soil composition. The system was non-functional during the site visit and the Air Force indicated that the system has yet to perform to a satisfactory level.

## 3.6 Ft. McCoy ANG-POL Facility, WI

The leak detection system is a Raychem TraceTek. It is a two cable system which operates on the same principals as the Permalert system installed at Elmendorf AFB and as such, has the same resolution and capabilities. They have had no problems with the monitor. About the beginning of August 1996 the leak detection system reported water in the conduit near the road. They are in the process of investigating the leak.

Technology




Drawing not to scale

| | |
|---|---|
| Cable diameter: | .240 inches nominal |
| Cable diameter with connector: | .510 inches nominal |
| Continuity and signal wires: | 2 x 26 AWG with insulation of fluoropolymer |
| Sensor wires: | 30 AWG with jacket of conductive fluoropolymer |
| Carrier: | fluoropolymer |
| Cable weight (50-ft length): | 2 lbs |

Figure 5. Raychem TraceTek cable diagram

3.7 Whiteman AFB, MO

Tracer Research provides the intermittent testing of the pipeline integrity by inoculating the stored fuel with a proprietary marker gas (which is compatible with the JP8 fuel) at trace levels about 1 week prior to testing. Technicians then sample each of the approximately 1400 sensor wells spaced at 20 ft. intervals along the pipeline. The soil gas sample is then analyzed using a portable gas chromatograph to detect the trace levels of the marker gas which would result from a fuel leak.

The difficulties experienced with the Tracer Research system at this site are generally due to leaks from leaking connections in the fueling pits which release fuel into the pits. The fuel then migrates through either a crack in the pit wall or through the air and is detected in one of the nearby sample wells. There is also a non-functioning Argus Technologies vapor detection system at this site which the site personnel tested first by placing the sensor tube alongside a pan of JP8, then by covering both the pan and the sensor tube with a sheet of plastic, and then finally by immersing the sensor tube in the JP8 at which point the system finally registered hydrocarbon levels above normal background levels.

3.8 Ellsworth AFB, SD

Ellsworth uses an AZI leak detection system with wells spaced at 200 ft. intervals. The system takes a soil gas sample from each well and passes the sample across an electronic hydrocarbon detector to measure hydrocarbon concentration in ppm. Each well is connected to a perforated tube buried approximately 1 ft. above the fuel line. The sampling of each well takes an average of 10 minutes per well with the closer (to the monitoring station) wells taking slightly less time.

The system has three wells which are in contaminated soil which are still indicating leaks even after having a chip with higher concentration level capabilities installed. The line with the indicated leakage has been verified to not be leaking by tank level measurements.

Often the sensor well restrictor assemblies will become blocked by water after a heavy rainfall. The proprietary restrictor assemblies are not dryable and must be replaced if they become immersed in water.

The sensor tube can be prone to splitting, which results in a "port open" malfunction of the leak detection system if the line is exposed to ultraviolet light (bright sunlight) for any substantial length of time before burial.

## 4. DISCUSSION

Two leak detection systems manufactured by Argus Technologies were surveyed and neither was functional. The system at Whiteman was abandoned in favor of the Tracer Research system when the

quoted repair price of the Argus system exceeded the installation cost of the new Tracer Research system. The system installed at Travis AFB was installed with the pipeline to specifications by the pipeline construction contractor, but has failed to perform satisfactorily. The system is based on sound scientific principals, however the system cannot be recommended due to two factors; 1) The time required for a given minimum leak to diffuse into the sensor requires the system to remain idle for so long that a leak of dangerous magnitude could remain undetected long enough to create a significant spill and 2) the system's apparent unreliable performance.

An AZI system in operation was surveyed at two sites, Pensacola NAS and Ellsworth AFB. These systems have proven themself in the field with the major drawback being the susceptibility of the system to water invasion and the resulting inability to monitor some sections of the piping system. In addition, experience has shown that the remote operation capabilities of the system can be a liability. Specifically, a lightning strike at the Pensacola NAS disabled several monitoring stations for several days. Another drawback to the AZI system is the location of the leak source. At the Pensacola installation, the sensor tubes cover 20 ft. of pipeline per sensor well. This means a leak indication can be located to within only 20 ft. of it's source. The detection levels for a given leak rate are also dependent on the installation of the system, particularly the backfill surrounding the sensor tubing and pipeline. AZI recommends a minimum percolation value that is to be obtained by a given backfill in order for the system to perform to it's minimum concentration detection levels.

The Tracer Research system was used at Travis AFB before the installation of the Argus Technologies system. The system Tracer was considered too maintenance intensive after several of the probe wells were damaged by construction and grounds maintenance equipment. The same type of wells are used at Whiteman AFB and have not experienced the same rate of attrition. The 20 ft. well spacing of the Tracer system allows leak location to within 10 ft. of the source by comparison of relative concentration levels. The deficiency of the Tracer system is similar to that of the Argus Technologies system in that it is not a continuous monitoring system. Leaks of dangerous magnitude can exist undetected until the next scheduled testing date.

Two volumetric systems were surveyed. A pressure differential system by Hansa Consult and a constant pressure volumetric system from Vista Research. Both systems are capable of detecting extremely small leaks, but leak location remains a problem.

Two cable systems were also surveyed, one by Permalert and one by Raychem. Both cable systems were performing as advertised and one was indicating a water leak condition. The disadvantage of the cable systems is that they require replacement of any length of cabling which comes in contact with liquid and they must be installed in a conduit pipe, effectively negating their applicability for an existing system and increasing the installation cost of a new system. The cable systems are ranked lowest in performance and cost. Water intrusion is a major problem for cable systems and since the cables must be protected, their use is limited to double-wall piping systems which increases the initial cost of system installation and prevents retro-fitting existing systems.

The acoustic leak detection technology was shown to be capable of detecting and locating small (0.1 gallons per hour) leaks in both the laboratory and small scale field testing. The SERDP project also proved the acoustic technology capable of locating a leak within a few inches of the source in a 200 foot long pipeline. It is estimated that the installation and operation of a finalized acoustic leak detection system will cost under $10.00 per foot of piping installed.

## 4.1 Cost Data

Questionnaires were sent to both installations and vendors to determine applicable current pricing on installation, materials, and maintenance costs for the system types surveyed. TABLE I. illustrates the relative breakdown of the cost data obtained. Vendors were supplied with a hypothetical piping system 1000 ft long, carrying JP-8 in a single wall pipe buried 4 ft. beneath grade.

TABLE I. SURVEYED COST DATA

| Leak Detection System | Cost Data Source | Installation Cost | Equip. and Constr. Materials | Maintenance Cost (Annual) | Length of Pipline in feet | Total Cost in first Year | Total Cost Per Foot |
|---|---|---|---|---|---|---|---|
| Soil Sentry 12XP Pipeline and AST Environmental Monitoring System | Site Costs Pensacola NAS (Based on 26,400') | $274,000 | | $300 | 26,400 | $274,300 | $10.39 |
| AZI Soil Sentry (Tracer Research Tracer Tightness used on storage Tanks - not included in cost data) | Site Costs Ellsworth AFB (Based on 7908') | $104,000 | $40,000 | $300 | 7,908 | $144,300 | $18.25 |
| Soil Sentry 12XP Pipeline and AST Environmental Monitoring System | Manufacturer Estimate (Based on 1000') | $15,500 | $10,750 | $995 | 1,000 | $27,245 | $27.25 |
| Tracer Research: ALD 2000 | Manufacturer Estimate (Based on 5,000') | $134,941 | | $25,883 | 5,000 | $160,824 | $32.16 |
| Raychem: Trace Tek (Quote by Tracer Research) | Manufacturer Estimate (Based on 5,000') | $113,000 | | $8,000 | 5,000 | $121,000 | $24.20 |
| PermAlert: PAL-AT Leak Detection System | Manufacturer Estimate (Based on 5,000') | $49,246 | | | 5,000 | $49,246 | $9.85 |
| Vista Research: Model LT100 | Manufacturer Estimate (Based on 1,000') | $42,000 | | | 1,000 | $42,000 | $42.00 |
| Hansaconsult: TCS Tightness Control System | Manufacturer Estimate (Based on 1,000') and Converted to US Dollars | $66,000 | | | 1,000 | $66,000 | $66.00 |
| Argus Technologies | Manufacturer Estimate (Based on 5,280') | $209,457 | | | 5,280 | $209,457 | $39.67 |

## 5. CONCLUSIONS AND RECOMMENDATIONS

To achieve sufficient performance from a leak detection system, the piping system should first be verified for integrity, then have a continuous monitoring system installed and tested. The system must also be relatively maintenance free and inexpensive to operate. None of the systems surveyed or researched provide the optimal level of leak detection and location alone. Developing technologies, especially the current SERDP research into passive acoustic leak detection, show promise for an all encompassing solution to leak detection, quantification, and location.

Of the current COTS leak detection systems investigated, the most promising technology for reliable detection of fuel leaks in underground fuel piping systems appears to be the gas sniffing system. This system has proven it's ability to detect numerous hydrocarbons from natural gas, to hydraulic fluid, to JP8. However, the system is not applicable to water or energy pipe systems and susceptible to water invasion on some current systems. The AZI leak detection and location system provides sufficient sensitivity to detect smaller leaks and has the ability to continuously monitor the piping system, while giving leak location to within 10 feet.

The tracer gas systems are suitable for intermittent pipeline integrity tests and do not depend on prior knowledge of the pipeline condition. Cable systems are useful for both energy pipe systems and new potable water systems which incorporate double wall piping. There are also cables available for the detection of hydrocarbon liquids which makes this technology applicable to fuel, water, and energy pipe systems.

The gas sniffing systems are at present the best technology and commercial solution available for petroleum leak detection, followed by cables for overall leak detection (in double walled pipe), however, as advanced acoustic leak detection comes on line, its capabilities should meet or exceed those currently found in all of the previously researched systems.

# OPTIMIZING DOD INVESTMENTS IN OIL/WATER SEPARATORS AND CLOSED-LOOP RECYCLE TREATMENT SYSTEMS

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## ABSTRACT

Wastewater discharges associated with the maintenance of the Department of Defense's (DoD's) large fleets of tactical and non-tactical vehicles and equipment must comply with the Clean Water Act treatment and pretreatment requirements. Treatment methods for these wastewaters have traditionally focused upon the removal of the principal contaminants of sediment and POL (petroleum, oils, and lubricants). Typically, most current treatment/pretreatment systems employ the use of settling basins for the removal of sediments followed by an oil/water separator for the removal of oil and grease. If compliance problems are an issue with oil/water separators, closed-loop recycle treatment systems offer an alternative solution.

DoD installations currently purchase oil/water separators and closed-loop recycle treatment systems without adequate information as to whether they will be effective on their specific type of wastewater treatment requirements. Although manufacturers provide literature on their product's operation and performance, oil/water separators and closed-loop recycle treatment systems at Army washracks have not been independently evaluated and verified. Performance claims are frequently based on specific models operating under ideal conditions. These ideal conditions, however, almost never exist at DoD facilities. High solids loading and unique military use affect the performance and maintenance of oil/water separators and closed-loop recycle treatment systems in a manner which has not been evaluated. Some commercially available oil/water separator and closed-loop recycle treatment systems are available for purchase from the Federal government's GSA pricing list. However, limited "lessons learned" guidance addressing the purchase, operation, maintenance, and performance of these systems has been published to assist DoD customers.

To maximize the return on future DoD investments made in the design and purchase of oil/water separator and closed-loop recycle treatment system technologies, it is critical to provide the installation users with "lessons learned" and performance data obtained from non-vendor testing and evaluation. System designs based upon performance data generated from DoD operations will allow the "spin on" of commercially developed technologies to specific DoD applications and reduce the risk of regulatory non-compliance, reduce expenditures on non-performing technologies, and maximize savings through standardization of designs.

The multitude of combinations of off-the-shelf products and DoD applications make a comprehensive study to provide guidance for all situations unrealistic. However, the U.S. Army Environmental Center (USAEC) has initiated a study to provide guidance where it is most immediately needed. USAEC has directed the U.S. Army Construction Engineering Research Laboratories (USACERL) and the U.S. Army Aberdeen Test Center (USAATC) to test and evaluate two models of closed-loop recycle treatment systems and three oil/water separators. At the conclusion of these evaluations, a "lessons learned" report will be made available to all interested DoD users.

## INTRODUCTION

In order to maintain mission readiness, military units must periodically wash their vehicles. Vehicle washing is conducted in a designated area called a washrack. Washrack systems are designed to handle the wash water generated by either a single pass through treatment or by localized treatment allowing reuse of the water. Washracks designed to operate in a single pass through mode utilizing an oil/water separator are most common due to their low cost. However, oil/water separator issues are a chronic problem due to lack of maintenance, inadequate design, and characteristics of the wastewater influent. Closed-loop recycle treatment systems are becoming more popular due to limited discharging to the environment. However, closed-loop recycle treatment systems entail higher installation costs and create a considerable addition to the amount of operation and maintenance required.

## OIL/WATER SEPARATOR EVALUATION

Oil/water separators are the most common form of pretreatment for washrack wastewater. The main purpose of an oil/water separator is to separate free oil and solids from water that is being discharged to a sanitary sewer. There are several types of oil/water separators on the commercial market. Most installations have either gravity type or coalescing enhanced gravity oil/water separators.

Oil/water separators do not operate correctly if they are not properly maintained. Regularly scheduled operation and maintenance is required. A large portion of the oil/water separators at military bases are not operating as expected due to a lack of adequate maintenance. Making installations aware of conducting regular maintenance is crucial to maintaining compliance and reducing new system purchases.

In the summer of 1996 a mail survey was conducted at a number of Army installations to determine what problems installations were encountering regarding oil/water separators. The results from the survey showed that a majority of installations were planning to purchase closed-loop recycle treatment systems in order to end all of their environmental discharging problems. Others were planning to install newly purchased oil/water separators because their old separators were not functioning properly.

From this summer 1996 survey installations are planning on purchasing and installing closed-loop recycle treatment systems. But have the installations considered all options? Purchasing and installing closed-loop recycle treatment systems will increase the operation and maintenance requirements. In many cases, installations may just need to upgrade their existing oil/water separator or develop operation and maintenance schedules. The purpose of the USAEC, USACERL, and the USAATC project is to accomplish: 1) emphasizing the need and encourage installations to develop regular operation and maintenance schedules, 2) help the installation become a more educated consumer when purchasing an oil/water separator, 3) determine performance characteristics of various commercial systems in specific

applications, and 4) make the installation fully aware of all the possibilities of keeping their existing oil/water separator before purchasing a closed-loop recycle treatment system.

The USAEC, USACERL, and USAATC oil/water separator evaluation is currently being conducted at two Army sites and one Air Force site. The selection criteria was based on whether the installation had purchased and installed an oil/water separator within the past three years. The California and South Carolina Army National Guard have volunteered oil/water separator sites for evaluation. In coordination with the U.S. Air Force Armstrong Laboratory's Environics Directorate, the third site for the evaluation will be at Wright Patterson Air Force Base. An initial site visit was conducted to get an idea of what type of waste streams flow into the oil/water separator. Grab samples of the influent and effluent were then taken to determine how adequate the oil separation process works in the separator for total petroleum hydrocarbon (TPH). Treatment performance for the particular wastestream and operational conditions will be compared to typical discharge criteria. Operation and maintenance records will also be kept to determine frequency and duration as well as maintainability. At the conclusion of the evaluation period the TPH data from the effluent will be compared to manufacturer's stated literature. Operation and maintenance records will also be checked to see if additional operation and maintenance is required due to the Army's complex waste stream.

At the conclusion of the evaluation, a "lessons learned" report will be made available for all installations considering the purchase of an oil/water separator. Within this report will be a guide help an installation consider all alternative low cost options before purchasing a new oil/water separator or if a closed-loop recycled treatment system is necessary for that installation.

## CLOSED-LOOP RECYCLE TREATMENT SYSTEM EVALUATION

Closed-loop recycle treatment systems are very popular due to zero discharge capability. Many installations that are having problems with their existing oil/water separators are looking toward purchasing and installing closed-loop recycle treatment systems. However closed-loop recycle treatment systems are more labor intensive with regards to operation and maintenance, and in some cases, more time is required for the operation and maintenance of closed-loop recycle treatment systems than oil/water separators. For this reason, the U.S. Army Military District of Washington along with the U.S. Army Training and Doctrine Command, the U.S. Army Forces Command, and the U.S. Army National Guard Bureau requested that USAEC look into evaluating closed-loop recycle treatment systems for reliability and maintainability data.

The USAEC Environmental Technology Division has partnered with USACERL and USAATC to evaluate two commercial off the shelf closed-loop washracks at an USAATC depot level maintenance shop. Each system was evaluated for a 13 week period generating reliability, maintainability and treatment performance data. At the present time, one system evaluation has been completed and the other is nearing completion.

In the spring of 1996, a phone survey was conducted on all known closed-loop recycle treatment system owners within the DoD. Results from that survey show that installations have decided to purchase closed-loop recycle treatment systems as an alternative to discharging wastewater through an oil/water separator. Another statistic from that survey showed that installations purchased closed-loop recycle treatment systems based on the sales representative's claims and suggestions. For this reason, it is important that installations have better knowledge as to what closed-loop recycle treatment systems are best suited for their particular requirements.

At the conclusion of the first evaluation, several important factors regarding closed-loop recycle treatment systems were documented. Some factors include the following:

- it is important that closed-loop recycle treatment systems be installed and operated inside a closed and heated building due to environmental factors such as freezing pipes
- daily operation and maintenance is required, sometimes up to 30 minutes each day
- it is important to ensure that the manufacturer's contract provides: training, on-site support and troubleshooting, a user's manual that is easy to understand and assist in daily, weekly, and monthly maintenance record keeping
- limited handling of hazardous materials may be required (e.g. Aluminum Sulfate for coagulant, Sodium Hydroxide for pH control, etc.)
- wastewater contained within a closed-loop recycle treatment system will eventually need to be discharged into a sanitary sewer (accumulated levels of contaminants require monitoring)
- periodic inspections are necessary to insure the system is operating in closed-loop mode (problems can be encountered due to a limited size of the washrack basin, sump pump reservoir, or recycle treatment system controls)
- closed-loop systems do require make-up water for water that was lost to evaporation or water carried off on vehicles
- system overflows are possible if problems occur with system controls.

At the conclusion of the two system evaluation, a "lessons learned" package will be made available for installation use for those considering purchasing and installing closed-loop systems. Within this package will be a checklist as to whether the installation has considered all possibilities before purchasing a closed-loop recycle treatment system.

## DECISION TREE FOR WASHRACKS AND OIL/WATER SEPARATORS

A decision "tree" was developed to help installations considering washrack upgrades. Figure 1 is a copy of the decision tree that will be published in the "lessons learned" report.

## CONCLUSIONS

At the conclusion of both evaluations, USAEC, USACERL, and USAATC will be able to provide important information to installations regarding the purchase of oil/water separators and closed-loop recycle treatment systems. The goal of this project is to ensure the Army user is a more educated consumer when considering how to improve their washrack capabilities. Making the user a more educated consumer has the potential to save the government millions of dollars.

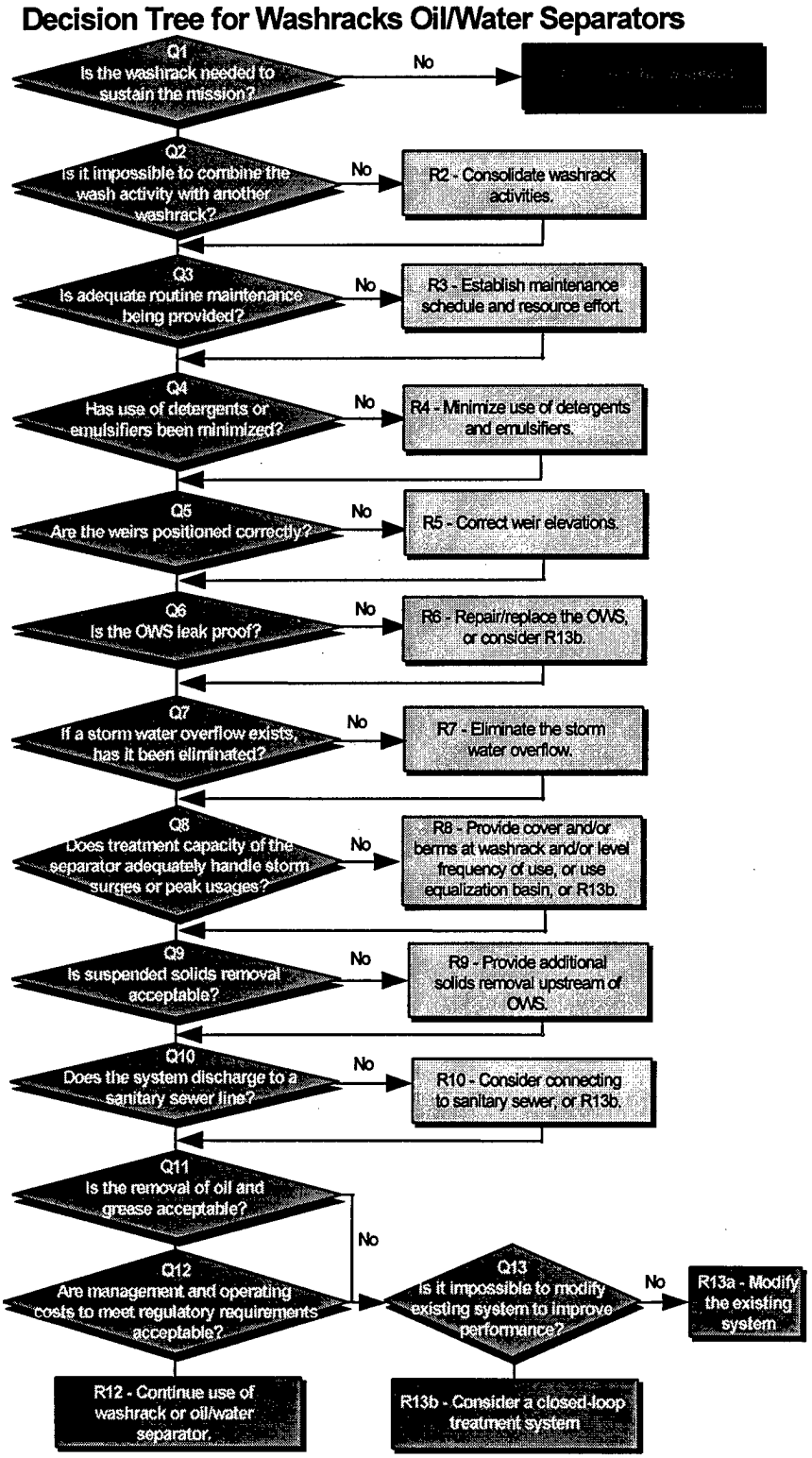



Figure 1. Decision tree for washracks and oil/water separators.

# APPLICATION OF A CONTINUOUS FLOW IMMUNOSENSOR FOR ONSITE ENVIRONMENTAL ANALYSIS

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## ABSTRACT

The Naval Research Laboratory (NRL) has developed a biosensor for onsite environmental monitoring that relies on specific interactions between an antibody and a target analyte as a means of detection. This continuous flow immunosensor is capable of detecting the explosives trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) at parts per million (ppm) to parts per billion (ppb) concentrations in environmental samples, even in the presence of other pollutants. The device is designed to have significant advantages over laboratory analytical detection methods, including low cost (negative samples can be analyzed with effectively no cost), rapid analysis (generally 2-3 minutes per sample), and ease of use (minimal technical skills required). The NRL biosensor has previously been shown to be effective at detecting explosives in groundwater and leachate samples at several Superfund sites, including Umatilla Army Depot and SUBASE Bangor. A new field-portable device engineered by Research International, Woodinville, WA, is currently being used in field tests at designated remediation sites to demonstrate field detection capabilites in groundwater and soil and to validate instrument performance for EPA certification.

## 1. INTRODUCTION

Due to past munitions manufacturing and disposal practices, the DoD has numerous installations contaminated with explosives that require extensive remediation. To meet EPA-regulated contaminant levels, the cleanup plan must specify a means of accurately measuring explosives levels, both during initial characterization and ongoing remediation. An accepted laboratory method for confirmation and quantitation of explosives is U.S. EPA SW846 Method 8330 High Performance Liquid Chromatography (HPLC) (1). This analytical method is accurate and reliable, but involves sending samples to an EPA-certified analytical laboratory for analysis by skilled personnel. Though several field test kits and immunoassay methods have become available (2,3), these methods can be time-consuming and require sample preparation or multiple steps. A field instrument which could perform quanititative analyses of samples onsite would be a valuable tool for project managers. It would provide timely, detailed site information and significantly reduce the costs incurred in laboratory determinations. In response to this need, NRL has developed a biosensor that detects the explosives TNT and RDX in environmental samples and is adaptable for use in a variety of circumstances. The biosensor is described here in terms of assay design, application in environmental monitoring, and instrument development.

## 2. BIOSENSOR OPERATION AND ASSAY DESIGN

The NRL sensor uses antibody/labeled antigen complex for signal generation. As described in detail previously (4,5), antibodies to a specific analyte, such as TNT, are first

immobilized on a support medium, such as an activated membrane or glass, and saturated with a fluorescently-labeled analog of the explosives. After washing to remove non-specifically bound fluorescent label, the support is placed in a column and connected to a flow stream. A sample of 100-150 µL is then injected directly into the flow stream. If the analyte is present, dye-labeled antigen is displaced in proportion to the antigen concentration and is measured downstream within a few minutes by a fluorescence detector. This biosensor can be readily used with discrete samples injected by hand or valving systems that divert a sample from a processing flow stream at selected intervals. Samples which do not contain detectable amounts of contaminants will not displace a significant quantity of dye conjugate, thus allowing the sensor to test a large number of negative samples without loss of performance.

## 3. FIELD STUDIES AND ENVIRONMENTAL SAMPLE ANALYSIS

Application of this biosensor technology to onsite analysis was first demonstrated in EPA-sponsored field trials at two military bases on the Superfund cleanup list (6). Conducted at Umatilla Army Depot Activity (UMDA), OR (a former munitions storage and handling depot), and Naval SUBASE Bangor, WA (an active military installation previously used as a wastewater lagoon for a nearby segregation facility), the onsite tests illustrated that the biosensor could effectively measure explosives in environmental samples. During the trials, groundwater samples were collected from monitoring and extraction wells and tested for TNT and RDX. Concentrations of these explosives varied from non-detectable levels to greater than 3000 *u*g/mL at each well, providing a broad range of explosives. Serial dilutions of samples were also performed at both sites to test the linear response for both the TNT and RDX assays. To quantitate biosensor measurements, the total fluorescence intensity for each sample was recorded and converted into concentration units (µg/mL) based on calibration standards applied to the system after each positive response. For data validation, laboratory splits were analyzed by an independent EPA-approved laboratory using EPA SW846 Method-8330.

**Table I - Comparison of EPA Method 8330 and NRL Analysis of Groundwater Samples**

| Well # | TNT Detection (ug/L) | | RDX Detection (ug/L) | |
|---|---|---|---|---|
| **Umatilla** | **EPA** | **NRL** | **EPA** | **NRL** |
| Well 4-1-2 | 198 | 276 | 160 | 194 |
| Well 4-18-0 | 3624 | 2952 | 1700 | 1639 |
| Well 4-18-2 | 299 | 368 | 170 | 150 |
| Well 4-2 | nd | nd | 0.16 | nd |
| **Bangor** | | | | |
| BEW-2 | 30 | 56 | 640 | 543 |
| BEW-3 | 65 | 62 | 290 | 263 |
| BEW-4 | nd | nd | 13 | 33 |

TNT and RDX assay results for several wells from both UMDA and Bangor (shown in Table 1) illustrate excellent agreement typically observed between the EPA method and the NRL biosensor. Linear regression plots of the data showed correlations between samples analyzed by the biosensor vs EPA Method-8330, with slopes of the curve ranging between 0.97 and 1.2, and correlation coefficients ($r^2$) values falling between 0.90 and 0.98, suggesting good accuracy for the NRL biosensor method.

In additional tests of system performance, soil samples from UMDA were extracted using the method of Jenkins, et al. (2). After extraction with acetone, samples were dried down, resuspended in biosensor buffer and injected into the system. As with the groundwater samples, total fluorescence intensities were recorded and compared to TNT/RDX standards for quantitation. Soil test results, shown in Table II, demonstrate that the biosensor also performs well for more complex samples. In general, the field method and laboratory method data are comparable. Measurable differences between the two are most likely due to the heterogeneous nature of soil samples.

**TABLE II - Analysis of Umatilla Soil Samples by Method 8330 and the NRL Biosensor**

| Sample ID# | EPA 8330 RDX* | NRL Biosensor RDX | EPA 8330 TNT | NRL Biosensor TNT |
|---|---|---|---|---|
| G18-L6 | 15 | ND | 3.4 | ND |
| G10-L3 | 21 | 39 | 10 | ND |
| G51-L1 | 25 | 0 | 24 | 19 |
| HS-04 | 44 | 39 | 29 | ND |
| G18-L3 | 51 | 55 | 36 | 26 |
| G21-L2 | 130 | 19 | 55 | 40 |
| G16-L2 | 190 | 86 | 11 | 99 |
| G17-L1 | 340 | 219 | 480 | 503 |
| G55-X | 1400 | 896 | 2800 | 1690 |

*Units=μg explosives/g of soil

## 4. PORTABLE FIELD BIOSENSOR

Initial assay development and field demonstrations were accomplished using the laboratory version of the biosensor. A portable device is currently being tested in expanded field trials to validate performance and onsite capabilities. The portable biosensor, known as the FAST 2000, with integrated sample testing and data analysis, has been developed in collaboration with Research International, Woodinville, WA . The device, including pumps and fluorometer, weighs approximately two pounds, is 4"x6" in size and is controlled by a laptop computer via the PCMCIA interface (Figure 1). The laptop computer also supplies power for the instrument, thus allowing for short periods of battery operation in remote locations. To run assays, a disposable cartridge containing the antibody/fluorescent-antigen complex is inserted into the unit and samples are introduced via a sampling port. Results

can be viewed in real time or stored on the computer for later data analysis and storage. A representative sample peak from a TNT assay of a SUBASE Bangor groundwater sample is shown in Figure 2. By comparing the intergrated peak area for this sample to that of a TNT standard, a calculated value in parts per billion (ppb) or ng/mL units can be determined.

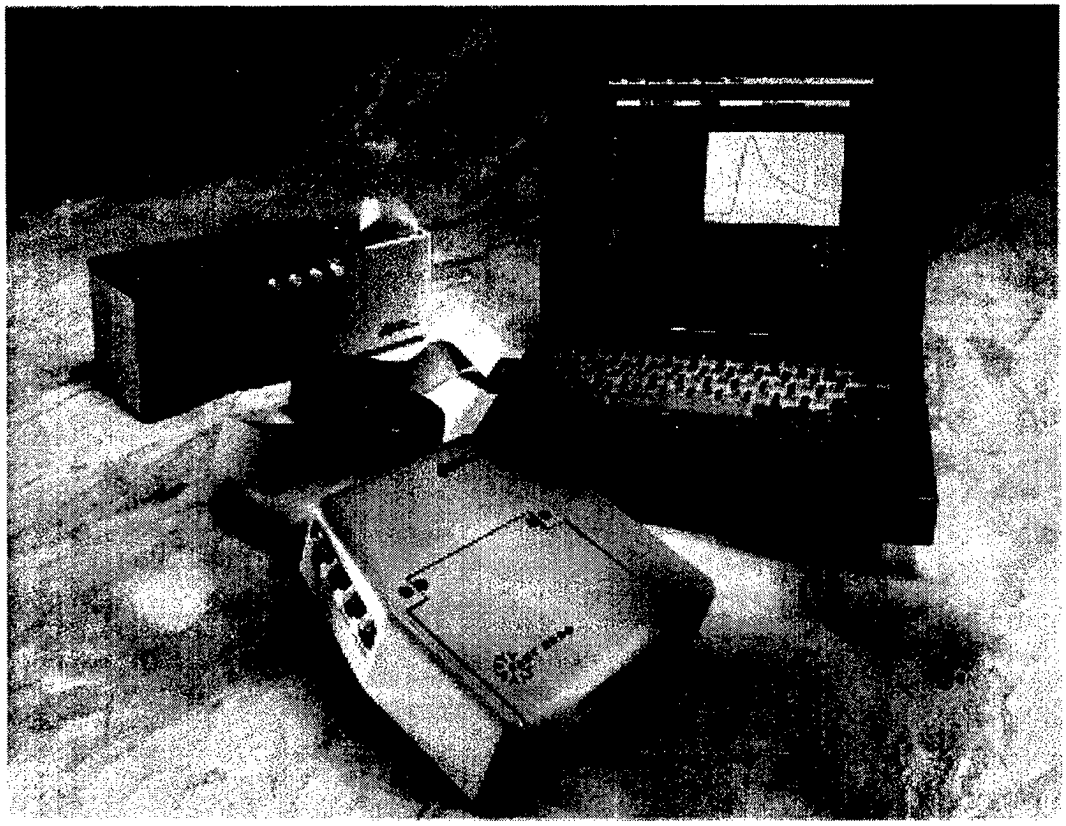


**Figure 1 - Portable field biosensor, the FAST 2000, developed for NRL by Research International.**

## CONCLUSIONS

Laboratory and field results from Umatilla Army Depot and Naval SUBASE Bangor have demonstrated that the NRL biosensor is capable of detecting low part per billion (ppb) levels of TNT and RDX with accuracy and precision. The assay system requires minimal sample volume (100-200 *u*L) and analyzes samples in less than 3 minutes. The instrument has proven to be quantitative, with a lowest detectable limit (LDL) of 20 *u*g/mL for both TNT and RDX. Statistical analysis based on regression curves that compare this biosensor to the accepted EPA Method-8330 for explosives detection consistently show a high degree of correlation between the two. This technology is expected to be particularly relevant for testing groundwater, streams and lakes for wastes from explosive manufacture, for monitoring chemical and fuel storage, and for checking the progress of bioremediation efforts. If adapted for field preparation of soil samples in solvent extracts, the device can also be used for monitoring ground contamination, with significant cost savings and

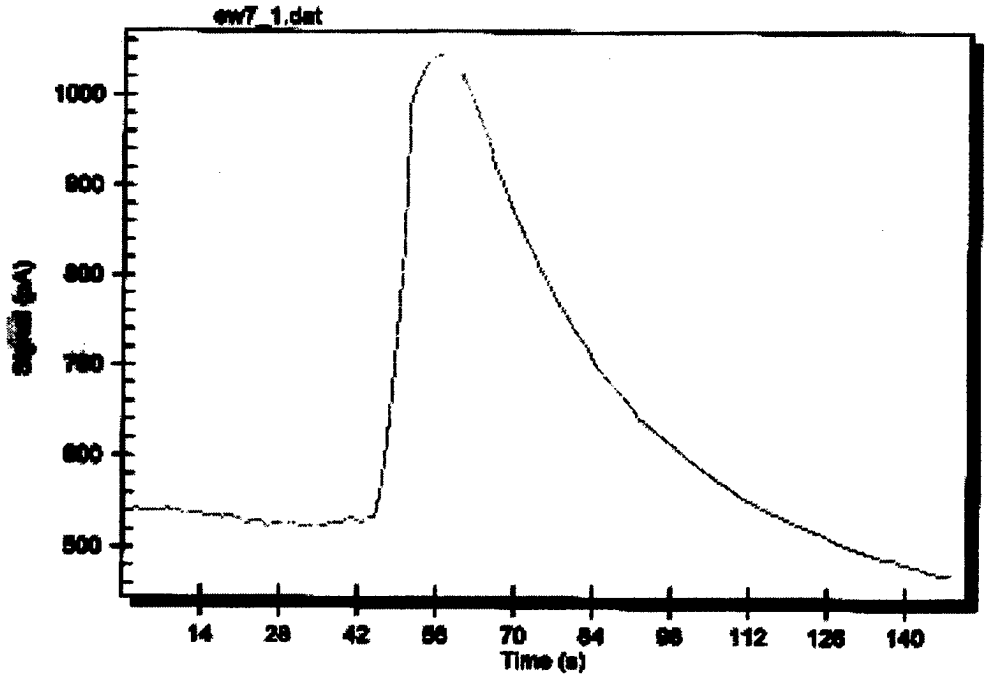



**Figure 2. FAST 2000 data for TNT analysis of groundwater sample from SUBASE Bangor extraction well #7.**

improved response times. Continued research will focus on completing EPA-certification of the TNT and RDX assays in the FAST 2000 field-portable system, as well as development of antibody-based assays for other explosives and priority environmental pollutants.

## ACKNOWLEDGEMENTS

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# POLLUTION PREVENTION I

# FURY: A REMOTE UNDERGROUND STORAGE TANK INSPECTION/ASSESSMENT SYSTEM

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## Abstract

Nationwide it is estimated that there are over 300,000 metallic Underground Storage Tanks (USTs). Near the end of 1998, Federal regulations (40 CFR 280) will require that all of these tanks be brought into regulatory compliance to avoid environmental contamination. Replacing all existing USTs would be prohibitively expensive. One allowed alternative is to retrofit existing USTs with cathodic protection for continued use. However, there is need for more cost-effective and reliable condition assessment methods for USTs in order to support better informed management decisions.

To meet this need a remote robotic UST condition inspection/assessment system named "Fury" is being developed and is currently undergoing field testing and validation. Fury enters the UST through an existing riser (4-inch diameter minimum) or manway and navigates using magnetically coupled wheels to access virtually all of the end cap and cylindrical wall area. A sensor sled takes multiple (approximately 90,000 per hour) ultrasonic thickness measurements while in motion and relays the readings along with position information to a computer. In its final form Fury is intended for immersion into fuel while filling the head space with a protective blanket of inert gas, thus allowing no interruption of normal operations.

In addition to providing a non-destructive evaluation tool which offers considerably more pertinent quantitative data compared to existing assessment technologies, a Fury UST inspection will also be significantly faster. An equally important benefit is the avoidance of the expense and danger associated with confined space entry.

Fury is being developed by the U.S. Army Construction Engineering Research Laboratories (USACERL) in conjunction with RedZone Robotics, Inc., of Pittsburgh, PA. The effort is being funded by the Small Business Innovation Research Program (SBIR), the Environmental Security Technology Certification Program (ESTCP) and the Army Petroleum Center.

## Introduction

According to Federal law 40 CFR 280 and 281, in order to minimize environmental contamination, all existing steel USTs must be upgraded to one of the allowed alternatives not later than 22 December 1998 [1]. In addition to removal/replacement and closure, these alternatives include the option of upgrading with cathodic protection. For USTs which are 10 years or older it is required that the tank first pass a precision tightness test to assure that there is

no current leakage. Subsequently, an assessment of the tanks integrity is required prior to upgrade. Currently available methods for assessment of tank integrity are expensive, time consuming, provide a wide range of reliability, and often necessarily involve the hazard associated with confined space entry. The Fury robot, however, does not require human entry for inspection and provides many multiple direct and quantitative measurements of the single most important aspect of UST integrity—remaining wall thickness.

External pitting is by far the most prevalent form of corrosion responsible for UST perforations. One study examined 500 steel USTs immediately after excavation [2] and another analyzed test data from 1,635 steel USTs [3]. It was determined from both studies that external pitting corrosion was the cause of perforation at least 70-80% of the time. Further, internal corrosion, weld failure, or seam failure each lead to less than 10% of the perforations. With Fury's capabilities, in situ measurements are made of the wall thickness which lend themselves immediately to statistical analysis of the tanks current condition and suitability for upgrade. Furthermore, having direct wall thickness measurements serves to improve the accuracy of existing UST life prediction models more robust.

The Fury robotic system (Figure 1) consists of a steerable tractor with an attached measurement sled. The tractor has permanent magnetic wheels which enable the robot to adhere to the tank wall in all orientations while driving in either the forward or backward direction. Transition levers allow movement onto and off of the tank end caps while various bump sensors assist the operator in navigation and obstacle avoidance. The measurement sled consists of an ultrasonic thickness transducer flanked by surface preparation and cleaning devices located on both sides of the sensor. During measurements a hydraulic system is used to press the measurement sled against the tank wall while a continuous supply of couplant is supplied. The entire robot fits through a 4-inch diameter opening and can make approximately 30 wall thickness measurements per second.

## Procedures and Results

In order to validate and demonstrate the capabilities of the robotic system older USTs at both Ft. Lee, VA and Hunter Army Air Field, GA were assessed for their current condition and suitability for upgrade with cathodic protection. The Ft. Lee tank, being scheduled for removal, was used mainly for validation purposes. In addition to an inspection in accordance with ASTM ES40-94 [4], a number of performance capabilities were documented on videotape. This included a real time video feed from inside the tank to an outside monitor. The capabilities documented included: entry/exit through a riser pipe, adherence to the inner tank wall in all orientations, movement in the forward and reverse directions, obstacle sensing and avoidance, traversal of lap joints, transitions to and from endcap walls, navigational accuracy, surface cleaning and ultrasonic thickness measurements. After the tank was removed a third party inspection was performed by MRI, Inc. in accordance with procedures developed by the EPA [5].

At Hunter Army Air Field a demonstration of the Fury robotic system was performed. Three USTs of 50,000 gal. capacity were assessed according to ASTM ES40-94. This information will be used to make better informed management decisions concerning upgrade versus replacement. The full replacement of 30 tanks at Hunter has been estimated at $10M. If some or all of these tanks are found to be suitable for upgrade then a significant cost will be avoided.

A full ASTM ES40-94 assessment also includes historic information, operational procedures, and various structural corrosion potential and soil chemistry measurements. These

procedures were performed in accordance with the standard. However, for the purposes of this paper only the wall thickness data obtained with the Fury robot will be emphasized.

Selected Validation Results from Ft. Lee

One of the most critical comparisons was that of the Fury in situ ultrasonic thickness measurements to other reference methods. Three 5x5 square grids with 10 cm. spacing were located near the center bottom, one approximately one half the distance to the end cap near the bottom, and one on one end cap. These test grids were marked out with wax pencil and stamp markers. Each measurement location was circled using a vibrating engraver and a robot template positioner. The template was used to assure that in-situ comparison measurements with a hand held ultrasonic thickness gauge were taken from exactly the same position. Both the robot sensor and the hand held thickness gauge were calibrated on the same step block before and after each group of measurements. After the tank was pulled the grids were cut out of the tank, sectioned, and the same measurements were performed using a standard mechanical micrometer capable of an accuracy of 1/1000 of an inch. The in situ Fury and laboratory micrometer measurements are shown in Figures 1 through 3.

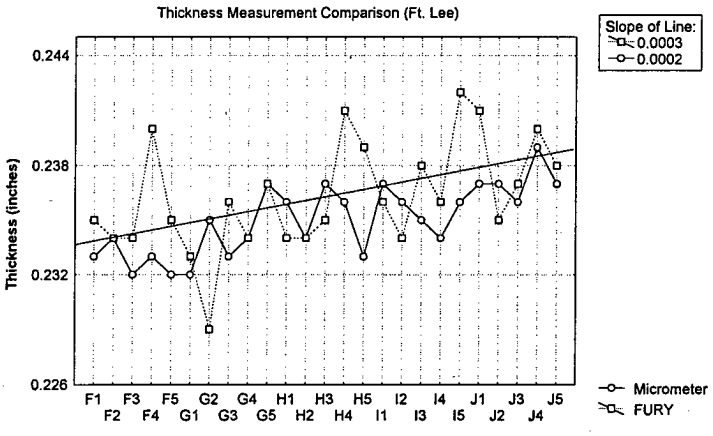



Figure 1. Bottom, Middle Mechanical vs. Fury Thickness Measurement

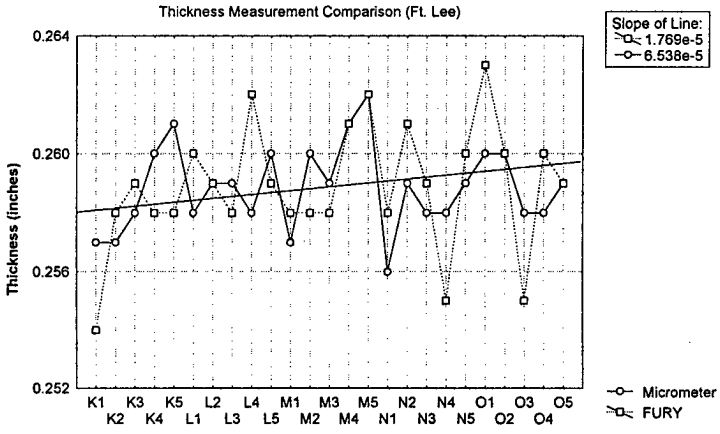



Figure 2. Bottom, Quarter Mechanical vs. Fury Thickness Measurement

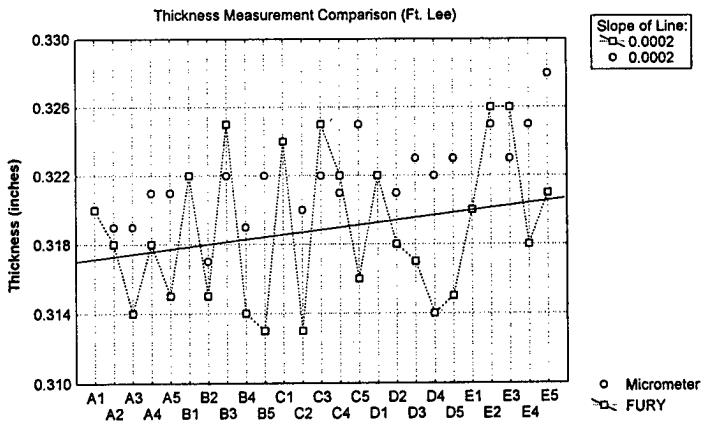



Figure 3. End Cap Mechanical vs. Fury Thickness Measurement

Laboratory analysis of the three 5x5 grid pattern readings were performed in accordance with ASTM G46 [6]. In addition, MRI, Inc. performed independent ultrasonic measurements on a different grid system in accordance with an EPA procedure for the field evaluation of USTs. The comparison of the measurements are given in Table 1. It is worth noting that the external hand held ultrasonic measurements taken by MRI, Inc. are almost identical to those called for by NLPA 631 and, considered alone, were inadequate to determine the tanks condition. In fact, no measurement indicating a remaining wall thickness less than 50% of the original value was found.

TABLE 1. Statistical Comparison of Ft. Lee Thickness Data Sets

| Method | Position | valid n | mean(in) | min(in) | max(in) | std dev(in) |
|---|---|---|---|---|---|---|
| Fury Robot | wall | 111952 | 0.255 | 0.071 | 0.543 | 0.033 |
| Micrometer | wall | 50 | 0.247 | 0.232 | 0.262 | 0.012 |
| Ultrasound* | wall | 77 | 0.245 | 0.222 | 0.274 | 0.012 |
| Fury Robot | far end cap | 3683 | 0.324 | 0.251 | 0.485 | 0.0100 |
| Fury Robot | near end cap | 18 | 0.234 | 0.071 | 0.441 | 0.124 |
| Micrometer | end cap | 20# | 0.322 | 0.316 | 0.327 | 0.003 |
| Ultrasound* | North end cap | 9 | 0.325 | 0.318 | 0.331 | .005 |
| Ultrasound* | South end cap | 9 | 0.322 | 0.312 | 0.328 | 0.006 |

*= MRI ultrasonic tank thickness measurements
# = five samples were rendered unusable by the cutting torch
n= number of data points
mean = average thickness of section
min = minimum thickness measured in section
max = maximum thickness measured in section
std. dev = standard deviation from the mean thickness

One of the main advantages of the Fury robotic system is its ability to rapidly take data while in motion. Virtually all of the data taken at Ft. Lee was during the last day of a week long effort after a number of other validation tasks had been completed. Table 2 shows the results of

a statistical analysis for the full data set as separated into tank wall and end caps (which typically have a larger initial wall thickness). The Fury data can be displayed in a number of ways. With position coordinates associated with each measurement the positions of the thinnest measurements can be displayed. Figure 4 shows the four thinnest ranges of measurement for the curved tank wall (displayed as if viewed from above and opened to each side from a longitudinal top seam). A feature along a lower circumference approximately eight feet from the southern end cap is evident. This feature was visually confirmed after the tank was removed. One possible explanation is that during installation a lifting strap caused some initial damage which over time lead to differential corrosive attack.

TABLE 2. Statistical Analysis of Complete Ft. Lee Data Set

| Position | valid n | mean(in) | min(in) | max(in) | std dev(in) |
|---|---|---|---|---|---|
| wall | 111952 | 0.2549 | 0.0707 | 0.5426 | 0.0333 |
| far end cap | 3683 | 0.3244 | 0.2508 | 0.4845 | 0.0100 |
| near end cap | 18 | 0.2336 | 0.0707 | 0.4412 | 0.1243 |

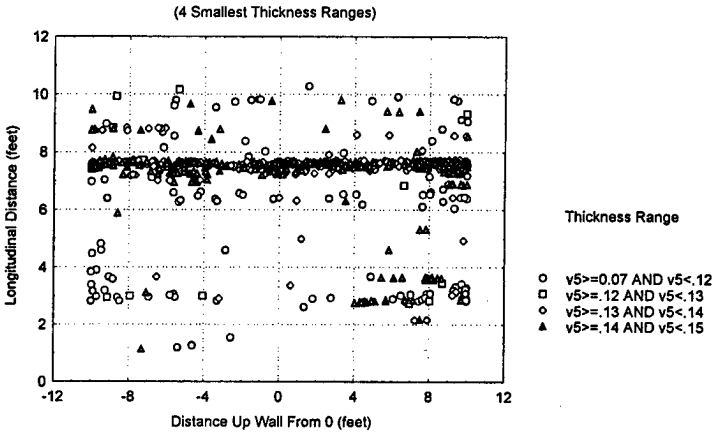



Figure 4. Location Distribution of 1000 Thinnest Wall Thickness Measurements

Validation and Results at Hunter Army Airfield

Fury collected in excess of 940,000 measurements from three USTs at Hunter Army Airfield. Each of the tanks were selected from three separate pump stations each consisting of a bank of 10 tanks. Measurements on the bottom one-third were emphasized in order to provide a conservative assessment. Table 3 summarizes the results obtained after correction for an internal epoxy coating. The data was then sorted according to thickness. Table 4 shows the results of an analysis of the 500 thinnest measurements. Histograms showing the number of measurements within successive ranges of wall thickness are shown in Figures 5 - 10. Tanks 3 and 4 appear to be in pretty good shape while Tank 5 clearly shows a large number of observations at the lower thickness ranges. Taken together with the findings from the other procedures detailed in ASTM ES40-94 tanks 3 and 4 are considered suitable for upgrade while tank 5 is not.

From a corrosion engineering viewpoint the character of the wall thickness histograms is intriguing. It may be that as a tank undergoes the accumulated damage of corrosive degradation the condition represented by Figures 6 and 8 evolves more toward a condition represented by Figure 10. The statistics of these so called "extreme values" (e.g., the thinnest measurements) is currently being examined. The potential benefits include a further improvement in knowing a

tanks condition, with either an equal or lesser amount of data, as well as a greater understanding of the degradation process itself.

TABLE 3. Descriptive Analysis of Hunter Airfield Data Set

| Tank | Valid n | mean(in) | min(in) | max(in) | std. dev(in) |
|---|---|---|---|---|---|
| 3 | 463408 | 0.38945 | 0.07096 | 0.56196 | 0.03232 |
| 4 | 321919 | 0.37601 | 0.07563 | 0.58053 | 0.03305 |
| 5 | 157183 | 0.36974 | 0.07034 | 0.57284 | 0.06551 |

TABLE 4. 500 Thinnest Data Points at Hunter Army Airfield

| Tank | mean(in) | min(in) | max(in) | std. dev(in) |
|---|---|---|---|---|
| 3 | 0.12664 | 0.07096 | 0.14700 | 0.02270 |
| 4 | 0.13498 | 0.07563 | 0.14973 | 0.01299 |
| 5 | 0.07252 | 0.07034 | 0.07614 | 0.00164 |

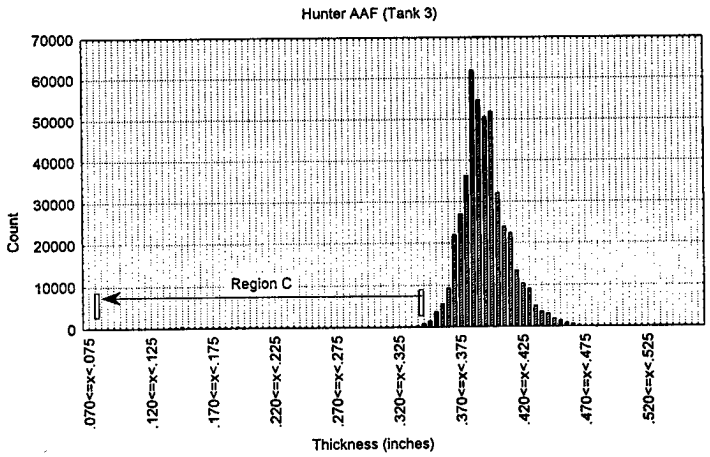



Figure 5. Thickness Distribution in Tank 3

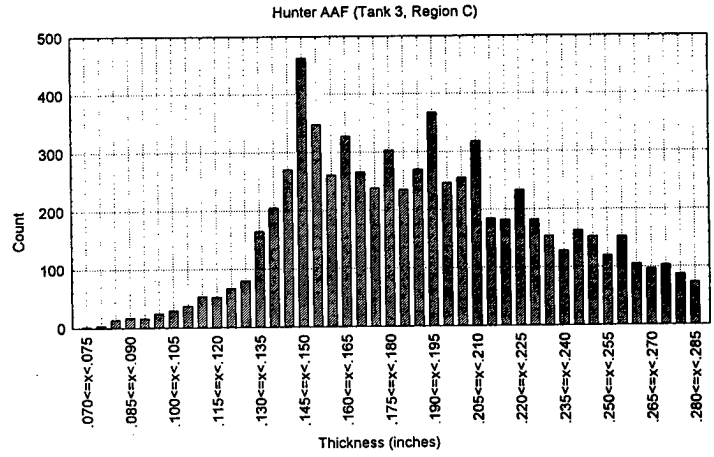



Figure 6. Thickness Distribution Region C in Tank 3 (Figure 5)

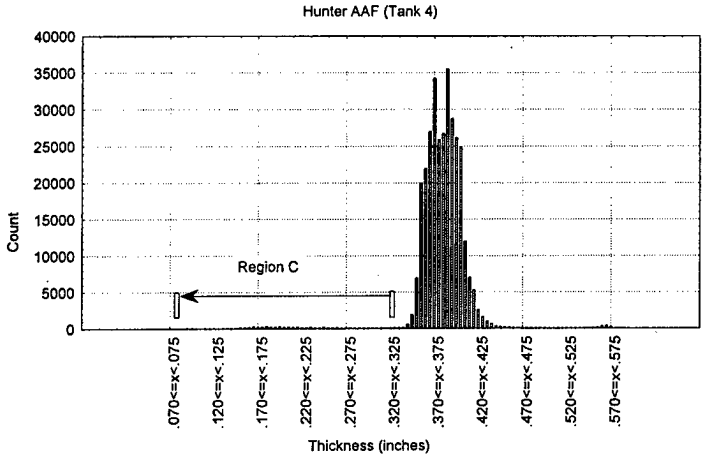



Figure 7. Tank 4 Thickness Distribution

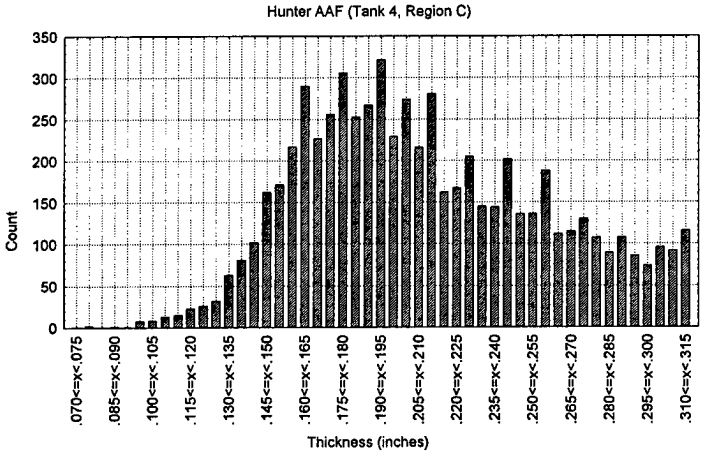



Figure 8. Region C Thickness Distribution in Tank 4 (Figure 7)

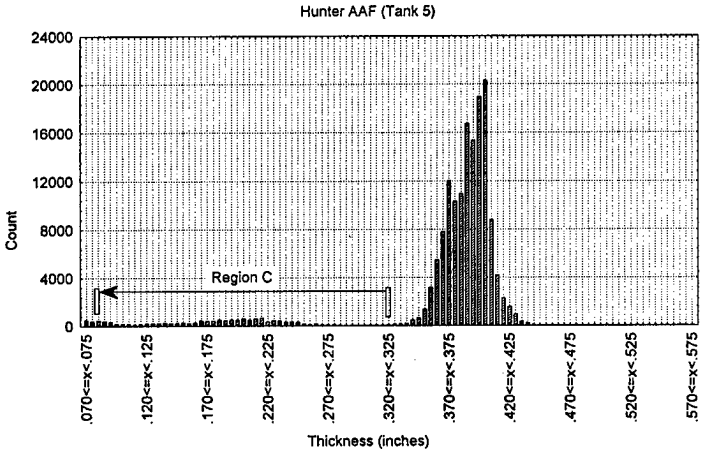



Figure 9. Tank 5 Thickness Distribution

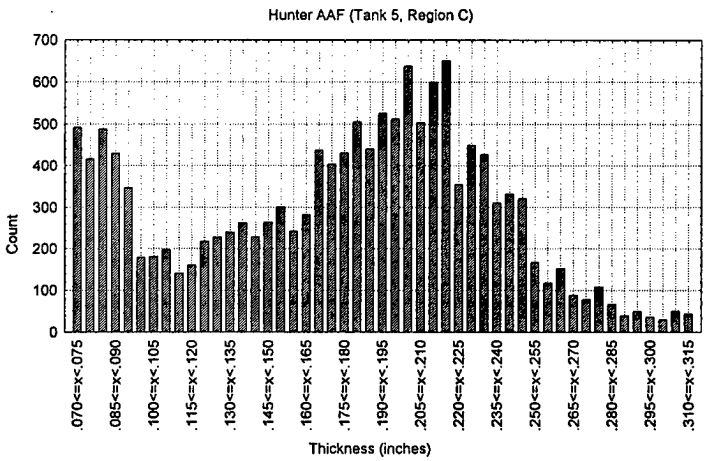


Figure 10. Region C Thickness Distribution Tank 5, (Figure 9)

## CONCLUSION

A remote robotic UST inspection and condition assessment system has been both validated and demonstrated at two separate sites on a total of four tanks. Virtually all the capabilities of the system were verified and documented. In terms of wall thickness data acquisition Fury advances the state of the art by three or four orders of magnitude compared to current methods. Another benefit is the ability to inspect a tank without requiring human entry. The results obtained from the Hunter AAF inspections are representative of how Fury can be used as a tool in order for owners to make better informed decisions about UST management. In addition, it will also allow tank owners to more cost effectively comply with federal, state and local requirements prior to the 1998 deadline and beyond.

## ACKNOWLEDGEMENT

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# CLEAN TECHNOLOGIES FOR THE REMOVAL OF LEAD-BASED PAINT FROM HOUSING

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## ABSTRACT

The foremost cause of childhood lead poisoning in the United States today is lead-based paint (LBP) found in older housing. Exposure to lead in paint can come from the paint chips themselves, from dust caused by abrasion of paint on friction surfaces, or from caulking of exterior paint. The U.S. Army Construction Engineering Research Laboratory, under funding from the U.S. Environmental Protection Agency's Office of Research and Development, National Risk Management Research Laboratory, conducted a study to demonstrate LBP removal from architectural wood components in unoccupied residential housing using four technologies: granulated carbon dioxide ($CO_2$) blasting, pelletized $CO_2$ blasting, encapsulant paint remover (EPR), and wet abrasive blasting with an engineered abrasive (WAB-EA). The three former technologies were demonstrated on interior components, the latter on exterior components. An x-ray fluorescence (XRF) spectrum analyzer (K-shell) was used to quantify the change in lead levels on the substrate before and after paint removal. Inductively-coupled plasma atomic emission spectroscopy (ICP-AES) was used to quantify the change in lead levels of airborne particulate and settled dust wipe samples before and after paint removal. Aerodynamic particle size distributions of lead particulates were measured using a multi-stage personal cascade impactor.

The paint removal effectiveness of the EPR and WAB-EA technologies were comparable with overall residual lead levels below the U.S. Department of Housing and Urban Development (HUD) Guideline (1 $mg/cm^2$); both technologies removed the paint to bare substrate with no apparent damage (minimal sanding prior to painting) to the underlying substrate. The $CO_2$ technologies yielded residual paint levels of >5 $mg/cm^2$ and rendered the substrate unusable for its intended purpose. Although the airborne particulate and settled dust levels varied with LBP abatement technology, the EPR technology consistently showed the lowest levels.

## INTRODUCTION

The foremost cause of childhood lead poisoning in the United States today is lead-based paint (LBP) found in older housing[1]. The Agency for Toxic Substances and Disease Registry (ATSDR) estimated that in 1984, 17 percent of all American preschool children had blood lead levels greater than 15 micrograms per deciliter (a level at which the Centers for Disease Control and Prevention (CDC) currently recommends intervention.)[2] Exposure to lead in paint can come from the paint chips themselves, from dust caused by abrasion of paint on friction surfaces, or from chalking of exterior paint. Lead was a major ingredient in most interior and exterior oil house paints prior to 1950, with some paints containing as much as 50 percent lead by dry weight. The U.S. Department of Housing and Urban Development (HUD) estimates that three-quarters of pre-1980 housing units contain some LBP.[3] The likelihood and extent that a particular housing unit will contain LBP increase with the age of the structure.

The Lead-Based Paint Poisoning Prevention Act of 1971, as amended by the Housing and Community Development Act of 1987, established 1.0 milligram of lead per square centimeter of surface area ($mg/cm^2$) as the federal threshold requiring abatement of LBP on architectural components in public and Indian housing developments nationwide. The Residential Lead-Based Paint Hazard Reduction Act of 1992 (commonly referred to as "Title X") mandated the evaluation and reduction of LBP hazards in the nation's existing housing. Title X also established 0.5 percent lead by weight as an alternative to the 1.0 $mg/cm^2$ threshold. The EPA-HUD Comparative Field Study[4] found that a level of 1.0 $mg/cm^2$ was roughly equivalent to 1.0 percent by weight and a level of 0.5 percent by weight was roughly equivalent to 0.5 $mg/cm^2$.

The EPA is sponsoring a program aimed toward the reduction of lead emissions in the environment from demolition and renovation projects in commercial buildings, non-industrial structures, and residential dwellings. As part of this program, the U.S. Army Construction Engineering Research Laboratories (USACERL) and the U.S. Environmental Protection Agency (EPA) conducted a study to demonstrate and evaluate environmentally clean technologies for removal of LBP from architectural wood components in residential housing.

## OBJECTIVE

The overall objective of this study was to conduct a pilot demonstration of LBP removal from architectural wood components in unoccupied residential housing using four technologies: (1) granulated carbon dioxide blasting, (2) pelletized carbon dioxide blasting, (3) encapsulant remover paint system, and (4) wet abrasive blasting with and "engineered abrasive." The specific objectives of the study are divided into two performance areas: engineering and economic.

The specific objectives for engineering performance were:

- Evaluate the effectiveness of three technologies (granulated carbon dioxide blasting, pelletized carbon dioxide blasting, and an encapsulant paint remover system) to remove LBP from interior architectural wood components (e.g., baseboards, door and window moldings, etc.) in residential housing.

- Evaluate the effectiveness of a wet abrasive blasting technology to remove LBP from exterior wood siding on residential housing.

- Evaluate the contamination potential of each removal technology on the work area.

- Evaluate the potential for each removal technology to generate airborne lead particulate levels in excess of the Occupational Safety and Health Administration (OSHA) Action Level (AL) of 30 $\mu g/m^3$, 8-hour time-weighted average (TWA).

The specific objective for economic performance was:

- Develop estimates of the cost of paint removal using the different LBP removal technologies.

## DESCRIPTIONS OF TECHNOLOGIES EVALUATED

Four lead-based paint removal technologies were evaluated in this pilot demonstration.

### GRANULATED AND PELLETIZED CARBON DIOXIDE BLASTING

Carbon dioxide blasting offers a number of potential benefits as a paint removal method. The process uses solid carbon dioxide ($CO_2$), or dry ice, as an abrasive media. The solid $CO_2$ is a soft abrasive material, which was expected to be effective on relatively soft substrates such as wood. After blasting, the abrasive media will sublime and dissipate, leaving only the volume of paint solids as the waste to be disposed. The carbon dioxide blasting technologies were represented by two manufacturers. Granulated $CO_2$ blasting was represented by Alpheus Cleaning Technologies Corporation, Rancho Cucamonga, California. The pelletized $CO_2$ blasting was represented by Cold-Jet Incorporated, Loveland, Ohio.

Although the technologies are similar in principle, primary differences between the technology are the size, density, and application feed rate of the $CO_2$ blasting media. One other primary difference is that the Alpheus technology uses block dry ice, which is shaved to create a fine, crystalline blasting medium, whereas the Cold-Jet technology uses uniform pellets. The Alpheus system uses a block of dry ice approximately every 20 minutes during blasting, whereas the Cold-jet system must be reloaded with pellets approximately every 15 minutes during operation.

The mechanism responsible for removal of the paint coating is a combination of several operations. First is the mechanical abrasion caused by the movement of one solid material against another. The second is the spalling of the materials surface that is caused by the rapid expansion of the carbon dioxide during sublimation. The third is thermal fracturing where the significant thermal differential between the substrate and the coating material causes these materials to expand and contract at different rates, resulting in fracturing of the coating.

### ENCAPSULANT PAINT REMOVER TECHNOLOGY

The encapsulant paint remover technology is manufactured by Kwick Kleen Industrial Solvents, Inc., Vincennes Indiana. The spray-applied encapsulant remover is a two-part liquid system consisting of potassium hydroxide and a proprietary polymer.

The equipment for the application of the encapsulant remover consists of two diaphragm pumps mounted to containers containing the respective solutions. The solutions are sprayed with an applicator gun that

employs an external mixing technique. The applicator gun facilitates a flat spray pattern for uniform coverage of the surface. The dwell or residence time is dependent upon the type and number of layers of paint, temperature, and other environmental factors. After the paint is absorbed into the remover matrix, the paint remover material is removed as a semi-solid material with a putty knife. The encapsulant paint remover is reapplied if visible paint remains on the surface. Following removal of the paint remover waste, a vacuum device equipped with a low-pressure/low volume sprayer is used to rinse the surface with a trisodium phosphate solution. The surface is then sprayed with a weak acid solution to neutralize the wood substrate.

## WET ABRASIVE BLASTING TECHNOLOGY

This technology, the Torbo® wet abrasive blasting system, is manufactured by Keizer Technologies Americas, Inc., Fort Worth, Texas. The system uses conventional blasting abrasives (such as coal slag or silica sand) mixed with water (80% abrasive to 20% water) in a pressure vessel.

The Torbo® system combines an abrasive media and water to create a slurry-mixture that is fed to a blast nozzle much like a conventional blasting system. In concept, the system encases every particle of the abrasive in a thin layer of water. It utilizes this coating to both reduce the heat generated by friction and as a cohesive bond for the dust created by the blasting process. Water pressure from as system piston pump forces the mixture from the vessel to a compressor-generated airstream where it is accelerated to the blasting nozzle. The blast media consumption and water consumption are both adjustable during operation. The paint coating is removed by the kinetic energy/mechanical abrasion of the blast media striking the surface.

A chemical stabilizer, Blastox®, is added at a 25 percent mixture to the abrasive/water media prior to blasting of the surface to create an "engineered abrasive." Blastox®, manufactured by the TDJ Group, Inc., is a di- and tri-calcium silicate-based material similar in chemical composition to Type I cement. This materials and lead in the paint waste react chemically to stabilize the leachable lead as lead silicate with stabilization mechanisms similar to those of Portland cement. Chemical substitution mechanisms reportedly render the lead nonleachable based on EPA's Toxicity Characteristic Leaching Procedure (TCLP).

## STUDY DESIGN AND METHODS

The study was conducted in unoccupied single-family and two-family residential housing units in the City of Buffalo, New York. Although the housing units were not randomly selected, they did include different housing components (e.g., baseboards, door and window moldings), paint thicknesses, and lead levels. Each technology was evaluated two or three times during a one-week period (depending on the logistical and technical problems experienced). The same operator demonstrated each of the four technologies. The operator (an experienced and licensed lead abatement contractor) was trained by each of the manufacturers on proper use of their respective technology. In addition, a manufacturer's representative was present during the demonstration of their technology to ensure its proper application. Table 1 presents a summary of the study design and the environmental measurements.

TABLE 1. SUMMARY OF STUDY DESIGN FOR ENVIRONMENTAL MEASUREMENTS

| Removal Technology | Surface Type | Environmental Data Collected | | |
|---|---|---|---|---|
| | | Paint Removal Effectiveness | Work Area Contamination | Site Control |
| EPRS[a] | interior wood | • XRF: pre/post removal<br>• surface evaluations: post removal | • settled dust: pre/post removal<br>• airborne dust: pre/during removal[b] | |
| Pelletized $CO_2$ | interior wood | • XRF: pre/post removal<br>• surface evaluations: post removal | • settled dust: pre/post removal<br>• airborne dust: pre/during removal[b] | • Gaseous $CO_2$ |
| Granulated $CO_2$ | interior wood | • XRF: pre/post removal<br>• surface evaluations: post removal | • settled dust: pre/post removal<br>• airborne dust: pre/during removal[b] | • Gaseous $CO_2$ |
| WAB-EA[c] | exterior wood | • XRF: pre/post removal<br>• surface evaluations: post removal | • airborne dust: pre/during removal | • soil: pre/post removal<br>• abrasive debris: post removal |

[a] Encapsulant Paint Remover System.
[b] Also includes personal samples on the technology operator and helper during paint removal.
[c] Wet Abrasive Blasting with an Engineered Abrasive.

## SITE PREPARATION

Each demonstration site was carefully prepared to ensure that lead concentrations in dust and air were attributable to the work being conducted, not previous contamination of the site. Interior wall and ceiling surfaces of the defined work area (excluding the surfaces to be abated) were covered with on layer of 6-mil flame-resistant polyethylene sheeting and the floors with two layers of sheeting. All seams were overlapped 12 inches (minimum) and sealed with spray adhesive and duct tape. The polyethylene sheeting was fastened to the surfaces with staples. To ensure stability of the containment during demonstration of the $CO_2$ blasting, wood furring strips were also fastened along edges of the polyethylene sheeting at corners, baseboards, window an door moldings. Entrance to the work area containment was through a two-stage airlock with double-flap doorways. After construction of the area containment, but no sooner than 18 hours prior to commencement of the experiment, all floor surfaces were wet wiped with a trisodium phosphate detergent.

The exterior work areas were prepared for the wet abrasive blasting experiment with a fully-enclosed flame-resistant tarpaulin work area containment. A 30-feet by 40-feet tarpaulin was used as the vehicle shell and aluminum extension ladders were places at each end and in the middle of the containment. The tarpaulin was stapled to the wood siding of the house and clamped to the ladders to create a stable and tight containment. The ground was covered with two layers of six-mil flame-resistant polyethylene sheeting and it was sealed to the foundation of the housing unit to avoid any further soil contamination. The polyethylene sheeting extended a minimum of 10 feet from the base of the housing structure. The edges of the polyethylene sheeting were rolled up and hard clamped to the tarpaulin. The area of the structure's foundation below the wood siding was covered with one layer of 6-mil polyethylene sheeting. The interior of all windows in the work area were covered and sealed with 6-mil polyethylene sheeting to ensure that no dust would infiltrate the housing unit. The entrance to the work area containment was through a two-stage airlock with double-flap doorways.

## SAMPLING AND ANALYTICAL METHODS

Table 2 provides a summary of the sampling and analytical methods employed in these experiments. In addition, measurements were made of the levels of gaseous carbon dioxide during the application of the $CO_2$ blasting technologies.

TABLE 2. SAMPLING AND ANALYTICAL METHODS

| Substrate | Method |
|---|---|
| paint film thickness | ASTM D 4138-88 |
| lead in paint | HUD / XRF (K-shell, 15-seconds) |
| paint chips | HUD / EPA SW-846 3050 / 6010 |
| lead in air | NIOSH 7300 |
| lead particle size | Cascade impactor / NIOSH 7300 |
| waste characterization | TCLP / EPA SW-846 3015 / 6010 |

## RESULTS AND OBSERVATIONS

The abatement demonstrations were conducted at eight family housing units in Buffalo, New York in June and July of 1996. The following sections summarize the general observations made during the demonstration of the encapsulant paint remover, granulated carbon dioxide blasting, pelletized carbon dioxide blasting, and wet abrasive blasting technologies. These observations are based on conditions (e.g. environmental conditions) that existed during the demonstration study; hence, they may not be representative of other conditions. The cost analysis was performed based on the total field data from the actual test demonstrations.

### ENCAPSULANT PAINT REMOVER

- **Site Preparation:** Full containment with mechanical ventilation usually not necessary. Protect surfaces with polyethylene sheeting.

- **Residual Lead on Substrate:** Overall levels reduced to below 1 $mg/cm^2$. Up to three applications needed, depending on paint thickness. Removal more difficult on ornate, non-flat surfaces.

- **Wood Substrate Aesthetics:** No visible damage, but some softening of the wood. Neutralization of caustic compounds required prior to repainting.

- **Paint Removal Rate:** 10.3 $ft^2/hr$ in this demo. May be better where multiple areas can be abated concurrently.

- **Airborne Dust Level:** Low.

- **Weather Limitations:** Temperature sensitive. Like any chemical reaction, product will work slower with lower ambient temperature.

- **Training Required:** Minimal

- **Personal Protection:** Respirators not required under the conditions evaluated. Chemical-resistant gloves, disposable coveralls/shoe covers, and goggles or face shield should be worn.

- **Hazardous Waste Generation**: Potentially high. Lead-containing caustic waste and rinse water are a hazardous waste. Volume can be reduced by using the manufacturer's onsite water filtration system to remove lead and particulate solids from the wastewater, which can then be safely discharged to a municipal sewer. Remaining material to be disposed as a solid hazardous waste.

- **Applicability:** Interior or exterior use on wood components. May also be applicable to masonry.

- **Total Paint Removal** Cost: $\$1.88/ft^2$ (includes equipment, materials, labor and waste disposal).

- **Additional Comments:** Application of the encapsulant paint remover system is quick and easy; Odiferous emissions are very minimal. Due to solubility of paint remover in water, cleanup is easy.

## GRANULATED AND PELLETIZED CARBON DIOXIDE BLASTING

- **Site Preparation:** Full containment required, including covering all surfaces with 4- or 6-mil plastic sheeting. Edges must be fastened with furring strips to prevent dislodgment. Area must be ventilated with outdoor air to control gaseous $CO_2$ levels to below the OSHA Permissible Exposure Limit.

- **Residual Lead on Substrate:** Overall, residual lead levels were >5 mg/cm$^2$. Removal of the paint was sporadic and complete paint removal was generally accompanied by severe wood damage.

- **Wood Substrate Aesthetics:** Poor. Wood was severely gouged, abraded or splintered.

- **Paint Removal Rate:** 140 ft$^2$/hr for both systems, but with incomplete paint removal.

- **Airborne Dust Level:** High.

- **Weather Limitations:** Moisture in blasting supply lines restricts flow and causes clogging.

- **Training Required:** Moderate.

- **Personal Protection:** Supplied airline respirator and 5-minute self-contained breathing apparatus required, unless $CO_2$ levels can be kept below the OSHA Permissible Exposure Limit, which would allow a full-facepiece air purifying respirator equipped with high efficiency particulate air (HEPA) cartridges.

- **Hazardous Waste Generation:** Low. There is no secondary waste, since the blasting media sublimes from a solid to a gas.

- **Applicability:** Not suitable for architectural wood components, but may be used effectively on metal and masonry substrates.

- **Total Paint Removal Cost:** \$0.43/ft$^2$ (includes equipment, materials, labor and waste disposal).

- **Additional Comments:** Operator may experience cold stress; high noise levels; high levels of gaseous $CO_2$ and poor visibility in the containment.

## WET ABRASIVE BLASTING WITH A BLASTOX® ENGINEERED ABRASIVE

- **Site Preparation:** Full containment, including covering the ground with a tarpaulin or double layer of 6-mil plastic sheeting. Effective seal at the foundation and ground interface is necessary to prevent soil contamination.

- **Residual Lead on Substrate:** Overall, the residual lead levels were reduced to < 1 mg/cm$^2$. Completely removes paint from flat surfaces; less effective in crevices or corners.

- **Wood Substrate Aesthetics:** Minimal damage to wood substrates; grain is slightly raised, but is suitable for repainting.

- **Paint Removal Rate:** 134 ft$^2$/hr.

- **Airborne Dust Level:** High.

- **Weather Limitations:** Most likely will not work at low ambient temperatures, i.e., 40 $^{o}$F.

- **Training Required:** Moderate.

- **Personal Protection:** Full-facepiece respirator equipped with HEPA filter cartridges, or one-half facepiece respirator depending on air levels. Disposable suit with attached hood and shoe covers, and hearing protection.

- **Hazardous Waste Generation:** Potential none, due to the waste stabilization effects of the engineered abrasive.

- **Applicability:** Exterior wood surfaces, and is expected to be effective on metal and masonry as well.

- **Total Paint Removal Cost:** $2.24/ft$^2$ (includes equipment, materials, labor and waste disposal).

- **Additional Comments:** Application of the technology is easy and effective paint removal is quick.

## CONCLUSIONS

The following are the principal conclusions reached during this study.

- The encapsulant paint remover technology effectively removed lead-based paint from interior architectural wood components to bare substrate with no apparent damage, yielding a substrate that required little preparation prior to painting. Overall, residual lead levels (0.8 mg/cm$^2$) measured by and XRF spectrum analyzer (K-shell) were below the HUD Guideline of 1 mg/cm$^2$.

- The granulated and pelletized carbon dioxide blasting technologies were not effective in removal of the lead-based paint from interior architectural wood components without severe damage (abraded/gouged) to the underlying substrate. Overall, residual lead levels (5.6 and 6.0 mg/cm$^2$, respectively) measured by an XRF spectrum analyzer (K-shell) exceeded the HUD Guideline of 1 mg/cm$^2$.

- The wet abrasive blasting technology with an "engineered abrasive" mixed with Blastox® effectively removed lead-based paint from exterior architectural wood components to bare

substrate with no apparent damage, yielding a substrate that required little preparation prior to repainting. Overall, residual lead levels (0.93 mg/cm$^2$) measured by an XRF spectrum analyzer (K-shell) were below the HUD Guideline of 1 mg/cm$^2$, except that the residual level was within the inconclusive range (0.7 to 1.3 mg/cm$^2$) of the instrument.

- The smallest increase in work area contamination of settled lead dust and airborne lead dust resulted from the encapsulant paint removal technology. Overall, the settled lead dust levels on floors and walls (measured by ICP-AES analysis of wipe samples) increased approximately 40, 532, and 1619 times for the encapsulant paint remover, granulated carbon dioxide blasting, and pelletized carbon dioxide blasting technologies, respectively. The work area levels of airborne lead increased approximately 4, 167, and 305 times, respectively.

- The wet abrasive blasting technology resulted in a significant increase in the soil levels of lead as well as airborne levels of lead. Overall, the soil levels of lead increased approximately 2.5 times. This finding is somewhat anomalous as the ground was covered with a tarpaulin. The levels of airborne lead increased approximately 304 times.

- The encapsulant paint remover technology did not result in personal exposures to airborne lead above the OSHA Action Level (30 μg/m$^3$). The granulated carbon dioxide blasting, pelletized carbon dioxide blasting, and wet abrasive blasting technologies exceeded both the OSHA Action Level and Permissible Exposure Limit (50 μg/m$^3$).

## ACKNOWLEDGMENTS

We acknowledge the City of Buffalo, New York for providing the residential housing units to conduct this study. We also acknowledge the suppliers of the technologies including Kwick Kleen Industrial Solvents, In. for providing the encapsulant paint remover system, Alpheus Cleaning Technologies Corporation for providing the granulated carbon dioxide blasting technology, Cold-Jet Inc., for providing the pelletized carbon dioxide blasting technology, Keizer Technologies of Americas, Inc., for providing the Torbo® Wet Abrasive Blasting System, and TDJ Group, Inc. for providing the Blastox® engineered abrasive.

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# REMEDIATION II

# PERFORMANCE AND COST EVALUATION OF FLAMELESS THERMAL OXIDATION FOR VAPOR-PHASE VOC TREATMENT

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## ABSTRACT

Parsons Engineering Science, Inc. (Parsons ES) has been retained by the Air Force Center for Environmental Excellence to perform performance and cost evaluations of a flameless thermal oxidation (FTO) vapor-phase treatment technology at four Air Force sites nationwide. The innovative FTO technology is effective in treating chlorinated aliphatic hydrocarbon (CAH) and petroleum hydrocarbon vapors. The FTO technology utilizes a packed-bed reactor with an inert, porous ceramic matrix that heats the influent vapor stream to temperatures that promote efficient flameless oxidation of the hydrocarbon vapors. Where CAHs are present, the chlorine is converted to hydrochloric acid (HCl), which, if necessary, is removed in an air quench/scrubber system following the oxidizer.

To demonstrate the FTO technology, the Air Force purchased a trailer-mounted Thermatrix Model GS120M FTO treatment system that includes a 6-horsepower regenerative blower with ancillary equipment. The FTO system is capable of treating flow rates up to 120 cubic feet per minute (cfm), and includes a quench/scrubber system. The FTO system was demonstrated at a former fire training area where soils are contaminated with petroleum hydrocarbons and CAH compounds. During this demonstration, influent volatile organic compound (VOC) concentrations ranged from 12 to 6,000 parts per million, by volume (ppmv). The maximum concentrations of trichloroethene (TCE) and perchloroethene (PCE) were 120 and 71 ppmv, respectively. The destruction/removal efficiency

(DRE) evaluation indicated that the FTO unit was 99.96 percent efficient at removing total VOCs, and between 99.98 and 100 percent efficient at removing benzene, TCE, and PCE from extracted soil vapors. The total cost for FTO system monitoring and operation for a total of 210 days over a 30-week period from August 27, 1996 to March 25, 1997, was $73,934, which is equivalent to $352 per day. A total of 8,162 pounds of VOCs was removed over 139 days of vapor extraction. The treatment cost ranged from $6.00 per pound (based on 139 days of vapor extraction) to $9.05 per pound (based on 210 days on site). Once periodic and initial mechanical problems were corrected and air flow conditions were balanced, the system proved to be reliable, and was in operation 96 percent of the time between December 6, 1996 and March 25, 1997.

# 1. INTRODUCTION

The Air Force Center for Environmental Excellence (AFCEE) has sponsored an ongoing program to promote the use of cost-effective soil vapor treatment technologies to be used in conjunction with soil vapor extraction (SVE) for remediation of fuel- and solvent-impacted sites. Parsons Engineering Science, Inc. (Parsons ES) was requested by the Air Force to provide services to evaluat the flameless thermal oxidation (FTO) vapor-phase treatment technology for off-gas abatement at various Air Force sites worldwide. At the direction of the Air Force, Thermatrix, Inc. (Thermatrix) of Knoxville, Tennessee provided their GS Series FTO treatment system to be evaluated during the demonstrations. Four Air Force installations were identified for demonstrating the Thermatrix FTO system, including a former fire training area (Site FT-002) at Plattsburgh Air Force Base (AFB), New York.

## 1.1 PURPOSE AND SCOPE

The SVE and volatile organic compound (VOC) vapor treatment demonstration was performed at Plattsburgh AFB, New York, Site FT-002, from August 27, 1996 through March 25, 1997. The technology demonstration was conducted over a 30-week period, and soil vapors were extracted from 14 site wells. The FTO system was tested on individual wells, or pairs of wells, for a period of up to 2 weeks per well (or well pair) to determine the optimum vacuum/extraction flow rate and soil vapor VOC concentrations for each of the wells. The 30-week demonstration served two primary purposes: 1) evaluation of the FTO technology, and 2) collection of test data to support the design and operation of a full-scale SVE system that was installed in 1996 at Site FT-002 by another contractor. A complete evaluation of the effectiveness of the FTO system during the Site FT-002 field demonstration, a summary of FTO system performance, operational costs and reliability, and an evaluation of full-scale treatment system application for Site FT-002 is presented in a more detailed *Site-Specific Technical Report*[1].

## 1.2 SITE BACKGROUND

Site FT-002 is a former fire training area that was used from the mid- to late 1950's through 1989. Training activities involved the release of waste fuels and solvents into unlined pits, where the fuels were ignited and extinguished. Uncombusted fuels and solvents percolated into the soils, resulting in contamination of soils and groundwater. Several site investigations have been conducted at Site FT-002, to characterize soil and groundwater contamination. A full-scale SVE system, installed at the site during 1996, includes 14 vapor extraction/vent wells (VE/VWs) spaced an average of 120 feet apart, a vacuum blower, and ancillary equipment. The SVE system was designed to treat approximately 5 acres of contaminated soil at Site FT-002. The VE/VWs have provided the source hydrocarbon vapors for testing the FTO system.

## 2. DESCRIPTION OF TECHNOLOGY

FTO is a technology that can be used to treat extracted soil gas vapors that contain chlorinated and/or petroleum hydrocarbons. The extracted vapors are heated to temperatures sufficient to oxidize chemical constituents and form carbon dioxide and water vapor, and, in the case of chlorinated hydrocarbons, hydrochloric acid (HCl). The type of FTO system tested at Site FT-002, system treatment capabilities, and acceptance of the technology by regulatory agencies are reviewed in the following paragraphs.

