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Handbook

Approaches for the Remediation of Federal Facility Sites Contaminated with Explosive or Radioactive Wastes

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HANDBOOK:

APPROACHES FOR THE REMEDIATION OF FEDERAL FACILITY SITES CONTAMINATED WITH EXPLOSIVE OR RADIOACTIVE WASTES

OFFICE OF RESEARCH AND DEVELOPMENT
CINCINNATI, OH 45268

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Chapter 1: *Introduction,* compiled by Eastern Research Group, Inc. (ERG), Lexington, Massachusetts, based on information provided by several authors of later chapters

Chapter 2: *Safety Concerns When Investigating and Treating Explosives Waste,* Jim Arnold, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

Chapter 3: *Field Screening Methods for Munitions Residues in Soil,* Tom Jenkins, Cold Regions Research and Engineering Laboratory, U.S. Department of the Army, Hanover, New Hampshire

Characterization of Radioactive Contaminants for Removal Assessments, Jim Neiheisel, Office of Radiation and Indoor Air, U.S. EPA, Washington, DC

Chapter 4: *Overview of Approaches to Detection and Retrieval Operations,* Richard Posey, Environmental Health Research and Testing, Lexington, Kentucky

Detection, Retrieval, and Disposal of Unexploded Ordnance (UXO) at U.S. Military Sites, James Pastorick, International Technology (IT) Corporation, Washington, DC

Detection and Sampling of White Phosphorus in Sediment, Harry Compton, Environmental Response Team, U.S. EPA, Edison, New Jersey

Chapter 5: *Biological Treatment Technologies, Wet Air Oxidation, Low Temperature Thermal Desorption, Solvent Extraction,* and *Volume Reduction,* Major Kevin Keehan, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

Incineration of Soils and Sludges, Charles Lechner, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

Open Burn/Open Detonation, Steven Whited, Hercules Incorporated, Rocket Center, West Virginia

Ultraviolet Oxidation and *Granular Activated Carbon,* Wayne Sisk, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

Compressed Gas Cylinder Handling and *Reactive Chemical Handling,* Irwin Kraut, Emergency Technical Services Corporation, Schaumburg, Illinois

Reuse/Recycle Options for Propellants and Explosives, William Munson, Thiokol Corporation, Brigham City, Utah

Chapter 6: *Wet-Based Volume Reduction for Radioactive Soils,* Michael Eagle, Office of Radiation and Indoor Air, U.S. EPA, Washington, DC

Dry-Based Volume Reduction for Radioactive Soils, Ed Bramlitt, Defense Nuclear Agency, Kirtland Air Force Base, New Mexico

Treatment of Radioactive Compounds in Water, Thomas Sorg, Drinking Water Research Division, U.S. EPA, Cincinnati, Ohio

Incineration of Radioactive and Mixed Waste, Patrick Walsh, Scientific Ecology Group, Inc., Oak Ridge, Tennessee

In Situ Vitrification, Tim Voskuil, Equity Associates, Knoxville, Tennessee, with assistance from Edwin Barth, CERI, U.S. EPA, Cincinnati, Ohio

Polymer Solidification, Paul Kalb, Brookhaven National Laboratory, Upton, New York

In Situ Grout Injection, Michael Gilliam, Martin Marietta Environmental Systems, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Electrokinetic Soil Processing, Yalcin Acar, Louisiana State University (LSU), Baton Rouge, Louisiana, with assistance from Robert Gale, LSU

Appendix A: *Search for a White Phosphorus Munitions Disposal Site in Chesapeake Bay,* Gary Buchanan, IT Corporation, Edison, New Jersey; Harry Compton, Environmental Response Team, U.S. EPA, Edison, New Jersey; John Wrobel, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

Appendix B: *Case Study: Remedial Action Implementation, Elizabeth, New Jersey,* Norman Abramson, Earth Resources Corporation, Ocoee, Florida

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Chapter One
Introduction

1.1 Document Overview

The information in this publication is based primarily on presentations at two technology transfer seminar series sponsored by the U.S. Environmental Protection Agency (EPA), the Department of Defense (DOD), and the Department of Energy (DOE): the Seminar Series on Technologies for Remediating Sites Contaminated with Explosive and Radioactive Wastes, and the Radioactive Site Remediation Seminar Series. Additional information has been provided by technical experts from EPA, DOD, DOE, academia, and private industry. The reader is cautioned not to infer that there is a connection between explosive waste and radioactive waste. Both topics have been combined because of the possibility of finding both types of waste at federal facility sites. In addition to explosive and radioactive wastes, reactive chemical and compressed gas cylinder handling also are discussed in the document.

This document provides an overview of technical issues related to remediating soil and ground water contaminated with explosive and radioactive wastes at federal facility sites. The document covers a range of sampling approaches and treatment technologies, both those that have been successfully demonstrated and applied and those that have not yet been successfully implemented. For successfully demonstrated technologies, the document provides background information, and information on treatable wastes and media; operation of the technology; applications at the laboratory, bench, pilot, or field scale; and advantages and limitations of the technology.

The document is intended to assist remediation contractors considering technical issues and sampling and treatment options at federal facility sites, but it should not be used as a detailed manual for undertaking remedial activities. The document presents a sampling of techniques used for remediating explosive and radioactive wastes, but is not a comprehensive presentation of all available techniques and technologies. In addition, although the document provides previously published cost data from applications of certain technologies, the reader is cautioned against using these data to compare specific technologies, because of the different costing assumptions used in each study.

Section 1.2 in this chapter outlines the technologies available for treating explosive and radioactive waste, the types of explosive and radioactive waste typically encountered at federal facility sites, and common sources of these wastes. Chapter 2 covers safety concerns associated with investigating and treating explosive waste. Chapter 3 focuses on laboratory-scale methods for developing detailed characterizations of explosives-contaminated sites. Chapter 4 covers detection and retrieval of buried munitions, both over large fields of operation overseas and at military installations in the United States. Chapter 5 describes the biological, thermal, and physical/chemical technologies available for remediating explosive waste, and Chapter 6 covers treatment technologies for radioactive waste sites.

1.2 Technical Introduction

1.2.1 Treatment Technologies for Explosive and Radioactive Waste at Federal Facilities

Most of the treatment technologies for explosive waste discussed in this document currently are being developed or implemented. These include biological technologies, incineration, ultraviolet oxidation, granular activated carbon treatment, and reuse/recycle options. Similarly, all of the radioactive waste treatment technologies discussed in Chapter 6, including volume reduction, polymer solidification and encapsulation, incineration, in situ vitrification, in situ grout injection, and electrokinetic soil processing, have been successfully demonstrated. This document also discusses four treatment technologies that have not been successfully implemented for explosive waste: wet air oxidation, low temperature thermal desorption, solvent extraction, and volume reduction. For additional information on treatment technologies for 2,4,6-trinitrotoluene (TNT) explosive waste, please see *Installation Restoration and Hazardous Waste Control Technologies* (U.S. ATHAMA, 1992).

1.2.2 Explosive Waste

1.2.2.1 Types of Explosive Waste

The term explosive waste commonly is used to refer to propellants, explosives, and pyrotechnics (PEP), which technically fall into the more general category of energetic materials. These materials are susceptible to initiation, or self-sustained energy release, when exposed to stimuli such as heat, shock, friction, chemical incompatibility, or electrostatic discharge. Each of these materials reacts differently to the aforementioned stimuli; all will burn, but explosives and propellants can detonate under certain conditions (e.g., confinement). Figure 1-1 outlines the various categories of energetic materials. The emphasis of this document is on soil and ground water contaminated with explosives rather than propellants or pyrotechnics.

Explosives

Explosives are classified as primary or secondary based on their susceptibility to initiation. Primary explosives, which include lead azide and lead styphnate, are highly susceptible to initiation. Primary explosives often are referred to as initiating explosives, because they can be used to ignite secondary explosives.

Secondary explosives, which include TNT, cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX or cyclonite), High Melting Explosives (HMX), and tetryl, are much more prevalent at military sites than are primary explosives. Since they are formulated to detonate only under specific circumstances, secondary explosives often are used as main charge or boostering explosives. Secondary explosives can be loosely categorized into melt-pour explosives, which are based on TNT, and plastic-bonded explosives (PBX), which are based on a binder and a crystalline explosive such as RDX. Secondary explosives also can be classified according to their chemical structure as nitroaromatics, which include TNT, and nitramines, which include RDX. Figure 1-2 shows the chemical structure of TNT and RDX. In the TNT molecule, NO_2 groups are bonded to the aromatic ring; in the RDX molecule, NO_2 groups are bonded to nitrogen.

Table 1-1 shows how frequently various nitroaromatics and nitramines occur at explosives-contaminated sites with which the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and the Missouri River Division (MRD) have been involved. TNT is the most common contaminant, occurring in approximately 80 percent of the soil samples found to be contaminated with explosives. Trinitrobenzene (TNB), which is a photochemical decomposition product of TNT, was found in between 40 and 50 percent of these soils. Dinitrobenzene (DNB), 2,4-dinitrotoluene (2,4-DNT), and 2,6-DNT, which are impurities in production-grade TNT, were found in less than 40 percent of the soils. Figure 1-2 shows the chemical structures of common explosive contaminants.

Propellants

Propellants include both rocket and gun propellants. Most rocket propellants are either (1) Hazard Class 1.3 composites, which are based on a rubber binder, an ammonium perchlorate (AP) oxidizer, and a powdered aluminum (Al) fuel; or (2) Hazard Class 1.1 composites,

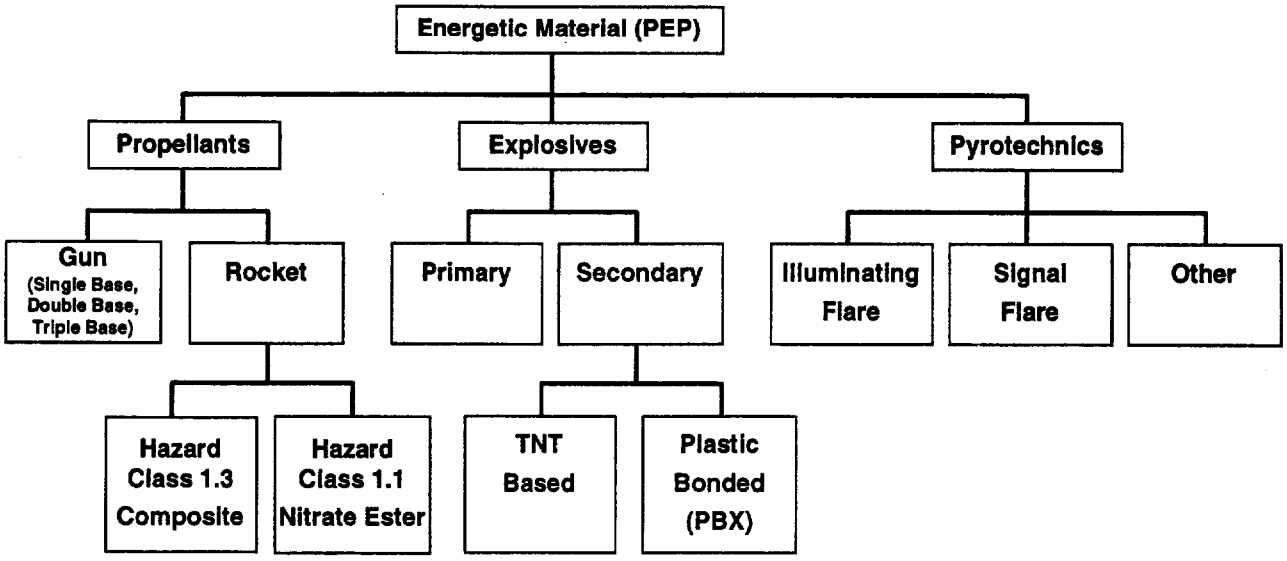

Figure 1-1. Categories of energetic materials.

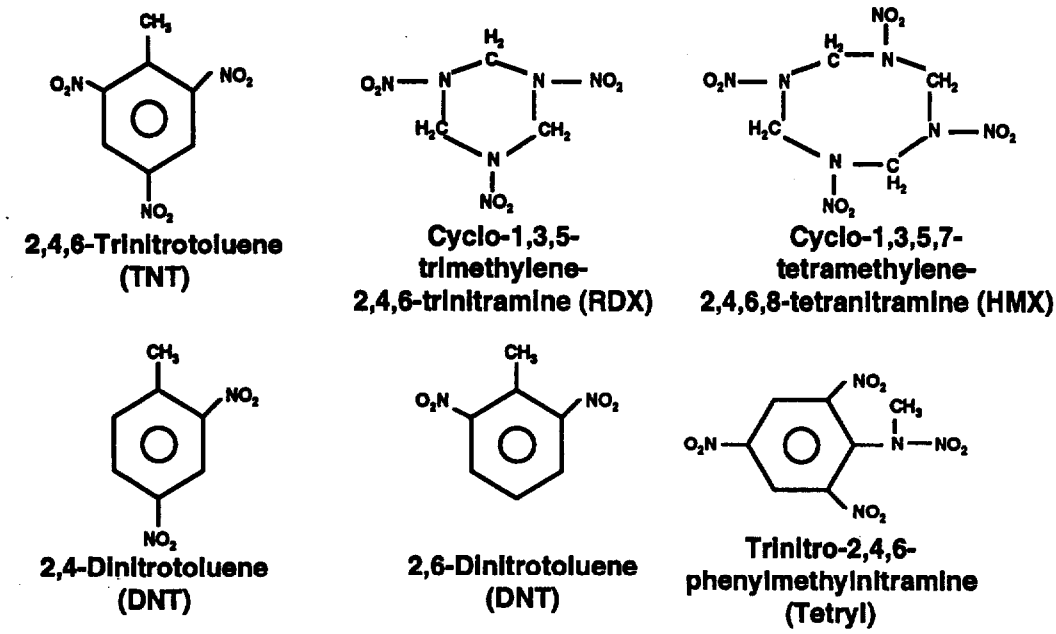

Figure 1-2. Chemical structures of common explosive contaminants.

Table 1-1. Nitroaromatics and Nitramines Detected by CRREL and MRD in Explosives-Contaminated Soils from Army Sites

		Frequency (%)	
Category	**Contaminant**	**CRREL**	**MRD**
Nitroaromatics	TNT	85	76
	TNB	53	38
	DNB	25	19
	2,4-DNT	41	17
	2,6-DNT	*	*
	4-Amino-DNT	6	3
	2-Amino-DNT	27	11
	3,5-DNA	**	**
Nitramines	RDX	44	28
	HMX	27	4
	Tetryl	8	14

*Often not separated from 2,4-DNT.
**Peak often observed but only recently identified.
Source: U.S. Army CRREL, 1993.

which are based on a nitrate ester (usually nitroglycerine [NG]), nitrocellulose (NC), HMX, AP, and Al.[1] The nitrate ester propellants can be plastisol-bound (high NC) or polymer-bound (low NC). If a binder is used, it usually is an isocyanate-cured polyester or polyether. Some propellants contain combustion modifiers, such as lead oxide. Gun propellants usually are single base (NC), double base (NC and NG), or triple base (NC, NG, and nitroguanidine [NQ]). Some of the newer, lower vulnerability gun propellants contain binders and crystalline explosives and thus are similar to PBX.

Pyrotechnics

Pyrotechnics include illuminating flares, signaling flares, colored and white smoke generators, tracers, incendiary delays, fuzes, and photo-flash compounds. Pyrotechnics usually are composed of an inorganic oxidizer and metal powder in a binder. Illuminating flares contain sodium nitrate, magnesium, and a binder. Signaling flares contain barium, strontium, or other metal nitrates.

[1] Hazard Class (HC) is a designation given to energetic materials by the defining documents for military explosives (U.S. Army, U.S. Navy, U.S. Air Force, and U.S. Defense Logistics Agency, 1989; United Nations, 1992). HC 1.1 materials will mass detonate; HC 1.3 materials will mass deflagrate. The distinction is made through a series of tests defined in the document test protocol.

1.2.2.2 Sources of Explosive Waste

Many DOD sites are contaminated with explosive waste as a result of explosives manufacturing; munitions load, assemble, and pack operations; explosives machining, casting, and curing; open burn and open detonation operations; and laboratory testing of munitions. Based on the experience of the U.S. Army Environmental Center (AEC) of DOD, one of the major explosive wastes of concern at DOD sites are residues from land disposal of explosives-contaminated process water.

Explosives-contaminated waters are subdivided into two categories: red water, which comes strictly from the manufacture of TNT; and pink water, which includes any washwater associated with load, assemble, and pack operations or with the demilitarization of munitions involving contact with finished TNT. Despite their names, red and pink water cannot be identified by color. Both are clear when they emerge from their respective processes and subsequently turn pink, light red, dark red, or black when exposed to light. The chemical composition of pink water varies depending on the process from which it is derived; red water has a more-defined chemical composition. For this reason, it is difficult to simulate either red or pink water in the laboratory.