### 2.1 DESCRIPTION OF THERMATRIX FLAMELESS THERMAL OXIDATION UNIT

Thermatrix of Knoxville, Tennessee has developed a proprietary technology for FTO of VOCs in vapor streams. The Thermatrix GS Series FTO system employs a "packed-bed" ceramic matrix that is resistant to moisture and acid, noncatalytic, and has a temperature rating of up to 2,500 degrees Fahrenheit (°F). The oxidation of VOCs in the influent vapor stream occurs in a reaction zone contained within the ceramic matrix (Figure 1). Typical operating temperatures are between 1,600 and 1,850°F. Supplemental fuel (e.g., propane) is required to maintain reactor bed operating temperatures. System exhaust gases are discharged directly to the atmosphere, or can be routed through a caustic scrubber to remove HCl if the influent vapors contain chlorinated VOCs. The caustic scrubber was not used during operation at Site FT-002 because estimated mass emission rates for HCl were less than New York State Department of Environmental Conservation (NYSDEC) annual guideline concentration for air emissions [7 micrograms per cubic meter ($\mu g/m^3$)].

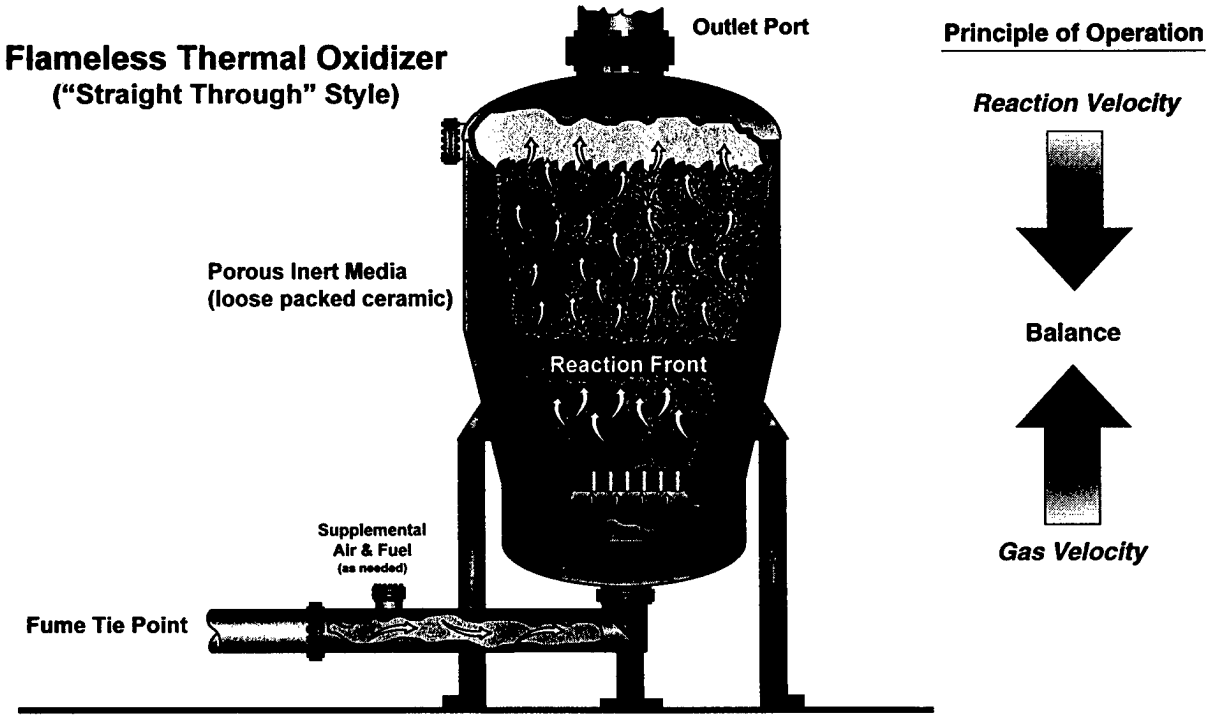



Figure 1. Schematic of FTO Treatment Process

The FTO system for the Plattsburgh AFB demonstration site was designed to extract and treat contaminated vapors at flow rates between 20 to 120 cubic feet per minute (cfm), and to reduce the influent VOC concentrations by not less than 99.99 percent. The FTO system is self-contained and skid-mounted on a trailer with a dedicated electrical distribution system. The system is designed to operate within single-circuit, 480-volt, 3-phase, 100-amp electrical power limitations. The electrical system is enclosed to provide weather protection for system controls that could be affected by temperature, moisture, and windblown particulates. Supplemental fuel was supplied by a local vendor to a 500-gallon propane tank mounted on the FTO system trailer.

## 2.2 SYSTEM CAPABILITIES

Previous performance tests by Thermatrix have demonstrated the 99.99-percent and greater destruction/removal efficiency (DRE) of the FTO system for a wide variety of VOCs, including chlorinated hydrocarbons[2,3]. Tests also have measured typical nitrogen oxide emissions of less than 2 ppmv and carbon monoxide emissions of less than 10 ppmv. Single-component and mixed organic vapor streams have been successfully treated, with vapor constituents that have included benzene, carbon tetrachloride, dichloromethane, ethyl chloride, isopropanol, methane, paint solvent mixtures, propane, and toluene. These compounds are chemically representative of many types of industrial VOCs, including chlorinated aliphatic hydrocarbons (CAHs). The test procedures, analytical methods, and performance results for the GS Series FTO unit are detailed in a separate vendor report[3].

In many flame-based devices, some of the soil vapor can bypass the flame zone, which can result in the formation of products of incomplete combustion. The configuration of the flameless oxidizer is designed to eliminate these problems by directing all of the vapor through the reaction zone before it exhausts from the oxidizer as carbon dioxide, water, and HCl (Figure 1). Thermatrix has performed a series of tests that have demonstrated the inherent safety of the FTO system[2]. Conditions considered to be worst case from a safety standpoint were investigated by Thermatrix, and under all test conditions, no flashback or detonation occurred.

Complete conversion of the VOCs to harmless byproducts and HCl occurs rapidly in the reaction zone of the FTO unit because of the intimate premixing of the influent contaminated vapors with air (oxygen) and the heat transfer properties of the ceramic matrix. Previous testing by Thermatrix has shown that a residence time of 0.15 second in the FTO can result in greater than 99.99 percent DRE for hydrocarbon vapors. The GS series flameless oxidizer tested at Plattsburgh AFB has a nominal vapor residence time of 0.5 second[3].

The FTO technology is capable of processing batch or variable-flow vapors or fumes because of the heat retention and radiant heat properties of the ceramic matrix design. It can treat VOC vapor spikes above nominal capacity, or accommodate a complete interruption in vapor flow, and remain functionally on-line with no upset condition or safety concerns (as could occur with a flame blow out).

Although, influent vapors can vary in hydrocarbon concentration, a minimum of 12 percent oxygen within the influent vapor system is required to sustain the oxidation process. Because many hydrocarbon contaminated sites have low, initial soil gas oxygen levels, ambient air dilution of the influent vapor stream is often required to ensure that 12 percent oxygen enters the oxidizer.

## 2.3 CAPITAL EQUIPMENT

Table 1 provides the total capital cost for the Thermatrix GS Series FTO treatment system purchased by the Air Force from Thermatrix on a "shared cost" basis for this demonstration. The

Thermatrix contribution was $40,000, which is the difference between equipment funding requested by the Air Force and the established commercial value of the FTO system. Therefore, the cost paid by the Air Force for the FTO system was $235,265, versus an actual commercial cost of $275,265.

TABLE 1. SUMMARY OF CAPITAL EQUIPMENT COSTS

| Item | Cost |
|---|---|
| Thermatrix Engineering and Project Management | $16,000 |
| Basic FTO Treatment Unit | $164,000[a/] |
| Quench/Scrubber System (optional) | $62,000 |
| FTO System Trailer | $19,500 |
| SVE Blower and Knockout Drum | $3,615 |
| Electrical Equipment | $4,900 |
| Control Valves | $4,500 |
| Miscellaneous Items | $750 |
| TOTAL | $275,265 |

[a/] This cost includes $40,000 contributed by Thermatrix for the design and fabrication of the FTO system.

To determine the prorated capital cost for the 210-day Plattsburgh AFB demonstration, the total capital cost of $275,265 was averaged over an estimated 3-year life of the FTO system [($275,265/1,095 days) x 210 days = $52,790]. Because use of the quench/scrubber was not necessary to meet NYSDEC recommended annual air guideline concentrations for HCl, the capital cost for the Plattsburgh AFB demonstration was calculated to be $40,900, which excludes $62,000 for the quench/scrubber [($213,265/1,095 days) x 210 days = $40,900].

## 2.4 REGULATORY ACCEPTANCE

Acceptance of Thermatrix FTO systems by regulatory agencies has been widespread, and approval of this technology for site remediation has been received from state environmental agencies and local air quality districts. Based on information provided by Thermatrix, the following states have permitted Thermatrix FTO systems to date:

| | | |
|---|---|---|
| California | Georgia | Idaho |
| Indiana | Louisiana | Maryland |
| Massachusetts | Michigan | Mississippi |
| Montana | New Jersey | New York |
| North Carolina | Pennsylvania | South Carolina |
| Tennessee | Texas | |

Also, Canada, England, and France have approved the use of this system. Additional projects are in progress in the Netherlands and Taiwan.

For the technology demonstration at Site FT-002, an application for a permit to construct/ certificate to operate a process, exhaust, or ventilation system was submitted to NYSDEC. As part of the application process, an air emissions regulation review was conducted, and mass VOC emission rates were calculated using Site FT-002 soil gas data collected in January 1996. Based on the regulatory review and the soil gas analytical results, off-gas control is required for full-scale SVE at the FT-002 site. Benzene, trichloroethene (TCE), and perchloroethen (PCE) exhaust concentrations were shown to be above NYSDEC annual guideline concentrations when no off-gas treatment was used. Despite HCl formation during FTO vapor treatment, the emissions calculations indicated that a scrubber to remove HCl is not necessary to meet the NYSDEC annual guideline concentration for HCl air emissions (7 $\mu g/m^3$).

## 3. FIELD DEMONSTRATION RESULTS

Testing of the FTO system was conducted over a 30-week period from August 27, 1996 to March 25, 1997, and soil vapors were extracted from 14 site wells. Individual wells and/or pairs of wells were tested for a period of up to 2 weeks per well (or well pair) to determine the optimum vacuum/extraction flow rate balance among all wells and soil vapor VOC concentrations for each well. Test data collected for design and operation of a full-scale system included soil vapor concentrations and vapor extraction rates (Section 3.1). The performance of the FTO system during the demonstration at Site FT-002 is described in Section 3.2.

### 3.1 EXTRACTION RATES AND SOIL VAPOR CONCENTRATIONS

The primary chemicals of concern at Site FT-002 are benzene, TCE, and PCE. Data collected during FTO unit testing included laboratory analysis of influent and effluent vapor samples using US Environmental Protection Agency (USEPA) Method TO-14; soil vapor extraction rates; and field measurements of oxygen, carbon dioxide, and total hydrocarbons in soil vapors.

The SVE flow rates for individual extraction wells ranged from 40 to 90 cfm. The influent vapor flow rate to the FTO unit was maintained at 100 cfm. Initial soil vapor oxygen concentrations at the vent wells ranged from 0 to 19 percent. It was necessary to manually bleed in ambient air to maintain oxygen concentrations of greater than 12 percent in the influent FTO vapor.

The concentrations of total VOCs detected by the laboratory in the influent vapor stream samples ranged from 12 to 6,000 ppmv. During the field demonstration a total of 8,162 pounds of VOC vapors were recovered from the soil during 139 days of extraction. The maximum concentration of benzene detected by the laboratory in the influent vapor stream samples was 16 ppmv, and the maximum detected concentrations of TCE and PCE were 120 and 71 ppmv, respectively.

### 3.2 FTO PERFORMANCE

The performance of the Thermatrix FTO system was evaluated based on three primary criteria: hydrocarbon vapor DRE, cost, and reliability and maintainability. Performance evaluation results are presented in the following subsections.

#### 3.2.1 Contaminant Destruction/Removal Efficiency

FTO DREs for total VOCs, benzene, TCE, and PCE are presented in Table 2, and were calculated using the following equation:

$$DRE = \frac{Concentration_{Influent} - Concentration_{Effluent}}{Concentration_{Influent}} \times 100$$

The contaminant DRE of the Thermatrix FTO system was evaluated using analytical results for samples collected during the March 1997 testing period. The influent and effluent vapor streams of the FTO unit were sampled using 1-liter SUMMA® canisters, and samples were analyzed by Air Toxics, Ltd. of Folsom California for VOCs using USEPA Method TO-14. Based on March 1997 data, the FTO unit was 99.96 percent efficient at removing total VOCs, and between 99.98 and 100 percent efficient at removing benzene, TCE, and PCE from extracted soil vapors (Table 2).

TABLE 2. SUMMARY OF FTO DESTRUCTION/REMOVAL EFFICIENCY

| Date Sampled | Extraction Well | Days of Operation | Pre-Dilution Oxygen (percent) | Post-Dilution Oxygen (percent) | FTO Influent Vapor Concentrations (ppmv)[a/] VOCs[b/] | Benzene | TCE[c/] | PCE[d/] | Well Air Flow Rate (cfm)[e/] | FTO Inlet Air Flow Rate (cfm) | FTO Effleunt Vapor Concentrations (ppmv) VOCs | Benzene | TCE | PCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3/5/97 | VEW/VW-6 and -14 | 9.34 | 12.0 | 17.1 | 1,500 | 3.7 | 12.0 | ND[f/] | 60.0 | 100 | ND | ND | ND | ND |
| 3/6/97 | VEW/VW-6 and -14 | 0.75 | 11.8 | 15.8 | 1,700 | 5.2 | 16.0 | ND | 66.7 | 100 | 0.860 | 0.005 | 0.019 | ND |
| 3/11/97 | VEW/VW-6 | 0.10 | 14.0 | 16.8 | 2,300 | 5.0 | 15.0 | ND | 66.7 | 100 | 1.400 | ND | 0.004 | ND |
| 3/18/97 | VEW/VW-6 | 3.69 | 15.2 | 16.0 | 2,600 | 7.1 | 22.0 | ND | 89.7 | 100 | ND | ND | ND | ND |
| 3/19/97 | VEW/VW-14 | 0.98 | 15.9 | 18.0 | 170 | ND | 31.0 | 0.2 | 62.5 | 100 | 0.240 | 0.009 | ND | ND |
| 3/20/97 | VEW/VW-14 | 1.02 | 13.8 | 16.9 | 83 | ND | 24.0 | 0.2 | 74.6 | 100 | ND | ND | ND | ND |
| 3/25/97 | VEW/VW-14 | 4.85 | 16.7 | 18.3 | 98 | ND | 19.0 | 0.3 | 78.7 | 100 | ND | ND | ND | ND |

| | | FTO System Destruction/Removal Efficiency (percent removal) VOCs | Benzene | TCE | PCE |
|---|---|---|---|---|---|
| 3/5/97 | VEW/VW-6 and -14 | 100 | 100 | 100 | NA[g/] |
| 3/6/97 | VEW/VW-6 and -14 | 99.95 | 99.90 | 99.88 | NA |
| 3/11/97 | VEW/VW-6 | 99.94 | 100 | 99.97 | NA |
| 3/18/97 | VEW/VW-6 | 100 | 100 | 100 | NA |
| 3/19/97 | VEW/VW-14 | 99.86 | NA | 100 | 100 |
| 3/20/97 | VEW/VW-14 | 100 | NA | 100 | 100 |
| 3/25/97 | VEW/VW-14 | 100 | NA | 100 | 100 |
| | Average = | **99.96** | **99.98** | **99.98** | **100.00** |

[a/]ppmv = parts per million by volume, as determined by the analytical laboratory.

[b/]Values given are for total volatile organic compounds referenced to heptane (molecular weight =100).

[c/]TCE = Trichloroethene.

[d/]PCE = Perchloroethene.

[e/]cfm=cubic feet per minute.

[f/]ND = not detected.

[g/]NA = Not applicable, compound not detected in influent vapor stream.

### 3.2.2 Operating Costs

The costs for the FTO system demonstration are summarized in Table 3. The total cost for FTO system monitoring and operation for a total of 210 days during the period from August 27, 1996 to March 25, 1997, was $73,934, which is equivalent to $352 per day (exclusive of quench/scrubber costs). During the field demonstration, a total of 8,162 pounds of VOC vapors was recovered from site soils during 139 days of vapor extraction. The treatment cost ranged from $6.00 per pound (based on 139 days of vapor extraction) to $9.05 per pound (based on 210 days on site). Excluded from these costs are Parsons ES labor costs and the cost of vapor and air emission sampling, which would be relatively consistent for other vapor treatment technologies. Approximately 5 labor hours per week were required for system sampling and maintenance, including removal of liquid condensate collected in the knock-out tank. During the testing, approximately 100 gallons of condensate was removed and disposed of at the Site FT-002 groundwater treatment plant.

TABLE 3. SUMMARY OF FTO TECHNOLOGY DEMONSTRATION COSTS

| Cost Item | Subtotal without Quench/Scrubber |
|---|---|
| Capital Costs | $40,900[a/] |
| Thermatrix Mobilization/Startup | $12,360 |
| Transportation of Treatment Unit to and from Site | $6,246 |
| Electricity[b/] | $900 |
| Propane[c/] | $10,777 |
| Thermatrix Demobilization | $2,751 |
| **TOTAL** | $73,934 |

a/ Capital cost is the total vendor capital costs (excluding the quench/scrubber) averaged over an estimated 3-year life of the FTO system [$213,265/1,095 days) x 210 days = $40,900].

b/ Excludes power costs for site SVE blower and assumes $0.10 per kilowatt hour.

c/ Costs based on actual propane use and average cost of $1.15 per gallon.

### 3.2.3 Reliability and Maintainability

Once mechanical and operational problems were resolved and air flow conditions from the VE/VWs were balanced, the system proved to be reliable. The FTO system operated for 156.5 days over a 210-day period, which is equivalent to 75-percent availability. The majority of the down time was due to heavy rains causing damage to the variable frequency drive (VFD) controller, which occurred on two separate occasions. A redesigned VFD was installed in December 1996, and the system was restarted. The FTO treatment unit was operational 96 percent of the time from December 6, 1996 to March 25, 1997, including 100 percent of the time during the month of February 1997.

In January 1997, the FTO system shut down twice due to a low supplemental fuel pressure propane reading that was caused by very cold ambient temperatures (-27°F). The pressure regulator for supplemental fuel located at the propane tank was increased, which alleviated the problem of shut down associated with low-vapor-pressure readings due to extreme cold temperatures.

A special consideration for operation of the FTO unit is the influent vapor oxygen concentration. During the week of October 14, 1996, Thermatrix conducted performance tests to determine the lowest influent oxygen concentration at which the unit can operate. During the tests, it was determined that the FTO unit could operate effectively at an influent oxygen concentration of 12 percent[4]. The influent oxygen concentrations prior to dilution (i.e., direct from the vent wells), typically ranged from 0 to 19 percent. Post-dilution influent oxygen concentrations were typically above 12 percent. The oxygen

content is critical to ensure complete stoichiometric combustion of all chemical constituents present in the vapor stream.

Regular monthly maintenance for the Thermatrix FTO system is minimal. Regular maintenance, which requires approximately 1 to 3 hours per week, would typically include checking the supplemental fuel and emptying the condensate tank. If a scrubber were required, regular maintenance could require an additional 8 hours per week of technical oversight.

## 4. COST COMPARISON OF VAPOR TREATMENT TECHNOLOGIES

A cost comparison was developed for five soil vapor treatment technologies, including FTO, resin bed adsorption, thermal oxidation, catalytic oxidation, and activated carbon. The purpose of the cost comparison was to develop an approximate range of expected costs necessary to treat soil vapors at Site FT-002 over a 3-year period. Full-scale design considerations included operation of a soil vapor treatment system at a vapor flow rate of between 500 and 600 cfm with a required DRE for TCE of 87 percent.

Several vendors were requested to provide cost proposals for a soil vapor treatment system assuming: a soil vapor flow rate of 500 cfm, average influent VOC concentration of 1,100 ppmv, average influent TCE concentration of 21 ppmv, and a required DRE of 87 percent for TCE. Based on a 500-cfm flow rate, the expected chemical mass recoveries are 204 pounds per day of VOCs, and 5.1 pounds per day of TCE.

The results of the comparative cost evaluation are summarized in Table 4 and presented graphically in Figure 2. The results of the cumulative cost comparison show that over a 3-year period of operation, capital and operation and maintenance costs for thermal, catalytic, or resin bed soil vapor treatment systems range from $264,000 to $310,000. Activated carbon treatment (cumulative cost of $3.8 million) was not considered a cost-effective treatment technology for this site. The soil vapor treatment vendors indicated that their respective treatment technologies are capable of achieving a minimum required DRE of 87 percent for TCE. The costs of treating VOCs using the thermal, catalytic, or resin bed treatment technology range from approximately $1.86 to $3.45 per pound of VOCs removed over a 1-year period, and approximately $1.27 to $1.48 per pound over a 3-year period of operation.

The most appropriate treatment technology for any given site will be a function of the duration of system operation and the expected changes in soil vapor concentrations over the period of operation. More detailed vendor cost estimates would be required prior to selecting the most appropriate treatment technology. Consideration also should be given to factors such as vendor product warranties, durability of system components, component replacement costs and frequency of replacement, and overall vendor reliability.

## 5. CONCLUSIONS

The DRE evaluation indicated that the FTO unit was 99.96 percent efficient at removing total VOCs and between 99.98 and 100 percent efficient at removing benzene, TCE, and PCE from extracted soil vapors. The DREs represent the percent reduction in concentrations between constituents detected by the laboratory in the FTO system influent and effluent vapor streams.

The total cost for FTO system monitoring and operation for a total of 210 days over a 30-week period from August 27, 1996 to March 25, 1997, was $73,934, which is equivalent to $352 per day.

## TABLE 4. COST COMPARISON OF FULL-SCALE VAPOR TREATMENT TECHNOLOGIES

| Vapor Treatment Technology | Capital Costs | Shipping Installation and Setup | Annual Costs (365 days) | | | Expected DRE % | Cummulative Annual Costs over Cost Per Pound of VOC Treated[a/] | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Labor | Electricity | Fuel[b/] | | 1 year | 2 year | 3 year | |
| **Thermatrix FTO** | $200,000 | $12,000 [c/] | $5,000 [c/] | $1,500 | $21,900 | 99.99 | $240,400<br>$3.45 | $268,800<br>$1.93 | $297,200<br>$1.42 | Thermatrix estimate<br>Does not include SVE blower. |
| **Thermatrix Resin Bed** | $200,000 | $12,000 [c/] | $10,000 [c/] | $13,140 | $0 | 95 | $235,140<br>$3.37 | $258,280<br>$1.85 | $281,420<br>$1.35 | Thermatrix estimate<br>Does not include SVE blower. |
| **E Products Thermal Oxidation** | $43,111 | $12,000 [c/] | $5,000 [c/] | $3,000 [c/] | $76,957 | 99 | $140,068<br>$2.01 | $225,024<br>$1.61 | $309,981<br>$1.48 | E Products estimate<br>Does not include SVE blower. |
| **Therm Tech Thermal Oxidation** | $50,500 | $12,000 [c/] | $5,000 [c/] | $3,000 [c/] | $59,367 | 95 | $129,867<br>$1.86 | $197,233<br>$1.41 | $264,600<br>$1.27 | ThermTech estimate<br>Does not include SVE blower. |
| **Therm Tech Catalytic Oxidation** | $75,800 | $12,000 [c/] | $10,000 [c/] | $3,000 [c/] | $49,472 | 90 | $150,272<br>$2.16 | $212,744<br>$1.53 | $275,216<br>$1.32 | ThermTech estimate<br>Does not include SVE blower. |
| **Carbon** | $50,000 [c/] | $12,000 [c/] | $10,000 [c/] | $1,500 [c/] | $1,241,000 [c/] | | $1,314,500<br>$18.86 | $2,567,000<br>$18.41 | $3,819,500<br>$18.26 | Parsons ES estimate assuming 204 lb/day mass VOC load, 15 % carbon load rate per day, $2.50/lb carbon regeneration, 2 x 20K lb vessels |

Notes:

a/ The cost per pound of THC treated equals the cummulative costs divided by the cummulative number of days of operation, assuming mass recovery of THC at 204 lb/day, and vapor flow rate of 500 cfm.

b/ Actual propane fuel costs at Plattsburgh AFB were $1.15/gallon or $12.55/million BTU assuming 91,600 BTU, per gallon.

c/ Estimated cost.

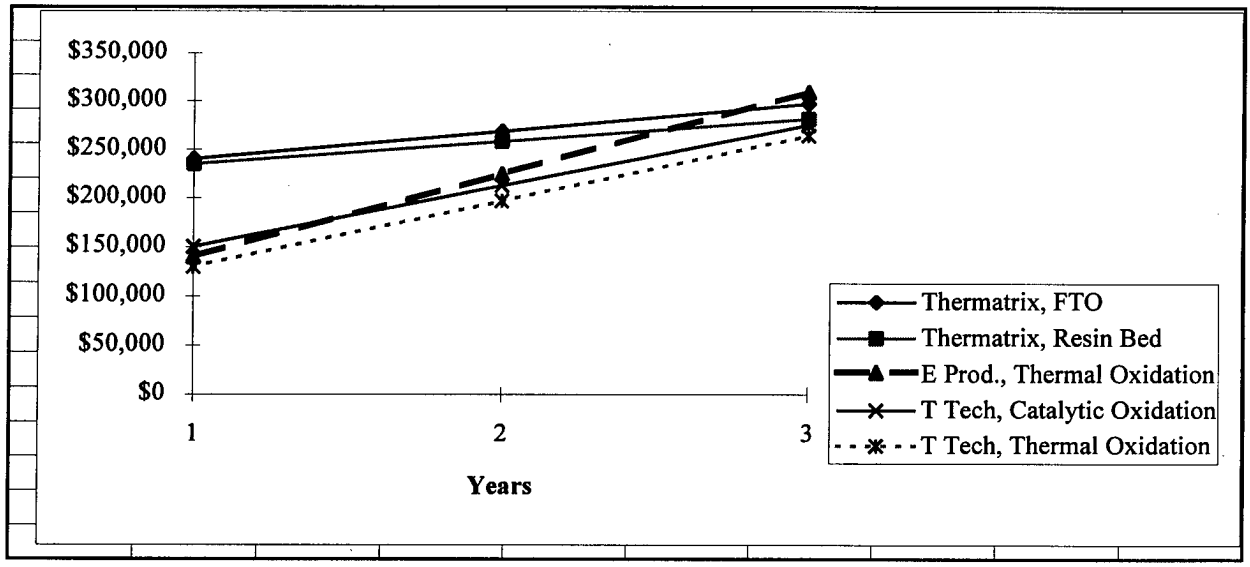



Figure 2. Cumulative cost comparison among full-scale vapor treatment alternatives for Site FT-002, Plattsburgh AFB.

A total of 8,162 pounds of VOCs was removed over 139 days of vapor extraction. The treatment cost ranged from $6.00 per pound (based on 139 days of vapor extraction) to $9.05 per pound (based on 210 days on site). During this pilot study, influent VOC concentrations ranged from 12 to 6,000 ppmv.

Once periodic and initial mechanical problems were corrected, and air flow conditions were balanced, the system proved to be reliable and was operational 96 percent of the time between December 6, 1996 and March 25, 1997. The Thermatrix GS Series FTO system is designed to operate unmanned; however, approximately 12 hours per month should be anticipated for maintenance and monitoring activities. System checks, influent/effluent sampling, disposal of condensate, and supplemental fuel monitoring will require approximately 3 hours of technician labor each week.

Based on vendor information and the Site FT-002 demonstration at Plattsburgh AFB, the Thermatrix FTO technology is an effective method of treating a mixed vapor stream consisting of aromatic and CAHs in extracted soil vapors at this site. For a full-scale application at the Plattsburgh AFB site, the costs of treating VOC vapors using thermal, catalytic, or resin bed treatment technology may range from approximately $1.86 to $3.45 per pound, over a 1-year period, and approximately $1.27 to $1.48 per pound over a 3-year period of operation.

## ACKNOWLEDGEMENTS

Parsons ES was contracted by the Air Force Center for Environmental Excellence (AFCEE) Technology Transfer Division (ERT) to perform a technology demonstration of the Thermatrix, Inc. GS Series Flameless Thermal Oxidizer at Site FT-002, Plattsburgh Air Force Base, New York. The work was performed for AFCEE/ERT under Contract F41624-94-D-8136, Delivery Order 28. Parsons ES would like to thank Mr. Jim Gonzales of AFCEE/ERT for his continued support during this project, and Mr. Brady Baker (AFBCA/OL3A) at Plattsburgh AFB for support during the Plattsburgh AFB demonstration. In addition, the authors would like to thank the Parsons ES field engineers who

collected the site data and performed FTO system operation and monitoring: Ms. Kim Makuch, Mr. John Mackey, and Mr. John Mastracchio.

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**Preliminary Report**
**Permeable Reactive Wall Remediation of Chlorinated Hydrocarbons in Groundwater**
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## ABSTRACT

The permeable reactive wall or barrier is an innovative technology for the remediation of groundwater contaminated with chlorinated hydrocarbons or solvents, such as trichloroethene (TCE), perchloroethene (PCE), dichloroethene (DCE), vinyl chloride (VC), and others. This technology is based on a chemical reaction, in which zero-valent iron particles react with chlorinated hydrocarbons in groundwater to produce less toxic, readily biodegradable, light hydrocarbon compounds, iron and chloride ions, and hydroxides. Remediation of contaminated groundwater by conventional pump-and-treat systems is very difficult, costly, and generally ineffective. The unique benefit of the permeable reactive wall technology is that it can passively remediate the chlorinated hydrocarbons in groundwater using the natural flow properties of a site. Compared to pump and treat technology, permeable reactive walls should remediate groundwater more effectively with lower operation and maintenance costs. The reactive barrier technology has been identified by the EPA[1] as an emerging technology for cleanup of groundwater contaminated with chlorinated solvents.

Moffett Field was placed on the U.S. Environmental Protection Agency (EPA) Superfund National Priorities List in June 1987, and the remedial investigation and feasibility study (RI/FS) process was initiated thereafter. The U.S. Navy identified and evaluated past hazardous waste activities at the site in an effort to control the spread of contamination and identify remedial solutions. Several investigations have identified extensive groundwater contamination from dissolved chlorinated hydrocarbons, much of which originated from offsite upgradient sources (Silicon Valley plume). The primary contaminants of concern at the site are TCE, PCE, and cis 1,2-DCE (cDCE). The present remedial solution for the site, as identified in the EPA Record of Decision (ROD), is to implement a very costly groundwater pump-and-treat system. In an effort to reduce remedial costs and investigate alternative solutions, the Naval Facilities Engineering Service Center (NFESC) and Navy Engineering Field Activity (EFA) West initiated a pilot-scale permeable barrier demonstration project at the former NAS Moffett Field, Mountain View (San Francisco Bay Area), California in late 1995. Battelle Memorial Institute and PRC Environmental Management were subsequently tasked by the NFESC to develop and implement a Performance Monitoring Plan (PMP) for the permeable barrier project at Moffett Field. This project is being sponsored and funded by the U.S. Department of Defense (DoD), Environmental Security Technology Certification Program (ESTCP), for the purpose of evaluating the technical performance and cost effectiveness of the technology application.. At the end of this project, a final technology evaluation report is planned for distribution in March 1998, with the anticipation that this technology can be used at other Navy and DoD solvent contaminated sites. The results of this demonstration project will also be distributed to others through working groups involved in this technology, such as the EPA Remediation Technologies Development Forum (RTDF) and the Interstate Technologies Regulatory Cooperation (ITRC), a group that contains regulators from 29 states.

## 1. INTRODUCTION

After the bench-scale testing and permeable barrier design activities, a 50-foot wide X 10-foot long X 25-foot deep permeable reactive wall using a funnel-and-gate system was installed in the chlorinated solvent contamination plume at Moffett Field in April 1996. Preliminary or baseline monitoring of groundwater conditions in the vicinity of the permeable barrier was conducted in June 1996. The preliminary findings indicated positive results, as chlorinated hydrocarbons were either reduced to below maximum contaminant levels (MCLs) or to non-detect (ND) within the iron treatment cell. Additional performance sampling in September 1996 and January 1997 has further substantiated the preliminary findings. In most cases, TCE concentrations were detected at greater than 1,200 micrograms per liter (ug/L) upgradient of the barrier and were reduced to ND levels within the first 2 feet (ft) of the permeable cell (gate). Slug testing, flow velocity meter testing, and tracer testing were also performed at the site, which are presently being evaluated to determine flow direction and velocities, preferential pathways, and capture efficiencies of the funnel-and-gate system. Inorganic chemical and microbiological data are also being evaluated to determine the potential for long term precipitate effects on the iron particles. Monitoring will be conducted quarterly for a total of about 1 year to evaluate the performance of the permeable barrier system. This preliminary report is derived from portions of Battelle's publications: Groundwater Modeling[2], Draft-Final Performance Monitoring Plan[3], and Groundwater Monitoring Reports[4]. Further details on this demonstration project can be found in these reports.

## 2. TECHNOLOGY DESCRIPTION

Research performed by the scientific community in the last 6 years, primarily in Canada at the University of Waterloo - Groundwater Research Centre and EnviroMetals Technologies, Inc. (ETI), has shown that when dissolved chlorinated solvents come into contact with the granular iron, the chlorinated compounds are degraded abiotically[5]. Degradation occurs through reduction as electrons are transferred from the iron to the chlorinated compounds within an in-situ permeable barrier system. Researchers have proposed that several different mechanisms are responsible for the degradation of the chlorinated organic compounds[6]. Central to each of the possible mechanisms lies the fundamental oxidation-reduction chemistry of iron. Most familiar is the process of corrosion in which iron metal is oxidized by molecular oxygen to form aqueous ferrous species ($Fe^{2+}$). This reaction can occur when oxygenated groundwater contacts the iron. It is a relatively fast reaction and usually occurs in the first few inches of the iron medium. The net effect is a release of ferrous iron and an increased pH due to production of hydroxyl ions. When dissolved oxygen is negligible, the interaction of groundwater with iron causes a reaction in which water is reduced to form hydrogen gas. Following is the general equation, which represents the overall reaction taking place:

$$Fe^0 + X\text{-}Cl + H_20 \rightarrow Fe^{2+} + X\text{-}H + Cl^- + OH^-$$

Other mechanisms and combinations thereof are also thought to exist. For example, evidence that C1 to C5 range light hydrocarbon byproducts (methane, ethane, ethene, acetylene, and others) suggest that the actual process of reductive dechlorination is not as straightforward as described[7]. The chlorine molecules are replaced with hydrogen, which form the ethanes and ethenes. Sorption may also play an important role in controlling the formation and release of degradation byproducts. Another important factor in the degradation process is elevated pH, which can cause chemical precipitates to form on the iron particles and can potentially clog the reactive cell and reduce the flow velocity or treatment capacity[8].

In a typical field application of a permeable reactive barrier, a trench or pit filled with granular iron is placed in the flow path of a chlorinated solvent plume. A funnel-and-gate configuration is typically used to capture a larger portion of the plume and direct it toward the reactive cell that contains the iron (Figure 1).

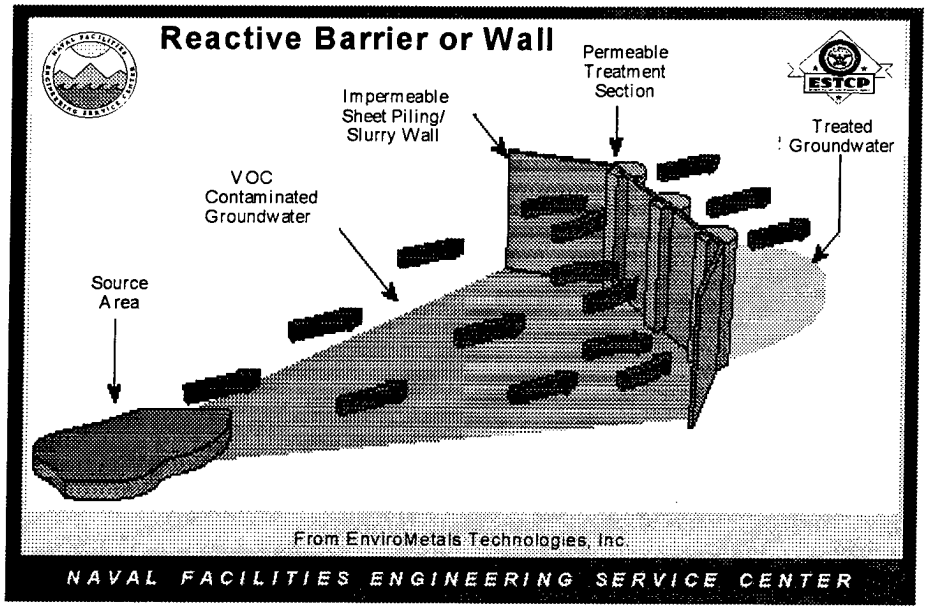



Figure 1. Funnel and Gate System Conceptual Design

## 3. SITE DESCRIPTION

Moffett Field is located in Santa Clara Valley, California, near the southern end of San Francisco Bay. The installation encompasses about 2,200 acres and is bordered by the cities of Mountain View on the west and Sunnyvale to the south. The reactive barrier demonstration project is located beneath a parking lot on the west side of Moffett Field. Until recently, Moffett Field has been in continuous operation since 1933.

### 3.1 HYDROGEOLOGIC SETTING

The subsurface sediments at the Moffett Field permeable barrier site have been identified as a mixture of alluvial-fluvial clay, silt, sand, and gravel. The sands and gravels form lens-shaped, interbraided channel structures that are incised into the clay and silt layers. The channel deposits are divided into A, B, and C aquifers[9]. The A aquifer extends from about 5 to about 60 ft below ground surface (bgs) and is divided into the A1 and A2 aquifer zones. The A1 aquifer extends from approximately 5 to 25 ft bgs near the permeable barrier site. A discontinuous semiconfining clay or aquitard layer ranging from 1 to 15 ft in thickness at intermittent locations separates the A1 and A2 aquifer zones. The A2 aquifer ranges up to 25 ft in thickness. The B and C aquifers underlie the A aquifer and continue to more than 200 ft bgs.

Four pumping tests were conducted on the west side of Moffett Field to determine the hydraulic properties of the A1 and A2 aquifer zones[10]. Average linear flow velocities were calculated at about 1 to 4 ft/day. Hydraulic conductivity values for the A1/A2 aquitard layer were calculated from slug and pump tests and ranged from $10^{-5}$ to $10^{-3}$ ft/min. Soil porosity values in the silts and sands ranged from 30 to 45%. The average hydraulic gradient near the barrier was calculated to be about 0.005 ft/ft and in a general north-northeast direction for both A1and A2 aquifer zones. Water-level measurements from monitoring wells at Moffett Field indicate fluctuations up to about 4 ft annually, with highs in the Spring and lows in the Fall.

### 3.2 WATER QUALITY CONDITIONS

The primary dissolved chlorinated hydrocarbons found in the vicinity of the barrier include TCE, PCE, and cDCE and are confined to the A1 and A2 aquifer zones. The plume is more than 10,000 ft long, about

5,000 ft wide, and oriented to the north/northeast (Figure 2). TCE is the most widespread contaminant at Moffett Field, which has primarily originated from the offsite Silicon Valley plume. TCE was reported by IT Corp.[11] at Moffett Field exceeding 5,000 ug/L. PCE levels, from a former onsite dry cleaning operation, were about 1,000 ug/L in the A aquifer. More recently, TCE levels of greater than 2,000 ug/L and PCE levels of about 150 ug/L were observed in the June 1996 sampling event near the permeable barrier.

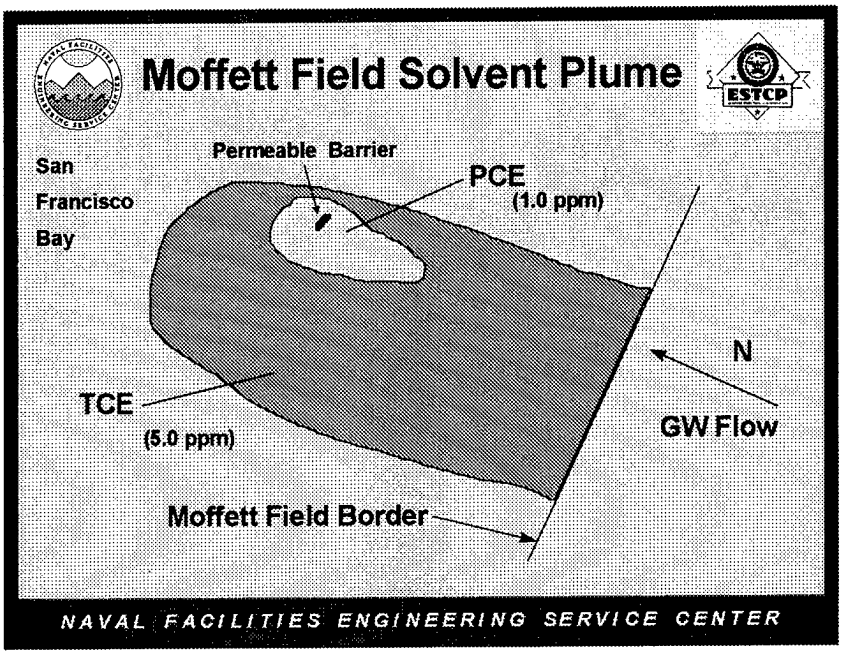



Figure 2. Moffett Field Solvent Plume

Inorganic parameters also have a considerable bearing on the performance of the barrier. The high alkalinity from the carbonates present in the groundwater is an important aspect of the natural buffering capacity of the groundwater. Elevated levels of chloride at the site are typical of shallow groundwater in the San Francisco Bay area. Elevated calcium and magnesium levels observed at the site could also contribute to precipitate formation in the reactive cell. Nitrates and sulfates observed in the groundwater also have the potential under certain conditions to promote microbial growth and sulfide precipitation. Although the levels of inorganics may suggest that biological or chemical precipitates could occur in the reactive cell, it is uncertain as to any effects on the flow or treatment capacity, because of varied kinetics.

## 4. PRE-DEMONSTRATION ACTIVITIES

Prior to installing the pilot-scale permeable barrier, bench-scale studies were conducted to evaluate the treatability of the site groundwater. In both batch and column tests, a mixture of reactive granular iron and sand was used. Batch tests were initially performed by mixing iron samples from four different industrial sources with the contaminated water. The granular iron samples from Peerless Metal Powders, Inc. were found to have the greatest sustained treatment efficiency for TCE and PCE and were subsequently used in the column tests. Batch tests were also conducted with and without buffers in the solutions to determine the correlation between pH and degradation rates (or half-life)[12]. Column tests were performed with a 4-ft long, 4-inch diameter, ported glass column filled with 50:50 mixture of Peerless iron and construction grade sand. Porosities in the mixture were reported to be about 38%. The flow rate through the column was calibrated at about 7.7 ft/day, which was slightly faster than natural site conditions, but was anticipated to be more representative of the velocity in the reactive cell using a funnel-and-gate system. Water samples

were collected at timed intervals from the inflow and outflow ports, and at seven intermediate ports along the length of the column. The column test results indicated that average calculated half-lives were about 0.9 hour (hr) for TCE, 0.5 hr for PCE, 3.1 (hr) for cDCE, 4.7 hr for VC, and 9.9 hr for 1,1 DCA.

Groundwater modeling was conducted to assist in the barrier design and placement location of the funnel-and-gate system[13]. MODFLOW[14] and MODPATH[15] were used to simulate the flow regime at the site. Hydraulic parameter values used in the model were obtained from the site pumping tests, cone penetrometer investigations, and bench scale studies. Three scenarios were simulated in the modeling study: pre-installation without the barrier, post-installation, and post-installation with extraction wells. Particle flow velocities in the models ranged from about 4 ft/day. Modeling indicated that the proposed funnel-and-gate system design should adequately capture the targeted portion of the groundwater plume at the site.

The pre-demonstration studies concluded that by using the calculated half-lives and with predicted flow velocities from the modeling, a reactive cell thickness of 6 ft and no buffering would be adequate to treat TCE, PCE, and other chlorinated compounds at the site. However, in the final design a reactive cell consisting of 100% granular iron was used instead of an iron and sand mixture, mostly as a safety factor and to promote more rapid and complete degradation of the chlorinated solvents.

## 5. REACTIVE BARRIER DESIGN

The permeable barrier project at Moffett Field was designed with the assistance of ETI using a funnel-and-gate system (Figure 3). The reactive cell, containing granular zero-valent iron [$Fe^0$], is 10-ft wide, 6-ft long, and 25-ft deep. Two feet of pea gravel is positioned both in front of and in back of the iron cell. The pea gravel homogenizes and disperses the flow from the heterogeneous aquifer as it passes into and out of the reactive cell. The funnel walls consist of interlocking steel sheet piles and are 20 ft in length on each side of the gate. A total of 48 multilevel PVC monitoring wells with 1 ft screened sections are located at approximately 10, 15, 20, and 25 ft depth intervals within the iron treatment cell and pea gravel. A total of 19 PVC monitoring wells (8 of which are clustered, WIC 5-12) with 5 and 10 ft screens are located at variable depths in the A1 aquifer zone both upgradient and downgradient of the permeable barrier.

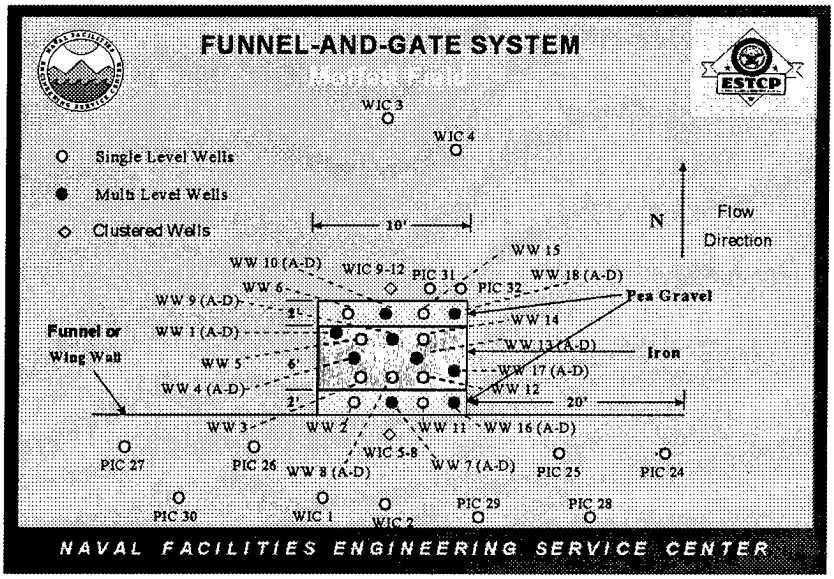



Figure 3. Funnel-and-Gate System at Moffett Field

Although both A1 and A2 aquifer zones are contaminated, the permeable barrier demonstration project was constructed to penetrate only the A1 aquifer and was not intended to be a full scale remediation. The other primary reason for positioning the permeable barrier in the A1 aquifer was that conventional excavation techniques can easily be used up to depths of 25 to 30 ft. The barrier was also installed to just above the A1/A2 aquitard, because of the fear of excavating through the semiconfining layer, which is estimated to be only 1 to 2 feet thick at that location. The barrier was placed towards the middle of the contaminant plume instead of at the leading edge or at the side to ensure that it would be exposed to higher contaminant concentrations in the short time available for the pilot study.

## 6. PERFORMANCE MONITORING

Since the reactive barrier was installed at Moffett Field, four water quality sampling events have been performed, one baseline monitoring (June 1996) and three subsequent quarterly sampling rounds (September 1996, January 1997, April 1997). In January 1997, for about one month, continuous monitoring of reduction oxidation potential (Eh), pH, temperature, precipitation, and water levels were used to evaluate the changing conditions of the site relative to the permeable barrier. Slug tests, flow/velocity meter testing, and tracer testing were also performed at the site from February to April 1997, to verify flow characteristics of the site and that groundwater was actually flowing through the treatment cell.

Performance monitoring activities for this study were planned for about 1 year following the baseline sampling. However, it is not anticipated that significant changes in the reactivity and performance of the reactive cell would occur in this time frame. Experience at past reactive barrier installations (the Waterloo site at Borden [Canada], where a pilot barrier has been functioning for more than 6 years and the Intersil site at Sunnyvale [California], where a full-scale barrier has been operating for almost 3 years) suggests that no loss of performance has occurred or may take place for several years.

### 6.1 FLOW AND TRANSPORT MODELING

The original version of MODFLOW was modified to increase the grid resolution near the permeable barrier location to obtain more detailed information. RWLK3D[16] was the transport model used to simulate particle tracking and to delineate capture zones of the permeable barrier. Flow variations have important implications in performance of the reactive cell and in plume capture, which will be assessed after further review of the monitoring and tracer testing results. The modeling was also used to locate new monitoring wells in determining capture efficiency, the effects of mineral precipitation, reduced permeability in the reactive cell, the existence of preferential pathways in and under the reactive cell, and in calculating volumetric water budgets. Modeling has indicated that for permeable barriers to effectively treat contaminated groundwater, a balance between the residence time of water within the cell, the volumetric flow through the cell, and the effective capture zone must be struck. Sediment clogging, iron encrustation, and precipitates would decrease the efficiency of the barrier by decreasing flow through the gate. A significant conclusion from the modeling is that the heterogeneous nature of a site also greatly impacts the capture zone of the funnel-and-gate system.

### 6.2 TECHNICAL OBJECTIVES

Table 1 lists the general technical performance criteria from Battelle's PMP that will be used to evaluate the effectiveness of the Moffett Field pilot barrier. Except for the criteria that treated groundwater should desirably meet the beneficial use MCLs or be ND for the contaminants of concern, other criteria are based more on the expectations incorporated in the design of the permeable barrier and projections based on the current understanding of the technology.

Table 1. Technical Performance Criteria for Evaluating the Permeable Barrier

| No | Objective | Technical Performance Criteria |
|---|---|---|
| 1 | Evaluate the reactivity characteristics of the permeable barrier | • Chlorinated solvent concentrations in the reactive cell wells should be below MCLs or ND when compared to upgradient background conditions.<br>• Increased levels of abiotic degradation byproducts should be observed in the reactive cell and potentially in the downgradient pea gravel.<br>• Tracer tests within the barrier should indicate the desired residence time in the reactive cell is being achieved and flow is being transported in the cell.<br>• Perform mass balance calculations. Slug tests or cell corings may indicate if chemical/biological precipitates are forming and may inhibit reactive process.<br>• pH levels should remain below 11 to help minimize precipitate formation. |
| 2 | Evaluate the downgradient water quality | • The permeable barrier should not allow any breakthrough of contaminants or introduce any sustainable levels of by-products into the aquifer above the MCLs (e.g., dissolved iron, chlorides, other hydrocarbon byproducts). |
| 3 | Evaluate the hydraulic capture efficiency of the barrier | • The capture zone should cover at least the portion of the plume targeted in the pilot-scale design.<br>• The barrier should be able to handle any seasonal water-level fluctuations or changes in flow direction. |
| 4 | Estimate operating and maintenance costs | • The permeable wall design and construction should be a cost-effective alternative to groundwater pump-and-treat.<br>• The barrier should retain its reactivity and capture efficiency for many years. |
| 5 | Evaluate pea gravel conditions | • Investigate the issue of contaminant underflow, lateral flow, or backflow and the potential contamination of the downgradient pea gravel. |

## 6.3 PRELIMINARY MONITORING AND QUARTERLY SAMPLING RESULTS

Based on a review of the baseline and first two quarterly sampling results, the overall performance of the permeable barrier was impressive. Several preliminary observations can be made from the monitoring and sampling events and are highlighted, as follows:

- TCE levels of around 1,100 to 1,400 ug/L, cDCE levels of around 210 to 260 ug/L, and PCE levels of around 6 to 15 ug/L in WIC-1 from the baseline and quarterly sampling results are representative of the highest levels of observed contamination entering the barrier.

- Dissolved chlorinated solvent concentrations were reduced to ND for TCE and PCE and to either below the MCL or ND for cDCE in the reactive cell for all of the quarterly sampling events. In most cases the reduction occurred within the first array (1-2 ft) of monitoring wells in the treatment cell.

- The chlorinated compound degradation product VC was ND in the upgradient aquifer wells near the barrier. However, VC was detected slightly (4 ug/L) in the first array of wells in the permeable cell (1-2 ft), suggesting degradation or reduction was occurring. In the next array of downgradient wells within the treatment cell (2-4 ft), VC was again ND, suggesting its cleanup.

- The analytical results from the September 1996 quarterly period (which are typical for each sampling event) for the primary contaminants of concern (TCE, PCE, and cDCE) are shown in Figure 4. However, the small VC concentration detected in the first array of wells in the iron cell could not be plotted because of the scale of the graph.

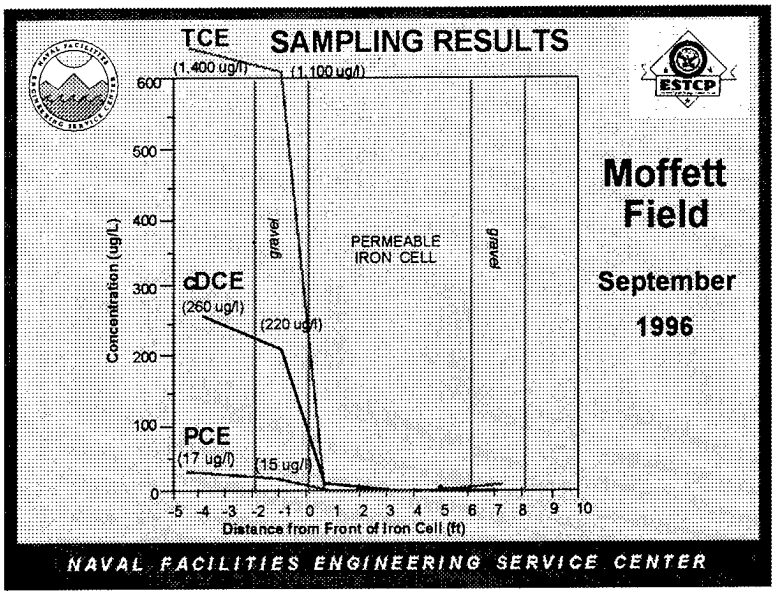



Figure 4. Quarterly Sampling Results for September 1996

- Inorganic byproducts of the abiotic degradation ($Cl^-$, $Fe^{2+}$) and light hydrocarbon gasses (methane, ethene, ethane, etc.) were also observed in the permeable cell, again suggesting the success of the chemical reaction. Eh and pH showed expected trends in the reactive cell. The pH rose to about 11.0 at some points in the reactive cell. Eh dropped as low as -600 millivolts, indicating strong reducing conditions favorable to abiotic degradation. Eh and pH returned to their background values as the water exited the reactive cell and mixed with the untreated aquifer water.

- Inorganic analytes exhibited distinct behaviors within the reactive cell. Charge balance calculations performed on the inorganic data are of good quality (within 10% error). Redox sensitive ions such as nitrates and sulfates also appeared to be significantly degraded along the flow path. Calcium, magnesium, and alkalinity also decreased along the flow direction, which may be resulting in the formation of precipitates. Declining calcium and alkalinity and the relatively constant saturation index for calcite may be evidence of precipitation in the reactive cell. Proposed cell corings should substantiate these concerns.

- Water level data a few months after reactive barrier installation and during the rainy season (October 1996 to February 1997) indicated that mounding was present at various times in the reactive cell, which suggests that a potential backflow condition may have occurred. After the rainy season, the water levels stabilized and a natural forward flow gradient returned to the reactive cell. Tracer testing became a very significant objective in verifying actual flow through the cell.

- Water level measurements and flow velocity meter testing indicated that the actual capture zone of the funnel-and-gate system appeared to be slightly smaller in reality than in modeling. Flow and velocity meter testing indicated general flow through the permeable cell in a northeasterly direction.

- Initial tracer testing of the reactive barrier was completed in April 1997. Twelve liters of a Bromide solution (3,000 mg/L) was injected into the pea gravel at a rate of 100 mL/min for 2 hours. Rapid dispersion occurred (within 8 hours) in the upgradient pea gravel from the injection point (WW-2) to WW-7, WW-11, and WW-16. After dispersion in the upgradient pea gravel, Bromide was detected in a linear path using continuous monitoring equipment within the permeable cell from WW-2 to WW-3,

WW-4, WW-5, and potentially at low concentrations (above background levels) in the downgradient pea gravel (WW-10), where dispersion likely occurred again. A Bromide path was also detected in a northeasterly direction from WW-2 to WW-8 and WW-13. Further evaluation of this data is ongoing.

- The flow rate was estimated to be about 0.5 ft/day, which was somewhat less than the modeled or anticipated results. However, it was still encouraging to know that groundwater flow appears to be generally moving through the cell in a natural downgradient (northward) direction, and if backflow conditions did exist, they were likely temporary in nature. Further evaluation of the slug tests, tracer testing data, and hydraulic measurements will provide some insight as to whether the design of the funnel-and-gate system may potentially be restricting flow from the aquifer through the treatment cell.

## CONCLUSIONS

The predominance of groundwater contamination and the lack of methods to treat the contamination in an effective and economical manner is a problem of great concern to the EPA and the regulated community. Chlorinated solvent contamination in groundwater has the potential to persist for several decades, despite efforts to pump-and-treat it. The EPA has identified six abiotic technologies that are emerging as possible cleanup remedies for recalcitrant sites. Permeable treatment barriers technology is one of them, which has several advantages over conventional groundwater pump-and-treat systems, such as:

- The permeable wall technology is passive in nature using gravity flow, no external energy is consumed.
- It has the potential for treating chlorinated solvents in groundwater to very low or ND concentrations.
- No hazardous waste streams are generated requiring subsequent disposal.
- No aboveground structures are required.
- It has the potential for a long-term, unattended, and cost-effective operation with low maintenance.

The proposed year of study at the Moffett Field demonstration project should allow for an evaluation of (1) how well the performance of the barrier achieves its design goals, and (2) how well the barrier is able to handle any seasonal changes in flow direction and volume. These findings should provide enough information to design a full-scale barrier at Moffett Field, and verify the technology for use at other sites. Detailed investigation results will be published in a final evaluation report in about March, 1998.

The issue of longevity of the permeable barrier technology has not been fully addressed by the scientific community. Research is presently under way by RTDF group members to reduce any potential precipitates that may be formed by controlling the pH in the reactive cell. For the past 6 years, the University of Waterloo permeable barrier at Borden has not required any maintenance, which is encouraging. Currently, most users of the permeable barrier technology have attempted to address the concern of longevity by incorporating safety factors into the design, such as extra reactive iron cell thicknesses or widths. One can easily estimate the construction costs of a barrier project, however the longevity or maintenance costs would be more difficult to estimate. ETI has suggested that maintenance costs be assumed to equal a value of replacing 25% of the iron every 10 years. Of course, in a best case scenario, the current installation could be left in the ground until the entire chlorinated solvent plume has been treated.

Members of the RTDF, permeable barriers workgroup, are optimistic about the growing acceptance of the permeable barrier technology by the regulators. The U.S. Air Force and RTDF group has prepared a design guidance manual for permeable barrier applications[17]. The ITRC has also been meeting in the past year to review permeable barrier applications and to develop a permeable barrier design protocol document[18] for eventual use by site managers and regulators. At the Intersil semiconductor manufacturing facility in Sunnyvale (regulated by the California Regional Water Quality Control Board), a full-scale iron

permeable barrier was installed to remediate a chlorinated solvent plume and has been in operation since December 1994 without any breakthrough of contaminants and/or byproducts.

A pump-and-treat system is scheduled to be installed at Moffett Field in late 1997 to remediate the groundwater contaminant plume. If the pilot-scale barrier project is consistently successful at the site, as has been indicated in the preliminary evaluations of performance monitoring, remedial plans could be revised to incorporate this potentially more effective and economical technology. The objectives of this demonstration project have been designed to answer questions of regulators concerning contaminant destruction, contaminant byproducts, water quality conditions downgradient from the barrier, and hydraulic capture efficiency. Regulators are increasingly considering cost-effective remedial alternatives to groundwater pump-and-treat systems, and should be involved early in the decision process.

## NOTICES

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# FUEL AND CHLORINATED SOLVENT REMEDIATION AT NAS FALLON: BIOSLURPING FREE PRODUCT AND NATURAL ATTENUATION MONITORING OF THE SOLUBLE PLUME

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## ABSTRACT

Bioslurping is an in situ technology that removes free-phase fuel from the water table and capillary fringe through vacuum skimming. While fuel biodegradation is accentuated by vadose zone and groundwater aeration, which may be promoted by bioslurping, remediation of highly chlorinated solvents such as perchloroethene (PCE) requires anaerobic soil conditions. Determining the interactions among bioslurping and fuel and chlorinated hydrocarbon natural attenuation processes was a goal of this field study, which was at a site co-contaminated with mixed fuels (gasoline, diesel, JP-5), waste oil, and chlorinated solvents. Bioslurping was shown to increase vadose zone aeration at distances up to 30 ft from vacuum extraction wells and to aerate groundwater in the immediate vicinity of these wells. However, increases in the groundwater gradient promoted by bioslurping under low flow conditions may have the greatest influence on altering saturated zone chlorinated solvent and less chlorinated daughter product concentrations. Vapor and aqueous transport of chlorinated solvents and daughter products through the vadose zone need to be considered in assessing spacial and temporal natural remediation rates. Complete reductive dechlorination of PCE appears to be occuring at the source area. Vinyl chloride is being produced but it is not accumulating at levels above 5 ug/L, despite high sulfate concentrations. Consequences of fuel biodegradation on reductive dechlorination rates need long-term assessment. Depletion of the more soluble monoaromatic fraction, which is known to degrade under anaerobic conditions, may also decrease the energy and hydrogen source required for biological reductive dechlorination. Sampling, analytical and site subsurface variability may confound short-term spacial and temporal data evaluation.

## INTRODUCTION

Bioslurping is an innovative in situ technology that simultaneously removes light nonaqueous phase liquid (LNAPL) from fuel-saturated soil and biovents the contaminated vadose zone through vacuum-assisted pumping at or near the water table. Natural attenuation monitoring involves determining the natural subsurface processes (e.g., dilution, sorption, dispersion and biodegradation) and rates that provide for reduction of human and ecological risk before potential receptor exposure pathways are completed.

Since LNAPL acts as a source area for soluble contaminants in groundwater, its removal is important in controlling the ultimate spread and decline of the contaminant plume. This is especially true when the LNAPL contains chlorinated solvents, such as perchloroethene (PCE) and trichloroethene (TCE), since the bulk of the chlorinated solvents and perhaps some transformation products may be strongly bound to and released slowly from the fuel.

Desorption and biotransformation rates of chlorinated hydrocarbons associated with fuel hydrocarbons may be governed by the fuel composition and its biodegradability under both aerobic and anaerobic conditions. Aerobic degradation may increase the chlorinated hydrocarbon solubilization rate through accentuated fuel degradation (thus potentially expanding the chlorinated hydrocarbon plume) while anaerobic fuel degradation processes could supply an energy and carbon source to the anaerobic bacteria that are responsible for the reductive dechlorination reactions[1].

Facultative anaerobic bacteria (denitrifiers) have recently been found capable of partially dechlorinating PCE to cis-1,2- dichloroethene (cis-DCE) at concentrations approaching its solubility in water (1 mM; 165 mg/L)[2] while obligate anaerobic bacterial consortia were shown to completely dechlorinate PCE to nontoxic ethene gas at concentrations as high as 55[3] and 90 mg/L[4]. However, different microbial consortia generally appear to direct the dechlorination of PCE to dichloroethene (DCE), through TCE; DCE to vinyl chloride (VC), and VC to ethene (and probably ethane), respectively. High nitrate concentrations can inhibit the initial step[2], while high sulfate concentrations could inhibit the second step because of microbial competition for $H_2$ (electron donor) between the sulfate reducing and dehalogenating bacteria[5]. This inhibition could be minimized if the food source releases hydrogen slowly because dehalogenation is favored thermodynamically over sulfate reduction and methanogenesis[5].

Laboratory studies using dehalogenating microbial consortia often show a buildup of cis-DCE until most of the PCE and TCE has been removed[4]. The greater difficulty in dechlorinating the lower chlorinated daughter products (DCE, VC) through anaerobic bacterial reductive respiratory (electron accepting) processes can result in their buildup under certain conditions. However, VC readily partitions to the vapor phase and can be degraded as a primary food source[6] or cometabolically[7] under the aerobic conditions that often exist down-gradient from the source area. The use of cis-DCE as a primary food source has not been substantiated and only cometabolic biodegradation under aerobic conditions has been proven, and probably only at relatively low levels because of its toxicity to the cometabolic bacteria[8]. These factors, combined with a declining food source down-gradient to sustain anaerobic or cometabolic processes, may be responsible for cis-DCE often being the dominant chlorinated hydrocarbon in down-gradient groundwater samples. However, the MCL for cis-DCE is fairly high (75 ug/L).

This report outlines results from an initial assessment of an old fire training pit site at Naval Air Station (NAS), Fallon, Nevada, that is co-contaminated with mixed fuels and oil and chlorinated solvents (PCE and probably TCE). This site (Site 1) is the location of field demonstrations of: bioslurping (for LNAPL removal), natural attenuation efficacy monitoring (intrinsic remediation), and enhanced microbial reductive dechlorination of the soluble plume. Since bioslurping can potentially aerate both the vadose zone and groundwater, an initial field evaluation was performed to help determine how active fuel and groundwater removal through vacuum skimming could affect natural reductive dechlorination processes in the soil and groundwater. The potential for intrinsic remediation of fuel and chlorinated hydrocarbons at this site was also assessed as part of a long-term investigation. The enhanced reductive dechlorination project will not be discussed.

## FIELD SITE AND BIOSLURPER SYSTEM

The field demonstrations are at the Old Fire Training Pit (Site 1) at NAS Fallon. The contaminated site soil and aquifer zone consist primarily of medium sand on a regional clay aquitard and the

contaminants are mixed fuels (JP-5 jet fuel, diesel, gasoline) and waste oil which are co-contaminated with PCE (possibly also TCE). PCE in free LNAPL has been measured at up to 1500 mg/kg and in source area soils at up to 38 mg/kg. The free LNAPL plume covers approximately a one acre area and is the site of the bioslurper system. The free LNAPL is limited, with most wells initially showing less than 0.1 ft of free product and at system startup fuel was not detected in any of the extraction wells.

The bioslurper system consists of 30 2-inch-diameter extraction wells interconnected to a 10 hp liquid ring vacuum pump through a 3-inch-diameter vacuum manifold system. A detailed description of bioslurping systems is available elsewhere[9]. Pumped groundwater is treated sequentially by passage through a trough containing coarse-spun polypropylene (furnace type) filters to remove heavy emulsion, a 10 gpm oil-water separator, and a 1500 gallon storage tank to allow for further gravity separation of the fuel from the water (with the bottom water discharged to the sewer). Figure 1 shows the locations of the bioslurper system, monitoring wells and points.

## INTRINSIC REMEDIATION METHODS

Historical data for borehole soil and groundwater analyses were assessed in conjunction with more recent sampling protocols conducted in February and April 1997. The recent protocols included data on potential primary food sources for reductive dechlorination: total petroleum hydrocarbons (TPH) as extractable and purgeable; benzene, toluene, ethylbenzene, xylenes (BTEX); and soluble total organic carbon (TOC); potential respiratory electron acceptors for intrinsic remediation: $O_2$, nitrate, total iron, sulfate and $CO_2$; common electron acceptor reduced products: soluble iron, soluble manganese, and methane; and chlorinated solvents and potential anaerobic daughter products: PCE, TCE, DCEs (cis-DCE, trans-DCE, 1,1-DCE), vinyl chloride (VC), ethene, ethane, and acetylene. Propane was monitored to determine if the end product gases were from recent biogenic or geological processes. Most of the historical data lacked these important parameters and monitoring was often incomplete.

Water samples were collected with a bailer after slow well purging with a peristaltic pump (usually 1 to 2 well volumes removed). Water samples for volatile organic compound analyses were placed in completely filled VOA vials and water for dissolved gases in completely filled 1-liter bottles. Samples for soluble constituents were immediately filtered (0.45 um) in the field using a hand syringe. Laboratory analyses were made by standard procedures (GC, GC/MS, and ion chromatography).

A Hydrolab™ was used immediately after sampling for in- well water measurements of dissolved oxygen, conductivity, pH, and temperature. Field instruments were used to analyze soil gas samples for $O_2$, $CO_2$, and petroleum hydrocarbons (using hexane as a standard). Soil gas was collected from immediately above the capillary fringe zone, after initially removing 2 liters from each sampling point, using Tedlar™ bags. Soil gas for other measurements (chlorinated hydrocarbons and end-product gases) was collected in 6-liter stainless steel SUMMA canisters and analyzed by accepted USEPA air sample laboratory procedures. All samples were kept on blue ice until analyzed.

## RESULTS AND DISCUSSION

### BIOSLURPER SYSTEM OPERATION

Fuel was not recovered from the bioslurper system during the initial 9 days of operation, which was initiated in late September 1996. However, after this time an average of four gallons has been collected daily, with minor variability. Groundwater discharge from the entire system (30 wells) was about 8 gpm initially but the rate was reduced to about 4 gpm after a month of operation. The total petroleum hydrocarbon (extractable TPH) concentration in the discharge water has averaged about 50 mg/L and the

air discharge (initial sampling) was 210 ppmv (1.8 lb/day at 15 cfm flow rate) as purgeable TPH. Benzene, PCE, TCE, and DCE (96% as cis- isomer) were discharged at 640, 510, 390, and 1148 ppbv, respectively. Total VOC discharge, at an average rate of 15 cfm, did not exceed Nevada air discharge limits and thus off-gas treatment is not required. Pump head and well head vacuums have averaged about 15 inches of mercury and 15 inches of water, respectively.

Figure 2 gives average soil gas concentrations of $O_2$, $CO_2$, and volatile hydrocarbons (TPH) for 13 soil gas points, measured over a four month period following bioslurper system startup. Initially, prior to startup, most soil gas samples in the lower vadose zone at distances up to 50 ft from extraction wells (average of about 30 ft) were already aerated, probably because of high water table conditions that may have covered most of the LNAPL smear zone. Over the course of the monitoring, $O_2$ concentrations increased about 2%, from around 12 to 14%. Simultaneously, the $CO_2$ and TPH concentrations declined by about 6% and 450 ppm, respectively. These data suggest that the vadose zone sampling point locations are generally under the vacuum control of the bioslurper system, despite two points showing little to no oxygenation during the monitoring program. There appeared to be a positive correlation between significant TPH (>500 ppm) and depressed $O_2$ concentrations, indicating that biodegradation of fuel vapor could be maintaining the low $O_2$ readings during bioslurper operation. Laboratory soil gas analyses (Table 1) further substantiate this assumption, such as at MP-4, where high BTEX concentrations were present.

Hydrolab™ data were collected from bioslurper extraction wells (BS) to compare groundwater conditions with those in monitoring wells (MW) generally outside the vacuum influence of the bioslurper system (Table 2). In comparing extraction well with down-gradient monitoring well data, it is apparent that bioslurping significantly aerates the water within the BS extraction wells, with the exception of those having appreciable free LNAPL (BS-11). However, only BS-26 was purged prior to field analysis, for sample collection purposes. This well showed low dissolved oxygen, with no measurable free LNAPL, but it is in an area known to have high BTEX concentrations (near soil gas MP-4) and a black precipitate was present which, based on high total iron levels (13 mg/L), appeared to be iron sulfide. Thus additional field measurements need to be made prior to and after removal of varying purge volumes to determine if bioslurping has a significant effect on groundwater aeration. Extensive groundwater aeration is not expected since the bioslurper system pulls water continuously into extraction wells.

## INTRINSIC REMEDIATION: SPACIAL VARIABILITY

Recent groundwater data (Feb 97) for BTEX, chlorinated solvents and daughter products are presented in Figure 3. These data show a rapid decline in BTEX concentrations, from 2.15 mg/L at the source (MW-51U) to 0.01 mg/L 300 ft down-gradient (MW- 16U). Benzene constituted 5.5% of the BTEX at the source area compared to 85% at MW-16, which indicates that anaerobic biodegradation may be an important component for the BTEX decline, due to the known poor biodegradation rate for benzene under anaerobic conditions. However, rather unusual data was obtained for the chlorinated hydrocarbons. Although high PCE has recently been measured in the free fuel (0.15%), rather low PCE and TCE concentrations were detected in groundwater at MW-51U, at 26 and 36 ug/L, respectively. In contrast, cis-DCE (the only DCE isomer detected) was measured at 1100 ug/L and similar data were noted at the down-gradient BS-26 well, which showed cis-DCE at 520 ug/L. Both of these wells are within the LNAPL plume but only MW-51 showed free product of 0.15 ft prior to well purging. MW-16U, (300 ft down-gradient from MW-51) showed PCE, TCE and cis-DCE at 11, 170 and 160 ug/L, respectively, and trans-DCE at 99 ug/L. MW-15U, 600 ft down-gradient from MW-51, showed PCE, TCE, cis-DCE and trans-DCE at 2.9, 11, 7.2 and 3.9 ug/L, respectively, with total BTEX at non-detectable levels. These data indicate that the reductive dechlorination rate has slowed appreciably beyond MW-16, probably because of a lack of food source needed to sustain reducing groundwater conditions and supply the energy needed to promote the use of the chlorinated compounds as electron acceptors. Groundwater dissolved oxygen concentrations at MW-15U indicate that aerobic conditions exist in the upper aquifer 600 ft down-gradient

(Table 2). TOC data suggest that soluble organic compounds other than BTEX are present at MW-16U (but not at MW-15U), as soluble TOC was 160 mg/L, compared to 250 mg/L at the source area (MW-51U).

## INTRINSIC REMEDIATION: TEMPORAL VARIABILITY

The low PCE and TCE concentrations measured in February 1997 at MW-51U differ from data collected in October 1993, prior to bioslurper system operation (Figure 4). The earlier data show PCE and TCE concentrations at 680 and 340 ug/L, respectively, and DCE was below detection (although it is possible that only the trans-DCE isomer was reported as this was a common fuel additive). The difference could be promoted by the operation of the bioslurper system, combined with recent high seasonal precipitation for this arid region. Although the total pumped groundwater is small, the site has a flat water table with a groundwater flow rate calculated from a pump test of 0.07 ft/day. A significant increase in the groundwater gradient may move soil pore water toward the bioslurper wells at a faster rate than the PCE desorption rate from the LNAPL. Therefore, the soluble phase concentrations would decline. Soil gas data presented in Table 1 show almost no measurable DCE, despite very high PCE and TCE values at MP-4. This may indicate that the high cis-DCE concentrations measured in groundwater beneath the LNAPL plume were flushed from the vadose zone following rainfall or snow melt events, which have intensified since 1993 and especially during 1996. The cis- isomer of DCE has a strong affinity for the water phase, although it was readily stripped from the groundwater during bioslurping.

Data presented in Figure 5 show problems inherent in evaluating older analytical data or in conducting long-term monitoring, especially where samples are collected by different personnel and analyzed by different laboratories. Some data was excluded because of known problems with the particular laboratory. However, the abrupt decline in DCE data over a summer period of two months (months 21 and 23 in Figure 5) appears to be unusual. The DCE data for October 1993 may have been only for trans-DCE, but this is not certain. The more recent data suggest that the soluble chlorinated hydrocarbon plume may be expanding. However, the variability is great and the older data is suspect. Therefore no conclusion can be drawn until additional sampling occurs.

Figure 6 shows historical data for MP-15U, approximately 600 ft down-gradient from MW-51U. These data also indicate an expanding soluble chlorinated hydrocarbon plume. Data for 1991 (not shown) give total chlorinated hydrocarbon concentrations at 42 ug/L from the deeper profile well (MW-15L), compared to the April 1997 data from the same well of 58 ug/L. Future extensive monitoring therefore appears necessary to resolve these observed relatively small temporal fluctuations.

## DCE DECHLORINATION POTENTIAL

Detectable concentrations of VC have appeared only twice during extensive monitoring that occurred at Site 1 between April 1991 and July 1995. These occurrences were at MW-51U of 3.0 ug/L in April 1992 and at MW-16U of 2.2 ug/L in July 1995. However, the USEPA sampled groundwater from 39 boreholes emplaced immediately northeast and southeast of the bioslurper wells in September 1995 and detected VC in almost every water sample that contained measurable DCE (25 of 28 wells). Eighteen well samples contained VC at measurable concentrations of between 1.0 and 2.9 ug/L. There was a very large range in DCE concentrations (mostly cis-DCE) for the wells displaying measurable VC, ranging from 10 to 658 ug/L. VC was also detected at 4.6 ug/L in groundwater from MW-16U during the February 1997 monitoring, which is the highest value recorded at Site 1. MW-15U contained a unquantifiable trace (<1.0 ug/L) of VC, despite aerobic groundwater conditions and total DCE at 11.1 ug/L. These findings suggest that VC is forming readily at Site 1 and at all sampling stations (including the source area). However, a build up of VC in anaerobic or aerobic groundwater does not seem to be occurring at this site. Soil gas sample analyses failed to show VC, with a detection limit of 1.0 ppbv. However, ethene and ethane gases

were detected at MP-4 at 1300 and 200 ppbv, respectively. MP-4 showed very high BTEX concentrations, especially toluene, in the soil gas and showed no detectable $O_2$ (Table 1). The absence of VC and presence of ethene and ethane in the soil gas further suggest that VC is not accumulating and PCE is being dechlorinated completely at this site, despite high sulfate concentrations. Recent data indicate that under highly reducing conditions acetylene may be an intermediate product in reductive dechlorination. However, lower detection limits appear to be required for this highly reactive gas. If detected, a pathway that avoids VC formation could be postulated[10]

## INTRINSIC REMEDIATION ELECTRON ACCEPTORS

The primary electron acceptors used by anaerobic bacteria to degrade fuel hydrocarbons (nitrate, manganese, iron, sulfate, and $CO_2$) are similarly used, at low concentrations, to promote reductive dechlorination. However, since the chlorinated compound is also an electron acceptor, high concentrations of primary electron acceptors may be inhibitory. This is because the bacteria may favor the more readily available oxidized substrate (e.g., sulfate) even if the chlorinated hydrocarbon is at a higher oxidation state. Generally, the highly chlorinated organics are less oxidized than nitrate but at a higher oxidation state than sulfate or $CO_2$. Since some dehalogenators of PCE and TCE are denitrifiers, high nitrate could be inhibitory. High nitrate would also limit use of electron acceptors at lower redox potential, such as the chlorinated compounds.

Site 1 has very high sulfate concentrations, with values up to 12,000 mg/L (Table 3). These levels should be inhibitory to the dechlorination of DCEs if the microbial consortia that dechlorinate DCEs work primarily in the sulfate reducing or methanogenic redox range, which has been postulated. Molybdenum, a known inhibitor of sulfate reduction, is also at high levels at Site 1, with average soluble concentrations near 1 mg/L. Therefore, it is possible that the anticipated high sulfate reduction rate may be inhibited, thus avoiding DCE build up to toxic levels. Also, the anaerobically degraded fuel hydrocarbons probably release $H_2$ slowly, which would favor the dehalogenating bacteria. Future monitoring at NAS Fallon could clarify some of these problem areas.

Table 3 shows the primary natural electron acceptor concentrations in groundwater at Site 1. Nitrate appears to follow a curve down-gradient that suggests that it is being utilized in intrinsic remediation. It is most likely being utilized to anaerobically degrade soluble fuel hydrocarbons (mostly BTEX) as a slow rebound is experienced down-gradient of the major BTEX decline (before MW-16). Sulfate also shows a major decline down-gradient, with no discernible rebound. However, high natural spacial variability in sulfate concentrations has been observed at site 1, with vertical stratification also noted in the groundwater. Additional monitoring from multiple wells will be required to verify if the observed sulfate decline down-gradient is real. Soluble manganese showed no discernible trends, based on the data available. Iron appears to become solubilized in the area of the LNAPL plume, perhaps through sequestration with the organics as no decline in pH was noted. Chloride concentrations are one to two times the sulfate concentrations. Thus it is not anticipated that chloride concentration will show a noticeable change as a result of dechlorination activity. However, chloride could be used as a tracer to help determine if changes in sulfate concentrations are caused by anaerobic biodegradation processes.

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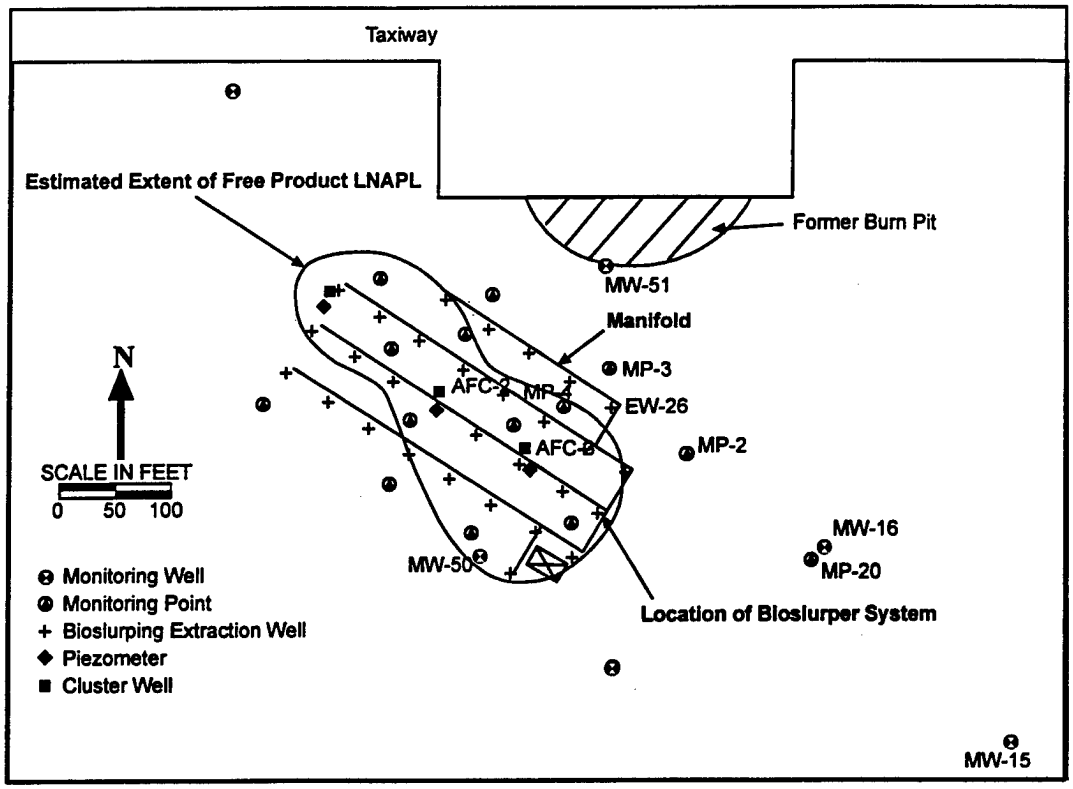



Figure 1. Bioslurper system, free product plume and sampling locations at Site 1, NAS Fallon.

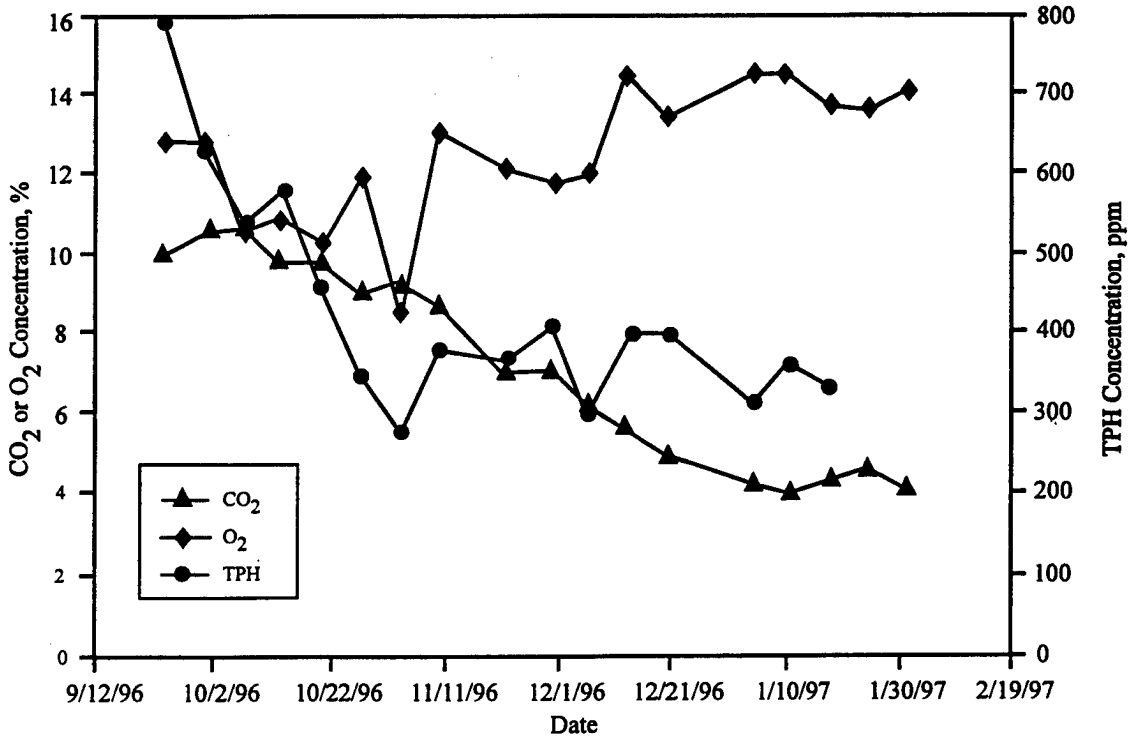



Figure 2. Average soil gas concentrations of $O_2$, $CO_2$, and Total Petroleum Hydrocarbons (TPH) within and adjacent to the bioslurper system at Site 1, NAS Fallon.

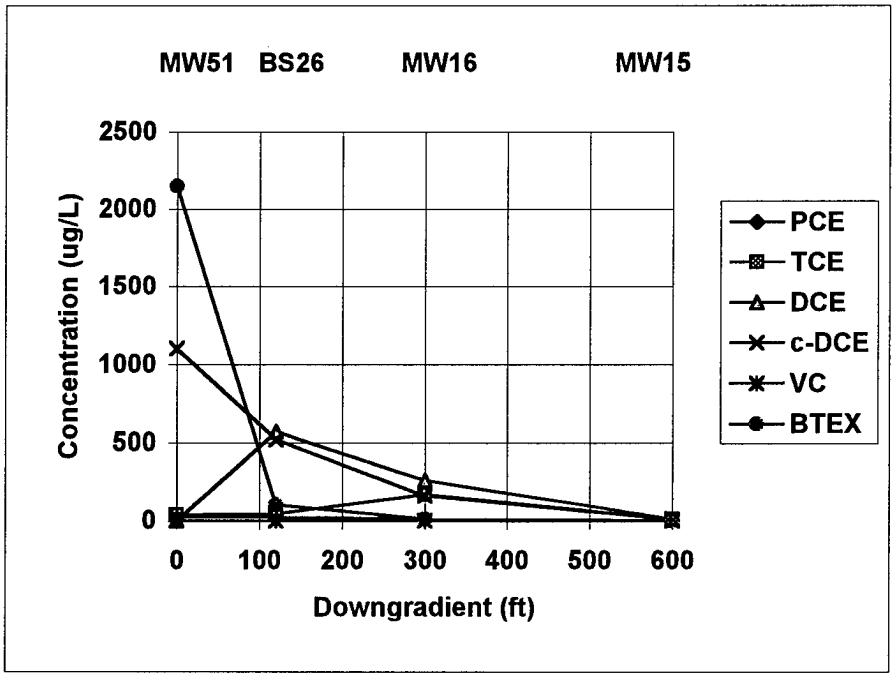



**Figure 3. Downgradient contaminant concentrations in groundwater - NAS Fallon Site1.**

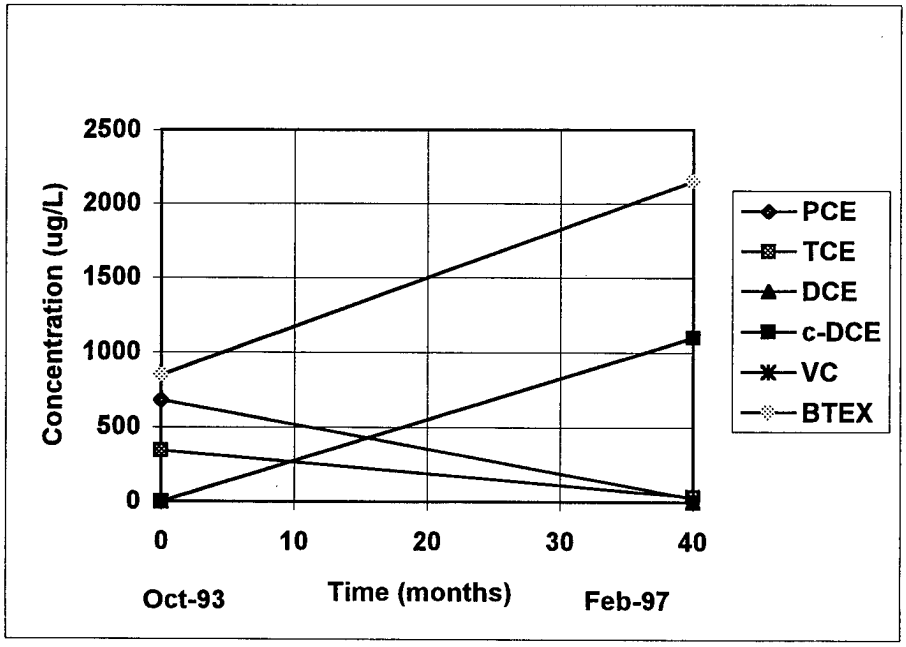



**Figure 4. MW 51 - Concentrations of chlorinated ethenes in groundwater - NAS Fallon Site 1.**

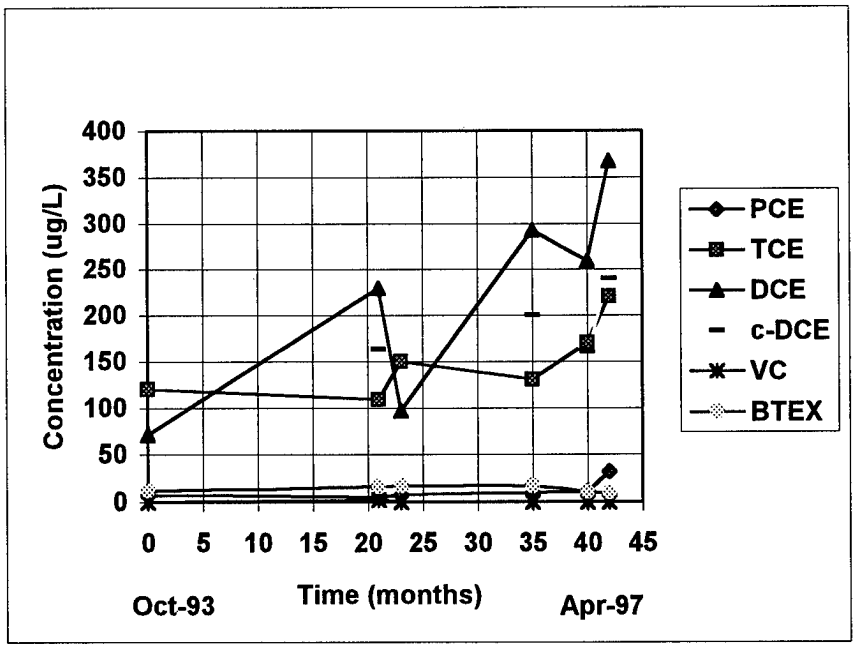



**Figure 5. MW 16 - Concentrations of chlorinated ethenes and BTEX, NAS Fallon Site 1**

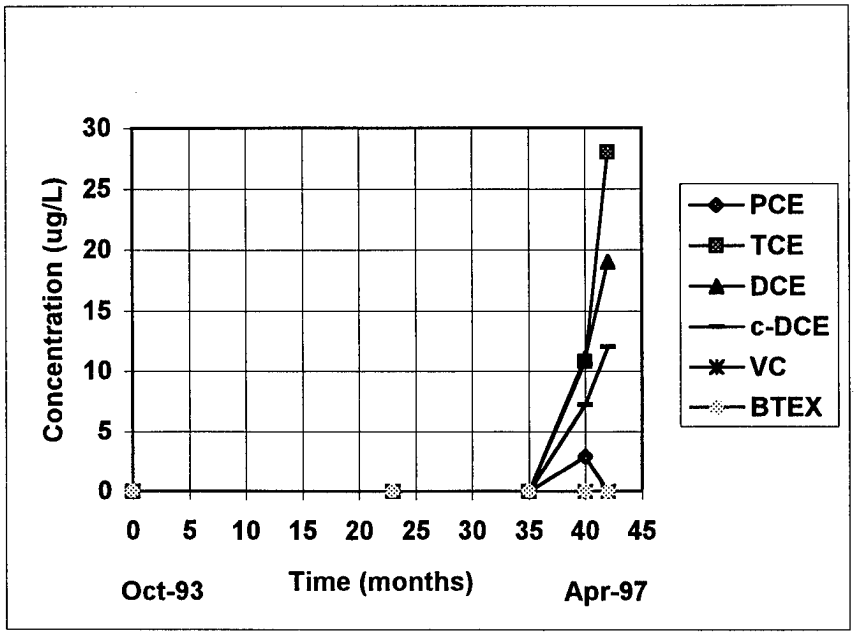



**Figure 6. MW 15 - Concentrations of chlorinated ethenes and BTEX, NAS Fallon Site 1**

TABLE 1. CONTAMINANT CONCENTRATIONS IN SOIL GAS FOR SITE 1 NAS FALLON (FEB 97)

| Parameter (ppbv) | Sample ID | | | |
|---|---|---|---|---|
| | MP-3 (100 ft.) | MP-4 (125 ft.) | MP-2 (175 ft.) | MP-20 (300 ft.) |
| PCE | 9403. | 19849. | 34.9 | 17.0 |
| TCE | 252. | 4105. | 36.8 | 65.5 |
| DCE | <1.0 | 9.0 | <1.0 | <1.0 |
| cis-1,2- DCE | <1.0 | <1.0 | <1.0 | <1.0 |
| Vinyl Chloride | <1.0 | <1.0 | <1.0 | <1.0 |
| Ethylene | <200. | 1300. | <200. | <200. |
| Ethane | <200. | 200. | <200. | <200. |
| Acetylene | <200. | <200. | <200. | <200. |
| Methane | 2600. | 5500. | 32000. | 1200. |
| Benzene | <5.0 | 550. | <5.0 | <5.0 |
| Toluene | <5.0 | 31770. | <5.0 | <5.0 |
| Ethylbenzene | <5.0 | 2634. | <5.0 | <5.0 |
| Xylenes | <5.0 | 2383. | <5.0 | <5.0 |
| Oxygen (%) | 17.0 | 0.0 | 20.6 | 20.8 |
| $CO_2$ (%) | 1.0 | 5.0 | 0.0 | 0.1 |
| Hydrocarbons (%) | 110.0 | 660. | 78. | 64. |

TABLE 2. HYDROLAB DATA FROM SITE 1 BIOSLURPER AND MONITORING WELLS NAS FALLON, NEVADA.

| Station ID | Depth Below Water Table | Purge Volume | D.O. mg/L | Conduct. mS/cm | Temp. C | pH |
|---|---|---|---|---|---|---|
| MW -15U | 2 ft. | 1.4 gal | 4.4 | 12.7 | 16.95 | 8.37 |
| MW-16U | 2 ft. | 2.6 gal | 0.7 | 36.5 | 15.6 | 7.40 |
| MW-51U (fuel) | 2 ft.<br>3 ft. | 4.0 gal | 0.75<br>0.85 | 53.1<br>57.3 | 17.35<br>17.5 | 7.77<br>7.69 |
| PW-02 (background) | 3 ft.<br>8 ft. | 3.5 gal | 4.7<br>5.4 | 69.3<br>68.8 | 13.45<br>14.45 | 7.30<br>7.45 |
| BS-26 | 2 ft. | 2.0 gal | 0.9 | 37.9 | 15.95 | 7.65 |
| BS-18 | 2 ft. | none | 7.3 | 58.1 | 14.9 | 7.38 |
| BS-09 | 2 ft. | none | 6.25 | 63.7 | 15.0 | 7.41 |
| BS-13 | 2 ft.<br>3 ft. | none | 8.8<br>6.5 | 52.9<br>56.2 | 15.25<br>15.6 | 7.20<br>7.20 |
| BS-04 | 2 ft.<br>3 ft. | none | 6.6<br>8.0 | 57.2<br>59.1 | 13.55<br>14.05 | 7.09<br>7.12 |
| BS-11 (fuel) | 2 ft.<br>3 ft. | none | 1.0<br>1.1 | 56.1<br>59.7 | 14.6<br>15.2 | 7.26<br>7.32 |

**BS = bioslurper well; BS-26 showed black particulates in the groundwater.**

TABLE 3. ELECTRON ACCEPTOR CONCENTRATIONS IN GROUNDWATER - NAS FALLON SITE 1

| Sample Location | Parameter (mg/L) | | | |
|---|---|---|---|---|
| | Iron | Mn | Sulfate | Nitrate |
| MW PW02 | | | 12000 | 5.3 |
| MW 51 | 0.48 | 0.35 | 4600 | ND |
| BS 26 | 0.92 | 0.59 | 6100 | ND |
| MW 16 | ND | 2.2 | 7100 | 0.87 |
| MW 15 | ND | ND | 1000 | 2.6 |

# THE INTERNAL COMBUSTION ENGINE AS A LOW-COST SOIL VAPOR TREATMENT TECHNOLOGY

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## ABSTRACT

A low-cost and innovative soil vapor extraction (SVE) system using modified internal combustion engines (ICEs) to extract and destroy fuel hydrocarbons is being demonstrated at multiple United States Air Force sites. The ICE systems with advanced emissions controls were manufactured by VR Systems, Inc., formerly of Anaheim, California. Parsons Engineering Science, Inc., under contract to the Air Force Center for Environmental Excellence, is collecting cost and performance data to compare the ICE technology to traditional fuel hydrocarbon vapor treatment technologies and to provide recommendations for full-scale treatment, including estimates of operating and capital costs.

This paper presents a description of the ICE vapor extraction and treatment technology, and case studies for three sites in Arizona and one site in the District of Columbia, where the SVE/ICE technology is being used for remediation of unsaturated soils at these sites. Destruction/removal efficiencies (DREs) for the four ICE systems have averaged greater than 99.9 percent. A full-scale SVE system using ICE technology has successfully operated at Davis-Monthan Air Force Base (AFB), Arizona for 21 months, and has removed more than 700,000 pounds of total volatile hydrocarbons (TVH) at an average cost of $0.14 per pound. The ICE system operating at Luke AFB, Arizona has removed 169,000 pounds of TVH in 9 months of operation at an average cost of $0.23 per pound. At Bolling AFB, Washington D.C., the ICE system has operated for 7 months and removed over 47,000 pounds of TVH at an average cost of $0.54 per pound. At Williams AFB, Arizona, the ICE system has operated for 4 months and removed over 200,000 pounds of TVH at an average cost of $0.06 per pound. The higher costs per pound represent lower influent TVH concentrations and increased use of supplemental fuel as a result of decreasing extracted hydrocarbon concentrations. The TVH removal rate has ranged from 378 to 3,417 pounds per day and the weighted average influent TVH concentration ranged from 10,000 to 90,000 ppmv.

## 1. INTRODUCTION

A low-cost and innovative soil vapor extraction (SVE) system using modified internal combustion engines (ICEs) to extract and destroy fuel hydrocarbons from vadose zone soils is successfully being demonstrated at multiple United States Air Force sites. The ICE systems with advanced emissions controls were manufactured by VR Systems, Inc., formerly of Anaheim, California. The sites are contaminated with either JP-4 jet fuel or gasoline, and are located in Arizona and the District of Columbia. Parsons Engineering Science, Inc. (Parsons ES), under contract with the Air Force Center for Environmental Excellence (AFCEE), is collecting cost and performance data to compare the ICE technology to traditional vapor treatment technologies and to provide recommendations for full-scale treatment system designs, including projected operating and capital costs.

This paper presents a description of the ICE technology, a history and description of four sites that are successfully being remediated using the ICE technology, performance data for the ICE systems, and a comparison of the performance and cost of each system.

## 2. DESCRIPTION OF ICE TECHNOLOGY

Vapor extraction and combustion is an innovative technology that uses an ICE with advanced emission controls to extract and burn nonchlorinated hydrocarbon vapors from the vadose zone. Vapors are extracted from the subsurface by the intake manifold vacuum of the engine via vent wells (VWs) screened in contaminated intervals. The extracted vapors are then burned as fuel to run the engine. The ICE exhaust gases pass through a standard catalytic converter for complete oxidation before being discharged to the atmosphere. VR Systems, Inc. manufactured vapor recovery systems in three sizes: the single-engine V2C and V3, and the dual-engine V4. The performance specifications for the three VR Systems units, are provided in Table 1. A schematic diagram of a Model V4 is provided as Figure 1.

TABLE 1. PERFORMANCE SPECIFICATIONS
FOR VR SYSTEMS MODELS V2C, V3, AND V4

| Feature | V2C | V3 | V4 |
|---|---|---|---|
| Max. Hydrocarbon Destruction Rate | 15 lbs/hr | 55 lbs/hr | 110 lbs/hr |
| Destruction Efficiency for TVH/BTEX[a/] | >99% | >99% | >99% |
| Engine Size in Cubic Inch Displacement | 140 | 460 | 920 (2 x 460) |
| Max. Flow Rate in Cubic Feet/Min | 65 | 250 | 500 |
| Max. Vacuum in Inches of Mercury/Approx. Inches of Water | 18/245 | 18/245 | 18/245 |
| Required Soil Gas Hydrocarbon concentration (ppmv as gasoline)[b/] | 40,000 | 40,000 | 40,000 |

a/ TVH = total volatile hydrocarbons; BTEX = benzene, toluene, ethylbenzene, and xylenes.

b/ Per vendor specifications, the recommended influent vapor concentration in parts per million, volume per volume (ppmv) required to sustain >99% destruction efficiency without the addition of supplemental fuel (e.g., natural gas) to maintain efficient engine operation.

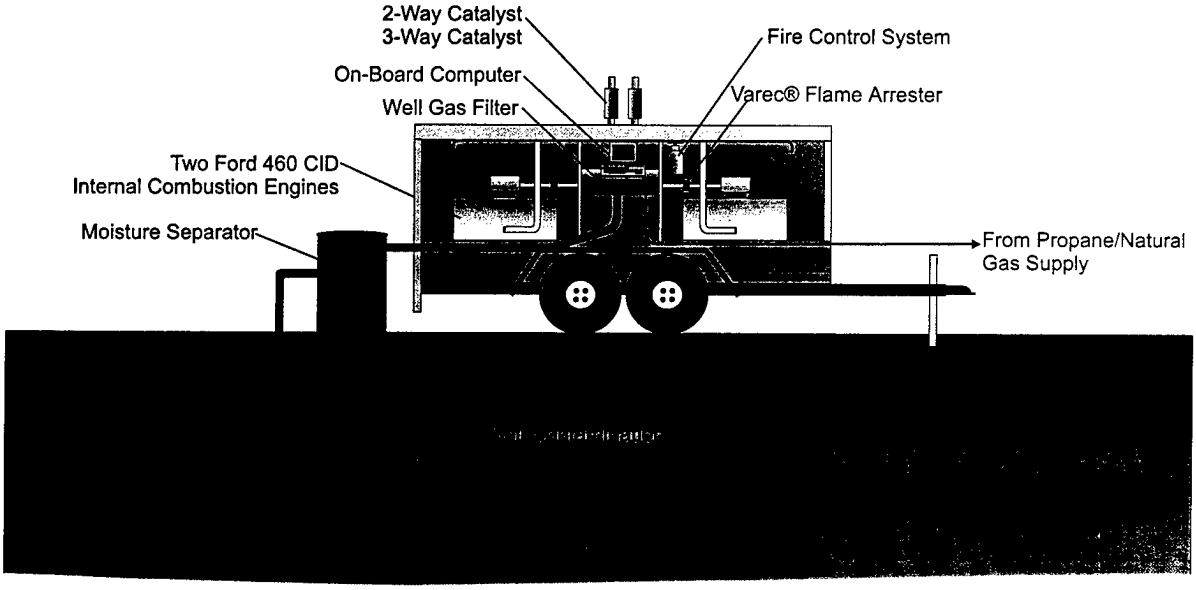



Figure 1. Model V4 ICE unit schematic.

The engines in the VR Systems units are modified Ford® gasoline-powered engines. Each VR Systems ICE/SVE system is equipped with an on-board computer system that provides the necessary monitoring for engine control. The 16-channel data reporting system monitors the engine's oil pressure/temperature, coolant temperature, exhaust temperature, exhaust percent oxygen, and engine speed and performance (extraction flow rate, inches of vacuum, supplemental fuel consumption, air/fuel ratio, and engine hours).

External electrical power is not required for these systems because the electronic ignition is battery-powered. The ICE units are equipped with a cellular phone modem for remote monitoring and to make necessary adjustments to engine speed to optimize engine performance and minimize supplemental fuel consumption. The remote monitoring capability allows for adjustments to be made while the unit is operating, and/or for the ICE unit to be started remotely.

Supplemental fuel (propane or natural gas) is used to provide smooth operation of the engine as extracted soil gas total volatile hydrocarbon (TVH) concentrations fluctuate. Soil vapor TVH concentrations in excess of 30,000 to 40,000 parts per million, volume per volume (ppmv) (depending on the British thermal unit [BTU] value of the influent soil vapors) generally are sufficient to sustain the engine speed without the need for supplemental fuel. The on-board computer regulates the fuel requirements of the engine through a master control unit. The control unit makes adjustments in the supplemental fuel flow to compensate for the changing influent hydrocarbon concentrations and to maintain the stoichiometric air-to-fuel ratio. By maintaining the proper air/fuel ratio, the TVH vapor destruction/removal efficiency (DRE) typically exceeds 99 percent, eliminating the need for air emissions permitting.

The regulatory acceptance of this technology for treatment of hydrocarbon vapors in soil gas has been widespread. VR Systems, Inc. ICE units have been approved for air treatment in the District of Columbia, Arizona, California, and 26 other states.

## 2. SITE HISTORIES AND DESCRIPTIONS

The following sections provide an overview of the history, site description, and ICE operation for each of the four sites.

### 2.1 Davis-Monthan AFB, Arizona

#### History

Site 35 is a jet fuel pumphouse consisting of nine 40,000-gallon and one 50,000-gallon underground storage tanks (USTs) containing JP-4 jet fuel, and an underground piping system that conveys the fuel to a fueling island. In 1985, a leak was detected in an underground fuel line, and an estimated 1.7 million cubic feet of soil was found to be contaminated. From 1989 to 1993, remedial investigations and feasibility studies were completed under the U.S. Air Force Installation Restoration Program (IRP). The remedial alternative selected for the site included SVE followed by air injection bioventing.

#### Site Description

Based on previous site investigations, soil contamination extended from near the ground surface to a depth of approximately 260 feet below ground surface (bgs). A maximum total fuel hydrocarbon concentration of 320,000 milligrams per kilogram (mg/kg) and a maximum soil gas TVH concentration of 140,000 milligrams per liter (mg/L) were measured at the site. Groundwater, which occurs at approximately 300 feet below ground surface, has not been impacted by the jet fuel spill.

#### ICE Operations

In 1993, a pilot-scale SVE test was performed, and based on the results, a full-scale SVE system was designed that consisted of a series of 28 vapor extraction wells (VWs), a blower system, a moisture separator, thermal oxidizer and catalytic oxidizer air treatment systems, a propane tank, and associated piping and controls. The system was designed to operate at a maximum flow rate of 3,000 standard cubic feet per minute (scfm) with an operation period of 4 to 6 years in the SVE mode, then 2 years in a bioventing (low-flow air injection) mode. The construction/installation cost was estimated to be $1.72 million, with an operating cost of $23,400 per month for 4 to 6 years, for a total SVE remediation cost of between $2.84 and $3.40 million (excluding the 2-year period of bioventing treatment).

Because of the prohibitively high cost for full-scale SVE treatment using thermal/catalytic oxidation, AFCEE contracted with Parsons ES to review alternative treatment technologies, including bioventing and the use of an ICE system for vapor extraction and treatment. Results from a 1-year bioventing pilot test indicated that biological degradation rates for fuel residuals were too slow (10 to 50 mg/kg/yr) to remediate the highly contaminated soils.[1] Following the bioventing pilot test, the SVE/ICE technology was evaluated to determine the technical feasibility and potential cost savings of this technology. A redesigned, full-scale SVE system using an ICE unit was installed in July and August 1995. The system included six VWs completed at varying depths to focus vapor extraction in the most contaminated soil intervals, and seven vapor monitoring points (VMPs) to monitor remediation progress. A remotely monitored, automated valving and flow rate control system was fabricated for this site so that the vapor flow from individual extraction wells can be remotely blended to provide optimum engine performance and minimum supplemental fuel use.

Start-up of a Model V4 ICE system occurred in September 1995, and the system operated through October 1996. On October 31, 1996, approximately 450 days from start-up, the decreased extracted TVH concentrations and the resulting increased supplemental fuel use led to a decision to replace the

dual-engine Model V4 ICE with a single-engine Model V3 ICE system, which currently is operating at the site.

## 2.2 Bolling AFB, Washington, DC

### History

The former Car Care Center at Building 41 served as an auto repair and fueling facility for Bolling AFB from 1936 through 1982. During this period, the station used several USTs for storage of gasoline and waste oils. The waste oil tanks were abandoned in place in the early 1980s, and removed in 1995. The gasoline USTs were removed in 1983 and 1994. Site personnel have indicated that spills from, and overfilling of, the former USTs located north and west of Building 41 are the most likely sources of subsurface fuel contamination documented at the site.

### Site Description

The maximum detected soil TVH concentration was 16,000 mg/kg in a soil sample collected at 20 to 21 feet bgs. The maximum detected soil total benzene, toluene, ethylbenzene and xylenes (BTEX) concentration was 670 mg/kg, in a soil sample from 18 to 20 feet bgs. The maximum TVH concentration detected in soil gas was 580,000 ppmv in a sample collected from the 9.5- to 10-foot bgs interval during installation of two vapor extraction/air injection VWs and two VMPs that were installed in September 1996 to support an ICE demonstration at this site. Groundwater at the former Car Care Center is typically encountered at depths of 18 to 20 feet bgs. Groundwater contamination consists of mobile light nonaqueous-phase liquid (LNAPL) and dissolved fuel contamination. Mobile LNAPL has historically been observed in site monitoring wells at a maximum measured thickness of 0.81 foot; however, attempts to recover the mobile LNAPL have not been productive, and only approximately 500 gallons of mobile LNAPL has been recovered.

### ICE Operations

A demonstration to test the effectiveness of an SVE system using an ICE to extract and treat volatile fuel hydrocarbons began in November 1996. A Model V4 ICE system, extracting vapors from two VWs, operated at the site from November 13, 1996 until January 16, 1997, and a Model V3 ICE system began operating on January 21, 1997, and is currently in operation.

## 2.3 Luke AFB, Arizona

### History

Site SS-42 is located at the bulk fuels storage yard at Luke AFB. A former oil/water separator and associated 1,000-gallon UST system that received condensate from two adjacent aboveground storage tanks (ASTs) are present at the site. The oil/water separator system and ASTs were installed in 1954. Prior to 1960, aviation gas and JP-4 were delivered to the bulk fuels storage area by rail car and off-loaded through a hydrant system to the ASTs. From 1960 to 1993, the fuel delivery system consisted of a combination of aboveground and underground distribution pipelines. In 1992, a fuel release from the oil/water separator system was detected. In September 1993, the oil/water separator and associated 1,000-gallon UST were removed.[2]

### Site Description

In May 1995, three air injection VWs and four multi-depth VMPs were installed and sampled near the former oil/water separator as part of a bioventing treatability study.[2] Total petroleum hydrocarbon

(TPH) results from soil sampling ranged from 4.3 mg/kg in a sample from 150 feet bgs to a maximum of 12,000 mg/kg in a sample from 70 bgs. The maximum detected soil BTEX concentration was 414 mg/kg in a soil sample from 70 feet bgs. A sample at 200 feet bgs had a TPH concentration of 5.2 mg/kg, and no detected BTEX. Currently, the top of the groundwater table occurs beneath the site at a depth of approximately 320 feet bgs. Groundwater sampling data indicate that the groundwater beneath the site has not been impacted by the released petroleum hydrocarbons.[2]

ICE Operations

A demonstration of a Model V3 ICE system to extract and treat fuel hydrocarbons began at the site on August 6, 1996. The system was shut down from November 21, 1996 until January 16, 1997 because chlorinated solvents were thought to be present in the soil gas. The Model V3 ICE system was restarted on January 16, 1997, and is currently in operation.

2.4 Williams AFB, Arizona

History

Site ST-12 is a former liquid fuels storage area located at the former Williams AFB. The site has been impacted primarily by releases of JP-4 and AVGAS, which were attributable to multiple documented fuel spills and leaks between 1977 and 1989, and possibly to other undocumented fuel spills and leaks that have occurred since Williams AFB initiated operations in 1942.

Site Description

During a 1993 deep soils investigation, 384 soil samples were collected from 16 soil boreholes. TPH as JP-4 were detected in 227 of the 384 samples at concentrations ranging from 0.42 to 35,000 mg/kg. The maximum TPH concentration of 35,000 mg/kg was detected in a soil sample from 174 feet bgs. The maximum soil BTEX concentration of 1,151 mg/kg was detected in a soil sample from 195 feet bgs.

Shallow groundwater elevations have steadily increased since 1989, due to the decrease in agricultural use of the surrounding area, and the current depth to water is 200 to 210 feet bgs. Groundwater contamination consists of mobile LNAPL and dissolved fuel contamination. Mobile LNAPL thickness data have been collected from site wells since 1990. The maximum measured thickness has been 15 feet. Volume estimates of LNAPL in the subsurface at Site ST-12 range from 0.65 to 1.4 million gallons.[3]

ICE Operations

A demonstration to test the effectiveness of an SVE system using ICE technology to extract and treat volatile fuel hydrocarbons from the unsaturated soils began in February 1997. One dual-phase extraction (DPE) well and four VMPs were installed in September 1996. Two Model V4 ICE systems are presently operating at the site. The first ICE system (V4A) was started on February 6, 1997, and the second system (V4B) was started in April 1997.

## 3. FIELD DEMONSTRATION RESULTS

During operation of the ICE systems at each site, monthly sampling events, that include collecting influent and effluent samples from the ICE systems, are being conducted by Parsons ES to evaluate the performance of each of the systems. The influent and effluent vapor streams of the ICE systems were sampled using 1-liter SUMMA® canisters, and samples were analyzed by Air Toxics, Ltd. of Folsom

California for TVH and BTEX using USEPA Method TO-3. This section provides a summary of TVH removal rates and costs, TVH DREs, and reliability and maintainability of the ICE systems.

## 3.1 Hydrocarbon Removal Rates

The total pounds of TVH removed for each site are presented in Figure 2 as a function of total days from startup, and the TVH removal rate (pounds per day) and average influent TVH concentration are presented in Table 2.

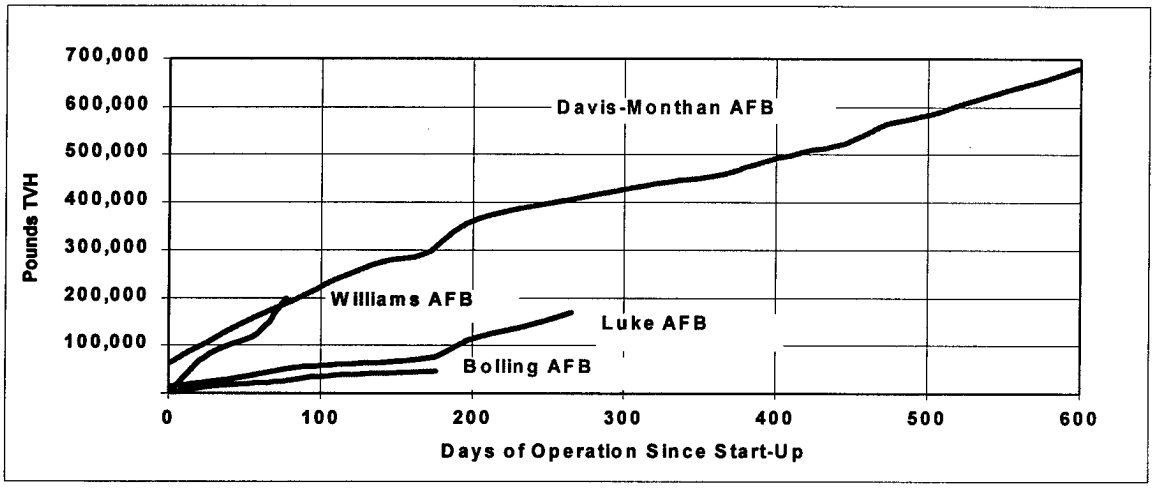



Figure 2. Total pounds TVH removed.

TABLE 2. AVERAGE INFLUENT TVH CONCENTRATIONS AND AVERAGE DAILY TVH REMOVAL RATES

| Site Name | Weighted Average Influent TVH Concentration (ppmv) | Average Daily TVH Removal Rate (pounds/day) |
|---|---|---|
| Davis-Monthan AFB, AZ | 24,000 | 1,249 |
| Bolling AFB, DC | 8,800 | 321 |
| Luke AFB, AZ | 21,000 | 940 |
| Williams AFB, AZ | 90,000 | 3,417 |

The total pounds of TVH removed to date has ranged from 47,550 pounds at Bolling AFB (378 pounds per day) during 148.3 days of actual operation, to over 700,000 pounds at Davis-Monthan AFB (1,249 pounds per day) during 561 days of actual operation. Site ST-12 at Williams AFB has the highest TVH soil gas concentrations (90,000 ppmv weighted average), which currently are capable of supporting two Model V4 ICE units with less than 10 percent supplemental fuel required to maintain smooth operation of the engines. The average TVH removal rate at Site ST-12 has been 3,417 pounds per day. Approximately 169,000 pounds of TVH has been removed at Site SS-42, Luke AFB, during 179.6 days of actual operation, and the average TVH removal rate has been 940 pounds per day.

## 3.2 Hydrocarbon Removal Costs

The cost per pound of TVH removed was estimated based on a prorated 30-day month with the capital cost of each ICE unit averaged over an estimated 3-year life of the ICE unit. Also included in the daily cost were labor and other direct costs for operation, maintenance, and sampling (including laboratory costs), and actual supplemental fuel cost during operation. For example, the capital costs for

the Model V3 ICE units operating at Bolling AFB and Luke AFB are $60,170. The capital costs for the two Model V4 ICE units operating at Williams AFB is $85,000 (ICE unit V4A) (includes engine rebuild), and $75,954 (ICE unit V4B). The V4A unit at Williams AFB also was used during the initial 450 days of the ICE demonstration at Davis-Monthan AFB.

The actual cost per pound of TVH removed and treated by the ICE has ranged from $0.04 to $0.93 per pound (Figure 3). The average cost per pound of TVH removed has ranged from $0.06 per pound at Site ST-12, Williams AFB to $0.54 per pound at the former Car Care Center, Bolling AFB. The higher costs per pound represent lower influent TVH concentrations and increased use of supplemental fuel as a result of decreasing extracted hydrocarbon concentrations. Where appropriate, the ICE systems have been optimized to increase influent TVH concentrations and decrease supplemental fuel use. For example, at Davis-Monthan AFB in August 1996, approximately 325 days from the start-up, one of the 460-cubic-inch engines was turned off to reduce supplemental fuel use, and the flow from individual wells was readjusted to optimize engine performance and minimize supplemental fuel use. At Davis-Monthan AFB on October 31, 1996, approximately 450 days from start-up, and at Bolling AFB on January 21, 1997, approximately 60 days from startup, the decreased extracted TVH concentrations and the resulting increased supplemental fuel use led to decisions to replace the Model V4 ICE with a Model V3 ICE system at each of these sites.

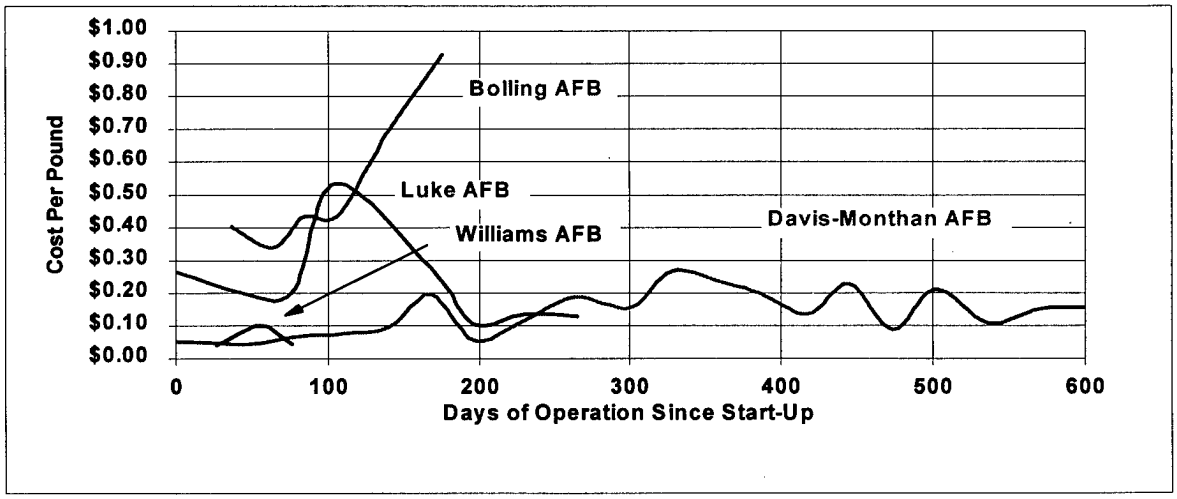



Figure 3. Cost per pound of hydrocarbon removed.

3.3 Hydrocarbon Destruction/Removal Efficiencies

DREs for the ICE systems were calculated using the following equation:

$$DRE = \frac{Concentration_{Influent} - Concentration_{Effluent}}{Concentration_{Influent}} \times 100$$

The influent and effluent vapor streams of the ICE systems were sampled using 1-liter SUMMA® canisters, and samples were analyzed by Air Toxics, Ltd. of Folsom California for TVH and BTEX using USEPA Method TO-3. Each of the ICE systems have been an average of 99.8 percent efficient at removing TVH from extracted soil vapors.

The ICE/SVE systems used at each site have met the air emission standards for the respective regulating authorities with one exception at Bolling AFB due to the oxygen sensor requiring

replacement. The average daily TVH air emissions for the ICE units operating at each of the sites are shown in Table 3 and the total daily TVH emissions is shown in Figure 4. System performance monitoring will continue to ensure compliance with state and local emissions regulations and to determine when site closure soil sampling should be conducted.

TABLE 3. DAILY TVH EMISSIONS

| Site Name | Average Daily TVH Emissions (pounds/day) | Air Emissions Standards (pounds/day) |
|---|---|---|
| Davis-Monthan AFB, AZ | 0.70 | 2.4 (Pima County, AZ) |
| Bolling AFB, DC | 0.84 | 1.0 (DC Air Resources Div.) |
| Luke AFB, AZ | 0.22 | 3.0 (Maricopa County) |
| Williams AFB, AZ | 1.28 | 3.0 (Maricopa County) |

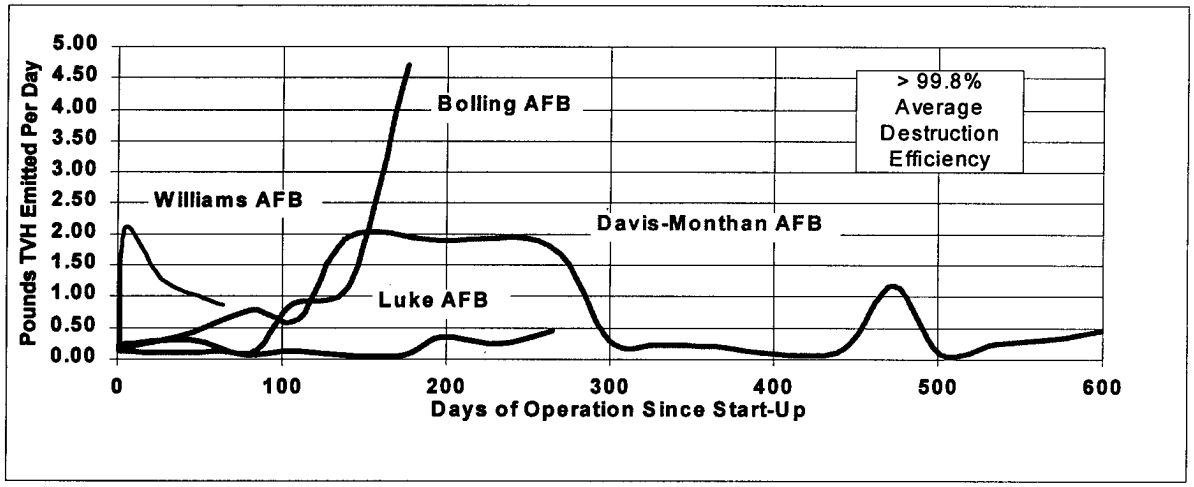



Figure 4. Total daily TVH emissions.

3.4 Reliability and Maintainability

The ICE systems have proved to be a reliable SVE technology. The operational efficiency as a percent of total possible engine hours is presented for each site in Table 4.

TABLE 4. SYSTEM RELIABILITY

| Site Name | Model ICE System(s) Operating at Site | Operational Efficiency (Percent) |
|---|---|---|
| Davis-Monthan AFB, AZ | V4, V3 | 87 |
| Bolling AFB, DC | V4, V3 | 84 |
| Luke AFB, AZ | V3 | 86 |
| Williams AFB, AZ | 2 V4s | 82 |

The primary ICE system components with a potential for mechanical problems include the alternator/voltage regulator, the battery (especially in hot climates), and the oxygen sensor. Long-term maintenance issues include an engine rebuild being required following 10,000 to 15,000 engine hours. The cost of the engine rebuild is approximately $10,000, including parts, labor, and shipping the unit to and from the site. The catalytic converters require replacement every 5,000 to 10,000 engine hours at

an approximate cost of $450 each. In addition, problems with the on-board computer system may arise due to dust and engine vibrations.

Regular monthly maintenance for the ICE systems requires approximately 8 hours per month, and includes draining the moisture separator, changing the engine oil and oil filter, replacing the carburetor air filter and spark plugs, and checking engine coolant level, battery charge, and water pump. Approximately 8 additional hours per month should be anticipated for unexpected shutdowns.

## 4. CONCLUSIONS

The DRE evaluation indicates that each of the ICE units have been 99.9 percent efficient at removing TVH from extracted soil vapors. The ICE/SVE systems used at each site have met the air emission standards for each regulating authority. The actual cost per pound of TVH removed and treated by the ICE systems has ranged from $0.04 to $0.93 per pound. The average cost per pound of TVH removed has ranged from $0.06 per pound at Site ST-12, Williams AFB to $0.54 per pound at the former Car Care Center, Bolling AFB. The higher costs per pound represent lower influent TVH concentrations and increased use of supplemental fuel as a result of decreasing extracted hydrocarbon concentrations. The TVH removal rate has ranged from 321 to 3,417 pounds per day and the weighted average influent TVH concentration ranged from 8,800 to 90,000 ppmv.

The ICE systems have proven to be a reliable SVE and vapor treatment technology. The operational efficiency as a percent of total possible engine hours for each of the four Air Force demonstration sites ranged from 82 to 87 percent. Regular monthly maintenance for the ICE systems requires approximately 8 hours per month, and approximately 8 additional hours per month should be anticipated for unexpected shutdowns.

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# *IN SITU* BIOVENTING: RESULTS OF THREE PILOT TESTS PERFORMED AT US ARMY INSTALLATIONS

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## ABSTRACT

*In situ* bioventing is defined as soil ventilation for the enhanced aerobic biodegradation of hydrocarbon contaminants in vadose zone soils. The US Air Force Center for Environmental Excellence (AFCEE) has initiated bioventing pilot tests at over 145 sites nationwide, and has concluded that bioventing is a cost-effective technology for soil remediation at most of these sites (1). The US Army Environmental Center (USAEC) recently contracted with Parsons Engineering Science, Inc. (Parsons ES) through AFCEE to perform bioventing pilot tests at three Army sites.

The pilot test sites included a former gasoline underground storage tank (UST) site at Fort Bliss, Texas; a former waste disposal pit at Fort Rucker, Alabama; and a former gasoline and diesel fuel UST site at Fort Carson, Colorado. A soil gas survey also was performed at a former petroleum UST site at Camp Ripley, Minnesota. The survey established that oxygen was present at concentrations high enough to support aerobic hydrocarbon biodegradation, and demonstrated that vadose zone soil remediation was unnecessary.

Each bioventing pilot test consisted of initial and extended phases. During the initial phase, a vent well (VW) and several soil vapor monitoring points (MPs) were installed at each site, baseline site conditions were characterized, and a blower system was installed and optimized. Oxygen levels were depleted, and carbon dioxide concentrations were elevated in soil gas samples collected from fuel-impacted soils. Based on these indicators, aerobic petroleum hydrocarbon degradation was demonstrated at all three sites. *In situ* respiration rates ranged from 75 to 1450 milligrams (mg) of fuel per kilogram (kg) of soil per year. Air permeability testing demonstrated that oxygen could be delivered uniformly through a variety of soil types, including silty clays. Radii of influence for these single-VW pilot-scale systems ranged from 30 to at least 45 feet. Although a zone of perched groundwater at the Fort Rucker site and some low-permeability soils at the Fort Carson site interfered with oxygen delivery, bioventing was generally found to be a feasible remedial technology at all three sites during the initial phase of testing. The systems installed at the Fort Bliss and Fort Rucker sites were capable of providing full-scale treatment in permeable, unsaturated soils in the contamination source areas. Because the areal extent of soil contamination at the Fort Carson site exceeded the zone of influence of the pilot-scale system, the system was expanded by installing five VWs, six MPs and an upgraded blower system.

The bioventing systems installed at the Fort Rucker and Fort Carson sites are currently operating for a 12-month extended testing phase to determine the long-term influences of air injection on petroleum hydrocarbon biodegradation rates and concentrations in soil gas. At the end of the 12-month operating period, respiration testing and soil gas sampling will be conducted to determine the degree of cleanup that has been achieved. One year of system operation has been completed at the Fort Bliss site, and year-end testing showed minor decreases in petroleum hydrocarbon levels and significant decreases in biological oxygen demand, indicating that continued operation of the air injection bioventing system would not be effective. Low-flow-rate soil vapor extraction (SVE) has been recommended to complete the cleanup of vadose zone soils at the Fort Bliss site.

## 1. INTRODUCTION

A growing emphasis is being placed on implementing remedial technologies that are inexpensive yet protective of human health and the environment. One such technology for the remediation of fuel-contaminated soil is *in situ* bioventing, defined as soil ventilation for the enhanced aerobic biodegradation of hydrocarbon contaminants in vadose zone soils.

In the United States, researchers from the Texas Research Institute (2), Chevron (3), and the US Air Force (4,5) were among the first to observe or utilize enhanced petroleum hydrocarbon biodegradation through the use of soil ventilation. The most extensive project in the bioventing arena to date has been carried out by AFCEE through their Bioventing Pilot Test Initiative. This initiative included pilot testing activities at 145 sites to examine the feasibility of bioventing for the remediation of petroleum-contaminated soils in a variety of soil and climatic conditions, and on a wide range of petroleum contaminants, including automotive gasoline, aviation gasoline, jet fuel, diesel fuel, and heating oil. Pilot tests were conducted according to standard protocol procedures (6) in 38 states, including Hawaii and Alaska, and in all 10 US Environmental Protection Agency (USEPA) regions. Pilot testing activities were conducted from April 1992 through June 1996. Bioventing was found to be effective under a wide variety of soil and climatic conditions, and a significant data set was compiled and used to complete a bioventing principles and practices manual (7).

Due to the success of its bioventing initiative, AFCEE retained Parsons ES for an extended bioventing program to continue activities at 52 petroleum-contaminated sites across the country. The extended bioventing program started in September 1994 and will continue through 1999. The objectives of this program are to perform bioventing pilot testing at a number of new sites (sites that were not tested during the bioventing initiative), to continue or expand bioventing remediation at sites tested during the bioventing initiative, and to justify regulatory closure following the completion of treatment. A general Engineering Evaluation and Cost Analysis (EE/CA) for the bioventing technology also was prepared (8).

In September 1995, USAEC retained Parsons ES through the AFCEE extended bioventing program to perform bioventing pilot tests at the subject sites. USAEC provided funding and liaison with the Army installations, while AFCEE provided the contracting mechanism and technical oversight in this interagency effort. This cost-effective technology, developed in large part by AFCEE, is being transferred to the Army, providing the Army with an excellent opportunity to apply the technology at several of its facilities. Pilot tests were originally programmed for Building 675 at Fort Bliss, Texas; Solid Waste Management Unit (SWMU) #14 at Fort Rucker, Alabama, and the Building U-3 Petroleum, Oils, and Lubricants (POL) site at Camp Ripley, Minnesota. The pilot test at Camp Ripley was later reprogrammed for Building 8200 at Fort Carson, Colorado.

## 2. BIOVENTING PILOT TEST PROCEDURES

Each bioventing pilot test was performed in accordance with AFCEE protocol procedures (6). The objectives of each test were 1.) to determine if native soil microbial populations could biodegrade petroleum hydrocarbon contaminants, 2.) to quantify the rate at which the microbial populations could biodegrade fuel when stimulated with a supply of oxygen, and 3.) to determine if oxygen could be uniformly supplied throughout contaminated soil zones.

A preliminary soil gas survey was conducted at most of the sites to determine if oxygen was depleted and confirm that bioventing would be required (9). At each oxygen-depleted site, a VW was installed near the center of the contaminated soil region, and three or four MPs were installed to monitor soil gas conditions at various distances from the VW. The subsurface was characterized, and soil samples were collected and analyzed for total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene, xylenes (BTEX), and several inorganic and physical parameters.

Initial soil gas conditions were then characterized. The objectives of the initial soil gas characterization were to measure the initial concentrations of total volatile hydrocarbons (TVH) and BTEX in the soil gas, and to determine if aerobic fuel biodegradation was occurring in contaminated soils. The uptake of oxygen and the production of carbon dioxide are indicators of hydrocarbon biodegradation. A site suitable for the application of bioventing will have depleted oxygen and elevated carbon dioxide concentrations in contaminated soil zones.

*In situ* respiration testing was conducted at each site to determine the rates of microbial oxygen utilization and petroleum hydrocarbon biodegradation. Air was injected into contaminated soils using vacuum pumps at rates of approximately 1 cubic foot per minute (cfm) per MP screened interval for periods of approximately 20 hours. After air injection ceased, the rates of oxygen consumption were monitored. Observed oxygen utilization rates, estimated air-filled porosity values, and stoichiometric equations were used to estimate the rates of aerobic petroleum hydrocarbon biodegradation at each point.

Air permeability testing was performed at each site to determine if oxygen could be uniformly supplied through the fuel-contaminated soils. At each site, air was injected into the VW at flow rates of approximately 0.5 to 1 cfm per foot of screen while pressure response and changes in soil gas composition were observed at surrounding MPs. Optimal air injection flow rates, air injection pressures, and radii of influence are the critical parameters required for the design of full-scale bioventing systems, and these parameters were determined during the permeability test.

Following the initial testing phase, a small bioventing blower system was installed onsite for continuous operation during a 1-year extended period of air injection into the VW(s). Following the completion of the 1-year extended testing phase, the blower units will be shut down for a 30-day period to allow the subsurface to return to equilibrium conditions. Soil gas sampling and respiration testing will then be conducted to determine the degree of remediation achieved over the year of pilot-scale system operation. Following the interpretation of data, recommendations will be made for future action at the sites. Generally, recommendations can include the installation of additional VWs, MPs, and a larger blower system for full-scale treatment; continued operation of the existing pilot-scale system; or confirmation soil sampling to support site closure. If the year-end testing results show that additional periods of air injection bioventing would be ineffective, an alternative treatment technology will be recommended.

## 3. SITE DESCRIPTIONS, RESULTS, AND RECOMMENDATIONS

### 3.1 BUILDING 675 AT FORT BLISS, TEXAS

The Building 675 site was a gasoline service station from 1951 to 1985. In 1991, the gasoline underground storage tank (UST) system, included three 10,000-gallon USTs and associated product piping, was removed. Soil contamination was observed during UST system removal.

In April 1996, bioventing pilot testing activities began with an initial soil gas survey using a Geoprobe® unit. The survey demonstrated that oxygen levels were depleted in contaminated soil zones, indicating that the site could be remediated using bioventing. A single VW and three MPs were subsequently installed in contaminated vadose zone soils. A hydrogeologic cross-section illustrating the lithology of the Building 675 site is included as Figure 1. Petroleum-contaminated soils were encountered at depths of 18 to 55 feet below ground surface (bgs).

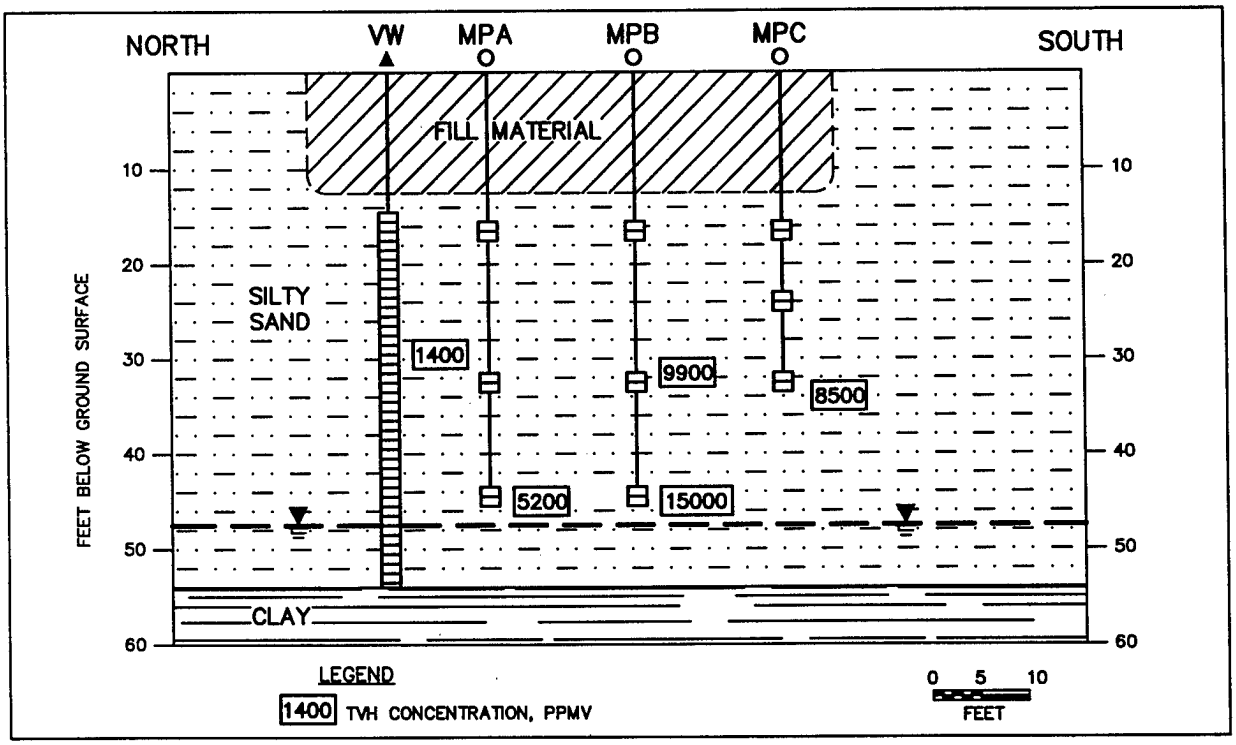



**Figure 1. Building 675 (Fort Bliss, Texas) hydrogeologic cross-section.**

Oxygen was depleted, and carbon dioxide concentrations were elevated (as high as 13 percent) in contaminated soil zones. During the permeability test, a radius of oxygen influence of at least 40 feet was observed at an air injection rate of 16.5 cfm (approximately 0.5 cfm per foot of VW screened interval in unsaturated soils). Initial hydrocarbon biodegradation rates (Kb) ranged from 1,080 to 1,700 milligrams of fuel per kilogram of soil per year (mg/kg-yr), and averaged 1,450 mg/kg-yr. A 1-horsepower regenerative blower system was installed, and air was continuously injected into the VW until late March 1997. After 1 month of system shutdown, soil gas sampling and *in situ* respiration testing were performed. Results of initial and year-end sampling and testing are summarized in Table 1.

TABLE 1. CHANGES OBSERVED DURING ONE YEAR OF BIOVENTING AT BUILDING 675.

| Parameter | Units | Sampling location and depth bgs | | | | Average |
|---|---|---|---|---|---|---|
| | | MPA-45 | MPB-32 | MPB-45 | MPC-32 | |
| Initial TVH | ppmv | 5200 | 9900 | 15000 | 8500 | 9650 |
| Year-end TVH | ppmv | 14000 | 4500 | 21000 | 5600 | 11275 |
| Initial BTEX | ppmv | 559 | 1440 | 2290 | 1830 | 1530 |
| Year-end BTEX | ppmv | 705 | 49.5 | 1813 | 195 | 690 |
| Initial Kb | mg/kg-yr | 1080 | 1700 | 1330 | 1700 | 1450 |
| Year-end Kb | mg/kg-yr | 76 | 270 | 210 | 330 | 220 |
| Initial oxygen | percent | 0 | 0 | 0 | 0 | 0 |
| Year-end oxygen | percent | 16 | 8 | 9.5 | 6 | 9.9 |

Average TVH concentrations in soil gas increased slightly across the site. Increases in TVH concentrations were greatest at sampling locations immediately above the perched water table, indicating that contaminants are being transported from the perched water into the soils via smearing (fluctuations in the groundwater surface) and/or volatilization. In comparison, the average BTEX concentration decreased by 55 percent, indicating preferential weathering and biodegradation of the BTEX compounds. Average hydrocarbon biodegradation rates decreased by 85 percent, and static oxygen concentrations averaged 10 percent after an entire month of system shutdown. These results indicate significant decreases in biological activity at the site. The soil microbial population may be limited by the lack of moisture or nutrients (total Kjeldahl nitrogen concentrations were below the 5-mg/kg detection limit). Regardless of the cause, aerobic hydrocarbon biodegradation rates dropped significantly over 1 year of bioventing, indicating that extended periods of air injection bioventing will not be effective in further reducing concentrations of hydrocarbon contaminants. Insignificant oxygen demand in fuel-contaminated soils has been observed previously at Air Force sites in Albuquerque, New Mexico; Las Vegas, Nevada; Phoenix, Arizona; and Tucson, Arizona, indicating that bioventing may not be suitable for long-term treatment of soils at many sites in the desert southwest.

Because TVH are still present at high concentrations in soil gas at the Building 675 site, it is unlikely that soil hydrocarbon concentrations have been remediated below Texas Natural Resources Conservation Commission (TNRCC) risk-based action levels. Low-flow-rate SVE has been recommended to complete treatment of soils at this site. The perched water layer, which appears to be impacted by petroleum hydrocarbons, must also be characterized.

### 3.2 SWMU #14 AT FORT RUCKER, ALABAMA

SWMU #14 at Fort Rucker, Alabama, is a former waste POL disposal pit. From 1978 to 1980, the pit was used for the disposal of contaminated JP-4, tanker truck washout fluids, and possibly motor oil. The pit was closed in 1980 by adding clay to absorb waste POL material, and the top was mounded to promote surface water runoff.

In May 1996, bioventing pilot testing activities began with the installation of a nested pair of VWs and three MPs in contaminated vadose zone soils. A hydrogeologic cross-section illustrating the lithology of SWMU #14 is included as Figure 2. Petroleum-contaminated soils were encountered from near the

surface to approximately 45 feet bgs, where groundwater was encountered. A saturated soil zone was encountered; the base of this zone occurred at depths of 15 to 17 feet bgs and coincided with a low-permeability soil unit that contained layers of tar, marking the former bottom of the disposal pit. Bentonite seals were placed in the boreholes at these depths to prevent contaminated perched groundwater from migrating to the water table aquifer. TPH concentrations in this saturated zone were as high as 25,000 mg/kg. Total BTEX concentrations in soils were as high as 11,000 micrograms per kilogram (µg/kg).

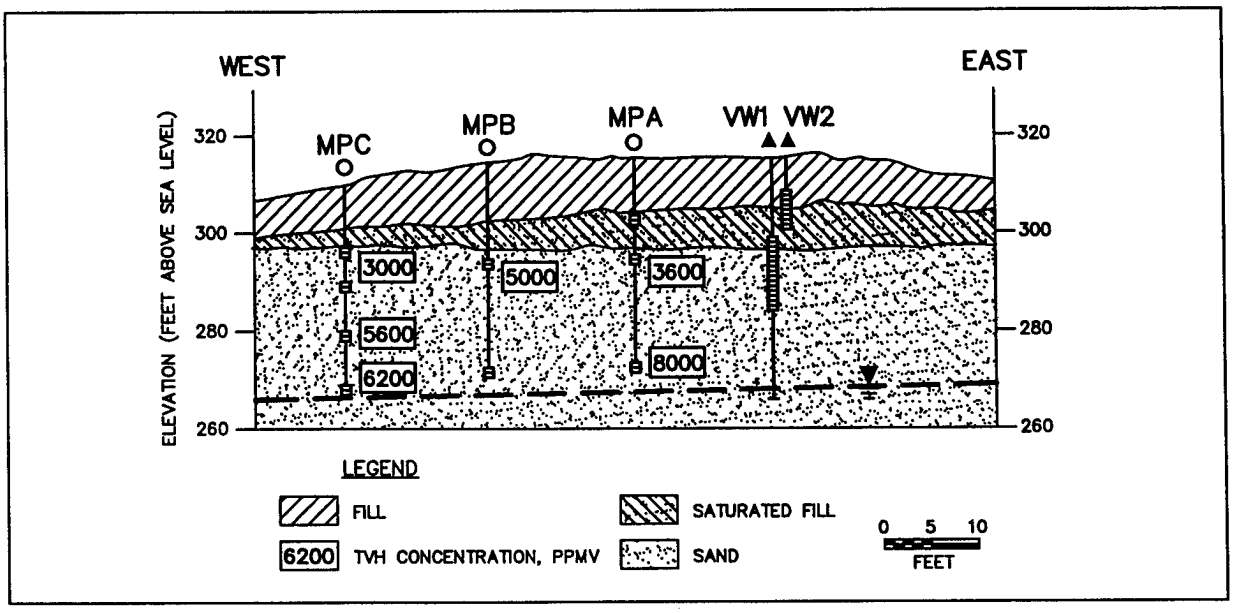



**Figure 2. SWMU #14 (Fort Rucker, Alabama) hydrogeologic cross-section. Oxygen influence was achieved at all depths except the saturated layer at the bottom of the former disposal pit.**

Oxygen was depleted and carbon dioxide concentrations were elevated (as high as 15 percent) in contaminated soil zones. During the air permeability test, a radius of oxygen influence of at least 45 feet was observed in unsaturated soils after 40 hours of air injection into VW-1 at a rate of 16 cfm (Table 2). Based on pressure response and the rapidity of oxygen response observed at MPC, the radius of oxygen influence could be 70 feet or greater. Hydrocarbon biodegradation rates ranged from 400 to 870 mg/kg-yr, and averaged 640 mg/kg-yr. A 2-horsepower regenerative blower system was installed for continuous air injection into the nested VW until June 1997. Year-end testing is scheduled for July 1997.

TABLE 2. OXYGEN INFLUENCE OBSERVED AT SWMU #14.

| Location | Distance From VW-1 | Screen Depth (feet bgs) | Initial $O_2$ (percent) [a/] | Final $O_2$ (percent) [b/] |
|---|---|---|---|---|
| MPA | 15 | 12 | saturated | saturated |
| | | 20 | 0.0 | 13.5 |
| | | 40 | 0.0 | 21.0 |
| MPB | 30 | 20 | 8.0 | 1.1 |
| | | 40 | 0.0 | 20.5 |
| MPC | 45 | 14 | 11.0 | saturated |
| | | 20 | 8.0 | 0.0 |
| | | 30 | 0.0 | 15.9 |
| | | 40 | 0.0 | 17.1 |

a/ Measurements were taken prior to air injection.
b/ Measurements were taken after 40 hours of air injection into VW-1.

It is anticipated that soil remediation will be complete after 1 year of treatment in unsaturated soils. Although the perched water layer interfered with oxygen delivery during initial pilot testing, it is possible that some of these soils were oxygenated during long-term air injection. Air permeability will likely increase as moisture levels decrease during drier summer and autumn months. Additionally, air flow through shallow soils should increase as injected air gradually depresses the perched water surface and displaces some moisture in the soil pore space. Soils that remain saturated over the extended testing phase may also be oxygenated by diffusion across the perched water surface. A soil sample will be collected from this saturated layer, and dissolved oxygen (DO) measurements will be collected to determine if system operation increases DO levels in the perched groundwater layer.

## 3.3 BUILDING U-3 POL SITE AT CAMP RIPLEY, MINNESOTA

The Building U-3 POL site at Camp Ripley, Minnesota, is a former truck service area where fuels were stored and dispensed. A 10,000-gallon diesel fuel UST, a 10,000-gallon gasoline UST, a 5,000-gallon gasoline UST, and a dispenser pump island were removed in 1992. The 5,000-gallon UST and the dispenser island were believed to be the primary sources of fuel contamination at the site. Numerous soil borings, groundwater monitoring wells and wells for SVE and air sparging pilot testing had been installed to characterize the hydrogeologic conditions and define the extent of petroleum hydrocarbon contamination.

The Building U-3 foundation is slab-on-grade, and the area surrounding the building is paved with asphalt. Soils at the site consist primarily of medium-grained sands, and groundwater occurs at a depth of approximately 18 feet bgs. Benzene and gasoline-range TPH had been detected in soils near the groundwater table at concentrations as high as 4.5 mg/kg and 1,000 mg/kg, respectively. Benzene concentrations in groundwater were as high as 570 micrograms per liter (µg/L), and the groundwater contaminant plume is approximately 500 feet long by 300 feet wide. SVE and air sparging pilot testing had been performed by other parties prior to the initiation of bioventing pilot testing activities.

In March 1996, Parsons ES collected soil gas samples from all accessible wells in the contamination source area to characterize subsurface conditions in preparation for the bioventing pilot test. Table 3 summarizes the initial soil gas chemistry at the site. Oxygen was present at near-atmospheric concentrations, ranging from 19.8 to 20.7 percent. Also, carbon dioxide was present at low concentrations, ranging from 0.3 to 1.5 percent. Initial TVH concentrations in soil gas ranged from 31 to 195 ppmv, which are near-background levels. Results of the soil gas survey showed that any volatile fuel hydrocarbon contamination in the vadose zone has either naturally biodegraded or was removed during earlier SVE pilot testing. At this site, further vadose zone remediation using either SVE or bioventing is unnecessary. Funding for the Camp Ripley pilot test was subsequently transferred to Fort Carson, Colorado.

TABLE 3. INITIAL SOIL GAS CHEMISTRY AT THE BUILDING U-3 POL SITE.

| Well | Oxygen (percent) | Carbon Dioxide (percent | TVH (ppmv) |
|---|---|---|---|
| EV-1 | 20.4 | 0.95 | 140 |
| MW-2 | 19.8 | 1.5 | 195 |
| MW-3 | 20.7 | 0.3 | 38 |
| MW-4 | 20.6 | 0.3 | 31 |
| MW-5 | 20.3 | 0.7 | 115 |

This case study demonstrates the importance of soil gas surveys for site screening and remedial action planning (9). Prior to the soil gas survey, a full-scale SVE/air sparging system had been recommended to the Army at a total cost of $360,000. For a cost of approximately $3,500, this soil gas survey demonstrated that active remediation was unnecessary.

## 3.4 BUILDING 8200 AT FORT CARSON, COLORADO

The Building 8200 site at Fort Carson, Colorado, is a former fueling system that consisted of four 20,000-gallon USTs (one containing gasoline and the others containing diesel fuel) and associated fuel lines and pump islands. The tanks and pump islands were removed from the site in November 1996, following completion of the initial bioventing pilot test. Site investigations performed in 1992 and 1994 indicated the presence of petroleum-contaminated soils at the site.

Bioventing pilot testing activities began in April 1996 with a soil gas survey using existing groundwater monitoring wells. The survey indicated that oxygen levels were depleted in zones of contaminated soil. In July 1996, one VW (VW2) and seven MPs (MPA through MPG) were installed in contaminated vadose zone soils (Figure 3). Soils consist of dense, brittle silt and clay soils overlying siltstone bedrock. Groundwater occurs at depths between 16 and 19 feet bgs, and perched water is present in thin layers of more permeable soil. Petroleum-contaminated soils were encountered from 14 and 20 feet bgs in the VW2 and MPE boreholes, and were encountered in all boreholes at depths corresponding to the perched water zones. TPH concentrations in soils were as high as 1,350 mg/kg. Total BTEX concentrations in soils were as high as 17,000 µg/kg.

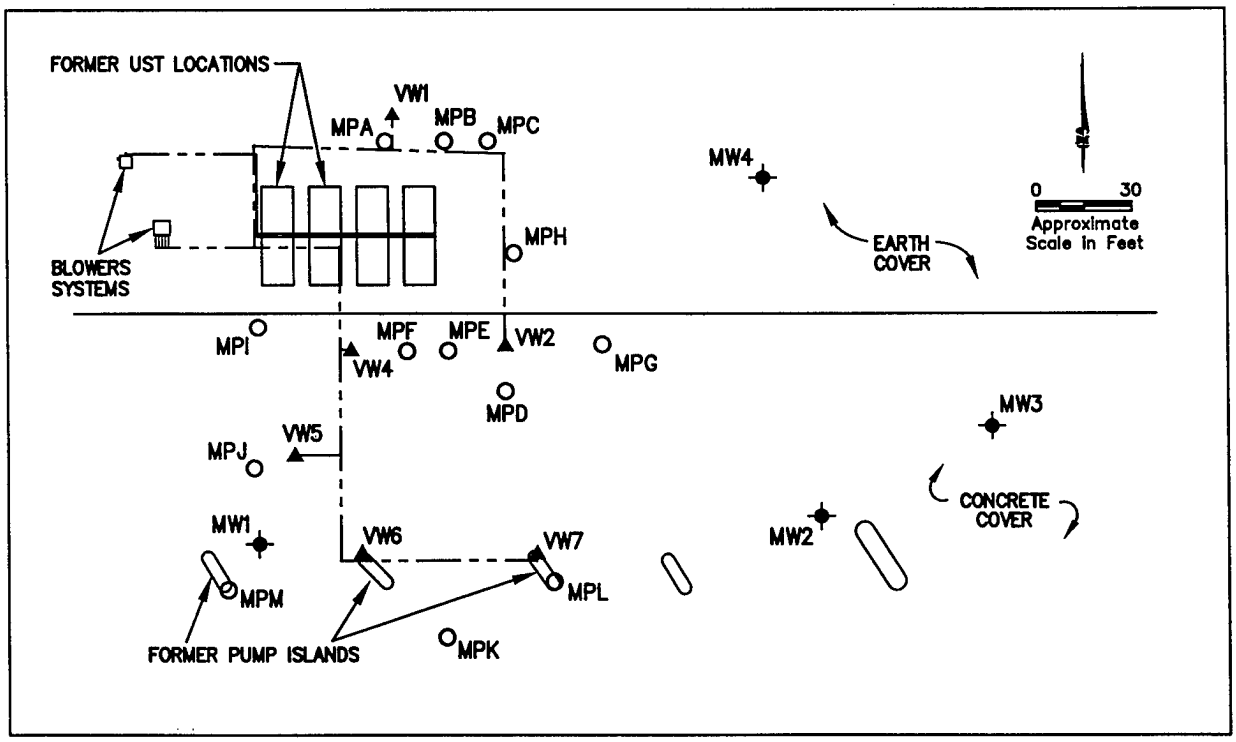



Figure 3. Layout of Building 8200 (Fort Carson, Colorado) site. The initial pilot test was performed using VW2, and an expanded system was designed and installed after completion of the pilot test.

Oxygen was depleted, and carbon dioxide concentrations were elevated (as high as 9 percent) in contaminated soil zones. During the air permeability test, a radius of oxygen influence of approximately 30 feet was observed at an air injection rate of 20 cfm into VW2. Oxygen concentrations dropped, and TVH concentrations increased in monitoring well MW-1 during air injection, indicating that the radius of oxygen influence could be 95 feet or greater in the more permeable soil lenses. Air could not be injected into VW1 (an existing groundwater monitoring well), and soil gas samples could not be collected from MPA, MPB, or MPC, indicating that a low-permeability soil unit exists north and northeast of the UST locations (Figure 3). Hydrocarbon biodegradation rates ranged from 40 to 84 mg/kg-yr, and averaged 70 mg/kg-yr. Although these rates are low, a 2-horsepower regenerative blower system was installed for air injection into VW1 and VW2. VW1 was manifolded to the blower system because soil permeabilities often increase over long periods of pressurization/air injection due to moisture displacement and the development of preferential airflow pathways.

The system was expanded in April and May 1997 by installing additional VWs and MPs south of the former UST locations towards the pump islands. A horizontal VW also was installed in the bottom of the UST excavation following the removal of the tanks. A rotary-vane compressor, capable of injecting air at much higher pressures than regenerative blower systems, was installed so that higher air injection flow rates could be achieved. Full-scale oxygenation has been achieved in permeable soils in the source areas using this expanded system, and the aerobic hydrocarbon biodegradation rates in a respiration testing event performed during system installation ranged from 77 to 218 mg/kg-yr, and averaged 150 mg/kg/yr.

Although very low-permeability soils were encountered at this site, it is estimated that over 80 percent of the affected soil volume is now receiving oxygen. Soil gas sampling has not been able to confirm oxygenation in the low-permeability soil unit north and northeast of the former UST location. Permeability in this area will likely increase as pressure is maintained in the subsurface by the system over long periods of time. The expanded scale system was optimized, and will run until June 1998, when year-end testing will be performed.

## 4. PROJECT COSTS

Table 4 provides the total project costs incurred at each site as of May 30, 1997, and also provides the estimated unit costs for each cubic yard of soil that was oxygenated. At Fort Bliss, the total cost includes a site visit, preparation of a work plan, obtaining regulatory approval for the work, performing the pilot test (including an initial soil gas survey, drilling, and well installation) and reporting the results, one year of system operation and maintenance (excluding electrical power), and year end testing and reporting. The total cost at Fort Rucker includes all of the above activities except the year end testing and reporting, which has not yet been performed. The Camp Ripley cost includes a site visit, an initial soil gas survey, and preparation of a results report. At Fort Carson, the cost includes a site visit, preparation of a pilot test work plan, performing the pilot test and reporting the results, preparing a remedial action plan and designing the expanded-scale system, obtaining regulatory approval for the work, and installing the expanded-scale system.

Unit costs at Fort Bliss and Fort Rucker are under $6 per cubic yard of soil. Unit costs are higher at Fort Carson because the system was installed in multiple mobilizations, manifold installation was required to supply air to multiple VWs in areas covered with 12-inch thick reinforced concrete, and two blower systems were installed at the site. Contaminated soils here were also less permeable and at shallower depths than the other sites, meaning that a much smaller volume of contaminated soil could be treated per VW. However, a unit cost of approximately $20 per cubic yard is still very reasonable when

compared with excavation and disposal, which could easily exceed $80 per cubic yard due to the presence of the concrete cover. Bioventing also benefits from an economy of scale. For sites with more than 20,000 cubic yards of contaminated soil, capital costs of less that $5 per cubic yard can be achieved. Sites with less than 2,000 cubic yards of contaminated soil will generally exceed a unit cost of $20 per cubic yard (10).

TABLE 4. PROJECT COSTS.

| Site | Total Cost | Cubic Yards of Oxygenated Soil | Cost per Cubic Yard |
|---|---|---|---|
| Fort Bliss | $73,000 | 12,700 | $5.75 |
| Fort Rucker | $60,000 | 20,000 | $3.00 |
| Camp Ripley | $3,500 | not applicable | not applicable |
| Fort Carson | $119,000 | 6,500 | $18.31 |

## 5. CONCLUSIONS

These bioventing pilot tests were successful in demonstrating that petroleum-contaminated soils could be aerated, and that native soil bacteria were capable of biodegrading petroleum hydrocarbons under aerobic conditions. The extended testing results at the Fort Bliss site illustrate that at some sites in arid climates in the southwestern United States, long-term fuel biodegradation rates can be very low, and bioventing treatment may be ineffective. At these sites, SVE will provide more cost-effective treatment of volatile fuel constituents, which typically are of greater regulatory concern. Although zones of saturated and low-permeability soils were encountered at the Fort Rucker and Fort Carson sites, respectively, the majority of the contaminated soil volumes are receiving oxygen. It is possible that oxygen will be supplied to low-permeability or saturated soils during extended system operation.

Bioventing is an excellent low-cost technology for the removal of toxic, "risk-driving" compounds (e.g., benzene) from soil. Based on soil sampling results from more than 100 sites during the nationwide AFCEE bioventing initiative, an average BTEX reduction of 97 percent was achieved during 1 year of bioventing. TPH levels were reduced by an average of 24 percent (1). Although biodegradation rates are much lower for TPH than they are for BTEX, it should be noted that TPH is not an accurate indicator of risk to human health and the environment. States are moving away from the TPH standard and are adopting risk-based regulations based on compound-specific action levels. Due to its widespread feasibility, simplicity, low cost, and minimum operation and maintenance requirements, bioventing is the most cost effective cleanup technology available for unsaturated, fuel-contaminated soils at most sites, and should be considered before more complicated or expensive remediation alternatives are recommended.

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# OPERATIONS & READINESS II

# SUBSURFACE ORDNANCE CHARACTERIZATION SYSTEM

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ABSTRACT

The Subsurface Ordnance Characterization System (SOCS) is a demonstration system that can be used for detecting, identifying, and mapping unexploded ordnance (UXO). The U.S. Army Environmental Center in partnership with the Naval Explosive Ordnance Disposal Technology Division and Wright Laboratories Robotics Laboratory has developed SOCS to serve as a standardized platform for evaluating different UXO detection sensors.

SOCS consists of five major subsystems: tow vehicle, sensor platform, sensor array, data acquisition unit, and the navigation and target localization unit. The tow vehicle operates in an autonomous mode while serving as the power system for the multi-sensor platform. The sensor platform carries multiple sensors in an open architecture to facilitate making changes in the sensor array. The current sensor array consists of both magnetometers and ground penetrating radar; and data is simultaneously collected from these two sensor types. The data acquisition unit is the heart of SOCS. It supervises the sensor operation and monitors the system status. Path planning and target localization are monitored through use of a differential global positioning system and an inertial navigation system. These subsystems have been fully integrated to provide accurate data collection autonomously while the system operator monitors the operation remotely.

Currently SOCS is capable of performing autonomous surveys for characterization of UXO. Modifications to the current system are planned to facilitate use of different UXO sensor systems. With these modifications SOCS may then be used as a standardized platform for sensor capability evaluations. The initial testing of the SOCS platform has shown possibilities for the commercial application of this type system for UXO site work. Also, architecture changes to improve durability and rough terrain capabilities are being considered. These changes along with the utility of autonomous operation and versatile sensor configurations would provide an alternative to current UXO survey practices.

## 1. BACKGROUND

The Subsurface Ordnance Characterization System, SOCS, was developed through an extensive cooperative effort between the U.S. Army Environmental Center, U.S. Air Force's Wright Laboratories Robotics Laboratory and the Naval Explosive Ordnance Disposal Technology Division. The driving purpose behind SOCS development is to advance the state of the art in UXO characterization systems. More specifically, SOCS has been developed to serve as a standardized testbed for evaluating the performance characteristics of different types of sensors. The basics of these evaluations may be described as completing an operational survey procedure that has been designed to describe the performance of a sensor, sensor operational environment, or data algorithms. As an example, a particular sensor may be evaluated to

determine the height above ground level where that particular sensor provides optimum performance. SOCS accomplishes these evaluations by exploiting the reliable robotics capabilities inherent in the SOCS platform design.

In August 1995, SOCS was tested at Jefferson Proving Ground in an effort to determine the overall system performance of SOCS. This test and subsequent similar tests have helped identify the capabilities and limitations of SOCS. The SOCS team has taken many steps to resolve major system limitations and has taken action to modify the SOCS platform to reach state of the art performance levels.

## 2. SOCS SUBSYSTEMS

SOCS consists of five major subsystems: tow vehicle, multiple sensor platform (MSP), sensor array, data acquisition unit, and the navigation and target localization unit. These subsystems work in concert to provide the precision, accuracy and reliability of a testbed platform. The first subsystem of SOCS is the tow vehicle which consists of a John Deere Gator ® 6X4 base vehicle that has been modified to accept electromechanical actuators for computer control. The tow vehicle is required to tow the sensor platform and carry acquisition unit and the navigation and target localization unit. This model of vehicle was chosen based on all-terrain capability, towing and carrying capacity, cost and ease of integration (Brown and Gluckman, 95). From the 1995 JPG SOCS test and subsequent tests the tow vehicle has proved to be a limiting factor in the overall SOCS performance. Tests have been plagued with physical failures of the tow vehicle. These failures manifest as a durability issue that the SOCS team is currently working to resolve.

The multiple sensor platform is the second SOCS subsystem and serves to carry the SOCS sensors. The MSP consists of a structure fabricated from aluminum and composite materials chosen to minimize magnetic influence (Brown and Gluckman, 95). The MSP has been developed with an open architecture to facilitate sensor attitude changes as well as changes in the basic sensor type. The MSP is connected to the tow vehicle by a three degree of freedom hitch that measures the MSP's pitch, roll and yaw in relation to the tow vehicle carrying the navigation control. With this capability MSP and sensor position can be accurately recorded. As with the tow vehicle, durability as been an issue with the platform and likewise is being addressed by the SOCS team.

The sensor array is the third SOCS subsystem and originally consisted of total field magnetometers and a ground penetrating radar. SOCS carries four cesium vapor magnetometers manufactured by Geometrics. These magnetometers are carried on the very rear of the MSP and are normally spaced one foot apart. The original GPR was designed and developed specifically for SOCS. This is a chirp stepped GPR system that utilizes synthetic aperture radar processing to produce images of subsurface objects. The size and weight (450 lb.) of this GPR antenna has shown to be somewhat problematic for SOCS and may have contributed to some of durability problems. As a result, this original GPR is being replaced by a new antenna design that is designed to be more easily carried by the MSP. This new antenna, which is expected to weigh approximately 30 lb., is planned on being mounted and tested on SOCS in September 1997. The SOCS team is currently in the process of identifying other sensor types to integrate into the platform and plans on having capacity to carry 5 sensor types.

The fourth SOCS subsystem is the data acquisition unit SiDCAPS (Simultaneous Data Collection And Processing System). SiDCAPS serves as the nerve center of SOCS and is responsible to collect and store sensor data during a survey. A very basic description of SiDCAPS purpose is that it collects sensor data and appends that data with a time and position stamp.

The final SOCS subsystem is the navigation and target localization unit that provides guidance for the tow vehicle and provides position data to SiDCAPS. This subsystem consists of a hybrid position system developed by integrating a Global Positioning System and an Inertial Navigation System though the use of an external Kalman Filter (Brown and Gluckman, 95). The GPS provides position data at 1 Hz while the INS provides position data at 20 Hz. Additionally the INS provides vehicle heading, pitch, roll and yaw.

SOCS is controlled through a Mobile Command Station (MCS) which houses the operator interface, GPS base station, radio base station, teleoperation control and other features. The SOCS operator uses the systems in the MCS to perform autonomous surveys, teleoperated functions, review SOCS system diagnostics and review video. Rather than viewing the MCS a completely separate subsystem of SOCS, the MCS is seen more as the interface between the operator and SOCS.

## 3. SOCS PROGRAM

As previously mentioned SOCS is a system that was created to serve as a testbed for UXO characterization technology advancements. The SOCS team has recently reviewed the overall program in an effort to characterize the success and failures of SOCS. This effort has resulted in a redefining of the SOCS program goals. First, SOCS will be used primarily as a testbed for UXO characterization technology advancements as it was originally intended. Second, the SOCS working to create a more robust version of SOCS that resolves the system durability issues that have been a part of the SOCS program from the start. This revised system is being designed to create a reliable platform that can operate successfully in rough terrain and that carries a complete UXO characterization sensor suite. Completion of this revision to SOCS promises to establish a baseline for UXO characterization performance.

## 4. SUMMARY

SOCS is a demonstration system that can be used for detecting, identifying, and mapping unexploded ordnance (UXO). The U.S. Army Environmental Center, the Naval Explosive Ordnance Disposal Technology Division, and Wright Laboratories Robotics Laboratory have developed SOCS to serve as a standardized platform for evaluating different UXO detection sensors. SOCS consists of five major subsystems that have been fully integrated to provide accurate data collection autonomously while the system operator monitors the operation remotely. Currently SOCS is capable of performing autonomous surveys for characterization of UXO. Modifications to the current system are planned based on results from testing SOCS at a number of sites. The planned revisions to SOCS are designed to facilitate use as a standardized platform for sensor capability evaluations as well as establishing a baseline for UXO characterization capabilities.

## 5. REFERENCES

H. Edward Brown and Sidney Gluckman, Operational and Functional Demonstration of the Subsurface Ordnance Characterization System (SOCS), Wright Laboratory, Tyndall AFB, FL, Jan 95.

# WEIGHING THE COSTS OF EXCESS FACILITIES

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## ABSTRACT

The recent significant changes in the Army's facility requirements resulting from base realignments and downsizing have forced facility planners to face tough decisions regarding what to do with the excess buildings now in the Army's inventory. The expense of keeping these facilities places tremendous strains on shrinking operations and maintenance budgets, yet uncertainty about future requirements and the possible historical significance of many of these facilities raises questions about the wisdom of disposing of them. Choosing a cost-effective strategy is complicated not only by the sheer difficulty of gathering and processing all of the life-cycle costs associated with each alternative but also by 1) the lack of data for such key areas as layaway/caretaker costs and building deterioration rates, 2) the regulatory requirements and costs of hazardous materials cleanup, and 3) the consideration of preservation requirements when the facility is historic.

This paper reports on the results of studies currently underway at the U.S. Army Construction Engineering Research Laboratories to develop a quick-turnaround automated tool for estimating the cost differences of three alternatives for a given excess facility. The work has been funded by the BRAC Office and by the U.S. Army Environmental Center. The three alternatives analyzed during the study are: 1) maintain the status quo by keeping the facility in move-in condition, 2) demolish and construct a new facility later if needed,and 3) mothball/walk away from the facility until needed. The work includes assembling and, in some cases, constructing the necessary cost databases, designing a decision analysis model of the alternatives, and the developing an easy-to-use computer tool to perform the calculations and present the results. The paper places special emphasis on environmental and historic preservation issues associated with excess facilities.