The United States stopped production of TNT in the mid-1980s, so no red water has been generated in this country since that date (Hercules Aerospace Company, 1991). Most process waters found in the field are pink waters that were generated by demilitarization operations conducted in the 1970s. In these operations, munitions were placed on racks with their fuzes and tops removed. Jets of hot water then were used to mine the explosives out of the munitions. The residual waters were placed in settling basins so that solid explosive particles could be removed, and the remaining water was siphoned into lagoons. Contaminants often present in these lagoon waters and the surrounding soils include TNT; RDX; HMX; tetryl; 2,4-DNT; 2,6-DNT; 1,3-DNB; 1,3,5-TNB; and nitrobenzene.

1.2.3 Radioactive Waste

Several radioactive elements, including uranium, radium, and radon, occur naturally in soil and ground water. Radioactive contamination also can result from processes associated with the production of nuclear energy and nuclear weapons. Common radioactive-contaminated materials include dry active wastes, such as paper, plastic, wood, cloth, rubber, canvas, fiberglass, and charcoal; ion exchange resins used to polish condensate from nuclear power plants; sewer sludges and lubricating oils contaminated with radioactive materials; and air pollution control equipment. For the purposes of this document, radionuclides should be considered to have properties similar to those of other heavy metals.

The Nuclear Weapons Complex (NWC) is a collection of enormous factories devoted to metal fabrication, chemical separation processes, and electronic assembly associated with the production of nuclear weapons. In approximately 50 years of nuclear weapons production, these factories have released vast quantities of hazardous chemicals and radionuclides to the environment. Evidence exists that air, ground water, surface water, sediment, and soil, as well as vegetation and wildlife, have been contaminated at most, if not all, nuclear weapons production facilities. Table 1-2 shows the types of wastes often found at NWC sites.

Contamination of soil, sediments, surface water, and ground water is widespread at the NWC, and contamination of ground water with radionuclides or hazardous chemicals has been confirmed at almost every facility. Most sites in nonarid locations have surface water contamination as well. Almost 4,000 solid waste management units (SWMUs) have been identified throughout the NWC, and many of these units require some form of remedial action. Substantial quantities of waste have been buried at the NWC, often with inadequate records of the burial location or composition of the waste buried. DOE estimates that a total of about 0.2 million m^3 of transuranic waste and about 2.5 million m^3 of low-level radioactive waste have been buried in the complex. Most of this buried waste is "mixed waste," meaning that it is mixed with Resource Conservation and Recovery Act (RCRA) hazardous wastes. For additional information on radioactive waste sites, refer to *Complex Cleanup: The Environmental Legacy of Nuclear Weapons Production* (U.S. Congress, 1991).

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Table 1-2. Nuclear Weapons Site Contaminants and Contaminant Mixtures[a]

Inorganic Contaminants					
Radionuclides	**Metals**	**Other**	**Organic Contaminants**	**Organic Facilitators[b]**	**Mixtures of Contaminants[c]**
Americium-241 Cesium-134, -137 Cobalt-60 Plutonium-238, -239 Radium-224, -226 Strontium-90 Technetium-99 Thorium-228, -232 Uranium-234, -238	Chromium Copper Lead Mercury Nickel	Cyanide	Benzene Chlorinated hydrocarbons Methylethyl ketone, cyclohexanone, acetone Polychlorinated biphenyls and select polycyclic aromatic hydrocarbons Tetraphenylboron Toluene Tributylphosphate	Aliphatic acids Aromatic acids Chelating agents Solvents, diluents, and chelate radiolysis fragments	Radionuclides and metal ions Radionuclides, metals, and organic acids Radionuclides, metals, and natural organic substances Radionuclides and synthetic chelating agents Radionuclides and solvents Radionuclides, metal ions, and organophosphates Radionuclides, metal ions, and petroleum hydrocarbons Radionuclides, chlorinated solvents, and petroleum hydrocarbons Petroleum hydrocarbons and polychlorinated biphenyls Complex solvent mixtures Complex solvent and petroleum hydrocarbon mixtures

[a] This contaminant list is being updated as new information becomes available.
[b] Facilitators are organic compounds that interact with and modify metal or radionuclide geochemical behavior.
[c] Information on mixture types is sparse, and concentration data are limited.
Source: U.S. DOE, 1990.

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Chapter Two
Safety Concerns When Investigating and Treating Explosives Waste

2.1 Background

Safety precautions must be taken at sites contaminated with explosives wastes. AEC, which has been involved in sampling and treating explosives waste sites since the early 1980s, has developed protocols for identifying sites that require explosives safety precautions and for handling explosives wastes at these sites. This section discusses AEC's sensitivity testing protocol, specific precautions required for sampling and treating explosives wastes, and some laboratory safety issues associated with analyzing explosives-contaminated samples. The section does not cover statistical site characterization or the work and health and safety plans suggested by the Occupational Safety and Health Administration (OSHA).

2.2 Sensitivity Testing

When AEC began to investigate explosives waste sites in the early 1980s, the only available guidance on sampling and treating explosives-contaminated soils was 40 CFR 261.23, which vaguely specifies waste identification. Consequently, AEC developed its own protocol for determining whether soils contaminated with explosives wastes are susceptible to initiation and propagation, and, if so, how best to handle them. This original protocol involved many tests, including impact tests, friction tests, and shock gap tests. AEC quickly determined that the original protocol was too expensive and unwieldy, due to the variety of available tests, and developed a two-test protocol. This protocol involved (1) the deflagration-to-detonation test (DDT), which measures an explosive material's reaction to flame; and (2) the Bureau of Mines' zero gap test, which measures an explosive material's reaction to shock. Both of these tests are extremely conservative, rendering additional tests unnecessary. The drawback to this protocol was that both tests required relatively large volumes of soil to be excavated and shipped, often at great expense, to specially qualified laboratories.

AEC eventually developed its current protocol, which involves chemical compositional analysis. By analyzing the composition of samples from a site, AEC can determine quickly and inexpensively whether materials at the site are susceptible to initiation and propagation. According to the DDT, soils containing more than 12 percent secondary explosives by weight are susceptible to initiation by flame; according to the shock gap test, soils containing more than 15 percent secondary explosives by weight are susceptible to initiation by shock. As a conservative limit, AEC considers all soils containing more than 10 percent secondary explosives by weight to be susceptible to initiation and propagation and exercises a number of safety precautions when sampling and treating these soils. Sampling and treatment precautions are exercised when handling soils that contain even minute quantities of primary explosives.

The reliability of compositional analysis depends on obtaining enough samples to generate a statistically valid characterization of the site. CRREL has developed field screening methods to reduce the number of samples that must be analyzed in the laboratory (see section 3.1). If contamination is in the parts per million (ppm) or parts per billion (ppb) range by weight, the samples could be shipped off site for analysis; if contamination is in the percent range, special analytical arrangements must be made.

2.3 Sampling and Treatment Precautions

Work, sampling, and health and safety plans for explosives waste sites should incorporate safety provisions that normally would not be included in work and sampling plans for other sites. AEC works with other laboratories such as the Bureau of Mines to conduct site-specific hazards analyses for every proposed operation at explosives waste sites, including remedial investigation, remedial design, and remedial action. These analyses include hazards identification, hazards evaluation, risk assessment, and risk management.

The most important safety precaution is to minimize exposure, which involves minimizing the number of workers exposed to hazardous situations, the duration of exposure, and the degree of hazard. To reduce the degree of hazard at explosives wastes sites, operations usually are conducted on materials that have been

diluted to a wet slurry. If necessary, distilled water can be added to the soil to achieve the desired moisture content. Water desensitizes the explosives and reduces the effects of heat and friction. Water, however, also can cause a localized detonation to propagate throughout a soil mass, so moisture content should be adjusted on a site-by-site basis. As another safety precaution, nonsparking tools, conductive and grounded plastic, and no-screw tops, which were developed for manufacturing explosives, are standard equipment at explosives waste sites. For example, nonsparking beryllium tools are used instead of ferrous tools.

If contamination is above the 10 percent limit in some areas of a site, the contaminated material could be blended and screened to dilute the contamination and produce a homogenous mixture below the 10 percent limit. This blending is not by itself a remedial action but a safety precaution; soils containing less than 10 percent secondary explosives by weight occasionally experience localized detonations but generally resist widespread propagation. Foreign objects and unexploded ordnance within the contaminated soil often impede the blending process and require unexploded ordnance contractors (see section 4.2).

Once blending is completed, soil treatments such as incineration and bioremediation can proceed. Equipment used in treatment must have sealed bearings and shielded electrical junction boxes. Equipment also must be decontaminated frequently to prevent the buildup of explosive dust.

AEC conducts periodic safety audits to ensure that proper safety procedures are being followed. Field operations must have DOD approval from the Explosives Safety Board and corporate approval from any private contractors involved.

2.4 Laboratory Analysis of Explosives-Contaminated Samples

Although TNT and RDX are the most common contaminants at explosives waste sites, many sites also are contaminated with impurities in production-grade TNT, such as DNB, 2,4-DNT, 2,6-DNT, and products of photochemical decomposition of TNT, such as TNB. These impurities and decomposition products are thermally labile and hydrophilic and consequently should not be analyzed using certain tests and solvents. For example, gas chromatography (GC), in particular, is not the best choice to screen for these chemicals, because thermally labile compounds decompose in GC equipment. High-performance liquid chromatography (HPLC) (SW846 method 8330) has been selected for routine laboratory analysis of soils from military sites.

Chapter Three
Laboratory-Scale Analytical Methods

3.1 Field Screening Methods for Munitions Residues in Soil

3.1.1 Background

Laboratory analysis of samples from sites contaminated with explosives wastes is expensive and time consuming. Due to heterogeneous waste distribution at many sites, it would not be unusual for 80 to 90 percent of the soil samples from a given site to contain no contamination. As a result, developing a site characterization with good spatial resolution is extremely expensive. Field screening methods determine quickly and less expensively which samples are contaminated with explosives residues, thereby reducing total analytical costs. For example, field screening was found to be acceptable for determining soil contamination areas at a military site (Craig et al., 1993). This section discusses the field screening procedures developed by CRREL and advantages and limitations of CRREL's procedure. The section does not cover soil sampling procedures.

3.1.2 Field Screening Methods

In developing the field screening methodology, CRREL considered several design criteria. The method needed to detect contaminants that were present at most military sites. Based on data from sites investigated by CRREL and MRD, CRREL determined that most sites could be adequately assessed by methods that screen first for TNT and RDX, and secondarily for 2,4-DNT, TNB, DNB, and tetryl. The equipment needed to be portable, so it could be shipped easily to sites, and simple to operate, because field operators would not necessarily have experience in analytical chemistry. Field screening procedures also needed to use only low toxicity solvents and have a quick turnaround time, a large analytical range, a linear calibration scale, and a sufficiently low detection limit. In addition, the results of the procedure needed to correlate well with results from standard laboratory methods.

CRREL's methodology has three steps: extraction, TNT screening, and RDX screening.

3.1.2.1 Extraction

CRREL's procedure begins with a simple extraction process. A 20-g sample of undried soil from the site is mixed with 100 mL of acetone. The sample is shaken for at least 3 minutes, allowed to settle, and filtered with a syringe filter. Very heavy clays might require longer extraction periods, but 3 minutes is often sufficient for most sandy and loamy soils. The efficiency of acetone extraction is 95 percent that of standard laboratory methods. The filtered extract then is subjected to CRREL's TNT and RDX screening procedures. For more detailed information on these procedures, see U.S. Army CRREL, 1990, and U.S. Army CRREL, 1991.

3.1.2.2 TNT Screening

In the TNT screening procedure, the initial absorbance of the acetone extract at 540 nanometers (nm) is obtained using a portable spectrophotometer. The extract is amended with potassium hydroxide and sodium sulfite, agitated for 3 minutes, and filtered again. The extract then can be analyzed visually. If it has a reddish or pinkish color, it contains TNT; if it has a bluish color, it contains 2,4-DNT. Figure 3-1 shows the reaction—known as the Janowsky Reaction

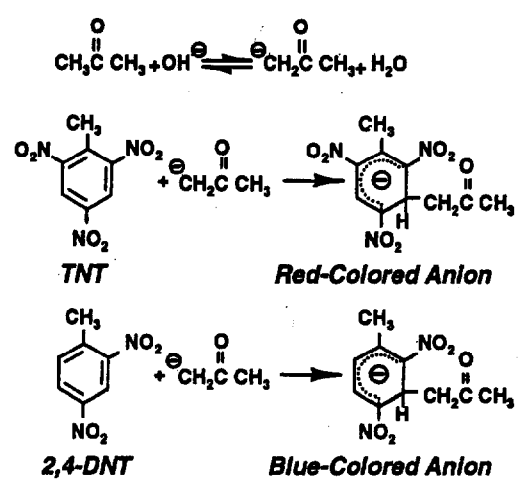

Figure 3-1. Schematic of the Janowsky Reaction (1886) for TNT and 2,4-DNT.

(1886)—that produces the reddish-colored anion from TNT and the bluish-colored anion from 2,4-DNT.

Absorbance measurements can be used to obtain quantitative results. Figure 3-2 illustrates the visible absorbance spectrum of the Janowsky Reaction product of TNT, showing the maximum absorbance at 460 and 540 nm. CRREL uses the peak at 540 nm to verify the presence of TNT, even though the absorbance at 460 nm is greater, because of the potential for interference from humic substances at 460 nm. Figure 3-3 illustrates the visible absorbance spectrum of an acetone extract of uncontaminated potting soil before and after Janowsky Reaction reagents are added, showing the greater absorbance near the 460-nm as opposed to the 540-nm wavelength.

The results of TNT screening, which reflect the sum of the TNT and TNB concentrations, correlate well with results obtained in the laboratory. Table 3-1 compares the sum of the TNT and TNB concentrations as determined by colorimetric analysis with the sum of the TNT and TNB concentrations as determined by laboratory analysis for homogenized, field-contaminated (i.e., not spiked) soil samples from seven sites. Figure 3-4 shows the strong correlation (R^2 = 0.985) between results of colorimetric analysis and the standard HPLC laboratory procedures for homogenized soil samples. Table 3-2 compares colorimetric and HPLC results from the Umatilla Army Depot site in Oregon, showing a slightly lower correlation due to the high concentrations of TNT at the site. At the Savanna Army Depot site in Illinois, Dames and Moore, Inc., reported a correlation of 0.959 between the results of laboratory and field analyses. At the Seneca Army Depot site in New York, Aquatec reported that colorimetric analysis identified 15 contaminated and 46 uncontaminated samples. Laboratory analysis revealed only 2 false positives and confirmed all 46 negative results.

3.1.2.3 RDX Screening

Field screening for RDX is similar to, but slightly more complicated than, field screening for TNT. As in the

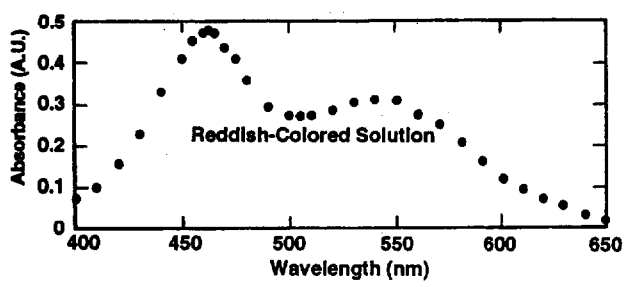

Figure 3-2. Visible absorbance spectrum of the Janowsky Reaction product of TNT.

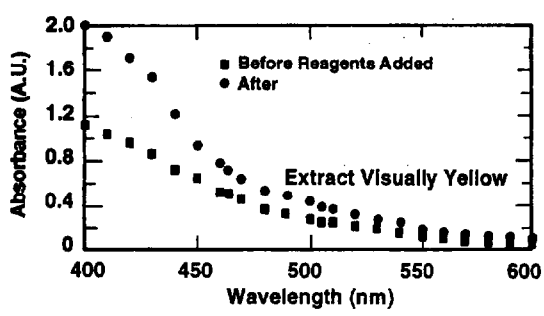

Figure 3-3. Visible absorbance spectrum of acetone extract of potting soil before and after addition of Janowsky Reaction reagents.

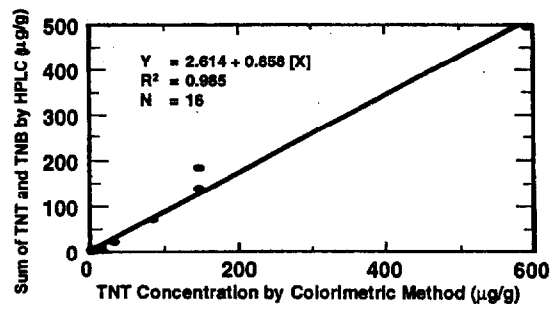

Figure 3-4. Correlation of TNT and TNB analysis by colorimetric and standard RP-HPLC procedures.

Table 3-1. Comparison of TNT and TNB Concentrations as Determined by Field and Laboratory Procedures

	Colorimetric (µg/g)	HPLC (µg/g)	
Sample Origin	**TNT+TNB**	**TNT**	**TNB**
Vigo Chemical Plant (IN)	14	12	<d
Hawthorne Army Ammunition Plant (NV)	6	5	<d
Nebraska Ordnance Works (NE)	2	0	3
Nebraska Ordnance Works (NE)	592	340	157
Hastings Ind. Pk. (NE)	85	68	3
Hawthorne Army Ammunition Plant (NV)	1	1	<d
Nebraska Ordnance Works (NE)	146	64	74
Lexington-Bluegrass Depot (KY)	15	6	<d
Sangamon Ordnance Plant (IL)	33	22	1
Raritan Arsenal (NJ)	85	72	<d

Source: U.S. Army CRREL, 1990.

procedure for TNT, acetone is used to extract contaminants from soil samples. The extract then is passed through an anion exchange resin to remove nitrate and nitrite. Zinc and acetic acid are added to the extract, thereby converting RDX to nitrous acid. The extract then is filtered and placed in a vial with a Hach NitriVer 3 Powder Pillow. If the extract has a pinkish color, it contains RDX. Figure 3-5 shows the reaction sequence, including the Griess Reaction (1864), that produces the pinkish-colored molecule (Azo dye) from RDX.

Table 3-2. Comparison of Colorimetric and HPLC Results from Umatilla Army Depot

	TNT Concentration Estimate (µg/g)	
Sample #	Colorimetric Method	Standard HPLC Method
1b	1,060	2,250
2a	3,560	7,430
3b	704	1,180
3a	3,180	4,030
4a	4,490	8,520
5a	2,530	3,990
6a	84	131
8a	102,000	38,600
9a	6,610	7,690
11a	716	1,300
12a	109	183

a = Surface soil
b = Soil from 18 in. depth
Source: Jenkins and Walsh, 1992.

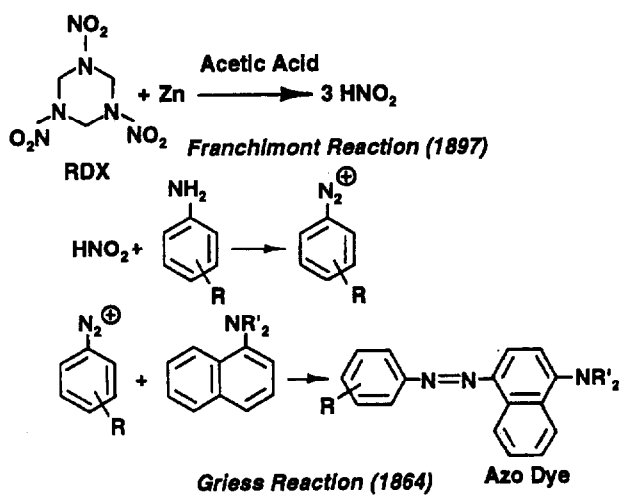

Figure 3-5. RDX reaction sequence, including production of pinkish-colored anion (Azo dye) by Griess Reaction (1864).

As in the TNT detection procedure, quantitative analysis of the extract can be obtained from absorbance measurements. Figure 3-6 is the visible absorbance spectrum of the NitriVer 3 reaction product, showing the absorbance maximum at 507 nm. Colorimetric analysis of uncontaminated soil after acidification and addition of the Griess Reaction reagents shows no background absorbance (see Figure 3-7).

The results of RDX screening, which reflect the sum of the concentrations of RDX and HMX, correlate well with results obtained in the laboratory. Table 3-3 compares RDX and HMX concentration estimates from field and laboratory analysis of soil samples from three sites. Figure 3-8 shows the strong correlation (R^2 = 0.986) between these field and laboratory results. Table 3-4 also shows a strong correlation between RDX concentration estimates from field and laboratory analysis of homogenized, field-contaminated soil samples collected from the Newport Army Ammunition Plant site in Indiana.

3.1.3 Advantages and Limitations of the Methodology

CRREL's methodology has several advantages, including:

- *Speed.* The TNT and RDX detection procedures take about 30 minutes per sample, including the

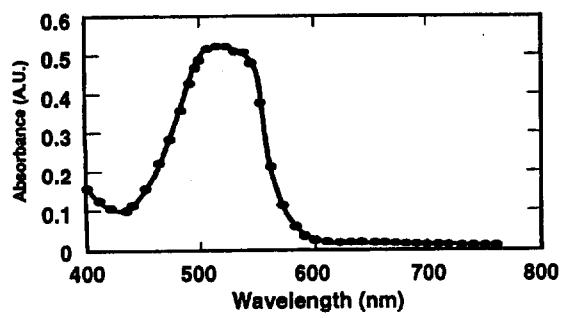

Figure 3-6. Visible absorbance spectrum of NitriVer 3 reaction product.

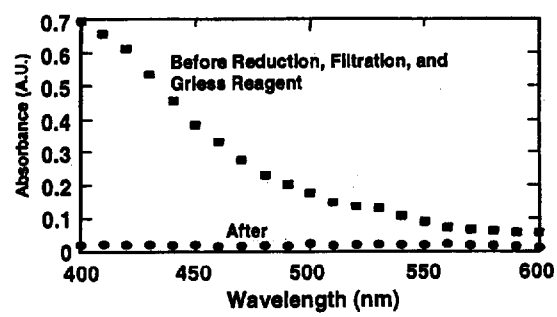

Figure 3-7. Visible absorbance spectrum of acetone extract of uncontaminated soil before and after addition of Griess Reaction reagents.

Table 3-3. Comparison of Colorimetric and HPLC Results for Several U.S. Army Sites

Sample Origin	Colorimetric (µg/g) RDX+HMX	HPLC (µg/g) RDX	HPLC (µg/g) HMX
Nebraska Ordnance Works (NE)	1,060	1,250	115
Hawthorne Army Ammunition Plant (NV)	233	127	56
Raritan Arsenal (NJ)	11	4	t
Nebraska Ordnance Works (NE)	3	4	t
Nebraska Ordnance Works (NE)	1,100	1,140	105
Nebraska Ordnance Works (NE)	10	19	3
Hawthorne Army Ammunition Plant (NV)	6	3	<d
Nebraska Ordnance Works (NE)	129	104	12
Nebraska Ordnance Works (NE)	16	14	2
Nebraska Ordnance Works (NE)	21	60	13
Nebraska Ordnance Works (NE)	2	<d	<d

Source: U.S. Army CRREL, 1991.

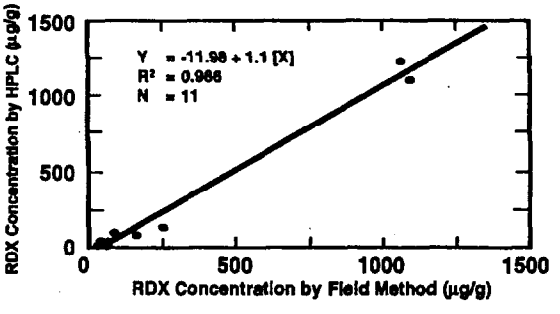

Figure 3-8. Correlation of RDX analysis by colorimetric and standard HPLC procedures (Jenkins and Walsh, 1992).

15-minute color development stage. Typically, 25 samples can be analyzed per day for both RDX and TNT.

- *Cost.* The solvents used in these tests are very inexpensive. The total cost for materials to process each sample is about $20, relatively inexpensive compared to other analytical methods.
- *Simplicity.* The calibration of the colorimetric analysis is linear, and the test has a zero intercept, meaning that all associated calculations are very simple.

Table 3-4. Comparison of Colorimetric and HPLC Results for Newport Army Ammunition Plant

Sample #	RDX Concentration Estimate (µg/g) Colorimetric Method	RDX Concentration Estimate (µg/g) Standard HPLC Method
1	0.55	0.05
2	2.86	1.31
3	4.55	3.15
4	6.62	15.5
5	5.87	8.45
6	253	299
7	17.4	38.6
8	45.4	258
9	674	1,800
10	2,430	3,170
11	7,690	12,200

Source: Jenkins and Walsh, 1992.

- *Laboratory correlation.* The results of colorimetric analysis show strong correlation with those obtained by HPLC procedures.
- *Low incidence of false negatives.* This is important since the procedure is used to screen for explosives-contaminated soils.
- *Low detection limits.* The procedure can detect explosive residues at concentrations as low as 1 g/g.

The limitations of CRREL's procedure include:

- *Water content.* Samples must contain 2 to 3 percent water by weight. Samples from sites with dry conditions must be wetted with distilled water prior to color development.
- *Interferences.* The TNT procedure detects other nitroaromatics and is subject to positive interference from humic materials. These interferences can be reduced by careful visual analysis prior to colorimetric analysis. The RDX procedure detects other nitramines and nitrate esters such as nitrocellulose and nitroglycerine.

3.1.4 TNT and RDX Test Kits

A private firm has developed and tested a field screening kit based on CRREL's methodology. A "how to" videotape explaining the procedure is available from Martin H. Stutz at the U.S. Army Environmental Center at Aberdeen Proving Ground, Maryland 21010. Requests must be submitted in writing.

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3.2 Characterization of Radioactive Contaminants for Removal Assessments

3.2.1 Background

In 1987, EPA's Office of Radiation and Indoor Air (ORIA) developed a characterization protocol for determining the feasibility of reducing the volume of soils contaminated with radioactive wastes at Superfund sites. ORIA's protocol is more extensive than standard protocols, which require only gamma spectroscopy of bulk samples to determine the levels of radioactive constituents. In ORIA's protocol, sieving and sedimentation techniques are used to separate soils into size fractions. Each fraction then undergoes petrographic and radiochemical analysis to determine the values of certain parameters, such as grain size distribution, mineral composition and percentages, and physical properties of radioactive contaminants, that affect the feasibility of volume reduction. This section discusses the potential applicability of ORIA's protocol to radioactive soils at federal facilities, examines the two tiers of the protocol, and presents a case study of a radium-contaminated site where the protocol was applied.

3.2.2 Applicability to Military Installations

ORIA's protocol potentially could be used to characterize soils at military sites contaminated with radioactive wastes. For example, at an Air Force base in California, it was speculated that radium paint buried in a bunker was contributing to elevated uranium levels in the well water of a nearby field. Radiochemical analysis would have indicated that radium paint does not contain the parent compound, uranium-238, so uranium at the site could not have been derived from radium paint in the bunker. Similarly, at an Air Force base in New Mexico, researchers conducted an analysis for radium contamination near a particular bunker where radium paint also might have been buried. This analysis found radium only at background levels. A petrographic analysis of the soil would have revealed natural radioactive minerals and led to the same conclusion.

ORIA's protocol is relatively inexpensive. Petrographic analysis of five representative soil samples takes a petrographer about one week and costs about $5,000. Radiochemical analysis takes three times as long and costs about $15,000. Thus the total cost to develop a detailed characterization of soil from a military installation, as a feasibility study for remediation considerations, would be approximately $20,000.

3.2.3 ORIA's Soil Characterization Protocol

ORIA's methodology was developed based on investigations at thorium-contaminated sites in Wayne and Maywood, New Jersey; radium-contaminated sites in Montclair and Glen Ridge, New Jersey; and plutonium surrogate host soil at the Nevada Test Site. These investigations led to the development of a two-tiered protocol: Tier 1 is a feasibility study; Tier 2 is an optimization study.

3.2.3.1 Tier 1: Feasibility Study

The Tier 1 feasibility study has two stages: fractioning and analysis.

Fractioning

Bulk samples are dried at 60°C and examined by high resolution gamma spectroscopy. Samples then are split into representative 300-gram portions by prescribed separation methods, and each portion to be tested is placed in a beaker to create a slurry of five parts deionized water to one part solids. After 24 hours, the slurry is stirred and poured through a nest of increasingly fine sieves to separate the bulk sample into size fractions of coarse, medium, and fine sand and silt.

Analysis

The fractions obtained by sieving undergo three separate analyses. First, the fractions are analyzed to obtain the sample's grain size distribution curve, which identifies each size fraction's contribution to the total weight of the sample. Figure 3-9 is a grain size distribution curve for soils from the Nevada Test Site. Second, the fractions are analyzed for radioactivity as a function of particle size. Figure 3-10 is a graph of radioactivity versus particle size for radium-, thorium-,

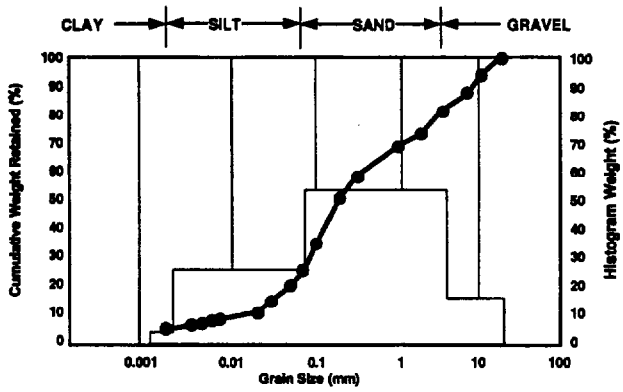

Figure 3-9. Grain size distribution curve and histogram for soil from the Nevada Test Site.

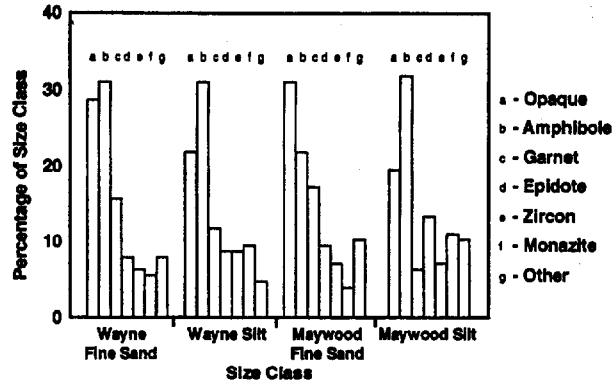

Figure 3-11. Heavy mineral composition of soil from the Wayne and Maywood, New Jersey, sites.

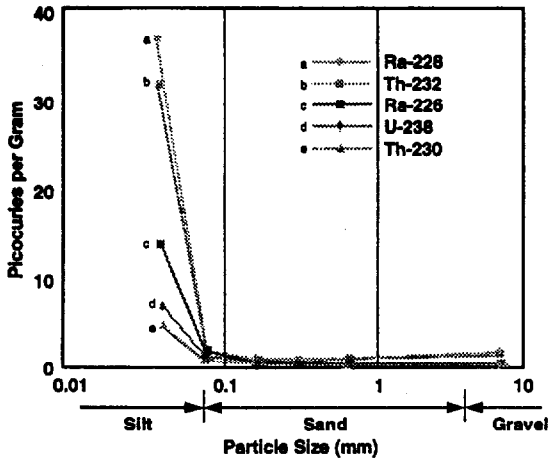

Figure 3-10. Radiochemical analysis showing radioactivity as a function of particle size.

and uranium-contaminated soils, from Maywood, New Jersey, showing increased radioactivity in the silt-size fraction. Third, the size fractions undergo petrographic analyses, which generate precise statistical counts of the various particles in the soil. Coarse-size materials, which are greater than 0.6 mm, are analyzed visually. Medium-size materials, which are between 0.038 and 0.60 mm, are immersed in index oil and examined under petrographic and binocular microscopes. Fine-size materials, which are less than 0.038 mm, are examined by X-ray diffraction. Finally, medium-size materials undergo a second petrographic analysis in which a separatory funnel containing sodium polytungstate is used to extract minerals with specific gravities greater than 3.0. These minerals, which usually represent a small percentage of the total sample, contain disproportionately high levels of radioactive materials. Figure 3-11 shows the heavy mineral composition of soil from the Wayne and Maywood, New Jersey, sites. The heavy mineral fraction of the soil from this site contains all of the radiation contaminants. Monazite, which contains almost all of the radioactivity, represents only about 10 percent of the heavy mineral fraction and comprises less than 1 percent of the total sample. Zircon, which can contain up to 4 percent substitution of thorium or uranium in the crystal lattice, constitutes the remainder of the radioactive material at this site.

3.2.3.2 Tier 2: Optimization Study

If Tier 1 suggests that volume reduction is feasible, further analyses can be performed to characterize the contaminated soil. Size fractions can be broken down into more precise increments by hydroclassification and centrifuge. In addition, chemical assays can be used to quantify the mineral analysis if a chemical element is known to be solely associated with a particular contaminant. For example, at one of the radium-contaminated sites, the ore minerals for radium include a uranal vanadinate. Since vanadium is rare, it can be used as a "chemical signature" to determine the weight percentage of this ore mineral of radium. Instruments such as the scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX) also can be useful in identifying the morphology and elements of specific particles in the submicroscopic size range.

3.2.4 Case Study: Montclair/Glen Ridge Superfund Site

From 1915 to 1926, acid leach tailings from the manufacture of radium were deposited in open field pits in Montclair and Glen Ridge, New Jersey. After operation ceased in 1926, residential housing was developed in the area. Most of the contamination, which consists primarily of precipitates and coprecipitates from the acid leach process, is within 8 ft of the surface. Ground water contamination is confined to areas directly surrounding the dump areas, and there is no ground water contamination in the bedrock, which is 20 ft below the surface. Consolidated glacial till, along with

other materials that were dumped in the pits, is the host material for the radium-contaminated tailings. The cost to remove, transport, and dispose of all 300,000 yd^3 of soil from the site is estimated at close to $300 million, making volume reduction an attractive option.