## 1. INTRODUCTION

The fall of the Berlin wall in November of 1989 came to symbolize the end of the Cold War. It could also symbolize the beginning of the current down-sizing trend in the U.S. Army. As a consequence of that trend, many army buildings have become excess facilities, and thus candidates for demolition. Paradoxically, the demolition of the infamous wall in Germany made many DOD facilities around the world candidates for demolition also. Although the decision to demolish the Berlin wall was unanimous and straightforward, the decision to demolish excess facilities in DOD now may not be as obvious.

Many of these excess facilities still have a considerable economic life left to them and demolishing them could be a waste. Transferring these excess facilities to other agencies or to the public may not be feasible. This is the case of excess facilities located inside an active installation. In this case, transferring the facilities for non-military use will disrupt the mission of the whole installation. An alternative to demolishing these facilities is to keep them for future use, hence retaining the economic life left to them.

The uncertainty of future facility requirements calls for the evaluation of different scenarios. On the one

hand, demolishing excess facilities saves money in Operation and Maintenance (O&M) in the down-size period. On the other hand, if there is a build-up period in the future, and facilities are needed again, building new facilities from scratch may become very expensive. It has always been the case in recent U.S. history that every down-size period in DOD has been followed by a build-up one. Hence, in the event of a build-up scenario, reuse of property previously considered to be excess facilities may be the most economic alternative.

Either demolishing or keeping the excess facilities costs money and a careful Economic Analysis (EA) is required to support the request for funds. The information required to do that EA is scattered around different systems and publications and its compilation is time-consuming. Many of these facilities are potentially historic and any action concerning them requires extra information and documentation to support it with state and federal preservation organizations. Furthermore, in the case of historic facilities, a careful EA is required in order to determine if the action is a high cost undertaking. Therefore, there is a need at the U.S. Army installations for a tool that simplifies the EA of excess facilities and helps to document the decision.

The objective of this paper is to report the ongoing effort at USACERL to develop an economic model of facility layaway. This project is sponsored by the BRAC Office and by the U.S. Army Environmental Center. This effort will produce a methodology to support installation and HQ personnel in deciding whether or not to mothball their excess facilities. In addition, this research will provide an estimate of the resources required to accomplish their decision successfully. As a consequence, installation managers will save scarce resources by allocating them to worthy facilities and by avoiding unnecessary risk of future resources.

This paper is organized as follows: first, different sources of uncertainty obscuring this decision are reviewed; second, the alternatives of the decision maker are discussed; third, several decision rules are suggested.

## 2. FACILITY LAY AWAY DECISION MODEL.

The decision of what to do with excess or underutilized facilities is driven by several factors namely: expected cost, future facility requirements, future functional requirements, and future cost of historic preservation and environmental clean-up. Figure -1- shows the influence diagram of this decision. The decision is represented by the rectangle, and its outcome is represented by the rhomboid. The three sources of uncertainty influencing the outcome are represented by the tree circles.

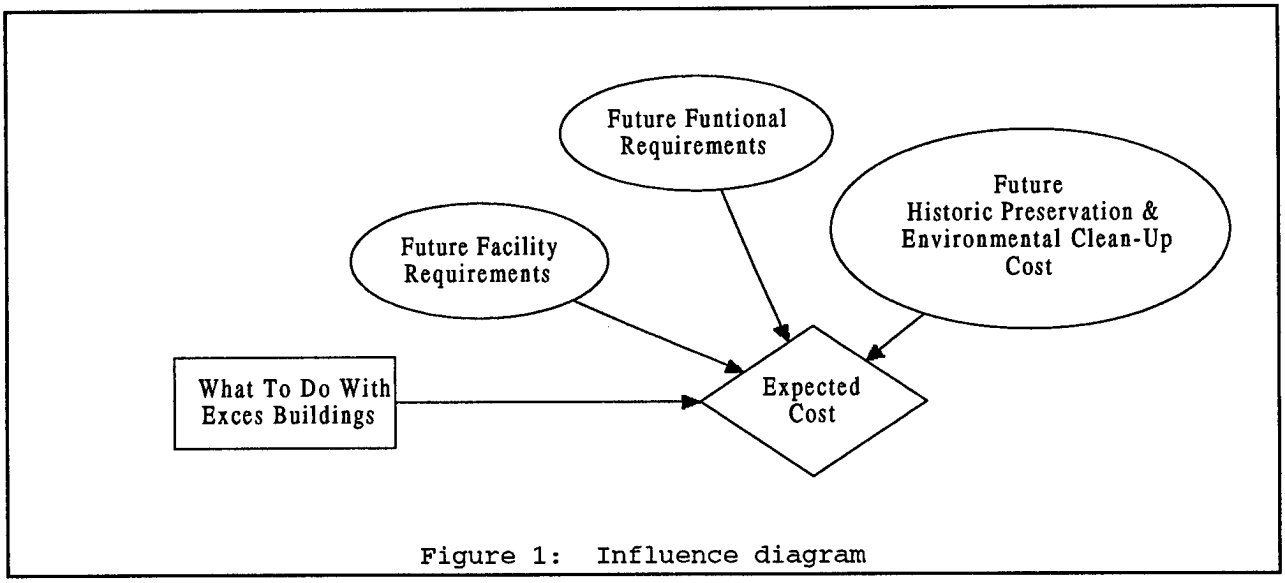



Figure 1: Influence diagram

If the decision maker knows with certainty whether a specific facility is going to be needed or not and, if so, when, then the decision of whether to lay a facility away or to demolish it is a straightforward one and it can be supported by a benefit-cost analysis. If the facility is not needed, the least cost alternative is demolition. If the facility is going to be needed in the future even though it is not needed now, the decision maker could either demolish it now and build it later, or lay it away now and reactivate it later. The optimal policy to follow will be to choose the alternative with the least Net Present Value (NPV). Unfortunately, future events are never certain.

*Sources of uncertainty:*

The first source of uncertainty is the future facility requirement. If the decision maker does not know with certainty his/her facility requirements, this decision becomes a risky one. In this case, the cost (*c*) of building the new facility if the need arises, is not a certain cost and hence the NPV comparison of above is not possible. If the decision maker knows the probability of needing the facility (*pNedFac*) in the future, then he/she can compute the expected cost as the product of *c* and *pNedFac*. In this case, the alternative with the least expected cost will be the appropriate one, provided the decision maker can accept the risk involved in it. If the decision maker has to make this decision repeatedly with many buildings and independently of one another, then the risk is diluted and the least expected cost alternative will be the best alternative to choose each time.

This decision model contemplates two possible future events regarding facility requirements namely: Need facility, or don't need facility. In addition, each event has a probability associated with it and the model is able to carry sensitivity analysis regarding the likelihood of each event.

The second source of uncertainty is the functional requirements the facility will have to meet in the future. Take for instance a training facility that meets today's standards and is mothballed now. Ten years from now, because of emerging technologies in training, the facility may be obsolete and the cost of bringing it up to acceptable standards may be high. The probability of this happening depends upon the type of building and its age.

The model contemplates two possible future events namely: the facility will be functionally obsolete in the future, or it will be adequate. Again, each event has a probability associated with it and the model is able to carry sensitivity analysis regarding the likelihood of each event.

The third source of uncertainty is the future cost of Historic Preservation & Environmental Restoration (HP & ER). In the case of historic preservation issues, this uncertainty is derived from the need to consult with the State Historic Preservation Officer (SHPO) as well as the Advisory Council on Historic Preservation (the Council). In the case of environmental issues, this uncertainty is due to the continuous change in environmental regulations. For instance, removing asbestos from a building is more expensive now than it was 15 years ego. Also, future technological improvements will very likely reduce the cost of historic preservation and environmental clean up; hence making the future cost of historic preservation more uncertain. For instance, new technology and procedures, on the works now at CERL, for removing lead based paint will reduce the future cost of HP & ER.

The model contemplates two possible events namely: different HP & ER, or same HP & ER cost. Moreover, the model performs sensitivity analysis regarding the amount of the difference as well as the likelihood of it.

The combinations of all these possible future events can be represented in a "tree" form like the one in Figure -2-. In this tree, each branch represents a different combination of future events, or in other words, a different scenario. There are a total of 6 possible scenarios to be considered in this decision and they are

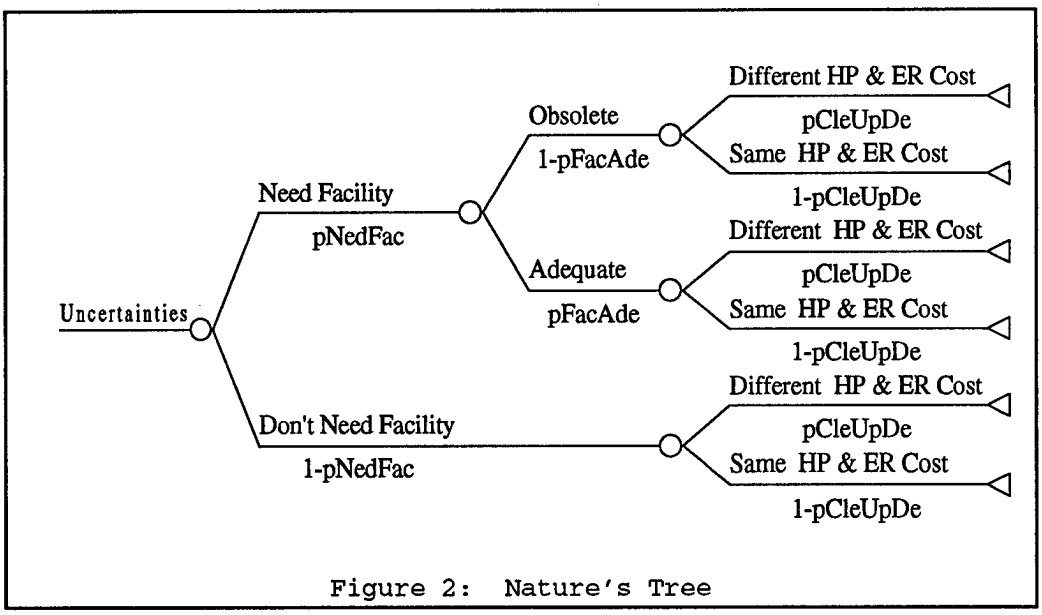



Figure 2: Nature's Tree

represented in figure -2- by the 6 right hand branches. Above each branch is the name of the scenario it represents and right below it is the probability associated with that scenario.

*Decision Alternatives:*

This model contemplates three possible alternatives when faced with excess facilities namely: keep the status quo, layaway/walk away from it, or demolish it. The status quo alternative refers to the decision of keeping the facility in a move-in condition, under utilizing it, hoping to find new tenants in the near future. Under this alternative, if the facility is still in excess or under utilized after 10 years, then the facility is demolished after mitigating the adverse effect, and the sight is cleaned up. This alternative tends to be the least cost alternative when the probabilities that the facility will be needed and adequate in the near future are both high. By the same token, this alternative tends to be the most expensive one if either one of the two probabilities is low.

In the layaway/walk away alternative, the facility is mothballed according to standard procedures and minimally maintained for up to 10 years. Under this alternative, the facility is reactivated at the end of the analysis period if it is needed or it is demolished if it is not needed. In both cases the adverse action is mitigated and the sight is cleaned up at the end of the analysis period. The mothballing effort involves controlling the long-term deterioration of the building while it is unoccupied as well as protecting it from sudden loss by fire or vandalism. This requires securing the building from unwanted entry, providing adequate ventilation to the interior, and shutting down or modifying existing utilities.

In the demolish alternative, the facility is demolished after mitigating the adverse effect at the beginning of the analysis period and the sight is cleaned up. If the facility is needed at the end of the analysis period, a new facility is built. This alternative tends to be the least cost alternative if the probability of needing the facility in the future is none . This alternative tends also to be the least cost alternative if the probability that the facility will be obsolete in the future is very high. On the contrary, this alternative tends to be very costly if the probabilities that the facility will be needed and that it will be adequate are both high.

# Table 1: LEA Decision Matrix:

| *Future Facility Needs* | **Need Facility** | | | | **Don't Need Facility** | |
|---|---|---|---|---|---|---|
| *Future Functional Needs* | **Obsolete** | | **Adequate** | | | |
| *HP & ER Cost* | **Different** | **Same** | **Different** | **Same** | **Different** | **Same** |
| *Likelihood of Scenario* | *(pNedFac) * (1-pFacAde) * (pCleUpDe)* | *(pNedFac) * (1-pFacAde) * (1-pCleUpDe)* | *(pNedFac) * (pFacAde) * pCleUpDe* | *(pNedFac) * (pFacAde) * (1-pCleUpDe)* | *(1-pNedFac) * (pCleUpDe)* | *(1-pNedFac) * (pCleUpDe)* |
| **Status Quo** | Keep Facility in move-in condition for up to 10 Years, then demolish it after mitigating the adverse effect and clean up with new HP & ER cost, and build a new one. | Keep Facility in move-in condition for up to 10 Years, then demolish it after mitigating the adverse effect and clean up, and build a new one. | Keep Facility in move-in condition for up to 10 Years, then mitigate and clean up with new HP & ER cost and use it fully. | Keep Facility in move-in condition for up to 10 Years, then clean up and use it fully. | Keep Facility in move-in condition for up to 10 Years, then demolish it after mitigating the adverse effect and clean up with new HP & ER cost. | Keep Facility in move-in condition for up to 10 Years, then demolish it after mitigating the adverse effect and clean up. |
| **Lay Away Walk Away** | Lay facility away and keep it so for up to 10 Years, then demolish it after mitigating the adverse effect and clean up with new HP & ER cost, and build a new one. | Lay facility away and keep it so for up to 10 Years, then demolish it after mitigating the adverse effect and clean up, and build a new one. | Lay facility away and keep it so for up to 10 years, then reactivate the facility by renovating and mitigating it, and cleaning up at new HP & ER, and use it fully. | Lay facility away and keep it so for up to 10 years, then reactivate the facility by renovating and mitigating it and cleaning up, and use it fully. | Lay facility away and keep it so for up to 10 Years, then demolish it after mitigating the adverse effect and clean up with new HP & ER cost. | Lay facility away and keep it so for up to 10 Years, then demolish it after mitigating the adverse effect and clean up. |
| **Demolish** | Demolish facility now after mitigating the adverse effect and clean up. Then build a new one. | Demolish facility now after mitigating the adverse effect and clean up. Then build a new one. | Demolish facility now after mitigating the adverse effect and clean up. Then build a new one | Demolish facility now after mitigating the adverse effect and clean up. Then build a new one | Demolish facility now after mitigating the adverse effect and clean up. | Demolish facility now after mitigating the adverse effect and clean up. |

Table 1: LEA Decision Matrix, summarizes the actions entailed by each alternative under each scenario. Each scenario is represented by one column. The first three rows of the matrix describe the scenario. The fourth row, *Likelihood of Scenario*, represents the probability of that scenario. The last three rows represent the three alternatives mentioned above namely: Status Quo, Lay Away/Walk Away, and Demolish. Finally, each cell describes the actions to be taken in the building for that alternative and that scenario.

The LEA model estimates the cost of each cell in the last three rows of the LEA Decision Matrix in order to identify the least expected cost alternative. The cost estimates are best estimates taken from Maintenance and Repair Resource Prediction Model (MRPM), Means, Computer Aided Cost Estimating System (MCASE), Air Force Parametric Cost Engineering System (PACES), and so forth. As a consequence, each cell in the last three rows of the decision matrix has a cost associated with it and represents the cost of performing the described activities. The expected cost of each alternative is then the vectorial product of its row times the likelihood row.

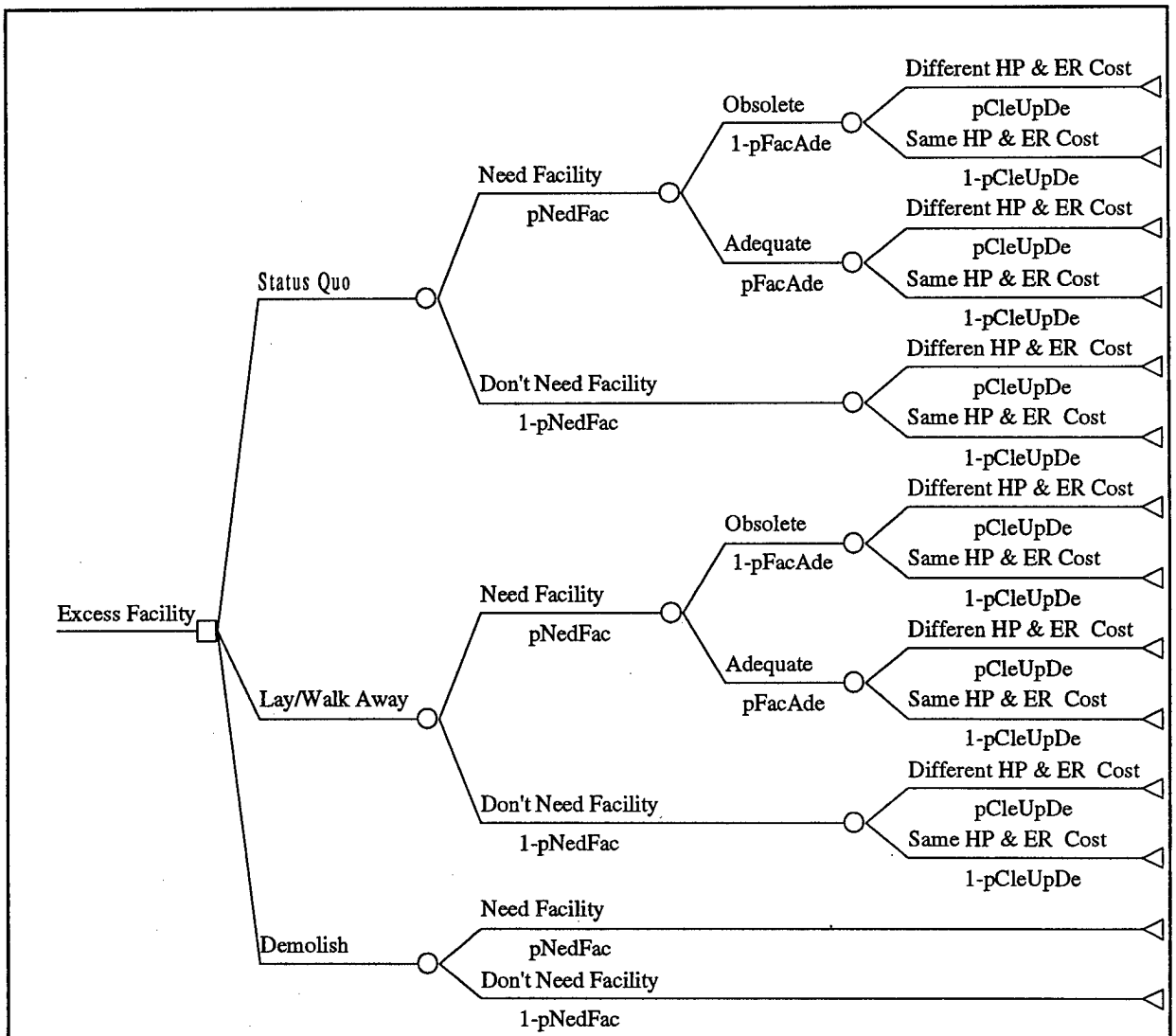



Figure 3: LEA Decision Tree

Another way to represent the different scenarios and their probabilities is with a decision tree. Figure 3; LEA Decision tree, represents the same decision as that in Table 1, but in tree form. This tree shows that the three alternatives result in fourteen different paths each one with a different probability of happening and a different cost.

Decision Rule

The optimal rule to follow for making this decision depends upon the amount of information the decision maker has at the time and it also depends upon his/her attitude towards risk. If the decision maker knows the probabilities associated with the chance nodes of Figures 1 and 2, then the model computes the total cost and the probability of each leaf. The risk associated with each alternative is described by the probability distribution of all the paths following that alternative, and different decision makers may react differently towards it.

On one hand, if the decision maker is making this decision with several buildings of similar characteristics, then the risk of the actual cost being different from the expected cost in the long run is minimum, and the least expected cost decision rule is the best rule. On the other hand, if the decision maker cannot bear the risk associated with the probability of the worst case scenario happening, then the best decision rule is to chose the alternative with the least maximum cost.

Those two extremes described above may well be the cases for decision makers at the MACOM level and at the installation level respectively. On one hand, at the MACOM level the decision maker is faced with large numbers of similar buildings scattered around different installations. As a consequence of the large number of buildings the total average cost of the rule will approximate the expected total cost. On the other hand, at the installation level the decision maker faces a smaller number of buildings, and as a consequence, the total cost may significantly differ from the expected cost. Hence, minimum expected cost may not be the optimal rule at the installation level.

If the decision maker does not know the probabilities associated with the chance nodes of the tree or is not able to estimate them satisfactorily, then it is not possible to compute the expected cost and hence not possible to choose the alternative with the least expected cost. This situation is called "decision making under uncertainty" by decision theorists, and the optimal decision rule is more abstract. The most popular decision rules are the following: Laplace Rule, Minimax Rule, Minimin Rule, and Minimax Regret Rule. A description of them can be found in reference 2.

Each rule has a different objective and hence recommends a different alternative as optimal. For instance, the Minimax rule will assume the worst-case scenario for each alternative and choose the one with the least worst-case cost. This decision rule will be the preferred one by a pessimistic decision maker. Moreover, the Minimin rule assumes that nature will do its best for each alternative and will recommend the alternative with the least minimum cost. This decision rule will be the preferred one by an optimistic decision maker. In other words, there is not a unique optimal alternative and the recommended alternative depends upon the personality of the decision maker and his/her perception of the natural events. Therefore, there is a need for both a qualitative and quantitative understanding of the uncertainties involved in this decision.

## 3. Summary and Conclusion

The decision of whether to lay a facility away for future use or to demolish it and build a new one later if needed involves risk and hence straightforward comparison of Net Present Value (NPV) of each alternative is not an appropriate method. The three elements of risk are: future facility needs, future functional

requirements, and future cost of historic preservation and environmental restoration. In the case of historic preservation issues, this uncertainty is derived from the need to consult with the SHPO as well as the Council. In addition, future technological improvements will very likely reduce the cost of historic preservation and environmental clean up; hence making the future cost of historic preservation more uncertain. To account for these elements of risk in an EA, it is necessary to estimate the probability of future scenarios in order to compute expected cost.

There is a need at the installation level and at the HQ level for a methodology to perform economic analysis of excess facilities for two reasons. First, the alternatives to the status quo namely; mothballing and demolition have some risk associated with them that needs to be evaluated and accounted for before making a decision. Second, in the case of historic facilities, a careful and well documented EA is required in order to determine if the action is a high cost undertaking.

The optimal rule to follow for making this decision depends upon the amount of information the decision maker has at the time, and it also depends upon his/her attitude towards risk. In other words, there is not a unique optimal alternative and the recommended alternative depends upon the personality of the decision maker and his/her perception of the future events. Therefore, there is a need for both a qualitative and quantitative understanding of the uncertainties involved in this decision.

In the case of excess historic facilities, the alternative to demolishing now has to consider the likelihood of needing a similar facility in the future. After accounting for that probability, demolition is only the most economical alternative if the probability of needing a similar facility in the future is very low, or if the probability that the facility will be adequate is also low. On the contrary, demolition tends to be a very costly alternative for dealing with excess facilities if the probabilities that the facility will be needed and that it will be adequate are both considerable.

References:

1. Uzarski, et al; Layaway Procedures for U. S. Army Facilities, Volume I: Decision Criteria an Economics.; USACERL Technical Report M-91/23; July 1991.

2. Thuesen, G. J. and Fabrycky, W. J.; Engineering Economy; Eighth Edition; Prentice Hall.

3. Subick et al; Facility Layaway Economic Analysis.; USACERL Technical Report 96/81; August 1996

4. TRADOC Guide for Historic Structures: A Framework for Decision Making.; January 1996

# POLLUTION PREVENTION II

by a sales representative from the respective corporation. During the one year evaluation, four vehicles from the installation's maintenance motor pool were selected for the evaluation. These vehicles were drained of their existing antifreeze, the used antifreeze was recycled, and then poured back into the vehicle. A sample was taken before the antifreeze was put back into the vehicle and the characteristics of the recycled antifreeze were compared to fresh antifreeze. Samples were then taken every three months and were tested for reserve alkalinity, pH, freeze point, formate, glycolate, and total dissolved solids and again compared to characteristics of fresh MIL-A-46153.

During the one year field evaluation each participating installation kept records regarding suggestions on how to make recycling antifreeze as simple as possible. Each participating installation submitted comments to the MTCB that could help other installations starting up an antifreeze recycling program. Some suggestions included a start-up kit containing pH strips, a batter tester, drum stirrers, and clear plastic drums.

## APPROVED SYSTEMS

KFM Corporation Cool'r Clean'r Coolant Purification System (formally BG Products):
The Cool'r Clean'r Coolant Purification System (CCCPS) was tested by MTCB and verified to meet the specifications of MIL-A-46153. Formerly called the BG Products Cool'r Clean'r Coolant Purification System, this system operates as an ion exchange process. The CCCPS is a similar design to a kidney dialysis machine and removes all dissolved solids from the used antifreeze. The coolant is processed through the system at approximately 180 gal/hr and once processed, the waste coolant returns to pure ethylene glycol and deionized water. The only hazardous waste generated is from the spent filters. A sketch of the CCCPS is as follows in Figure 1.

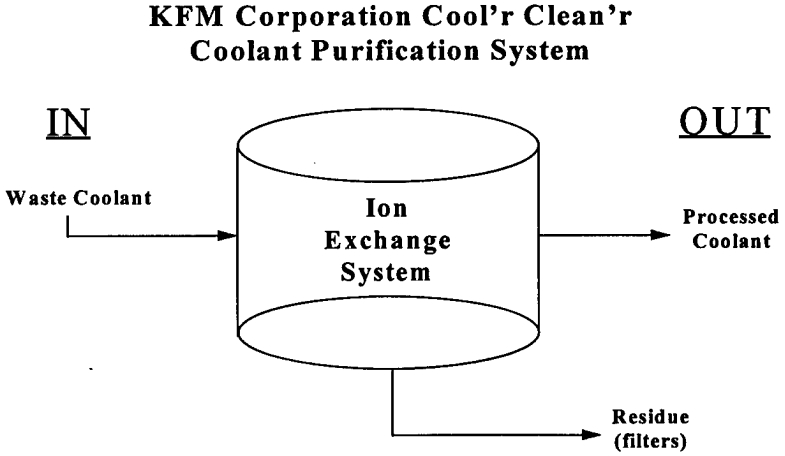



Figure 1. Sketch of the CCCPS

During the one year site demonstration, samples were taken to see how the characteristics of the recycled antifreeze performed against characteristics of fresh antifreeze. With the CCCPS tests completed, the recycled antifreeze has met the MIL-A-46153 specification for reserve alkalinity, pH, and freeze point. Table 1 gives a breakdown of the quarterly samples.

Table 1. CHEMISTRY DATA FOR ONE CCCPS EVALUATION

| Time (months) | Reserve Alkalinity | pH | Freeze Point |
|---|---|---|---|
| 0 | 9.6 | 7.7 | -50 |
| 3 | 11.9 | 8.1 | -62 |
| 6 | n/a | n/a | -60 |
| 9 | 13 | 8 | -60 |

Finish Thompson BE-Series Coolant Reclaimer Systems:
The BE-Series Coolant Reclaimer Systems were tested by MTCB and verified to meet the specifications of MIL-A-46153. The BE-Series comes in two different size units, BE-15C and BE-55C. The BE-55C system was tested in this field evaluation at two Army installations. The BE Series Coolant Reclaimers operate as vacuum distillation units. Waste coolant is processed at flow rates between 1-3.2 gal/hr. Hazardous waste generated from this process is the distillation bottoms.

An Air Force installation discovered a process to reduce their hazardous waste disposal using the BE-Series Reclaimers. This installation purchased a BE-55C Coolant Reclaimer for recycling used coolant. The distillation bottoms from the BE-55C were collected and placed in a drum. This installation also purchased a BE-15C Coolant Reclaimer and recycled the distillation bottoms using this system. After each distillation bottom batch was processed, the installation collected the distillation bottoms from the prior batches and continued to recycle the distillation bottoms until there was no usable quantity left to process. This Air Force installation only disposed of 3 gallons of hazardous waste in one year using this process.

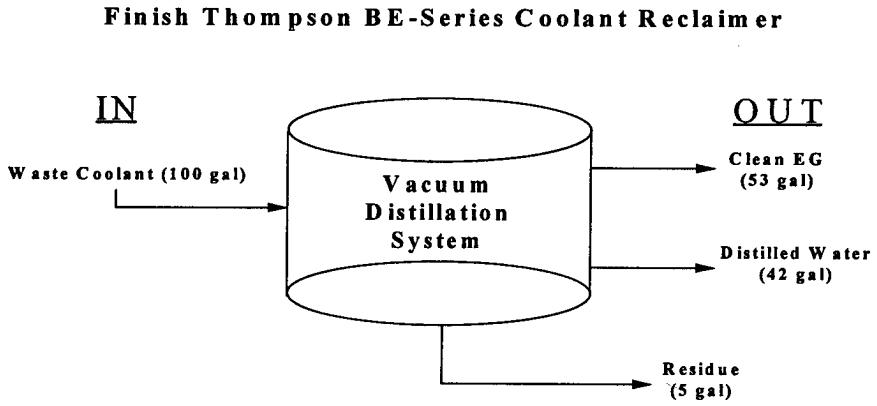



Figure 2. Sketch of the BE-Series Coolant Reclaimer

A sketch of the BE-Series Coolant Reclaimer System is found in Figure 2. Chemistry data for the BE-Series Coolant Reclaimer System is not available at the present time.

## CONCLUSIONS

Antifreeze recycling is a cost effective alternative to purchasing and disposing antifreeze. With improved guidance for field use, installations should have no trouble recycling antifreeze on-site. The KFM Corporation Cool'r Clean'r Coolant Purification System and the Finish Thompson BE-Series Coolant Reclaimers generally have a payback period of 1-2 years depending on the amount of use.

# Field Demonstration of an Acid Recovery Process Using Diffusion Dialysis

**Second Tri-Service Environmental Technology Workshop**

**11 June 1997, St. Louis, Missouri**

Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140-2390

52353-03

## Table of Contents

# Acid Recovery Using Diffusion Dialysis


I. Background

II. Technology Description

III. Demonstration Site Selection

IV. Equipment Design and Operation

V. Preliminary Results

VI. Preliminary Economic Analysis

# The demonstration of diffusion dialysis for recovery of mineral acids is sponsored by the Naval Facilities Engineering Service Center (NFESC), Port Hueneme , CA.

- NFESC, working under the direction and in support of the Strategic Environmental Research and Development Program (SERDP), has been involved in developing technologies to extend the service life of metal preparation and finishing baths.

- Under this sponsorship, NFESC has conducted laboratory-scale testing of diffusion dialysis for the reclamation and reuse of mineral acids commonly used in naval plating facilities.

- The next step in the development process is to demonstrate and validate the technology at a DOD activity.

# The objective of the field demonstration is to utilize full-scale equipment in a production environment of a metal finishing shop to demonstrate the use of DD to recover mineral acids.

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# Acid Recovery Using Diffusion Dialysis


I. Background

II. Technology Description

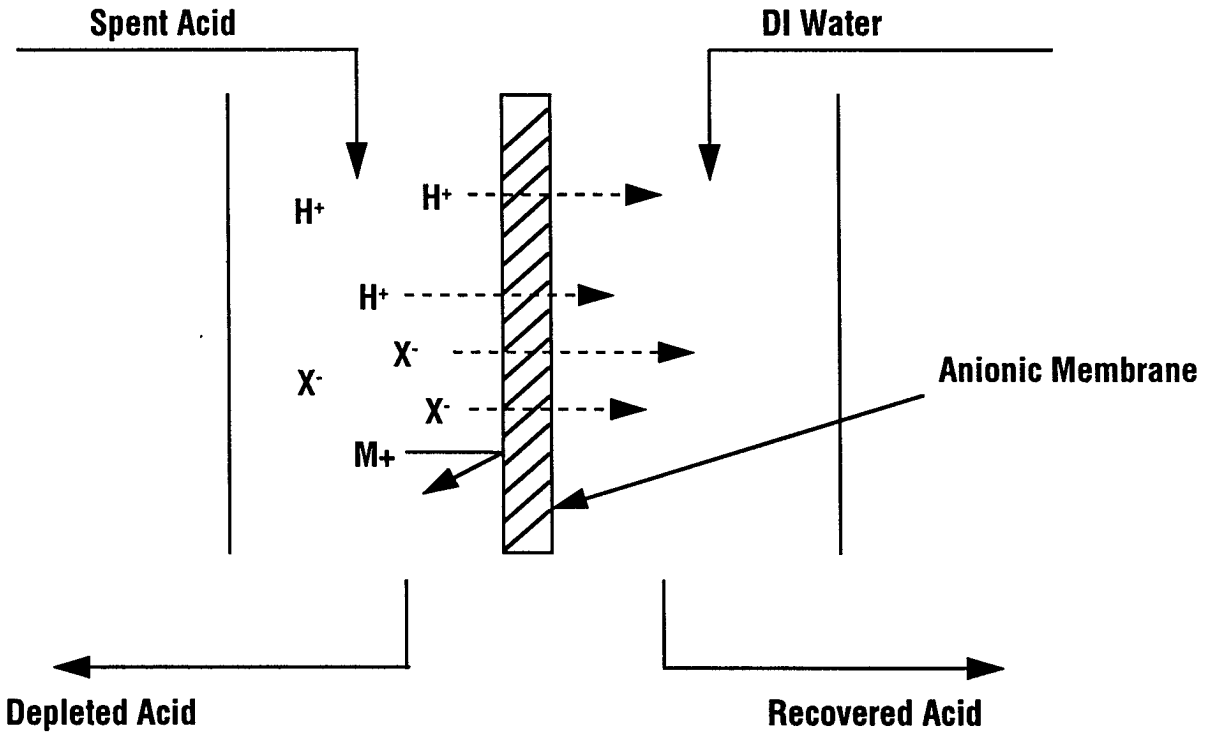
III. Demonstration Site Selection

IV. Equipment Design and Operation

V. Preliminary Results

VI. Preliminary Economic Analysis

# Diffusion Dialysis is a concentration driven separation process that involves the movement of acid ions across an anionic membrane into distilled water. The small, highly mobile hydrogen protons easily diffuse across the membrane to maintain electrical neutrality. The positively charged metals are rejected.



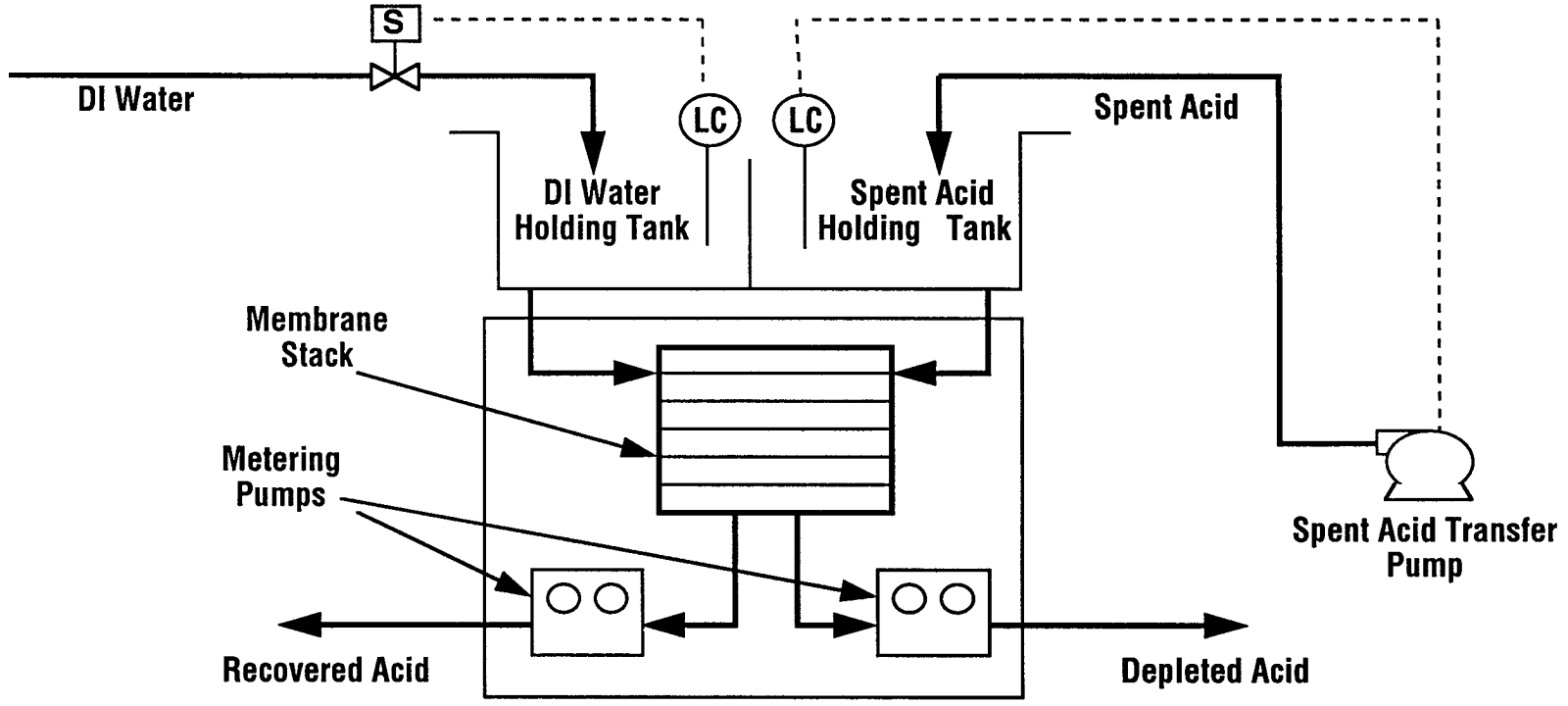
The primary variables in designing and operating a DD system are acid concentration, membrane surface area, flow rate of the DI water, and flow rate of the spent acid.

- Acid concentration determines the required membrane surface area to provide sufficient residence time for acid recovery.
- Increased DI water flow rate, relative to the spent acid flow rate, increases the concentration gradient and thus maximizes the acid recovery. However, the concentration of the acid will be lower due to the dilution effect.
- Increased spent acid flow rate minimizes residence time in the membrane and thus maximizes metal rejection.

# Laboratory testing results showed good recoveries for most acids and good rejection efficiencies for metals.

| Parameter | Acid Recovery (%) | Metal Rejection (%) |
|---|---|---|
| Hydrochloric Activation Solution | 93% | Fe - 65% |
| Sulfuric Acid Anodizing Solution | 79% | Al - 97% |
| HNO3/H3PO4 Pickling Solution | HNO3 - 88%<br>H3PO4 - 50% | Cu - 70% |
| HNO3/NH4HF2 Pickling Solution | HNO3 + HF - 73%<br>NH4HF2 - 40% | Fe - 87%<br>Ni - 81%<br>Cr - 90% |

# A typical equipment arrangement for a commercially available DD system utilizes gravity flow for the spent acid and deionized water. The systems are skid mounted and include a feed pump and two recovery pumps.



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# Acid Recovery Using Diffusion Dialysis


I. Background

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# The site selection process involved interviewing personnel at several DOD sites to determine whether the site met the following selection criteria.

- Use of mineral acid baths in their plating shop
- Generation of spent acid baths at a frequency to allow a reasonable time period for the demonstration.
- Desire to operate the DD systems after the completion of the demonstration phase testing.

# Tobyhanna Army Depot (TOAD), located in Tobyhanna, PA, met all of the selection criteria.

| Acid Bath | Application | Volume Disposed/Year |
|---|---|---|
| Hydrochloric Acid (32% w/w) | Pickling | 2500 |
| Nitric Acid (34% w/w) H2SO4 (66% w/w) | Stripping | 750 |
| Nitric Acid (76% w/w) Ammonium Bifluoride (6% w/w) | Stripping | 275 |

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# Acid Recovery Using Diffusion Dialysis


I. Background

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III. Demonstration Site Selection

IV. Equipment Design and Operation

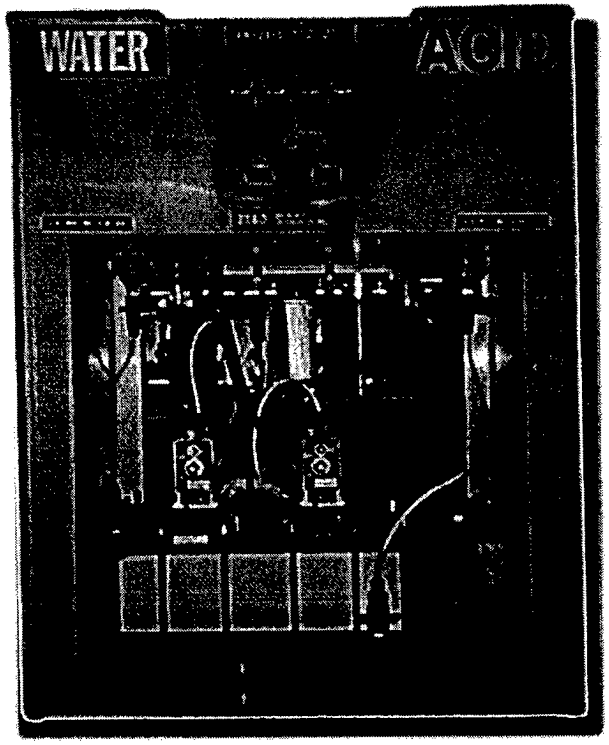
V. Preliminary Results

VI. Preliminary Economic Analysis

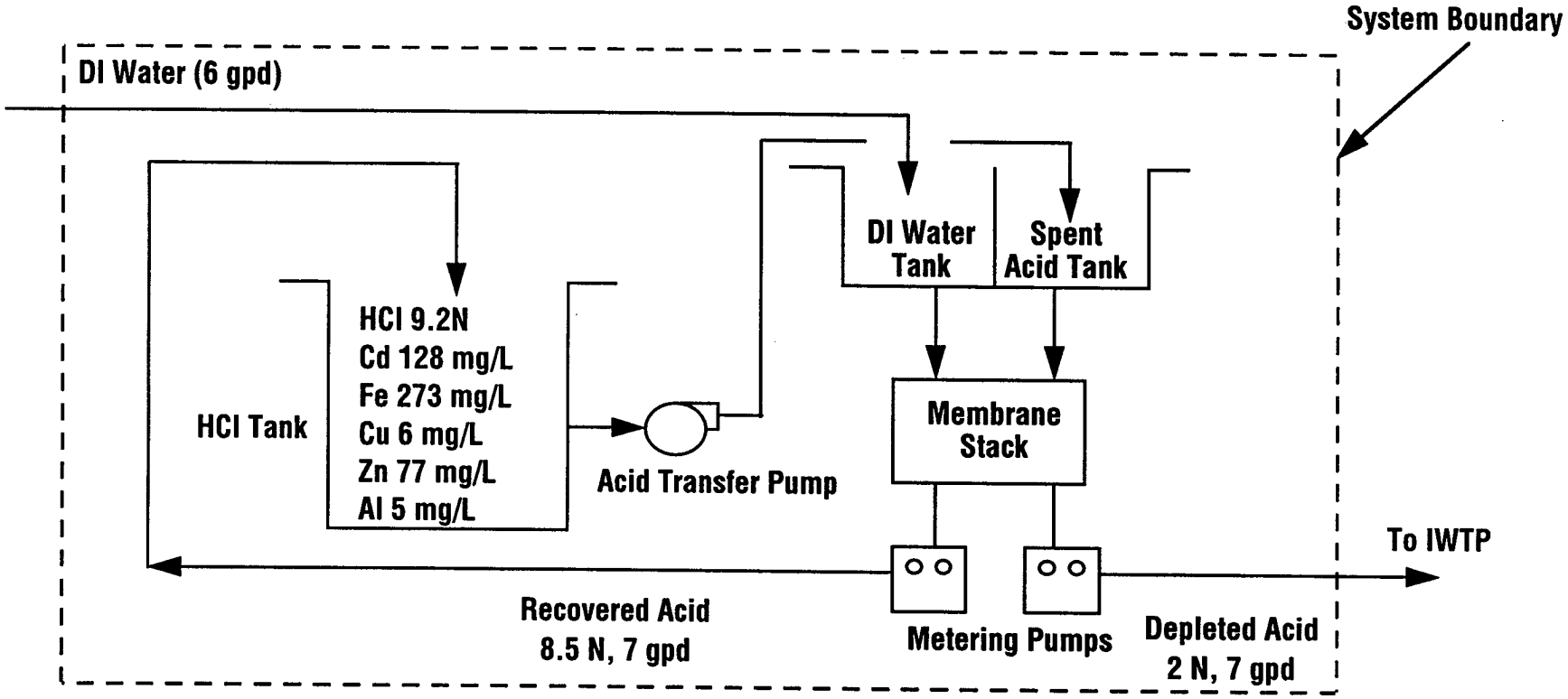
# Two DD systems were purchased for use at TOAD.

- Both systems were specified to treat 10 gpd of acid.
- One system has been dedicated to the recovery of the 100 gallon HCl pickling bath and is operating in a continuous mode.
- The second system has been dedicated to the remaining smaller acid baths and operates in a batch mode.
- Both systems were installed and started up in April 1997.

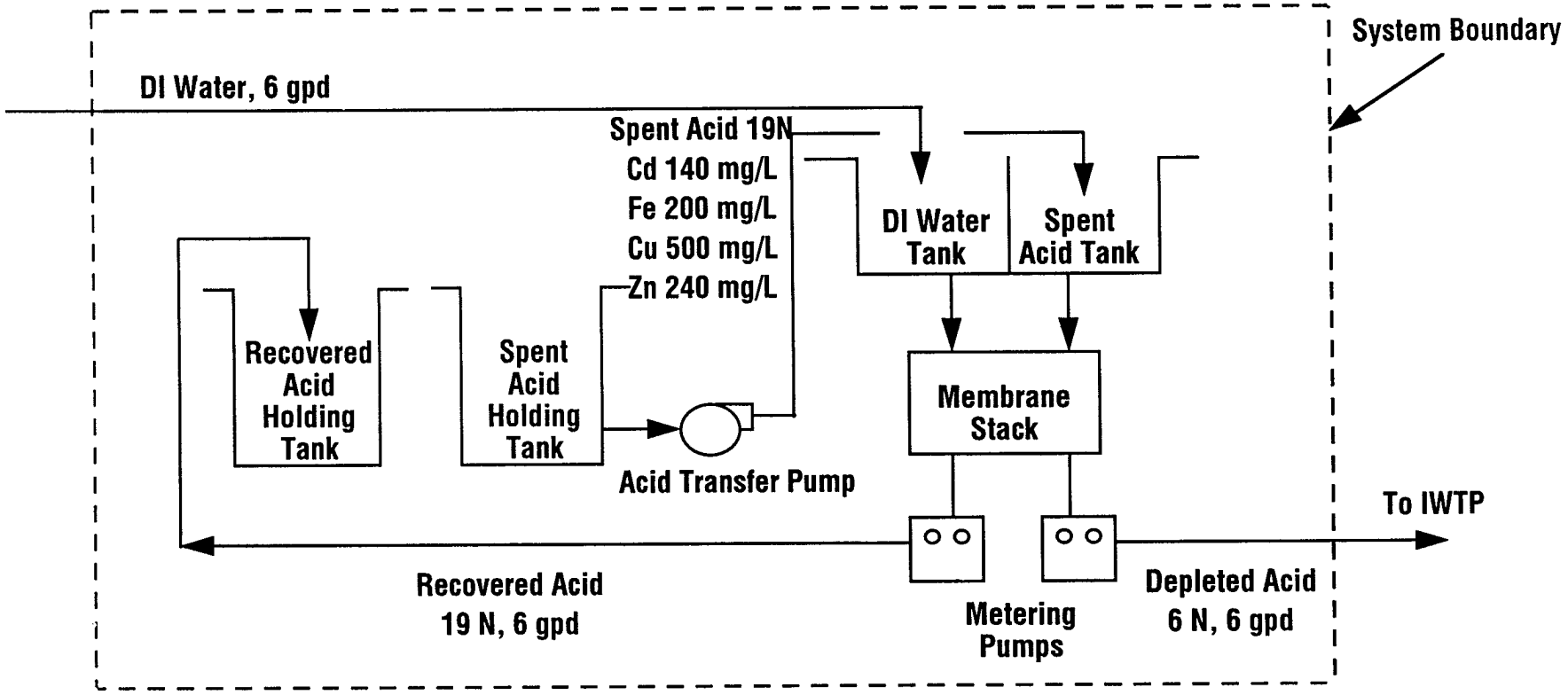
# Two DD systems were purchased with approximately 5200 sq. inches of membrane surface area.



# One system has been dedicated to the recovery of the 100 gallon HCl pickling bath and has been in operation in a continuous mode since 9 April 1997.



# The second DD system has been dedicated to recovering the smaller stripping baths. Two spent stripping baths have been recovered since start-up in April.



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# Acid Recovery Using Diffusion Dialysis


I. Background

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VI. Preliminary Economic Analysis

# Acid recoveries of up to 93% have been achieved with the HCl recovery system operating continuously.

| Parameter | Acid Recovery (%) | Metal Rejection (%) |
|---|---|---|
| HCl | 93% | — |
| Total Metals | — | 40 - 57% |

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# Results are available for only one batch run of the HNO3/H2SO4 stripping bath processed with the second DD system.

| Parameter | Acid Recovery (%) | Metal Rejection (%) |
|---|---|---|
| HNO3 | 80 - 90% | — |
| H2SO4 | 50 - 75% | — |
| Total Metals | — | 70 - 90% |

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# Acid Recovery Using Diffusion Dialysis


I. Background

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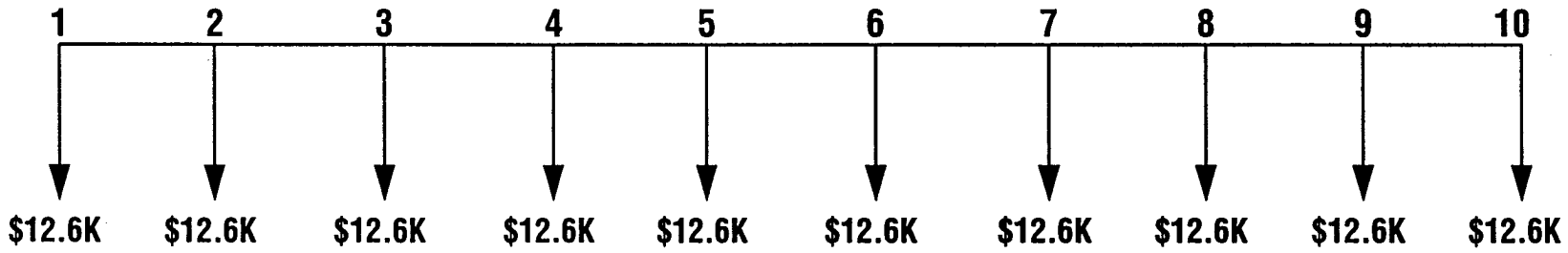
VI. Preliminary Economic Analysis

# A Preliminary Economic Evaluation indicates less than a 3 year payback for the investment based on the following assumptions:

- 100 HCl bath is changed over and disposed of 25 times per year.
- Current method of disposal is as a hazardous waste at $0.38 dollars per pound.
- Chemical replacement costs are approximately $138 per change over.
- Metals treatment/sludge disposal estimated to be $265 per change over.
- Labor requirements are not significantly changed when utilizing DD.
- Capital cost for a DD system estimated at $15,000.
- Project life is 10 years.
- Interest rate, i, = 6%.

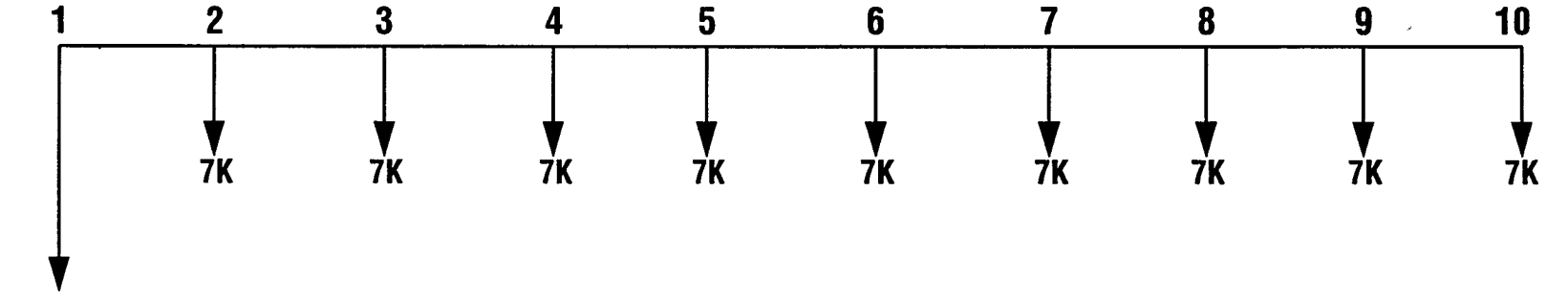
# Preliminary Economic Evaluation is favorable.

(Alternative A - Status Quo)




NPV = $92,700

(Alternative B - Diffusion Dialysis)




NPV = $68,000

# BIODEGRADATION OF AMMONIUM PERCHLORATE: OPERATIONAL IMPLEMENTATION

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## ABSTRACT

Ammonium Perchlorate (AP) is the primary solid rocket propellant oxidizer used in boosters for the Minuteman, Peacekeeper, Shuttle, Titan, and other major strategic, tactical and space systems. Propellant manufacture, testing, and disposal activities generate large quantities of AP contaminated waste water. The EPA recently proposed a preliminary reference dose for ammonium perchlorate that could regulate aqueous discharges to less than one ppm. In response to this problem a very robust and cost-effective biodegradation process has been developed by Armstrong Laboratory's Environics Directorate and its support contractor Applied Research Associates. In this process the perchlorate ion is biologically reduced to chloride. Aqueous solutions of perchlorate up to 1.5% can be treated to below the detectable limit (< 0.5 ppm). In 1995 a continuous-flow pilot system capable of treating up to 1000 gallons per day of effluent was designed, fabricated, and successfully tested at Tyndall AFB, Florida. In 1996 optimization studies were accomplished to transition this process to industry. Through a Cooperative Research and Development Agreement (CRDA) with Thiokol Corporation, Defense and Launch Vehicle Division, this process is being modified to treat perchlorate waste water containing salts, corrosion inhibitors, and other contaminants. A production-scale biodegradation process will be integrated into existing waste treatment processes at Thiokol's production facility near Brigham City, Utah, and will be operated by Thiokol under the CRDA. The capacity of the production-scale system will be over 3000 gallons per day, depending on perchlorate and salt concentration, and will directly complement other perchlorate recovery and reuse operations. The production-scale implementation of this process represents the culmination of six years of research and development efforts sponsored by the Air Force, the Joint Ordnance Commanders Group, and the Environmental Security Technology Certification Program Office.

## INTRODUCTION

This program was initiated in 1989 under the sponsorship of the Air Force Office of Scientific Research (AFOSR) and the Air Force Armstrong Laboratory, Environics Directorate, Tyndall AFB, FL. At that time biodegradation was recognized as a viable process to treat dilute AP waste streams and remediate contaminated soil and ground water. An organism capable of reducing perchlorate was isolated by Attaway and Smith[1] and the bacterium designated HAP-1. Laboratory studies were conducted in batch mode and in continuous stirred tank reactors (CSTRs). The process variables that affect perchlorate

reduction performance were addressed in laboratory studies. These included temperature, pH, nutrient type, nutrient concentration, residence time, and perchlorate ion concentration. Nutrients had to be commercially available, relatively low cost, and demonstrate good performance with respect to perchlorate reduction. The most promising nutrients were dried brewer's yeast and yeast extracts. Typical treatment conditions identified were:

| | |
|---|---|
| Temperature | 37-42°C |
| pH | 6.5-7.6 |
| Residence Time | 8-24 hours |
| Perchlorate Concentration | < 6000 ppm |
| Degradation Rates | 125 mg/l per hr |

## PILOT-SCALE DEMONSTRATION

The results of the laboratory studies were used to design, fabricate, and demonstrate the operability of a complete AP biodegradation system using actual effluent from the wash out of Minuteman stage 2 propellant by the Aerojet Propulsion Division. The design of the pilot-scale system was centered around a 350 gallon anaerobic reactor capable of treating up to 1000 gallons per day of dilute AP waste water. A new facility was constructed to house the pilot bioreactor system at the Tyndall AFB, Florida. Construction of the pilot system was performed by Case Engineering, Lakeland, Florida. The modular designed, skid mounted pilot system was delivered to Tyndall AFB in October 1994 on three trailers and completely assembled in only one week. The entire system, shown in the Figure 1 below, occupies a 40 ft by 52 ft concrete pad that is enclosed on three sides. In May 1995, the pilot system was operated in the continuous mode for over 600 hours using an extract prepared from dried brewer's yeast to reduce a 3000 ppm perchlorate feed to less than the detectable limit. The pilot system was also operated for over 900 hours, at residence times as short as 12 hours, on a commercially available, water-soluble yeast extract called BYF-100. Both nutrients performed well. The BYF-100 nutrient is more expensive than dried brewer's yeast but, also, more efficient and can result in a lower biological oxygen demand (BOD) for the effluent.

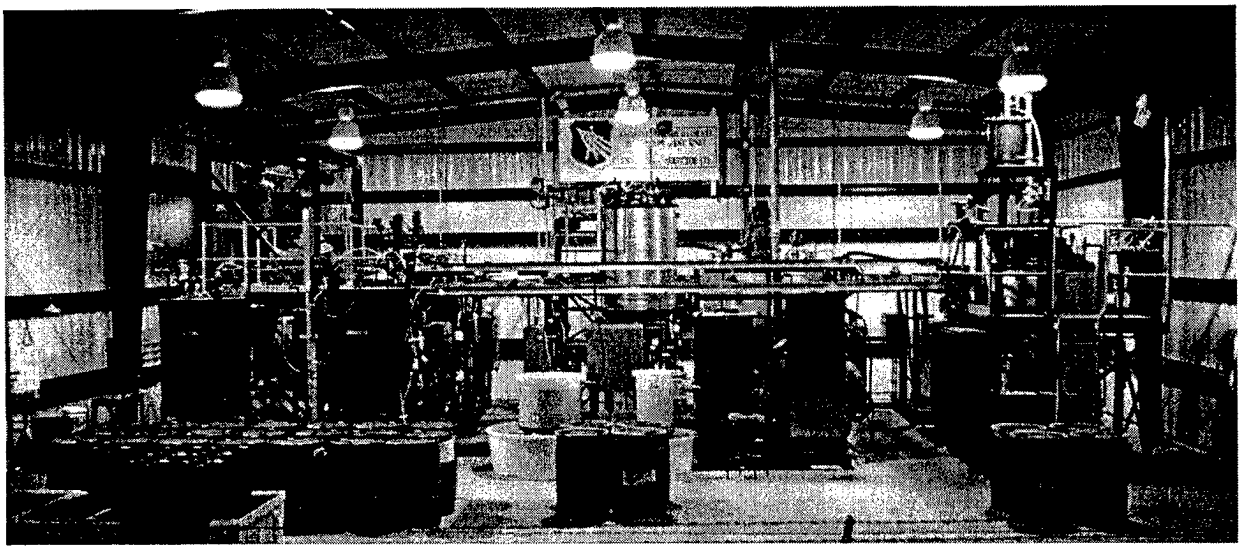


Figure 1. Photograph of the pilot-scale AP biodegradation system at Tyndall Air Force Base, Florida.

## RECENT DISCOVERIES

Laboratory efforts have culminated in the positive identification of the specific genus and species of the bacterium responsible for perchlorate reduction as *Wolinella succinogenes*[2]. This has enabled us to take advantage of the scientific data and literature on this organism and has led to promising process enhancements. One discovery is the microaerophilic nature of *Wolinella succinogenes*. This means that this organism may prefer small concentrations of oxygen or that oxygen could compete with perchlorate reduction as an alternate electron acceptor. Previously it was assumed that oxygen did not play a critical part in perchlorate reduction because other microbes in this mixed culture would consume the oxygen to maintain anaerobic conditions. However, when strict anaerobic conditions were maintained using nitrogen, very stable, predictable perchlorate reduction was obtained at rates exceeding 0.5 g/l per hour. In addition, it was successfully demonstrated that the HAP-1 mixed culture can destroy AP and other components of more complex aqueous wastes from class 1.1 propellants containing nitroglycerin, nitramines, stabilizers, and plasticizers. One patent (5,302,285)[3] has been granted on this process. Additional patents are pending.

## OPTIMIZATION STUDIES

Additional studies have demonstrated that this biodegradation process is much more durable, flexible, and predictable than originally perceived. Process optimization efforts have focused on reducing operating cost, tailoring the process variables, and reconfiguring operations to treat representative industrial wastes. These efforts resulted in an increased robustness of the process which can effectively treat effluents containing over 1.5 percent (15,000 ppm) perchlorate. Perchlorate can also be reduced in effluents with a high salt content (> 2.3 % $Na^+$, $K^+$, $Cl^-$), other impurities ($NO_2^-$, $NO_3^-$, $SO_4^=$), and over a broad temperature range (20-40°C). Lower cost nutrients were successfully demonstrated that significantly lower this primary operating expense. Dried brewer's yeast can be used directly, without extracting the critical nutrients. This increases BOD in the effluent but reduces the total nutrient requirements. Preliminary studies have shown that dried, sweet cheese whey may also be an effective nutrient by itself or in mixtures with brewer's yeast. The cheese whey is more soluble than brewer's yeast and is only one fourth the cost. Nutrient costs may be reduced even further by using unprocessed yeast and cheese whey wastes.

## OPERATIONAL IMPLEMENTATION

Industrial applications were evaluated and a waste stream at the Thiokol Corporation was targeted for further testing. This effluent was a brine containing perchlorate, nitrates, and nitrites. The laboratory studies described above indicated that the perchlorate in this effluent could be effectively treated. In order to demonstrate performance at a larger scale, the existing pilot plant was modified to enable operation of the larger (720 gallon), aerobic reactor as an anaerobic reactor. A nitrogen generation system was used to control anaerobic conditions. The perchlorate in a high salt (>2.3% with $NO_2^-$ and $NO_3^-$ impurities), low perchlorate (1000 ppm) effluent was easily reduced to below detectable limits at 35°C and 24 hour residence time using low-cost, whole brewer's yeast and cheese whey nutrients. A summary of the test conditions and results are provided in Table 1. Condition #1 is the start-up condition on yeast extract (BYF-100). The perchlorate concentration in the feed was elevated and the salt concentration kept low. Condition 2 represents operational levels of perchlorate and salt. At condition #3 the nutrient was switched to dried, whole brewer's yeast. At condition #4 a corrosion inhibitor was added to the feed to determine the effects of nitrite and nitrate on perchlorate and anion reduction. At condition #5 the nutrient was switched to a blend of 75% dried, sweet cheese whey and 25% dried brewer's yeast. Condition #7 was a dormancy test to determine if the ability of HAP-1 to reduce perchlorate could be retained over an extended period of time without perchlorate in the feed. Condition

#8 demonstrated that the original perchlorate reducing capability of the microbes could be re-established in less than two days.

TABLE 1. SUMMARY OF HIGH-SALT, PILOT-PLANT TESTS

| Condition ID | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **Days Operated** | 7 | 11 | 6 | 7 | 7 | 7 | 14 | 7 |
| **Residence Time, hours** | 24-48 | 24 | 24 | 24 | 24 | 24 | 360 | 24 |
| **Feed Composition (Avg.)** | | | | | | | | |
| $ClO_4^-$, ppm | 2433 | 1366 | 1112 | 1053 | 1224 | 1011 | 0 | 2727 |
| $NO_2^-$, ppm | 0 | 0 | 0 | 391 | 559 | 0 | 0 | |
| $NO_3^-$, ppm | 0 | 57 | 14 | 137 | 157 | 0 | 0 | |
| BYF-100, g/l | 7.04 | 3.02 | | | | | 30 | 113.4 |
| Dried yeast, g/l | | | 4.04 | 3.97 | | | | |
| Whey + 25% yeast, g/l | | | | | 4.01 | 3.99 | | |
| Nutrient Ratio (N:AP) | 2.89 | 2.21 | 3.63 | 3.77 | 3.28 | 3.95 | - | 4.91 |
| Total salts, wt% | 0.23 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | < 2.3 | ~0.9 |
| **Effluent Analysis (Avg.)** | | | | | | | | |
| $ClO_4^-$, ppm | 0 | 0 | 0 | 0 | 0 | 6 | - | 0 |
| $NO_2^-$, ppm | 0 | 0 | 2 | 34 | 0 | 0 | | |
| $NO_3^-$, ppm | 2 | 3 | 3 | 5 | 3 | 0 | | |
| COD, ppm | | | | 3400 | 4340 | 4340 | | 6020 |

## PROTOTYPE DEMONSTRATION

A contract was awarded to Applied Research Associates and Case Engineering, the engineering and construction firm who built the existing pilot plant. Under this contract the existing pilot system is being redesigned and modified. This new production-scale system will undergo testing at Tyndall AFB before being shipped to Thiokol and integrated into existing wastewater treatment facilities for demonstration and validation. As part of the CRDA with the Air Force Armstrong Laboratory, Thiokol will conduct a two-year operational validation of this technology. During the validation, performance will be reported and data made available to all interested government and industrial parties. A schematic of the Thiokol production-scale system is shown in Figure 2. At the time of this writing, the redesign and modifications were complete. The system is currently undergoing functional testing on actual Thiokol effluents at Tyndall AFB.

## OPERATING COST

The most attractive aspect of ammonium perchlorate biodegradation is the low operating and investment costs. The Figure 3 clearly shows that operating costs to treat dilute perchlorate effluents are very acceptable. These costs are based on actual and predicted costs for all of the components shown. As the concentration of perchlorate increases, operating costs increase almost linearly due to decreased capacity and increased nutrient requirements. The implication is that at high concentrations of perchlorate, recovery may become a more cost-effective approach. However, even recovery processes will directly benefit from this low-cost method of treating their by-product streams and mixed or contaminated perchlorate wastes.

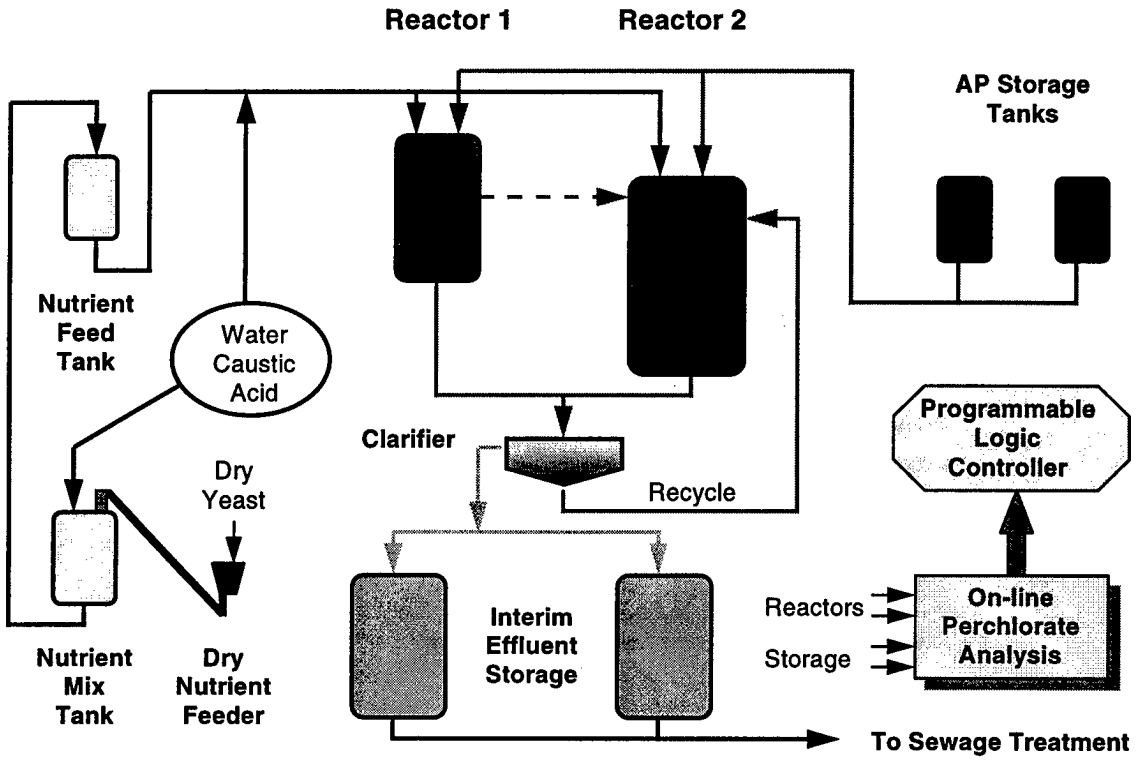



Figure 2. Schematic of the Thiokol production-scale system.

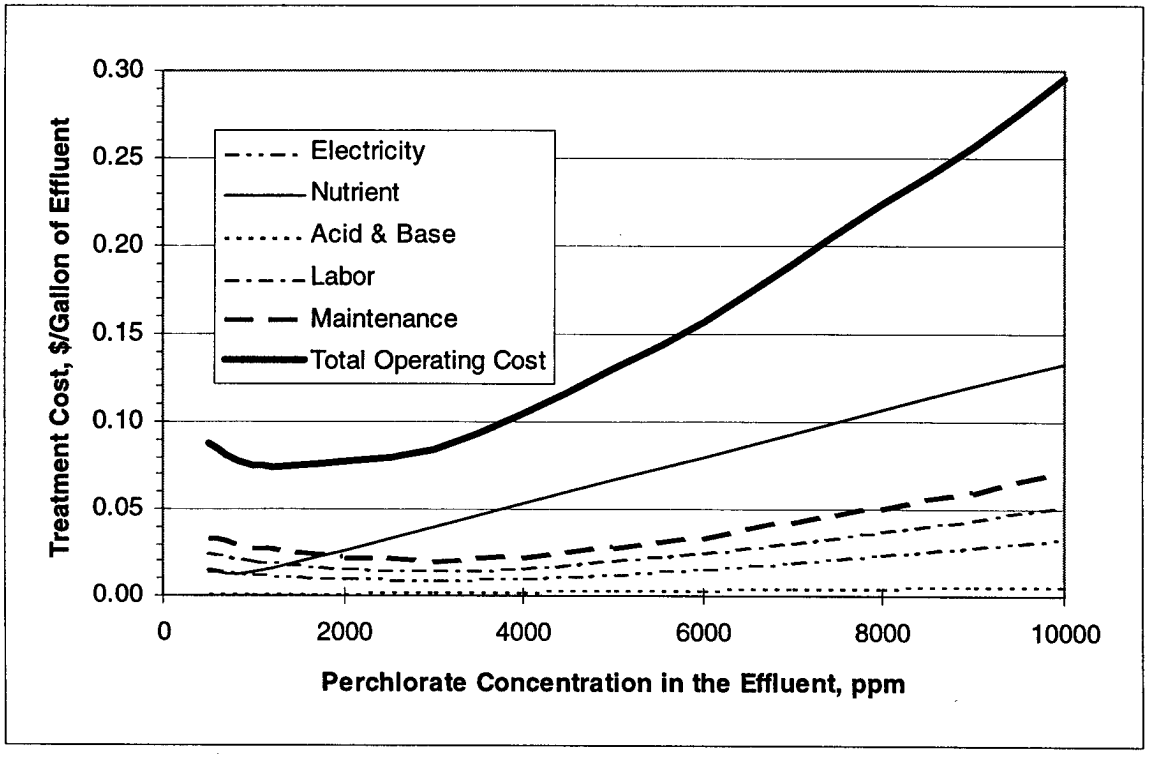



Figure 3. Projected operating costs for the Thiokol production-scale system.

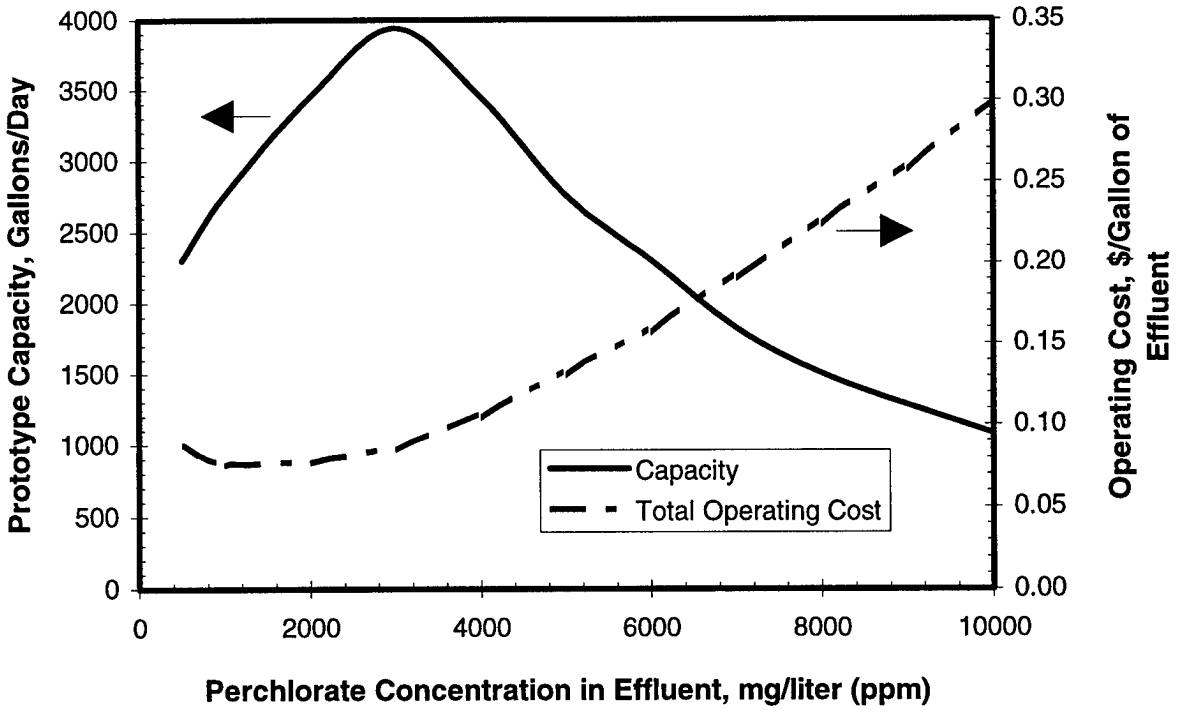



Figure 4. Capacity of the Thiokol production-scale system as a function of perchlorate concentration.

Figure 4 shows that the treatment capacity of the Thiokol production-scale system is near maximum when the perchlorate concentration in the effluent is in the 3000-4000 ppm range. At this concentration the elevated nutrient requirement results in efficient microbial growth and high perchlorate reduction rates. At lower perchlorate concentrations less nutrient is used. This lowers the perchlorate reduction rate resulting in increased residence time and decreased throughput. Higher perchlorate concentrations require increased residence time to reduce the additional perchlorate. Above 6000 ppm perchlorate, the system is operated in the series mode and overall residence time is increased further in order to accomplish complete reduction of the perchlorate ion.

## CONCLUSION

The Silo-Based ICBM Systems Program Office (SBICBM SPO) has planned and programmed for the remanufacture of the Minuteman III propulsion systems. Preliminary engineering and development programs are in progress. The SPO has already decided to reuse the stage 1 and 2 motor cases which would result in saving the production program an estimated $1-2 billion. Water washout of the solid propellant is the accepted, safe method to accomplish this case recovery and has been proposed for stage 1 remanufacture. The ability to safely recover and dispose of over 6 tons of propellant per day, on a continuous basis, is critically important to the success of the Minuteman III remanufacture program. In addition, the Titan Program Office recently awarded a contract to Thiokol to washout up to 57 Titan solid rocket booster segments (over 4 million pounds of propellant). This program is also dependent on propellant and component recovery that is made possible by the ability to dispose of dilute perchlorate waste streams through the implementation of this biodegradation process. In addition, production of

other rocket motors at Thiokol, including the Space Shuttle Solid Rocket Motor segments, will directly benefit from the implementation of this process.

The process described in this paper is a proven, low-cost approach to addressing the many perchlorate treatment needs brought about by more stringent and widespread environmental regulation. Disposal of ammonium perchlorate from production, remanufacturing, test and evaluation, and remediation is currently an industry wide problem. The ability to effectively biodegrade dilute ammonium perchlorate wastes will enable continued use of this critical defense material in both rocket motors and ordnance items.

## REFERENCES

1. Attaway, H., and Smith, M. 1993. "Reduction of Perchlorate by an Anaerobic Enrichment Culture." Journal of Industrial Microbiology. 12: 408-412

2. Wallace, W., Ward, T., Breen, A., Attaway, H. 1996 "Identification of an Anaerobic Bacterium Which Reduces Perchlorate and Chlorate as *Wolonella succinogenes*." Journal of Industrial Microbiology. 16: 68-72

3. United States Patent 5,302,285. "Propellant Wastewater Treatment Process." April 12, 1994

# REMEDIATION III

# SAMPLING STRATEGY FOR SITE CHARACTERIZATION AT EXPLOSIVES-CONTAMINATED SITES

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## ABSTRACT

This study assessed sampling strategies for characterization of explosives-contaminated sites as impacted by substantial short- and mid-range spatial heterogeneity of analyte distribution. Soil samples were collected and analyzed individually and as composites by colorimetric and immunoassay-based on-site methods, as well as standard laboratory protocols. Short-range heterogeneity was assessed at 10 sampling sites on four installations contaminated with TNT, DNT, HMX, or ammonium picrate. Mid-range heterogeneity was investigated at an active antitank range contaminated with residues of HMX and TNT. In all cases, results from on-site analysis were compared with those from laboratory analysis to assess how well sites could be characterized using on-site methods.

Substantial short-range heterogeneity was encountered at all 10 sampling locations, independent of the type of explosive present or the mode of contamination. For six sampling locations, the short-range heterogeneity was enormous; thus sampling error overwhelmed analytical error. For the other four sampling locations, short-range variability was less extreme and normal distribution statistics were used to fractionate total error variances. Standard deviations due to sampling were greater than that due to analysis by factors ranging from 2.6 to 22.8, whether on-site or laboratory analyses were used.

Analytical results from colorimetric on-site methods and standard laboratory protocols were in excellent agreement in nearly every case. This was particularly true for TNT, which was the major contaminant encountered at seven of the 10 sites investigated. Results for HMX were equally impressive using the colorimetric-based "RDX" test, although HMX was the major contaminant at only one of the 10 sites investigated.

An active antitank range was characterized for explosives concentrations using a combination of "area-integrated" sampling, in-field sample homogenization, compositing to produce representative grid samples, and on-site analysis. The depth of contamination and the dimensions of sampling grids were determined using on-site methods. Overall this approach appears to be an efficient, cost-effective means of providing representative data for making remediation decisions at sites contaminated with residues of high explosives.

## 1. INTRODUCTION

The ultimate goal of site characterization for HTRW sites is to provide sufficient information so that an informed decision can be made with regard to the need for remediation. To accomplish this goal, potentially contaminated sites are generally divided into small geographically defined units (grids) and samples are collected and analyzed to characterize the concentrations of contaminants within these zones. The surface areas of these grids can range from hundreds to many thousands of square feet, and often a single core sample is collected within the grid, divided into depth intervals, and the various depth related samples analyzed at an off-site commercial laboratory. Decisions regarding the need for cleanup are made by comparing contaminant concentrations obtained from the analysis of these samples to action levels determined by risk assessment.

An unstated assumption of this approach is that the concentration of contaminants of interest in the samples collected and analyzed adequately represents the average concentration of those contaminants at the collected depths within grid boundaries. Discussion with both the personnel conducting site characterization activities and those within the government that oversee these activities indicate that some of the shortcomings of this approach are recognized, but that financial considerations have precluded the analysis of sufficient numbers of samples to adequately address the problem. The high cost of laboratory analyses, in particular, is often quoted as an impediment to the analysis of the number of samples necessary to truly characterize the distribution of contaminants.

Explosives represent a fairly unique set of environmental contaminants. The most commonly encountered explosives, environmentally, are TNT (2,4,6-trinitrotoluene) and RDX (1,3,5-hexahydro-1,3,5-trinitrotriazine)[1]. TNT, RDX and other secondary explosives are solids at environmental temperatures and were generally released into the environment as particulates. Thus the bulk of contamination generally resides in near-surface soils. These compounds have low vapor pressures, and hence no special precautions are needed during sample collection and homogenization to mitigate vapor losses. They are relatively polar, particularly for neutral organic compounds, and do not sorb strongly to soils by hydrophobic interactions. TNT and RDX have aqueous solubilities in the 50- to 150-mg/L range at environmental temperatures and, from a kinetic point of view, dissolve slowly into aqueous solution. Because of these factors, high concentrations of these compounds can persist in near-surface soils for decades. Once they are dissolved in water, though, they can migrate through the unsaturated zone to the water table and form plumes in underlying aquifers, miles in length.

The particulate nature of these contaminants in near-surface soils leads to the potential for substantial levels of spatial heterogeneity in contaminant distribution. Thus use of a single discrete sample to represent even a small geographical area is risky, unless there is some knowledge of the distribution of these contaminants. Recently we presented some initial information on the short-range heterogeneity of explosives contaminants at several contaminated sites.[2,3]

## 2. OBJECTIVES

The first major objective of this work was to further characterize the short-range spatial heterogeneity of contaminants in near-surface soils at explosives-contaminated sites. This was done by conducting field sampling and analysis studies at 10 explosives-contaminated sites on four installations that varied in explosives analytes present, mode of contamination, soil type and geohydrology. Statistical analyses of the results were conducted to determine the following:

1. Analytical error estimated from the pooled variances from duplicate analyses of seven grab samples collected within a localized area. Short-range sampling error was estimated from the variance computed from the differences of mean values of the seven grab (soil) samples.

2. The degree to which some form of composite sampling could be used to reduce sampling error.
3. Whether inexpensive, colorimetric on-site analysis methods were adequate to provide an accurate description of contaminant distribution and a reliable estimate of sampling error.

The second major objective was to develop a sampling strategy for characterizing explosives-contaminated sites that provides representative samples and a) takes advantage of the ability to generate near real-time information from on-site analyses, and b) overcomes the problem of large localized spatial heterogeneity in contaminant concentrations. To overcome heterogeneity problems, a combination of collecting an "area-integrated sample" combined with a simple compositing approach was evaluated for obtaining representative samples within defined geographic (grid) boundaries.

The third objective of this work was to document the levels of accumulation of HMX and TNT on an active firing range, where the munition fired was a 66-mm M72 rocket filled with octol, a melt-cast explosive composed of a 70:30 mixture of HMX and TNT.

## 3. EXPERIMENTAL SECTION

### 3.1 SAMPLING LOCATIONS

Sampling studies were conducted at four installations: 1) Monite, a Bureau of Land Management installation near Sparks, Nevada; 2) Hawthorne Army Ammunition Plant (AAP), Hawthorne, Nevada; 3) Volunteer AAP, Chattanooga, Tennessee; and 4) the Canadian Force Base, Valcartier (CFB-Valcartier), Courcelette, Quebec. Information regarding sampling sites at these installations is presented in Table 1. Detailed descriptions of the individual sampling locations are presented elsewhere.[3,4]

TABLE 1. SAMPLING LOCATIONS.

| Sampling location | Installation | Contamination cause | Major contaminant |
|---|---|---|---|
| 1 | Monite, Nevada | Commercial reprocessing | TNT |
| 2 | Monite, Nevada | Commercial reprocessing | DNT |
| 3 | Monite, Nevada | Commercial reprocessing | TNT |
| 4 | Hawthorne AAP, Nevada | Dust from crates of explosives | TNT |
| 5 | Hawthorne AAP, Nevada | OB/OD (open burning–open detonation) | TNT |
| 6 | Hawthorne AAP, Nevada | Disposal lagoon | AP* |
| 7 | Volunteer AAP, Tennessee | Spills from TNT washhouse | TNT |
| 8 | Volunteer AAP, Tennessee | Drainage ditch for pink water | TNT |
| 9 | Volunteer AAP, Tennessee | Remote location, source unknown | TNT |
| 10 | CFB-Valcartier, Quebec | Antitank firing range | HMX† |

*Ammonium picrate
†1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine

## 3.2 SOIL SAMPLING PROCEDURE FOR SHORT-RANGE ASSESSMENT

A common sampling pattern was used at all 10 locations. A plastic template was placed on the ground with the center at the selected sampling location and oriented with sample numbers 2 and 5 oriented north–south. Seven samples were collected in a wheel pattern with sample number 1 in the center. The radius of the wheel was 61 cm, and samples arranged around the wheel were separated by 61 cm.

All seven soil samples were collected at the surface from 0 to 15 cm using a manual 5.0-cm-i.d. stainless-steel hand corer. When vegetation was present, it was removed. Cores were transferred to plastic Ziploc bags and taken to a processing area.

## 3.3 SOIL SAMPLING PROCEDURE FOR MID-RANGE ASSESSMENT

To assess larger-scale heterogeneity at the CFB-Valcartier site, the area around two target tanks was divided into 6- × 6-m grids (labeled D1 through D11, and C4 through C10) and each grid was subdivided into four 3- × 3-m subgrids, labeled A, B, C, and D. Samples within each subgrid were obtained as follows. A spading shovel was used to scrape the top 5 cm of soil from a 20-cm wide circular path of radius 77 cm located in the center of each subgrid; this path sampled about 10% of the surface within the subgrid. The soil scraped from the surface was piled in the center of the circle and mixed thoroughly with the spading shovel and a small hand shovel. Pieces of metallic and ceramic debris from munition detonation were removed by hand and a subsample of about 1 kg of soil was collected from random locations in the pile. Duplicate portions of soil from these soil piles were collected in nine randomly selected subgrids from the total of 40 to assess the degree of uncertainty due to subsampling the pile. Samples prepared in this manner were designated *area integrated.* In these same nine subgrids, duplicate area-integrated samples were prepared in a manner identical to that described above, except that the sampled area was offset from the initial one. This was done to assess the uncertainty due to the fact that only about 10% of a subgrid was included in any one area-integrated sample. All samples were returned to the processing area in plastic Ziploc bags in a cooler.