Tier 1 analyses indicated that the contaminated material consists of 15 percent ores, such as carnotite and uraninite, and 85 percent anthropogenic materials. Within the latter group, most of the radioactivity is located in the fine silt and clay fractions, particularly in the 10- to 20-µm fraction. A linear density gradient analysis was used to separate the 10- to 20-µm fraction into light, medium, and heavy particles (see Table 3-5). These three groups of particles then underwent Tier 2 analyses, including gamma spectroscopy, X-ray diffraction analysis, SEM/EDX analysis, photomicrography, and autoradiography. Figures 3-12 and 3-13 illustrate the results of some of these analyses. The light particles, which are mostly amorphous silica, were found to contain about 25 percent of the radium; the heavy particles, which are mostly radiobarite, were found to contain about 50 percent of the radium.

Table 3-5. Linear Density Gradient Analysis of 10- to 20-µm Size Fraction of Soil from Glen Ridge, New Jersey, Site

Density	Weight %	Ra-226 Activity	% Ra
Light 2.10-2.25	32.20	1,640 pCi/g	25.21
Medium 2.25-2.71	55.69	1,040 pCi/g	27.55
Heavy 2.71	12.01	8,270 pCi/g	47.24

Source: U.S. EPA, 1989.

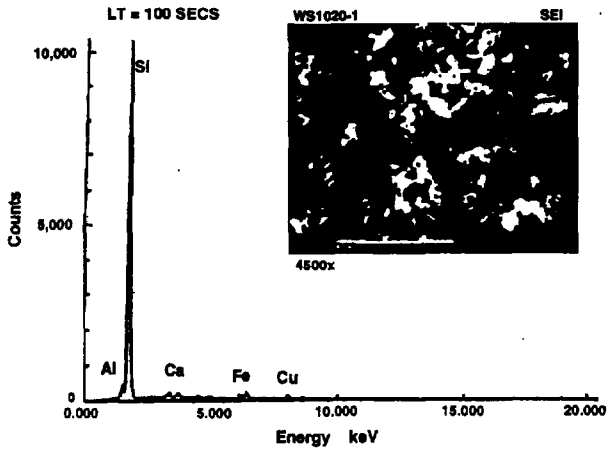

Figure 3-12. SEM (inset) and EDX analysis of amorphous silica from the 2.10-2.25 density fraction of the 10- to 20-µm grain size of radium-contaminated soil from Glen Ridge, New Jersey.

Based on the results of the characterization, site engineers decided to remove the fine silt particles from the site and wash the remaining sand-size particles of any residual clay. In laboratory testing, these procedures reduced 30 to 40 percent of the material to a target level of 12 to 15 picocuries per gram of radium 226 (see Figure 3-14).

3.2.5 References

References Cited

U.S. EPA. 1989. U.S. Environmental Protection Agency. Characterization of contaminated soil from the Montclair/Glen Ridge, New Jersey, Superfund sites.

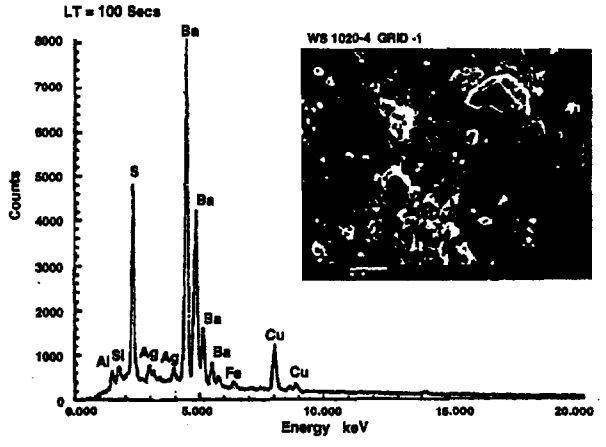

Figure 3-13. Autoradiograph (SEM) showing radiation etch tracks from radiobarite (inset) and EDX of radiobarite in the heavy fraction of 10- to 20-µm grain size of radium-contaminated soil from Glen Ridge, New Jersey.

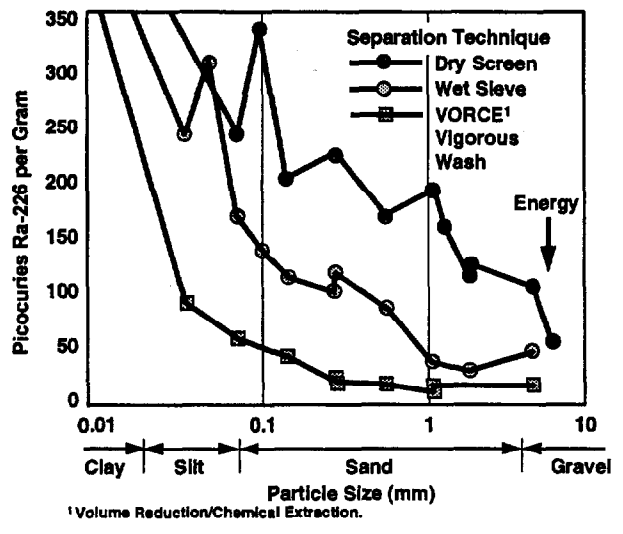

Figure 3-14. Radium reduction produced by laboratory-scale water washing and wet sieving of soil from Montclair and Glen Ridge sites.

EPA/520/1-89/012. U.S. EPA, Office of Radiation Programs.

Additional References

Neiheisel, J. 1992. Petrographic methods in characterization of radioactive and mixed waste. Proceedings of HMC/Superfund 1992, December 1-3, Washington, DC, 192-195.

U.S. EPA. 1992. U.S. Environmental Protection Agency. Characterization protocol for radioactive contaminated soils. Pub. No.: 9380, 1-10FS. U.S. EPA, Office of Solid Waste and Emergency Response.

Chapter Four
Detection and Retrieval of Buried Munitions

This chapter covers several aspects of detection and retrieval of buried munitions. Section 4.1 is an overview of approaches to munitions detection and retrieval, primarily in large fields of operation, such as large firing ranges or war-ravaged countries. Section 4.2 discusses retrieval and management of unexploded ordnance at military sites in the United States, and section 4.3 examines detection and sampling of white phosphorus munitions.

4.1 Overview of Approaches to Detection and Retrieval Operations[1]

This section examines various approaches for planning activities related to detection and retrieval of buried munitions, while emphasizing the importance of the site-specific operations planning document, which is designed to anticipate procedural problems and ensure the procurement of equipment compatible with specified tasks. This section also considers the means of anticipating hazards and potential problems and provides an operations planning checklist.

4.1.1 Site Assessment and Operations Planning

The factors to consider when assessing a site for detection and retrieval of munitions can be as varied as the types of explosives waste that can be encountered. Along with the instability and unpredictability of the munitions themselves, however, a comprehensive assessment also must take into account several other site-specific factors. These factors include:

- Proximity of population centers, which introduces the possibility of evacuation and can restrict open burning or detonation.
- Particular terrain, which can be inaccessible or saturated with metal and thus influence the detection equipment used.
- Seasonal weather, particularly temperature, which determines the type of protective clothing and detection equipment used.
- Breadth and depth of contamination, and the presence of underground obstacles, such as water lines and electric power cables, which influence the selection of detection equipment.
- Potential environmental impact of retrieval.

Based on these considerations, retrieval operations at a munitions firing site would be carried out quite differently than retrieval of an explosive encountered during excavations for an addition to a local hospital. Ultimately, the extent of any operation will be determined by constraints on time, technology, and financial resources.

When assessing the nature of the munitions buried at a site, the operations planner must be fully aware of the challenges associated with specific types of explosives. The following items are particularly problematic in terms of safety and procedural planning:

- Dud-fired munitions, which are fuzed and armed.
- White phosphorus munitions, which, if damaged or leaking, ignite on contact with air and pose problems in recovery, handling, transportation, and disposal.
- Chemically filled and depleted-uranium munitions, which require several safety precautions, such as protective clothing, decontamination lines for personnel and equipment, and downwind hazard areas.

Table 4-1 presents a checklist of factors to consider in operations planning. While not intended to be comprehensive, it covers major categories of issues regarding buried munitions sites and is intended to be used in the planning stages of a site-specific document. Using a think-tank approach with subject matter experts, each applicable section should be reviewed for problem areas and the development of the operations plan. Consideration of the factors listed in Table 4-1 will make it possible to answer several questions that are key to the planning effort:

- What type of munitions are likely to be encountered?

[1] The approaches described in Section 4.1 are based on experience in foreign countries and might not be applicable to operations conducted in the United States.

Table 4-1. Checklist for a Site-Specific Detection/Retrieval Plan

I. Background

A. Site history

1. Abstracts (e.g., old records, aerials, archives)

2. Range history

3. Battlefields/targets

4. Ammunition Supply Point (ASP) records/storage facilities and dumps (e.g., anticipated munitions and degree of deterioration)

B. Level-one assessment

1. Current aerials/satellite photographs

2. Recent surveys (boundaries/borders, both physical and political)

3. Utility company records (e.g., wires, cable, piping)

4. Environment

a. Climatic conditions/restrictions

b. Sensitive floral and faunal species

5. Topography

6. Subsurface/surface soils and stratigraphy

a. Ground water interference (also impact of retrieval operations on local water and mineral resources from chemical munitions)

b. Limitations on detection and retrieval equipment

7. Walk-Through

a. Evidence of dispensers and other delivery systems

b. Presence of physical obstacles not readily apparent

c. Craters or other physical evidence not apparent from aerials or surveys

d. Surficial evidence of buried munitions/chemical leaks, high explosives, or ordnance components

C. Regulatory restrictions

1. National

2. Regional

3. State

4. Local

5. Political (foreign restraints)

6. Sociological

7. Rerouting of utilities

8. Economic (e.g., interruption of businesses or access to natural resources)

II. Scope of Work

A. Geographic extent

B. Quantity of contamination anticipated/types of contamination

C. Time for completion

D. Quality controls

1. Determination of completeness

2. Internal/external controls/monitoring

E. Remediation required (e.g., reclamation)

III. Equipment Requirements

A. Mine detector

B. Computerized subterranean visual location

C. Ferrous ordnance locators (deep)

D. Mass detectors

E. Retrieval equipment (manual or remote)

F. Heavy equipment (e.g., modified heavy equipment)

1. Soil handling

2. Gaining access to ordnance items

3. Removal of ordnance items

IV. Personnel Requirements

A. Explosive ordnance disposal/unexploded ordnance (EOD/UXO) specialists

B. Support personnel

1. Administration

2. Safety/medical support

3. Laborers

4. Heavy equipment operators

5. Technical support (e.g., instrument personnel)

6. Maintenance

C. Political agents/liaisons

D. Trainers

V. Safety Requirements

A. Remote retrieval equipment

B. Chemical/Hazardous materials protection

1. Communications

2. Medical monitoring

3. Decontamination of personnel and equipment

C. Environmental protection

D. Contingency Plan/Accident Prevention Plan

E. Training program

VI. Financial/Budgetary Restraints

A. Cost vs. operational size

B. Quality of detected information vs. cost and utility

C. Time allotted for completion

- What is the required end result?
- What is the scope of the project?

4.1.2 Selection of Detection Equipment

When selecting munitions detection equipment, the operations planner must weigh the advantages and disadvantages of various technologies in relation to the particular site. For example, munitions detection equipment used in the remediation of a 5-acre military storage facility might not be appropriate for a larger scale operation, such as the removal of land mines from 100 square miles of a former militarized zone. Equipment used for the larger scale operation would have to be portable and could not require long setup and operation times.

High-end munitions detection equipment is quite sophisticated. A recently developed computer technology has made it possible to generate a three-dimensional, enhanced "snapshot" of as much as an acre of subsurface contamination. Selected views of the area can be generated that eliminate such obstructions as utility lines in order to portray subsurface contamination with great accuracy. A limitation of this technology is that it detects only metallic objects; also, certain soil compositions can undermine the accuracy of such equipment. Moreover, because it takes most of a day to generate a readout, such equipment is best suited to relatively small-scale operations.

On the other end of the detection technology spectrum is the conventional metal detector (i.e., the mine detector). Metal detectors vary in sensitivity and signal type. Some detectors have a depth range of up to 60 ft; others have a range of only 1 ft. Relatively unsensitive detectors might be appropriate for clearing an artillery impact area where large amounts of ordnance fragments are within 6 ft of the ground surface. Figure 4-1 shows a metal detector being used to perform a quality control check for ordnance in a demolished bunker. A more sensitive detector would be required to locate an unexploded bomb dropped from an airplane, since ordnance dropped from a high altitude can penetrate deep into the ground surface—in loose soil, to as deep as 60 ft.

In the past, mass detectors were used to search for nonferrous materials. These detectors were sensitive to variation in density and thus capable of detecting explosive materials containing no metal. At present, however, mass detectors are considered to be an antiquated technology.

Figure 4-1. A quality control check to a depth of 6 ft to assure that no ordnance items remain in a demolished bunker.

4.1.3 Minimizing Hazards in Retrieval Operations

Personnel safety with chemicals and explosives is the primary consideration when carrying out a buried munitions retrieval operation. Indeed, although the dangers inherent in certain aspects of munitions retrieval operations cannot be eliminated, thorough planning can reasonably minimize hazards. A "least hazardous" method for a particular procedure usually can be developed through hazard analysis studies, the application of modern loss-control techniques, and adherence to safety recommendations and regulations. Most cases of "failure" in munitions retrieval operations can be traced to insufficient site-specific safety planning.

A general approach to follow in munitions retrieval operations is to expose a minimum number of personnel to hazards for a minimum amount of time. This approach suggests that remote retrieval procedures should be used whenever possible. Remote procedures can be as unsophisticated as attaching a line to a piece of buried ordnance and retrieving it from a safe distance. Or they can involve elaborate technologies such as remote-controlled tools and computer-operated robots. Since using remote retrieval procedures is not always practical, the operations planner must determine which approaches can be used with minimum risk. Type of ordnance is the determining factor in most cases. Remote initial movement would be advisable, for instance, when retrieving either antitank munitions fuzed with piezoelectric crystals and a dud-fired, graze-sensitive feature or extensively damaged white phosphorus munitions. Conversely, manual retrieval might be reasonable for either a dud-fired illumination round with a powder-train time fuze or an unarmed and undamaged explosive projectile.

For some situations, readily available equipment can be modified to fulfill operational requirements. For example, an area saturated with small-blast or blast-and-fragmentation munitions might be cleaned up with a conventional D-8 bulldozer after a "rake" has been added and the operator's cab has been armored. For other situations, it might be feasible to enhance such a bulldozer with the addition of remote controls or to use the heavy equipment itself as a barrier between the ordnance and the operator. Figures 4-2 and 4-3 show examples of modified vehicles used in munitions recovery. The operations planner should be prepared to use whatever will accomplish the task without posing an unacceptable risk of injury to personnel.

When retrieving munitions that pose a respiratory hazard, such as chemical ordnance, personnel must wear protective clothing. In such cases, the operations planner needs to consider several questions in regard to equipment use, including:

- Can the equipment controls be manipulated by personnel wearing protective clothing?

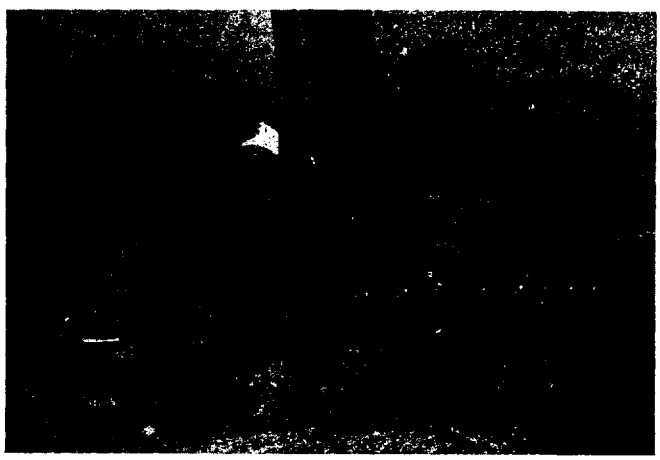

Figure 4-2. Track hoe in use as munitions recovery vehicle.

Figure 4-3. Locally modified "armored cab" track hoe.

- Will climate and fatigue limit the length of time personnel can operate equipment?
- Can the equipment be decontaminated after the operation?

After all logical attempts have been made to limit exposure of personnel to operational hazards, certain aspects of an operation still might need to be performed manually. For such cases, the operations planner will face difficult decisions concerning acceptable risks. The basis of any such decision-making has to be a recognition of the dangers that are inherent to the task of clearing weapons of destruction—some only partially detonated—from a site. Operations often require that procedures be developed at the site and then implemented without benefit of thorough testing. Only through careful planning can an operation be designed to minimize hazards and the threat of injury.

4.2 Detection, Retrieval, and Disposal of Unexploded Ordnance (UXO) at U.S. Military Sites

4.2.1 Background and Definitions

Ordnance and explosive waste (OEW) is technically defined as:

> anything related to ordnance designed to cause damage to personnel or materiel through explosive force, incendiary action, or toxic effects. OEW includes bombs and warheads; guided and ballistic missiles; artillery, mortar, and rocket ammunition; small arms ammunition; antipersonnel and antitank land mines; demolition charges; pyrotechnics; grenades; torpedoes and depth charges; containerized and uncontainerized high explosives and propellants; depleted uranium rounds; military chemical agents; and all other related components, explosive in nature or otherwise designed to cause damage to personnel or materiel (e.g., fuzes, boosters, bursters, rocket motors). Uncontainerized high explosives/propellants or soils with explosive constituents are considered explosive waste if their concentration is sufficient to be reactive and present an imminent safety hazard.[2]

One component of OEW is unexploded ordnance (UXO), technically defined as:

> explosive ordnance which has been primed, fused [sic], armed, or otherwise prepared for action, and which has been fired, dropped,

[2] This definition of OEW was developed by the Huntsville Mandatory Center of Expertise (MCX) and is used frequently in their statements of work to contractors.

launched, projected, or placed in such a manner as to constitute a hazard to operations, installations, personnel, or materiel, and remains unexploded either by malfunction or design or for any other cause.[3]

This section discusses the authority and qualifications for handling UXO projects, types of UXO projects, UXO detection and excavation tools and techniques, and UXO identification and disposal.

4.2.2 Authority and Qualifications for Handling UXO

4.2.2.1 Authorities and Programs

In 1986, Congress established the Defense Environmental Restoration Program (DERP) under Public Laws 99-190 and 99-499 to investigate and remediate OEW. The two subprograms established under DERP are the Installation Restoration Program (IRP), which deals with active DOD installations, and the Formerly Used Defense Sites (FUDS) Program, which deals with sites formerly owned or used by DOD, but no longer under DOD control.

The Huntsville Division of the U.S. Army Corps of Engineers (COE) was designated on April 5, 1990, as the Mandatory Center of Expertise (MCX) and Design Center for UXO. As the UXO MCX, Huntsville is responsible for investigating and remediating OEW under the IRP and the FUDS program. The Huntsville Division MCX works in cooperation with local COE districts, local officials, and interested citizens to examine and remediate OEW contamination.

4.2.2.2 UXO Personnel

Specialized training in ordnance disposal for personnel from all four branches of the armed forces has been standardized at the U.S. Naval School of Explosive Ordnance Disposal (EOD), at the Naval Ordnance Station in Indian Head, Maryland. This site has been the main EOD training center for the U.S. armed services since World War II. In the future, a recently opened satellite facility of the U.S. Naval School of EOD at Eglin Air Force Base, Florida, might assume a larger role in EOD training.

While civilian- and military-trained specialists are distinguished by title—UXO specialists and EOD technicians, respectively—skill classifications in this field are roughly equivalent. Civilian skill classifications of UXO Specialist, UXO Supervisor, and Senior UXO Supervisor generally correspond to the military designations of Basic EOD Technician, Senior EOD Technician, and Master EOD Technician (also known in the military as "Master Blaster"). All UXO specialists working for contractors under contract to the Huntsville MCX must be former EOD technicians who have attended and graduated from the U.S. Naval School of Explosive Ordnance Disposal.

4.2.3 Types of UXO Projects

UXO projects fall into two main categories: UXO remediation/investigation and UXO support services. These two types of projects are described below.

4.2.3.1 UXO Remediation/Investigation

UXO remediation/investigation involves the location and disposal of UXO. The explosive hazard presented by UXO is the overriding safety concern in UXO remediation/investigation.

While the organization of a UXO remediation project varies depending on the project's size and the site conditions, UXO work crews generally work most efficiently when divided into distinct teams to accomplish specific objectives. A field work team typically is staffed by a group of 3 to 10 UXO specialists, assistants, and skilled laborers under the direction of a UXO supervisor. The exact number and type of personnel depend on the project's work objective. A large surface survey team, for example, could have several skilled laborers trained as magnetometer operators. UXO work crews performing intrusive operations, such as UXO excavation, will consist entirely of UXO specialists because a high level of training is required to perform that operation safely.

4.2.3.2 UXO Support Operations

In contrast to the goal of removing and disposing of UXO in remediation/investigation, UXO support operations focus on protecting site personnel who are not EOD trained from the hazards presented by UXO in their work area.

An example of a UXO support operation is any remedial investigation/feasibility study (RI/FS) that requires the generation of field data from an active or formerly used DOD installation. Whenever an installation has been used by DOD, the possible presence of UXO or explosives should be considered. If the site history indicates that UXO was used or disposed of near project sampling activities, the project management authority typically requires that the work plan and safety plan consider UXO hazards and requests Huntsville MCX oversight of UXO operations.

During environmental sampling efforts, UXO specialists might be employed to remove UXO hazards to allow access to well drilling sites, or to perform downhole

[3] Definition of UXO from the "Department of Defense Dictionary of Military and Associated Terms," Joint Publication 1-02, December 1, 1989.

magnetometer checks during well drilling operations to preclude contact with UXO. UXO specialists also might escort field sampling teams to locate potentially hazardous UXO and ensure that such items are avoided.

UXO support operations usually are staffed with the minimum number of UXO specialists required to ensure the safety of field sampling personnel. Generally, the level of UXO staffing required is one UXO specialist for each individual field operation to be simultaneously conducted. For example, if two well drilling rigs and one soil gas sampling team are working simultaneously in areas that could contain UXO, a total of three UXO specialists would be used to ensure the safety of the three sampling teams. Each sampling team should have an assigned UXO specialist responsible for the detection and avoidance of UXO.

Because UXO disposal typically is not included in the statement of work for UXO support operations, UXO discovered during such operations should be reported to the area's military EOD team. Planning for UXO support operations always should include deciding who would have custody of and responsibility for UXO that might be discovered during the project. The group or agency responsible for disposal of the UXO also should ensure adequate security to prevent unauthorized access to the hazardous UXO.

The disposal of UXO hazards usually is not possible during a UXO support project, because sufficient UXO personnel are not available. Intrusive activities, such as excavation of suspected UXO items, require at least two UXO specialists, with additional support personnel available in case of emergency. This staffing level is rarely available on a UXO support project, which has other field priorities and usually involves only the minimum number of UXO specialists to escort the sampling teams. As a result, disposing of UXO discovered during a support operation takes a long time, because the contracting authority must shift from the UXO support staff to the Huntsville MCX.

4.2.4 UXO Detection and Excavation

The equipment and techniques commonly used for UXO detection and excavation are described below.

4.2.4.1 Geophysical Detection Equipment

While locating UXO by sight is sometimes possible, most UXO is extremely difficult to locate without the aid of detection equipment, because UXO usually is deteriorated and camouflaged by soil, grasses, and leaves. Geophysical instruments are used to locate potential UXO anomalies. The most common types of geophysical instruments used on UXO projects are the low-sensitivity magnetometer, the high-sensitivity magnetometer, and the metal detector.

Low-Sensitivity Magnetometer (LSM). The LSM is the most commonly used instrument for UXO location because it is inexpensive, effective, and easy to use. LSMs used for UXO detection typically are the dual-fluxgate type originally developed for the detection of underground utilities. Completely nonintrusive, LSMs do not emit any electromagnetic radiation, which is a potential source of initiation for some electrically initiated UXO. A minor disadvantage of LSMs is that they detect only ferrous items; nonferrous UXO, however, is fairly rare. LSMs are used most frequently to supplement visual observation during surface and near-surface UXO searches and during safety escort operations.

High-Sensitivity Magnetometer (HSM). While operating on the same principle as the LSM, the HSM also can be calibrated and has a greater detection capability. Some HSMs are designed specifically for subsurface UXO detection and are so used by military EOD teams. Some specific models have been tested extensively by the U.S. Naval EOD Technology Center and can locate large UXO up to 20 ft underground. Some HSMs are equipped with a fluxgate sensor probe, which can be detached from the electronics package to perform underwater and downhole investigations. The HSM's primary disadvantages are cost ($17,000 compared to $650 for the LSM) and increased weight and bulk. An HSM, therefore, is used only when additional sensitive detection capabilities are required or as a quality control tool to check areas previously searched by the less capable LSMs.

Metal Detector. Metal detectors, similar to commercially available treasure finders, are useful for projects requiring a second method of UXO detection. These inexpensive instruments can locate nonferrous metallic objects. They emit low-frequency radiation, however, which presents the remote possibility of initiating certain UXO under ideal conditions. Underwater versions also are available for use by divers.

4.2.4.2 Geophysical Detection Techniques

UXO specialists surveying an area for UXO typically begin by marking the site boundaries with stakes. They then divide the area into 5-ft-wide search lanes by stringing surveyors' lines across the site to stakes at each end of the survey area. The UXO survey team then uses the low-sensitivity magnetometer to examine each survey lane.

Upon detecting a possible subsurface UXO, the UXO specialist will mark the spot with a pin flag or spot of spray paint. A team of two UXO specialists then will

excavate the marked items when the magnetometer survey team has advanced beyond the area that would be hazardous in the event of an accidental detonation caused by the excavation team.

4.2.4.3 UXO Excavation Tools and Techniques

Anomalies suspected to be UXO can be positively identified by a trained UXO specialist only after excavation, which allows access to the item. Excavation does not involve removal or movement of the item; these activities would be considered part of the disposal process. At most UXO sites, the vast majority of UXO are located within 2 ft of the surface. Various common hand tools are used to excavate such relatively shallow UXO. For large projectiles and bombs that can be imbedded from 10 to 20 ft underground, a backhoe can be used by a skilled UXO specialist/equipment operator.

Upon locating and unearthing the suspected item, excavation team members attempt to classify it. First, they will determine if the item is UXO. If it is not UXO and is not hazardous, such as a scrap of metal, the nonhazardous metallic item may be removed and the hole backfilled. If the item is identified as UXO, the excavation team next will attempt to positively identify it. All excavation results should be recorded in a field excavation log.

4.2.5 Positive Identification

UXO is discovered most often in a deteriorated condition after years of exposure, which can make positive identification difficult or impossible. Positive identification is even more difficult for UXO specialists, since, unlike EOD technicians, they do not have ready access to EOD 60 Series publications, reference documents with detailed information on the identification and functioning of specific ordnance. These publications are frequently classified and available to UXO specialists only on an as-needed basis from the Huntsville MCX. UXO specialists are not authorized to maintain EOD 60 Series libraries, which would have to be guarded with the proper security and updated when the publications are changed by the EOD Technology Center in Indian Head, Maryland.

UXO specialists, therefore, frequently are required to identify UXO based on their experience alone. Required to err on the side of safety, specialists must consider a UXO not positively identified unless it is a common UXO with characteristics and operation that are thoroughly familiar to them. If a UXO cannot be positively identified, it must be considered unsafe to move. Unidentified UXO potentially could have been exposed to a number of stresses, including being buried for a long time, being fired downrange and failing to function as designed, or being kicked out of an improperly constructed disposal detonation by the force of the detonation rather than being consumed by the detonation. It often is impossible to determine how the UXO was affected by such stresses.

4.2.6 UXO Disposal

Once a UXO has been positively identified, the decision to move a UXO is based on the UXO's fuzing and condition, i.e., whether the UXO fuze has been armed. Fuze arming is designed to occur when the ordnance is fired or otherwise deployed. Therefore, UXO that has been deployed, but failed to function, is considered to be armed.

While the general rule of thumb is that unarmed UXO is safe to move and armed UXO is not, some exceptions exist. Although armed UXO usually is disposed of without being removed, some specific UXO is safe to move even if armed. Knowledge of the specific UXO is required to move any UXO safely. Conversely, even if a UXO is considered to be unarmed, the UXO specialist may decide based on its appearance that it is not safe to move. The UXO specialist should always err on the side of safety and opt not to move any questionable UXO.

The ideal method of handling UXO that is positively identified as armed and unsafe to move is to dispose of it where it is found. For UXO that is unarmed and safe to move, disposal by detonation in a prepared disposal area is a feasible option. Since transporting UXO can be extremely problematic, time consuming, and costly, transportation to an offsite disposal area should be considered only if the UXO's current location cannot withstand a high-order detonation, thereby precluding onsite disposal methods.

The following sections discuss the accepted methods of UXO disposal and the critical factors that must be considered when designing a safe and efficient UXO disposal operation. Figure 4-4 is a logic diagram illustrating the rationale and logic for the proper handling and disposal of UXO.

4.2.6.1 Onsite Disposal and Handling

UXO that is positively identified as armed and unsafe to move commonly is disposed of using the blow-in-place (BIP) method, which involves detonating UXO where it is found. In BIP, a small initiation charge of explosives is placed in contact with, or very near to, the UXO.

When neither BIP nor movement of the UXO is possible, a render safe procedure (RSP) is a viable option. Huntsville MCX, however, allows only EOD technicians, not UXO specialists, to perform this operation because needed information on particular RSPs is available only from classified EOD 60 Series publications, to which civilian UXO specialists do not have easy and routine access. The RSP disrupts the UXO's explosive train,

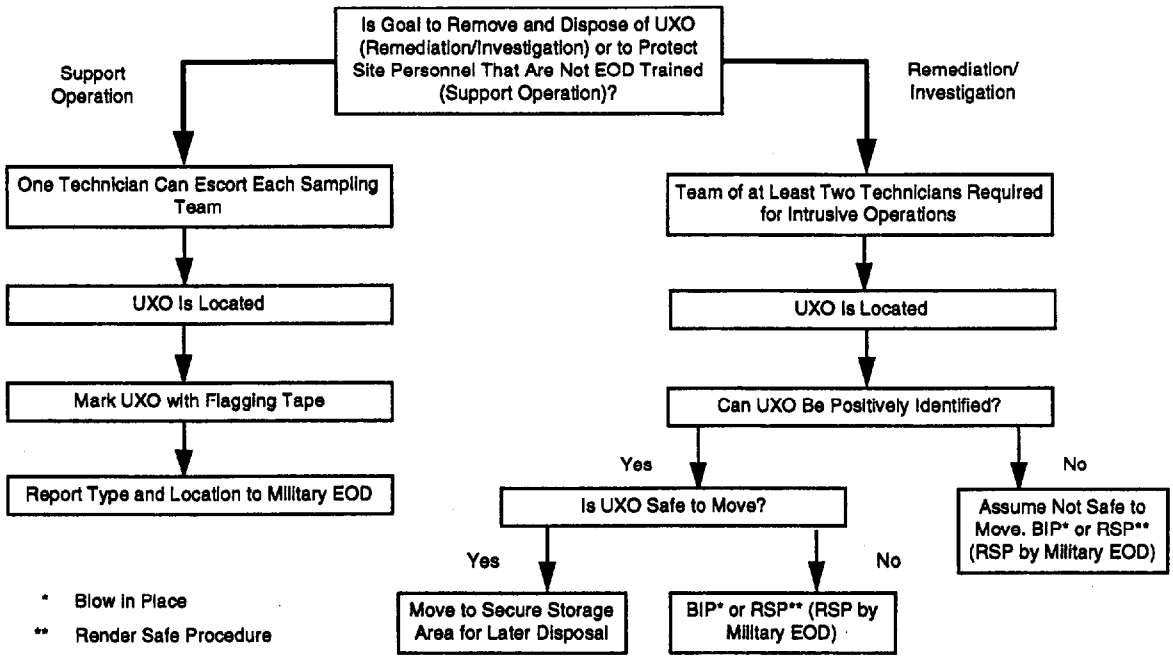

Figure 4-4. UXO disposal operations.

which is the series of events that causes an armed UXO to detonate. This procedure is extremely time consuming and possibly hazardous, so it is most efficient to BIP these armed items and transport only those that are safe to move in the condition in which they were found.

RSPs are designed to eliminate the possibility of UXO detonation, typically through fuze removal or disablement. Since performing an RSP is inherently hazardous, preparations should be made in advance for a high-order detonation in case the RSP is not successful. EOD technicians frequently perform RSPs remotely to ensure their safety in case of accidental detonation. Since performing RSPs is time consuming and costly, the process should be used only when BIP or movement of the UXO for disposal in a prepared disposal area is not possible.

4.2.6.2 Disposal in a Prepared Disposal Area

Disposal in a prepared disposal area is most efficient for larger projects where a secure onsite storage area is constructed and maintained to collect UXO and store working explosives. In any UXO disposal operation, the goal is to minimize shock and fragmentation associated with the operation, thereby avoiding excessive disturbance of the surrounding area. Large disposal detonation is more efficient than a series of BIP operations and has less of a lasting environmental impact.

For consolidation, however, UXO must be moved to the disposal site and possibly stored until enough UXO is amassed for an efficient disposal detonation. For large disposal detonation, the disposal site is chosen, rather than being dictated by where the UXO was found, as in BIP. Previously disturbed sites can be selected for the UXO disposal area, thereby limiting unnecessary additional environmental impact to other areas. The environmental impacts are contained in the selected area, which can be completely remediated after UXO disposal operations.

Large disposal detonation is much more efficient than performing a series of BIPs. While setting up one large disposal detonation takes slightly longer than preparing a BIP, a much larger quantity of UXO can be disposed of simultaneously in such a detonation area. In contrast, a BIP is effective only for disposal of a single UXO, or a cluster of UXO found together.