## 3.4 SOIL SAMPLE PROCESSING AND ANALYSIS

Soil samples were kept cold until processed, either the same day they were collected or the morning following collection the previous afternoon. Soil samples varied somewhat in moisture content and texture from location to location. Some soils were quite dry and consisted mainly of sands and gravels while others had a much greater level of moisture and had a much greater clay or organic content. Individual samples were further homogenized in the soil processing area and subsamples were removed for on-site analysis and for subsequent laboratory analysis. Details on the processing of discrete samples, methods used for subsampling and preparation of composite samples are presented elsewhere[3,4].

For on-site colorimetric analysis, 20-g soil samples from all sampling locations were extracted with acetone as described in detail elsewhere[2,3] and analyzed on site using the EnSys colorimetric TNT and RDX methods[5]. The EnSys RDX method was used to estimate HMX concentration using an HMX standard for calibration. A short extraction kinetic study was conducted with the initial samples collected at each site and the extraction times were selected based on these results[3,4]. At Monite and Hawthorne, a 3-minute extraction was adequate, while at Volunteer and CFB-Valcartier, a 30-minute extraction was required. At CFB-Valcartier, these same acetone extracts were returned to CRREL and analyzed by reversed-phase high-performance liquid chromatography (RP-HPLC) using the separations described in SW846 Method 8330[6]. Separate subsamples of soil from all 10 sampling locations were also analyzed RP-HPLC analysis according to SW846 Method 8330[6].

## 4. RESULTS AND DISCUSSION

### 4.1 SHORT-RANGE HETEROGENEITY

The degree of short-range spatial heterogeneity was assessed at 10 sampling locations at four installations. The major contaminant at seven of these locations was TNT; 2,4-DNT (DNT), ammonium picrate (AP) and HMX were each the major contaminant at one site. A summary of the analytical results for discrete soil samples from these locations are presented in Table 2. The total uncertainty associated with site characterization using single discrete sample collection and analysis was fractionated into sampling and analytical error for the five locations where the data were sufficiently normal to allow this procedure (Table 3). Generally, sampling error was a factor of 10 or greater than that due to analysis, whether on-site or laboratory results were used. Results from analysis of composites prepared from the seven discrete samples at each location, however, indicated that they provided concentration estimates that were in good agreement with the mean of the discrete samples with a relative standard deviation of about 10% compared to a relative standard deviation (RSD) for discrete samples of about 115% (Table 4). Thus much more representative data can be obtained through the use of homogenization of discrete samples and compositing prior to on-site analysis, than is currently being produced using typical sampling protocols based on analysis of discrete samples.

TABLE 2. COMPARISON OF MEASURES OF ANALYTICAL PRECISION, ACCURACY AND DISCRETE SAMPLE REPRESENTATIVENESS FOR EXPLOSIVES ANALYTES AT MONITE (M), HAWTHORNE (H), VOLUNTEER (V) AND CFB-VALCARTIER (C).

| | Precision | | | | Accuracy | Local heterogeneity | |
|---|---|---|---|---|---|---|---|
| | Relative Standard Deviation (RSD) of duplicates (%) | | Largest concentration ratio of duplicates | | Slope of 0-intercept model | Ratio of highest mean concentration vs. lowest for discrete samples | |
| Sample location | On-site | Lab | On-site | Lab | On-site vs. lab | On-site | Lab |
| M-1 (TNT) | 3.9 | 11.1 | 1.16 | 1.47 | 0.815 | 243 | 315 |
| M-2 (DNT) | 23.0 | 10.0 | 1.66 | 1.46 | 0.350 | 10.6 | 33.4 |
| M-3 (TNT) | 16.7 | 6.5 | 1.82 | 1.19 | 1.464 | 50.0 | 98.1 |
| H-4 (TNT) | 12.5 | 13.5 | 1.70 | 1.99 | 0.911 | 69.0 | 58.1 |
| H-5 (TNT) | 3.3 | 4.9 | 1.13 | 1.16 | 0.847 | 28.9 | 29.5 |
| H-6 (AP) | 11.6 | 11.9 | 1.50 | 1.88 | 0.967 | 688 | 43,000 |
| V-7R (TNT) | 4.9 | 5.1 | 1.27 | 1.21 | 0.677 | 3.8 | 3.0 |
| V-8 (TNT) | 19.7 | 4.5 | 1.73 | 1.19 | 1.070 | 53.1 | 55.6 |
| V-9 (TNT) | 4.1 | 5.1 | 1.13 | 1.17 | 1.032 | 8.2 | 5.7 |
| C-10 (HMX) | 6.9 | 19.2 | 1.82 | 2.54 | 0.988 | 20.2 | 34.3 |
| C-10 (TNT) | ** | ** | 1.60 | 3.60 | 1.051* | >7 | >7 |
| Mean (TNT only) | 9.3 | 7.2 | 1.42 | 1.34 | 0.983 | 65.1 | 80.7 |

*Slope for model with intercept. Intercept was 0.63, but was found to be statistically signicant at the 95% confidence level.

**RSDs could not be computed because many values were less than detection limits for one ot the duplicates.

TABLE 3. FRACTIONATION OF TOTAL ERROR INTO ANALYTICAL AND SAMPLING COMPONENTS.

| | Standard deviation | | | | Ratio | |
|---|---|---|---|---|---|---|
| | Analytical | | Sampling | | Sampling/analytical | |
| Sampling location | On-site | Lab | On-site | Lab | On-site | Lab |
| Hawthorne location 4(TNT) | 217 | 265 | 1,970 | 2,150 | 9.1 | 8.1 |
| Hawthorne location 5(TNT) | 5.3 | 11.0 | 121 | 131 | 22.8 | 11.9 |
| Volunteer location 7R(TNT) | 5,120 | 6,320 | 24,700 | 27,600 | 6.1 | 4.4 |
| Volunteer location 9(TNT) | 1.0 | 1.0 | 10.4 | 12.4 | 10.4 | 12.4 |
| CFB-Val. location 10(HMX) | 10.9 | 38.1 | 123 | 135 | 11.3 | 3.5 |

*Data unavailable.

TABLE 4. COMPARISON OF RESULTS FROM DISCRETE AND COMPOSITE SAMPLES FOR EXPLOSIVES ANALYTES AT MONITE (M), HAWTHORNE (H), VOLUNTEER (V) AND CFB-VALCARTIER (C) FROM COLORIMETRIC ON-SITE ANALYSES.

| | | Concentration (mg/kg) | | | |
|---|---|---|---|---|---|
| | Major | Discrete samples | | Composite samples | |
| Location | analyte | Mean | RSD* | Mean | RSD** |
| M-1 | TNT | 13500 | 124% | 13100 | 4.1% |
| M-2 | DNT | 16100 | 72% | 23800 | 13.2% |
| M-3 | TNT | 19.8 | 212% | 12.6 | 9.5% |
| H-4 | TNT | 1970 | 101% | 1750 | 10.1% |
| H-5 | TNT | 156 | 78% | 139 | 11.9% |
| H-6 | AP | 869 | 184% | 970 | 3.3% |
| V-7R | TNT | 57500 | 44% | 54800 | 10.7% |
| V-8 | TNT | 9920 | 121% | 11300 | 17.8% |
| H-9 | TNT | 13.7 | 132% | 16.6 | 9.0% |
| C-10 | HMX | 158 | 78% | 176 | 7.4% |
| | | Discrete mean RSD = 115% | | Composite mean RSD = 9.7% | |

*Computed from the seven means of duplicates from individual discrete samples.
**Computed from replicate composites prepared from discrete samples, $n = 7$ except for C-10 where $n = 3$.

## 4.2 AGREEMENT OF RESULTS FROM ON-SITE COLORIMETRIC METHODS WITH SW846 METHOD 8330

Analytical precision was estimated by the pooled RSD for replicates. RSDs for the on-site methods were very similar in magnitude to those for laboratory analysis (Table 2). The accuracy of the on-site methods was assessed relative to the standard laboratory method (EPA SW846 Method 8330) from the slope of the

zero intercept regression relationship between the on-site and laboratory methods. For TNT, these slopes ranged from 0.68 to 1.46 with a mean value of 0.98. Thus the TNT method was quite accurate in all cases. The accuracy of the AP and HMX were also excellent at 0.97 and 0.99, respectively, while a lower accuracy estimate was obtained for DNT (0.35). This lower value for DNT was in part due to obtaining the final absorbance measurement after allowing only one minute for the reaction of DNT with the reagent to take place. Subsequently, the manufacturer of the test recommended waiting 30 minutes for the reaction to go to completion. A more thorough discussion of the results of the short-range heterogeneity study is presented elsewhere[2–4].

## 4.3 MID-RANGE HETEROGENEITY

HMX results from analysis of subgrid and grid composite samples from CFB-Valcartier are presented in Table 5. Concentration estimates for the grid composites were generally within 25% of the mean of the four subgrid samples for HMX concentrations above 100 mg/kg. Thus we were able to prepare composite samples in the field that accurately represented the mean of the discrete samples, even where the highest concentration among individual subgrids divided by the lowest concentration subgrid within a grid varied by a mean value of 4.7 (subgrid variability ratio) for the same series of grids.

TABLE 5. COMPARISON OF HMX CONCENTRATION ESTIMATES USING THE ON-SITE COLORIMETRIC RESULTS FOR INDIVIDUAL SUBGRIDS, MEAN OF FOUR SUBGRIDS, AND GRID COMPOSITES AT CFB-VALCARTIER.

| Grid no. | HMX (mg/kg) Subgrid A | B | C | D | Mean | Composite | % Diff.* | Subgrid variability ratio** | Replicate variability ratio† |
|---|---|---|---|---|---|---|---|---|---|
| D1 | 120 | 121 | 32 | 59 | 83 | 80 | 3.6 | 3.8 | — |
| D2 | 279 | 271 | 316 | 41 | 227 | 212 | 6.6 | 7.7 | 1.5†† |
| D4 | 631 | 148 | 254 | 680 | 428 | 479 | 11.9 | 4.6 | 1.3 |
| D5 | 53 | 33 | 86 | 54 | 57 | 41 | 28.1 | 2.6 | — |
| D7 | 209 | 1000 | 729 | 1140 | 770 | 812 | 5.5 | 5.5 | 1.3 |
| D8 | 878 | 286 | 202 | 208 | 394 | 322 | 18.3 | 4.3 | — |
| D9 | 10 | 180 | 20 | 14 | 56 | 35 | 37.5 | 18.0 | 36.4 |
| D10 | 25 | 5.1 | 2.4 | 6.4 | 9.8 | 4.7 | 52.0 | 10.4 | 1.02 |
| C4 | 1910 | 721 | 995 | 2160 | 1447 | 1636 | 13.1 | 3.0 | 1.1†† |
| C5 | 461 | 79 | 129 | 301 | 242 | 180 | 25.6 | 5.8 | — |
| | | | Means | 371 | 380 | 20.2 | | | |
| | | | | | | | Mean (all) | 6.6 | |
| | | | | | | | Mean (except D9 and D10) | 4.7 | |

Paired *t*-test (composite vs. subgrid mean) $t = 0.382$***

% Diff. mean (all values) 20.2%

% Diff. mean (conc. > 50) 14.1%

*Absolute value of [100% – (composite/subgrid mean × 100)]

**Highest subgrid concentration / lowest subgrid concentration

***Composite and mean of subgrids not significantly different at 99.9% confidence level

†Ratio of replicates samples from same subgrid within grid

††Mean of two estimates from different subgrids within grid

Independent subgrid replicate samples were collected in eight randomly selected subgrids. For the six subgrids where the HMX concentration was above 100 mg/kg, the mean ratio for the replicates was 1.3, indicating that we were able to reproduce subgrid area-integrated samples with good precision for these areas (Table 5). For subgrid D9C, though, where the mean HMX concentrations was 26 mg/kg, the ability to reproduce subgrid samples was much poorer.

It is instructive to compare the reproducibility of discrete grab samples, collected in a manner commonly used, with area-integrated subgrid samples collected as described above. The seven discrete samples collected in the wheel pattern at CFB-Valcartier were taken in grid D2. HMX values ranged from 16 to 324 mg/kg, with a ratio of highest divided by lowest of 20.3. Two sets of replicate area-integrated samples where collected from grid D2. HMX concentrations for the two pairs were 210 and 337 mg/kg, and 111 and 165 mg/kg, respectively. The two ratios for these replicates were 1.6 and 1.49, respectively, compared with the ratio of 20.3 from the discrete samples. Thus the ability to obtain reproducible samples from grid D2 was much improved when the area-integrated approach was used.

## 4.4 CONCENTRATIONS OF HMX AND TNT FOR THE ANTITANK RANGE AT CFB-VALCARTIER

The concentrations of HMX and TNT obtained for grid composite samples at CFB-Valcartier, using the colorimetric on-site methods, are shown in Table 6. HMX concentrations ranged from 1640 mg/kg in grid C4, between two target tanks, to 4.7 mg/kg for grid D10, about 15 m in front of target tank D. TNT concentrations ranged from 23 mg/kg for grid C4 to <1 mg/kg for grid D10. Mean values of HMX and TNT for these 10 grids were 381 mg/kg and 4.4 mg/kg, respectively, with a mean HMX to TNT ratio of 87. The weapon fired at the antitank range at CFB-Valcartier was a 66-mm M72 light anti-armour weapon (LAW) rocket filled with octol, a melt-cast explosive composed of a 70:30 mixture of HMX and TNT. It is interesting that HMX has accumulated in the surface soils at Valcartier to a much greater degree than has TNT. The reason for this is uncertain, but we believe it is due to the much lower aqueous solubility of HMX compared to TNT, and perhaps a much slower rate of dissolution. In addition, TNT is known to biotransform to isomers of monoaminodinitrotoluene under the aerobic conditions typical of surface soils, while no aerobic degradative mechanism for HMX has been proposed.

TABLE 6. CONCENTRATIONS FOR HMX AND TNT IN SOILS AT ANTI-TANK RANGE AT CFB-VALCARTIER FROM ON-SITE COLORIMETRIC ANALYSES.

| Grid number | HMX (mg/kg) | TNT (mg/kg) | HMX/TNT ratio |
|---|---|---|---|
| D1 | 80 | <1 | >80 |
| D2 | 212 | 1.2 | 177 |
| D4 | 479 | 3.4 | 141 |
| D5 | 41 | 1.7 | 24 |
| D7 | 812 | 2.9 | 280 |
| D8 | 322 | 4.8 | 67 |
| D9 | 35 | 1.8 | 19 |
| D10 | 4.7 | <1 | >4.7 |
| C4 | 1640 | 23 | 71 |
| C5 | 180 | 3.2 | 56 |
| Mean | 381 | 4.4 | 87 |

## CONCLUSIONS

1. Sampling error exceeds analytical error by about an order of magnitude, when sites contaminated with explosives are characterized using discrete soil samples.

2. On-site colorimetric methods generally provided results in excellent agreement with those from standard laboratory protocols.

3. Homogenization of discrete samples, combination to form composites, and on-site analysis provides a reliable, inexpensive approach to characterizing sites contaminated with high explosives.

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# BIOTREATMENT TECHNOLOGIES FOR EXPLOSIVES-CONTAMINATED SOILS

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Although uncertainties exist with efforts to quantify the problem, energetics have been determined to be the largest environmental cleanup challenge at Army sites. Depending on the concentrations present, these explosives-contaminated soils can pose both a reactivity and toxicity hazard. Treatment of the contaminated soils is necessary to prevent the migration of hazardous substances and the potential for groundwater contamination. While incineration is the current proven treatment technology, its capital and operating costs are high, and public acceptance has diminished.

Bioremediation technologies are currently being developed by the U.S. Army Environmental Center (USAEC) as alternatives to incineration. The application of landfarming to treating explosives-contaminated soils gained early interest due to its success in treating other organic wastes: petroleum hydrocarbons, pentachlorophenols, and polycyclic aromatic hydrocarbons. The potential for landfarming has not been realized. A 1991 pilot-scale study of landfarming explosives-contaminated soils in California failed to achieve the target cleanup levels.

Fungal degradation of explosives has been shown to be successful in repeated laboratory studies involving pure cultures of white rot fungus. However, subsequent pilot-scale demonstrations had difficulties overcoming competition from native bacterial populations, toxicity inhibition, chemical sorption, and the inability to meet treatment levels.

In 1992, USAEC demonstrated the effectiveness of windrow composting of explosives-contaminated soils. Composting is currently being employed as the remedial action in a Superfund site at Umatilla Depot Activity, OR, and is being considered for other sites.

Slurry phase biotreatment, in which contaminated soils are biodegraded in an aqueous suspension, was successfully demonstrated at Joliet Army Ammunition Plant, IL in 1995. This system, which uses a native microbial consortium, molasses as a co-substrate, and alternating electron acceptor conditions, consistently achieved TNT removal rates above 99%. In addition, pilot tests of a proprietary anaerobic bioslurry process have generated interest among researchers in its promise of degradation along a different metabolic pathway.

The presentation will compare the results of tests of these processes, and their relative advantages. This review will address the Army perspective on these biotreatment techniques, including the challenge to develop engineering and cost data to make these technologies fieldable. This is becoming increasingly important, as remediation schedules at many explosives sites call for cleanup to begin in the next few years.

# COST AND DESIGN FOR APPLICATION OF COMPOSTING AND BIOSLURRY TREATMENT OF EXPLOSIVES-CONTAMINATED SOILS

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The magnitude of explosives contamination of soils at military installations makes it one of the Army's greatest cleanup challenges. Forty installations have reported explosives contamination at one or more sites, with total volumes estimated at over 1.2 million tons. The U.S. Army Environmental Center (USAEC) has dedicated years of effort to developing and fielding biotreatment alternatives to the conventional technology, high temperature incineration.

In 1992, USAEC demonstrated the effectiveness of windrow composting of explosives-contaminated soils. Based on its capacity to reduce explosives concentrations by over 99% and toxicity by 90-98%, composting was selected in a 1992 Record of Decision as the remediation process for a Superfund site at Umatilla Depot Activity, OR (UMDA). Contracting for cleanup with an innovative technology presented unique challenges in providing sufficient design and technical information to generate reliable bids.

Follow on studies charted the success of the first full scale application of windrow composting at UMDA. A new report documents the remedial design and determines a unit cost of $250-299 per ton.

Slurry phase biotreatment was successfully demonstrated at Joliet Army Ammunition Plant, IL in 1995. Bioslurry consistently achieved removal rates above 99%, with a high rate of mineralization. 1996 studies performed in support of Feasibility Studies at Joliet and Iowa Army Ammunition Plants developed comprehensive concept designs and cost estimates for full scale application of aerobic and anaerobic bioslurry processes. The studies found that bioslurry systems have higher construction and facility costs, but lower operation and maintenance costs when compared to composting. An estimated unit cost of $290-310 per ton is surprisingly close to that of windrow composting.

Bioslurry costs are dominated by two factors; process time and the ultimate disposal of the soil. If dewatering and subsequent water treatment is required, the cost can increase at a minimum of $25-65 per ton. Disposition of the treated soil must be carefully considered within risk-based goals and future land use.

This presentation will review the full scale design and process costs for these biotreatments, and offer lessons learned in contracting for innovative technologies.

# INSTALLATION RESTORATION
# AT NAVAL WEAPONS STATION EARLE
# REMEDIAL ACTION AT CLOSED PISTOL RANGES
# NAVY AND CONTRACTOR PERSONNEL - PARTNERING IN CLEAN UP

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## ABSTRACT

Installation Restoration Sites 24 and 25 were formerly used pistol ranges at Naval Weapons Station Earle. The sites were targeted for cleanup in order to mitigate the potential for runoff of metals (primarily lead) in surface water and ground water. The clean up objective was to remove 90% of the small caliber projectiles deposited in sandy berms, without interfering with mission critical operations. Therefore, the cleanup work required a tight execution schedule, and close communication between Navy and contractor personnel.

A clean up approach maximizing the use of Naval Weapons Earle personnel and equipment in the clean up process was implemented. The strengths of Station personnel and equipment were supplemented with those of Metcalf & Eddy, a contractor accessed via the Navy's Remedial Action Contract (RAC) administered by Northern Division, Naval Facilities Engineering Command.

Initially, dry screening and disposal were evaluated to separate the lead from berm soils. However, a treatability study of this method indicated as much as 59 percent of the berm material would be co-mingled with the lead, making recycling impractical. Subsequent soil washing feasibility studies indicated more than 95 percent of the berm material could be recovered for re-use in restoration, while recovering over 98 percent of the lead in the berm. Based on these findings, soil washing was selected for implementation.

Over the period September 3, 1996 through October 3, 1996, the clean up was executed. The Station not only provided direct labor to the job, such as heavy equipment operators, truck drivers and hazardous waste handlers, but also support personnel and infrastructure. Additionally, the Station's Explosives Ordnance Disposal team was on standby, and was consulted when live rounds were found. The Station's Fire Department also issued hot work permits and monitored the job from start to finish. The Navy forces were augmented by construction management personnel, process operators, and field sampling personnel from Metcalf & Eddy.

## INTRODUCTION

The mission of Naval Weapons Station Earle is to receive, store, segregate and issue ammunition to the United States Navy Atlantic Fleet. Operations which have taken place in the past included ordnance maintenance activities such as washout, stripping, painting and restenciling of items such as mines, torpedoes, and demilitarization of ammunition items. Areas of the 12,000 acre Station were used for training, and for disposal of domestic and industrial wastes. Training areas included the two outdoor pistol ranges which were closed after approximately 25 years of use. The subject clean up of those ranges were addressed under the auspices of the Installation Restoration Program at Naval Weapons Station Earle.

## OVERVIEW OF REMEDIATION PROGRAM

The Installation Restoration Program at Naval Weapons Station Earle addresses sites where previous activities may have caused, or have the potential to cause environmental impact. There were 29 of these type of sites identified by an Initial Assessment Study in 1983. The focus of the Program is to evaluate those sites in order to identify those that will require either remedial action, further study, or no further action. To date, approximately 60% of the sites identified in the 1983 Study have been remediated, or further investigations (e.g., soil analysis, groundwater analysis, etc.) have proven that no further action is warranted. The two closed pistol ranges addressed by this paper were identified as "Sites 24 and 25" under the Installation Restoration Program.

As a consequence of the use of Sites 24 and 25 as pistol ranges, a significant amount of small caliber bullets, as well as empty casings, were deposited in the sandy impact berms and in the firing line areas. The primary contaminant of concern was lead, as the ranges were to be closed, and converted into multi-use recreation areas. In accordance with the U.S. Environmental Protection Agency and the New Jersey Department of Environmental Protection, a minimum of 90 percent of the projectiles would have to be removed, with the soil clean up goal for these sites set as a total lead level not to exceed 400 mg/kg.

A removal action was selected as the most appropriate method to meet the required cleanup goals as this alternative would serve to minimize the potential for run off of metals in surface water and groundwater from the sites, and reduce the potential for people coming in contact with the contaminants after range closure. The removal action was consistent with Navy policy to close existing small arms ranges that are no longer necessary to support mission requirements in a manner that is protective of human health and the environment.

## SCHEDULING CONSTRAINTS

One of the logistical challenges of this project was to ensure the availability of equipment and personnel for ship loading/off-loading operations; this project had to be scheduled such that those mission critical operations could be adequately supported. Therefore, phasing of labor and equipment for mobilization, project execution, and demobilization required close attention to the demands of port operations. The tight scheduling constraints required solid planning on the part of management personnel. This aspect of the project demonstrated command commitment and teamwork to bringing this task to successful completion; Station personnel and equipment were positioned at the sites when needed. The entire project was completed in about one month.

## FEASIBILITY STUDY

Prior to mobilization, a feasibility study[1] was conducted on one five-gallon sample of soil from each range to evaluate three removal alternatives: non-hazardous direct disposal; screening/recycling; soil washing/recycling. Of the three, it was originally anticipated that the direct disposal option could be the most cost effective. However, initial assessment of the berm soils showed the total lead levels to range from 19,346 mg/kg to 38,529 mg/kg. In addition, the corresponding TCLP lead levels exceeded the 5 mg/L RCRA level, whereby all of the berm material had to be classified as "characteristically hazardous", and disposed of as hazardous waste. In addition to the higher cost of this option was the never-ending long term liability associated hazardous waste disposal.

The second option evaluated was screening/recycling. Since the samples consisted of a well graded sand with the bulk of the lead present in the form of "particulates" larger than ¼ inch, it seemed logical that passing the berm soils over a ¼ inch "dry screen" would remove the larger than ¼ inch lead in a form suitable for recycling, while rendering the balance of the soil suitable for reuse. To evaluate this option in the lab, the soil was screened into nine size fractions, with total lead analysis conducted on each fraction. Elevated lead levels were found not only in the larger than ¼ inch material, but also in material down to 28 mesh sand particles, and clays finer than 150 mesh. As such, the screening option would have required removal of all material larger than 28 mesh, and all material smaller than 150 mesh, which represented 59 percent of all material at the site. While the lead content of this material was in percent concentrations, it was not high enough to recover any salvage value, and in fact, recycling this material would have required payment similar to that for hazardous waste disposal. The recycling option, however, does break the "cradle to grave" chain of responsibility associated with disposal.

To further reduce the amount of material going off site, soil washing, a water based process combining both physical and gravity separation was also evaluated. As with the screening option, the soil was first screened into nine size fractions. Those fractions with lead levels above the cleanup goals then under went a subsequent gravity separation step, further separating the lead fragments from similar sized sand/stone particles. This process resulted in recovery of over 99 percent of all lead present, with over 95 percent of the berm material meeting the cleanup goal, and suitable for reuse. As such, this option could save more than $134,000 over either of the other two, and it was selected for implementation.

While the feasibility study was being conducted, Navy personnel were preparing the site, and stockpiling impacted materials. These concurrent activities shortened an already tight project schedule by more than a week, and allowed for implementing the field activities without delay after the remedy was selected.

## PROJECT TEAM

This project was made unique by joining the process expertise of Metcalf & Eddy, subcontracted by the Navy's Remedial Action Contractor, Foster Wheeler, with the manpower, equipment and support infrastructure of Naval Weapons Station Earle. In this era of fiscal austerity, the partnership established on this project team enabled a substantial savings to be realized in contrast to the conventional turn-key remediation contract.

The use of heavy earth moving equipment located on Station reduced the mobilization cost and demurrage charges; use of Station, qualified personnel to operate equipment assured an accessible workforce for the job, reducing the need to pay for travel expenses for equipment operators and laborers. Maintenance mechanics were available to repair hydraulic equipment in the event of failure. Non-hazardous process water (6500 gallons) was disposed of at the Station's wastewater treatment plant. Additional support to the job was provided by the Station Fire Department to ensure effective oversight of the job from a Safety perspective. The Station's Explosives Ordnance Disposal Unit was also available to respond in the event of the discovery of unfired rounds. A Navy Industrial Hygienist also monitored the workers for lead exposure on site; he also conducted the required Site Safety and Health briefings.

## SOIL PROCESSING

The objectives of the project were to remove at least 90 percent of the lead in the berm, with soils containing less than 400 mg/kg total lead deemed suitable for reuse. To expedite field activities and minimize material handling, the process equipment was set up at the larger of the two ranges. It was staged on a polyethylene liner and configured to mimic the process proven effective during the feasibility study. Water for the processing was recycled in a closed loop, with makeup water obtained from a nearby fire hydrant.

Approximately 85-90% of the metal bullets were found to be located between the surface soil and as much as 18 inches below the ground surface. Careful excavation and close coordination between Navy personnel and the contractors sample technicians performing post excavation sampling resulted in "surgical" removal of contaminated material, resulting in a 500 ton reduction of material requiring treatment versus the original anticipated volume.

The soil washing system deployed provided three output streams: concentrated lead (bullets); washed sand; and fine clays. The washed sands were conveyed to a Navy dump truck, and staged on plastic to await post treatment confirmation samples. The fine clays collected were also sampled for reuse criteria, and the bullets were collected in drums for subsequent recycling. In accordance with the U.S. Environmental Protection Agency and the New Jersey Department of Environmental Protection, the soils had to test below 400 mg/kg lead in order to be reused on site. The recovered bullets were sold to a recycle for their scrap value, with the proceeds used to fund subsequent quality of life projects at the base. The clays were either reused (less than 400 mg/kg total lead) or solidified and recycled at a local asphalt plant (more than 400 mg/kg total lead).

## PARTNERING

Call it partnering, teamwork, or cooperation, this remediation project was a reflection of a what a dedicated group of Navy, contractor, regulatory personnel, and concerned citizens can accomplish working together toward a clear goal. The willingness to attempt an unconventional project collaboration, but one that made sense from the perspectives of technical merit and cost, contributed to drive this project to success.

Naval Weapons Station Earle, in consonance with the Policy of the Chief of Naval Operations (CNO) had established a Restoration Advisory Board [RAB] of concerned local citizens that supported the need

for and the approach of this project before it was undertaken. This project also proved that partnering with the community is an essential ingredient to effective execution.

Subsequent to a RAB meeting of 14 Nov 96, the Asbury Park Press published a very positive article, on 15 Nov 96, entitled "10 TONS OF BULLETS CLEANED UP AT EARLE." Additionally, the Environmental Protection Agency stated in their letter of 9 Aug 96, "we are very supportive of the Navy's efforts through this removal action to address environmental concerns at NWS Earle." Further, in their letter of 27 Mar 97, the EPA offered [in reference to the pistol range clean ups], "Excellent coordination with your contractor (Metcalf & Eddy) and Navy Northern Division [Naval Facilities Engineering Command] and good communication with EPA and NJDEP helped ensure a quick, efficient and professional operation."

The Navy's Remedial Action Contractor, Foster Wheeler, also realized the advantage of subcontracting with Metcalf & Eddy, who delivered key personnel, equipment and technology in a timely manner. Notwithstanding, Foster Wheeler played a major role in the disposal of process residuals, and in managing tight schedule constraints.

## CONCLUSIONS

The objectives were met. 1500 tons of soils were processed and 10 tons of bullets were recovered and recycled. About 70 tons of clay fines required recycling at an asphalt batch plant. The remainder of the soils processed met the criteria and were reused on the sites, with residual total levels ranging from 14.6 mg/kg to 92.2 mg/kg.[2] The combination of proven, commercially available soil washing equipment, an existing contract, and a "can-do" project team enabled the successful completion of the project within the schedule constraints, and without disrupting mission critical operations. The benefits of partnering afforded all concerned the opportunity to achieve a successful remediation effort. With all of the above considered, the tangible benefit of this Navy-contractor team yielded a project cost savings of approximately 30% over more traditional approaches.

## REFERENCES


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2. Naval Weapons Station Earle Pistol Range Remediation Final Report, Prepared for Foster Wheeler by Metcalf & Eddy, Inc., October 3, 1996

demonstration was conducted in two phases: Test 1 involved direct placement of contaminated soil on an impermeable liner system; Test 2 used a hammer mill to pulverize the contaminated soil prior to placement on the liner system, and also involved the construction of a separate control pile. In addition, after several months of operation, the Test 2 treatment pile was dismantled and reconstructed (hereafter referred to as "reformed").

## SYSTEM DESIGN AND INSTALLATION

Prior to construction of Test 1, a treatability study consisting of a mineralization ($CO_2$ evolution) and $O_2$ uptake study and a soil column study was conducted to identify optimum nutrient amendment rates (100 mg/kg nitrogen [N] and 25 mg/kg phosphorus [P]) and to predict biopile performance.

Test 1 soils consisted of brown silty sand with a trace of clay (35 percent passing a No. 200 sieve), with capillary pressure-derived field capacity of 12 to 17 percent by weight, and contaminated with primarily diesel fuel. Test 2 soils consisted of brown clayey silt (52 percent passing a No. 200 sieve), with capillary pressure-derived field capacity of 16 to 18 percent by weight, and contaminated with a combination of diesel fuel and heavier fuel oils. In both tests, the petroleum hydrocarbons were found to be already significantly degraded or weathered as evidenced by the absence of normal alkanes.

Each biopile was constructed with 500 cy (380 m3) of soil arranged in a pile approximately 52 x 52 x 8 ft (16 x 16 x 2.4 m) on a 60-mil (1.5 mm) HDPE liner. Nutrients in the form of liquid ammonium polyphosphate and ammonium thiosulfate were sprayed on the soil during treatment pile construction. Instrumentation installed in the soil pile included 6 to 9 soil gas monitoring points (respirometry probes), capacitance probes (moisture sensors), and thermistors (temperature sensors). Figure 1 illustrates the design of the biopile.

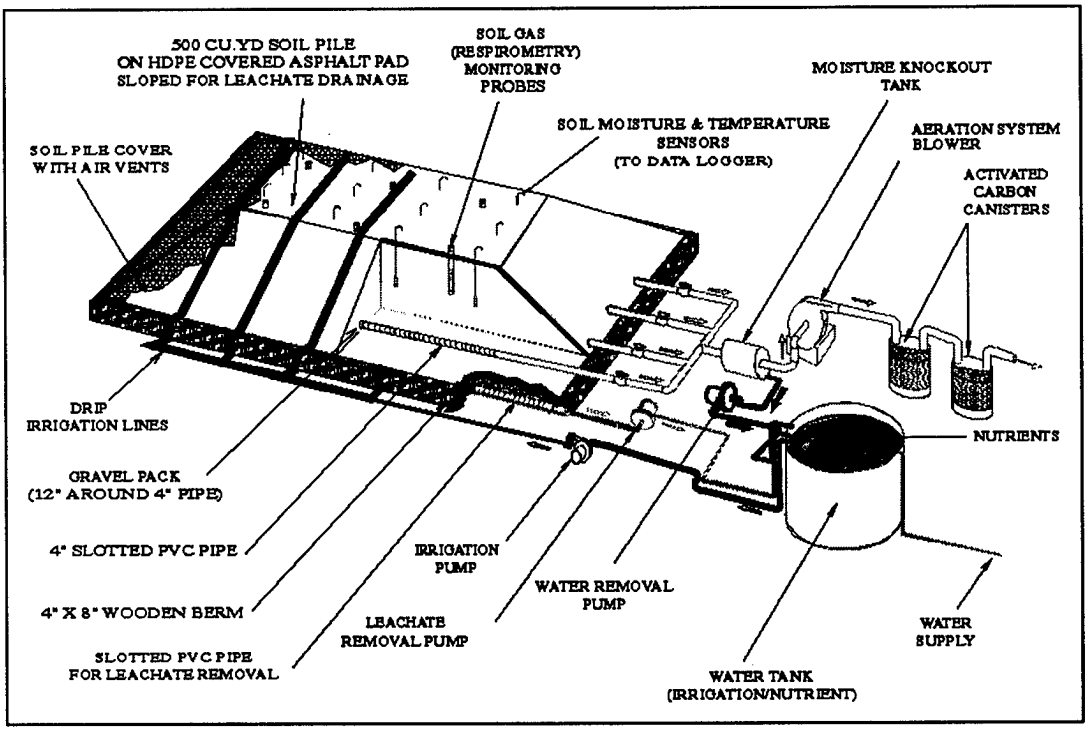



**FIGURE 1. Biopile Treatment System**

An aeration system - consisting of slotted PVC piping in the base of the pile and a positive displacement blower - to deliver oxygen, and an irrigation system - consisting of polyethylene tubing with internal drip emitters - to allow future moisture and nutrient additions were installed for the Test 1 and 2 treatment piles. The piles were covered with polyethylene, and an activated carbon emission control system was installed to comply with local air permitting requirements.

The control pile during Test 2 was constructed similarly to the treatment piles, with the exception that nutrients were not added and an aeration system and irrigation system were not installed.

**Sampling and Analyses.** The demonstration included rigorous procedures for soil sampling and analyses, and data validation to ensure data quality. Sampling of biopile soil, leachate, and blower air emissions was conducted at the start of each test and at periodic intervals during system operation. A spreadsheet-based random number generator was used to select soil sampling locations within the biopile. To minimize the effects of soil contaminant variability, between 4 and 12 soil samples were collected during each sampling event. Six to seven sampling events were conducted during each test.

TEPH analysis was performed using modified EPA method 8015 preceded by solvent extraction. Additional analyses were performed for soil moisture, nutrients, total organic carbon (TOC), general minerals, microbial population enumeration, cleanup of polar biogenic material (biomass) and other degradation compounds, and quantitation of individual hydrocarbon constituents.

**Field Monitoring.** Field measurements to monitor system performance included continuous recording of temperature and moisture within the piles, and periodic respirometry testing to calculate biodegradation rates. Respirometry testing consisted of turning off the blower and measuring $CO_2$ and $O_2$ concentrations in the biopile over a 24 to 72 hour period. The respirometry test procedure was modeled after the in situ protocol developed by Hinchee et al.[2] with the primary exception that the test duration was shorter because of the higher $O_2$ uptake rates observed (up to 1 percent per hour) in the biopile. Biodegradation rates in terms of mg/kg TEPH per day were calculated using $O_2$ uptake measurements and assuming complete mineralization of the TEPH to $CO_2$.

## RESULTS AND DISCUSSION

**Hydrocarbon Degradation.** During Test 1, the petroleum hydrocarbons were reduced by 88 percent in the diesel range (<C22) from an average 1,990 mg/kg to 232 mg/kg during 51 weeks. During 47 weeks of operation, Test 2 achieved a 88 percent reduction in the diesel range (<C22) from an average 4,769 mg/kg to 592 mg/kg and a 71 percent reduction in the motor oil range (>C22) from an average 5,638 mg/kg to 1,617 mg/kg. In both Tests 1 and 2, the largest reductions occurred during the first 4 weeks of soil pile operation, and TEPH degradation rates slowed dramatically after 6 to 8 weeks of operation. TEPH concentrations in the control pile also decreased, but as to be expected at lower rates than the treatment piles. Figures 2(a) and 2(b) present TEPH diesel range (<C22) and motor oil range (>C22) concentrations versus time.

During Test 2, soil samples were also analyzed with and without a silica gel column cleanup (SW846 Method 3630A) to remove polar non-petroleum hydrocarbon biogenic or other degradation products prior to TEPH analysis. The fraction of erroneously reported TEPH concentrations removed by silica gel cleanup steadily increased from approximately 4 percent at the start to over 27 percent after 32 weeks of operation.

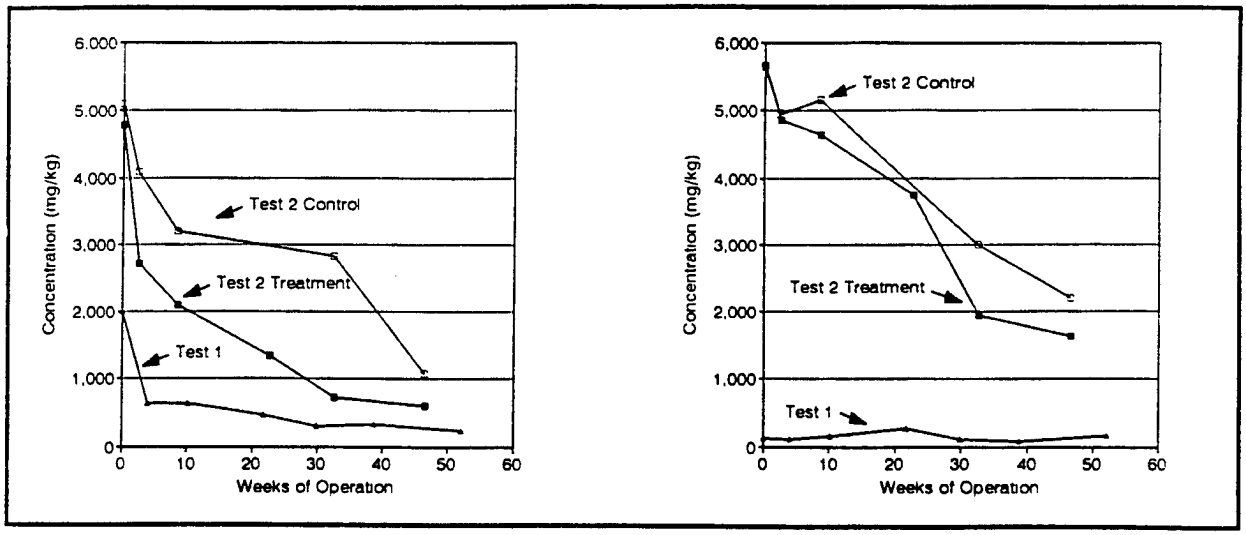



**FIGURE 2. TEPH Concentrations**
**(a) Diesel Range/<C22. (b) Motor Oil range/>C22**

**Respirometry Testing.** $O_2$ uptake rates were used to calculate TEPH degradation rates for each respirometry test. During both Test 1 and 2, biodegradation rates appeared to diminish with respect to treatment time at a fairly constant rate for the first 6 to 8 weeks of each test. After 8 weeks of treatment, hydrocarbon biodegradation rates showed little change with respect to the time of treatment system operation. Calculated degradation rates for Test 2 are shown in Figure 3(a) with individual probe results.

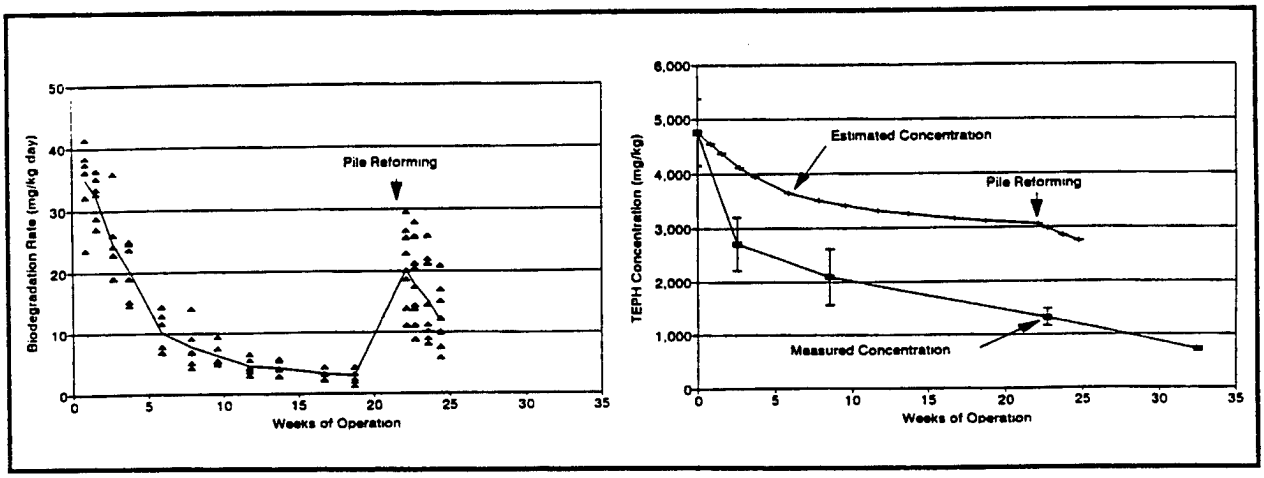



**FIGURE 3. Test 2 Respirometry Testing Results. (a) Biodegradation rates calculated from oxygen uptake rates. (b) Comparison of TEPH Concentrations Predicted From Respirometry Testing With Actual TEPH Analytical Results.**

Five months after the start of Test No. 2, the treatment pile was dismantled and reformed in order to remove any preferential flow paths or stagnant zones that may have developed in the biopile. As shown in Figure 3(a), an eight-fold increase in the average $O_2$ uptake rate was observed in the treatment system when measurements before and after pile reconstruction are compared.

The respirometry-based biodegradation rates were also used to calculate theoretical TEPH losses with respect to time. The calculated TEPH concentration estimates were then compared to actual TEPH analytical results for each sampling event. Average TEPH (diesel range, <C22) soil concentrations are superimposed on plots of respirometry-based TEPH estimates for Test 2 in Figure 3(b). In general, field respirometry-based biodegradation rates provided a good overall estimate of actual diesel range TEPH degradation with the exception of the first few weeks of operation. For both Test 1 and 2, hydrocarbon removal rates were underestimated during this period of time.

**Carbon Mass Balance.** In order to assess potential transformations that petroleum hydrocarbons underwent during biopile treatment, carbon (C) mass balance calculations were performed using field and laboratory analytical data from soil, leachate, and air emission samples. Four transformation pathways were evaluated in addition to carbon remaining as undegraded TEPH:

- C as vapor phase hydrocarbons in air emissions.
- C as $CO_2$ (complete mineralization of TEPH) based on $O_2$ uptake rates measured during respirometry testing.
- C as biomass and other non-petroleum hydrocarbon degradation compounds based on TOC analysis.
- C as liquid-phase hydrocarbons in leachate generated from the biopile.

Figure 4 displays the relative distribution of these pathways (C as hydrocarbon in leachate was calculated to be less than .1 percent of total C). Results do not add up to 100% because of inaccuracies in individual pathway measurements.

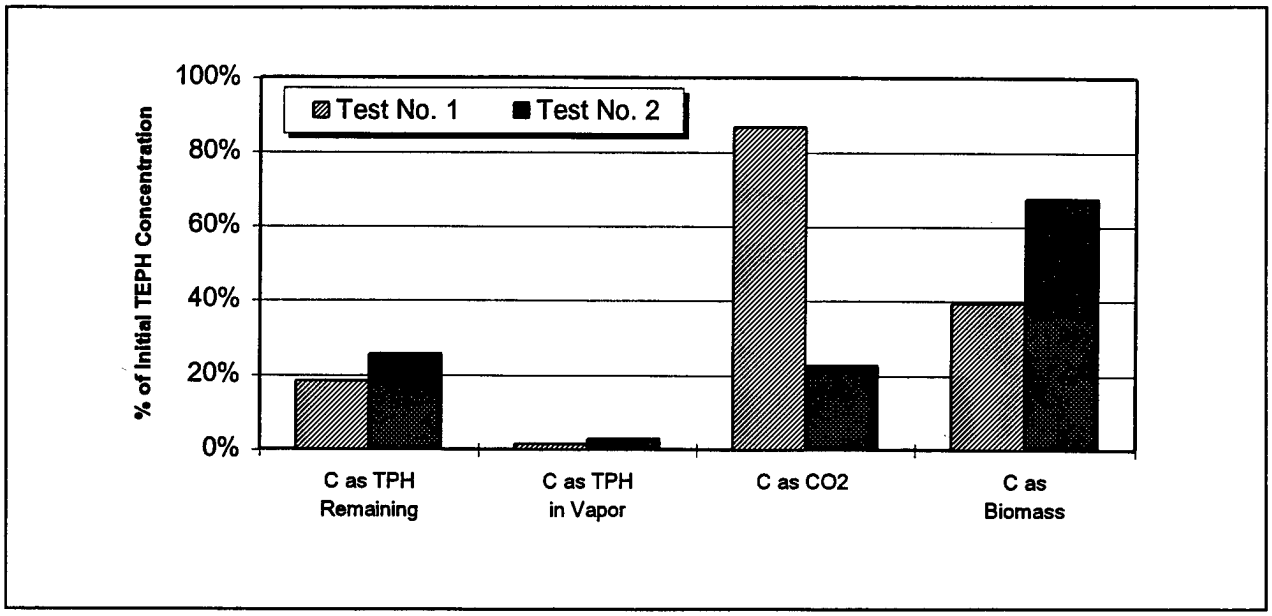



**FIGURE 4. Relative Distribution Of Carbon Transformation Pathways**

## CONCLUSIONS

Biopile technology effectively degrades petroleum hydrocarbons without transferring them significantly to other media such as via air emissions or leachate water generation. The decrease in degradation rates observed at 6 to 8 weeks is attributed to the development of preferential air flow pathways and stagnant zones in the soil during operation. Dismantling and reforming the ex situ bioremediation treatment system on Test No. 2 served to disrupt these preferential pathways and stagnant zones and dramatically increased degradation rates. The soil pulverization used during Test 2 pile construction successfully broke up clods in the clayey soil, the presence of which would otherwise be expected to inhibit air flow and bioremediation; the comparable performance of Test 2 compared to Test 1 with less clayey soils is attributed to this method of pretreatment. The use of $O_2$ respirometry testing proved effective in monitoring the progress of bioremediation. After sampling for TEPH at the start of the treatment system and 1 to 2 months after startup, respirometry testing can be used as a reliable measure to estimate diesel range hydrocarbon degradation. This eliminates the need for sampling and analyzing for TEPH until confirmation samples at the conclusion of the remediation program and thus reduces the overall cost of the remediation program.

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2. Hinchee, R. E., S. K. Ong, R. N. Miller, D. C. Downey, and R. Frandt. 1992. *Test Plan and Technical Protocol for a Field Treatability Test for Bioventing.* Prepared for U.S. Air Force, Center for Environmental Excellence.

# REMEDIATION IV

# APPLICATION OF THE CHEMTECH SOIL TREATMENT PROCESS TO CLEAN UP METALS CONTAMINATED SOILS FROM NAVAL INSTALLATIONS IN THE SAN FRANCISCO BAY AREA

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## ABSTRACT

The newly patented ChemTech soil treatment process was piloted in January 1997 to demonstrate the removal of antimony, copper, chromium, lead, and zinc from the former Naval Shipyard at Hunter's Point in San Francisco, California. The demonstration also included use of Energy Dispersive X-ray Fluorescence (EDXRF) analyses of metals concentrations to optimize the ChemTech treatment parameters. This evaluation was part of the Bay Area Defense Conversion Action Team (BADCAT) demonstration program for emerging and innovative technologies. The BADCAT Environmental Technology Project is a partnership of regional business organizations, federal and state regulatory agencies, and the US Navy to assist with remediation of the region's closing military bases. This paper describes the results of that demonstration program, and addresses the applicability of the technology to other sites, and provides estimates of unit clean up costs.

The ChemTech process employs two mechanisms to remove contaminants from soil: ***physical scouring*** of the soil particle surface, and ***chemical leaching*** of the contaminants from the soil particles. Physical scouring of the slurried soil is accomplished in a mechanically simple but physically intense three phase fluidized bed where high air velocities provide for turbulent mixing and extensive interparticle contact. Chemical leaching of the contaminants occurs in the fluidized bed as well as in the classifiers. The combined effects of extremes of pH (either highly acidic or highly basic), addition of surfactant, and near boiling temperatures rapidly remove petroleum hydrocarbons and metal contaminants from soil. These design features result is a simple but flexible, high capacity system with attractive operating and capital costs, well suited to environmental cleanup of a range of soil and sediment types.

Tests of the ChemTech soil treatment system at Hunter's Point in January 1997 have demonstrated rapid and cost competitive removal of metal and hydrocarbon contaminants from soil. Field EDXRF analyses for metals were used to evaluate the efficacy of the process and compared with fixed laboratory results.

Industrial cleanup levels were achieved for each of the following target metals: antimony, copper, chromium, lead, and zinc. Residential permit levels were met for copper, chromium, and zinc, but not for lead or antimony due to the presence of metal particulates such as sandblasting grit, lead battery casings, and wire debris. Subsequent to the pilot plant demonstration, treatability testing indicated that longer treatment times would enable residential levels to also be met for lead and antimony. The leachable (Toxicity Characteristic Leaching Procedure or TCLP) levels of the treated soil were significantly decreased compared to the untreated soil, well below permit levels. Hydrocarbon concentrations were decreased even under the acidic conditions to target metal removal. Under alkaline conditions, approximately 90% of the petroleum hydrocarbons in the feed soil were removed after a 5 minute residence time in the fluidized bed.

# 1. INTRODUCTION

The remediation of soils and sediments contaminated with heavy metals and heavy petroleum hydrocarbons is generally difficult and therefore expensive. In many cases, excavation and disposal in a secure landfill is the only available option. Robust techniques are required which can readily adapt to variable soil types and contaminant levels, while maintaining reasonable time frames and costs.

Currently the two most widely accepted approaches to remediation of metals contaminated soil are excavation with off-site disposal, and soil washing (DOD Environmental Technology Transfer Committee, 1994). While excavation and off-site disposal alleviates the contaminant problem at the site, it does not treat (that is, react, destroy, separate, or stabilize) the contaminants. Key factors which may limit this option include: transportation distance to landfill, on-going legal liability for disposed contaminants, and limits of both total and leachable contaminant levels at landfills.

Soil washing is a water-based ex-situ process to remove contaminants by means of chemical leaching and/or by particle size separation. Factors which limit the widespread application of soil washing include: mechanical complexity of commercial systems and their labor requirements, management of residuals which require further treatment or disposal, and cost.

## 1.1 THE IDEAL SOIL TREATMENT SYSTEM

The ideal system to treat contaminated soil would segregate metal contaminants into a very small fraction. It would be adaptable to a variety of soils and contaminants, and have a high capacity. Rapid treatment would enable the apparatus to be small and mobile so that it, rather than the contaminated soil, could be easily transported to site. The setup would be mechanically simple, leading to a requirement for few operators and minimal maintenance. The process would not discharge wastes into the sewer or to the air, and would use neither incineration nor hazardous chemicals. The costs to apply the process would be significantly less than to landfill the soil. These attributes describe the ChemTech process.

## 1.2 DESCRIPTION OF THE CHEMTECH SOIL TREATMENT SYSTEM

ChemTech Analysis Inc.'s soil treatment system configures conventional unit operations from the chemical process industry to result in a flexible, high capacity system with comparatively low cleanup costs. The soil treatment process is a portable treatment system which removes both metals and petroleum hydrocarbons from soils or sediments. Figure 1 illustrates the process.

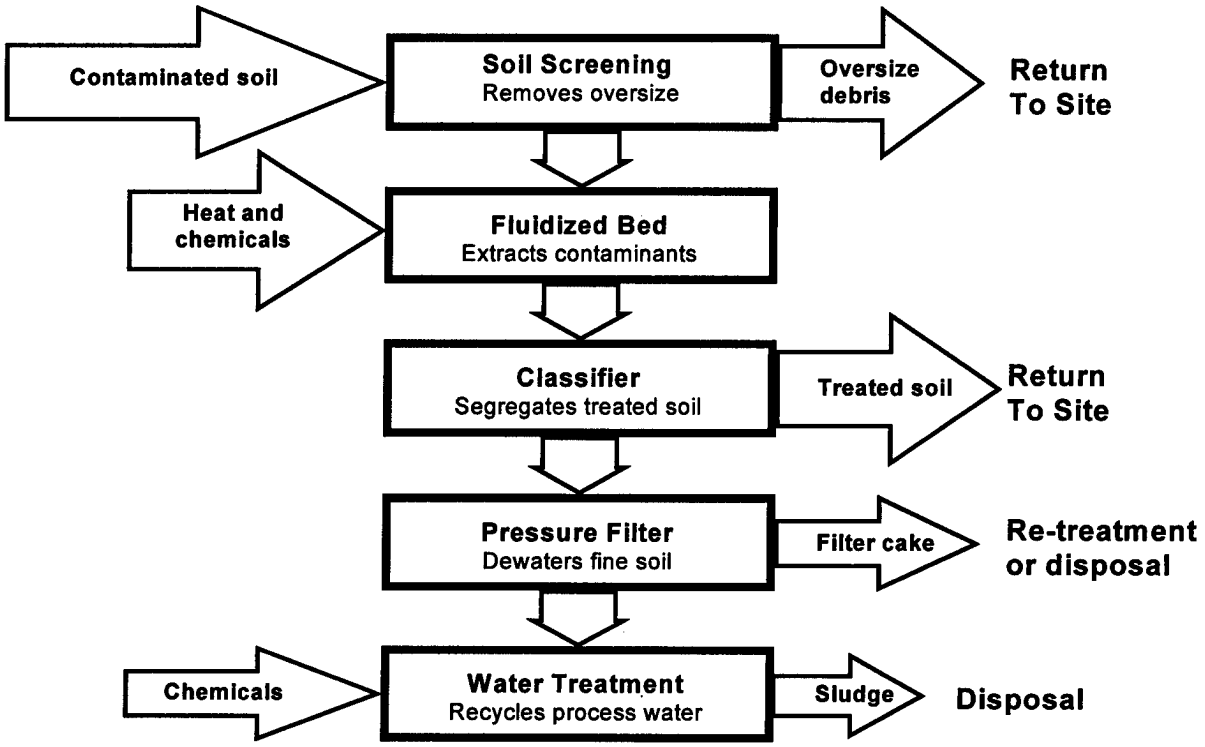



Figure 1. Schematic of the ChemTech soil treatment system

The heart of the ChemTech process is a fluidized bed/classifier. The mechanically simple but physically intense three phase fluidized bed is an enclosed vessel which blasts air through a hot acid or hot alkaline slurry of soil. In the classifier, process water which is pumped in an upflow direction washes out fine particles from the readily settleable coarse soil particles. These integrated unit operations enable two contaminant removal mechanisms to be employed simultaneously: ***physical scouring*** of the soil particle surfaces, and ***chemical leaching*** of the contaminants from the soil particles. Physical scouring of the slurried soil is accomplished in the fluidized bed where high air velocities provide for turbulent mixing and extensive interparticle abrasion. Rapid chemical leaching of the contaminants occurs in the fluidized bed and also in the classifiers. The combined effects of extremes of pH (either highly acidic or highly basic), addition of soap, and near boiling temperatures rapidly remove petroleum hydrocarbons and metal contaminants from soil. Addressing the shortcomings of commercially available systems, the ChemTech process is a second generation soil washing system.

## 1.3 ENERGY DISPERSIVE X-RAY FLUORESCENCE

ONSITE Environmental Laboratories, Inc. demonstrated the use of Energy Dispersive X-ray Fluorescence (EDXRF) to perform rapid analysis of soil samples for metals on-site to help direct the treatment process and associated field work. EDXRF is an analytical technique where the elemental components of a solid, liquid, or powder sample are "excited" by X-rays impinging on it. This results in the emission (fluorescence) of X-rays from the sample that are characteristic of the elements present. Quantification is achieved by measuring the intensity of the X-ray emission. Fluoresced X-rays are simultaneously detected and can be displayed in real time for rapid identification of the elemental components. The elemental sensitivity range of EDXRF is great, generally covering most of the periodic table. A portable Spectrace 6000 EDXRF unit was set up in a mobile lab in the field.

## 1.4 SELECTION OF THE CHEMTECH SYSTEM AND XRF ANALYSES FOR BADCAT DEMONSTRATION

The Bay Area Defense Conversion Action Team Environmental Technology Partnership (BADCAT ETP) is a program to expedite clean-up and conversion of the twelve closing military bases in the San Francisco Area through application of emerging and innovative environmental technologies. Klohn-Crippen Consultant's ChemTech soil treatment process and ONSITE Environmental Laboratory's Energy Dispersive X-Ray Fluorescence (EDXRF) metal detection technology were selected by the BADCAT ETP from 21 proposed technologies for pilot scale demonstration based on efficiency, cost effectiveness, and innovativeness. The BADCAT ETP is a public-private partnership of the Bay Area Economic Forum (BAEF), Bay Area Regional Technology Alliance (BARTA), California Environmental Protection Agency (Cal EPA), US Environmental Protection Agency (US EPA), Engineering Field Activity West - Naval Facilities Engineering Command, Naval Facilities Engineering Service Center, Chevron Research and Technology Company, Pacific Studies Center, and other technical experts.

In 1996, BADCAT ETP identified areas where new environmental technologies were needed by assessing the total contaminant mass for Bay Area Navy bases identified by Cal EPA's Military Base Contaminant Inventory Project. This information indicated that petroleum hydrocarbons (TPH) and inorganic contaminants are commonly found at Navy Bay Area BRAC bases in significant volumes. In the Bay Area alone there are acres of soil contaminated with metals and petroleum hydrocarbons. Approximately 84% of the total contaminant mass is comprised of total petroleum hydrocarbons and inorganics which together are found at 90 of 135 sites at eight San Francisco Bay Area closing Naval installations. Incentives to identify and apply efficient, cost effective, and innovative technologies for these multiple sites include saving time (quicker closure of sites and transfer of property), money (declining budgets can go further), and ensuring a better product (cleaner sites allow for flexible re-use of the property).

# 2. METHOD

Field screening for total metal concentrations in soil was performed by ONSITE Environmental Laboratories by means of X-Ray Fluorescence (XRF). Confirmation testing of the field assays was performed by Environmental Chemical Corporation according to EPA method 6010A (ICP). Total hydrocarbons were assayed by EPA Total Recoverable Petroleum Hydrocarbons (TRPH). The leachability of metals was performed according to TCLP.

## 2.1 CHEMTECH APPROACH TO SITE CLEANUP

In order to optimize performance and minimize clean-up cost, our approach to site clean-up comprises four stages: site characterization, treatability testing, feasibility assessment, and commercial scale clean-up. Table 2 outlines these four stages and their rationale.

## 2.2 DEMONSTRATION OF PILOT PLANT OPERATION

A pilot scale ChemTech process was constructed to fit on a 8 by 16 feet trailer. In order to process from one half to one ton per day on a semi-batch basis, it included the following components: feed soil auger, feed hopper and screw feeder, three phase fluidized bed, air blower, moisture separator, fine particle filter, two classifiers, a plate and frame pressure filter, pumps for recirculation and chemical metering, clarifiers for process water treatment, heaters, pH controllers, chemical feed tanks, and mixers. A report filed to BADCAT (Klohn-Crippen Consultants Ltd., 1997) contains details of the pilot plant operation.

TABLE 2. APPROACH TO SITE CLEAN UP

| Stage | Rationale |
|---|---|
| **Site Characterization** | ▸ What are the site clean-up objectives? |
| | ▸ Which contaminants are present? |
| | ▸ Where are the contaminants located? |
| | ▸ What are the contaminant concentrations? |
| | ▸ How much soil needs to be cleaned up? |
| | ▸ What is the physical and chemical nature of the soil? |
| **Treatability Testing** | ▸ What are the optimum chemical and physical conditions for contaminant removal from soil and water? |
| | ▸ What are the proportions of oversize, coarse, and fine soil which will affect their management in the system? |
| | ▸ How quickly can contaminants be removed? |
| | ▸ What final contaminant concentrations are practically achievable? |
| | ▸ Do final contaminant concentrations satisfy the clean-up objectives? |
| **Feasibility Assessment** | ▸ How long would commercial clean-up take? |
| | ▸ How much would commercial scale clean-up cost to meet clean-up objectives? |
| | ▸ What are the costs and time requirements of alternative remediation approaches? |
| | ▸ What environmental, health, legal, financial constraints must be met? |
| **Cleanup** | ▸ Meet clean-up objectives as fast and as inexpensively as possible. |
| | ▸ Minimize secondary environmental impacts: dust and air emissions, water discharge, spills of chemicals or soils. |

## 3. RESULTS

Pilot plant operation was as follows: nominally 80 ∘C, pH 1.0 adjusted by means of 75:25 hydrochloric acid, sulphuric acid, and solids residence time in the fluidized bed of less than 5 minutes. Table 3 shows that total metal concentrations were reduced to within the industrial limits for Hunter's Point. However, due to the presence of metal particulates such as sandblasting grit, lead battery casings, and wire debris, residential levels for lead and antimony were not obtained for this site during pilot scale testing.

There are two options to respond to the difficulty in consistently meeting target cleanup objectives for soils contaminated by metal particulates. The first is to increase the treatment time of the soil in the fluidized bed to dissolve the metal particulates in the hot and acidic process water. However, adding to treatment time correspondingly lowers the plant capacity and drives up the unit cost of site cleanup.

An alternative approach to cleaning up particulate metals contaminated sites would be to pursue a risk-based approach. Treated soil should generally be non-leachable under the TCLP standard test after having been subject to the tremendously aggressive chemical and physical environment of the ChemTech process (see Table 2). The leachable (TCLP) levels of the treated soil were significantly decreased compared to the untreated soil, well below permit levels (see also Table 6).

The results of bench scale testing for a number of industrially contaminated soils is presented in Table 4. This table illustrates that removing metals from soils was quite variable, an apparent function of both the soil and the metal itself. The treatment conditions for all metals except arsenic were as follows: pH 1 by means of hydrochloric acid addition, 80 ∘C, nominal treatment time of five minutes except where noted. Arsenic removal effectiveness was promoted under alkaline rather than acidic conditions.

TABLE 3. CHEMTECH DEMONSTRATION PERFORMANCE AT HUNTER'S POINT

| Description | Performance | | | | | | |
|---|---|---|---|---|---|---|---|
| | Antimony | | Copper | Chromium | Lead | | Zinc |
| | Pilot 5 min | Bench 15 min | | | Pilot 5 min | Bench 15 min | |
| **Average Total Concentration of Contaminant (mg/kg):** | | | | | | | |
| Untreated Soil | 87 | 53 | 2,270 | 267 | 2,407 | 1,450 | 2,773 |
| Treated Soil | 84 | 34 | 287 | 122 | 750 | 300 | 829 |
| Percent Removal | 3% | 36% | 87% | 54% | 69% | 80% | 70% |
| **Contaminant Leachable Concentrations (mg/kg)** | | | | | | | |
| Feed Soil TCLP | 0.10 | N/A | <0.02 | 3.7 | <1 | N/A | 22 |
| Treated Soil TCLP | <0.05 | N/A | <0.01 | 0.21 | <0.2 | N/A | 0.38 |
| Average Percent Reduction | - | N/A | - | 94% | - | N/A | 98% |
| **Cleanup Objectives (mg/kg)** | | | | | | | |
| Residential | 31 | | 2,800 | 210 | 400 | | 4,100 |
| Industrial | 680 | | 63,000 | 450 | 1,000 | | 100,000 |
| STLC | 15 | | 25 | 5.0 | 5.0 | | 250 |
| **Comparison With Cleanup Objectives** | | | | | | | |
| Residential | No | Nearly | Yes | Yes | No | Yes | Yes |
| Industrial | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Leachable | Yes | Yes | Yes | Yes | Yes | Yes | Yes |

TCLP = Toxicity Characteristic Leachate Procedure, STLC = Soluble Threshold Limit Concentration

Generally speaking, longer processing times result in higher treatment efficiencies. For a particular site, processing times and operating conditions would be selected to achieve the required contaminant reductions. Note that the permissible contaminant concentration for a particular site depends upon the individual regulatory jurisdiction and on the intended use of the property or soil.

TABLE 4. REMOVAL OF METAL CONTAMINANTS FROM VARIOUS SOILS

| Contaminant | Concentration (mg/kg) | | Removal Efficiency (%) |
|---|---|---|---|
| | Feed Soil | Treated Soil | |
| Antimony ** | 91 | 21 | 77 |
| Arsenic ** | 37,000 | 740 | 98 |
| Barium | 2,015 | 750 | 63 |
| Cadmium | 12.0 | 1.5 | 88 |
| Chromium | 267 | 122 | 54 |
| Copper ** | 505 | 46 | 91 |
| Manganese | 1,875 | 525 | 72 |
| Nickel | 133 | 48 | 64 |
| Lead * | 1,450 | 200 | 86 |
| Strontium | 1,538 | 269 | 83 |
| Zinc | 6,525 | 802 | 88 |

*15 minute treatment ,** 30 minute treatment

## 3.1 REMOVAL OF PETROLEUM HYDROCARBONS

Various bench and pilot scale studies of the ChemTech soil treatment process have shown it to effectively remove a variety of petroleum hydrocarbons contaminants from soils (Stephenson and Yan, 1996). Results of this test work for a number of different soils after five minutes of treatment are summarized in Table 5. Total recoverable petroleum hydrocarbons (TRPH) were removed from Hunter's Point soil at an average removal efficiency of 65%, under the hot acid conditions which were operated in the pilot plant. Hot alkaline conditions are better suited to hydrocarbon removal, and to demonstrate this effect bench scale testing was conducted on a Mare Island oiled soil. A raw soil petroleum hydrocarbon concentration of approximately 17,000 mg/kg was lowered to less than 2,000 mg/kg after 10 minutes of treatment. Recycling process water through a water treatment plant and more effective fluidization at pilot or commercial scales can be expected to increase treatment effectiveness.

TABLE 5. REMOVAL OF PETROLEUM HYDROCARBON CONTAMINANTS FROM SOILS

| Contaminant | Total Extractable Hydrocarbon Concentration (mg/kg) | | Removal Efficiency (%) |
|---|---|---|---|
| | Feed Soil | Treated Soil | |
| Diesel | 41,000 | 170 | 99 |
| Kerosene | 1,340 | 20 | 99 |
| Motor Oil | 213,170 | 1,350 | 99 |
| PAH | 1,620 | 80 | 95 |
| Creosote | 44,500 | 4,780 | 93 |

## 3.2 CHARACTERISTICS OF RESIDUALS

The soil treatment process concentrates contaminants into three residuals streams: pressure filter soil cake, water treatment sludge, and process water. The solid residuals must pass TCLP levels in order to permit landfill disposal and the process water must pass sewer discharge permit levels in order to allow discharge into the municipal sewer. For the Hunter's Point demonstration, both the lime/metals water treatment sludge and the pressure filter soil cake met the TCLP criteria. Process water met all US National Guidelines with the exception of phenol. This shortcoming could be addressed by either activated carbon adsorption or by the addition of alum in the water treatment step.

In spite of the high contaminant levels of these materials, their stability is evident by their very low TCLP levels (see Table 6). The stability of the pressure filter soil cake is due to the extremely aggressive chemical conditions which were used to extract the contaminants from the soil. The stability of the water treatment sludge is attributable to the addition of lime to precipitate the soluble metals as their stable metal hydroxides. The TCLP test is relatively benign when compared to the near boiling and turbulent acidic acid treatment which is applied in the ChemTech system. This lack of leachability would permit industrial landfill disposal.

TABLE 6. CHARACTERISTICS OF SOLID RESIDUALS FROM HUNTER'S POINT

| Parameter | Total Metal Concentration (mg/kg) | | Leachable Metal Concentration TCLP (mg/l) | |
|---|---|---|---|---|
| | Cal. Haz. Waste TTLC | Measured Average | Cal. Haz. Waste STLC | Measured Average |
| **Pressure Filter Soil Cake:** | | | | |
| Antimony | 500 | 89 | 15 | - |
| Chromium | 2,500 | 1,375 | 5.0 | <0.02 |
| Copper | 2,500 | **4,310** | 25 | 0.05 |
| Lead | 1,000 | **3,125** | 5.0 | 1.95 |
| Zinc | 5,000 | **7,890** | 250 | 200 |
| TRPH | - | 85 | - | - |
| **Water Treatment Sludge:** | | | | |
| Antimony | 500 | 47 | 15 | - |
| Chromium | 2,500 | 972 | 5.0 | 0.08 |
| Copper | 2,500 | 2,190 | 25 | 0.74 |
| Lead | 1,000 | **1,080** | 5.0 | 0.65 |
| Zinc | 5,000 | 4,240 | 250 | 200 |
| TRPH | - | <20 | - | - |

Note: shaded areas denotes permit level exceeded

## 3.3 ADEQUACY OF DATA QUALITY

Table 7 below summarizes the adequacy of the data quality which was generated during the program of pilot plant testing. This table shows that the ONSITE Environmental Laboratory XRF data quality approached the objectives for accuracy, substantially met the objectives for completeness, and did not even approximate those for precision. Similarly, ECC's verification laboratory achieved data quality objectives for accuracy, neared the objectives for completeness, and like the field XRF data, did not even approximate those for precision.

TABLE 7. ADEQUACY OF DATA QUALITY: PRECISION, ACCURACY, AND COMPLETENESS

| | Precision (%) | | | Accuracy (%) | | | Completeness (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Work Plan | Actual | | Work Plan | Actual | | Work Plan | Actual | |
| Assay | Obj. | XRF | Fixed Lab | Obj. | XRF | Fixed Lab | Obj. | XRF | Fixed Lab |
| Antimony | 25 | 43 | 56 | 90 | 69 | 99 | 80 | 79 | 78 |
| Chromium | 25 | 24 | 47 | 90 | 85 | 99 | 60 | 96 | 83 |
| Copper | 25 | 34 | 87 | 90 | 88 | 99 | 80 | 74 | 82 |
| Lead | 25 | 42 | 53 | 90 | 95 | 98 | 80 | 78 | 69 |
| Zinc | 25 | 41 | 33 | 90 | 95 | 100 | 80 | 79 | 68 |
| Leachable Metals | 10 | - | 3 | 95 | - | 99 | 95 | - | 100 |
| TRPH | 25 | 37 | - | 90 | - | - | 90 | 83 | - |

Table 8 shows that excellent correlations of the ONSITE versus fixed laboratory data were obtained for chromium (0.969), copper (0.891), and zinc (0.965). The correlation coefficients for antimony (0.528) and lead (0.744) indicates a weaker linear association of the two assay techniques, possibly due to poorly matched calibration standards, or low extraction efficiency of the confirmation lab. This indicates that the XRF technique was less effective as a predictive tool of commonly accepted fixed laboratory assays for antimony and lead for the samples submitted.

TABLE 8. CORRELATION COEFFICIENTS FOR XRF VERSUS FIXED LABORATORY ASSAYS

| Compare to Fixed Lab | Pearson Correlation Coefficient | | | | |
|---|---|---|---|---|---|
| | Antimony | Chromium | Copper | Lead | Zinc |
| XRF | 0.528 | 0.969 | 0.891 | 0.744 | 0.965 |
| Leachability | - | - | 0.989 | 0.646 | 0.994 |

## 4. CHEMTECH ECONOMIC PERFORMANCE

The factors which affect the technical and economic feasibility of ChemTech site cleanup include the following: soil type (sand versus clay); contaminant type, form, and concentration (metals, petroleum hydrocarbons, particulate metals); cleanup objective: (residential, industrial or risk-based (leachable) levels); and scale of the project. These factors dictate the optimum operating conditions, process kinetics, quantity of residuals, and operating costs. The estimated total cleanup cost for a 250 TPD capacity to treat 20,000 tons of soil, 20% oversize, 10% fines and 15 minutes solids residence time is around $US 100 per ton of contaminated soil. Table 9 itemizes these costs.

TABLE 9. CHEMTECH TOTAL CLEANUP COSTS FOR A METALS CONTAMINATED SOIL

| Cost Element | Cost/Ton ($US) |
|---|---|
| **Pre-Treatment:** | |
| Sampling, Treatability Testing, Analysis, Mobilization of Equipment, Spill Containment, Travel, Setup | 1.90 |
| **Soil Treatment:** | |
| Soil Handling Labour, Soil Treatment Labour, Chemicals, Utilities, Supplies, Analytical | 37.50 |
| **Post Treatment:** | |
| Treatment of Soil Cake, Water Treatment, Equipment Decontamination, Storage, Disposal, Disposal of Water Treatment Sludge, Disposal of Used PPE, Take Down, Demobilization, Site Restoration, Report. | 22.55 |
| **Cost of Ownership:** | |
| Amortization of capital, equipment rental, profit | 26.60 |
| **Indirect Costs:** | |
| Administration, marketing, accounting, legal, insurance, office | 10.10 |
| **Total Cleanup Cost Per Ton Of Soil** | $98.65 |

No general allowance was made for site restoration, since this cost is highly variable. The cost to purchase, install, and commission a 250 TPD mobile ChemTech soil treatment plant is estimated to be approximately $US 1.5 million.

The general effect of the above variables such as soil type, and cleanup objective on a 250 TPD soil processing is illustrated in Figure 2 for a site similar to Hunter's Point.

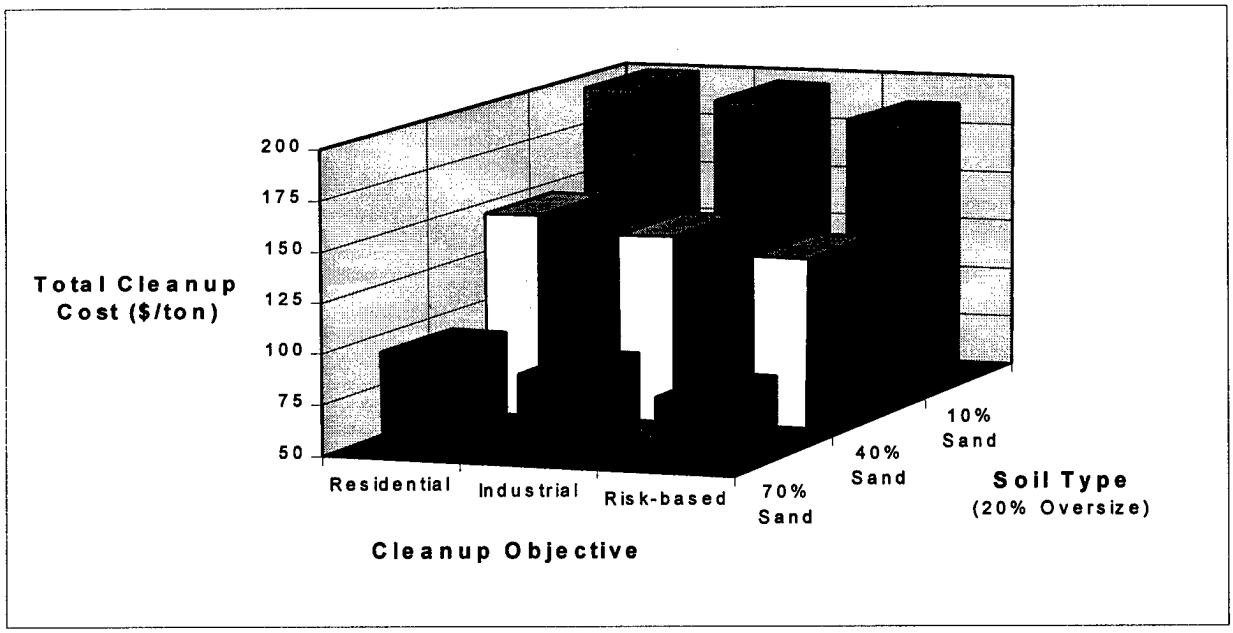



Figure 2. Effect of soil type and cleanup objective on total cleanup cost

Both soil type and cleanup requirement exert significant impacts on the total cleanup cost. Whereas predominantly sandy soil is readily treated in the process, contaminated soils which are rich in clay would typically require secondary processing in the fluidized bed in order to render the fine soil fraction suitable for return to the excavation site. Meeting the total contaminant concentrations of residential or industrial permit levels can be costly, especially if particulate metals are encountered on site. If a risk-based approach to site cleanup is feasible such that metal contaminants are not leachable and therefore are not transported by groundwater, then the total site cleanup cost could be significantly reduced. The same rationale can also be extended to estimate the cost of cleanup for other types of contaminants. Soils contaminated with light hydrocarbons such as gasoline, diesel, or kerosene are easily treated by this process and this is reflected in the high capacity (analogous to lower cleanup objective) and low unit costs. Soils which are contaminated with heavy hydrocarbons or heavy metals require longer treatment times and the diminished treatment capacity results in higher total cleanup costs.

## 5. ATTRIBUTES OF METALS ANALYSES BY XRF

The XRF demonstration project realized the following objectives:

1. Rapid Mobilization: The lab was connected to shore power and fully operational within two hours.

2. High Sample Throughput: Four samples were analyzed per hour, which translates to the forty sample per day rate. Traditional methods cannot provide a result within 15 minutes.

3. Data Quality: Data quality objectives for accuracy, completeness, and correlation were substantially achieved.

4. Cost effective: To measure 5 metals in a soil matrix, an off-site fixed laboratory would typically cost $65 per sample or $130 for a 24 hour rush turnaround premium. Assuming a daily rate of $1,350 per day for a ten hour day, EDXRF analysis of 30 samples per day, would cost $45 per sample. Based on

these assumptions, the EDXRF analysis is 35% of the cost of traditional methods, or a savings of 65%. The savings of using EDXRF increase as the number of elements requested increases.

5. Time: Using EDXRF to guide an excavation or site characterization will generally reduce the overall time required in the field due to the quick turnaround of the sample analysis.

## 6. ATTRIBUTES OF THE CHEMTECH PROCESS

Applications of the ChemTech process include removal of metals and heavy or light hydrocarbons from soils ranging from gravel to sand to clay. Since the process can employ combinations of the physical treatment and chemical extraction contaminant removal mechanisms, other soil-like materials such as marine sediments or sandblasting grit can also be treated in the same manner by this process.

The innovative application of a three phase fluidized bed, integrated with conventional mineral processing unit operations, affords the process the following attributes:

- Aggressive physical and chemical treatment results in high treatment capacities
- Mobile, high capacity system
- Adaptability to varying field conditions
- Mechanically simple system adds field reliability
- Closed air and water circuits is cheaper and environmentally friendly
- Solids residuals are non-leachable

### 6.1 PREFERRED APPLICATIONS

The most suitable match between the ChemTech process and contaminated soil is where the soil is coarse and contaminated by either metals and light hydrocarbons or by heavy hydrocarbons. Table 10 summarizes the applicability of the ChemTech soil treatment system to various soil types and contaminants. A suitable match of the system's technical and economic performance was rated as either superior, competitive, or marginal. As Table 10 illustrates, the process is feasible for predominantly sandy soils which are contaminated with either metals or hydrocarbons. Soils which are predominantly clay or silt are generally more costly to treat and therefore a lower performance rating was assigned.

TABLE 10. APPLICABILITY OF CHEMTECH SYSTEM TO SOILS AND CONTAMINANT TYPE

| Soil Type | Contaminant Type | | | | |
|---|---|---|---|---|---|
| | Metals | | Hydrocarbons | | Combined |
| | Dispersed | Particulate | Light | Heavy | Metals and Hydrocarbons |
| Predominantly Sand | ★★★ | ★★ | ★★★ | ★★★ | ★★ |
| Predominantly Clay or Silt | ★★ | ★ | ★★ | ★ | ★ |

★★★ Superior Performance, ★★ Competitive Performance, ★ Marginal Performance

Remediation difficulty is presented by soils where "contamination" is intrinsic to the soil (for example metal particulates, sandblasting grit, or mine tailings) rather than concentrated on the soil surface following chemical spillage, and by liquid contaminants which have impregnated porous materials such as wood debris or bricks. Performing risk based remediation to meet target leachable levels of contaminants may be appropriate for these sites.

As for all soil treatment processes, effective soil treatment may be difficult for some contaminants (chlorinated organics for example) due to the chemical characteristics of the contaminant and/or the permissible concentration as specified in contaminated site regulations.

## CONCLUSIONS

Tests of the ChemTech soil treatment process have demonstrated a capability to remove a range of both metals and hydrocarbons contaminants from soil. The compatibility of the physical and chemical systems promises a unique ability to remediate contaminated soils rapidly and effectively. The process is environmentally friendly, involving neither incineration nor hazardous chemicals, and recycling process air and water to result in minimal discharge to the environment.

The demonstration of XRF analyses by ONSITE Environmental Laboratories demonstrated a rapid setup, high throughput to result in improved decision making and reduced costs, met data quality objectives for accuracy and completeness, showed overall a strong correlation with confirmation data, and offered substantial savings over conventional, off-site methods.

Commercial scale application of the ChemTech system will lead to rapid and comparatively low cost clean-up of contaminated soils. Typical total clean-up costs for this system can be expected to be around $100 per ton, depending upon a number of site specific factors. Compared to the available alternatives for site clean-up such as landfilling soil, this lower cost could promote clean-up activity and the re-development of contaminated sites.

## ACKNOWLEDGMENTS

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# FIELD DEMONSTRATION OF AN IN-WELL AERATION TECHNOLOGY FOR AQUIFER REMEDIATION

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## ABSTRACT

Wasatch Environmental, Inc. is conducting a field demonstration of their in-well aeration technology called density-driven convection (DDC) at Keesler AFB in Biloxi, Mississippi. The DDC demonstration is part of a technology demonstration project being conducted by the Air Force Center for Environmental Excellence . The study is being performed in an unconfined, fine sand aquifer impacted by release of gasoline and diesel. The demonstration is being conducted in two phases: a pilot study conducted in April of 1995; and a large scale demonstration which began in May 1996. Results of the pilot study show a groundwater circulation rate of about 4 g.p.m. through a DDC well. Dye injected into the DDC well at the start of the pilot study was observed at a radial distance of 20 feet within 6 days of operation. A hydrocarbon removal rate of up to 1.6 lbs/day due to stripping in the DDC well was measured. The stripping efficiency of the DDC well was found to average 95 percent for total petroleum hydrocarbons during the pilot study and was over 90 percent for all aromatic hydrocarbons except benzene which averaged 76 percent. The large scale demonstration included installation and operation of 32 DDC wells (including the pilot study DDC well) and 6 SVE wells. Monitoring of the large scale system to date indicates an average in-well stripping efficiency of about 80% in DDC wells. The concentrations of petroleum hydrocarbons in soil has decreased approximately 90% after one year of operation.

## 1. INTRODUCTION

Wasatch Environmental, Inc. (Wasatch) is conducting a field demonstration of their in-well aeration technology called density-driven convection (DDC) at Keesler AFB in Biloxi, Mississippi. The DDC demonstration is part of a technology demonstration project being conducted by the Air Force Center for Environmental Excellence (AFCEE). The contract for demonstration was awarded in response to a broad agency announcement proposal submitted by Wasatch. The field demonstration is being conducted in two phases: a pilot study conducted in April of 1995; and a large scale demonstration which began in May 1996.

### 1.1 PHASE I -PILOT STUDY

Phase I of the field demonstration consisted of a pilot study using one DDC well and one soil vapor extraction (SVE) well. The principal objective of the pilot study was to develop design parameters based on DDC performance to help in its application at this and other sites. The pilot study involved a variety of activities to measure the groundwater circulation rate, flow pattern, and air stripping efficiency of the DDC well. It also included activities to measure the radius of influence and hydrocarbon removal efficiency of the SVE well. Results of the pilot study were used in the design of the large scale demonstration carried out under Phase II of the field demonstration.

## 1.2 PHASE II - LARGE SCALE DEMONSTRATION

Phase II of the field demonstration involved installing and operating a large scale demonstration system. The objective of Phase II was to demonstrate the effectiveness of DDC in promoting *in situ* bioremediation and in-well air stripping.

## 2. DESCRIPTION OF DDC TECHNOLOGY

DDC is a patented in-well aeration technology developed by Wasatch. It is based on a well design in which the well casing is screened across two separate intervals. Typically, the upper screen is installed across the water table and the lower screen is installed near the bottom of the aquifer interval to be treated. The screened intervals are separated by a section of blank casing which is installed with a corresponding annular seal. A diagram of a typical DDC well is shown in Figure 1.