4.2.6.3 Considerations for UXO Disposal

Points to consider in any UXO disposal detonation are discussed below.

Security

UXO disposal areas should be easily accessible to UXO personnel and also easily secured when UXO disposal operations are being conducted. If UXO is going to be stored until sufficient quantities are amassed for disposal, a secure storage area also must be provided.

Tamping

Common methods for reducing blast and fragmentation effects are to tamp each disposal shot by covering it with earth or sandbags. At a prepared UXO disposal site, the effects of blast and fragmentation can be minimized by tamping the disposal detonation. To tamp a disposal detonation, the UXO is placed in a hole and covered by at least 3 ft of earth, which helps contain the detonation and reduce the amount of blast and fragmentation. If the site is in or near a residential area, the amount of earth used to tamp the disposal detonation may be increased to further decrease the effect of the blast.

Monitoring

A seismometer can be used to record the amount of blast and shock produced by the detonation. This record of the audio and seismic effects of each disposal detonation can be used to confirm or dispute property damage claims from nearby residents.

Safe Distance

The safe distance from disposal detonations depends on site-specific conditions. For more information on safe distances for disposal detonations, see section 5.2.2.4.

4.3 Detection and Sampling of White Phosphorus in Sediment

4.3.1 Background

White phosphorus, a tetrahedral molecule with four phosphorus atoms, burns rapidly in air to form phosphoric oxide (P_4O_{10}) powder, which has had several military applications. In the past, munitions makers produced phosphorus shells for artillery use. These shells also were effective weapons, because small particles of burning phosphorus stuck to clothing and skin.

Shells disposed of under water can release phosphorus into the environment, resulting in environmental damage due to the toxicity of white phosphorus.

A major factor controlling the rate of disappearance of white phosphorus is whether it is dissolved or suspended. Dispersed white phosphorus could be quickly covered with sediment. Other potential problems with white phosphorus are that decomposition products are poorly defined and that white phosphorus has the potential to bioaccumulate in organisms higher in the food chain.

4.3.2 Analytical Methods

Elemental phosphorus can be extracted and analyzed using the method, Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography (Addison and Ackman, 1970). In this method, sediment and water samples are extracted with toluene and analyzed by gas chromatography/mass spectrometry. The mass spectrometer is used as the detector because it can be programmed to scan specifically for the P_4 molecule of elemental phosphorus. This eliminates the misidentification of phosphorus due to coeluting peaks or any interferences in the matrix.

4.3.3 Case Study: White Phosphorus Munitions Burial Area, Aberdeen Proving Ground

The White Phosphorus Munitions Burial Area (WPMBA) is located near Chesapeake Bay within the confines of the restricted waters of the U.S. Army Base at Aberdeen Proving Ground (APG), Maryland. An investigation of this site was conducted to determine the exact location of the WPMBA and the impacts of the area upon the surrounding ecosystem. This investigation is summarized below. For a more detailed description of this case study, see Appendix A, "Search for a White Phosphorus Munitions Disposal Site in Chesapeake Bay" (Buchanan et al., 1989).

4.3.3.1 Detection and Sampling

Several techniques were used during the investigation to determine the location of the WPMBA. A search was conducted to locate related information concerning the disposal, storage, and handling of white phosphorus. In addition, an initial geophysical survey was conducted during October 1988. The transects were completed in two phases because of safety constraints imposed by the nearby firing range.

In conducting the survey, a coarse grid was developed to screen the area with an underwater proton magnetometer. The magnetometer was used to detect the assumed large mass of ferrous material in the disposal area. Discrete areas exhibiting numerous or extremely large gamma changes were investigated in a second survey.

Based on the geophysical data, five areas were selected for sediment core analysis to determine if a burial site existed. Cores were collected off Black Point, in the channel, north of Gull Island; east of the channel; and west of the channel. In addition, cores were collected in the adjacent APG channel to assist in decision-making concerning future dredging. A reference area also was selected north of the site in Spesutie Narrows. The coring was conducted during August 1989 in each of the five areas. Because of safety concerns in dealing with the burial area and the known presence of unexploded ordnance on APG, a remote coring operation was necessary.

4.3.3.2 Sample Analysis

A total of 60 cores was obtained, ranging in depth from 1 to approximately 9 ft. Cores were screened on site for explosives using a portable gas chromatograph, and composite samples were collected for analysis. All samples were analyzed for elemental phosphorus, explosives, and RCRA characteristics. Select samples were analyzed for total organic carbon, grain size, and toxicity. Core liners (6-ft butyrate plastic tubes) were used throughout the investigation to collect, transport, store, and maintain the integrity of the cores.

Water samples also were collected at each of the areas, cored, and analyzed for elemental phosphorus and explosives. Water quality measurements were recorded in each area and included temperature, pH, conductivity, salinity, oxidation-reduction potential, and dissolved oxygen.

4.3.3.3 Safety Considerations

Steps were taken to prevent personnel from coming into contact with white phosphorus and white phosphorus munitions. The hazards posed to sampling personnel from white phosphorus included the potential for fire and explosion, and the inhalation of toxic fumes produced during its burning. The following contingencies were established to minimize this hazard.

A 55-gallon drum filled with water was placed in close proximity to all core handling operations so that cores could be submerged in the event of an isolated flare-up. A pressurized hose also was available to douse any core that could not be isolated and submerged. In the event of an incipient fire, personnel were instructed to don emergency respiratory equipment (self-contained breathing apparatus) and evacuate the area immediately. As a back-up to the water systems, wet mud also was available.

In addition, to control incidental skin contact with white phosphorus or other contaminants that may have been contained in sediments, personnel involved with sample handling wore butyl aprons, rubber boots, Nomex coveralls, and long sleeve butyl gloves. Hard hats equipped with face shields prevented sediments or contaminants from splashing into eyes. Frequent breaks between sampling events, construction of shaded areas, and an ample supply of fluids eliminated the hazards associated with the sun and hot weather conditions and reduced the potential for heat-stress-related injuries associated with the use of protective clothing.

4.3.3.4 Results

White phosphorus was detected in 11 of the 60 core samples at concentrations less than 6 μg/kg. No white phosphorus was detected in the water column. No explosive compounds were detected in the water or sediment samples. RCRA analyses indicated that the sediment cores would not be considered hazardous waste. Definitive boundaries for the WPMBA could not be determined because of the diffuse, isolated nature of the contamination. No impacts upon the aquatic ecosystem are expected. Release of white phosphorus is not expected unless the sediments are disturbed.

4.3.3.5 Further Investigation

The possibility of another location for the WPMBA was suggested by historical references. One reference alluded to munitions disposal in a tidal marsh near Black Point, an area currently covered with 2 ft of sediment. The Maryland Department of the Environment (MDE) requested that this site be investigated as a possible land disposal site. The survey location was selected based on MDE's review of historical references and aerial photographs.

The location identified by MDE was inaccessible by water or land, so the subsequent magnetometry survey was performed by a helicopter. The helicopter was equipped with a helium magnetometer in a towed "bird" configuration (an aerial tow). Navigation control was accomplished with a range-range positioning and global positioning system. The survey encompassed a 1,400-m by 1,600-m area.

The range-range and global positioning system with video display provided accurate navigation control. The aeromagnetic survey successfully identified the location of several magnetic anomalies the size of the target. Also detected was a single anomaly with a magnitude that correlated well with that predicted by a computer-generated model.

Ground investigation of the anomaly identified it as an old metallic residuals burial area. The location of the WPMBA remains undiscovered.

4.3.4 References Cited

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Buchanan, G.A., H.R. Compton, and J. Wrobel. 1989. Search for a white phosphorus munitions disposal site in Chesapeake Bay. Proceedings of the U.S. EPA's Forum on Remediation of Superfund Sites Where Explosives Are Present. December 5-6, 1989. San Antonio, Texas.

Chapter Five
Treatment Technologies for Explosives Waste

5.1 Biological Treatment Technologies

5.1.1 Background

Biological treatment, or *bioremediation,* is a developing technology that uses microorganisms to degrade organic contaminants into less hazardous compounds. Compared to conventional technologies, bioremediation has several advantages: (1) it actually degrades target compounds, rather than just transferring them from one medium to another; (2) it is publicly accepted, because it is a natural process; and (3) it is probably less expensive than incineration, especially for small volumes of contaminated soil.

Although the two terms occasionally are interchanged, biodegradation is not synonymous with mineralization. Mineralization, which is the process by which compounds are transformed into carbon dioxide and water, is only one of several fates of contaminants in biological treatment systems. Contaminants also may be volatilized, bind to organic materials, be assimilated into an active biomass, or be transformed into compounds other than carbon dioxide and water. Mineralization of contaminants is a desired, but rarely achieved, outcome of bioremediation. This section discusses the types of explosives that can be bioremediated and highlights five specific biological treatment technologies: aqueous-phase bioreactor treatment, composting, landfarming, white rot fungus treatment, and in situ biological treatment.

5.1.2 Treatable Wastes and Media

Bioremediation is most effective for dilute solutions of explosives and propellants. TNT in the crystalline form is difficult to treat biologically.

TNT degrades under aerobic conditions into monoamino-, diamino-, and hydroxylamino-DNT, and tetranitro-azoxynitrotoluenes. RDX and HMX degrade into carbon dioxide and water under anaerobic conditions. Researchers have not identified any specific organisms that are particularly effective for degrading explosives waste; a consortium of organisms usually effects the degradation.

5.1.3 Operation and Maintenance

DOD currently is developing or implementing five biological treatments for explosives-contaminated soils: aqueous-phase bioreactor treatment; composting, land farming, and white rot fungus treatment, which are solid-phase treatments; and in situ biological treatment.

5.1.3.1 Aqueous-Phase Bioreactor Treatment

DOD is considering two types of aqueous-phase bioreactors for the treatment of explosive contaminants. The first is the lagoon slurry reactor, which allows contaminants to remain in a lagoon, be mixed with nutrients and water, and degrade under anaerobic conditions. Figure 5-1 is a schematic of a lagoon slurry reactor. The second is the aboveground slurry reactor, which is either a concrete activated sludge basin or a commercially available bioreactor. Figure 5-2 is a schematic of aboveground bioreactor treatment, showing the excavation and screening of soils prior to treatment, dewatering of the treated soil, and recycling of the extracted water to the reactor.

Aqueous-phase bioreactors provide good process control, can be configured in several treatment trains to treat a variety of wastes, and potentially can achieve very low contaminant concentrations. A drawback of bioreactor treatment is that, unlike composting systems which bind contaminants to humic material, bioreactors accumulate the products of biotransformation. In addition, bioreactors have been shown to remediate explosives only at laboratory scale, so the cost of

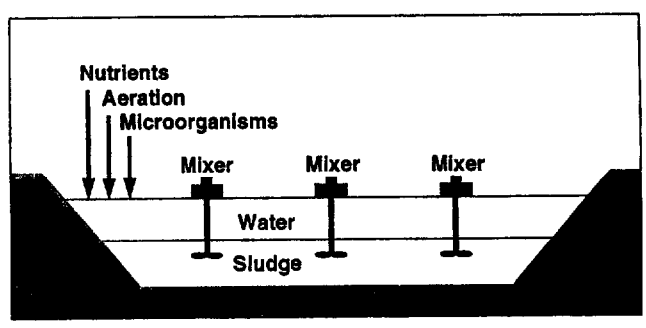

Figure 5-1. Schematic of lagoon slurry reactor.

full-scale bioreactor treatment is unknown. Full-scale bioreactors will have to incorporate a variety of safety features that will add to their total cost.

The Army is conducting a demonstration study to examine the effectiveness of treating explosives-contaminated soils from the Joliet Army Ammunition Plant (JAAP) in an aboveground sequencing batch bioreactor. The goal of this study is to determine the extent of degradation, byproducts, and total costs of full-scale bioreactor treatment. Soils will be excavated from the site, screened, and pumped into the reactor. Indigenous microorganisms from the site will be isolated and added to the reactor. Either malate or molasses will be used as a substrate. After processing in the reactor, soils will be drawn into a filter bed, where process waters will be removed. These process waters will be recycled back to the reactor, and any remaining discharges will be treated to meet National Pollutant Discharge Elimination System (NPDES) requirements. Initial laboratory testing of this system produced greater than 99 percent contaminant reductions within 14 days (see Figure 5-3).

5.1.3.2 Composting

DOD has been evaluating composting systems to treat explosives waste since 1982. To date, composting has been shown to degrade TNT, RDX, HMX, DNT, tetryl, and nitrocellulose in soils and sludges. The main advantage of this technology is that, unlike incineration, composting generates an enriched product that can sustain vegetation. After cleanup levels are achieved, the compost material can be returned to the site and covered with a soil cap. Another advantage is that composting provides both aerobic and anaerobic treatment, so it is effective for a range of wastes. The feasibility of composting can be limited, however, by the level of indigenous organisms in contaminated soil and the local availability of amendment mixtures. In addition, composting requires long treatment periods for some waste streams, and composting of unfamiliar contaminants potentially can generate toxic byproducts.

Composting methods fall into four categories: (1) static-pile composting; (2) in-vessel, static-pile composting; (3) mechanically agitated, in-vessel composting; and (4) windrow composting. In static-pile composting, contaminated material is excavated, placed in a pile under a protective shelter, and mixed with readily degradable carbon sources. The pile undergoes forced aeration to maintain aerobic and thermophilic (55 to 60°C) conditions, which foster the growth of microorganisms. Bulking agents, such as cow manure and vegetable waste, can be added to enhance biodegradation. Figure 5-4 is a schematic of static-pile composting. In-vessel, static-pile composting is similar to static-pile composting except the compost pile is placed in a vessel. Figure 5-5 is a schematic of an in-vessel, static-pile composting device. In mechanically agitated, in-vessel composting, contaminated material is aerated and blended with carbon-source materials in a mechanical composter. These devices have been used at municipal sewage treatment facilities and

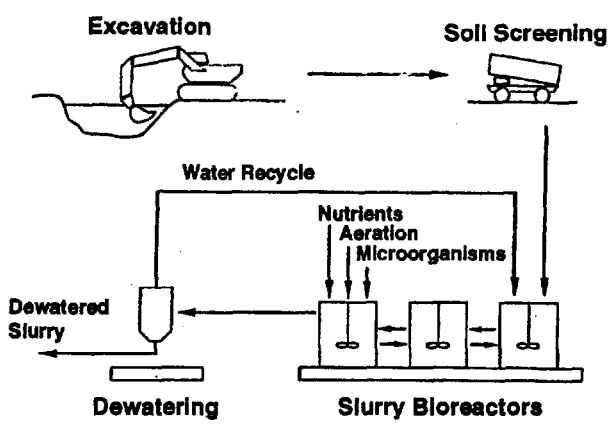

Figure 5-2. Schematic of aboveground slurry reactor treatment.

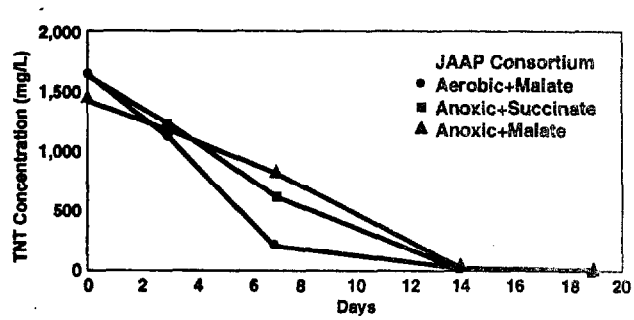

Figure 5-3. Contaminant reductions achieved in laboratory-scale testing of sequencing batch reactor treatment of soils from Joliet Army Ammunition Plant.

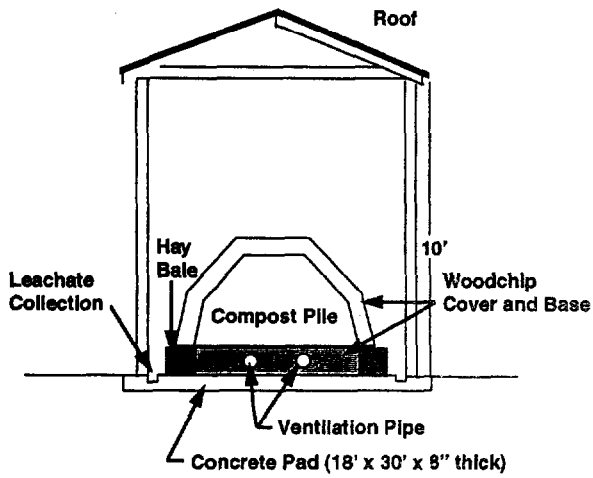

Figure 5-4. Schematic of static-pile composting, showing the compost pile, protective shelter, forced aeration system, and leachate collection pad.

applied to explosives waste. Figure 5-6 is a schematic of a mechanical composter. Windrow composting is similar to static-pile composting except that compost is aerated by a mechanical mixing vehicle, rather than a forced air system.

In 1988, the Army began a series of demonstration studies at the Louisiana Army Ammunition Plant to determine the effectiveness of composting explosives-contaminated soils. In the initial study, static-pile composting required 153 days to remediate soils contaminated with just 3 percent explosive waste by volume. Based on these results, the Army determined that static-pile composting would not be cost effective for remediating large volumes of explosives waste.