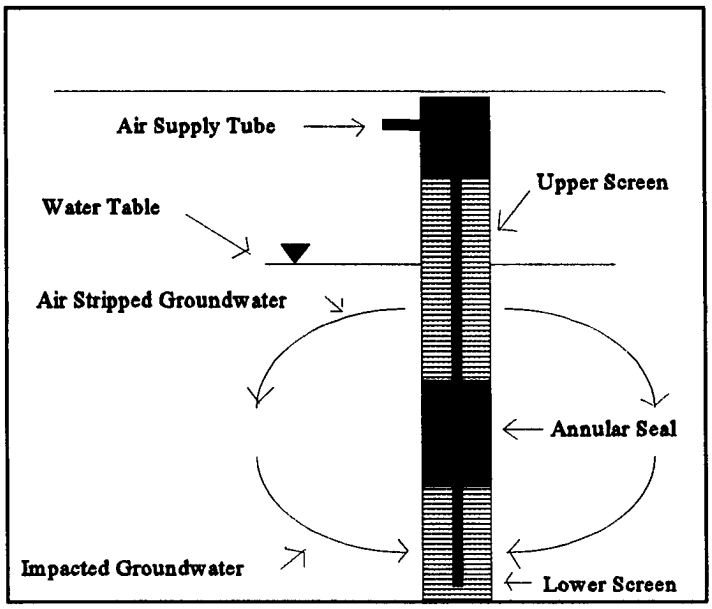



FIGURE 1. TYPICAL DDC WELL CONSTRUCTION

Air is injected at the bottom of the DDC well producing a less dense mixture of air and water within the well. The density difference between the air/water mixture inside the well and the static water outside the well results in flow of water from the aquifer into the lower screen as aerated water flows out the upper screen into the aquifer. The flow pattern DDC develops in the aquifer is shown in Figure 1.

Two mechanisms accomplish remediation of the groundwater and surrounding soil: first, dissolved volatile compounds are air stripped from the groundwater as it flows through the well; and second, bioremediation in the surrounding soil and groundwater is enhanced as air stripped, oxygenated groundwater flows out of and away from the DDC well. DDC can also enhance bioremediation in the vadose zone as air is introduced into the surrounding soil from the DDC well. DDC is well suited for use with SVE as it serves as a source of air to be drawn through the vadose zone.

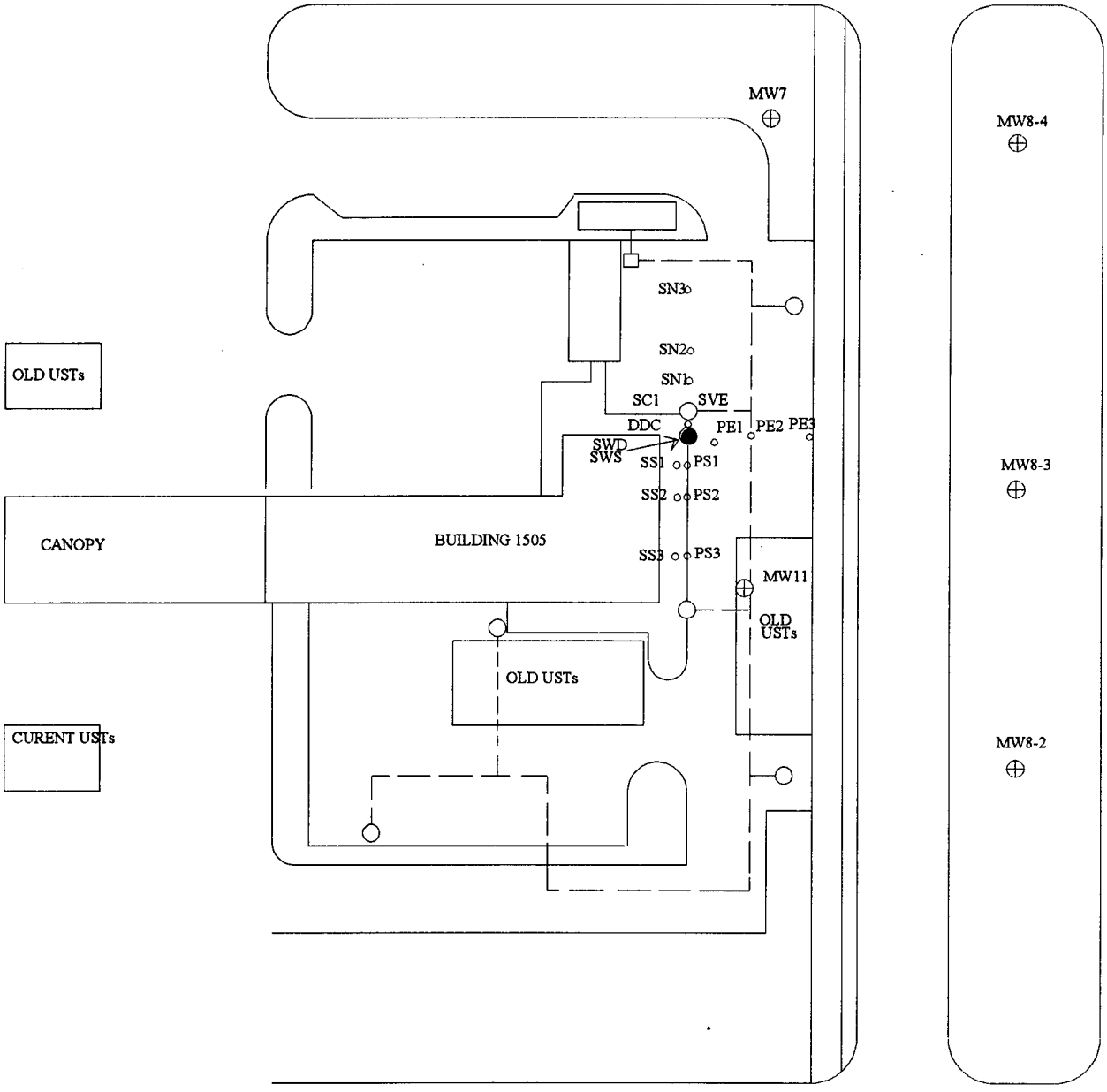
## 3. SITE DESCRIPTION AND BACKGROUND

### 3.1 GENERAL DESCRIPTION

Keesler AFB is located in Biloxi, Mississippi, approximately 80 miles east of New Orleans, Louisiana, and 60 miles west of Mobile, Alabama. The base is bordered on the north by the Back Bay of Biloxi (Back Bay) and on the west, south, and east by residential and commercial areas. The Mississippi Sound is approximately 0.5 miles south of the base. Keesler AFB comprises 1,494 acres of federally owned land. The base was activated in June 1941 as a training center for aircraft mechanics and continues to operate as a training center for the Air Force. The current mission focuses on technical training, medical care, flying operations, and support.

### 3.2 DEMONSTRATION SITE

The field demonstration site at Keesler AFB is the BX Service Station at the northwest corner of the intersection of Larcher Boulevard and Meadows Drive. The station is currently active and includes an automotive store (building 1504), service bays, and pump islands. A map showing the site features is presented as Figure 2, below.




o PIEZOMETER PAIR

⊕ MONITORING WELL

o SOIL GAS MONITORING POINT

○ BIOVENTING WELL

FIGURE 2: SITE MAP

Concrete and asphalt paving, or buildings cover the site, except several small grass-covered islands. The site topography is flat with an average elevation of approximately 20 feet above mean sea level. Surface runoff is to the northeast toward the Back Bay via a storm water drainage network.

The station has several active underground storage tanks (USTs) located southwest of building 1504. The currently active dispensers are beneath a canopy attached to the western side of the building. These USTs and associated dispensers were installed in 1995.

Several previous fueling systems were in use at the station over the years. The oldest system, which was removed in 1987, had ten USTs and three dispenser islands located east and south of building 1504. The approximate locations of these old USTs are shown on Figure 2. Evidence of petroleum hydrocarbon releases was observed in both UST excavations during removal activities.

The next oldest fueling system had five USTs, which contained gasoline and diesel fuels. The USTs were northwest of building 1504 and supplied product to dispensers which were under the canopy. The locations of these USTs are shown on Figure 2. Reportedly, several of these USTs failed tightness tests due to suspected leakage near the tops of the tanks. This fueling system was removed and replaced in 1995.

### 3.3 PREVIOUS INVESTIGATIONS AND TESTS

Several consults have conducted investigation of the site over several years. All of the monitoring wells used in this field demonstration had been installed by others. The locations of the monitoring wells used in the demonstration are shown on the accompanying figures.

Battelle conducted a bioventing test at the site as part of an AFCEE bioventing initiative. Six bioventing wells (three extraction and three injection wells) and buried piping were installed for the test. The bioventing test was conducted in the same area as the current field demonstration and a portion of the old system was used in the construction of the current system.

## 4. SITE CONDITIONS

### 4.1 SITE SOIL

The shallow aquifer at the site occurs in the Pamlico Sand, a Holocene or Pleistocene formation of unconsolidated terrace or alluvial deposits. Soils encountered during the demonstration consist of silty sand to a depth of about 3 to 4 feet, and fine to medium sand to a depth of 22 feet. Clay was encountered at a depth of about 22 feet.

### 4.2 SITE HYDROGEOLOGY

The demonstration was conducted in a shallow, unconfined aquifer. Groundwater at the site occurs from 7 to 9 feet below ground surface. Groundwater flows east or northeast under a horizontal hydraulic gradient of 0.004 to 0.005 ft/ft. Horizontal and vertical hydraulic conductivities measured during the pilot study are 32 ft/day and 9.5 ft/day, respectively.

### 4.3 NATURE AND EXTENT OF IMPACT

The source of contamination in the soil and groundwater was gasoline and diesel fuel leaked from the old USTs and dispensers. Results of previous investigations show that the aerial extent of impacted soil was approximately 20,000 $ft^2$. The highest concentrations were found near the oldest fueling system location. The aerial extent of impacted groundwater was approximately 130,000 $ft^2$. The plume extended approximately 400 feet down

gradient of the site. Monitoring conducted as part of the current field demonstration indicate that impacted groundwater and free product occur up gradient of the demonstration system. The source of this impact is likely the old USTs located northwest of building 1504.

## 5. PHASE I - PILOT STUDY RESULTS

The phase I pilot study was conducted over a 19 day period beginning April 18, 1995. Monitoring was conducted daily over the course of the study. The SVE system was operated only for the first ten days of the study.

### 5.1 SYSTEM DESCRIPTION

The pilot study system included installing and operating one SVE well and one DDC well. Seven piezometer nests and seven dual-level soil gas monitoring points were installed to monitoring operation of the wells. The locations of the wells and monitoring points are shown on Figure 2.

The SVE well was installed in the manhole of an old bioventing well. The old well was pulled out and a new, larger diameter well installed. Vacuum pressure was supplied to the new well by connecting it to the bioventing system's vacuum supply piping. The soil gas monitoring points were installed in a line running north (SN1 through SN3) and south (SC1, and SS1 through SS3) from the SVE well. Each monitoring point has two probes constructed of stainless steel pipe with 6-inch screens. One screen was installed to about 4 feet the other to about 6 feet deep.

The DDC well was installed approximately 8 feet south of the SVE well. It was constructed of 4-inch diameter PVC with screened intervals form 4 to 14 feet and 16.5 to 21.5 feet below ground surface. One piezometer pair was installed in the DDC well boring. One of the piezometers (SWS) was screened from about 8 to 9 feet and the other (SWD) was screened from about 18 to 19 feet below ground surface. Piezomters SWDand SWS provide sampling points for inflow to and outflow from the DDC well. Six other piezometer pairs were installed in lines running east (PE1 through PE3) and south (PS1 through PS3) from the DDC well. The pairs in both lines were installed at radial distances of 10, 20, and 40 feet. The screened intervals and construction of the piezometer pairs was similair to those in the pair installed in the DDC well boring.

### 5.2 SVE TESTS

#### 5.2.1 RADIUS OF INFLUENCE

The radius of influence for the SVE well was evaluated by installing vacuum gauges on each of the soil gas monitoing points and measuing reponces while appling a vacumm to the SVE well. For this test, the radius of influence was defined as the distance to one percent of the vacuum pressure applied to the SVE well. The radius of influence was determined by plotting the log of the normalized vacuum presure (the measured vacumm pressure divided by the vacuum at the SVE well) against the raidus from the SVE well. Results of the test showed a radius of influence of approxiamtely 60 feeet.

#### 5.2.2 SOIL GAS MONITORING

The concentrations of oxygen and carbon dioxide in soil gas were measured prior to operating the SVE system. The initial average oxygen concentration was 7.3 percent and that of carbon dioxide was 7.0 percent. The concentration of oxygen increased during the study while the concentration of carbon dixide decreased. The average concentrations of oxygen and carbon dioxie during the test were 17.4 and 2.6 percent, respectively. Although operation of the SVE well ceased after 10 days, the concentrations of oxygen and carbon dioxide did not change substancially during the remiander of the test. These results suggest that DDC is capable of supplying

adquate oxygen to support biremediation in the vadose zone.

## 5.3 DDC TESTS

### 5.3.1 FLOW TESTS

The rate of groundwater flow through the DDC well was evaluated by two methods: the first method involved injecting a slug of cold water into the bottom of the well and measuring the velocity with which it traveled upward through the; the second method involved plotting the air flow rate against produced head gradients and comparing them to plots from laboratory tests in which the flow rates were known. Results of these tests indicate that the flow rate of groundwater through the DDC well was about 3 to 4 gpm.

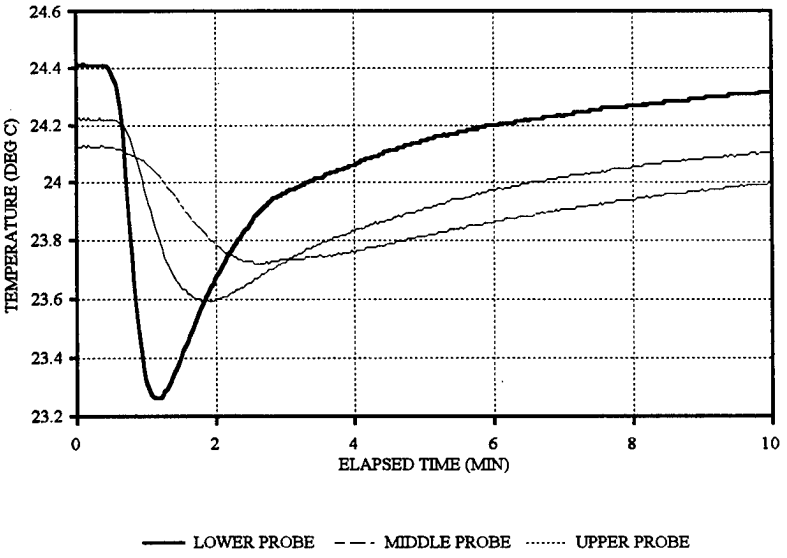



FIGURE 3: SLUG TEST RESULTS

### 5.3.2 RADIUS OF INFLUENCE

The radius of influence of the DDC well was evaluated by two methods: the first invloved injecting dye into the DDC well and monitoring its movement through the aquifer; the second invloved measuring for a hydraulic gradient within the piezometer nests.

The dye tracer study consisted of injecting a fluorecent dye into the DDC well at the start of the test. Groundwater samples collected from the piezometers were analyzed periodically throughout the test to evalute migration of the dye. Results of the test showed that dye had migrated a distance of 20 feet from the DDC well during the test period. Dye was observed 10 feet from the sparge well within 2 days of system startup and 20 feet from the sparge well within 6 days of system startup.

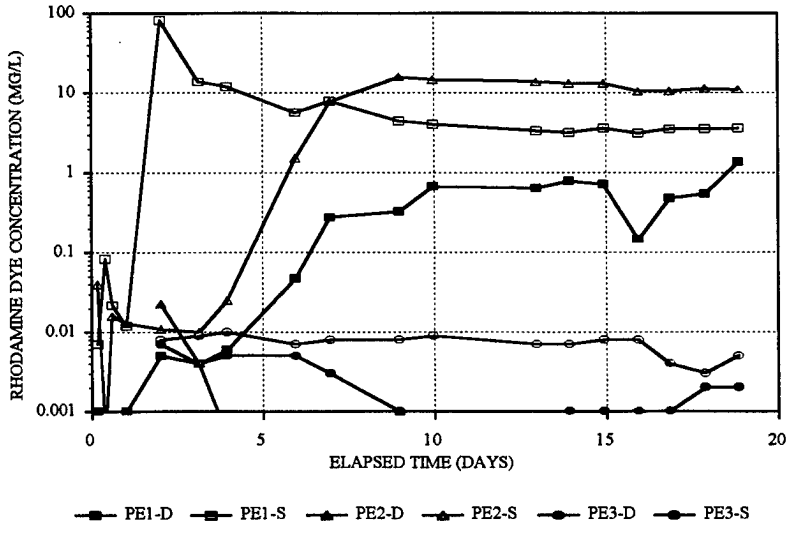



FIGURE 4: DYE TEST RESULTS

The pattern of dye migration matched the expected pattern of dye movement with the highest concentrations of dye detected in the shallow piezometers. Migration in the down-gradient direction (east) was higher than the cross-gradient direction (south) based on the concentrations of dye observed.

Baseline monitoring showed that there was no vertical gradient in the piezometer pairs prior to system startup. Operation of the DDC well produces downward vertical gradient within the aquifer. The produced gradient is apparent as differences in water levels between the pizometers pairs. The magnitude of these differences decline with distance from the DDC well and the radius of influence may extend beyond the measurebale gradient difference. The gradient measured in the piezometer pair installed in the DDC well boring was about 3.3 feet throughout the test. Gradients up to 0.3 feet were measured in piezometer pairs PE1 and PS1 which are 10 feet from the DDC well. Gradients up to 0.04 feet were measured in piezometer pairs PE2 and PS2 20 feet from the DDC well. No gradient was measured in piezometer pairs PE3 and PS3 which are 40 feet from the DDC well. These results show that the radius of influence of the DDC well is at least 20 feet at the demonstation site.

### 5.3.3 STRIPPING EFFICIENCY

The in-well stripping efficiency of the DDC well was evaluated by analyzing, groundwater samples collected from the piezometers SWS and SWD. The stripping efficiency was calculated as the change in petroleum hydrocarbon concentration between the effluent and influent screens, divided by the concentration at the influent. This calculation assumes that the concentrations in SWD and SWS representative of the average groundwater influent and effluent concentrations, respectively. The calculated stripping efficiencies averaged over 90 percent for TPH and all of the aromatic hydrocarbons except benzene which averaged 76 percent.

The hydrocarbon concentrations in the influent samples increased over the course of the test. This is believed to be due to the mechanics of dispersion of hydrocarbons in groundwater wherein concentrations decrease with depth in the aquifer. Due to the vertical groundwater circulation created by DDC within the aquifer, dissolved hydrocarbons are pulled downwards within the aquifer towards the lower screen of the DDC well increasing the influent concentrations. Stripping efficiencies increased with increasing influent concentration, presumably due to recirculation around the annular seal.

## 6. PHASE II - LARGE SCALE RESULTS

### 6.1 SYSTEM DESCRIPTION

Phase II of the feild demonstartion invloved the installation and operation of a large scale demonstartion system consisting of 6 SVE wells and 32 DDC wells. The locations of the large scale system wells are shown on Figure 5. Operation of the large scale demonstartion system began on May 15, 1996, results of system monitoing are presented below.

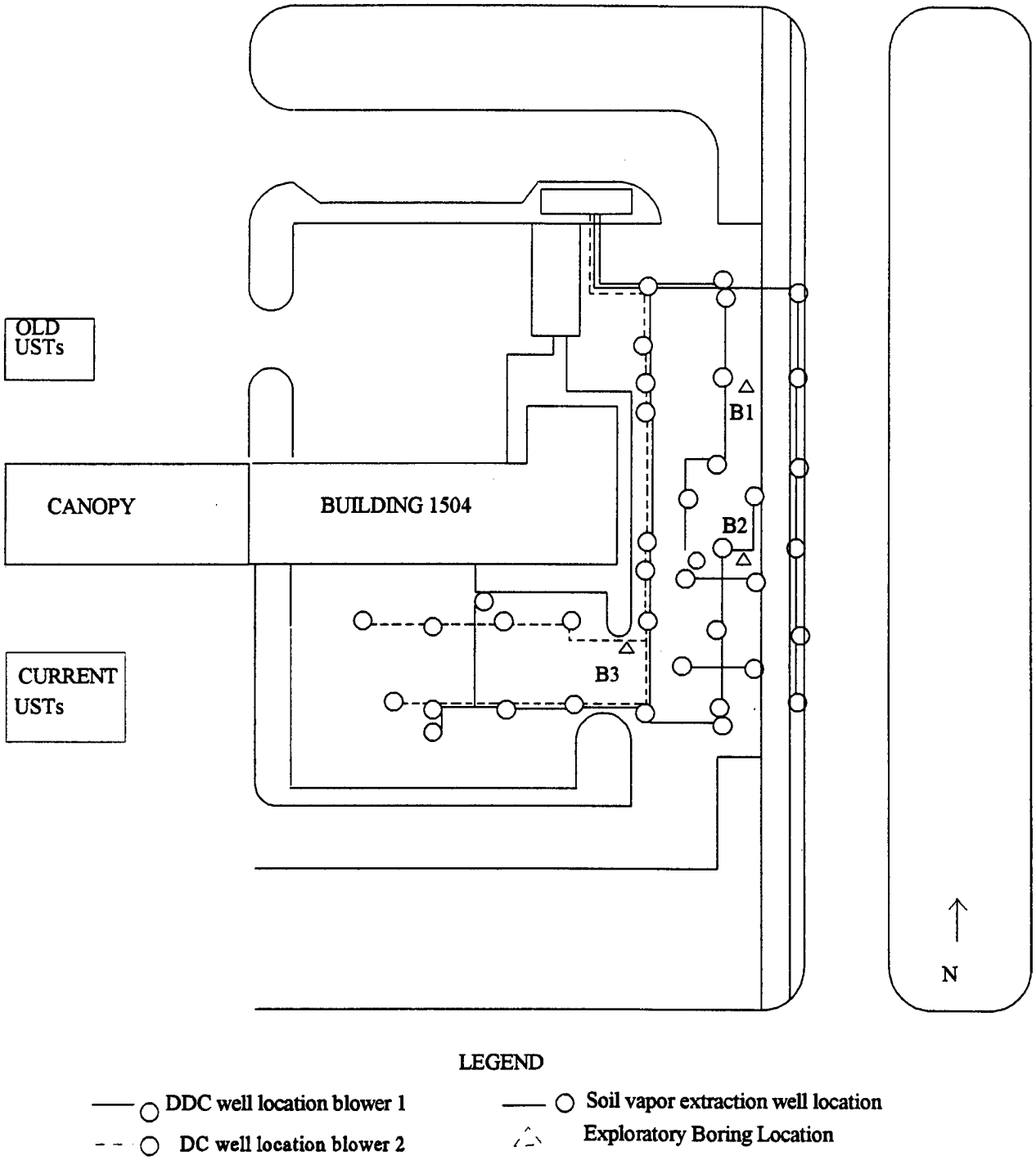



FIGURE 5: LARGE SCALE SYSTEM

## 6.2 SVE OPERATION

The SVE system has operated continuously since startup. Monitoirng shows that the concentration of carbon dioxide in the SVE emissions has decrease since startup from approxiametly 3 percent to approximately 1 percent after one year of operaton. In that same time, the concentration of oxygen has increased slightly from approximately 19 percent to approximately 20 percent.

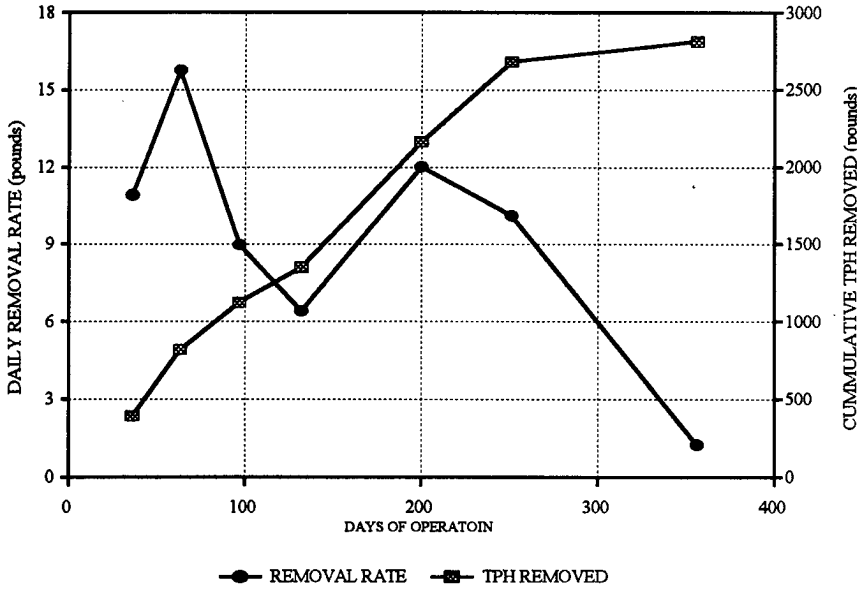



FIGURE 6: SVE EMISSION MONITORING

Monitoring of hydrocarbon vapors in the emissions shows the SVE system has removed approxiametly 2,800 pounds of hydrocarbon vapors during the first year of operation. Results of the vapor emission monitoring are shown in Figure 6.

## 6.3 DDC OPERATION

Two pressure blowers are used to supply air to the DDC wells, the smaller of the two blowers supplies 11 of the wells, and the larger blower supplies 21 wells. The small blower has operated continuously since startup. The large blower experienced recurrent failures and was replaced with a different brand in October 1996. Since then, both pressure blowers have operated essentially full time.

The average concentration of dissolved TPH has decresed since startup except for one increase after about 30 days of operation. The average concentration of cummulative BTEXN increased during the first 200 days of operation then began to decrese. Results of groundwater monitoring are shown on figure 7. The initial increase in dissolved

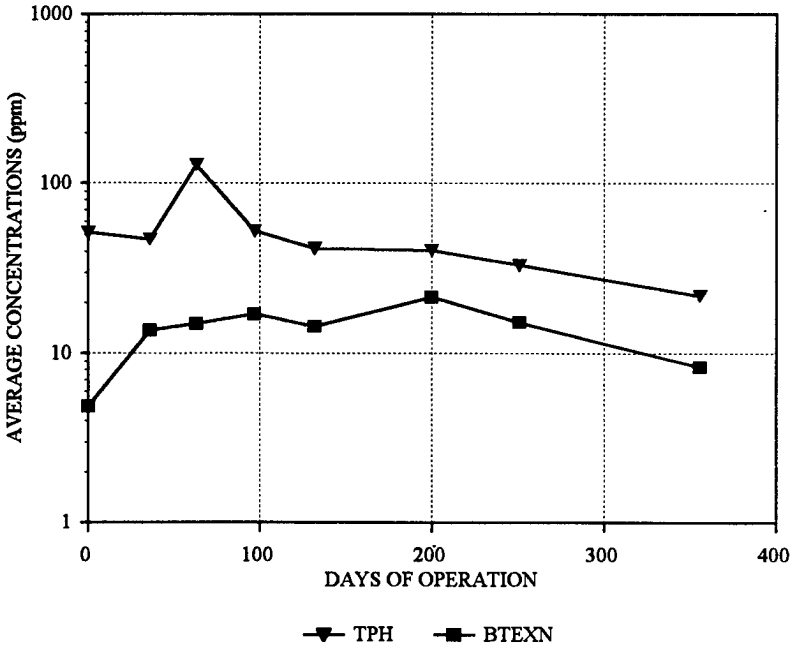
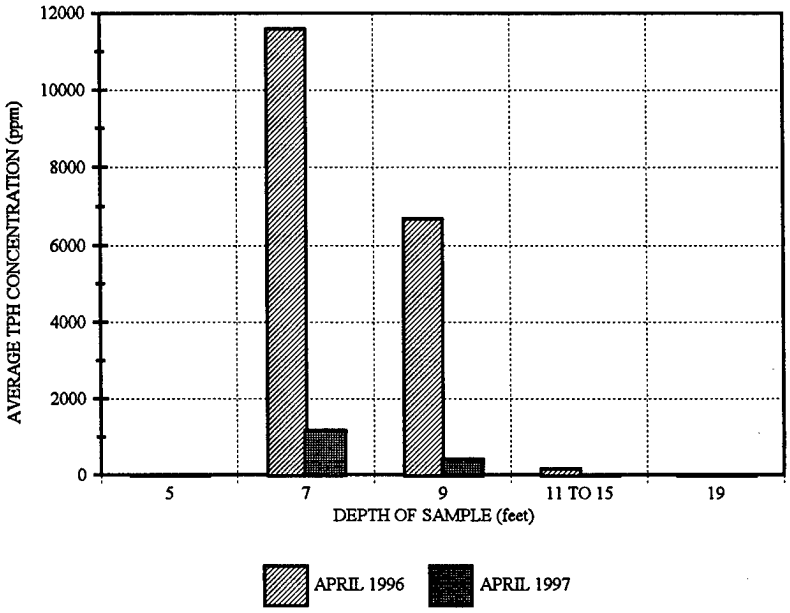



FIGURE 7: DISSOLVED HYDROCARBONS

concentrations is expected based observations at other full scale DDC sites. It is belived to result from the circulation of groundwater by DDC and desorption of hydrocarbons from soil.

The in-well stripping eficiecy of the pilot DDC well has averaged 68 percent since startup. However, this includes one sample event in which the influent and effluent samples had indentical concentrations of dissolved constituents resulting in a calculated stripping efficiency of zero for that event. The indientical concentrations in those samples suggest the possiblity of sampling or analytical error. Excluding this data from stripping efficiency calculations yields an average stripping efficieny of approximately 80 percent since startup.




Soil samples were collecetd from three borings drilled in the study area. The location of the borings are shown on Figure 5. The April 1996 samples were collected during the large scale system installation. The April 1997 samples were collected from borings drilled approximately one foot from the original borings. The average concentration of TPH with depth for the two sampling events are shown on Figure 8. Soil samples were collected at depths corresponding to the vadose zone (5 feet), immediately above the water table (7 feet), and at three depths below the water table.

The majority of the soil impact occured within the capillary fringe and immediately below the water table. The intial soil samples averaged about 11,600 ppm and 6,700 ppm at seven and nine feet, respectivily. Samples collected after one year of operation averaged about 1,200 ppm and 450 ppm at the same depths. These results indicate TPH concentration reductions of 89 and 93 percent in soil within the capillary fringe and immediately below the water table, respectively.

## CONCLUSIONS

The pilot study performed as Phase I of the field demonstartion provided information on aquifer properties, SVE well performance, and DDC well performance. Results of the pilot study indicate that an SVE well at the demonstartion site had a radius of influence of approximately 60 feet. The study radius of influence for a DDC well at the demonstration site was greater than 20 feet. Dye injected into the DDC well at migrated laterally a distance of 20 feet during the pilot study. Groundwater flow through a DDC well was approximately 4 g.p.m.

Phase II of the field demonstration involved installing and operating a large scale system which includes 6 SVE well and 32 DDC wells. The system has been operated for about one year during which the DDC well was shown an in-well stripping efficiency of approximately 80 percent. The concentration of hydrocarbons in soil has decreased approximately 90 percent since operation of the large scale system began.

# REMEDIATION V

# APPLICATION OF PHOTOCATALYTIC OXIDATION TO MILITARY PAINT BOOTH EMISSIONS

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## ABSTRACT

The Department of Defense (DOD) is responding to environmental concerns at military installations by investigating over 20,000 potentially contaminated sites comprising underground tanks, landfills, spill and storage areas, as well as hazardous VOC (volatile organic compounds) emissions as mandated by the Clean Air Act amendment of 1990. Sources of air pollution at military installations include VOC producing operations such as spray painting, plating and abrasive blasting, storage and handling of volatile fuels and solvents, fuel farms, waste water treatment facilities, and other sources.

One area in which light-driven environmental remediation technologies can provide nonpolluting and cost effective compliance is the treatment of VOCs in contaminated air streams. Recently, researchers from the National Renewable Energy Laboratory (NREL) field tested a new technology at paint booth facilities at Fort Carson US Army Installation and the US Air Force Academy, both located in Colorado Springs, Colorado. The air streams from the paint booths are permitted under the 1990 Clean Air Act (amended) Title V operating permit program in which emission limits are 25 tons/year for a combination of hazardous air pollutants (HAPs) and/or 100 tons/year of VOCs. This report will discuss the environmental problem, process and apparatus used in the field tests, preliminary test results, and applicability of the process to other VOC emissions.

## 1.0 INTRODUCTION

Painting operations for military vehicles and associated components are conducted in ventilated enclosures called paint booths. Filters in the exhaust ducts trap paint droplets from the paint overspray while the VOC-laden air is typically exhausted through roof vents. The vent emissions can contain several hundred parts per million (ppm) of the paint solvents, which continue to evaporate from the vehicle after painting is complete. Most types of paint generally contain significant amounts of VOCs such as toluene, a suspected carcinogen, as well as other hazardous solvents such as methyl ethyl ketone, methyl isobutyl ketone, hexanes, xylenes, n-butyl acetate, and other components in lesser amounts. Those solvents not considered hazardous are still organic

compounds known to contribute to smog and ozone problems in the atmosphere.

The amount of paint used at Fort Carson in 1994 was estimated to be 5200 gallons. The actual emissions, determined from the amount of paint used, are listed in Table 1.

**TABLE 1: ACTUAL AIR EMISSIONS (lbs/yr)**

| Paint Type | Total Usage (gal/yr) | VOC | HAP | MEK | Toluene | MIBK | Xylene |
|---|---|---|---|---|---|---|---|
| Solvent base | 5200 | 29,120 | 1,430 | 1,040 | 130 | 0 | 260 |
| Thinner | 260 | 1,914 | 191 | 146 | 0 | 46 | 0 |

Currently, no treatment of these hazardous air streams is required at either of these installations for painting operations. However, these air streams do contribute to the total permitted emissions and new requirements are expected to take effect in the near future that will necessitate some type of control device.

Before going on-site, a slipstream off the paint booth vents at both installations was analyzed to determine the components present. Then laboratory tests of the simulated mixtures, based on the component analysis, were conducted to determine the feasibility of using photocatalytic oxidation (PCO) to treat these streams. After finding that such streams are treatable with PCO, we then took a small field unit to both sites to determine how well we could treat actual streams. The small (20 liters/min) field tests provided the information necessary to scale up to a 5 SCFM system that used concentrated sunlight for a heat and light source.

### 1.1 TREATMENT PROCESS: PHOTOCATALYTIC OXIDATION

The photocatalytic oxidation process effectively destroys hazardous organic pollutants in both air and water streams. Although treatment systems will vary depending on the type of stream being treated, the basic process remains the same. The key ingredient is the photoactive catalyst titanium dioxide ($TiO_2$), which is an inexpensive, non-toxic material commonly used as a paint pigment. When $TiO_2$ is illuminated with lamps or natural sunlight, powerful oxidizing species called hydroxyl radicals form. These radicals then react with the organic pollutant to tear it apart and ultimately form carbon dioxide ($CO_2$) and water. Since PCO is not a high temperature process like incineration, no NOX emissions are produced.

Many organic compounds commonly found at DOD sites are quite susceptible to destruction by PCO. In addition, PCO systems are modular, portable, and ideally suited to treating point of use emissions. PCO may be competitive with conventional methods for treating emissions at low flows and low pollutant concentrations. Our goals for testing the paint booth emissions was to gather real-world treatability data and establish that both lamp- and solar-driven systems maintained performance during the duration of the testing.

## 1.2 APPARATUS: FIELD REACTOR SYSTEM

The small field test system consisted of a photoreactor packed with Degussa $TiO_2$-coated glass beads. Figure 1 shows a schematic of this system which operated with a flow rate of 20 liters/minute provided by a pump connected to the paint booth exhaust vent line. The reactor temperature could be varied from ambient to 200°C. The inlet VOC concentration was measured by a gas chromatograph (MTI Instruments, Model P200 gas analyzer) directly connected to the inlet line. The reactor outlet concentration was simultaneously measured with a second gas chromatograph. This arrangement provided real time monitoring of the inlet and outlet VOC concentrations during painting operations.

The larger (5 SCFM) solar-based system shown in Figure 2 was constructed by the Industrial Solar Technology Corporation of Golden, CO. This system consists of a parabolic trough reflector to focus incident sunlight onto a receiver tube containing the catalyst. The trough has a 91 cm (36") aperture width and is 243 cm (96") long. The reflective surface is covered with SA-85 (3M Company), a polymer film that reflects greater than 90% of the incident radiation onto the catalyst tube, providing both heat and light for reaction. The catalyst-containing receiver tube is a 3.81 cm (1.5") I.D. borosilicate tube packed with 1.9 cm (0.75") ceramic berl saddles coated with 2.0 wt% platinum on $TiO_2$ (P25, Degussa Corp.). Operating temperatures of 200°C were obtained, depending on cloud cover, during most of the day. Note that a thermally heated, lamp-illuminated system will provide the same performance as the solar-based system described here. The reflective trough rotates around the fixed receiver tubes by means of a gear motor. A control and photodiode arrangement activate the gear motor, permitting the trough to track the sun throughout the day. Paint booth emissions were sampled directly from the exhaust stream via 4 inch aluminum ducting. On-line analysis of the inlet and outlet concentrations was provided by sample lines connected to the MTI gas samplers.

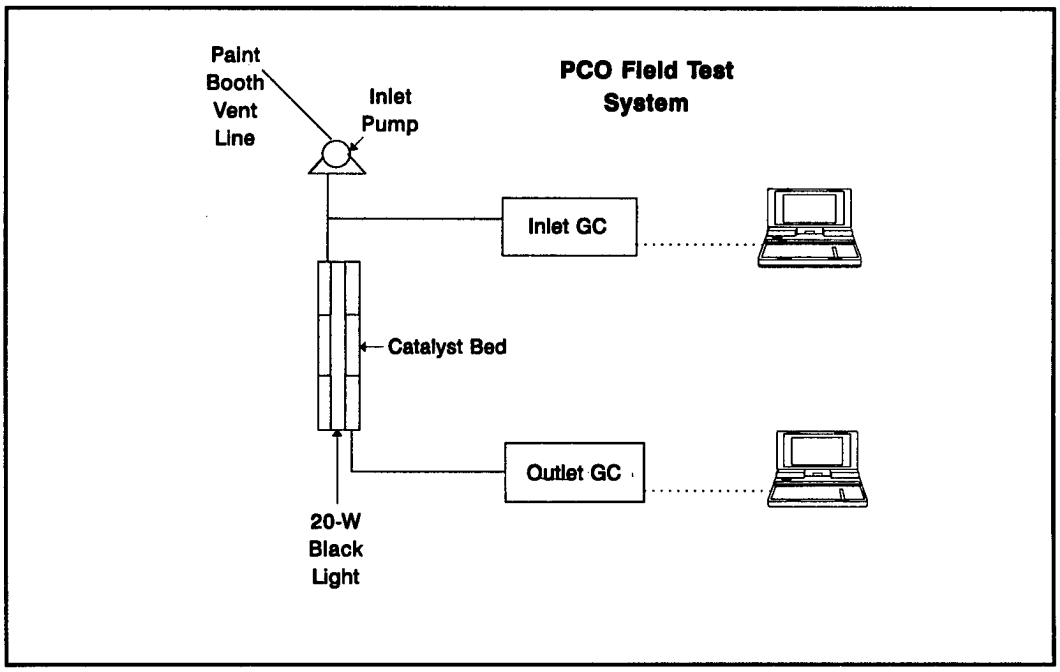



FIGURE 1: PCO FIELD TEST SYSTEM

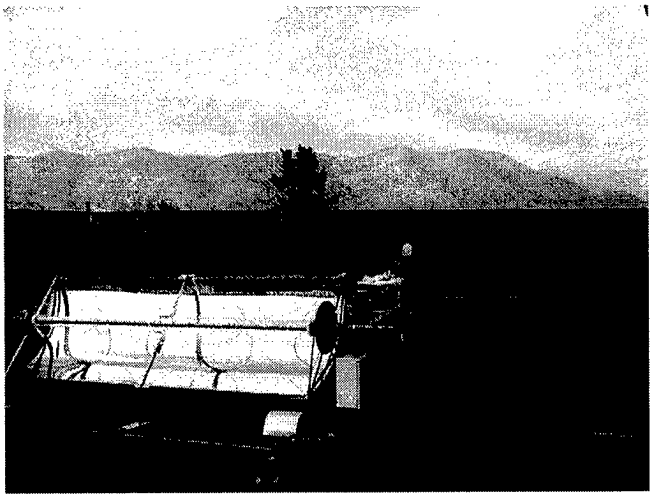


FIGURE 2: 5 SCFM SOLAR PHOTOTHERMAL REACTOR

## 1.3 FIELD TEST RESULTS AND DISCUSSION

Figure 3 shows the real time test results for VOC emissions from painting operations at Fort Carson. The inlet and outlet VOC concentrations are given in ppm. Test data begins at 8:10 AM on June 25, 1996 and ended at 11:55 for this run. The painting operations are conducted in a batch mode. Vehicles are placed in the paint booth, painted, then removed from the booth to the parking area, where they dry. The mixture of VOCs emitted from the aliphatic polyurethane green military paint being sprayed consisted of methyl ethyl ketone, methyl isobutyl ketone, toluene, n-butyl acetate, xylenes, and ethyl benzene.

When the reactor reached an operating temperature of 170 °C, complete VOC destruction was achieved for the entire run except for a period of peak VOC emissions beginning at 9:30 and ending at 9:45. Thus, during this four hour period, the PCO process destroyed virtually all of the VOCs in the slip stream from the paint booth exhaust. The total time averaged conversion is estimated to be greater than 95%.

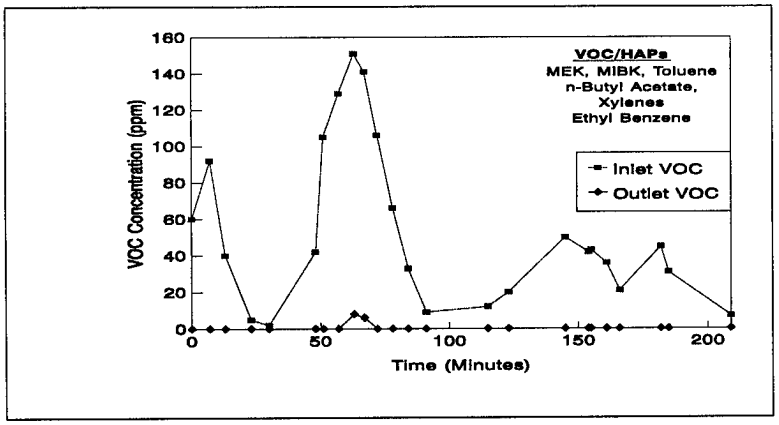



FIGURE 3: INLET AND OUTLET VOC CONCENTRATIONS FROM THE FORT CARSON PAINT BOOTH

Data from the Air Force Academy paint booth facility was gathered on June 27, 1996 with the same field test system. The Academy paint booth is approximately half the size of the Fort Carson facility and the paints used are a combination of military specification and commercial paints. Thus, we were able to treat different streams with lower concentrations of VOCs than those tested at Fort Carson. Figure 4 shows both inlet and outlet VOC concentrations as a function of real time. The inlet concentrations were much lower from this paint booth, which was spraying a white military specification paint. The primary VOCs were toluene, n-butyl acetate, and ethyl benzene. The flow rate remained the same at 20 liters/minute and the reactor operating temperature was 150°C at the inlet. Complete VOC destruction was achieved at all VOC concentrations. Note that the VOC scale for the Fort Carson emissions was approximately 30 times that of the Academy emissions.

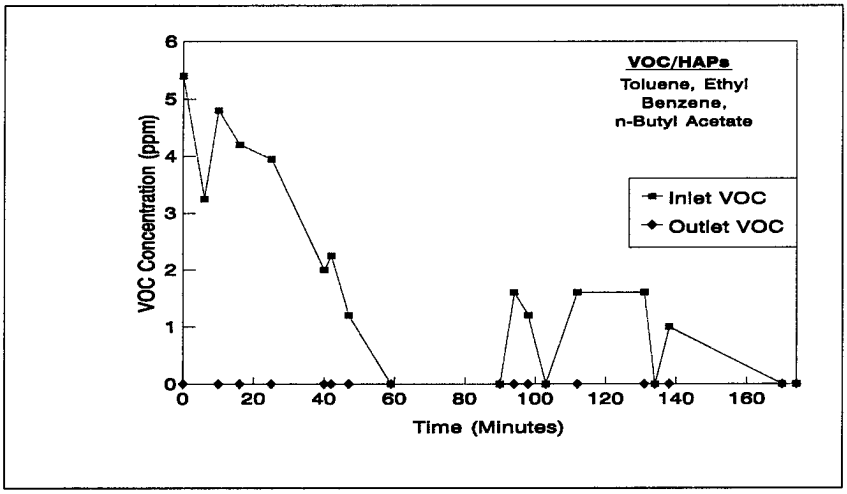



FIGURE 4: INLET AND OUTLET VOC EMISSIONS FROM THE ACADEMY PAINT BOOTH

Because the lamp-based tests were successful, our next step was to test a larger photoreactor system that used ambient sunlight to provide heat and light for reaction. The trough system described above was recently tested at NREL with the test compound methyl ethyl ketone, a paint solvent surrogate. Figure 5 shows the results of on-sun testing with this system. The Y-axis plots three factors: temperature in °C x100, conversion as a fraction with 1 equalling 100% conversion, and solar insolation as $mW/cm^2$. The X-axis plots illumination time in minutes. This test was performed on a hazy day with numerous clouds to evaluate the system under challenging conditions. Though conversion and reactor temperature parallel the insolation, they do so in a less than 1:1 ratio. This is likely due to the square root dependence of reaction rate on light intensity and to the heat transfer (insulative) characteristics of the ceramic support. 100% conversion was achieved when insolation levels were above 3.5 $mW/cm^2$ and reactor temperatures above 175°C. This system is planned for testing at the Fort Carson paint booths in FY1997.

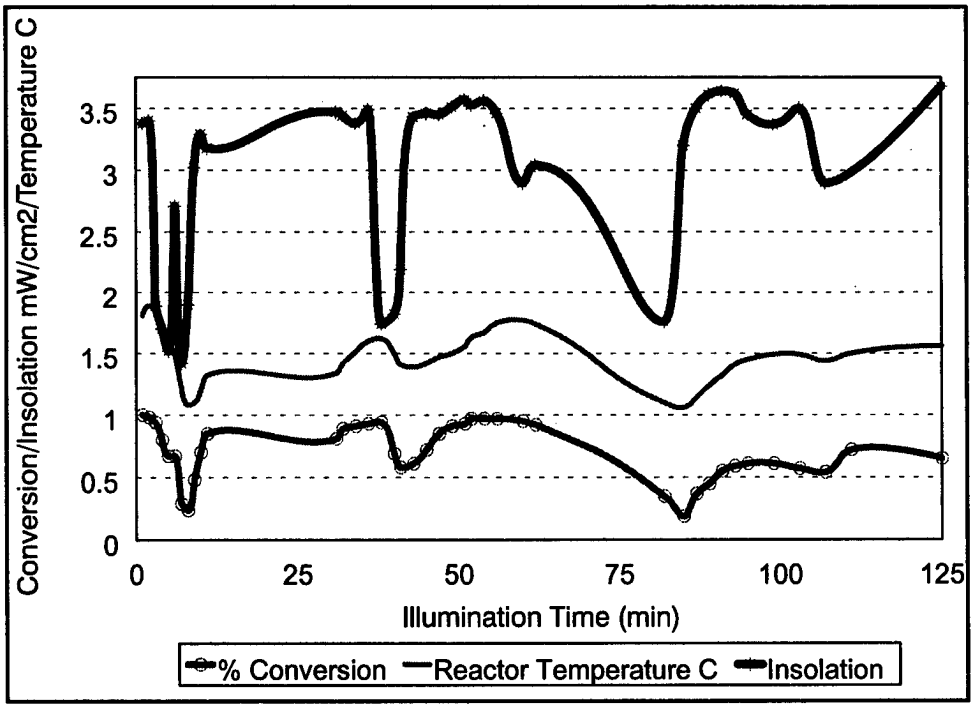



FIGURE 5: SOLAR PHOTOTHERMAL OUTDOOR TESTS WITH METHYL ETHYL KETONE

## CONCLUSIONS

In summary, preliminary field test results show the feasibility of using photocatalytic oxidation to efficiently treat hazardous VOC emissions from military paint booth operations. The PCO process works with both lamp and solar driven systems and under a variety of operating conditions that include fluctuating feeds, light levels, and reactor temperatures. We are currently working on testing the solar-driven system at the Fort Carson paint booths.

## ACKNOWLEDGEMENTS

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# DESTRUCTION OF HAZARDOUS MILITARY WASTES USING PLASMA ARC TECHNOLOGY

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## ABSTRACT

A Plasma Arc Technology (PAT) system treats hazardous wastes in a furnace, at temperatures of 2000° C, or higher, using a plasma torch. The organic components vaporize, decompose or oxidize. The off-gases consist of hydrogen, carbon monoxide, carbon dioxide and nitric oxides. A wet air scrubber is used to remove most of these gases. The scrubber water is treated and recycled. Metal-bearing solids are melted or vaporized. The solids are usually recovered as molten metal, or as non-leachable vitrified slag, suitable for disposal in a landfill.

A Plasma Arc Centrifugal Treatment system was used to evaluate this technology for destruction of the nine military hazardous wastes listed below:

1. Sludge from Longhorn Army Ammunition Plant, TX;
2. Agriculture Blast Media from Letterkenny Army Depot;
3. Glass and Plastic Glass Media from Letterkenny Army Depot;
4. Medical incineration ash from Aberdeen Proving Ground, MD; and
5. Contaminated soil from open burning/open detonation ground at Picatinny Arsenal, NJ.
6. Waste paint from a U.S. Navy facility;
7. Garnet blast media from a U.S. Air Force Base;
8. Simulated oil-contaminated sorbent, used by Tri-Services and private industry; and
9. Mendocino soil spiked with Dichlorobenzene, a surrogate for PCB.

The evaluation, Phases 1 and 2 of a two-phase program, included determining the process capability of PAT for the ultimate destruction of hazardous components; verifying the suitability of the resulting slag for regular landfill disposal; identifying potential hazards associated with the process emissions; and developing qualified cost estimates for the future utilization of the process on large scale operations.

Process variables such as feed rate, composition of off-gases, run duration, percentage of oxygen used in the secondary chamber, and chamber temperature were controlled. Material balance, destruction and removal efficiency (DRE), air emission quality, wastewater quality, and suitability of slag for landfill were determined. The results from these test runs and analyses are presented in this paper.

The ultimate success of PAT for destroying hazardous wastes depends on achieving a slag that is non-leachable and meets Resource Conservation and Recovery Act (RCRA) requirements, and off-gases and scrubber water that meet Clean Air and Clean Water Act standards.

Results of Phases 1 and 2 show that all slags passed Toxicity Characteristics Leaching Procedure (TCLP) tests, for land disposal requirements; air quality meets California standards, and scrubber water can be treated and recycled.

## I. INTRODUCTION

The National Defense Center for Environmental Excellence (NDCEE), operated by Concurrent Technologies Corporation (*CTC*), was tasked to evaluate the applicability of plasma arc technology (PAT) to treat complex military wastes. The U.S. Army Environmental Center (AEC), sponsor of this task, established a statement of work (SOW) containing two phases to accomplish the evaluation:

Phase I -- Identification and selection of candidate waste materials, identification and selection of a suitable plasma waste treatment system, and conduct of testing.

Phase II -- Identification and selection of additional candidate waste materials, conduct of testing, documentation of results, preparation of a procurement/design/fabrication guidance manual, and production of a video presentation.

## II. BACKGROUND

This paper reports the results of Phases I and II pilot-scale testing of candidate waste materials using PAT. PAT can be used to convert complex hydrocarbon molecules into common, simple molecules. PAT processing temperatures of 3632°F (2,000 °C) and higher lead to breakdown of the organic components of the waste into smaller molecules, while the non-volatile inorganic components are vitrified in the resulting slag. Plasma arc furnaces are currently used commercially for industrial and manufacturing applications, including iron ore reduction, titanium scrap melting, platinum and aluminum metal recovery, and steel ladle or tundish heating. During the past two decades, plasma arc technology has emerged as a very effective method of converting hazardous waste materials into recyclable, non-hazardous by-products. Plasma arc furnaces have the potential to stabilize weak foundation soils in-situ, produce energy, and destroy or immobilize waste materials in a cost-effective and environmentally safe manner.

Through a competitive bidding process, *CTC* subcontracted the pilot-scale testing to Retech, Inc. of Ukiah, CA. Retech proposed a Plasma Arc Centrifugal Treatment (PACT) system for this task. Retech designated their system the PACT-2, where 2 designates a furnace that is two feet in diameter. At the heart of the PACT-2 system is the RP-75T Plasma Torch, which is capable of a sustained output of 160 kilowatts (kW). This torch operates in the transferred arc mode, in which the rear electrode is the positive attachment point and the negative attachment point is the workpiece or molten material.

## III. RESULTS

The PAT testing program was divided into Phase I (tests 1-18) and Phase II (tests 19-31). Test #19 was a repeat of test #1 for Medical Ash because of operational problems with the latter. Actual number of valid tests performed per the SOW was 30. Phase I was divided into Phase IA (tests 1-6) and Phase IB (tests 7-18). Equipment modifications were completed after test 6 and after test 18. Nine different waste materials, listed in Table 1, were treated during Phase I and II testing. Feedstock materials were selected, based on existing waste disposal requirements at military installations. The selection criteria include: their hazardous waste status; the lack of satisfactory treatment and disposal procedures; the presence of energetics or heavy metals; potential cost benefit to treating the waste with a PAT; and the existing inventory of a particular waste. A total of 5203.52 lb. of waste was treated in the PACT-2 during Phases I and II. The results are summarized in Table 2 and 3.

**Table 1. Treated Waste Materials**

| Test Series | Waste Type | Source |
|---|---|---|
| Phase I | Longhorn Sludge (LS) | Longhorn Army Ammunition Plant, TX |
| | Open Burning Ground Soil (OBG) | Picatinny Arsenal, NJ |
| | Agricultural Blast Media (ABM) | Letterkenny Army Depot, PA |
| | Plastic and Glass Blast Media (PGBM) | Letterkenny Army Depot, PA |
| Phase I and II | Medical Incinerator Ash (MIA) | Aberdeen Proving Ground, MA |
| Phase II | Garnet Blast Media (GBM) | McClellan Air Force Base, CA |
| | Surrogate Absorbent Material (SAM) | Retech, CA |
| | Waste Paint (WP) | Norfolk Naval Base, VA |
| | Dichlorobenzene spiked Mendocino Soil (MS/DCB) | Mendocino County, CA |

**Table 2. Summary of Phase I PAT Testing Results**

| Retech Test No. | Waste Type | DRE | TCLP | CO | Amount Processed, lb | Rate, lb/hr | Scrubber Water[2] | Air Particulate Emissions, g/hr |
|---|---|---|---|---|---|---|---|---|
| 1R | MIA | 99.9999 | Pass | Pass | 162.5 | 31.0 | T.A. | Fail (8.46) |
| 2 | MIA | 99.9999 | Pass | Pass | 49.3 | 13.0 | T.A. | Fail (26.08) |
| 3 | MIA | N/A | Pass | Fail | 48.6 | 13.0 | T.A. | Fail (4.31) |
| 4 | MIA | 99.9999 | Pass | Pass | 48.6 | 16.0 | T.A. | Fail (21.59) |
| 5 | LS | N/A | Pass | Pass | 58.8 | 34.0 | T.A. | Fail (31.52) |
| 6 | LS | 99.9999 | Pass | Pass | 96.5 | 25.0 | T.A. | Fail (28.17) |
| 7 | OBG | N/A | Pass | Pass | 152.4 | 83.0 | T.A. | Pass (0.09) |
| 8R | OBG | 99.9999 | Pass | Pass | 105.8 | 90.0 | T.A. | Fail (6.94) |
| 9 | OBG | N/A | Pass | Pass | 303.98 | 134.0 | T.A. | Pass (0.01) |
| 10 | OBG | 99.9999 | Pass | Pass | 318.63 | 113.0 | T.A. | Pass (0.09) |
| 11 | LS | N/A | Pass | Pass | 244.07 | 82.0 | T.A. | Pass(0.11) |
| 12 | LS | 99.9999 | Pass | Pass | 177.19 | 59.0 | T.A. | Fail (0.17) |
| 13 | ABM | N/A | Pass | Fail | 138.8 | 36.0 | N.D. | Pass (0.09) |
| 14 | ABM | N/A | Pass | Fail | 166.36 | 32.0 | N.D. | Fail (0.92) |
| 15 | PGBM | N/A | Pass | Fail | 47.5 | 28.0 | N.D. | Fail (0.32) |
| 15R | PGBM | N/A | Pass | Fail | 101.0 | 34.0 | N.D. | N/A |
| 16 | PGBM | N/A | Pass | Fail | 108.02 | 30.0 | N.D. | Fail (0.14) |
| 17 | PGBM | N/A | Pass | Fail | 122.47 | 40.0 | T.A. | Fail (5.22) |
| 18 | PGBM | N/A | Pass | Pass | 137.4 | 36.0 | T.A. | Fail (4.90) |

**Table 3. Summary of Phase II PAT Testing**

| Retech Test No. | Waste type | DRE | TCLP | NO CO HCl | Amount Processed, lb | Rate, lb/hr | Scrubber Water[2] | Air Particulate Emissions, g/hr |
|---|---|---|---|---|---|---|---|---|
| 19 | MIA | 99.9999 | Pass | Pass | 598 | 124.6 | N.D. | Pass (0.47) |
| 20,21,22 | SAM | 99.9999 | Pass | Pass | 240 | 32.7 | N.D. | Pass (0.154) |
| 23,24,25 | GBM | N/A | Pass | Pass | 772 | 85.3 | N.D. | Pass (0.032) |
| 26,27,28 | MS/DCB | 99.991 | Pass | Pass | 654 | 68.3 | N.D. | Pass (0.067) |
| 29,30,31 | WP | 99.9999 | Pass | Pass | 351.6 | 34.9 | N.D. | Fail (0.334) |

[1]Dry weight [2] Scrubber water is hazardous waste and should be treated and recycled
N.D.= Non-Detection of SVOCs (tested for)
DRE = Destruction and Removal Efficiency, CO = Carbon monoxide, TCLP = Toxicity Characterization Leaching Procedure
T.A. = Trace Amounts of either SVOCs or VOCs (tested for).
SVOC = Semi-volatile organic compounds VOC = Volatile organic compounds

Because of the potentially large variation in the chemistry of materials processed in PAT systems, feedstock material was thoroughly analyzed prior to processing. This analysis yields important information regarding composition, which in turn influences process parameters (i.e. oxygen, gas flow values, potential metals emissions, etc.). Pre-qualification testing was performed to test and adjust system parameters prior to long term processing. Stack emissions were monitored closely, when increasing feed rates, to avoid overloading the off gas cleaning train.

One of the major objectives of any PAT system is to process hazardous wastes in a manner that allows the PAT solid effluent to be taken to a non-hazardous landfill. Based on the parameters measured for waste slag from a PAT system, the slag could be used for road bed materials, aggregate for hot and cold mix asphalt, blast media, abrasives, or filter media. In order to reduce the overall waste from the PAT System, the wet scrubber solution in Phase II was not changed after every test, only the solid sludge was removed. This solid sludge can be taken to a non-hazardous landfill.

## IV. LESSONS LEARNED AND RECOMMENDED EQUIPMENT MODIFICATIONS

### Equipment Changes Implemented after Phase I Testing

#### Throat Design:

The PC throat was fabricated from a high alumina castable, Novacon 95®, which replaced the silicon carbide and Ruby plastic used previously. This material produced a 10-fold improvement in throat life, thereby decreasing overall refractory maintenance.

#### Geometry:

Throat geometry was changed from a cylindrical to a parabolic cross-section. This geometry change aided in reducing throat closure during treatment as well as the quantity of unprocessed material falling through the throat.

#### Tub Materials:

The tub bottom refractory was changed from a graphite ring to Nuline *RS20*® (magnesia) conductive refractory brick. This change facilitated hot and cold torch starting and produced a better conductive path for both heat and electricity at the plasma-slag interface.

#### Auxiliary Torch Starter (ATS):

The auxiliary torch starter (ATS) is a slag heater used in the PACT-2 unit to transfer the primary torch when the slag skull is not molten. This system was used because chipping the tub bottom damaged the tub refractory, and direct transfer of the arc to the tub bottom severely eroded the refractory near the throat. In operation, the primary torch transfers to the ATS, effectively heating the relatively constant slag layer using the evolved hot gases. The plasma arc transfers once the slag layer reaches approximately 3,000 °F (1649°C). After plasma arc transfer occurs, the ATS is removed vertically from the tub by a hydraulic manipulator. A typical slag skull preheat cycle was about thirty minutes.

#### Tub Drive Upgrades:

The tub hydraulic drive was upgraded to produce higher torque during normal tub rotation. This upgrade reduced tub seizure due to refractory melt from the spool section, or from feed material depositing in the gap between the spool and tub.

The mold extractor interconnect arm was re-designed to ensure a constant grip around the mold. This redesign also reduced fatigue failure induced by cyclic heat and mechanical stresses.

Mold alignment software was debugged so that the mold consistently lined up with the mold extractor.

An Aerojet designed, platelet-cooled electrode replaced the standard Retech electrode to increase normal operating life by using diffusion-bonded, directionally-cooled surfaces and argon surface-arc diffusion at the arc termination-electrode interface.

The SCC baffle was removed to enhance combustion efficiency and to reduce the amount of refractory maintenance required during Phase I. The inlet and outlet of the SCC were changed to increase the off-gas residence time.

A feed rate calibration system was installed to properly determine the weight of material at a given feed rate, as determined by the requirements of an individual test.

Feeder can flight geometry was modified to produce a more constant feed to the primary chamber. The new flight geometry eliminated "spiked" cyclic feed behavior, and permitted better control of the combustion process.

A liquid lance with pumping unit was designed to feed waste paint and other liquids.

The off-gas filtering system was modified to provide two filtering stages. The first stage was a sintered, commercially pure (CP) titanium (Ti) metal filter placed at the exhaust of the wet scrubber. The filter had a nominal pore size of 10 micrometers, and acted as a coarse prefilter for the second stage. It was expected that the majority of the particulates would be kept in the scrubber water. The second stage was a 0.1 micrometer, sintered CP Ti filter located downstream from the 10 micron filter. The sintered metal filters were intended to be more resistant to moisture in the gas stream. These filters also can be cleaned and reused, thereby eliminating the disposal of a HEPA filter secondary waste stream.

Wet scrubber liquor was sampled after every test but was not changed. The liquor was pumped into a circulating holding tank, from which representative samples were taken. The liquor remained in the tank (not circulating) overnight to allow for settling of the particulate material. The supernatant liquor was then pumped back into the scrubber. The sludge was placed in sludge bins to be reintroduced into the system at a later date.

NOx and THC measurements were conducted before and after the wet scrubber (off-gas treatment system) in order to determine NOx and THC removal efficiencies.

Method and Procedural Modifications After Phase I Testing

The technique of adding hexachlorobenzene (HCB) seemed to work well as the principal, organic, hazardous constituent (POHC). Being a SVOC, it makes transportation to the laboratory for analysis much less critical than when using xylene. The spiked feed also can be stored without evaporation of the HCB. The HCB is easy to handle while weighing, because it is a granular solid.

The metal spikes did not work well for the fine, fluffy type wastes treated (such as MIA and ABM) because the metal spikes themselves were powders. The powders tended to be blown around in the system. Under ideal conditions, the metal spikes should coat the waste particles uniformly. This would better mimic the behavior of the actual waste and eliminate scatter in the elemental analyses of the feed.

A reliable and accurate analytical method for total metals is required for glassy silicate slags, because EPA Method 6010 is not adequate. Slag chemistry analyses show that analyses using EPA 6010 consistently report lower values than those concentrations actually present. The glassy slags require a digestion. The boiling nitric acid digestion called for in Method 6010 is not suitable.

The sampling procedures for heterogeneous wastes need to be re-evaluated in order to compensate for potential sampling inaccuracies. There is so much scatter inherently generated by the present techniques that a reliable, representative analysis cannot be obtained.

Chemical analyses on the as-received wastes are needed. Representative analyses should be requested from the waste suppliers, but analyses of the as-received wastes are essential in order to eliminate confusion caused by different parties performing different analyses at different laboratories. An accurate assessment of the waste to be treated is required before testing begins.

The standard metals, organics, and semi-volatile organic compounds analyses performed do not provide sufficient information from an operational standpoint. A moisture analysis and a method that determines the total organics available (such as loss on ignition or total organic content) are critical for controlling the treatment process.

Any future testing, which involves a chloride containing waste or a chloride spike, should allow for a chloride mass balance.

A better method to determine organic content of the waste, including free carbon, needs to be identified and used.

Two important process parameters are oxygen and carbon monoxide content in the PC off-gas pipe. These parameters are critical in assuring the correct combustion atmosphere (reducing or oxidizing). Gas sampling in this area is difficult because of the high temperature, the acid gases present, and the amount of particulates present. A sampling technique needs to be developed to solve this problem.

Equipment Modifications During Phase II Testing

The only design change implemented during Phase II testing was to increase the surface area of the CP Ti filters in the off-gas filtering system. It was doubled prior to test 22 (2.3 $ft^2$ to 4.6 $ft^2$) to increase run time when processing materials that generate large amount of particulate material.

## V. CONCLUSIONS

The PAT system tested successfully treated the wide variety of complex military wastes selected by the Army/*CTC* team. Nearly all tests met or exceeded the design feed rate recommended by the equipment supplier. Lower feed rates were used for the organic wastes because of their high volatile content, and higher feed rates were used for the inorganic wastes because of their low volatile content. For all wastes treated, the Destruction and Removal Efficiencies (DREs) were in excess of the Environmental Protection Agency (EPA) requirement 99.99%.

All slag materials formed passed Toxicity Characteristics Leaching Procedure (TCLP) testing, which demonstrates that PAT can be used to produce a product with commercial value, or one which can be landfilled. Gas emissions for nitrous oxide, carbon monoxide, (except for test 13-17) hydrochloric acid, or metals were below permit levels. Particulate emissions were below permit level for all wastes tested, with the exception of the paint waste, for which there were problems with soot build-up. Scrubber water, containing metals, particulates, and dissolved solids can be treated, for example, by processes such as reverse osmosis, to remove these impurities. The water then can be recycled.

## VI. RECOMMENDATIONS

- A portable PACT-5 or fixed PACT-8 system is recommended for future applications.
- The system should be installed at a regional location to treat wastes from surrounding bases which have sufficient materials for treatment and disposal.
- The system should be located in those states where permits are easily obtainable.
- For efficiency of the operation, the system should be run on a 24-hour basis, seven days per week.
- More pilot scale studies should be performed to evaluate the applicability of a PAT system to other hazardous wastes, e.g. chemical weapons.

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# Surfactant-Enhanced Aquifer Remediation for DNAPL Removal

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At least 2,000 DoD sites are contaminated with chlorinated solvents. When these compounds become trapped in soil pores due to the action of capillary and sorptive forces and remain as a separate organic phase, they are called dense non-aqueous phase liquids (DNAPLs) or residual DNAPL, because they are more dense than water and can not be removed as a free-phase product. Residual DNAPLs are most commonly found at the original source of the spill, leak, or disposal, which led to the contamination problems in the first place. As opposed to other organic contaminants which have similar densities to or are less dense than water, chlorinated solvents tend to sink until a confining layer (e.g. a clay aquitard) is reached, thus they are prevalent in the groundwater. At the same time, chlorinated solvents typically have low water solubilities and are not rapidly biodegraded. As a result, chlorinated solvents which become trapped as DNAPL will act as a long term contamination source for aquifers. Since many of these solvents are suspect carcinogens, these contaminated groundwaters pose a significant human health risk. Thus the removal of DNAPL is necessary in order to achieve rapid and cost-effective remediation of these groundwater sites.

The standard method of remediating or controlling groundwater contaminated with chlorinated solvents is the pump and treat technology. However, this technology is inherently a solution for a dissolved-phase problem. Because of the mass transfer limitations posed by DNAPL, i.e. slow rates of dissolution and biodegradation, pump and treat becomes very ineffective in meeting cleanup goals when DNAPL is present. While there are a variety of solutions for DNAPL removal in the vadose zone, there are no proven technologies for the saturated zone. Therefore, there has been considerable attention and effort placed on the investigation of methods to supplement the conventional pump and treat technology through the use of chemical additives such as surfactants and co-solvents. In surfactant-enhanced aquifer remediation (SEAR), a surfactant solution is used to flush the DNAPL contaminated zone. Approximately two to five pore volumes of a surfactant solution are used in the flushing process; this is followed by water flushing to remove any remaining surfactant and DNAPL. Surfactants accomplish the removal of DNAPL by increasing its aqueous solubility and by reducing the interfacial tension between the DNAPL and water phases.

At least five successful field trials of surfactant-enhanced aquifer remediation have been completed in the past year (1996). The demonstrations have shown effective performance of a surfactant system under field conditions for removal of DNAPLs and NAPLs. Recent cost analyses have shown that in a full-scale SEAR remediation, the cost of the surfactant is a significant portion of the overall cost of implementing the technology. There has been some investigation into surfactant recovery processes,

# FOLLOW-ON REACTIVITY STUDY
# of
# PRIMARY EXPLOSIVES in SOIL

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## ABSTRACT

An initial study, Phase I, of reactivity of soil and primary explosives performed in 1994 followed the methods used to characterize mixtures of soil and secondary explosives in a 1987 report. (USATHAMA AMXTH-TE-CR86096, 1987, Testing to Determine Relationship between Explosive Contaminated Sludge Components and Reactivity) [1]. The secondary explosive test methods proved inadequate to characterize primary explosives due largely to the reduced energy output of primary vs secondary explosive loads. This current project, Phase II, performed for the U.S. Army Environmental Center (USAEC), modified the standard tests to include reduced confinement, a modified witness system, modified initiator/booster sources, sensitive blast-pressure instrumentation and video observation of the tests. This was done by evaluating potential test methods, developing compaction techniques and preparing and testing mixtures of lead azide/soil and nitroglycerine (NG) /soil mixed at various soil and water concentrations and compaction levels. This work supports remediation efforts by government and industry contractors to safely sample, evaluate, and clean up sites contaminated with primary explosives or NG based compounds from manufacturing, demilitarization or unexploded ordnance. The reactivity level was used in the hazard analysis of generic field operations (sampling, excavation, handling, and remediation) to generate Safe Field Handling Criteria.

The test results for lead azide indicated that soil compaction was not a significant factor for reactivity in the baseline soil. The Threshold Initiation Level (TIL) for the shock test occurred at an explosive concentration of 2% lead azide at dry conditions. The TIL for the flame test occurred at an explosive concentration of 4% lead azide at dry conditions. The results showed that for moisture levels below 15% the reactivity was reduced. Moisture levels above 15% appeared to increase reactivity.

The results of probit testing with mixtures of NG and soil yielded a TIL for the Deflagration-to-Detonation Transition (DDT) test at an explosive concentration of 12% NG at dry conditions. The TIL for the U.S. Gap test occurred at an explosive concentration of 13% NG at dry conditions. Tests at 15% moisture saturated the NG soaked soil and corrupted the results. Tests were not performed.

Generic safe handling criteria were established for field operations related to sampling, excavating, handling and remediation operations. It is cautioned that these criteria be used as a guide and that hazard analysis for specific equipment or operations be performed prior to any activity with primary explosives.

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Distribution authorized to U.S. Government agencies only; premature dissemination; March 1997. Other requests for this document shall be referred to U.S. Army Environmental Center, SFIM-AEC-TSD, Aberdeen Proving Grounds, MD 21010-5401, Mr. William Houser, 410-612-6869.

## INTRODUCTION

TRW, under contract No. MDA970-89-C-0019 to the Defense Evaluation Support Activity (DESA) for the U.S. Army Environmental Center (USAEC), in cooperation with the Department of Defense Explosives Safety Board (DDESB) and the Department of Transportation (DOT), conducted a follow-on to work previously completed and reported to USAEC in May 1994 by GES and Roy F. Weston, Inc.[2] Alliant Techsystems, Global Environmental Solutions (GES) was selected as the sub-contractor to perform the work. The objectives of this program were to (1) characterize the flame and shock reactivity of soils contaminated with primary explosives including lead azide and lead styphnate, (2) perform probit testing with nitroglycerine (NG) contaminated soil, and (3) develop guidelines for safe handling criteria, similar to those already established for secondary explosives. The work was authorized by Task Order No. 04-25/00 and was performed at Allegany Ballistics Laboratory (ABL). This paper discusses the results of several of the major tasks performed under this study. The complete work is available from USAEC, William Houser, 410-612-6869.

### PRIMARY EXPLOSIVES

The focus of this program was to develop and conduct small-scale flame and shock reactivity tests with lead azide over a range of soil types, compaction levels, explosive concentrations, and moisture levels. Data from this program will support decisions regarding the safety of cleanup activities at sites contaminated with primary explosives.

### NITROGLYCERINE (NG)

Probit testing with NG and soil was performed as a continuation of the previous study on primary explosives.[2] Deflagration-to-Detonation Transition (DDT) and U.S. Gap tests were performed with NG concentrations between 10% and 18%.

### SAFE HANDLING CRITERIA

Safe handling criteria were developed for generic field operations for soils contaminated with primary explosives. A hazards analysis was conducted for sampling, excavating, handling, and remediation operations. Sensitivity lab data were generated for initiation of mixtures of lead azide and soil from impact, friction, and electrostatic discharge (ESD). These data were used as the basis for developing design and operating criteria to establish an acceptable level of risk for generic field operations. Since the analysis was conducted for generic operations, hazard analysis for specific field operations is recommended prior to conducting any remediation efforts.

## RESULTS AND DISCUSSION

### PRIMARY EXPLOSIVES

The first task was to review existing explosives reactivity tests including No. 8 Cap, Bonfire, U.S. Gap, and Deflagration-to-Detonation Transition (DDT). When these tests were applied to primary explosives such as lead azide, several shortcomings became apparent; these were attributed to insensitive witness systems, excessive (overly rigorous) reaction criteria, and the effects of variation in bulk density, confinement, and moisture content of the sample materials.

From the literature, 11 types of shock initiation tests and 17 flame tests were identified, described, and evaluated on the basis of the above criteria. The study concluded by defining, in concept, a new shock initiation test and a new flame initiation test. For both tests, the proposed response observation system would include a steel plate supported by force or pressure gauges, a video system, and sensitive overpressure (microphone) gauges.

The study recommended that alternative tests should meet the following criteria:

- Sufficient material under test to represent a homogeneous mixture of contaminated soil
- Amount of material under test minimized for safety
- Large ignitors not required for initiation
- Compaction and confinement of sample representative of field material
- Differentiation between effects of ignitor and sample initiation
- Observability of reaction indicators preceding detonation

The second task embodied the development and "fine-tuning" of the basic concepts for new small-scale shock and flame initiation tests. Development of the tests began with a 1-inch (2.54 cm) diameter pipe capped at one end. This pipe size was selected to reduce the quantity of explosives in the preliminary tests. A series of trials was conducted to determine the optimal material of construction (steel or PVC), pipe schedule, and length of the container, as well as the size (energy level) and type of the initiator.

The ignition source for the flame and shock tests was chosen based on system response. The reaction criteria were chosen so that the ignition source in an inert sample produced a measurable and repeatable response and did not totally destroy the test container. For the shock test, a no. 8 blasting cap and a J-2 cap were compared using a 2-inch (5.04 cm) thick Lucite cylinder as a witness system. The damage to the Lucite cylinder was slightly less for the no. 8 cap, but it was evident from the spalling and fracture patterns that the shock did propagate through the entire cylinder. The no. 8 cap was chosen in preference to the J-2 cap because of significantly lower cost per cap and because the no. 8 cap is commercially available, while the J-2 is a military (mil-spec) cap.

The flame test was ignited with a bag ignitor, consisting of an Atlas match as the ignition source for a small bag of powder or pyrotechnic compound. Several materials were compared for use in the bag ignitor including black powder, boron potassium nitrate ($BKNO_3$), thermite (powdered aluminum and iron oxide mixture), plus various small arms propellants. The quantity of each material was varied in order to obtain the desired results. $BKNO_3$ was chosen for the flame test ignitor because of a strong measureable and repeatable response and no container damage. The results of the 0.035 ounce (1 gm ) ignitor study are given in Table 1.

**TABLE 1**
**IGNITOR STUDY - 1 Gm AVERAGE**

| | Black Powder | $BKNO_3$ | Unique | Bullseye | Reloader 12 |
|---|---|---|---|---|---|
| Impulse lb/sec | 0.04 | 0.51 | 1.30 | 0.90 | 0.90 |
| (kg/sec) | 0.018 | 0.231 | 0.590 | 0.408 | 0.408 |
| MIC1 psi.sec | 0 | 0 | 0.05 | 0.04 | 0 |
| (Kpa/sec) | | | 0.345 | 0.276 | |
| MIC2 psi/sec | 0 | 0 | 0.03 | 0.02 | 0 |
| (Kpa/sec) | | | 0.207 | 0.138 | |
| Damage | ND | ND (5) | CB (1)<br>ND (2) | S (1)<br>ND (2) | ND (3) |
| S = Shot (container broken into shards); CB = Cap Broken (container split); ND = No Damage. | | | | | |

Tests were conducted using both compacted and uncompacted samples of soil containing lead azide. The density and uniformity of sample compaction was verified using compactions of inert simulant (lead citrate). For uncompacted soil the sample container (pipe and pipe cap) were lightly tapped to settle the sample during filling. Nominal density of the uncompacted samples was 111.12 lbs/ft3 (1.78 g / cm3). The average density of compacted samples was 132.97 lbs/ft3 (2.13 g/cm3) for the flame test and 140.46 lbs/ft3 (2.25 g/cm3) for the shock test.

Lead azide concentration was tested at 5% and 15%, based on the range observed in Phase I. The test setup for the compaction study is depicted in Figure 1. The manually operated air-over-hydraulic ram compressed the test sample with 300 pounds (136 kg) force for a period of one minute. The ram transferred the load to the sample through a 1 inch diameter dowel rod. The dowel rod was substituted for the wooden block for the compaction study. After compaction, a reduced ram load of 80 pounds (36 kg) was applied to the wooden dowel to maintain system confinement.

The graphs of peak load for flame and shock, comparing uncompacted and compacted results for 5% and 15% lead azide, are included as Figures 2 and 3, respectively. The data showed that compaction did not significantly affect the reactivity. Therefore, the uncompacted configuration was used for the probit study. The microphone data did not provide useful results, and their use was discontinued for future tests.

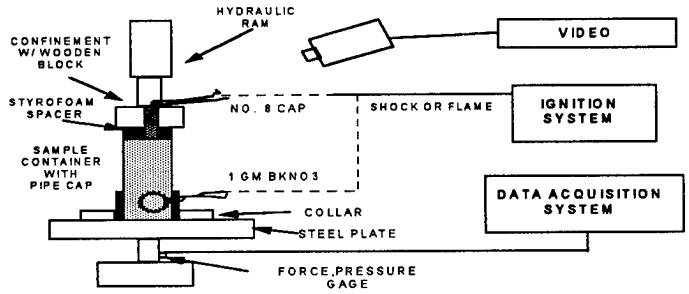



**Figure 1 - Flame and Shock Test Configuration**

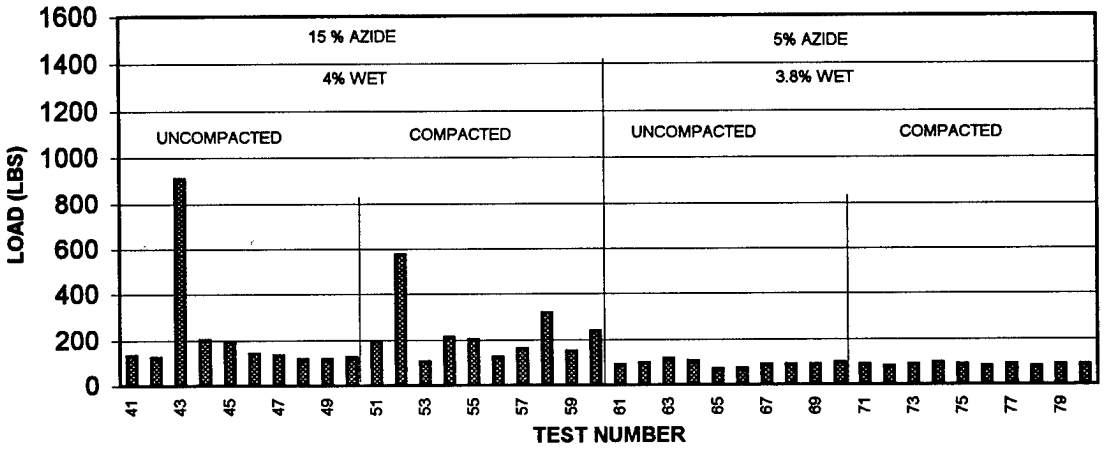



**Figure 2- Flame Test - Peak Load**

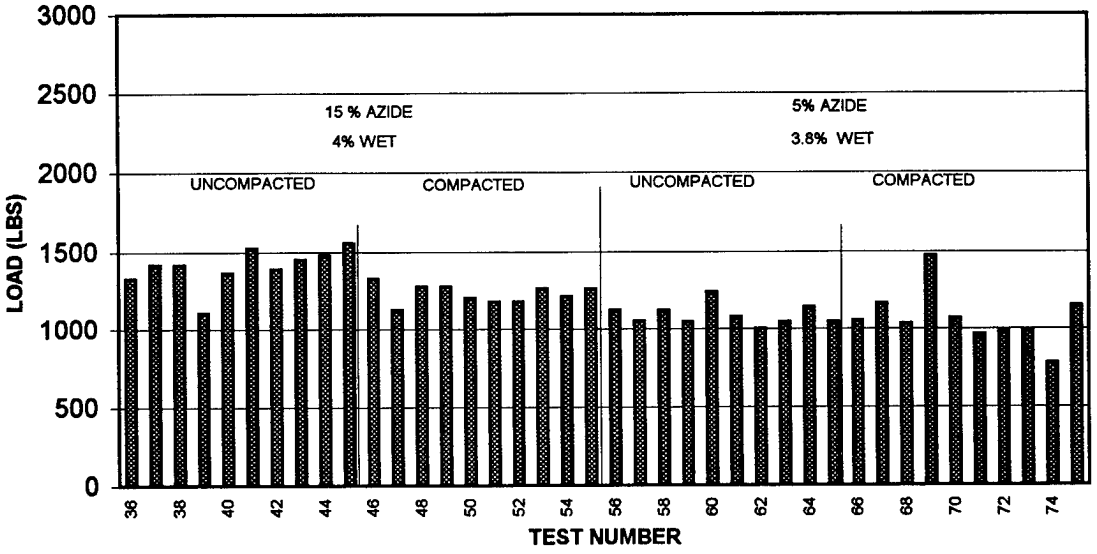



**Figure 3 - Shock Test - Peak Load**

## SHOCK AND FLAME PROBIT TESTS USING LEAD AZIDE

In this task the initial series of shock tests was conducted using uncompacted lead azide/soil mixtures to determine the TIL for each of three moisture levels (dry, 3% and 10% moisture). These levels correspond to soil found in natural or excavated conditions. The dry condition (<1% moisture) was achieved by drying the soil at 100°F for a minimum of 12 hours. The shock probit test configuration is shown in Figure 1.

Additional tests at other lead azide concentrations were then conducted at these moisture levels to generate probit data. Probit data express the probability of initiation of the test sample as a function of explosives concentration at a given moisture level and ignitor strength.

The results of the shock testing with lead azide and soil yielded probit data between 2% and 15% explosive concentration and moisture levels of dry, 3%, and 10% which are summarized in Table 2. The test results are listed based on two criteria. In the table, "L" indicates the number of positive reactions based on the load measurements. "D" indicates the number of positive reactions based on the pipe damage.

Based on test results from the Phase I study,[2] additional tests were run in this program at 15% moisture and several lead azide concentrations. The 15% moisture condition represents 100% saturation for the type of soil used in the tests. A thin layer of water was observed on the top of the soil, indicating a two-phase sample. This condition would tend to increase the concentration of the lead azide in the lower portion of the test sample.

**TABLE 2**
**SHOCK TEST PROBIT DATA**

| Moisture (wt%) | Basis | Lead Azide (wt%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 15% | 12% | 10% | 8% | 6% | 5% | 4% | 3% | 2% | 0% |
| 15% U | L | 6/10 | | | | | | 0/10 | | | 0/10 |
| | D | 10/10 | | | | | | 0/10 | | | 9/10 |
| 10% U | L | 0/10 | 1/10 | 0/20 | 0/10 | | | | | | 0/10 |
| | D | 0/10 | 0/10 | 0/20 | 0/10 | | | | | | 1/10 |
| 3% U | L | 7/10 | 4/10 | | 2/10 | 0/10 | 0/10 | 1/10 | | 0/20 | |
| | D | 3/10 | 0/10 | | 0/10 | 0/10 | 0/10 | 0/10 | | 0/20 | |
| Dry U | L | 5/5 | | 10/10 | 3/10 | 1/10 | | 1/10 | 1/10 | 0/20 | 0/20 |
| | D | 5/5 | | 10/10 | 3/10 | 1/10 | | 0/10 | 0/10 | 0/20 | 0/20 |

U = Uncompacted.
L = Load measurements; D = Pipe damage.
Probit data are expressed as the number of positive reactions per total number of trials.

The initial baseline testing was performed to determine reaction threshold. The reaction threshold was based on three criteria: (1) measured peak load from reaction, (2) test container (pipe) damage, and (3) review of video record. The load value chosen was obtained from calculating the average and standard deviation for 20 trials using dry soil and no lead azide. The average was 1048 pounds (476 kg) with a 108 standard deviation (sigma). The reaction threshold for load was set at three sigma above the average, 1374 pounds (624 kg). Load values for later tests that exceeded 1374 pounds (624 kg) would be designated as a positive reaction. Values below 1374 (624) were designated as "no reaction."

In addition to the load measurement, the container damage was also evaluated. The damage to the test container from a no. 8 cap (no lead azide) covered a broad range. For a baseline reaction the pipe cap may be undamaged, or the reaction may crack the pipe or split the cap in several pieces. At concentrations of lead azide below 15% the damage was similar make it difficult to distinguish between reactions and no reactions. Tests with high concentrations of lead azide (15%) resulted in total

reaction which destroyed the containers leaving only the base of the pipe cap. In several trials in this program, the measured load level was not deemed sufficient to be designated a reaction but the pipe cap was destroyed. For these trials the reaction was designated a reaction based on pipe damage.

The third criterion for evaluating the reaction level was video documentation. The video record of the test was reviewed and compared to other trials, looking for anomalies. Any anomalies detected would be considered in the final designation of the test result. No anomalies were observed.

The TIL for the shock test in ABL (C) soil based on the load data is 2% lead azide for dry and 3% moisture levels. For the 10% moisture level the TIL increased to 10% lead azide. This trend supports the theory that increased moisture decreases the reactivity of the soil/explosives mixture. At 15% moisture and 15% lead azide, however, the theory did not appear valid. Based on load results, there were 6 positive reactions at this level. A comparison was made of the dry and 15% moisture level with no lead azide present. These baseline data were similar, showing no effect of moisture content on measured reactivity of the ignition system alone.

Tests were also performed on samples containing 4% lead azide and 15% water. The load values were comparable to those observed for the 3% and dry moisture levels. The increased reactivity at higher levels of moisture and lead azide is of concern. Further investigation of the reactivity at higher moisture levels was beyond the scope of this program, but it is recommended that further study be undertaken to provide a better understanding of this phenomenon.

The flame probit tests followed the same general protocol used for the shock probit testing. The flame probit test configuration is shown in Figure 3.5.1. Tests were carried out in uncompacted mixtures of lead azide and soil to determine the TIL for dry, 3% and 10% moisture levels. These flame test data are summarized in Table 3.

As in the shock testing, an initial baseline reaction level was generated with 20 trials using dry soil samples with no lead azide. The same three criteria were used to evaluate the reactions: load, container (pipe) damage, and video record. The average load for the 20 trials without lead azide was 176 pounds (80 kg) with a standard deviation of 24. The reaction threshold for load was set at three sigma above the average, 248 pounds (113 kg). Load values for subsequent tests that exceeded 248 pounds (113 kg) were designated as positive reactions. Values below 248 (113)were designated as "no reaction."

The pipe damage criteria were different for the flame test. There was no pipe damage caused by the reaction of the ignitor alone, so any pipe damage was considered a reaction. The video record was more useful for the flame test. During review of the video, audible pops or snaps and smoke jets were observed several seconds after the ignitor pulse. These events were interpreted as a reaction of the lead azide and were designated as positive reactions. The pops and snaps observed in the video record were also recorded in load data. The data acquisition system would record nine seconds of data. Loads in excess of the ignitor were recorded during this period. Any peak after the ignitor peak was called a "multiple peak" and was deemed to be reaction of lead azide after the ignitor pulse and therefore a reaction. At lower concentrations of lead azide, the multiple peaks would result in no pipe damage, offering no visible evidence that lead azide was reacting. At higher concentrations the secondary peaks would correspond with the pipe damage. On several occasions the second peak would be delayed until the data acquisition period was complete, then the sample would react and the container would be destroyed. Based on container damage and video records, these trials were designated as reactions.

Using the load measurement results for ABL (C) soil, the TIL for the flame test is 4% lead azide for dry and 10% moisture levels. The TIL at the 3% moisture level is 6% lead azide. The 10% and 15% moisture level data raised some questions as to the validity of using a dry baseline level to evaluate samples which contain water. The dry baseline reactions were compared to results at 10%, 15%, and 20% moisture with no lead azide. The dry and 10% moisture conditions were similar in that their average and standard deviation of ten trials each were approximately the same. The average and standard deviations for the 15% and 20% moisture conditions were significantly higher (see Table 4). Consideration was given to providing a baseline for each moisture level, but there was a concern that the reaction of the lead azide may be masked by the effects of the increased moisture. The moisture appeared to contribute to the measured reaction. The water, when heated by the ignitor, generated steam which the instrumentation measured as increased load. The system was unable to distinguish between the load caused by the steam and the load caused by the reaction of small amounts of lead azide.

## TABLE 3
## FLAME TEST PROBIT DATA

| Moisture (wt%) | Basis | Lead Azide (wt%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 15% | 12% | 10% | 8% | 6% | 5% | 4% | 3% | 2% | 0% |
| 15% U | L | 10/10 | | | | | | 9/9 | | | 10/10 |
| | D | 0/10 | | | | | | 0/9 | | | 0/10 |
| 10% U | L | 10/10 | 6/10 | | 6/10 | 5/10 | | 0/20 | | | 0/10 |
| | D | 0/10 | 0/10 | | 0/10 | 0/10 | | 0/20 | | | 0/10 |
| | MP | | 1/10 | | | | | | | | |
| 3% U | L | 4/10 | 5/10 | | 5/20 | 0/20 | 0/10 | 0/10 | | | |
| | D | 3/10 | 1/10 | | 0/20 | 0/20 | 0/10 | 0/10 | | | |
| | MP | | 2/10 | | 4/20 | | | | | | |
| Dry U | L | 5/5 | 10/10 | 7/10 | 6/10 | 1/10 | 0/10 | 0/20 | | | 0/20 |
| | D | 5/5 | 10/10 | 5/10 | 0/10 | 0/10 | 0/10 | 0/20 | | | 0/20 |
| | MP | 1/5 | 10/10 | 6/10 | 1/10 | 1/10 | | | | | |

U = Uncompacted
L = Load Data; D = Pipe Damage; MP = Multiple Peak Data.
Probit data are expressed as the number of positive reactions per total number of trials.

Close examination of the reactions of the dry samples with lead azide levels greater than 6% showed reaction delays of several seconds after the ignitor fires until the lead azide reacts. This caused a second peak or multiple load peak. This secondary peak sometimes resulted in pipe rupture. One theory to explain this delay is that the sample has to be heated to sufficient temperature to begin decomposition of some of the lead azide. After the sample is at an elevated temperature, some of the lead azide decomposes and the reaction propagates through a portion of the sample. This delay phenomenon was present in all ten trials at the 12% lead azide level in dry soil (refer to Table 3). A secondary reaction took place from 1.5 to 6 seconds after the ignitor was fired in all ten trials.

## TABLE 4
## BASELINE REACTION AT VARIOUS MOISTURE LEVELS

| Moisture % | Average Load lb (kg) | Standard Deviation |
|---|---|---|
| 0 | 176 (80) | 24 |
| 10 | 139 (63) | 17 |
| 15 | 811 (369) | 87 |
| 20 | 958 (435) | 158 |

For the 10% lead azide level, there were seven positive reactions. Six of these trials had delayed second reactions. One trial had sufficient reaction with just the ignitor pulse to be classified as a reaction. The 8% and 6% level also had some multiple peak reactions. Below 6% there were no positive reactions recorded. At the highest lead azide level tested (15%), the reaction occurred during the ignitor reaction. The data showed a slight increase (less than 50 pounds, 23kg) in load over a 20 to 30

millisecond period, and then the sample reacted with loads in excess of 2700 pounds (1227 kg) and destroyed the sample container. The short period of time required for this reaction indicates a different reaction mechanism was responsible for the propagation.

At higher moisture levels, the reaction delay time should increase. In theory, the moisture should absorb some of the energy from the ignitor to produce steam. The reduction in ignition energy should reduce the sensitivity of the soil sample and increase the TIL concentration. The 3% moisture data supported this theory. The TIL increased to 6% and the reaction level decreased at correspondingly higher lead azide levels. For the 10% data, however, the TIL was again 4% and the higher lead azide levels did not correlate with the dry soil data. The measurements may be complicated by steam that was being generated, since it would be measured by the data acquisition system as load and the added load may have been of sufficient magnitude to exceed the baseline criteria. At the 15% moisture level, all three lead azide levels tested (0%, 4%, and 15%) yielded results well above the baseline criteria for dry soil.

A second factor which may affect the results at higher moisture levels was the inability of the sample container to vent the ignitor gases. At low moisture levels, air occupied the void space in the soil sample, making the sample gas-permeable. A path existed for ignitor gases to pass through the sample, heating the soil and lead azide. However, as the sample reached saturation, the water filled the void space, decreased the permeability of the sample, and effectively blocked the movement of ignitor gases through the sample. The test results supported this theory. At 10% moisture or less, the sample was not saturated (there was no standing water on the top of the sample in the container). After initiation of the ignitor, small amounts of gas and smoke were expelled at the interface between the top of the container and the wooden spacer block. Regardless of the source of increased pressure in the sample container, the pressure masked any reaction of the lead azide. Further study is required to understand the phenomena of increased reactivity at moisture levels above 10%.

## NITROGLYCERINE (NG)

The purpose of this task was to continue the work begun in Phase I and establish a probit analysis using the conventional DDT and U.S. Gap tests, using dry ABL (C) soil. In Phase I, limited testing was conducted with soil samples containing from 10% to 16.4% NG. The 16.4% NG level occurred due to a mixing error which was confirmed by sample analysis. In these tests, the soil mixtures reacted at 16.4% NG but not at 14%. The scope of Phase I did not include probit testing. Tests were performed dry at 15% moisture with no explosives in order to set a baseline for each test configuration. The 16% NG level was then tested in dry soil, based on results from the previous study. The concentration of NG was then reduced incrementally until a TIL was obtained. Once the TIL was established for each test, other levels were selected to obtain probit data. U.S. Gap and DDT test data for NG are summarized in Table 5.

**U.S. Gap:** The TIL for the U.S. Gap test is 13% NG in dry ABL (C) soil. Testing began with ten trials at a concentration of 16% NG. The result was 9 reactions in 10 trials. The concentration was then reduced to 14%. The last trial of this series detonated, yielding 1 reaction in 20 trials and requiring the concentration to be reduced to the next level to identify the TIL. The TIL was found at 13% NG. Ten trials were run with 15% NG, resulting in 1 reaction out of 10 trials. It would appear that a step function exists in the data between 15% and 16% NG concentration.

**DDT Test:** The TIL for the Deflagration-to-Detonation Transition (DDT) test is 12% NG in dry ABL (C) soil. Testing began with ten trials at a concentration of 16% NG. The result was 1 reaction out of 10 trials. The concentration was then reduced to 14%. One trial of this series detonated, yielding 1 reaction out of 10 trials. The concentration was reduced to 13% with the anticipation of a TIL as in the U.S. Gap test; however, the eleventh trial was positive and the concentration was decreased to 12%. The TIL was found at 12%. Since there was only 1 reaction out of 10 trials at 16% the concentration was increased to 18% with the result of 9 reactions out of 10 trials. At 17% the result was 10 out of 10. The DDT test for NG has a step function similar to that found in the U.S. Gap test.

**TABLE 5**
**US GAP AND DDT TEST DATA FOR NG**

| Moisture | NG Concentration | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Dry | 18% | 17% | 16% | 15% | 14% | 13% | 12% | 0% |
| US GAP | | | 9/10 | 1/10 | 1/20 | 0/20 | | 0/5 |
| DDT | 9/10 | 10/10 | 1/10 | | 1/10 | 1/11 | 0/20 | 0/5 |

## SAFE HANDLING CRITERIA

The objective of this task was to develop safe handling criteria for generic field operations involving explosives-contaminated soil. This task was accomplished by conducting a hazards analysis of the field operations (sampling, excavating, handling, and remediation support operations) and equipment (augers, sampling equipment, etc.) typically used in such operations[3]. Incorporated in the hazards analysis were sensitivity test data (probit and TIL) generated for soil mixtures containing various lead azide concentrations and moisture levels. On the basis of the hazards analysis, design and operating criteria were established, which should afford an acceptable level of risk in the field operations.[4]

**WARNING:** Hazards analysis of specific equipment used for remediation efforts is outside the scope of work for this project. This section deals with the hazards analysis of generic equipment and operations that could be used for remediation of soils contaminated with primary explosives. The safety criteria developed in this analysis are only guidelines and should not be construed to be the ultimate criteria for safe remediation efforts. Prior to remediation activities using specific pieces of equipment, it is recommended that quantitative hazards analysis be performed for the equipment and operations to be used for the remediation efforts.

The hazards analysis of generic field operations was carried out in four phases.

- **Sensitivity Testing:** Impact, friction, and electrostatic discharge (ESD) sensitivity tests were conducted on 2% and 10% lead azide in dry soil and on 10% lead azide in soil containing 10% moisture, in order to characterize the initiation sensitivity of field materials over a range of conditions. These tests were conducted to bridge the data gap between reactivity (flame and shock tests) and initiation sensitivity (impact, friction, and ESD) in order to characterize field materials over a range of conditions. The percentages selected for the sensitivity testing were within the reactivity range determined from the flame and shock testing phase of the program. The sensitivity data, converted to engineering terms, is used to support the quantification of hazards identified for field operations.

- **Hazard Identification:** Potential initiation scenarios were identified in each field operation and generic type of equipment likely to be used. For each scenario, the analysis gave a description of the hazard, the initiation source, the probable result of initiation, and supporting data such as design safety or recommendations for risk reduction.

- **Quantitative Analysis:** Critical hazards were selected for quantitative analysis, in which the estimated process potential energy to which the energetic material may be exposed was compared with the material response (sensitivity test data) in engineering units, to determine the probability of a fire or explosion.

- **Safety Criteria:** In the fourth phase of the analysis, the safety criteria for the field operations were developed on the basis of the information developed in the first three phases of the hazards analysis.

Samples of safety criteria for field operations are summarized in Table 6. These criteria were developed on the basis of the hazards analysis of generic operations and equipment. They are presented in the form of recommendations intended to reduce the risk of potential injury or damage from the hazards identified in the analysis. Difficulties were encountered when trying to establish specific criteria for safe operations involving explosives-contaminated soil, because of the large number of unknown factors involved in the field conditions. The type of explosives present in the soil, their concentration, whether the explosives is evenly distributed or concentrated in layers or lumps, the moisture content, and the presence of rocks, concrete, and other foreign objects or debris, are all factors which affect the sensitivity and reactivity of the explosives in the soil.

**Sampling and Handling:** The most hazardous field operations, from the standpoint of personal injury, are sampling and handling, in which the operator maintains a "hands-on" contact with the contaminated soil. The material is likely to be very sensitive to impact, friction, and mechanical shock, and somewhat sensitive to ESD. The best practice for operator protection during manual operations is to keep the material water-wet and to minimize the energy imparted to the energetic material. Most energetic materials in solid granular form become less sensitive to impact, friction, and ESD when water-wet. This may be due to the lubrication and thermal conductivity provided by the water, thus increasing the quantity of energy required to cause initiation; in the case of ESD the water also enhances electrical conductivity and reduces the presence of fine particles and dust.

## TABLE 6
## SAMPLE of SAFETY CRITERIA for FIELD OPERATIONS

| Operation or Equipment | Safety Criteria and Recommendations |
|---|---|
| Manual sampling (trowel, scoop, or hand auger) | 1. Do not use manual sampling tools in soil containing rocks or lumps of explosives.<br>2. Avoid sampling dry soil; soil should contain minimum moisture content of 10% by weight.<br>3. Use low force (20 lbs maximum, 9 kg) when pushing tool through soil; if heavy force is required for sampling, avoid sampling manually. Lesser force decreases probability of initiation.<br>4. Use low speed when pushing tool through soil: 2 ft/sec (0.6 m ) maximum. Lower speed decreases probability of initiation.<br>5. Use plastic trowels or augers (polypropylene, Teflon, etc.) instead of steel tools where possible, to reduce friction initiation hazards.<br>6. If a ram or pusher is used to remove the soil sample from the auger, use a wooden or plastic ram/pusher instead of metal. |
| Mechanized sampling (power auger) | |
| Handling explosives-contaminated soil | |
| Excavating (front end loader, back hoe, drill rig, truck) | |
| Screening (manual or mechanical shakers) | |
| Sludge pumps, sump pumps | |

Manual operations should be designed to minimize the energy imparted to the contaminated soil in terms of pressure, velocity, force, and electrostatic discharge. An example of this practice is the use of a small hand-trowel or scoop instead of a heavy spade. The trowel or scoop is a small tool designed for one-handed use, which limits the force exerted on the soil to a maximum of about 20 pounds (9 kg), whereas sampling the soil with a spade would allow the operator to exert a force nearly equal to his total body weight on the soil. Manual sampling should also be conducted slowly, using a tool speed of no more than 2 ft/sec (0.6 m). If hard-packed soil or solid materials are likely to be encountered, the use of a plastic scoop instead of a metal scoop is recommended. If the operator senses the presence of rocks or solid material in the soil, manual sampling should be discontinued.

ESD hazards are not likely to be encountered in the field, where the soil can be expected to contain a minimum of 3% moisture, unless a severe dust problem exists. ESD is usually more of a hazard in the laboratory, where the soil samples may become very dry and hence more sensitive to electrostatic energy. Materials with low conductivity can generate high charges when in motion, such as when being poured from one container into another, or during screening. Laboratory operators and other persons handling very dry or finely divided energetic materials should be properly grounded, and should use conductive containers and implements in handling the explosives. The operators should wear hand, face, and eye protection when handling explosives contaminated soils.

Walking over explosives-contaminated soil can be hazardous, particularly if the explosives exist in concentrated layers or agglomerates, if the moisture level is very low, or if rocks or foreign objects such as chunks of concrete or metal are present in the soil. If the explosive material is evenly distributed throughout the soil and is not concentrated, the pressure exerted upon the soil by an average person walking in smooth-soled shoes would be approximately 10 psi (68 Kpa), giving a wide margin of safety for friction (pressure) initiation. If small rocks or other hard objects were embedded in the soil, or if the explosives were

concentrated in layers or agglomerates, the pressure exerted by the operator's footsteps could be increased by one or two orders of magnitude, greatly reducing the margin of safety.

**Excavation:** When heavy machinery such as back hoes, front-end loaders, and drill rigs are used in contaminated soil, attempts to limit the energy imparted to the contaminant become largely academic. If the soil mixture is sufficiently sensitive to impact or friction, the energy imparted by the machinery is likely to cause initiation. In such an event, operator protection depends on the operator's position relative to the explosives. Normally the cab of the vehicle will afford the operator some protection, owing to the mass of metal between the operator and the soil. Backhoes and other heavy equipment can be fitted with thick Lexan panels to provide additional operator protection. Furthermore, an initiation would likely involve only a small quantity of material, unless an extensive concentration of explosives were present to support propagation. Machinery operators should remain in the cab of their vehicle when working in a contaminated field, and ground personnel should keep well clear of the vehicle when it is operating. Vehicles and machinery should be removed from the contaminated area before refueling or maintenance procedures are performed.

**Screening:** Explosives-contaminated solid material may be screened (classified) to remove oversize material such as rocks or site debris. In a typical screener, sources of initiation can include friction and impact from the movement of loose solid materials in contact with energetic materials, and friction or thermal energy from the effect of energetic material trapped between vibrating screen wires, frames, and other components of the machine itself. Thermal initiation can also occur if energetic material becomes pinched in stress cracks within vibrating components.

These hazards can be mitigated by the use of welded or punched-metal screens instead of loose-woven screens, by sealing or welding the crevices between components of the screen frames and discharge chutes, and by reducing the vibrational amplitude and frequency to the minimum required for efficient operation. The screener should be inspected at regular intervals for stress cracks and loose components. Tramp metal, debris, rocks, and other oversize materials should be cleared from the screener either continuously or at frequent intervals. The feed and discharge rates should be monitored closely to ensure that contaminated soil does not plug the screens or build up in the screener. If possible, contaminated soil should be kept water-wet during screening, to reduce initiation hazards and to prevent dust formation. All components of the screener should be constructed of conductive materials, with proper electrical bonding and grounding to prevent electrostatic charge accumulation.

**Pumping:** Remediation processes may require pumping of contaminated soil sludge or sump pumping. Initiation hazards in pumping explosives-contaminated slurries vary, depending on the type of pump used. For example, centrifugal pumps subject the slurry to high levels of shear and impact energy. Pumps with tight clearance between moving parts (such as piston, lobe, and screw pumps) can exert high frictional forces on the solids in the slurry, even when operating at low speed. Ideally an explosives-contaminated slurry should be handled by a low-shear, low-velocity, low-friction pump such as an air-operated double diaphragm pump. Valves in the slurry system should be avoided where possible; where required, rubber pinch valves would meet the same generic criteria outlined for pumps. Metal-to-metal couplings or quick-connects should be avoided if possible.

It is understood that the materials to be pumped may contain as much as 50% water, which should provide an adequate safety margin for impact/friction/thermal hazards provided that the explosives remain suspended in or mixed with the liquid. If the slurry is trapped or allowed to settle in the pump, valve, or pipe, the explosives can become dry or concentrated, which increases the initiation hazard. To prevent settling or drying of the explosives in the slurry, pumps and pipelines should be designed to be self-draining, and should be flushed with water following shutdown or prior to maintenance. Pumps should not be operated dry (empty) and should not be operated against a closed discharge (deadheaded).

## Regulatory Requirements

**Remediation:** Operations such as site visual survey and limited sampling may be done before obtaining DDESB approval for the final site remediation, if such sampling and survey are done for purposes of determining conditions that need to be known, in order to prepare the Clean-up Plan. The Clean-up Plan includes the Remediation Plan plus the Site Health and Safety Plan. To obtain DDESB approval for site remediation or clearance, the remediation vendor or contractor must submit the Clean-up Plan to the appropriate (Army, Navy, or Air Force) Service Headquarters, through the safety chain of command. The Service Headquarters explosives safety office, in turn, submits the plan to the DDESB. The headquarters explosives safety offices for the respective services are as follows:[5]

Army (including FUDS): Director, Defense Ammunition School
Attn: SIOAC-ES
Savanna, IL 61074-9639

AirForce: Director, Air Force Safety Agency
HQ AFSA/SEW
9700 Avenue G, Suite 130
Kirtland AFB, NM 87117-5670

Navy and Marine Corps: Commander, Naval Ordnance Center
Farragut Hall, Bldg. D-323
23 Strauss Avenue
Indian Head, MD 20640- 5555

DDESB contact: Chairman, DDESB
2461 Eisenhower Avenue,
Hoffman Building 1
Alexandria VA 22331-0060
Phone (703) 325-0152

**Transportation:** Off-site transportation of any explosives or explosives contaminated soil (including samples) must comply with all applicable requirements of the Department of Transportation (DOT) Hazardous Materials Regulations (49CFR). These requirements include (1) explosive hazard shipping classifications and (2) approved shipping containers. Explosives or explosives contaminated soil shipped to, by, or for DOD must comply with Army Technical Bulletin (TB) 700-2, the requirements of which are incorporated in 49CFR.

Before any Class 1 (explosive) material can be shipped off site, a shipping classification must be obtained. Procedures for obtaining shipping classifications are provided in 49CFR, Section 173.56. Explosive hazard shipping classifications are assigned to specific materials on the basis of the material's performance in a series of DOT tests that subject small quantities of the material to various stimuli which may be incurred during handling and transportation. These tests include but are not limited to thermal stability, no. 8 cap, small scale burning, and Bureau of Explosives (BOE) impact and friction sensitivity tests. 49CFR Part 173 Subpart C covers the classification and packaging procedures for Class 1 explosives. Additional details about testing and certification of packaging are contained in Part 178. The contact for information regarding the transportation of hazardous materials is the U. S. Department of Transportation, Associate Administrator for Hazardous Materials Safety, 400 Seventh Street S.W., Washington, D.C. 20590, or phone 1-800-467-4922.

## RECOMMENDATIONS FOR FUTURE WORK

### LEAD AZIDE/SOIL REACTIVITY AT ELEVATED MOISTURE

Several areas for future work have emerged from this project. Further study is required to understand the effects of moisture and different soil characteristics on reactivity. The effect of moisture is the most significant, since field operations can encounter soils ranging from very dry to pond sludge. The unanswered question that revolves around the results from the 15% moisture level for both the shock and flame tests is: Does increased moisture increase the reactivity of soil/lead azide mixtures?

A comparison of load vs. pipe damage results for the shock test showed that pipe damage is not as precise an indicator of reaction. It is recommended that the load measurement be used as the primary determinant of reaction level. Shock tests appeared to be more reactive at 15% moisture than at lower moisture levels. Further testing is needed at higher moisture levels and higher lead azide levels to better understand this test result.

A comparison of load vs. pipe damage results for the flame test showed that pipe damage may be a better indicator of reaction. For tests with alternate soil samples and with samples containing moisture, the load data seemed to overstate the reactivity of the samples. The unexpected high reactivity for high water content soil/lead azide mixtures may be the result of test container over pressurization due to vaporization of the water, and not lead azide reactivity. This phenomenon may be resolved by modifying the test container for the flame test to include vent holes which would relieve the pressure from the igniter reaction while maintaining the sensitivity of the system to measure the reaction of primary explosives. It is recommended that testing be performed at moisture levels from dry to 15% to evaluate this phenomenon further. The lead azide should range from 0 to 20%.

The settling of lead azide in high water content soil/lead azide mixtures may concentrate the lead azide at the bottom of the test sample container. If significant settling of the lead azide is occurring, it may explain the anomalous results at high water concentration. Settling can be examined by preparing a high water content soil/lead azide mixture in a test sample container, allowing it to dry, then sampling the mixture at specific depths.

The interaction of dextrin in the dextrinated lead azide with water/soil/lead azide mixtures may change the reactivity of the lead azide. Dextrin is incorporated in vendor-supplied lead azide stored in a water/isopropanol blend to prevent the re-crystallization of the lead azide into larger crystals. If the water/soil/lead azide mixture interacted with the dextrin in such a way that allowed the lead azide to re-crystallize as larger crystals, this could make the mixture more sensitive and could explain some of the anomalous results. A comparison of the size and shape of the lead azide crystals before and after exposure to the water/soil/lead azide mixture would reveal any possible interaction.

## SOIL CHARACTERIZATION STUDY

Some test results with alternate soils indicated that soil composition is a factor in the measurement of reactivity of a soil/explosives sample. Before continuing a test program to characterize reactivity, historical soil analysis and sampling data should be evaluated for the nine sites believed to contain primary explosives. If sufficient data on the sites are not available, then soil characterization should be performed. This should include the particle analysis and XRD for each soil. Sufficient inert soil should be obtained from each site so that shock and flame probit testing with lead azide can be performed at ABL. From this broader soil sampling, generalizations regarding reactivity and soil could be made. These tests would provide specific reactivity baselines for each site. The baseline data could be used for analysis of remediation techniques and recommendations on safety criteria that are site-specific.

## REMEDIATION SAFETY FIELD MANUAL

The current program provided the foundation for understanding the reactivity of soil and primary explosives. The logical next phase is to utilize the safety criteria and reactivity limits to generate a Remediation Field Manual. This manual would serve as a safety guide to persons cleaning up explosives contaminated sites. It would include guidelines for General Operations safety and offer specific direction for site characterization and sampling techniques. The manual would also provide equipment requirements for handling explosives and recommended practices for remediation and disposal.

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# CONTRIBUTED MANUSCRIPTS

# DEVELOPMENT OF A WASTEWATER TREATMENT PLANT SLUDGE MANAGEMENT STRATEGY FOR WEST POINT U.S. MILITARY ACADEMY

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## ABSTRACT

The U.S. Military Academy at West Point, NY operates the Target Hill Wastewater Treatment Plant (WWTP), which currently disposes its residual sludge by landfill. The WWTP uses a belt filter press, which can dewater sludge up to 15 percent solids content, a level below the 20 percent solids content required by New York State for landfilling. The sludge is consequently mixed with sand to meet the State requirements, a practice that places an unnecessary labor and materials burden on the WWTP. This report presents different technical alternatives and develops a strategy to manage Target Hill WWTP sludge more efficiently. Factors governing strategy development include compliance with U.S. Environmental Protection Agency's (USEPA's) new Part 503 regulations, economy, and simplicity of operation. Sludge must be stabilized, and stabilized biosolids should be beneficially used as a soil supplement to avoid landfill disposal. The study recommended composting Target Hill WWTP sludge at the Rockland County central composting facility currently under construction, and reusing the biosolids as a soil amendment at West Point Military Academy. This recommendation will result in annual savings of nearly $58,000. This project will also serve as a model for the cooperation between local and federal government in sludge (biosolids) management.

## 1. INTRODUCTION

Effective sludge management can be a difficult task for wastewater treatment plant (WWTP) operators. As sludge regulations become more stringent, more landfills are closed down, and many WWTPs are consequently forced to develop new and more effective residual management plans. Solids residual management is a global environmental problem. While it may appear that each nation takes a different approach for residual management, in reality individual WWTPs have unique combinations of environmental conditions and regulatory requirements. Thus, the best solution for solids residual problems can vary by location, and even by individual WWTP. Key factors affecting the success of good residual management for a WWTP include, but are not limited to:

- the regulatory framework and attitude of government
- available technologies and "know-how"
- economical feasibility and available resources
- public awareness and acceptance.

## 2. REGULATORY FRAMEWORK

Although manure and sludge have long been used for farming fertilizer, the scientific evaluation of sludge use is relatively recent. In 1928, Rudolfs determined the fertilizer value of various sludges at different wastewater treatment plants.[1] Almost five decades later, the Federal Water Pollution Control Amendments of 1972 recognized

land application of sludges as an alternative method for sludge disposal and recognized a need for land application research. In 1979, the USEPA implemented land application criteria including pH, cadmium application rates and PCB concentrations. In 1984, the USEPA issued its "Policy on Municipal Sludge Management," which actively promoted the beneficial use of sludge while maintaining and improving environmental quality and protecting public health. The beneficial use of sludge provides two benefits: (1) it saves landfill space and reduces liability from landfill, incineration, and ocean dumping, and (2) it improves soil properties and reduces the use of chemical fertilizers as soil amendments or organic fertilizers. In 1993, the USEPA adopted the most comprehensive, technically based sludge regulations, known as Part 503. These regulations encourage the beneficial use of biosolids.

Residual management strategy is greatly affected by different federal policies, laws, and regulations. In addition to Part 503 regulations, regulations applied to sludge use and disposal include: Marine Protection, Research and Sanctuaries Act; Toxic Substance Control Act; Clean Air Act Ambient Air Quality Standards, New Source Performance Standards, and National Emissions Standards for Hazardous Air Pollutants; Resource Conservation and Recovery Act; Clean Water Act; National Environmental Policy Act; Comprehensive Environmental Response, Compensation, Liability Act, and Superfund Amendments and Reauthorization Act.

## 2.1 Part 503 Overview

Title 40 of the Code of Federal Regulations, Part 503 was published on February 19, 1993 and became effective on March 22, 1993. Commonly referred as "Part 503," these regulations encourage the beneficial land application of biosolids. Land application requirements include pollutant limits, pathogen, and vector attraction reduction as well as site restrictions, management regulations, general requirements, monitoring, and recordkeeping and reporting requirements. Since Part 503 was published, many biosolids treatment processes that previously had not been used in the United States have been re-explored as technologies capable of meeting the new regulations.

Part 503 regulates the concentrations of ten heavy metals in land applied biosolids. All biosolids must meet the ceiling concentration limits shown in Table 1 to be applied to land. In addition to the ceiling concentration limits, at least one of the other requirements in Table 1 must be met.

In addition to the heavy metal requirements, Part 503 specifies pathogen reduction levels. Biosolids are classified as either Class A or Class B according to the amount of pathogen removal. Part 503 gives six options to meet Class A requirements and three options to meet Class B requirements. For example, a Class A option is to treat the biosolids in a Process to Further Reduce Pathogens (PFRP). Class A biosolids may be applied anywhere without site restrictions. An example Class B option is to treat the biosolids in a Process to Significantly Reduce Pathogens (PSRP). Class B biosolids may still contain some pathogens and site restrictions must be applied. These site restrictions ensure that Class B biosolids present no hazard to public health. Pathogen reduction should be performed prior to or concurrently with vector attraction reduction, with few exceptions.

Vector attraction reduction (VAR) requirements are necessary since vectors, such as flies, mosquitoes, fleas, rodents and birds, are capable of transmitting pathogens from wastewater sludge to humans and animals. Part 503 contains twelve options for the reduction of vector attraction. The first eight options reduce the attractiveness of the sludge to vectors. One of these options is to reduce the mass of volatile solids in the biosolids by at least 38% during treatment.

TABLE 1. POLLUTANT LIMITS

| Pollutant | Ceiling Concentration Limits for All Biosolids (mg/kg) | Pollutant Concentration Limits (mg/kg) | Cumulative Pollutant Loading Rate Limits (kg/hectare) | Annual Pollutant Loading Rate Limits (kg/hectare/year) |
|---|---|---|---|---|
| Arsenic | 75 | 41 | 41 | 2.0 |
| Cadmium | 85 | 39 | 39 | 1.9 |
| Chromium | 3,000 | 1,200 | 3,000 | 150 |
| Copper | 4,300 | 1,500 | 1,500 | 75 |
| Lead | 840 | 300 | 300 | 15 |
| Mercury | 57 | 17 | 17 | 0.85 |
| Molybdenum | 75 | — | — | — |
| Nickel | 420 | 420 | 420 | 21 |
| Selenium | 100 | 36 | 100 | 5.0 |
| Zinc | 7,500 | 2,800 | 2,800 | 140 |
| Applies to: | All biosolids that are land applied | Bulk biosolids and bagged biosolids | Bulk biosolids | Bagged biosolids |
| From Part 503 (EPA, 1993) | Table 1, Section 503.13 | Table 3, Section 503.13 | Table 2, Section 503.13 | Table 4, Section 503.13 |

The heavy metal, pathogen and vector attraction reduction requirements discussed above are used to determine which land application requirement is met. Four options, which are equally protective of public health through management practices, site restrictions and general requirements, are (in order of increasing regulatory requirements): Exceptional Quality (EQ), Pollutant Concentration (PC), Cumulative Pollutant Loading Rate (CPLR) and Annual Pollutant Loading Rate (APLR). The Exceptional Quality option is the most ideal in that site restrictions, general requirements, management practices, and tracking of added pollutants are not required. EQ is met by meeting the ceiling concentration limits and pollutant concentration limits in Table 1, Class A pathogen requirements, and one of the first eight VAR options.

## 3. TARGET HILL WWTP DESCRIPTION

The rated design capacity of the Target Hill WWTP is 2.06 million gallons per day (MGD), but the average flow is 1.5 MGD. Influent wastewater is primarily characterized by biochemical oxygen demand (BOD) and total suspended solids (TSS), which average 145 mg/L and 106 mg/L, respectively. The flow and wastewater characteristics are based on figures reported in an Operator Assistance Program report (ES Environmental Services, 1988). The permit limits on BOD and TSS are 30 mg/L (average) and 45 mg/L (maximum) for both.

Sludge is generated in the primary settling tanks and in the activated sludge system. Primary sedimentation tanks are used at the WWTP to remove readily settleable solids and floating material, thereby reducing the suspended solids content. Properly designed sedimentation tanks typically remove 50 to 70% of the suspended solids and 25 to 40% of the influent $BOD_5$. A previous study indicated that the loading on primary clarifiers were within typical design parameters at the rated flow rate of 2.06 MGD.

The activated sludge process follows primary treatment to remove carbonaceous organic matter (defined by BOD). To maintain an adequate concentration of organisms, a portion of the settled solids for the secondary clarifiers is returned to the aeration tanks. The removal of excess activated sludge, referred to as waste activated sludge (WAS), comprises the other major portion of sludge produced. Various properties of WAS make it difficult to dewater, as compared to other biological sludges and primary sludge.

At the Target Hill WWTP, the WAS is thickened, via processing in a dissolved air flotation (DAF) unit. The volume reduction achieved by thickening is beneficial to subsequent treatment processes, including digestion and dewatering, because it effectively increases the capacity of tanks and equipment, reduces the amount of chemicals required for sludge conditioning (e.g., polymers for dewatering), and reduces the amount of heat required by digesters.

The thickened WAS and primary sludge are combined in the anaerobic digestion process. Two-stage digestion is used at the Target Hill WWTP. The sludge is mixed and heated in the primary digester, where the biological reduction of the volatile organic matter principally takes place. After primary digestion, the sludge is sent to the secondary digester. The second tank stores and concentrates the digested sludge. A belt filter press is used to mechanically dewater the digested sludge. The filter press achieves between 13 and 15 percent dry solids. This amount is significantly below the landfilling requirement of 20 percent solids for sludge in the New York Codified Rules and Regulations (NYCRR), Part 360. To meet this standard Target Hill sludge is mixed with sand before transport.

The Target Hill WWTP is minimally impacted by industrial wastewaters, and therefore, there is little likelihood that a significant concentration of metal pollutants exists. This fact was verified by previous testing reported in a past U.S. Army Environmental Hygiene Agency (AEHA) land feasibility study done for West Point[2] and by USACERL data gathered for this study. The results indicate that West Point biosolids meet the highest 503 standards with respect to metals. This greatly reduces the burden of land application because there is no requirement to track and record the quantity of metals applied or to determine the amount previously applied to the desired site.

Anaerobic digestion, the current treatment at the Target Hill WWTP, is listed as a Process to Significantly Reduce Pathogens (PSRP) in Appendix B of Part 503 regulations. Minimum requirements for anaerobic digestion as a PSRP are that the biosolids be treated in the absence of air while the mean cell residence time (MCRT) and temperature be maintained between 15 days at 35 to 55°C and 60 days at 20°C. According to the study from the Operator Assistance Program done at West Point, the primary anaerobic digester has a design MCRT of 28 days at a flow rate of 2.06 MGD.[3] Assuming that the digester heating equipment is operating properly, the system will meet the PSRP requirements for anaerobic digestion, producing Class B biosolids. Properly operating anaerobic digesters have little problems meeting the 38% reduction of volatile suspended solids required to meet VAR requirements.

USACERL researchers collected technical data on how other municipal plants manage sludge in the region. In the New York State Department of Environmental Conservation Region 3 (Orange, Rockland, Sullivan, Westchester, Dutchess, Putnam and Ulster Counties, NY), only 3 WWTPs implement beneficial use of biosolids. About 39% of sludge was transported to out of state landfills. It was exciting news that Rockland County initiated construction of a central composting facility for its municipalities.

## 4. BIOSOLIDS MANAGEMENT ALTERNATIVES RELATED TO TARGET HILL WWTP

Sludge management consists of a few major steps, including: thickening, stabilization, conditioning, dewatering, and beneficial use or disposal. The objective of thickening, conditioning, and dewatering is to separate water from

solids. The purpose of stabilization and other sludge processes are to reduce volume, odors, pathogens, and putrescibility of the sludge so that biosolids can be beneficially used or effectively disposed. These steps should be compatible with each other, and the overall system management should be integrated to minimize total costs.

## 4.1 Stabilization

Conventional stabilization processes include anaerobic digestion, aerobic digestion, lime stabilization, and composting. Emerging stabilization processes include autothermal thermophilic digestion, alkaline stabilization, and new sludge dryers.[4]

### 4.1.1 Anaerobic digestion

Target Hill WWTP uses anaerobic digestion for sludge stabilization. Anaerobic digestion of sludge is a solubilization and reduction process of organic substances in the absence of oxygen. Three distinct groups of micro-organisms perform different functions:

1. Extracellular enzymes found in these micro-organisms hydrolyze complex organics (e.g., proteins, carbohydrates, and lipids) to soluble organics (e.g., glucose, amino acids, and fatty acids).
2. The acids producers convert soluble organics to short-chain organic acids (e.g., acetic, propionic, and lactic acids).
3. The methane formers convert the short-chain organic acids to methane, carbon dioxide, and other trace gases.

The microorganisms responsible for Steps (1) and (2) are often called "acids formers." Compared to acids formers, methane formers are more sensitive to environmental changes such as pH, temperature, and substrate compositions, and grow more slowly. Therefore, operators must closely monitor the methane formers population.

Many researchers have studied sludge anaerobic digestion to improve the process efficiencies. In the 1950s, heating and mixing were combined to make a high rate anaerobic digester. Most anaerobic digesters are operated in the mesophilic range. However, they can be operated in the thermophilic temperature range. Thermophilic digestion may offer several advantages over mesophilic digestion, including increased reaction rates, increased destruction of pathogens, and better dewatering characteristics. On the other hand, limitations of the process include extreme sensitivity of micro-organisms, high energy requirements, and more offensive odor from the digested sludge. Part 503 gives credit to thermophilic aerobic digestion for greater reduction in pathogens, but thermophilic anaerobic digestion is not included in Part 503. Thus, selection of thermophilic anaerobic digestion should be carefully evaluated for the claimed advantage. A relatively new configuration for anaerobic digestion is the egg-shaped digester, which has been extensively used in Europe. The egg-shaped digester helps to eliminate grit buildup.[5] Two-stage anaerobic digestion divides the functions of fermentation and solids-liquid separation into two separate tanks in series. By contrast, two-phase anaerobic digestion separates the acid formation phase from the methane formation phase. Based on a bench scale study,[6] full scale facilities[7] were built. The claimed advantages of the two phase system include higher rates of volatile solids reduction, increased higher quality methane production rates, higher pathogen reduction, and elimination of foaming. Although some benefits have been attributed to modifying anaerobic digesters as above, none of the modifications were recommended for Target Hill.

Anaerobic digestion typically produces Class B biosolids, which are suitable for restricted beneficial reuse on land.[8] Anaerobic digestion substantially reduces pathogen concentration but is not sufficient to meet Class A biosolids requirements. Detectable viruses and fecal coliform are reduced during anaerobic digestion by one to four orders of magnitude, with the higher reductions at thermophilic operating ranges. However, some helminth ova survive even after thermophilic digestion.[4]

4.1.2 Alkaline Stabilization

Advanced alkaline stabilization can meet Class A requirements of Part 503 regulations. Most advanced alkaline stabilization processes are proprietary. Chemicals in addition to lime that may be added include cement kiln dust, lime kiln dust, Portland cement and fly ash. One example of an advanced alkaline stabilization process is the N-Viro process. The N-Viro process is a patented system that is technically defined as "advanced alkaline stabilization with subsequent accelerated drying." Two different methods of conducting the N-Viro process have been approved by the U.S. Environmental Protection Agency as PFRP equivalent processes. In the first process, alkaline materials are added to and mixed with the sludge in sufficient quantity to achieve a pH of 12.0 or greater for at least 7 days. For example, Burnham used 35% kiln dust and a small amount of quicklime.[9] Following mixing, the alkaline-stabilized sludge is heated to a temperature of at least 53°C and is maintained at that temperature for at least 12 hours. In the second process, a pH greater than 12.0 is maintained for at least 72 hours. Concurrent with maintaining this high pH, the sludge is heated to a temperature of at least 53°C and is maintained at that temperature for at least 12 hours. Although advanced alkaline stabilization is a promising alterative to improve Target Hill WWTP biosolids management, it was not the selected technology for a couple of reasons. West Point soil is generally alkaline. Thus, adding biosolids which have increased alkalinity is not feasible. In addition, receiving a permit to build silos on the historically preserved grounds of the military academy is nearly impossible.

4.1.3 Composting

Composting is an aerobic sludge stabilization process. The heat generated from biochemical reactions destroys pathogens and the humus-like end product can be used as soil amendment meeting "Class A" requirements of Part 503 regulations. In composting, where temperatures reach the thermophilic range, practically all viral, bacterial, and parasitic pathogens are eliminated.[4]

The objectives of composting are to: (1) reduce pathogens to PFRP requirements in Part 503 regulations; (2) further stabilize biosolids by decomposing odor producing compounds; (3) dry the biosolids; and (4) produce a marketable product. The following major factors affect compost processes: biosolids and amendment characteristics (solids content, carbon/nitrogen (C/N) ratio, particle size and shape, porosity, biodegradability, and energy content); initial mix ratios; aeration rates; and detention time.[10]

The three types of composting systems[4] are:

1. *Aerated static pile,* in which dewatered cake is mixed with a coarse bulking agent such as wood chips, and the mixture is stacked over a porous bed with air piping connected to blowers. The piles are covered with a layer of finished compost to provide insulation and capture odor. Air is drawn downward or forced upward through the mixture. After composting, the pile is taken down and the bulking agent may be partially recovered by screening and then reused.
2. *Windrow process,* in which the mixture is stacked in windrows with a sufficient ratio of surface area to volume to provide aeration by natural convection and diffusion. The windrow is remixed periodically by a turning machine. The amendments are typically of a smaller particle size than with aerated static pile and may include recirculated compost. In the aerated windrow process, natural convection and diffusion are supplemented by forced aeration, as in the static pile process. Air is supplied through trenches in the paved working surface.
3. *In-vessel process,* in which the mixture is fed into one end of a silo, tunnel, or open channel and moves continuously toward the discharge end where it is outloaded after the required detention time. Air is forced through the mixture. The mixture may move as an undisturbed plug or be periodically agitated as it is moved through the vessel.

The bulking agent or amendments provide energy, are a source of carbon, provide structural integrity, and increase porosity and free air space. An initial total solids concentration of 40% is recommended. A wide variety

of bulking agents and amendments has been used: wood chips, sawdust, shredded yard wastes, processed agricultural wastes, and shredded tires. Lang and Jager reported that some amendments such as wood ash suppress compost odors.[11] Reducing particle size increases surface areas, thereby enhancing composting rates because the optimum conditions of decomposition occur on the surfaces of organic materials. However, reducing particle size reduces the pore size, limiting the movement of oxygen required for composting. Thus, an optimum range of particle size exists for each condition. For aerated static piles, this is between 12.5 and 50 mm (0.5 and 2 in.). Other process configurations may be able to manage smaller sizes. Coarse bulking agents can be recovered in post processing. Benedict indicated that compost screening typically results in the recovery of 65 to 85 percent of wood chips entering the composting process.[12]

Carbon and nitrogen are the principal nutrients that affect composting. Carbon-to-nitrogen ratios (C/N) between 20 and 40 have been cited as optimum. Low C/N ratios (less than 20) result in a loss of excess nitrogen from ammonia volatilization.[13] High C/N ratios (greater than 80) result in a slowing of decomposition rate and subsequent reduction of composting temperatures.[14]

The governing air flow rate for forced-aeration composting is dictated by either the need for moisture removal or for temperature control, with temperature control typically being most critical and most easily measured. During the early stages of composting, the temperature of the composting mass is a critical operational consideration. As the compost matures, moisture levels decrease to a point where the need to retain moisture becomes more of a concern than temperature control. At this point, forced aeration of the compost should be limited, and turning of compost piles can be a more effective way to control temperature. As a rule of thumb, aeration demands for temperature control should be approximately 0.2 to 0.25 standard $m^3$/ton.[10]

The USEPA established minimum requirements for composting as a PFRP listed in Appendix B of Part 503 regulations. They are: (1) using either the within-vessel composting method or the static aerated pile composting method, where the temperature of the biosolids is maintained at 55°C or higher for 3 days; and (2) using the windrow composting method, where the temperature for the biosolids is maintained at 55°C or higher for 15 days or longer. During the period when the compost is maintained at 55°C or higher, the windrow is turned a minimum of every 5 days.[8] Most composting facilities are designed and operated with much longer detention time than Part 503 limits. For example, most horizontal agitated systems are designed for 21 days and other in-vessel systems for 14 days aeration, followed by curing.

Odor control is an important aspect of successful composting operation. The treatment methods for compost odors include wet scrubbing; regenerative thermal oxidation; and the use of biofilters, masking agents, and carbon absorption.[4] It appears that biofilters using compost and bulking agents have become more popular for odor treatment at composting facilities in the United States.

West Point Military Academy will realize a substantial savings by composting the Target Hill WWTP sludge and using the resultant biosolids as a soil supplement. If a composting facility were built at West Point Military Academy, an in-vessel composting enclosure would be preferred because the Academy is a tourist attraction and a historically preserved site. Odor control is relatively easier in an in-vessel process. Three candidate sites were identified for in-vessel composting facilities. However, cost for construction, operation, and maintenance is relatively high. It was found that, in comparison with in-house composting facilities, using the Rockland County Solid Waste Management Authority (RCSWMA) composting facility and returning biosolids to West Point will result in substantial savings (i.e., an estimated $57,934 annually) to the West Point Directorate of Public Works. This savings was accomplished through reduced labor, elimination of tipping fees, elimination of sand additions, and free soil amendments. RCSWMA will begin operation of its composting facility to handle sludge generated at Rockland County's municipal WWTPs in January 1998. RCSWMA assured USACERL that the composting facility had sufficient capacity to process additional sludge. Contracting sludge composting with RCSWMA was

strongly recommended by this study, and the West Point DPW accepted the recommendation. On behalf of the West Point DPW, USACERL will execute a contract with RCSWMA for 2 years. This arrangement will serve as a model for local and federal government for better biosolids management.

## 4.2 Conditioning/Dewatering

Conditioning enhances the aggregation of suspended sludge particles by chemical and physical means. Conventional conditioning methods include the use of polymers, inorganic chemicals, and heat treatment. Dewatering is the removal of water from sludge to achieve a volume reduction greater than that achieved by thickening alone. Dewatering may be accomplished mechanically or naturally.

### 4.2.1 Reed Bed

Although it was started in Europe more than 10 years ago, reed bed dewatering is still an emerging technology in the United States. Reed bed technology has been largely used in the northeastern states, including New Jersey, Pennsylvania, Maine, and Vermont. Like sand drying beds, the reed bed is a natural dewatering system and is therefore well suited for smaller treatment plants. Compared to mechanical dewatering processes, O&M costs of reed beds are significantly lower because of the reed bed's low level of complexity, minimal requirements for operational attention, and reduced energy requirements. A disadvantage with such natural systems is the greater requirement for available land. The reed bed process can produce a much greater solids content than mechanical systems, with solids ranging from 30 to 60%.[15]

The reed bed process basically operates as a modified sand drying bed with a dense growth of reed vegetation. Therefore, the construction is similar to that of sand drying beds. An excavated trench is first lined with an impermeable barrier to contain the liquid. Precast Hypalon liners have been successfully demonstrated for lining the trenches at several installations. A layer of gravel is placed over the drainage pipe and is then covered with a layer of sand. The side walls are commonly made of concrete and include at least one meter freeboard. This freeboard insures adequate storage capacity of the sludge for a design period of ten years.

Once the beds are constructed, the reeds are planted at 1-foot centers. Several species are available, but usually the common reed *Phragmites* is used. *Phragmites* is well suited for reed bed use due to its great tolerance for variable climates and its elevated evapotranspiration rate. Once the reeds are established, sludge may be applied to the beds. Reed beds are designed to accommodate stabilized sludge that contains 3 to 4% solids.

Reed beds have some important advantages over other natural systems. The dried sludge removed at the end of bed is very similar in quality to compost with regards to pathogen content and stabilization. These results are mainly due to the long detention of the sludge, added microbial degradation due to oxygen provided through the root system and an additional storage period that follows the final sludge application. While not yet documented, it is believed that, if the sludge is allowed to weather for 1 year following the last sludge application, it will pass the EQ biosolids criteria.

Reed beds require very little operator attention. Typical operator attention is 200 hours per year to monitor sludge additions and perform other miscellaneous tasks. Unlike sand beds, which require the removal of the sludge after each individual sludge application, reed beds are designed to hold sludge for a period of 10 years. One relevant manpower requirement is for harvesting of the reeds each fall. Harvesting may be performed manually with hedge clippers, sickles, or mechanical devices. Alternately, the reeds may be burned after filling the bed with 2 in. of water, if local authorities permit.

At the time of disposal, the final volume is significantly lower than the total volume from a sand bed after 10 years, which results in disposal savings as well. Several ultimate disposal alternatives are available for the sludge

after it is removed from the beds. It is likely that the weathering of the sludge over the storage period will result in Class A biosolids. Therefore, the material could be used as freely as any commercial soil conditioner, in a similar manner to compost. In the worst case, the biosolids would meet the Class B standards and could still be beneficially applied to the land. The solids content of over 40% would facilitate ease of application. One problem that must be considered is the removal and extinction of the reed system from the final product. This may possibly be addressed by killing the reeds at the beginning of the 1 year holding period and by screening of the final product. Landfilling of the sludge is still an alternative. Landfilling would still be cheaper than currently practiced, since the volume of sludge would be reduced through organic destruction.

Winter operations are a concern when using natural, outdoor processes. Since reed dormancy during winter affects the rate of water uptake, sludge application is normally stopped. New Jersey experiences a downtime of only 20 to 30 days annually, but areas with more severe and extended winters will experience greater periods of reduced dewatering capability. If West Point cannot store the sludge through the worst winter months, provisions must be made to address this issue. Some sludge may still be applied to the reed beds even if the reeds are dormant or harvested, but care must be taken to ensure that the sludge level does not exceed the height of the remaining reed stalk. During this period, the freeze/thaw mechanism will effectively reduce the volume of sludge that is applied. Also, it would be advisable to empty the digester in the late fall to maximize the plant's storage capacity for the winter months.

Although reed beds is a promising technology for West Point, it would be very difficult to receive approval to convert Target Hill training area to reed beds due to its training priority. USACERL researchers were told not to pursue this option.

4.2.2 Agitated Drying Beds

Agitated drying is also a fairly new method. The Metropolitan Water Reclamation District of Greater Chicago uses an agitated drying method. Dewatered sludge from centrifuges or lagoons is placed on a mildly sloped, paved drying surface. The sludge is then spread out over the surface to a depth of about 45 cm. The sludge is agitated by a tractor equipped with a front mounted auger until the solids content reaches 30 percent. The biosolids are windrowed and periodically agitated until the solids content reaches 50 percent.[16] This method is worthy of a pilot trial.

4.3 Beneficial Use

Land application is application of biosolids to land either to condition the soil or to fertilize crops or other vegetation grown in the soil. Based on information in the Preamble to Part 503, 33.3 percent of U.S. sludge is land applied. More than 65 percent of land applied biosolids are placed on agricultural crop land. Of the remaining sludge, 34.0 percent is landfilled, 16.1 percent is incinerated, 10.3 percent is disposed into surface impoundments, and 6.3 percent is disposed by unknown means.[8] In the future, as the ability to landfill biosolids is continuously reduced, land application or beneficial use of biosolids will increasingly replace landfills. If West Point Military Academy uses the RCSWMA composting facility starting from 1998 and the processed compost meets EQ standards, then the compost may be freely used as a soil supplement for landscaping on parade fields, training fields, golf courses, and for erosion control.

## CONCLUSIONS

The Target Hill WWTP at West Point generates about 1,840 cu yd (about 250 dry tons) of sludge at 13 to 15 percent solids. The sludge is currently mixed with sand to meet the 20 percent solids content required by New York State before it is disposed at the Al Turi Landfill. This study has developed a sludge management strategy

for the Target Hill WWTP that considers the new USEPA Part 503 regulations, economic benefits, and simplicity of operation.

The authors recommend that the Target Hill WWTP compost its sludge at the Rockland County Central Composting Facility, which is expected to begin operation in January 1998 by the Rockland County Solid Waste Management Authority (RCSWMA), and use the composted biosolids as a soil amendment at the West Point Military Academy. Hopefully, the West Point and RCSWMA cooperation serves as a model for other DOD WWTP biosolids management.

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# ELECTROKINETIC DEMONSTRATION FOR THE REMEDIATION OF METALS CONTAMINATED SOILS NAVAL AIR WEAPONS STATION POINT MUGU, CALIFORNIA

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## ABSTRACT

Electrokinetics (EK) is an emerging remediation technology for the in situ removal of heavy metals, volatile organic compounds, and radionuclides from soils and sediments. Naval Air Weapons Station Point Mugu, California will host an EK technology demonstration. The demonstration will consist of installing and operating an EK system which is engineered to remove cadmium and chromium from former electroplating waste pits. The selected site is adjacent to and encroaches on an environmentally sensitive salt marsh area for federally protected wildlife. The electrokinetic process will be used to mobilize and extract heavy metals from the metals-contaminated soil by applying a low amperage direct current across an array of electrodes placed in the contaminated soil. The demonstration will focus on the effectiveness of the EK process for removing heavy metals from the tidal marsh area. The EK demonstration will be used to collect cost effective data necessary to address both the technical and economic feasibility of using this technology in areas where soils are porous, water is brackish, and the system is susceptible to tidal influences.

## 1.0 INTRODUCTION

The US Army Environmental Center (USAEC) is preparing to conduct a technology demonstration of EK as a method of removing heavy metals from soils. The demonstration is sponsored by the Environmental Security Technology Certification Program (ESTCP) and the Southwest Division, Naval Facilities Engineering Command (NAVFAC SOUTHWEST DIV). It will be conducted at the Naval Air Weapons Station (NAWS), Point Mugu, California, Site 5 - Old Area 6 Shops (the Site). The technology is being investigated for this ecologically sensitive area because of its potential to be a less invasive technology. A key element of the demonstration is to determine the costs associated with the use of the technology.

### 1.1 BACKGROUND

Located in Ventura County, California, NAWS Point Mugu Reservation comprises approximately 4,500 acres in the western portion of the Ventura Basin (Figures 1 and 2). The installation is approximately 50 miles northwest of Los Angeles and borders the western slopes of the Santa Monica Mountains.

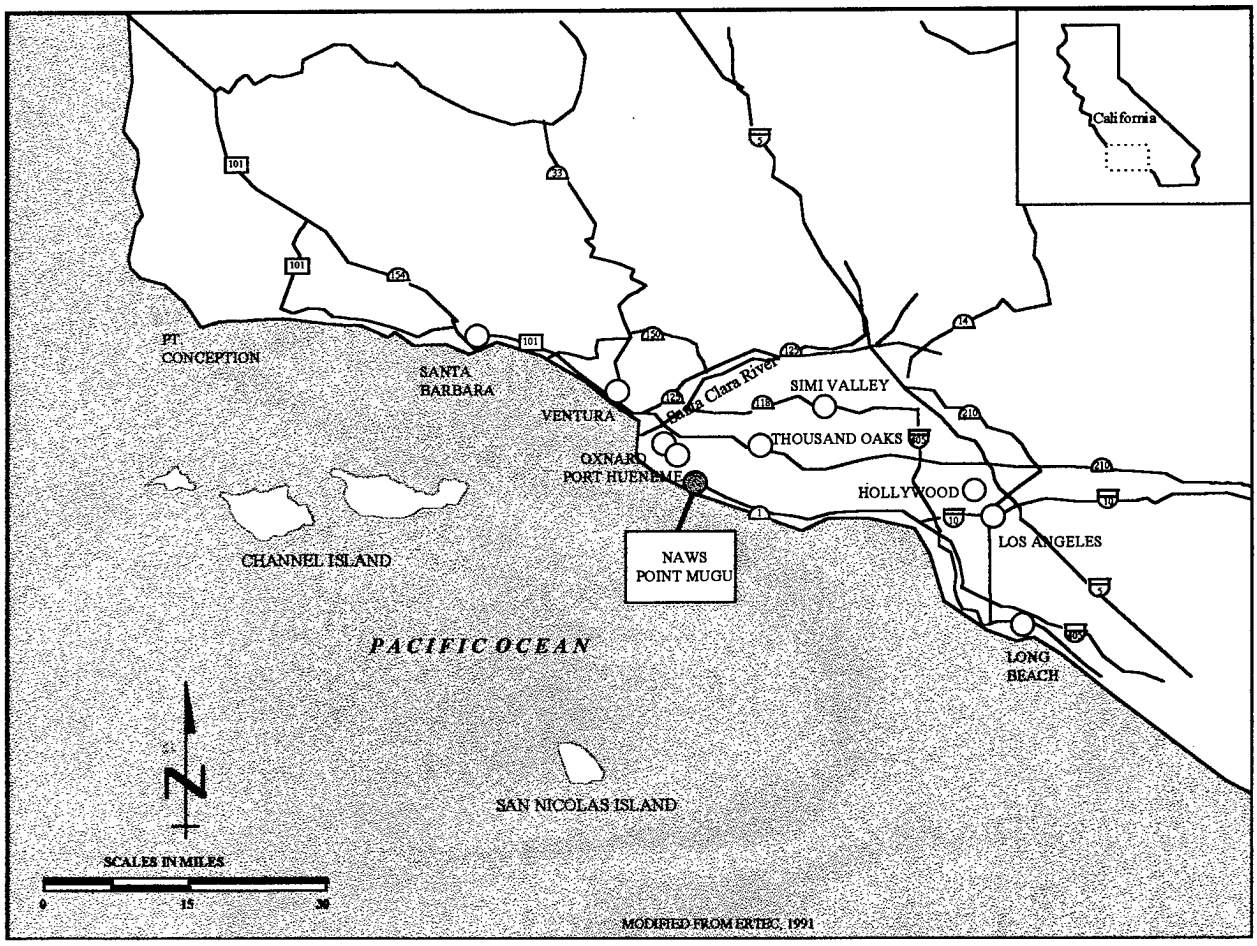



Figure 1: NAWS Point Mugu Regional Location Map

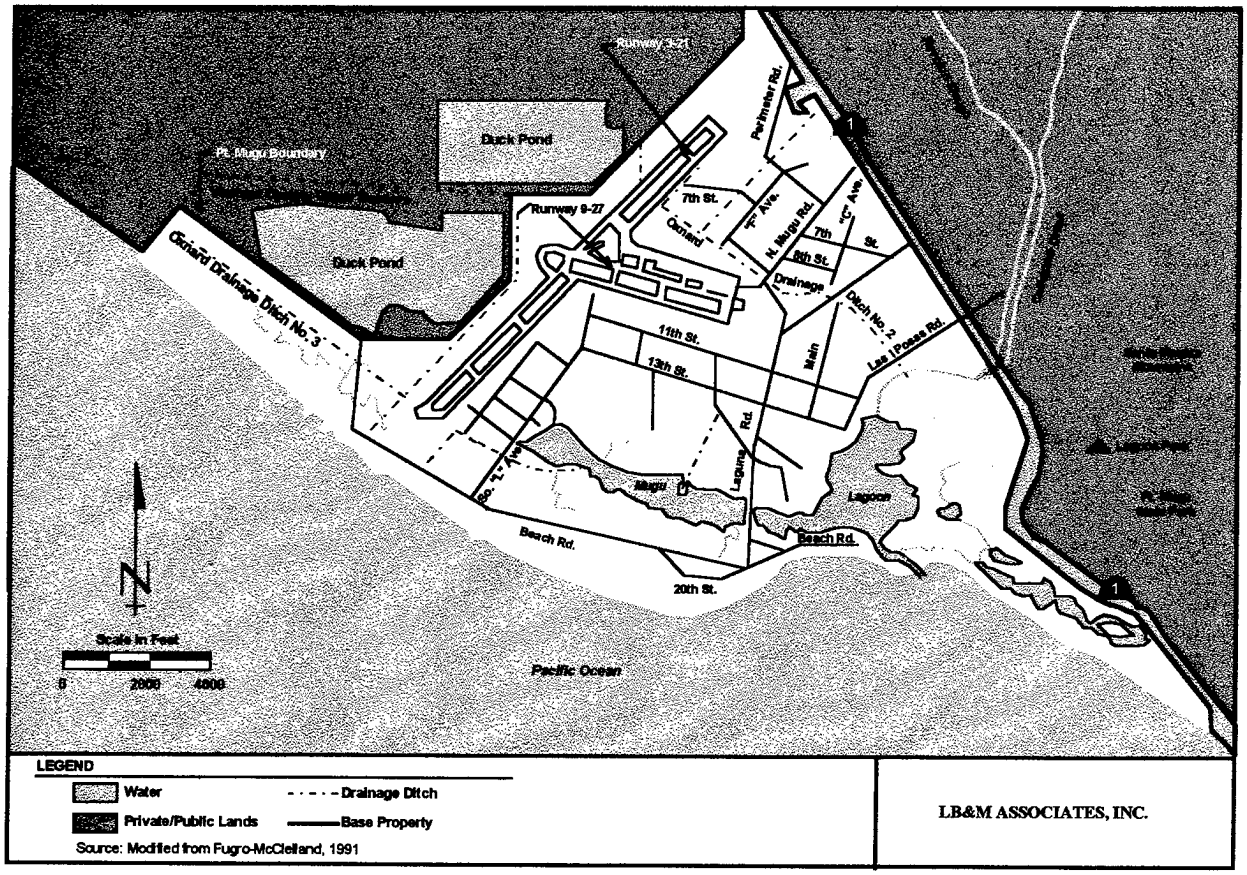



Figure 2: NAWS Point Mugu General Location Map

Past military and industrial operations at NAWS Point Mugu included electroplating and metal finishing processes, explosive and propellant manufacturing and use, and the use of lead-based paints. These operations resulted in large tracts of land being contaminated with metals (CBDCOM, 1996).

### 1.1.1 SITE 5 - OLD AREA 6 SHOPS

Site 5 is a large area where electroplating and metal finishing operations were conducted. The Old Area 6 Shops within Site 5 are located along Beach Road, just west of the south end of Laguna Road (Figure 3). The area of study is approximately 1/2 acre and includes two former waste pits located in the center of Site 5. The pits are unlined and were used between 1947 and 1978 to receive waste water discharge from electroplating and metal finishing activities. The largest waste generator in the area was the plating shop which reportedly disposed of an estimated 95 million gallons of plating rinsate between 1948 and 1965. Additionally, up to 60,000 gallons of waste photovoltaic fixer solution, and small quantities of organic solvents and rocket fuel were reportedly disposed of in the pits from the late 1940's until the early 1950's.

In 1988, surface soil and soil boring samples were collected from the Old Area 6 site and analyzed for a number of constituents. Soil samples collected from 10 surface and two boring points contained concentrations of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Only soil borings SB5-1 and SB5-2 and surface soil sample SS5-4 (Figure 3) are located about the waste

pits (PRC, 1993). All soil samples were analyzed for polychlorinated biphenyls (PCB) and pesticides. PCBs were only detected in a duplicate sample from one of the borings. Dichlorodiphenyltrichloroethane (DDT) and its metabolites were detected in only three surface samples. Metal analytes were detected in all locations. In 1994, the Navy authorized the emergency removal of 117 cubic yards of soil from the former waste pits.

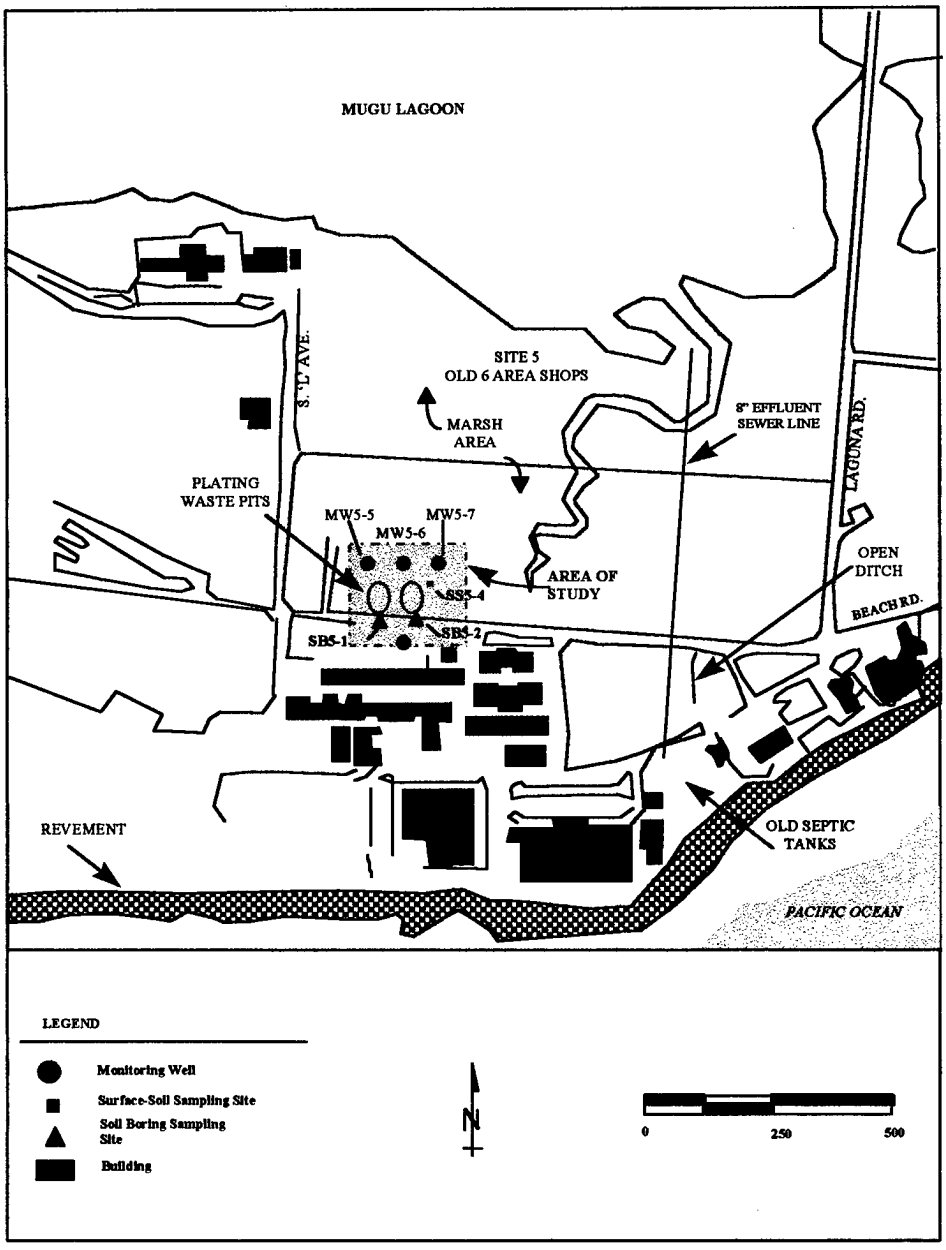



Figure 3: NAWS Point Mugu Site 5 Old Area 6 Shops Map

## 1.2 SUMMARY OF EXISTING SITE CONDITION

Following the 1994 emergency removal, surface sampling within the pits indicated that the levels of chromium and cadmium still exceeded allowable limits for California (22 CCR 66261.24). Because of the potential for damage to the marsh area, the state of California would not permit further excavation of soil from these two former waste pits for the purpose of remediation.

### 1.2.1 CONTAMINANTS OF CONCERN

The principal contaminants of concern at the Site are chromium, cadmium, copper, nickel and silver. Additional contaminants of potential concern include arsenic, beryllium, manganese, fluoride, tetrachloroethane, trichloroethene (TCE) and Aroclor-1260 (PCB trade name).

### 1.2.2 ENVIRONMENTAL CONSIDERATIONS

The Point Mugu area contains an extensive tidal marsh area, and is one of the larger remaining coastal wetlands in the US. The Site 5 characterization area is immediately adjacent to part of this coastal wetland. Impact on this area during field operations will be minimized through use of shortest paths to monitoring areas and keeping personnel intrusion to a minimum. The light-footed clapper rail, a federally and state listed endangered bird species, nests in this marsh area during the period 15 February - 15 September. Noisy or intrusive activities are not permitted during the nesting season. All activities must be cleared with the NAWS Point Mugu Wildlife and Natural Resources specialists charged with protecting this area.

# 2.0 TECHNOLOGY HISTORY

Initial observations of the electrokinetic phenomena are credited to Reuss (1809) who noted that water was transported through saturated soil when electric potential was applied (Mattson and Lindgren, 1994). Segall et al (1980) reported that electrokinetics may be applied to hazardous waste remediation from dewatering sludges rich in heavy metals. More recently, the Ukrainian government has been attempting to use electrokinetics in conjunction with hydraulic flushing to drive radionuclides deep into the soil profile to reclaim lost farming land from the Chernobyl accident (Mattson and Lindgren, 1994). Lageman et al (1989) has described field-scale removal of heavy metals from saturated soils in the Netherlands.

## 2.1 TECHNOLOGY DESCRIPTION

The electrokinetic process separates and extracts heavy metals from the metals-contaminated soil through the application of low amperage direct currents across an array of electrodes placed in the contaminated soil. The application of the electric field between the electrodes has several effects on the soil, water, and the contaminants:

- Electromigration;
- Electroosmosis;
- Changes in soil solution pH; and
- Electrophoresis.

### 2.1.1 ELECTROMIGRATION

Electromigration is the physical transport mechanism that is principally responsible for moving ions through water or moist soil by an applied direct current field (Kelsh, 1996). Ion migration rates will vary somewhat by species and generally conform to the transference measured for dilute aqueous solutions, but adsorption (the adherence of contaminants to soil particles) by soil can be influenced by contaminant characteristics such as speciation, ionic size, polarity, and concentration. This influence can be most severe for cations that are chelated by humic materials or react with soil anions to form precipitates, e.g., with carbonate or sulfide (Kelsh, 1996).

### 2.1.2 ELECTRO-OSMOSIS

Electro-osmosis is the movement of water through soil caused by an applied direct current field. It can be important in soils of low permeability, and has been used relatively successfully in sludge dewatering and soil stabilization (Kelsh, 1996). The effect is highly dependent on the nature of the electrical double layer of charge at the solid-liquid interface, with good transport observed for fine-grained sediments and soils (clays and silts) with high surface charges and low electrical conductivity (Kelsh, 1996).

### 2.1.3 CHANGES IN SOIL SOLUTION pH

pH changes occur under the influence of the current as a result of electrolysis reactions at the electrodes (USACEWES, 1997). Oxidation of water occurs at the anode and generates $H^+$ ions (Equation 1) (USACEWES, 1997). $H^+$ ions generate an acid front which slowly migrates to the cathode. In contrast, water is reduced at the cathode and generates $OH^-$ ions (Equation 2), which migrates as a base front towards the anode (USACEWES, 1997).

$$2H_2O - 4e^- \longrightarrow O_2 + 4H^+ \qquad \text{(Equation 1)}$$

$$4H_2O - 4e^- \longrightarrow 2H^+ + 4OH^- \qquad \text{(Equation 2)}$$

### 2.1.4 ELECTROPHORESIS

Electrophoresis refers to the movement of charged particles under the influence of the electric field (USACEWES, 1997). As with electromigration, positively charged particles migrate towards the cathode, and negatively charged particles migrate towards the anode. While electrophoretic transport occurs in soils, it is suspected to have less of an influence on contaminant treatment than the other phenomena discussed above (USACEWES, 1997).

## 2.2 ELECTROKINETIC EXPERIMENTATION

Electrokinetics has been tested predominantly in the laboratory with limited field trials. Laboratory (bench-scale) experiments employ small test cells with soils spiked with known amounts of contaminants or dyes that simulate contaminants and contaminant kinetics. Most of the present work has been bench-scale testing using soils and sediments from contaminated sites throughout the United States and Europe. Pilot-scale testing in the United States and Europe has been performed in clay-type soils and sediments contaminated with radionuclides and heavy metals.

Electrokinetic experiments at USACEWES using sand and gravel-type soils and sediments are still being performed in the bench- and isolated pilot-scale tests. The focus of the demonstration at NAWS Point Mugu is to validate the technology on sand and gravel sediments under the harsh conditions present in a saline tidal marsh environment.

## 3.0 GENERAL SYSTEM DESCRIPTION

NAWS Point Mugu was selected for a full scale electrokinetics demonstration to remove metal contaminants from the soil and groundwater. EK has the potential to remove metals, radionuclides, and chlorinated hydrocarbon contaminants from soil, sediment, mud, sludge, and marine dredging using electrochemical and electrokinetic processes to disassociate and then remove ionic contaminants.

### 3.1 SYSTEM DESIGN

The technology will involve the use of ceramic electrodes that are divided into cathode and anode arrays. Application of direct current (DC) or alternating current (AC) to the electrodes will initiate ion and water movement toward the electrodes (Figure 4). Metal ions, ammonium ions, hydronium ions and positively charged organic compounds move toward the cathode. Anions such as chloride, cyanide, fluoride, hydroxyl, nitrate, and negatively charged organic compounds move toward the anode. The electrodes are positioned inside permeable casings that are inserted into the waste material. After the annulus of each casing is filled with water, the current is turned on. The water passes from the anode casing into the waste and toward the cathode.

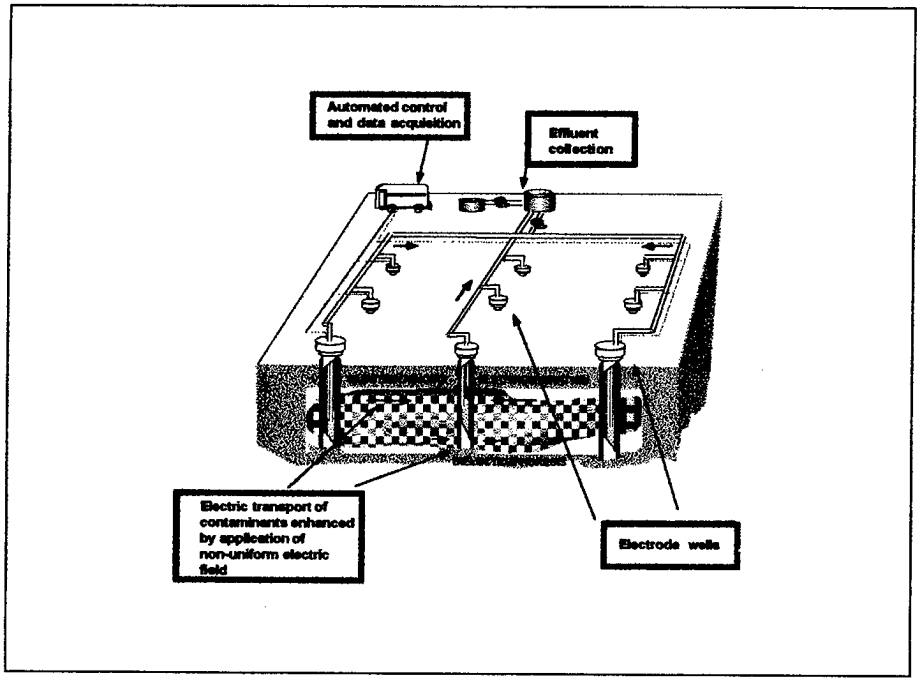



Figure 4: Electrokinetic Hardware Illustration

## 3.2 SYSTEM OPERATION

The technology demonstration will be conducted in two test cells at Site 5 - Area 6 on NAWS Point Mugu (Figure 5). Each test cell will be operated and monitored as separate units. The first test cell (TC #1) contains the two former waste pits and the surrounding berms (approximately 60 X 40 foot area). Contaminant depth to 11 feet was determined in this test cell from a 1997 Characterization Study done by LB&M Associates, Inc. (LB&M, 1997). An electrically non-conductive sheet pile barrier wall will be installed to a depth of 20 feet around the test cell to prevent uncontrolled movement of metal ions and contaminants outside of the test cell and to mitigate the effects of ground water flow and tidal effects within the test cell.

The second test cell (TC #2) will encompass a 30 X 100 foot area immediately north of TC #1 in the tidal marsh (Figure 5). Contaminant depth was determined to be 2 feet in this test cell (LB&M, 1997). No protective barrier will be installed around TC #2 and will be open to both ground water flow and tidal effects. Only after the EK system is shown to be operating within the confines of the TC #1 boundaries will the EK system in TC #2 be started.

Ground water and periodic soil samples will be taken to evaluate the dynamics of the technology process. Currently, ground water sampling events will occur twice monthly for 5 months; soil samples are scheduled for one per month throughout the life of the technology demonstration. Ground water samples will be taken from the three down gradient wells installed during the characterization phase of the project, and from the one existing up gradient well located north of Beach Road (Figure 5). Piezometers will be installed in the waste pits to monitor the performance of the technology; piezometers will also be placed outside of the barrier wall to detect breakthrough of target compounds.

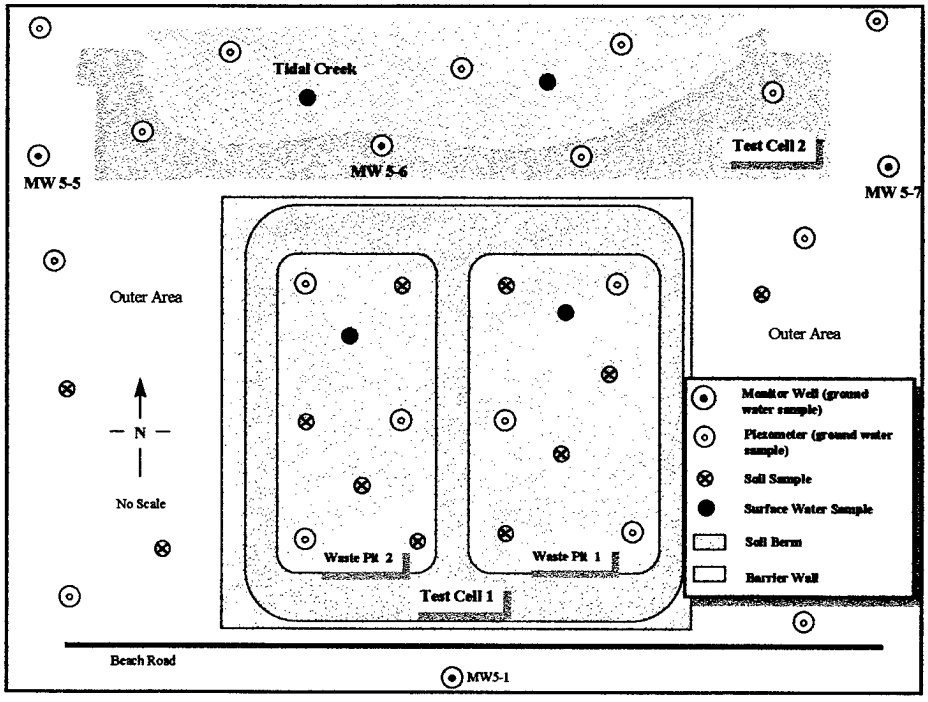



Figure 5: Site 5 Old Area 6 Shops Test Cell and Sample Locations

## 4.0 CONCLUSIONS

Since the technology has yet to be demonstration at NAWS Point Mugu, results and conclusions are not available. However, the objectives of the demonstration for the technology demonstration at NAWS Point Mugu will be as follows:

- To demonstrate the effectiveness of the EK technology in reducing chromium and cadmium concentrations at or below mandated California levels;
- To document the technology's performance effectiveness in removing contaminants in an environmentally hostile setting;
- To collect data and establish the cost-effectiveness of an emerging technology; and
- To test the technology in an environmentally sensitive area.

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# PINK WATER TREATMENT TECHNOLOGY EVALUATIONS

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## ABSTRACT

Processing operations at Army Ammunition Plants generate a waste stream known as pink water. In addition to photochemically-active TNT that colors the water, the waste stream may contain other energetic compounds, notably RDX and HMX[3]. Compositions of pink water are variable and dependent on materials processed, but typically the major constituent is about 200 ppm TNT.

Pollution minimization initiatives lead to a search for more effective pink water treatment technologies. This paper evaluates alternatives to the current activated carbon treatment of pink water, and describes five of the best technologies selected for further evaluation.

More than 27 different pink water treatment technologies were evaluated. Of these technologies, 18 passed preliminary screening for feasibility, with adequate data to support life-cycle cost analysis. Capital and operating cost data were obtained from published and unpublished sources, e.g., manufacturers, vendors, and technology owners. These data were used to calculate a total treatment cost for each process.

Technology evaluations were based on the following scored criteria, weighted as indicated: (1) total life-cycle cost, 35%, (2) effluent quality, 25%, (3) process operability, 15%, (4) flexibility, 10%, (5) health and safety, 10% and (6) commercial availability, 5%. Score weights reflected criteria importance and helped differentiate between candidate technologies.

Total scores, derived from the weighted selection criteria, ranked the best technologies for further bench-scale studies as follows:

| Technology | Mechanism |
|---|---|
| 1. GAC Thermophilic process | Biological destruction |
| 2. Fluidized bed bioreactor | Biological destruction |
| 3. Large aquatic plants | Biological destruction |
| 4. Fenton's chemistry | Chemical oxidation |
| 5. Electrolytic system | Electrolytic oxidation |

The first three processes clustered highest in overall score and could be differentiated from the bottom two. Process economics for all of these technologies were similar to the current GAC treatment costs. Quantification of effluent toxicity is a priority need for all future work. Bench-scale evaluations have been completed for all five selected technologies. Three technologies were found to meet the final selection criteria. It has been decided to proceed with testing GAC Thermophilic Process at the pilot scale with Fluidized Bed Bioreactor Process as a second choice, funds permitting.

## I. INTRODUCTION

### Origin and Composition of Pink Water

Army Ammunition Plants (AAPs) perform two functions that generate a waste stream known as pink water. These functions are (1) load, assemble, and pack (LAP), and (2) demilitarization of munitions. Associated housekeeping and processing operations create the waste water stream. Typical sources are wash down and wash out of munitions, and laundering workers' clothing. Pink water typically contains photochemically-active trinitrotoluene (TNT). The photoreactive products color the water. In addition to TNT, pink water usually contains cyclotrimethylene-trinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX). The composition of pink water is dependent on process materials and operations, and thus is highly variable. For purposes of discussion, the reference maximum value established in this work is 200 ppm dissolved energetic related materials.

## II. OBJECTIVE

The National Defense Center for Environmental Excellence (NDCEE), operated by Concurrent Technologies Corporation (*CTC*), was tasked by the U.S. Army Environmental Center (AEC), to identify and evaluate alternatives to the granular activated carbon (GAC) treatment of pink water. Currently, AAPs meet discharge requirements by using GAC to remove contaminants from pink water. The explosive-laden GAC, classified as a K045 hazardous waste, is then either regenerated for reuse or incinerated for disposal. More effective technologies are being sought to avoid the generation of this hazardous waste.