The Army conducted a second study to optimize the cost effectiveness of composting. This study used a less expensive carbon-source material, thereby cutting amendment costs from over $200 per ton to less than $50 per ton, and used a commercially available mechanically agitated composter rather than a static pile. These conditions led to more rapid and extensive degradation of the explosives, achieving cleanup levels of 10 to 20 ppm of TNT and RDX within 20 days. Nevertheless, this method also was determined to be economically infeasible, due to the initial cost of the commercial composter.

Finally, the Army conducted a study to examine the effectiveness of windrow composting. This study used cow manure, sawdust, and potato waste amendments and required the construction of a concrete pad leachate collection system. Temperatures were maintained at 55°C and the compost was turned once a day. This process produced 98 percent reductions of explosives contamination within 20 days, and degraded HMX, which formerly had resisted degradation (see Figure 5-7 and Table 5-1). Toxicological data from this study indicated that composting achieved 90 to 98 percent toxicity reductions, consumption of the compost material would not have been toxic to rats, the leachates exhibited no mutagenicity, and some of the TNT had been mineralized. Radiolabeled TNT studies indicated that strong binding had occurred between TNT and the humic compost. Since the initial costs were relatively

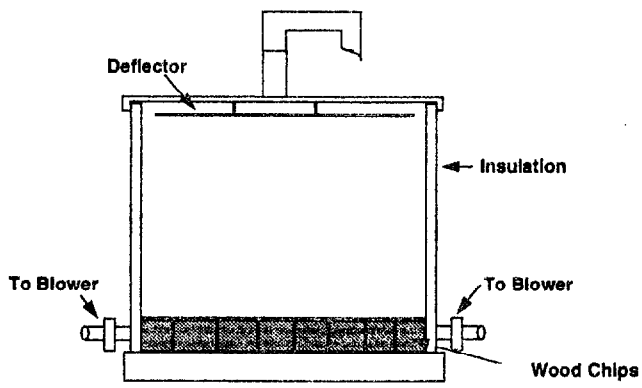

Figure 5-5. Schematic of in-vessel, static-pile composting equipment.

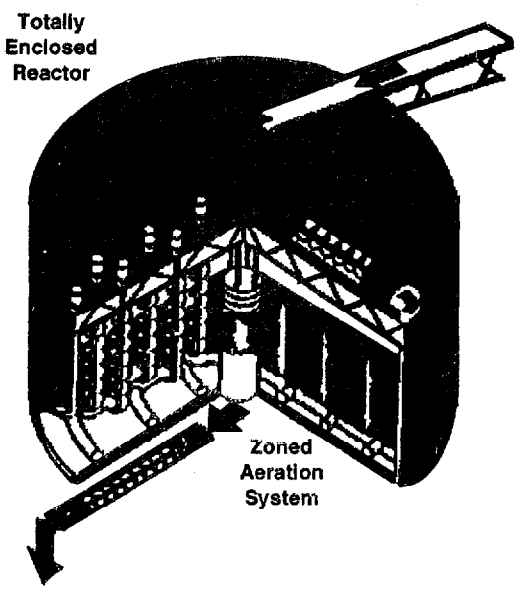

Figure 5-6. Schematic of a mechanical composter.

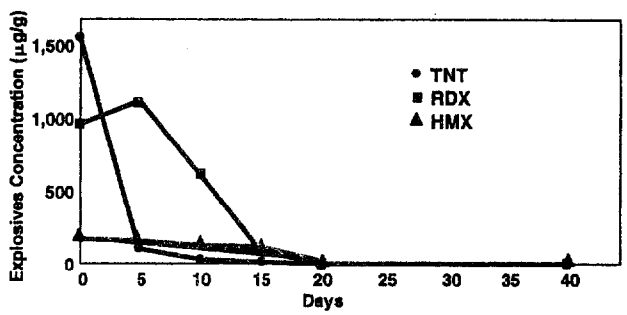

Figure 5-7. TNT, RDX, and HMX reductions achieved in windrow composting demonstration study at Louisiana Army Ammunition Plant.

Table 5-1. Actual and Percent Contaminant Reductions Achieved in Windrow Composting Demonstration Study at Louisiana Army Ammunition Plant

	Contaminant Level (µg/g)			Reduction (%)		
Day	TNT	RDX	HMX	TNT	RDX	HMX
0	1563	953	156	0.0	0.0	0.0
5	101	1124	158	93.5	0.0	0.0
10	23	623	119	98.5	34.6	23.7
15	19	88	118	98.8	90.7	24.4
20	11	5	2	99.3	99.5	98.7
40	4	2	5	99.7	99.8	96.8

low, windrow composting was determined to be an economically feasible alternative to incineration.

Composting methods were evaluated in a feasibility study at the Umatilla Army Depot TNT washout lagoons. In initial testing, composting compared well to incineration in terms of treatment performance but not in terms of cost. The Army then analyzed the factors affecting the cost of composting, including the specific composting method, volume of contaminated soil, soil throughput, amendment costs, and treatment time. This analysis suggested that for treating less than 10,000 tons of contaminated material, the cost would be $740 per ton for incineration, $651 per ton for mechanically agitated composting, and $386 per ton for windrow composting. Figure 5-8 shows estimated composting and incineration costs as a function of total soil volume treated. Based on these estimates, the Army elected to use windrow composting as the remedial action at the Umatilla site for 300 tons per day.

5.1.3.3 Land Farming

Land farming has been used extensively to treat soils contaminated with petroleum hydrocarbons, pentachlorophenol (PCP), and polycyclic aromatic hydrocarbons (PAHs), and potentially could be used to treat low to medium concentrations of explosives as well. In land farming, soils are excavated to treatment plots and periodically rototilled to mix in nutrients, moisture, and bacteria. Land farming typically achieves very slow degradation rates and can take many years to reach target cleanup levels.

In one pilot study at an explosives waste site in Hercules, California, soils contaminated with TNT and DNT were excavated to 1-yd^3 bins, inoculated with organisms indigenous to the site, and amended with brain/heart infusion agar, which is a common laboratory agar. This procedure failed to achieve the target cleanup levels of 30 ppm TNT, 5 ppm DNT, and 5 ppm DNB, achieving instead a 30 to 40 percent contaminant degradation.

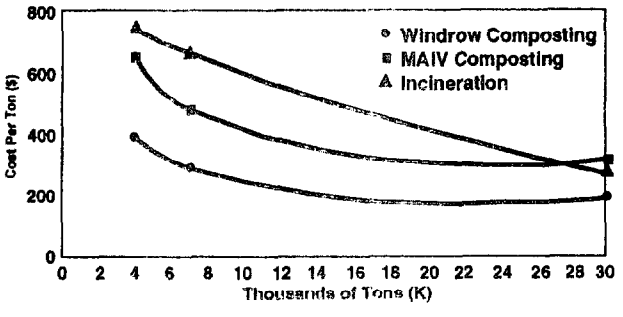

Figure 5-8. Comparison of costs for windrow composting; mechanically agitated, in-vessel composting (MAIV); and incineration of Umatilla Army Depot soils as a function of total soil volume treated.

5.1.3.4 White Rot Fungus Treatment

White rot fungus has been evaluated more extensively than any other fungal species for remediating explosives waste. Although white rot fungus degradation of TNT has been reported in laboratory-scale settings using pure cultures (Berry and Boyd, 1985; Fernando et al., 1990), a number of factors increase the difficulty of using this technology for full-scale remediation. These factors include competition from native bacterial populations, toxicity inhibition, chemical sorption, and the inability to meet risk-based cleanup levels.

In bench-scale studies of mixed fungal and bacterial systems, most of the reported degradation of TNT is attributable to native bacterial populations (Lohr, 1993; McFarland et al., 1992). High TNT concentrations in soil also can inhibit growth of white rot fungus. One study suggested that *Phanerochaete chrysosporium* was incapable of growing in soils contaminated with 20 ppm or more of TNT. In addition, some reports indicate that TNT losses reported in white rot fungus studies can be attributed to adsorption of TNT onto the fungus and soil amendments, such as corn cobs and straw (Spiker et al., 1992).

A pilot-scale treatability study was conducted using white rot fungus at a former ordnance open burn/open detonation area at Site D, Naval Submarine Base, Bangor, Washington. Initial TNT concentrations of 1,844 ppm were degraded to 1,267 ppm in 30 days and 1,087 in 120 days. The overall degradation was 41 percent, and final TNT soil levels were well above the proposed cleanup level of 30 ppm (Spectrum Sciences & Software, Inc., and Utah State University, no date).

5.1.3.5 In Situ Biological Treatment

In situ treatments can be less expensive than other technologies and produce low contaminant concentrations. The available data suggest, however, that in situ treatment may not be effective for explosives waste. In situ treatment of explosives might create more mobile intermediates during biodegradation. In addition, biodegradation of explosive contaminants typically involves cometabolism with another nutrient source, which is difficult to deliver in an in situ environment. Mixing often affects the rate and performance of explosives degradation. Finally, because in situ remediation takes place beneath the surface, the effectiveness of in situ treatment is difficult to verify both during and after treatment.

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5.2 Thermal Treatment Technologies

5.2.1 Incineration of Soils and Sludges

5.2.1.1 Background

AEC of DOD at Aberdeen Proving Ground, Maryland, oversees large-scale incineration of munitions, explosives waste, and explosives-contaminated soils as part of remedial actions at Army sites. This section discusses the types of wastes and media that can be incinerated, looks at various devices used to incinerate explosives waste, presents case studies of four sites where incineration has been applied to explosives-contaminated soils, and examines the advantages and disadvantages of incineration.

5.2.1.2 Treatable Wastes and Media

Incineration processes can be used to treat the following waste streams: explosives-contaminated soil and debris, explosives with other organics or metals, initiating explosives, bulk explosives, unexploded ordnance, bulky radioactive waste, and pyrophoric waste. In addition, incineration can be applied to sites with a mixture of media, such as concrete, sand, clay, water, and sludge, provided the media can be fed to the incinerator and heated for a sufficient period of time. With the approval of the DOD Explosives Safety Board, the Army considers incineration of materials containing less than 10 percent explosives by weight to be a nonexplosive operation. Soil with less than 10 percent explosives by weight has been shown by AEC to be nonreactive, that is, not to propagate a detonation throughout the mass of soil. (The military explosives to which this limit applies are secondary explosives such as TNT and RDX, and their manufacturing byproducts.)

The Army's first pilot-scale use of rotary kiln incineration utilized soil well above the 10 percent limit (up to 40 percent) with approval from the DOD Explosives Safety Board. A consideration in conducting the test was the fact that the kiln was not actually sealed and hence not thought to provide confinement for the small amount of explosives fed. Another consideration was a previous successful Army incineration of pure TNT without detonation in a deactivation furnace. Though the pilot-scale test experienced no detonation problems, the Army's full-scale incineration projects have incorporated a blending step to reduce the explosives concentrations below the 10 percent limit prior to feeding. The blending step is considered to be an explosives operation that requires the preparation and approval by the Army and DOD safety offices of a site plan/safety submission, which must include an explosives hazard analysis. Finally, even at explosives concentrations below 10 percent, each explosives project has unique elements, and a thorough safety review is a necessity.

The Army also has developed and tested a feed system capable of feeding reactive levels of explosives (up to 20 percent). The system includes multiple units with breaks in between to prevent propagation of a possible detonation throughout the system. Metal-to-metal contact also is minimized in the system to reduce the chances of detonation by friction or spark.

5.2.1.3 Operation and Maintenance

The Army primarily uses three types of incineration devices: the rotary kiln incinerator, deactivation furnace, and contaminated waste processor.

Rotary Kiln Incinerator

The rotary kiln incinerator is used primarily to treat explosives-contaminated soils. In rotary kiln incineration, soils are fed into a primary combustion chamber, or rotary kiln, where organic constituents are destroyed. The temperature of gases in the primary chamber ranges from 800 to 1,200°F, and the temperature of soils ranges from 600 to 800°F. Retention time in the primary chamber, which is varied by changing the rotation speed of the kiln, is approximately 30 minutes. Off gases from the primary chamber pass into a secondary combustion chamber, which destroys any residual organics. Gases from the secondary combustion chamber pass into a quench tank where they are cooled from approximately 2,000°C to 200°C. From the quench tank, gases pass through a Venturi scrubber and a series of baghouse filters, which remove acid gases and particulates prior to release from the stack. The treated product of rotary kiln incineration is ash (or treated soil), which drops from the primary combustion chamber after organic contaminants have been destroyed. This product is routed into a wet quench or a water spray to remoisturize it, then transported to an interim storage area pending receipt of chemical analytical results.

Deactivation Furnace

The deactivation furnace also is referred to as Army Peculiar Equipment (APE) 1236, because it is used almost exclusively by the Army to deactivate large quantities of small arms cartridges, 50-caliber machine gun ammunition, mines, and grenades. The deactivation furnace is similar to the rotary kiln incinerator, except that it is equipped with a thick-walled primary combustion chamber capable of withstanding small detonations. Deactivation furnaces do not have secondary combustion chambers, because they are intended not to completely destroy the vaporized explosives but to render the munitions unreactive. Most deactivation furnaces are equipped with air pollution control equipment to limit lead emissions. The operating temperature of deactivation furnaces is approximately 1,200 to 1,500°F.

Contaminated Waste Processor

The contaminated waste processor handles materials, such as surface-contaminated debris, that are lighter and less reactive than those processed in the deactivation furnace. Contaminated waste processors are thin-walled, stationary ovens that heat contaminated materials to about 600°C for 3 to 4 hours. The purpose of this process is not to destroy contaminated debris but to lower contaminant levels to meet Army safety standards. AEC currently is helping to develop standardized time and temperature processing requirements to meet these safety standards.

5.2.1.4 Case Studies

Cornhusker Army Ammunition Plant

The Cornhusker Army Ammunition Plant (CAAP) in Grand Island, Nebraska, was the site of 58 explosives wastewater washout cesspools and leaching pits. Explosives residues from these 10-ft deep pits created a contaminated ground water plume that extended into nearby residential areas. To prevent further ground water contamination, the Army opted to incinerate contaminated soils and sludges from the cesspools and leaching pits. For each contaminant, the Army established two cleanup criteria: (1) an excavation criterion, which was health risk based and determined the depth to which soils were excavated, and (2) an incineration criterion, which equaled the nondetection level for each contaminant. Table 5-2 shows the cleanup criteria for contaminants from the CAAP site.

Figure 5-9 is a schematic of the rotary kiln incineration system employed at the CAAP site. A three-stage feed system with a live bottom hopper, belt conveyor, and gravity tube was used to feed contaminated material to the incinerator. Ash from the incinerator was loaded into ash bins and subjected to compositional analysis. Once the ash was determined to be clean (i.e., to contain no detectable explosives), it was backfilled at a single location on the CAAP site. The CAAP project was completed successfully in 1988, after incinerating 40,000 tons at an average total cost of $260 per ton. Some of the difficulties encountered included (1) clogging of the quench tank by slag that fell from the walls of the secondary combustion chamber, (2) unwanted air infiltration through the air lock in the feed system, and (3) the need to winterize the unit for cold weather operations.

Louisiana Army Ammunition Plant

Over the years, wastewaters from ammunition load, assemble, and pack operations at the Louisiana Army Ammunition Plant (LAAP) in Shreveport, Louisiana, were shipped by truck to 16 leaching/evaporation lagoons at Area P in south-central LAAP. Explosives residues from these lagoons leached into the underlying

ground water, creating plumes of TNT and RDX. As at the CAAP site, the Army opted to incinerate soils and sludges from the LAAP lagoons and set the incineration cleanup criterion equal to the nondetection limit for each contaminant. Rather than assign each contaminant a specific excavation criterion, the Army specified that the concentrations of all contaminants total less than 100 ppm after 1 foot of lagoon material had been excavated. Table 5-3 shows the cleanup criteria for the LAAP lagoons.

The incineration system used at CAAP was transported to LAAP with a significant modification to the quench to allow workers to clean it without entering the tank. While operating at LAAP, some other modifications were made to correct the following difficulties: (1) clayey wet feed soil plugged and jammed the feed system and (2) buildup of soil on the secondary combustion chamber fell into the quench tank causing a steam overpressure. To remedy the first problem, the feed system was strengthened and a high-speed slinger belt conveyor was used as the final stage to throw the soil into the incinerator. To remedy the second problem, which may have been aggravated by the lime used to dry the feed, the quench was relocated in an offset position from the secondary combustion chamber. The project was completed successfully in 1990 after incinerating 102,000 tons of soil at an average total cost $330 per ton.