To meet these objectives, this task is divided into six phases:

- Phase 1 -- Process screening, evaluation, and down selection of identified technologies to the five most promising,
- Phase 2 -- Bench-scale testing of five technologies, and
- Phase 3 -- Planning for demonstration and implementation of up to three of the best technologies.
- Phases 4 -- Design, Fabricate, Install, and Debug Demonstration Plant(s)
- Phase 5 -- Operate and Evaluate the Demonstration Plant(s)
- Phase 6 -- Finalization and Follow-Through

## III. PHASE 1

### Objective: Evaluate Alternatives to Current Treatment Technology

The objective of Phase 1 was to evaluate alternatives to the current activated carbon treatment of pink water, and to select five of these technologies for further evaluation.

### Regulatory Requirements

The Phase 1 report identified regulatory issues that should be considered in the evaluation of alternative treatment technologies for pink water. The discharge of contaminated wastewater is a primary concern for AAPs. AAPs generating pink water must comply with all applicable wastewater effluent limitations before pink water wastes can be discharged. Current discharge limits for total nitrobodies at Crane, Kansas, Lonestar, and Milan AAPs were identified in the Phase 1 report. Also, because some observers have noted that discharge limitations for nitrobodies appear to be heading in the direction of the more stringent standards set for groundwater, the report identified the current U.S. EPA Drinking Water Health Advisories for chemicals found in the pink water. While these Health Advisories are not binding, state and local agencies often look to them for guidance when establishing groundwater treatment standards.

The treatment of pink water often results in the generation of hazardous waste. For this reason, applicable hazardous waste management and disposal requirements were also included. There has been a great deal of recent regulatory activity relating to the implementation of the Clean Air Act Amendments of 1990. These regulatory issues were also considered.

Alternative Technologies

The Phase 1 report evaluated potential methods for treating pink water, comparing these technologies against the standard of granular activated carbon (GAC) treatment followed by either off-site thermal destruction or regeneration. Alternative processes were classified into two categories, separation and destruction technologies.

The principal separation technologies evaluated were: 1) resin adsorption, 2) surfactant complexing, 3) liquid-liquid extraction, 4) powdered activated carbon, 5) carbon adsorption with regeneration, 6) ultrafiltration and 7) reverse osmosis. Because separation technologies require additional processing to destroy the contaminants, technologies that destroy these compounds directly are more advantageous. In addition, separation technologies may not be compliant with increasingly stringent environmental regulations. Therefore, separation technologies were not considered further.

The report reviewed more than 27 different destruction technologies relevant to pink water treatment. Of these technologies, 16 passed preliminary criteria screening for reasonableness, and had adequate data to permit life-cycle cost analysis. These technologies are listed without further comment in Table 1-2.

**Table 1-2 Destruction Technologies Reviewed**

| Technology | Technology | Technology |
|---|---|---|
| Base catalyzed hydrolysis | **Wet air oxidation (WAO)*** | Anaerobic expanded-bed GAC |
| **Advanced oxidation process, Vendor A*** | **Supercritical water oxidation (SCWO), Vendor A*** | **Anaerobic fluidized bed GAC*** |
| **Advanced oxidation process, Vendor, B*** | **Supercritical water oxidation (SCWO), Vendor B*** | Anaerobic-aerobic fluidized bed GAC |
| **Fenton's chemistry*** | **GAC with Supercritical water oxidation*** | **Aerobic GAC cycling batch thermophilic bioreactor*** |
| Mono-persulfate and $H_2O_2$ | **NitRem process*** | Aerobic rotary biological contactor |
| Ultraviolet and $TiO_2$ | Plasma arc technology | Algal turf scrubbing |
| Ultraviolet and $O_3$ | Gas-phase hydrogen reduction | Mixed microbial mats |
| **Electrolytic, Vendor A*** | **Electron beam, Vendor A*** | **Large aquatic plants (weeds)*** |
| **Electrolytic, Vendor B*** | **Electron beam, Vendor B*** | Enzymatic treatment |
| | | **Combinations, biological with carbon and WAO*** |

* Passed preliminary reasonableness screen and analyzed for life-cycle costs.

Evaluation Methods

The most promising separation and destruction technologies for pink water treatment were evaluated and compared. Process costs were compared on the basis of treating 20 gpm of pink water containing 200 ppm contaminants. Capital and operating cost data were obtained from published and unpublished sources, e.g. equipment manufacturers, vendors, and technology owners. Using these data, a total treatment cost was calculated for each process. Either direct or in situ destruction is recommended, rather than a separation process followed by secondary, off-site destruction.

Technology evaluations were based on the following criteria: 1) total life-cycle cost, 2) effluent quality, 3) process operability, 4) flexibility (technology mobility, ease of start up and shut down), 5) health and safety (process hazards analysis and safety review), and 6) commercial availability. The selection criteria were weighted to emphasize economics and effluent quality, 35% and 25%, respectively. Process operability was weighted 15%. Process flexibility and health and safety were weighted 10%. Commercial availability was weighted the least, namely 5%.

The most effective pink water destruction processes were judged to be:

1. Large aquatic plants (Biological destruction)
2. GAC thermophilic process (Biological destruction)
3. Fenton's chemistry (Chemical oxidation)
4. Electrolytic system (Electrolytic oxidation)
5. Fluidized bed bioreactor (Biological destruction).

The first three processes clustered in overall score and were differentiated from the bottom group. Process economics for all of these technologies were similar to the current GAC treatment costs. Quantification of effluent toxicity is a priority need for all future work.

A bench-scale test program to evaluate at least five technologies was recommended. The technologies were tested with identical pink water samples to enable relative performance comparisons. Both LAP plant pink water and demilitarization operations pink water were tested. Process testing was conducted by technology owners at one LAP plant. The permitting issues were addressed before the start of bench-scale testing. Effluent toxicity was a primary measurement for every technology. After bench scale testing, three of the five processes were selected for pilot-scale testing.

## IV. PHASE 2

The five technologies selected in Phase 1 for evaluation are shown in Table 1-2. The GAC thermophilic (biological) process is divided into two distinct processes. The "New" process, as the name suggests, requires construction of new carbon adsorption columns and associated plumbing. The "Retrofit" process proposes using existing equipment in place at AAPs. The retrofit process assumes that only minor additions to current equipment will be necessary.

**Table 1-2. Technologies Selected for Bench-Scale Studies**

| Order | Technology | Subcontractor |
|---|---|---|
| 1 | Fluidized Bed Bioreactor Process | University of Cincinnati |
| 2a | GAC Thermophilic (Biological) Process New | Center for Hazardous Materials Research (CHMR) |
| 2b | GAC Thermophilic (Biological) Process Retrofit | CHMR |
| 3 | Large Aquatic Plants (Biological) Treatment | Georgia Institute of Technology |
| 4 | Electrolytic (MIOX-UV) Process | Los Alamos Technical Associates |
| 5 | Fenton's Chemistry Process | Technotreat |

Pink water from both LAP and demilitarization operations were tested with each technology. LAP operation pink water was taken from McAlester Army Ammunition Plant (McAlester) and demilitarization operation pink water was taken from Milan Army Ammunition Plant (Milan). The five technologies were evaluated based on the same six criteria and weighting factors as in Phase 1, namely:

1. Economics
2. Effluent Quality (Toxicity)
3. Process Operability
4. Process Flexibility
5. Health and Safety
6. Technical Maturity

The results of the Phase 2 testing are shown in Table 1-3. The fluidized bed bioreactor process, GAC thermophilic (biological) process (new), and large aquatic plants (biological) treatment technologies effectively treated pink water. In addition, these technologies met minimum design criteria and have been recommended for pilot-scale evaluation. The electrolytic (mixed-oxidant-UV) and Fenton's chemistry technologies did not successfully meet the effluent quality, and the GAC thermophilic (biological) process (retrofit) is not technically proven. As a result, preliminary designs were not developed for these three technologies, and recommendations were made that these three technologies not be evaluated further.

**Table 1-3. Summary of Phase 2 Technology Evaluation**

| Technology | Passed Effluent Quality | Passed Other Criteria | Recommended for Pilot-Scale Testing |
|---|---|---|---|
| Fluidized Bed Bioreactor Process | √ | √ | √ |
| GAC Thermophilic (Biological) Process; New | √ | √ | √ |
| Large Aquatic Plants (Biological) Treatment | √ | √ | √ |
| Electrolytic (MIOX-UV) Process | Did Not Pass Minimum Evaluation Requirements | | |
| Fenton's Chemistry Process | Did Not Pass Minimum Evaluation Requirements | | |
| GAC Thermophilic (Biological) Process; Retrofit | Did Not Pass Minimum Evaluation Requirements | | |

√ signifies that a technology meets the requirements for the category.

As a result of the Phase 2 testing and evaluation, *CTC* recommended that the following three technologies should be investigated and tested on the pilot scale as funding permits. They demonstrated the ability to effectively treat pink water while remaining safe, cost effective, and technically viable. A pilot-scale study is required for full optimization as part of the implementation process.

- Fluidized Bed Bioreactor Process
- GAC Thermophilic (Biological) Process- New
- Large Aquatic Plants (Biological) Treatment

Because maximum production of pink water at Milan and McAlester does not exceed 20 gpm, *CTC*, AEC, and TACOM-ARDEC decided to downsize the pilot plant from 20 gpm to a flow rate of 1.5 to 2 gpm for Phase 3 (preparation of detailed engineering specifications). This lower flowrate would allow up to three technologies, if selected, to be installed and tested at either AAP, and would not exceed the total pink water flow capacity of the plant.

## V. PHASE 3

Objective

The objective of Phase 3 is to plan for the demonstration of up to three (3) technologies at the pilot scale level at an actual AAP. This Phase 3 report consists of: preliminary engineering specifications developed for each technology, a test and implementation plan, and a demonstration and validation proposal.

## VI. CONCLUSIONS

Twenty-seven technologies were identified and screened based on pre-determined criteria and weightings. As a result, five technologies were recommended for bench scale testing. Of these five technologies, three were deemed worthy of consideration for pilot scale testing. The three technologies are:

- GAC Thermophilic (Biological) Process- New
- Fluidized Bed Bioreactor Process
- Large Aquatic Plants (Biological) Treatment

## VII. RECOMMENDATIONS

A pilot scale test program for evaluating from one to three technologies is recommended. These technologies should be tested with identical pink water to ensure data comparability. Through a request for quotation (RFQ) process, a designer/builder should be contracted to build a plant for up to three technologies and test the pilot unit(s) before transporting to the selected Army Ammunition Plant (AAP) that has a supply of pink water to feed up to three pilot treatment units.

The demonstration site should be prepared by the AAP to accept the skid mounted plants. After installation, a demonstration study should be run for at least six (6) months. During these demonstrations, the influent and effluent waters will be tested at predetermined intervals. The samples will be sent for analyses to an independent, government-approved laboratory. Life cycle and implementation costs of up to three technologies will be developed after the plants have been built and operated at an AAP site. Upon conclusion of the demonstrations, a comparison will be made as to the most cost effective and environmentally safe technology that meets discharge goals. At least two technologies need to be tested at this pilot scale for comparison. This technology will then be transitioned to a second AAP for a similar test. After studying all of the test results and associated economic data, consideration should be given to selecting and installing a full sized treatment unit at an AAP that is interested in the selected technology.

## VIII. PHASES 4, 5, AND 6

It has been decided to proceed with testing the GAC Thermophilic Process at the pilot scale. Funds permitting, the Fluidized Bed Bioreactor will also be tested at the pilot scale. This project is scheduled to be completed by the end of year 2000.

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# THE SYNCHRONOUS SCANNING LUMINOSCOPE: A FIELD-PORTABLE, QUANTITATIVE, ANALYTICAL INSTRUMENT

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## ABSTRACT

The Synchronous Scanning Luminoscope (SSL) is a field-portable, synchronous, luminescence spectrofluorometer that was developed for on-site analysis of soil and ground water. The SSL is capable of quantitative analysis of polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs), total petroleum hydrocarbons (TPH), phenols, creosotes, and other fluorescent compounds. Soil and ground-water samples can be analyzed by the SSL in 15 minutes. Because of the speed of analysis and quantitative ability of the instrument, the SSL can reduce the cost of a site characterization up to 75% by eliminating the expenses for laboratory analyses and remobilizations. In addition, the SSL has the ability to 'fingerprint' or identify individual analytes or contaminant types in environmental samples. Recently, when tested on a Department of Defense (DoD) site, the SSL showed an excellent correlation when it was compared to the laboratory analyses for TPH, BTEX, and Napthalene. The following paper briefly describes the instrument and provides an example of a DoD site where the SSL was tested.

## INTRODUCTION

In the past several years, there has been an increased demand for cost-effective, field-portable analytical instrumentation in the environmental industry. While many qualitative methods have been introduced, few reliable quantitative instruments are available. To meet this demand, the SSL, a suitcase-sized spectrofluorometer was developed at Oak Ridge National Laboratory under U.S. Environmental Protection Agency (EPA) sponsorship. The SSL operation is based on luminescence principles and the characteristics of fluorescent high molecular-weight organic compounds. A brief description of the SSL and a comparison with laboratory analyses on a DoD site is provided.

## 1.0 INSTRUMENT DESCRIPTION

The SSL is a battery-operated, field-portable, quantitative analytical instrument which is controlled by a laptop computer. The SSL is enclosed in a suitcase which houses the optics and electronics necessary to perform the measurements. The optical components consist of a xenon flashlamp, two monochromators, focusing lenses, a sample holder, and a photomultiplier tube (Figure 1). The SSL weighs 30 lbs and has dimensions 16 in. x 16 in. x 9 in. A laptop computer provides SSL control, spectral display, quantification, and data storage.

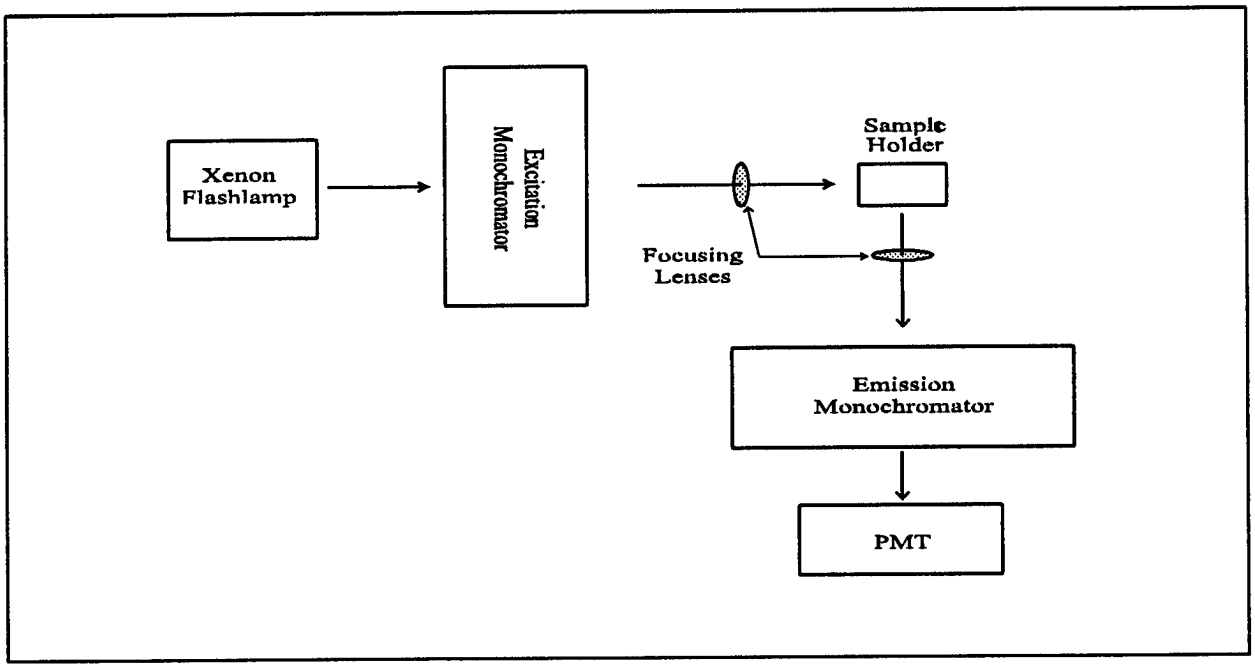



Figure 1. Optical components of the SSL.

## 2.0 THE SYNCHRONOUS SCAN

Unlike current portable filter fluorometers, the SSL incorporates two monochromators allowing synchronous wavelength scans. With a synchronous scan, both the excitation and emission monochromators are scanned simultaneously with a constant wavelength difference. The synchronous scan takes advantage of the overlap between the excitation spectra and emission spectra for a given compound, allowing for greater selectivity by producing simplified spectra in multicomponent analysis.

The SSL's synchronous spectrum is useful in two ways. First, the area under the spectrum is directly proportional to the concentration of contaminant within the sample. Second, an individual analyte or a contaminant type can be 'fingerprinted,' or identified by its spectral characteristics in an environmental sample. Therefore, the SSL is capable of performing quantitative and 'fingerprint' analyses of PAHs, PCBs, VOCs, TPH, phenols, and creosotes in soil and ground water.

## 3.0 ADVANTAGES OF THE SSL

In addition to its quantitative and fingerprinting abilities, the SSL has several other advantages. Samples do not pass through the SSL, instead they are placed in a cuvette which is in turn placed in the SSL for analysis. Therefore, heavy molecular-weight PAHs won't contaminate the instrument as is possible in a field-portable gas chromatograph. Another advantage is the low ppb range detection limit. Finally, soil and water samples can be analyzed in less than 15 minutes at a 75 % savings over conventional laboratory analysis. It is possible to analyze 20+ soil samples or 40+ water samples in one, eight hour shift. Based on the speed of analysis and quantitative ability of the SSL, on-site decisions can be made, eliminating laboratory costs and remobilizations typically required while waiting for laboratory results. For instance, the SSL can be used to find either non-detect samples or samples at an established regulatory limit in order to define a plume of contamination in one mobilization.

## 4.0 SAMPLE PREPARATION

### 4.1 Sample Preparation: Water

- Centrifuge or filter the sample
- Place in a cuvette
- Analyze

### 4.2 Sample Preparation: Soil

- Extract the contaminant from the soil into ethanol
- Centrifuge or filter the sample
- Place in a cuvette
- Analyze

## 5.0 TECHNOLOGICAL DEVELOPMENTS

The SSL is undergoing two new developments. The first is the capability of attaching a fiber optic probe for in-situ soil and ground-water analysis. The second is the ability to quantify benzene from a benzene, toluene, ethylbenzene, and xylene mixture. Both developments will be ready for field use by the Fall of 1997.

## 6.0 CASE HISTORY: A DEPARTMENT OF DEFENSE SITE

### 6.1 Site History

The site name and history is confidential and cannot be disclosed.

### 6.2 Fingerprinting

During the Summer of 1996, ESC in conjunction with International Technology Corporation, used the SSL on a Department of Defense site contaminated with JP4 jet fuel. The SSL was used on the first task of this project to 'fingerprint' ground-water samples. These ground-water samples were obtained both on and off-site using a direct-push technology. The assignment was to identify potential contaminant types (and then other potential sources) other than JP4, such as gasoline, diesel fuel, or hydraulic fluid. Each sample spectrum was compared to standard spectra of JP4, gasoline, diesel fuel, and hydraulic fluid to determine its source (Figures 2 and 3). The results showed that of 45 samples found to have contamination, 35 contained JP4, three showed some gasoline characteristics, four showed some diesel characteristics, and three were likely hydraulic fluid.

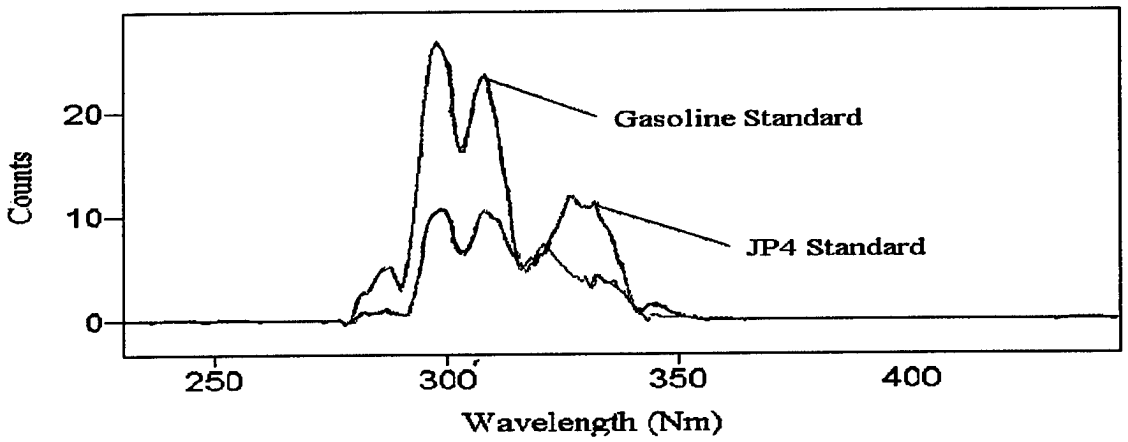



Figure 2. Standard spectra of JP4 and gasoline.

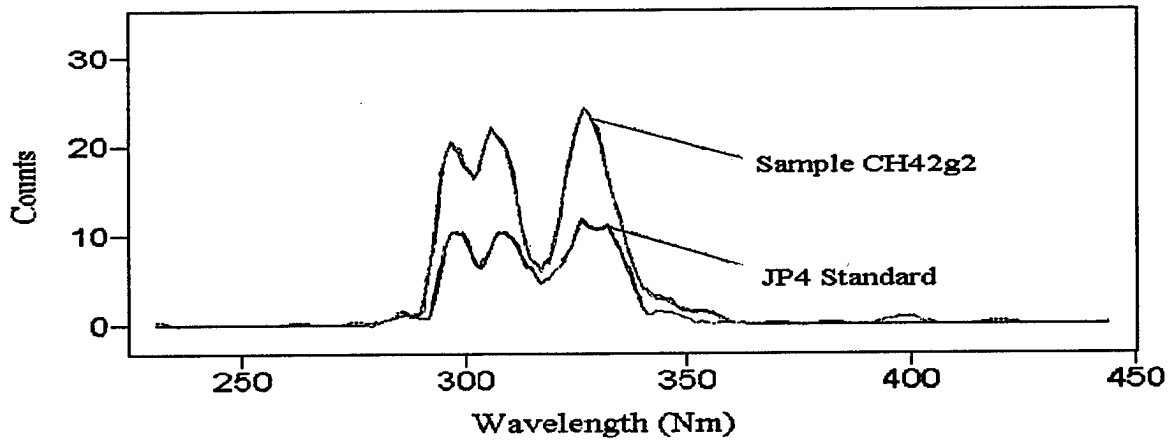



Figure 3. Comparison of sample CH42g2 to the JP4 standard.

6.3 Laboratory Comparison

During the second task of this project, the validity of the SSL's quantitative capability was determined by comparing results with an approved laboratory. For this task, 83 ground-water samples were analyzed by the laboratory and the SSL for TPH, benzene, toluene, ethylbenzene, xylene (BTEX), and Napthalene. These analyses correspond to EPA method numbers 8260 (BTEX), 3520/8015 (TPH-Diesel Range), and 8270 (PAH-Napthalene). The SSL values were taken from the area under three separate parts of the spectrum (Figures 4, 5, and 6). The SSL values and the laboratory values were plotted on an X-Y scatter plot and a best fit line

was applied to the graph. The closer the correlation coefficient of the best-fit line was to 1.0, the better the data correlated. The results showed an excellent correlation to laboratory analysis with correlation coefficients of 0.93 (TPH), 0.96 (Napthalene), and 0.90 (BTEX) (Figures 7, 8, and 9). As a result, the equation of the best-fit line can be used for subsequent SSL predictions of laboratory values. During the next sampling event, the SSL will be used exclusively to determine TPH, BTEX, and Napthalene concentrations. The results will be obtained in the field thus saving the client 75 % by avoiding conventional laboratory costs. This same method of calibrating the SSL to a site can be done with as few as five samples.

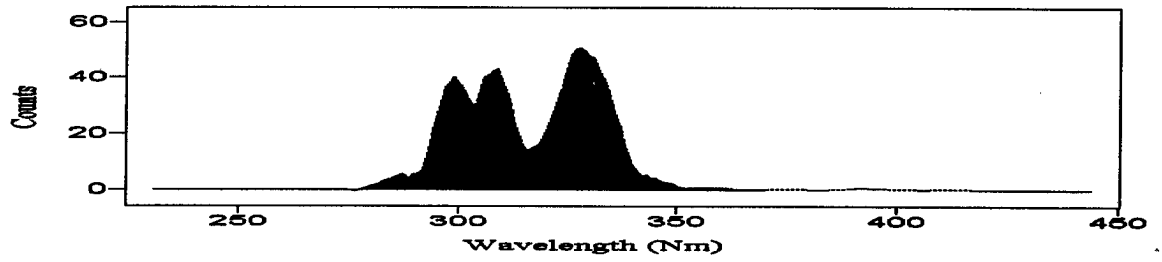



Figure 4. Area under the spectrum for TPH.

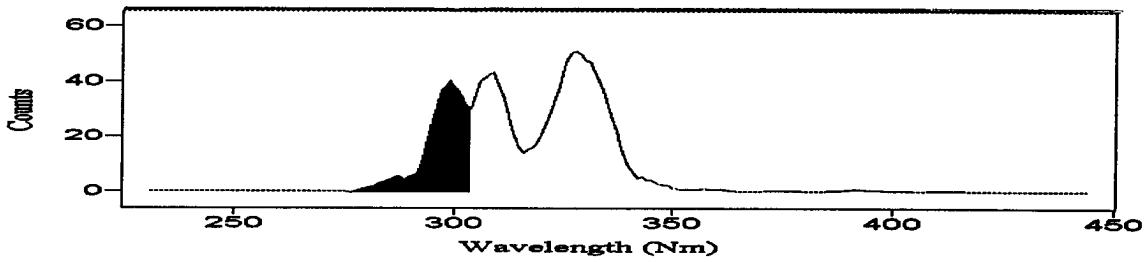



Figure 5. Area under the spectrum for BTEX.

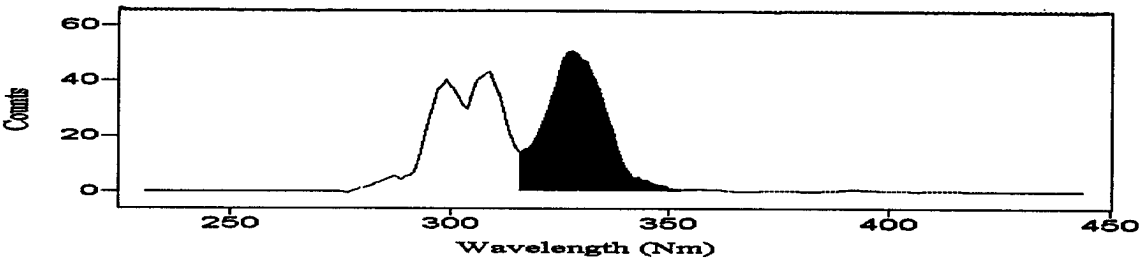



Figure 6. Area under the spectrum for Napthalene.

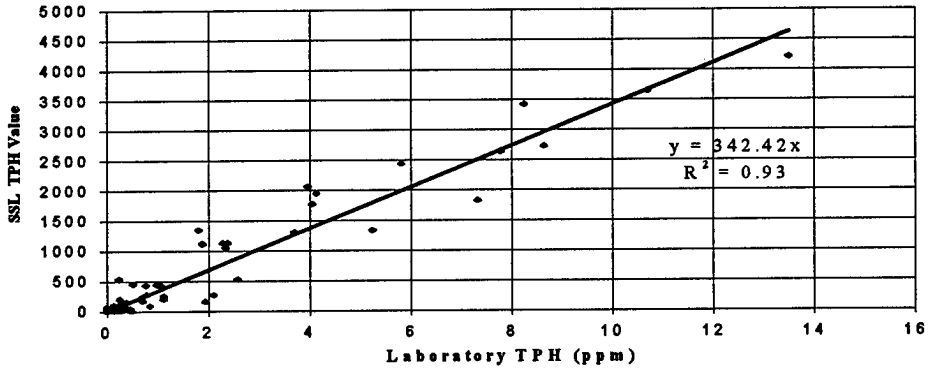



Figure 7. Comparison of SSL TPH values to laboratory TPH values.

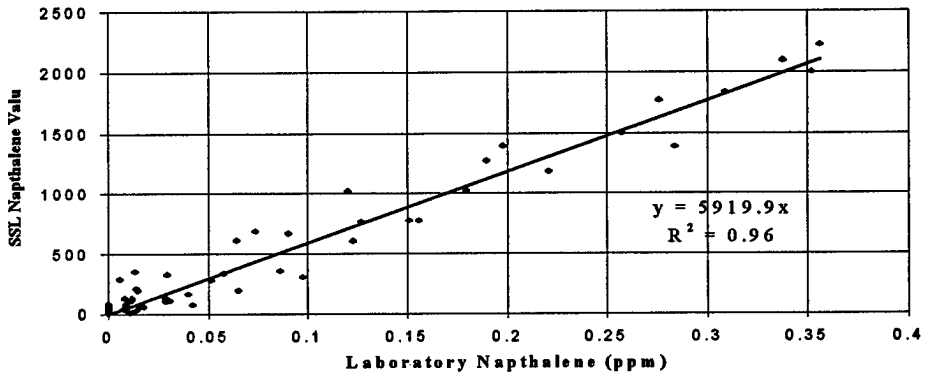



Figure 8. Comparison of SSL Napthalene values to laboratory Napthalene values.

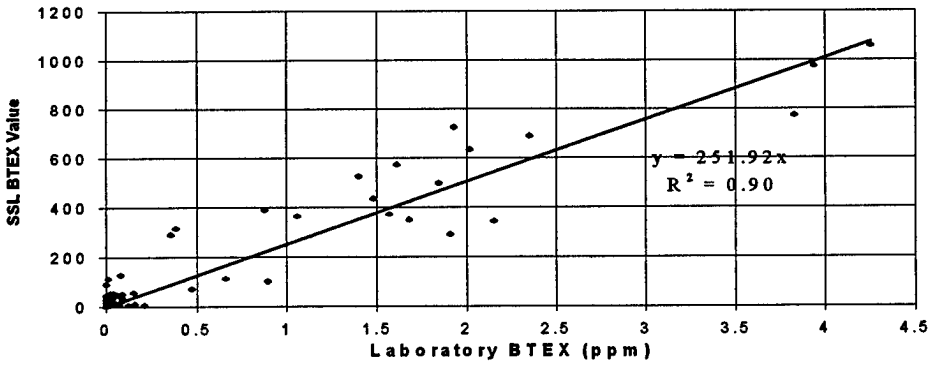



Figure 9. Comparison of SSL BTEX values to laboratory BTEX values.

## CONCLUSIONS

The Synchronous Scanning Luminoscope was developed for on-site, analysis of PAHs, PCBs, VOCs, TPH, phenols, creosotes, and other fluorescent compounds in the soil and ground water. Both soil and ground water samples can be analyzed in 15 minutes. With its speed and quantitative ability, the SSL can reduce site assessment costs by 75 %. In addition, the SSL has the ability to 'fingerprint' or identify individual analytes or contaminant types in environmental samples. On a recent DoD test site, the SSL showed an excellent correlation to laboratory results for 83 ground-water samples analyzed for BTEX, TPH, and Napthalene. The SSL fills the niche within the environmental industry for a cost and time-effective, field-portable, quantitative, analytical instrument.

# VALIDATION OF NATURAL ATTENUATION FOR REMEDIATION OF GROUNDWATER CONTAMINATED WITH FUEL HYDROCARBONS: THE COLUMBUS AFB FIELD EXPERIMENT

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## ABSTRACT:

A test release of a model weathered jet fuel is being used to study the geochemical and biochemical processes that contribute to natural attenuation of hydrocarbons in ground water. With well-known source conditions the initial development and stabilization of a dissolved plume can be studied. In this study a subsurface residual NAPL hydrocarbon mixture was emplaced in the well characterized and highly instrumented heterogeneous aquifer at the Columbus AFB, MS groundwater test site. The mixture, consisting of 1188.64 kg Decane (75.5%), Naphthalene (6.2%), p-Xylene (6.1%), Ethylbenzene (6.0%), Toluene (6.2%), Benzene (0.05%) and 2 Kg of KBr tracer were mixed with 30 $m^3$ of local aquifer material to create a 16 % residual phase and emplaced below the water table in the unconfined aquifer. Groundwater moving through the source zone under natural hydraulic gradients is dissolving the hydrocarbons and transporting the dissolved hydrocarbon and bromide plumes down-gradient.

Background sampling of groundwater and aquifer solids was done prior to source emplacement to characterize the site geochemistry and anaerobic and aerobic microbiology. The aquifer was initially oxygenated with DO levels ranging from 0.5 to 6.9 mg/L and generally <3.5mg/L. $NO_3$-N concentrations ranged from 0.02-0.3 mg/L, and sulfate concentrations ranged from 0.0 to 8.6 mg/L. Natural background dissolved $Fe^{2+}$ ranged up to 5.0 mg/L and was spatially variable. The solids which make up the aquifer contain are up to 1% iron by weight. Post emplacement sampling followed aquifer changes as the dissolved hydrocarbon plume developed and reached quasi-steady state. Continued sampling is characterizing changes in redox conditions and microbiological numbers and diversities associated with natural attenuation.

The dissolved hydrocarbon plume appears to have stabilized within a few weeks of emplacement, and aerobic and anaerobic microbial processes are limiting plume propagation to within 20 m down-gradient from the source. Dissolved oxygen depletion, the formation of $Fe^{2+}$

along with dissolved hydrogen and microbial evidence suggest that the plume has shifted from aerobic to anaerobic conditions near the source. Stable carbon isotope ratios confirm that microbial degradation is responsible for attenuation of the hydrocarbons. Observed natural attenuation can be correlated with microbial and geochemical changes in the aquifer.

## INTRODUCTION

Natural Attenuation (NA) is rapidly becoming the most commonly used method for remediation of groundwater contaminated with hydrocarbon fuels and solvents (Tremblay et al., 1995). In NA, subsurface physical, chemical and biological processes act to decrease groundwater contaminant concentrations down-gradient from a contaminant source. While there is extensive empirical evidence for NA (Mace et al., 1997; Rice et al., 1995; MacIntyre et al., 1993; Boggs et al., 1993), and protocols for implementing NA have been developed (Weidemeier et al., 1995; ASTM, 1996) the mechanisms and rates of these processes are not well understood. This ongoing study is designed to quantify these processes, and to show how they control plume development and hydrocarbon dilution, dispersion and degradation with a known source.

To simulate a subsurface release of fuel hydrocarbons, a model residual jet fuel mixture was emplaced below the water table in the highly heterogeneous surface aquifer at the Columbus AFB groundwater test site. The development of a dissolved hydrocarbon plume and the changes in chemical, physical and microbial conditions within the aquifer related to development and attenuation are being monitored. From this information mechanisms and rates of the individual processes which contribute to NA will be determined.

The objective of this project is to help solidify our understanding of the science underlying NA. Specifically, we plan to demonstrate quantitatively the natural attenuation process under known initial conditions, to define the contribution of chemical processes, aerobic and anaerobic microbial processes and geological surfaces to hydrocarbon degradation and to identify easily measured indicators of hydrocarbon degradation.

## MATERIALS and METHODS

### Source Emplacement

The hydrocarbon source was prepared by mixing of 1188.64 kg of decane (75.5%), naphthalene (6.2%), p-xylene (6.1%), ethylbenzene (6.0%) toluene (6.2%) and benzene (0.05%) with 30 $m^3$ of clean native aquifer material (Table 1). Two kg of KBr was added as a conservative tracer. Sheet piling was driven through the surfacial aquifer to an underlying clay layer to enclose an area 1 m wide by 15 long. Dewatering wells were installed around the enclosure and groundwater lowered below the source emplacement area. The aquifer materials within the enclosure were then excavated. The hydrocarbon-solid mixture was poured into the enclosure, and the trench backfilled with native material. The source zone formed was 1m thick, 1.7 m high and 15 m long approximately 6 m below the ground surface. After backfilling, the sheet pile was removed exposing the source to natural hydraulic conditions and gradients in the aquifer. The natural hydraulic gradient in the aquifer caused groundwater to flow through the source material forming a dissolved bromide and hydrocarbon plume.

Sampling Groundwater and Aquifer Solids

An existing network of more than 300 multilevel sampling wells representing 6000+ sampling points is used to collect groundwater for analysis. Additional wells are being installed as needed. Aquifer solids are collected by split spoon coring up-gradient, within and down-gradient from the plume. Groundwater and aquifer solids were sampled prior to source emplacement to measure background conditions in the aquifer. Since source emplacement, samples have been collected approximately quarterly. Groundwater is analyzed for dissolved hydrocarbons; bromide; electron acceptors including dissolved oxygen, nitrate, nitrite and sulfate; and microbial degradation reaction products including $CO_2$, dissolved hydrogen, methane, ferrous iron; and stable carbon isotopes. Aquifer solids are analyzed for aerobic microbial population and degradation activity; anaerobic microbial activity and bulk and iron mineralogy.

## RESULTS TO DATE

Sampling of groundwater and aquifer solids prior to source emplacement showed that the aquifer was initially oxygenated with DO levels ranging from 0.5 to 6.9 mg/L and generally <3.5 mg/L. $NO_3$-N ranged from 0.02-0.3 mg/L. Sulfate concentrations ranged from 0.0 to 8.6 mg/L, and dissolved $Fe^{2+}$ ranged up to 5.0 mg/L. Dissolved inorganic carbon, primarily as $CO_2$, was initially about 75 mg/L and $\delta^{13}C$ averaged 19.7. The natural distribution of dissolved oxygen and $Fe^{2+}$ varied spatially throughout the site, and zones of anoxic, iron reducing conditions were observed within the aquifer. Aquifer solids are up to 1% total iron by weight, mostly as goethite with some hematite and ferrihydrite. Amorphous iron oxides were not observed.

Post emplacement sampling followed aquifer changes as the dissolved hydrocarbon plume developed and approached steady state. The total mass of decane in the source has not changed significantly. The mass of benzene, xylene, toluene, ethylbenzene and naphthalene in the source has decreased by about one third to one half. The source pore water is saturated for all hydrocarbon compounds (Figure 1). The total mass of hydrocarbons in the dissolved plume initially increased with time. After about 10 months the mass of the hydrocarbons appears to has stabilized with a total dissolved mass of about 700 g in the plume. The mass of the individual compounds generally increased with some fluctuation in the mass of naphthalene and ethylbenzene (Figure 2).

Bromide distribution showed that groundwater flow rates in the aquifer were on the order of 0.5 m/day, consistent with rates measured in previous studies at this site (MacIntyre et al., 1993). The extent of the dissolved hydrocarbon plume appears to have stabilized within a few weeks of emplacement. Natural Attenuation processes are limiting the hydrocarbon plume to within 15 meters down-gradient from the source. Mono-aromatic hydrocarbons in the plume have stabilized with the leading edge at about 12 m down-gradient. The distribution of toluene, as shown in Figure 3, is typical of the distribution of mono-aromatic compounds in the plume. Naphthalene concentration was initially limited to the region nearest the source due to rapid degradation. In later samples naphthalene in the plume is seen to extended to the limit of the plume (Figure 4).

A zone of anaerobic conditions has developed immediately down-gradient from the source area (Figure 5). $Fe^{+2}$ concentrations greater then 10 mg/L occur within this zone (Figure 6) suggesting iron reducing conditions have developed. This increase in dissolved $Fe^{+2}$ along with

# Table 1. Hydrocarbon Source Mixture

| Compound | Mass Added | % |
|---|---|---|
| Decane | 897.40 kg | 75.5 |
| Naphthalene | 73.12 | 6.2 |
| p-Xylene | 72.54 | 6.1 |
| Ethylbenzene | 71.85 | 6.0 |
| Toluene | 73.66 | 6.2 |
| Benzene | 0.58 | 0.05 |
| Total | 1188.64 | |

2.0 kg KBr added as conservative tracer

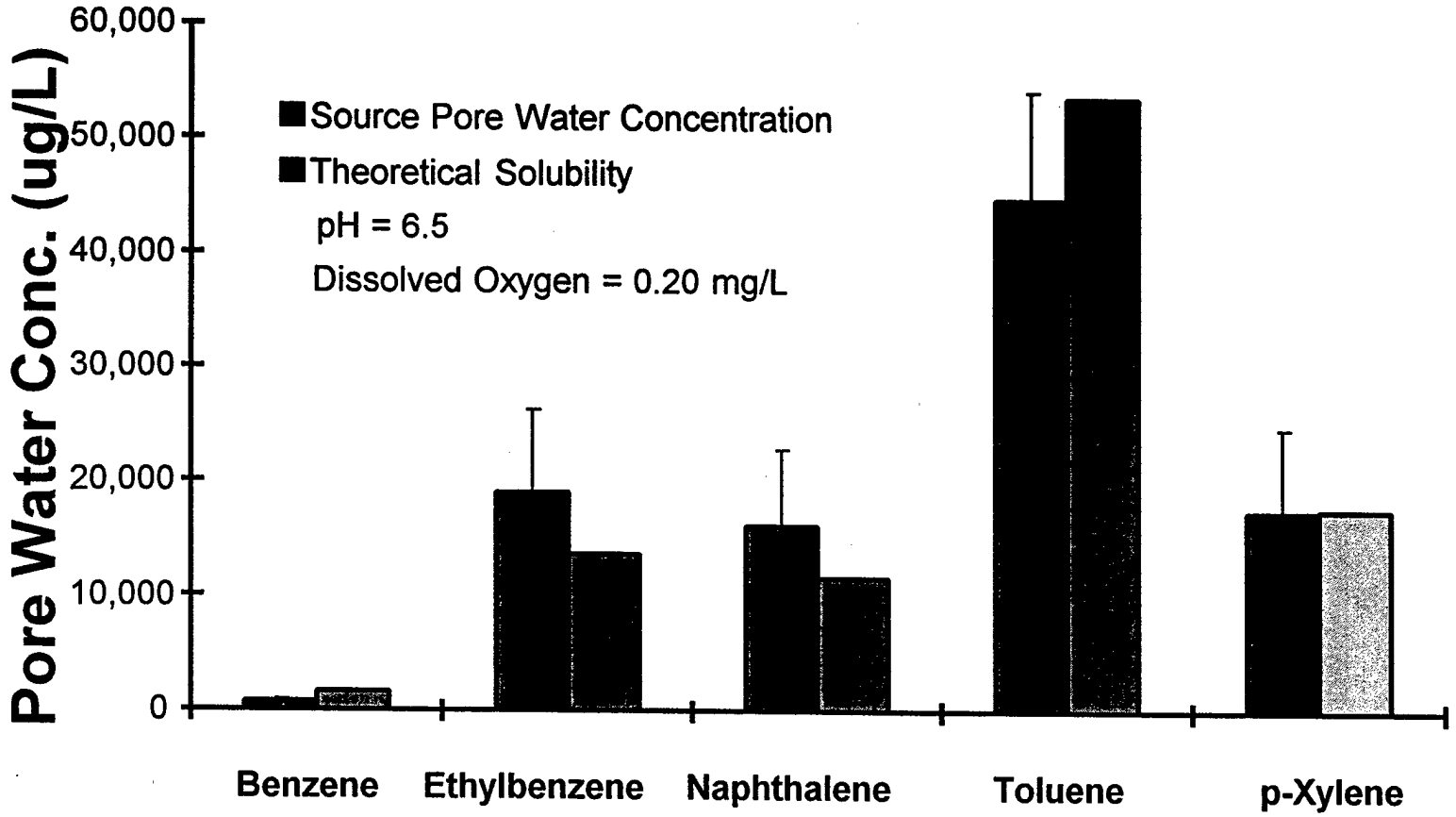



**Figure 1. Hydrocarbon Source Porewater Concentration 16 months after emplacement**

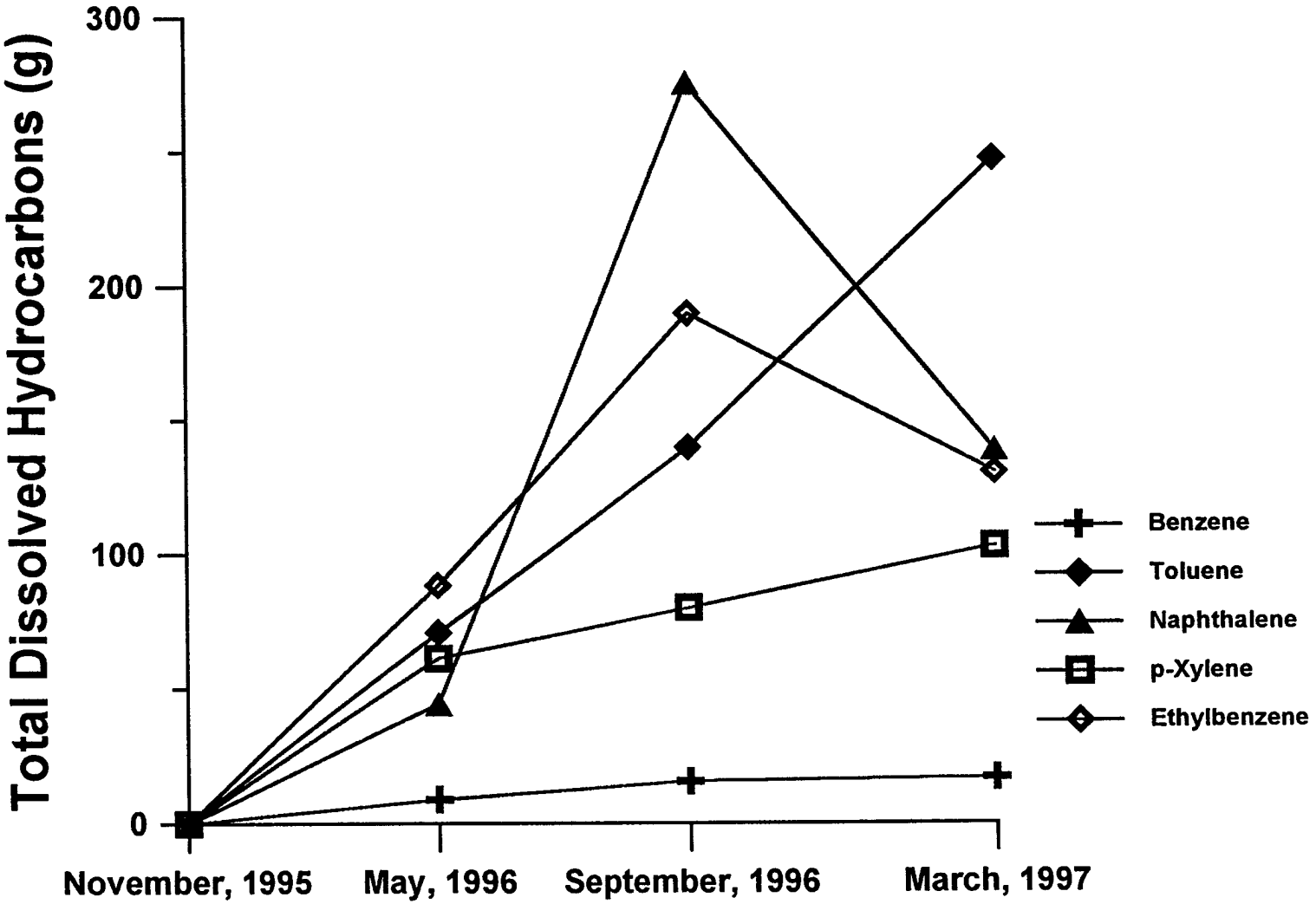



**Figure 2. Mass of Dissolved Hydrocarbons in Plume**

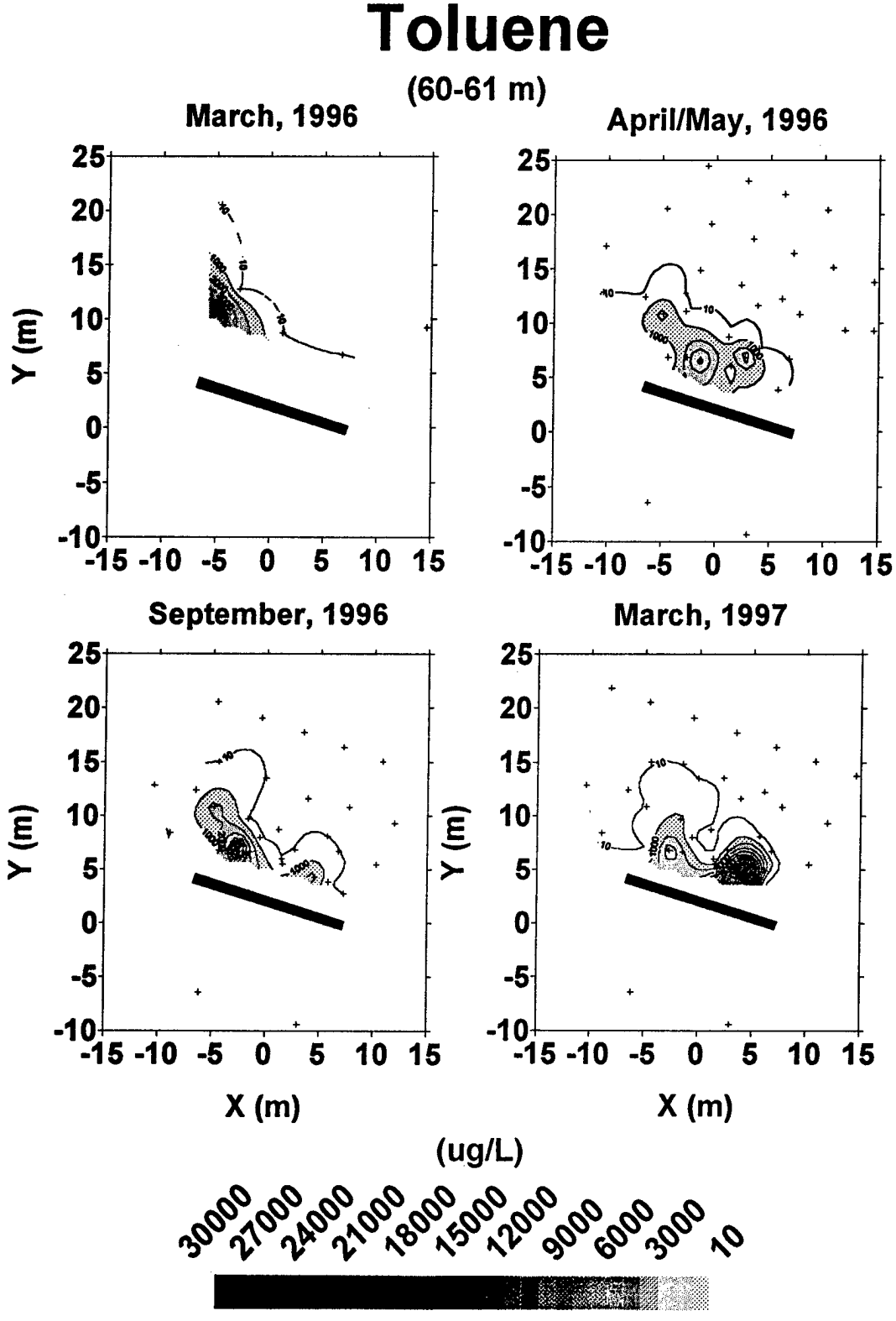



**Figure 3. Dissolved Tolune Plume**

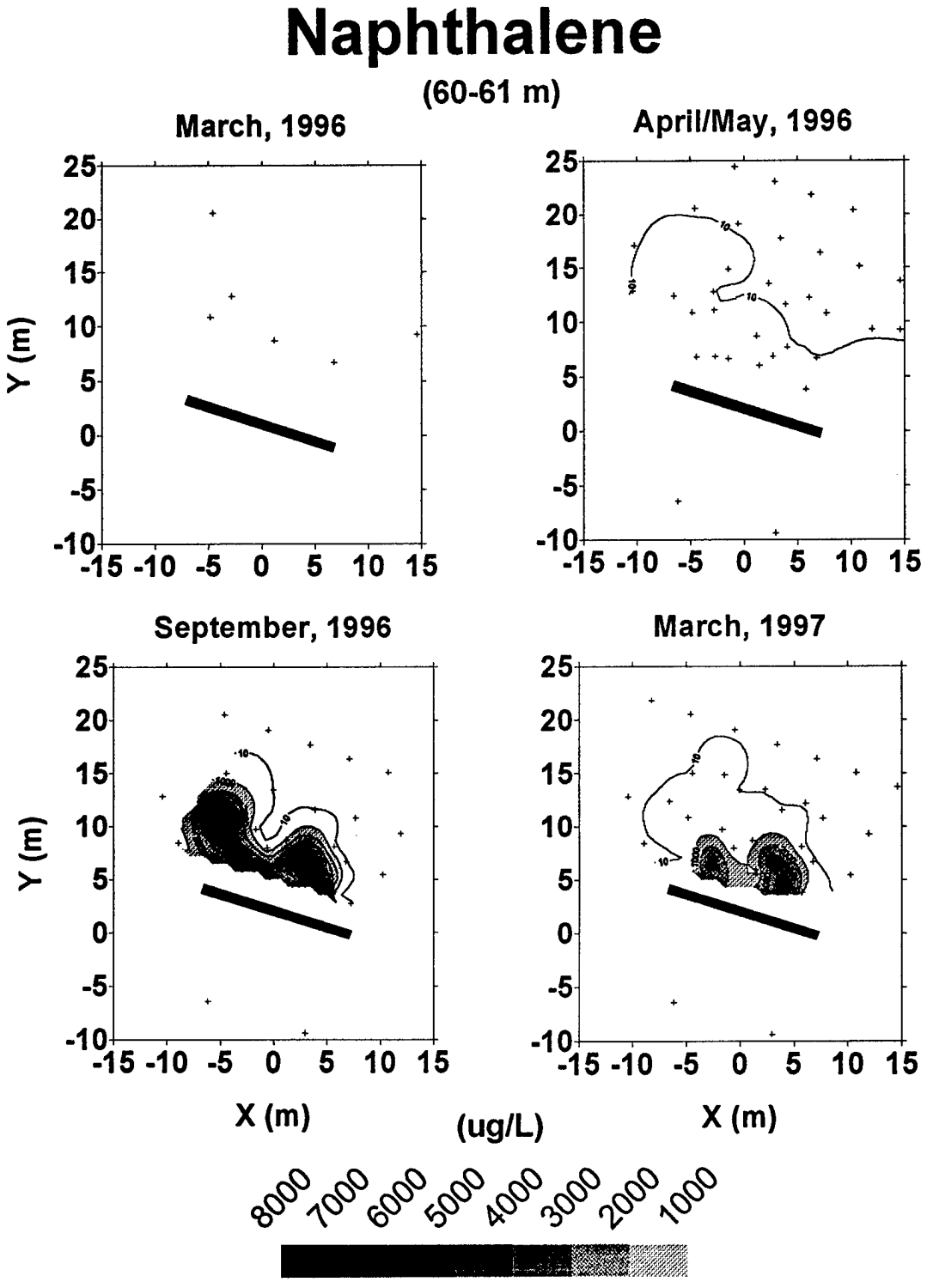



Figure 4. Dissolved Naphthalene

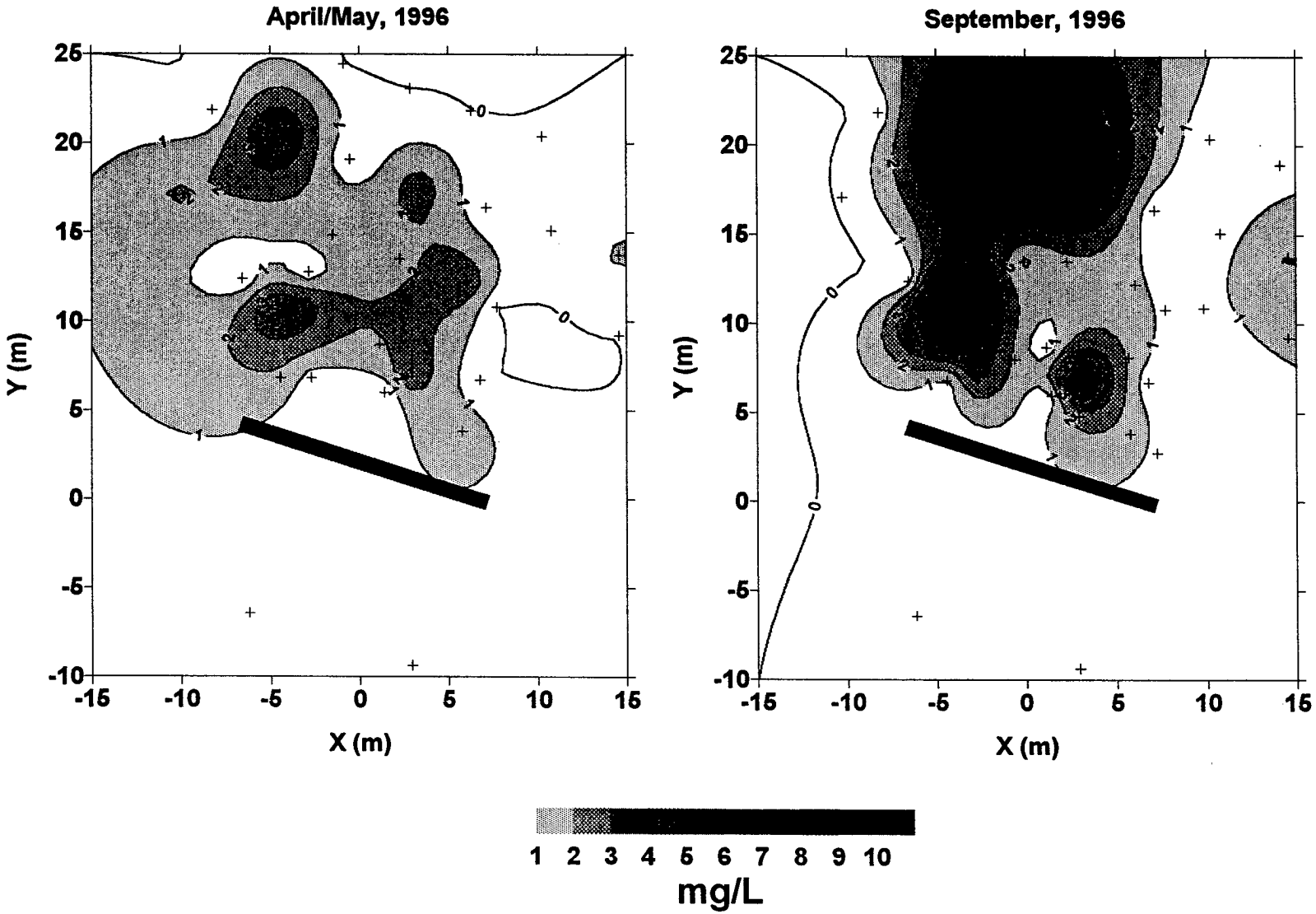



**Figure 5. Dissolved $Fe^{2+}$ Concentration Down-gradient from Source Area**

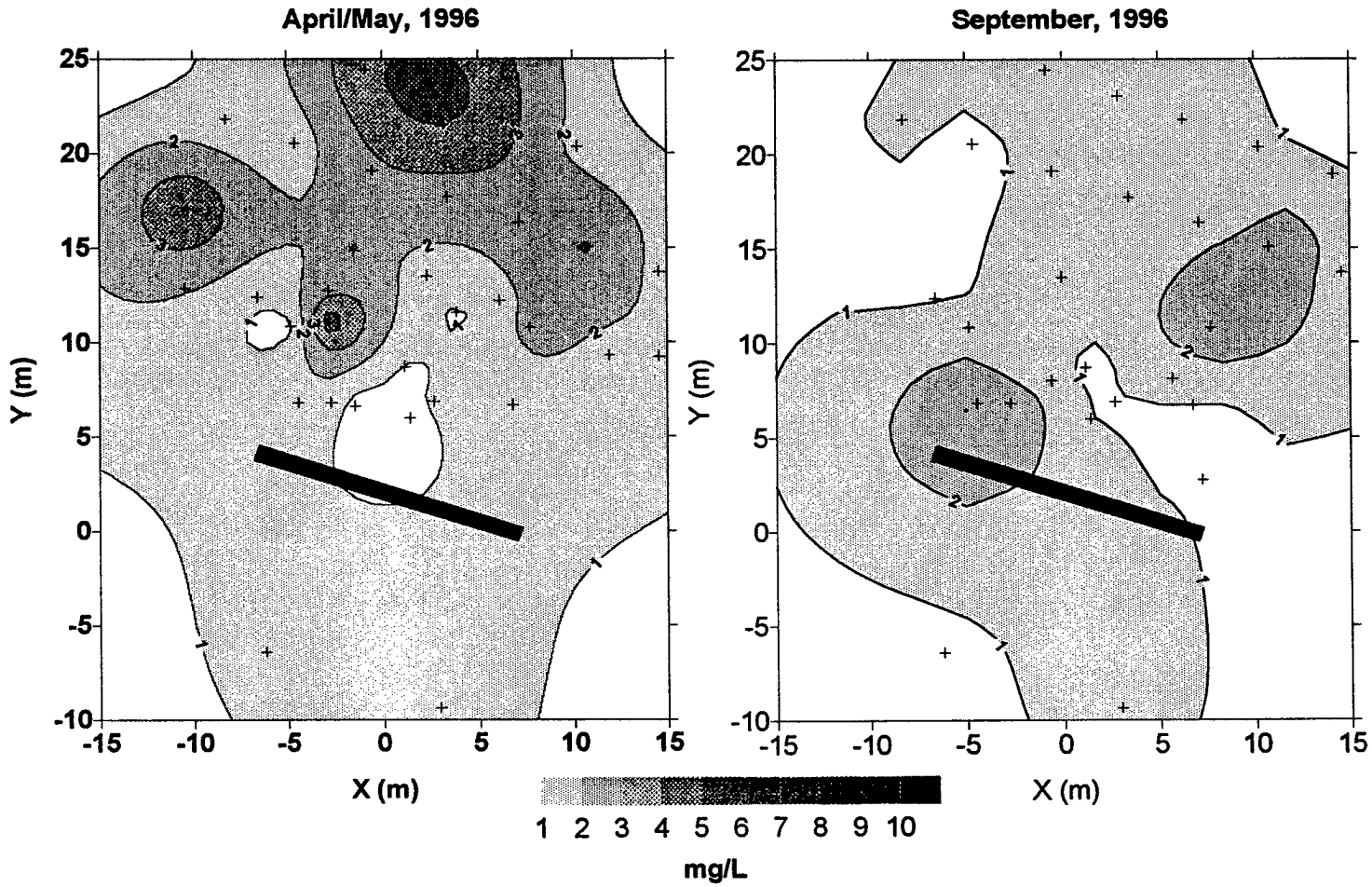



**Figure 6. Dissolved Oxygen Concentration Down-Gradient from Source**

the observed increased naphthalene stability is consistent with a shift from aerobic to anaerobic microbial processes. Aerobic microbial activity down-gradient from the source parallels the hydrocarbon distribution. Populations capable of degrading all of the hydrocarbon compounds were found in solids from cores within the plume. In 24 hour mineralization studies aquifer solids from cores immediately in front of the leading edge of the hydrocarbon plume had the highest aerobic degradation activity. In solids from the center of the plume aerobic degraders were present but not as active. Genetic probes have shown that measurable changes in the degradative populations were associated with changing conditions within the plume.

Anaerobic microbial populations were initially present in the aquifer. Changes in populations and activity due to the introduction of the hydrocarbons are not separable from background at this point. Attempts to delineate zones of redox conditions corresponding to zones of different electron acceptor utilization based on dissolved hydrogen concentration have not been successful.

Methane concentrations in the plume are significantly above background with levels in the interior, anaerobic portion of the plume are as high as 1.6 mg/L. Carbon dioxide concentrations in the plume have increased to as high as 180 mg/L. Carbon stable isotope ratios in aqueous $CO_2$ and in soil gas above the plume are lighter than those measured in natural background ($\delta^{13}C$ = -19 to - 20) and in areas unaffected by the source. $\delta^{13}C$ in the plume groundwater are as low as -21 confirming that the hydrocarbon compounds ($\delta^{13}C$ = -26 to-29) are being degraded.

## CONCLUSIONS

Analysis of plume movement and aquifer conditions demonstrate that Natural Attenuation is limiting the extent of the hydrocarbon plume. Geochemical and microbial indicators show that initially aerobic processes controlled the fate of the compounds. The system has developed an anaerobic zone in the center of the plume and anaerobic microbial processes are becoming more important. Changes in plume composition, such as greater naphthalene concentration, confirm a shift from aerobic to anaerobic microbial processes is occurring. Increased levels of $Fe^{+2}$ along with low dissolved oxygen suggest that the plume has become iron reducing. This is not confirmed by dissolved hydrogen concentrations, possibly because of the heterogeneous nature of the sediments which make up the aquifer.

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# VITRIFICATION AND REMOVAL OF LEAD-BASED PAINT FROM STEEL STRUCTURES USING THERMAL SPRAY

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## ABSTRACT

Lead-based paints and primers have been used to protect steel structures from corrosion. Structures in the DoD that commonly contain lead-based paint include bridges, catwalks, towers, water storage tanks, steel doors, hangar doors, trusses, exterior railings, steel post, poles, stairways, cranes, pontoons and boiler plant structural members. In addition to DoD facilities infrastructure, ship structures have also been coated with lead pigmented coatings. Paint removal is required before new paint can be applied especially if the old paint is peeling. Abrasive blasting is currently used to remove old lead-based paint. During abrasive blasting, Federal, state and local environmental requirements mandate the use of a containment structures to prevent contamination of air, soil, or water. The U.S. Occupational Safety and Health Administration (OSHA) requires the use of engineering controls methods when abating lead-based paint in construction. The thermal spray vitrification process to remove hazardous lead-based paint consists of thermal spraying a molten glass onto the painted surface from which the deteriorating paint is to be removed. Dried glass powder is melted in the high temperature flame of the thermal spay torch. When the glass strikes the substrate it is molten and reacts with the paint on the substrate. The organic components of the paint are pyrolyzed, while the lead ions are trapped on the glass surface. Quenching stresses in the glass cause the glass to crack and spall off the substrate. The resulting glass was collected and analyzed for lead content using the Toxicity Characteristic Leaching Procedure (TCLP). The results showed that the lead absorbed into the glass was partially vitrified during the thermal spray processing and the vitrification was driven to completion by remelting the deposits. During laboratory testing, airborne lead emission were below the OSHA action limit for personal exposure. Following the necessary monitoring, the advantages of the thermal spray vitrification process are the resulting savings from elimination of containment and increased worker productivity due to reduced worker protection requirements. Demonstrations of the thermal spray vitrification process are planned to remove lead-based paint from an Army bridge, an aircraft hangar and from ship structures.

## 1. INTRODUCTION

Red lead primer has been used on many steel structures to control corrosion. When old paint starts to peel, removal of the paint may be required prior to repainting. The most common method of removing paint from steel structures has been the use of a dense abrasive media as blasting grit. Often cheap material such as silica sand or coal slag can be used as highly effective blasting media. A collateral benefit of abrasive blasting is its tendency to roughen the surface, creating an anchor profile for

repainting the structure. While the method is highly effective and the procedure itself is cost-effective, abrasive blasting creates large amounts of hazardous dust and waste material. Most of the waste material consists of large chips of the coating and piles of spent blasting media, which must be removed from the site. However, a significant portion of the debris consists of airborne dust and small particles. In removal of lead-based paint systems, the presence of lead particles in the airborne dust and waste media creates an environmental risk that must be contained. The U.S. Environmental Protection Agency (EPA) requirements mandate the use of containment structures to prevent the contamination of air, soil or water. Inside the containment structures, stringent requirements must be met to protect the workers from the high concentration of lead dust[1].

Regulations that require the monitoring of exposed workers and the release of hazardous materials have greatly increased the cost of lead-based paint removal. The cost is dramatically escalated when the waste lead-based paint and removal media are determined to be hazardous waste by the EPA's Toxicity Characteristic Leaching Procedure (TCLP)[2]. When TCLP reveals that concentrations of hazardous species in lead-based paint removal wastes exceed the regulatory limits, a licensed special waste hauler must be employed to remove the material from the site and deliver it to a licensed hazardous material disposal site. Even if the waste material ultimately is found to be nonhazardous, the administrative and testing requirements add substantial costs to the overall project. Furthermore, the costs of worker health and environmental monitoring also dramatically raise the cost of LBP removal sometimes exceeding the cost of disposal by a factor of five[3]. Innovative technologies that could effectively remove LBP while rendering the wastes nonhazardous would be highly beneficial. One excellent candidate technology is thermal spray vitrification[4].

Vitrification is the process of heating constituent starting materials (oxides, carbonates, etc.) such that upon cooling, an amorphous noncrystalline glass is obtained. Vitrification technology has proven to provide superior leach resistance compared to other available forms of waste treatment. Because of the environmental stability of the glass based waste form, vitrification has been selected to be the Best Demonstrated Available Technology (BDAT) for high level nuclear waste and is being considered for treatment of other hazardous waste[5]. In the thermal spray vitrification process, molten glass is applied to a painted surface; the lead components of the paint react with the hot glass and are immobilized in the glass upon cooling. This process was patented by Kumar and Patreanu and assigned to the U.S. Army[6].

## 2. THERMAL SPRAY VITRIFICATION PROCESS DESCRIPTION

The principal equipment for the thermal spray vitrification process consists of a commercially available thermal spray torch, powder feeder, gas manifold, flow controllers, as well as compressed air, fuel and oxygen sources. These are connected with a series of gas and powder feed lines. A schematic of the thermal spray system is shown in Figure 1. The pressure of the oxygen and acetylene is controlled by the manifold and flow controllers. These are connected by separate gas feed lines to the thermal spray gun where they are combined. The glass powder is mixed with compressed air in the powder feeder and the air is used to transport it to the thermal spray gun. The oxygen and acetylene are ignited in the torch and the powder introduced into this flame. The flame melts the glass powder and propels the molten droplets onto the surface. The temperature of the flame from the thermal spray torch is about 2000°C (3600°F). This is sufficient to melt the glass powder. As the glass is propelled towards the substrate, it cools in the air and sticks to the substrate at a temperature of about 425°C (80°F).

The glass strikes the substrates and solidifies within a few seconds. The glass is reheated with the thermal spray torch 2 to 3 times and remains molten for a total of about 10 seconds. This allows the

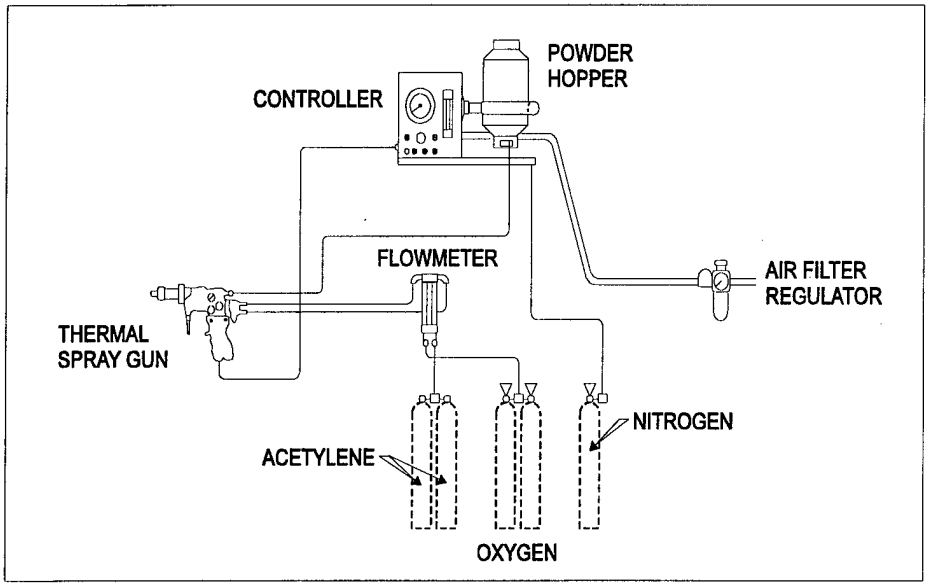



Figure 1. Schematic of the thermal spray process.

lead ions to diffuse into the glass network and become trapped in the silica tetrahedra of the glass structure, achieving partial vitrification. The difference in the thermal expansion coefficient between the sprayed glass layer and the metal substrate causes the glass to crack and spall from the surface as it cools. The paint is vitrified at the surface of the glass and additional layers of the paint are attached to this vitrified layer. They are removed when the glass spalls off the surface. The crumbled glass fragments can be easily removed from the steel substrate, leaving it free of lead-based paint. However, 2 to 3 applications of the vitrification process are required. The glass fragments may be remelted to ensure that the vitrification process is driven to completion.

During rapid cooling the glass develops thermal stresses that cause it to crack and spall off the substrate. The lead-based paint is attached to the glass surface and falls off with the glass. The small pieces of glass fall into the catch basin of a collector unit. The subsequent remelting of the glass immobilizes the lead inside the glass network, thereby preventing leaching. The concentration of lead in the leachate for the remelted glass as determined by TCLP analysis was below 5 ppm, the EPA's regulatory limit for classification as a hazardous waste.

The molten glass is very corrosive and acts like a cleaning agent which will restore the surface to a dull finish with the profile that it had before it was painted. For atmospheric exposure, the surface finish is not as critical as for immersion coatings. The surface finish produced by the thermal spray vitrification process requires a surface tolerant coating which is expected to provide up to 25 years of performance for atmospheric exposure. After application of the thermal spray vitrification process the steel surface has a dusting of loosely adhered powdery residue. This loosely adhered material must be removed prior to painting. The resultant surface needs to be free of all loose mill scale, loose paint, and other loose detrimental foreign matter prior to repainting with a surface tolerant coating system.

## 2.1 GLASS COMPOSITION

Thermal spray vitrification technology uses a glass compound designed for high lead solubility and

TABLE 1. GLASS COMPOSITIONS

| Species | Initial Composition A Wt. % | Modified Composition B Wt. % |
|---|---|---|
| $SiO_2$ | 54.1 | 54.1 |
| $B_2O_3$ | 6.8 | 10.0 |
| $Al_2O_3$ | 4.1 | 5.1 |
| $Na_2O$ | 10.3 | 16.5 |
| $Li_2O$ | 4.7 | 2.0 |
| $MnO_2$ | 2.9 | |
| NiO | 0.9 | |
| CaO | 1.5 | |
| MgO | 0.8 | |
| $Fe_2O_3$ | 12.3 | 12.3 |
| $ZrO_2$ | 1.2 | |

resistance to crystallization. These characteristics provide immediate reaction with the lead and upon subsequent remelting ensure containment of the hazardous material. The initial iron borosilicate glass system, Composition A, was selected because of its ability to accommodate a wide variety of hazardous species, its outstanding long-term chemical durability, and its corrosion resistance to a wide range of environmental conditions, Table 1[1].

A series of crucible melt experiments was conducted in the laboratory with Composition A prepared with between 0 and 40 wt.% PbO added to the glass. The lead loading experiment showed that the iron borosilicate glass was able to successfully immobilize up to 25 wt.% PbO such that it leached less than the 5 ppm Pb regulatory limit as determined using TCLP testing, Figure 2.

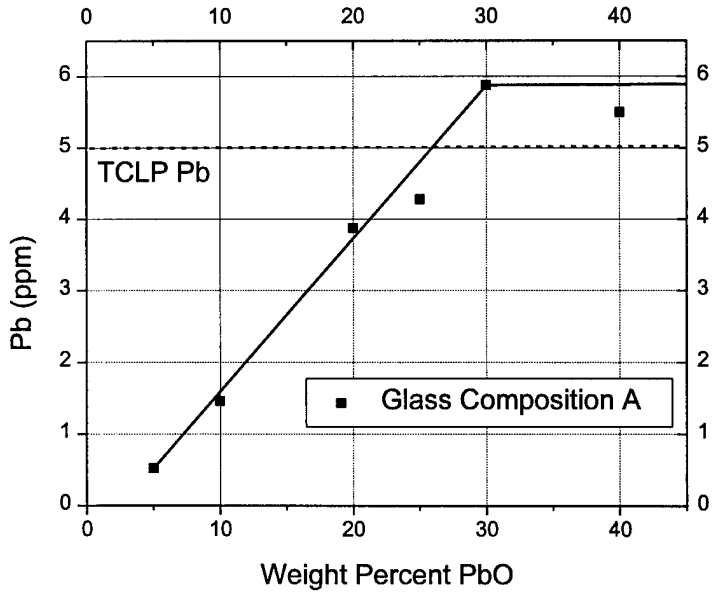



Figure 2. Effect of Lead Loading on the TCLP concentration of Pb.

TABLE 2. TCLP RESULTS FOR GLASS COMPOSITION B

| Hazardous Components (25% loading) | Pb (ppm) | Cd (ppm) | Cr (ppm) | Cu (ppm) |
|---|---|---|---|---|
| Pb | 2.8 | | | |
| 50% Pb /50% Cu | 2.4 | | | 3.9 |
| 80% Pb /10% Cd /10% Cr | 3.1 | 0.5 | 0.1 | |
| Regulatory Limit | 5.0 | 1.0 | 5.0 | |

To reduce the cost of the glass frit, the chemical formulation was modified by removing the elements considered nonessential. These included Mn, Ni, Ca, Mg and Zr. The modified composition B was scaled to 100% and is listed in Table 1. A series of laboratory experiment was conducted to determine the immobilization of lead, cadmium, chromium, and copper. Cadmium can be present on metal fasteners, chromium is a component of lead chromate primers, and copper is used as an antifouling agent in some paints for ship hulls. TCLP analysis was conducted on glass samples of composition B melted with 25% waste loading of the following hazardous permutations: 1) Pb only, 2) 50% Pb and 50% Cu, and 3) 80% Pb, 10% Cd and 10% Cr, Table 2. The regulatory limits for Cd and Cr release by TCLP testing are 1.0 and 5.0 ppm respectively. However, there is currently no Federal regulatory standard for release of copper by TCLP testing. The results showed that Composition B successfully immobilized lead, cadmium, chromium, and copper.

## 2.2 PROCESSING PARAMETERS OPTIMIZATION

The thermal spray application process was designed to operate with any industrial type fuel such as acetylene, propylene, or propane, with oxygen as the oxidizer. The powder-carrier gas can be either nitrogen, argon or compressed air. The flame spray gun may either be machine mounted or hand-held by attaching a pistol grip. All of the flame spray tests conducted during this investigation used acetylene as the fuel gas, oxygen as the oxidizer, and ultra dry industrial-grade nitrogen or compressed air as the carrier gas.

The effectiveness of the flame spray process is a function of the processing variables such as oxygen and acetylene flow rates, carrier gas flow rate, powder flow rate, particle size and uniformity, duration of flame spray pass, and stand-off distance. Any flame spray process is also influenced by particle molten state and velocity, particle chemical reaction with the environment during flight, heat transfer control to the substrate while spraying, and relative movement of spray gun to the substrate[7]. Although the spray parameters were optimized in this research, minor adjustments must be made in the field depending on the specific characteristics of the compound being flame sprayed. Spray parameters, such as fuel and oxygen pressures and flow rates, standoff distance, powder flow rate and powder carrier gas flow rate were optimized, Table 3. The use of a reducing atmosphere during the preheating of the substrate was found to improve the removal.

# 3. PAINT-REMOVAL EXPERIMENTS

The goal of the thermal spray vitrification process is remove the lead-based paint from the substrate for subsequent recoating with a surface tolerant system. Following removal of the lead-based paint, there may be a small amount of residual lead on the substrate surface. When the surface tolerant coating eventually needs to be removed for repainting, lead monitoring will have to be conducted to determine the airborne lead concentration and the necessary extent of work protection. Due to the significantly

TABLE 3. THERMAL SPRAY PROCESSING PARAMETERS

| Parameter | Initial Conditions | Reducing Preheat Condition |
|---|---|---|
| Acetylene Pressure (psi) | 15.0 | 15.0 |
| Acetylene Flow Rate (%) | 42.0 | 42.0 |
| Oxygen Pressure (psi) | 40.0 | 40.0 |
| Oxygen Flow Rate (%) | 32.0 | 10.0 |
| Carrier Gas ($N_2$) Pressure (psi) | 42.0 | 42.0 |
| Carrier Flow Rate (%) | 40.0 | 40.0 |
| Powder Feed Rate (g/min) | 88.0 | 0 |

lower lead concentrations, reduced requirements for worker protection would be expected. Traditional paint removal processes such as abrasive blasting can be utilized for the subsequent paint removal.

Carbon steel coupons measuring 4 in x 6 in x 0.5 in were painted with lead oxide-containing primer followed by an aluminized topcoat. These panels were cured in an oven at 60°C for 7 days for use as test specimen. The remnant lead in the panel was measured using x-ray fluorescence (XRF) lead-detection equipment. The test panels were preheated to about 150°C (300°F) to drive away the moisture, and the feedstock powder was sprayed and fused using the oxy-acetylene spray gun. Lead removal was tracked by XRF testing of the surface. The initial lead concentration ranged from 6.0 to 12.3 mg/cm$^2$. Following application of the thermal spray vitrification process the surface lead concentration ranged from 0.4 to 1.2 mg/cm$^2$. The accuracy of the XRF measurements is questionable at or below 1.0 mg/cm$^2$. Supplementary testing using scrape samples is recommended before making lead hazard control or worker protection decisions. Visual observations and XRF analysis showed that the thermal spray vitrification process successfully removed the lead-based paint from the substrate, Table 4. The resulting surface was suitable for repainting using a surface tolerant coating.

The glass fragments from the experimental samples were collected. TCLP analysis detected lead leaching from the glass collected. The rapid cooling of the glass on the substrate evidently had provided insufficient time for the lead to completely diffuse into the glass network while on the

TABLE 4. RESULTS OF LEAD REMOVAL EXPERIMENTS

| Sample | Initial Pb XRF Concentration mg/cm$^2$ | Final Pb XRF Concentration mg/cm$^2$ |
|---|---|---|
| 1 | 6.9 | 0.5 |
| 2 | 8.1 | 0.9 |
| 3 | 6.7 | 1.2 |
| 4 | 6.7 | 0.7 |
| 5 | 6.0 | 0.9 |
| 6 | 10.5 | 0.6 |
| 7 | 11.5 | 0.4 |
| 8 | 12.3 | 1.1 |

surface. Instead, lead was trapped on the surface of the glass where it was quickly liberated by the acid used in the TCLP test. However, remelting the glass fragments yielded a nonhazardous waste as determined by TCLP testing.

## 4. WORKER EXPOSURE AND AIR MONITORING

Both emission monitoring and personal monitoring of the airborne concentration of lead were. conducted during laboratory testing of the thermal spray vitrification process. Personal breathing zone samples were collected on the operator during each day's operation, i.e., the operator wore a personal sampling pump with filter assembly positioned in the worker's breathing zone. The personal breathing zone samples were collected on closed-face, 37 mm diameter, 0.8 μm pore size mixed cellulose ester membrane filters contained in a three-piece cassette. The filter assembly was attached to a battery powered vacuum pump operating at a constant flow rate of approximately 2 liters per minute.

The area air sampler was located in the exhaust hood area of the laboratory to determine the concentration of airborne lead particulate in the general area during the operation and until all work was completed. The air samplers were located in the same position at the same locations during all sampling events. Identical filters, filter assemblies, and pumps were used for the area-air sampling. Air cartridges were sent to an EPA-certified laboratory for analysis.

The U.S. Occupational Health and Safety Administration (OSHA) standards require all employers to conduct an initial exposure assessment for all jobs involving the use or removal of lead or lead-containing materials. The purpose is to determine if any employee is exposed to lead equal to or greater than the action level of 30 $\mu g/m^3$. The exposure assessment can include current results from exposure monitoring of employees, previous monitoring results, or other objective data. The specific product, process, operation, or activity involving lead cannot result in exposure above the action level under any circumstances. When the initial determination shows that no employee is potentially exposed to lead at or above the action level, further exposure assessment is not necessary until there is a change in the workplace[8].

Previous results where the employer has monitored employees for lead exposure can be used to satisfy the requirement for the initial determination providing the data was collected during the previous 12 months during work conditions closely resembling the processes, material types, control and containment methods, work practice, and environmental conditions used and prevailing in the current workplace[8].

The certified results show that airborne lead emissions during laboratory testing fell below the National Ambient Air Quality Standards (NAAQS) limit. The results of personal exposure monitoring during thermal spraying were below the OSHA action level of 30 $\mu g/m^3$.

## 5. FIELD DEMONSTRATIONS

The thermal spray vitrification process is scheduled to be demonstrated in August 1997 to remove lead-based paint from a 150 square ft test area on a highway bridge located at the Rock Island Army Arsenal, IL. The bridge has several coats of a non-lead alkyd top coat on top of a lead based primer. Measurements showed that the paint is on average 20 mils thick. The thickness is typical of other Department of Defense steel structures subjected to atmospheric exposure. Future demonstrations of the thermal spray vitrification process are planned to remove lead-based from an aircraft hangar in Hawaii and from a ship structure at Puget Sound, WA.

The State of Illinois Environmental Protection Agency (ILEPA) was contacted in regards to the planned demonstration at the Rock Island Arsenal. The ILEPA indicated that the remelting of the waste glass will not require a treatment or air permit via the Bureau of Land or the Division of Air Pollution Control. Essentially, the remelter furnace is considered tank treatment and since it will be operated at a temperature that is less than the lowest auto-ignition temperature of the contaminants present and not directly exposing the glass to a flame, no permit is required. Likewise, the ILEPA viewed the remelting of the glass as a typical lead-based paint removal operation which does not require a permit. However, the Contractor will still need to comply with the NAAQS for lead and particulate matter.

## CONCLUSIONS

Thermal spray vitrification is a dust-free process which minimizes airborne lead and reduces the need for total containment. The economic advantages of thermal spray vitrification for lead-based paint removal would be the savings realized through the reduction of containment and minimization of worker and environmental monitoring. Because the final glass residue would be nonhazardous, the waste material could be disposed though a standard waste hauler to a municipal waste landfill. DoD owns more than 200,000,000 square feet of steel structures such as bridges and aircraft hangars coated with lead-based paint. The savings because of reduced requirements for containment, worker protection, and hazardous waste disposal would be substantial.

## ACKNOWLEDGMENTS

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