Table 5-2. Cleanup Criteria for Cornhusker Army Ammunition Plant

Analyte	Excavation Criteria (ppm)	Incineration Criteria (Method Detection Limits [ppm])
RDX	<10	<2.2
2,4,6-TNT	<5	<1.3
1,3,5-TNB	<15	<1.25
2,4-DNT	<0.5	<0.24
2,6-DNT	<0.4	<1.26
HMX	NA	<2.9
1,3-DNB	NA	<1.2
NB	NA	<1.26
Tetryl	NA	<2.2
2A,4,6-DNT	NA	<1.25

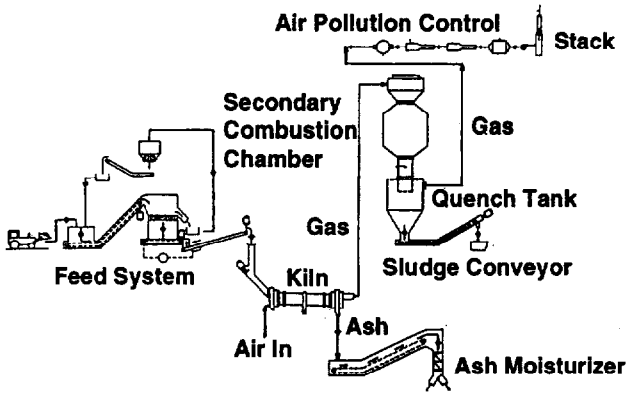

Figure 5-9. Schematic of rotary kiln incineration system employed at Cornhusker Army Ammunition Plant.

Savanna Army Depot

The Savanna Army Depot (SVAD) in Savanna, Illinois, formerly operated a washout plant where hot water was used to melt the explosives out of munitions. Wastewaters from these operations were pumped directly from the facility through a metal trough into washout lagoons. Recently, SVAD began piping wastewaters into two new washout lagoons on a sandy hill near the facility. Both the old and new lagoons are contributing explosives contamination to ground water beneath the site. The old lagoons are located in a flood plain of the Mississippi River, which runs about ½ mile west of the site. Periodically, the river floods the lagoons, spreading explosives contamination from the centers of the lagoons.

The entire site was screened for unexploded ordnance prior to the start of incineration operations. The Army then established health risk based excavation criteria and nondetection limit incineration criteria for the soils at the site (see Table 5-4). To reach the excavation criteria, some lagoons had to be excavated to a depth of 10 ft and excavation had to be done outside of the lagoons, apparently due to the periodic flooding by the Mississippi River. As a safety precaution, excavated soils were blended to reduce overall explosives levels to less than 10 percent by weight. Incineration currently is under way. Some problems have arisen with the feed system clogging due to the cold, wet conditions at the site, but incineration is expected to be completed in fall

Table 5-3. Cleanup Criteria for Louisiana Army Ammunition Plant

Analyte	Excavation Criteria (ppm)	Incineration Criteria (Method Detection Limits [ppm])
RDX	Sum of all less than 100 ppm after 1 foot excavation of lagoons	<2.2
2,4,6-TNT		<1.3
1,3,5-TNB		<1.25
2,4-DNT		<0.24
2,6-DNT		<1.26
HMX		<2.9
1,3-DNB		<1.2
NB		<1.26
Tetryl		<2.2
2A,4,6-DNT		<1.25

of 1993. The estimated quantity of soil to be incinerated is approximately 60,000 tons.

Alabama Army Ammunition Plant

In 1986, explosives- and lead-contaminated soils from the Alabama Army Ammunition Plant in Childersburg, Alabama, were excavated and placed on a concrete slab and in two containment buildings. These soils, totalling approximately 35,000 tons, are slated to undergo incineration over the next 2 years. Table 5-5 shows the excavation and incineration criteria for the site. The excavation criteria, which are health risk based, governed the initial excavation in 1986. The incineration criteria all are equal to nondetection limits. The Army anticipates two problems. First, the soils contain large amounts of debris and possibly pieces of explosive, which will have to be removed manually prior to incineration. Second, the soils contain lead, so the ash product may have to be stabilized prior to disposal.

Table 5-4. Cleanup Criteria for Savanna Army Depot

Analyte	Excavation Criteria (ppm)	Incineration Criteria (Method Detection Limits [ppm])
RDX	<5.75	<1
2,4,6-TNT	<21.1	<1
1,3,5-TNB	<3.7	<1
2,4-DNT	<9.3	<1
2,6-DNT	<4.3	<1
HMX	<3,722	<1
1,3-DNB	<7.4	<1
NB	<37.2	<1
Tetryl	<112	<1
2A,4,6-DNT	<1,191	<1

Table 5-5. Cleanup Criteria for Alabama Army Ammunition Plant

Analyte	Excavation Criteria (ppm)	Incineration Criteria (Method Detection Limits [ppm])
RDX	None	<1
2,4,6-TNT	<1.92	<1
1,3,5-TNB	<5.5	<1
2,4-DNT	<0.42	<1
2,6-DNT	<0.40	<1
HMX	None	<1
1,3-DNB	<1.1	<1
NB	None	<1
Tetryl	<1.7	<1
2A,4,6-DNT	None	<1

5.2.1.5 Advantages and Disadvantages

Incineration has many advantages, including:

- *Effectiveness.* With sufficiently long residence time and a sufficiently high temperature, incineration usually reduces levels of organics to below nondetection levels, which simplifies handling of treated soil and reduces overall site cleanup levels.
- *Demonstrated success.* Incineration is a proven technology; the literature on successful applications is extensive; many vendors offer incineration services, thereby driving down prices; and incineration equipment comes in many sizes to fit the needs of any site.
- *Regulatory requirements.* EPA's Land Disposal Restrictions (LDRs) specify incineration as a best demonstrated available technology (BDAT) for many types of wastes, meaning that these wastes must be incinerated prior to land disposal. Also, incineration results were used to set concentration-based BDAT standards for many contaminants and incineration probably has the best chance of continuing to meet these standards.

Incineration of TNT also has many disadvantages, including:

- *Safety concerns.* The foremost safety concern stems from exposing explosive materials to open flame, but this can be addressed through routine safety measures. Secondarily, hazards also are associated with erecting and operating the incinerator, which is a large piece of industrial equipment with moving parts and high temperature areas. For any explosives operation, DOD must approve the incineration work plan and may require a hazards analysis and site safety plan.
- *Noise.* The incinerator is driven by up to a 400 to 500 hp fan, which can generate substantial noise. Residents neighboring the Savanna Army Depot and the Louisiana Army Ammunition Plant have complained about the noise from incineration activity at these sites.
- *Air emissions.* Emissions from the stack may contain nitrous oxides (NO_x); volatile metals, such as lead; and products of incomplete combustion (PICs). Modeling may need to be conducted to predict the distribution of emissions.
- *Capital costs.* The capital mobilization and demobilization costs associated with incineration typically range from $1 to $2 million. Over time, for a large facility, incineration becomes more cost effective. Figure 5-10 shows the range of estimated incineration costs as a function of site size.

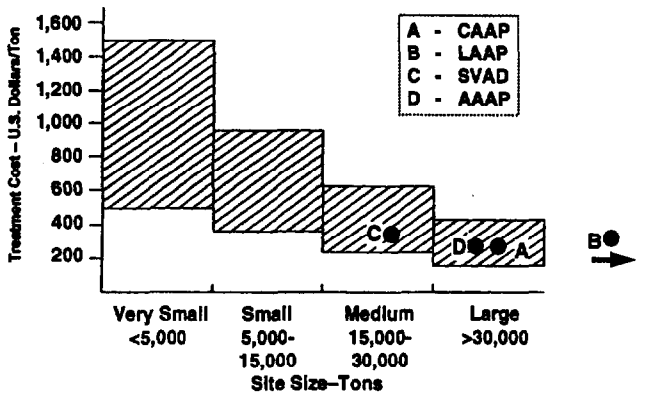

Figure 5-10. Range of expected incineration costs as a function of total volume of soils treated (U.S. EPA, 1990).

- *Public perception.* The public usually is wary of hazardous waste incineration. There may be public concern that a mobile incinerator will be established at a site and subsequently used to incinerate waste from other sites. The public must be assured that, most often, mobile incinerators are used only for single site cleanups and that incineration can be an effective way to treat explosives waste.
- *Required tests.* Before an incinerator can be used to treat a large volume of hazardous waste, it must pass a trial burn demonstrating that it can achieve a 99.99 percent organic destruction efficiency. If the soil at the site does not contain enough contamination to demonstrate the 99.99 percent destruction and removal efficiency, explosives might have to be shipped to the site to spike the feed soil for the trial burn.
- *Ash product.* Incineration of combustible materials produces a volume reduction, which can lead to higher concentrations of inorganic contaminants in the ash product and create leachability problems. Incineration of most contaminated soils produces only modest volume reductions, so inorganics are not significantly concentrated in the treated soil.
- *Materials handling.* Some soils can be difficult to feed to the incinerator, which has a small feed opening. Feeding sticky, high clay content soils can be particularly difficult. These soils require pretreatment by aeration and tilling to reduce moisture levels and decrease viscosity.
- *Electricity and water requirements.* Incineration operations require large supplies of electricity and water, both of which can be limited in rural areas.

5.2.1.6 Reference Cited

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5.2.2 Open Burn/Open Detonation

5.2.2.1 Background

Open burn (OB) and open detonation (OD) operations are conducted by DOD and some private companies to destroy unserviceable, unstable, or unusable munitions and explosive materials. In OB operations, explosives or munitions are destroyed by self-sustained combustion, which is ignited by an external source, such as flame, heat, or a detonation wave (that does not result in a detonation). In OD operations, detonable explosives and munitions are destroyed by a detonation, which is initiated by the detonation of a disposal charge. This section discusses types of wastes and media that can be destroyed in OB/OD operations, OB/OD procedures currently being used, safety precautions associated with OB/OD operations, and a method recently developed for quantifying the level of hazardous emissions from OB/OD operations.

5.2.2.2 Treatable Wastes and Media

OB/OD operations can destroy many types of explosives, pyrotechnics, and propellants. OB areas must be able to withstand accidental detonation of any or all explosives being destroyed, unless the responsible OB technicians used recognize that the characteristics of the materials involved are such that orderly burning without detonation can be ensured. Personnel with this type of knowledge must be consulted before any attempt is made at OB disposal, especially if primary explosives are present in any quantity.

5.2.2.3 Operation

OB and OD can be initiated either by electric or burning ignition systems. In general, electric systems are preferable, because they provide better control over the timing of the initiation. In an electric system, electric current heats a bridge wire, which ignites a primary explosive or pyrotechnic, which, in turn, ignites or detonates the material slated to be burned or detonated. If necessary, safety fuzes, which consist of propellants wrapped in plastic weather stripping, are used to initiate the burn or detonation.

The following design and procedural specifications for OB/OD operations are taken from paragraph 27-16d of the Army Materiel Command Explosives Safety Manual (U.S. AMC, 1985) and paragraph 8-44 of Air Force Regulation 127-100 on explosives safety standards (U.S. Air Force, 1990). OB of nonfragmenting explosives is conducted in burning trays, which are

designed without cracks or angular corners to prevent the buildup of explosive residues. The depth of explosive material in a tray may not exceed 3 in., and the net explosive weight of materials in a tray may not exceed 1,000 lb. The distance between the trays for explosive devices is determined by hazards analysis, but, in the absence of such analysis, trays are placed parallel to one another and separated by at least 150 ft. These distances may vary for OB of bare explosives or explosives-contaminated soils. When wet explosives are being burned, trays may be lined with nonexplosive combustible materials, such as scrap wood, to ensure complete combustion. An OB tray may not be inspected until 12 hours after the conclusion of the burn, and a tray may not be reused until 24 hours after the conclusion of the burn or until all ash and residues have been removed from the tray.

If there is a significant risk of fragmentation, OB operations are conducted in open pits, which must be at least 4 ft deep and have sloped sides to prevent cave in. The length and width of the pit is determined by the quantity of waste being burned. If necessary, nonexplosive combustible materials and fuel may be added to ensure complete combustion of explosive materials. As with burning trays, OB pits may not be inspected until 12 hours after the conclusion of the burn.

Facilities engineered specifically for OD operations are rare in practice. Consequently, almost all OD operations are conducted in pits that are at least 4 ft deep and covered with 2 ft of soil to minimize the risks associated with fragmentation. Detonating cords, which are plastic cords filled with RDX, are used to initiate buried disposal charges. Explosive components are arranged in the pits to be in close contact with the disposal charge.

To prevent partial or incomplete destruction, site personnel must ensure that the disposal charge is sufficiently powerful to propagate a detonation throughout the explosive material. High brisance explosives and shaped charges, which cut through metal casings, are very effective at propagating detonations. If a misfire occurs, personnel are required to wait at least 30 minutes before inspecting the point of initiation. The misfire may be inspected by no more than two personnel, who must follow specific operating procedures.

After each detonation, the surrounding area is searched for unexploded materials. Lumps of explosive material and unfuzed munitions are returned to the detonation pit; fuzed ordnance or munitions that may have damaged internal components are detonated in place.

5.2.2.4 Safety Precautions

During OB operations, munitions may rupture and produce fragments that travel relatively short distances, and explosive materials may detonate. OD operations always produce dangerous overpressures and various types of fragments, depending on the type of explosives being detonated. DOD has developed specific safety precautions for OB/OD operations, designed to expose the fewest individuals to the least degree of hazard for the shortest period of time. These precautions include minimum setbacks from OB/OD sites, provisions for the layout of OB/OD sites, optimum weather conditions for conducting OB/OD operations, and training requirements for OB/OD personnel.

Minimum Safety Distances

As a basic precaution, personnel are required to maintain a minimum distance from the OB/OD operation. This distance depends on the type of material being burned or detonated. The following minimum safety distances are outlined in paragraph 8-44 of Air Force Regulation 127-100 on explosives safety standards (U.S. Air Force, 1990). (Various Armed Services manuals contain distances that provide varying degrees of safety for exposure to the detonation.) For nonfragmenting explosive material, the minimum distance is either 1,250 ft or the explosive's actual maximum debris and fragment throw range, if known. For fragment-producing materials, the minimum distance is 2,500 ft. For bombs and projectiles with a caliber greater than 5 in., the minimum distance is 4,000 ft. For heavier case munitions, the minimum distance can be calculated by the following formula:

$$D = 300 \times (NEW)^{1/3}$$

where D is the minimum distance and NEW is the net explosive weight of the munitions in pounds. This distance is the radius in which most hazardous fragments will fall.

Even at the minimum distances, personnel may be exposed to some fragments. To minimize this exposure, the base plates and suspension lugs of bombs and projectiles should be pointed away from personnel prior to OB/OD.

Layout of the OB/OD Site

The following site layout specifications are taken from paragraphs 27-10 to 27-16 of the Army Materiel Command Explosives Safety Manual (U.S. AMC, 1985) and paragraph 8-44 of Air Force Regulation 127-100 on explosives safety standards (U.S. Air Force, 1990). (Specifications from other Armed Services manuals may vary.) The center of the OB/OD site typically consists of several burning trays, burning pits, and detonation pits. All combustible materials and loose stones are cleared within a 200-ft radius of the center of the site. Personnel shelters are located a minimum of 300 ft from the site, and holding areas for explosives

awaiting detonation are located a minimum of 1,250 ft from the site. Roadblocks are established at the perimeter of the site to restrict entry during the operation.

Weather Conditions

Weather conditions affect both the location and timing of OB/OD operations. OB/OD operations are sited so that prevailing winds carry sparks, flame, smoke, and toxic fumes away from neighboring facilities. The optimum wind speed for an OB/OD is 4 to 15 mph, because winds at these speeds tend not to change direction and, as a result, dissipate smoke relatively rapidly. OB/OD operations are never conducted during sand, snow, or electrical storms strong enough to produce static electricity, which might cause premature detonation.

Personnel Training

All OB/OD operations are supervised by a minimum of two experienced personnel with training in general OB/OD safety procedures and the handling of the specific materials being burned or detonated.

5.2.2.5 Emissions from OB/OD Operations

Quantifying the level of pollutants in the emissions from OB/OD operations is a difficult undertaking. Results from laboratory-scale studies translate poorly to the field, because only very small quantities of explosives can be tested. At this scale, the initiator or blasting cap contributes significantly to the total amount of pollutants in the system. Emissions from field-scale operations also are difficult to measure, because contaminants usually are not distributed homogeneously within the plume, and the plume dissipates quickly.

Personnel at Dugway Proving Ground in Utah recently developed a facility that is large enough to provide reliable, field-scale results while allowing the plume to be captured and analyzed by precise laboratory methods (Teer et al., 1993). The facility is a 1,000-m^3 enclosed hemisphere known as the *bangbox*. Preliminary studies conducted in the bangbox indicate that OB/OD operations emit traces of organics and small quantities of soot in addition to CO_2, N_2, and H_2O.

Based on data generated from bangbox studies, modeling was conducted to estimate the health risks associated with emissions of benzo(a)pyrene from OB/OD of TNT. The modeling assumed a cancer potency of 1.7×10^{-3} for benzo(a)pyrene and an emission factor of 3.01×10^{-6}—the highest factor calculated in any bangbox trial (and an order of magnitude higher than that of the second highest trial). It was determined that 500 tons of TNT would have to be destroyed in OB/OD operations to produce a 1 in 100,000 cancer risk from benzo(a)pyrene emissions. Since the assumed emission factor was very conservative, the health risks associated with emissions from OB/OD operations probably are minimal (Teer et al., 1993). Future bangbox studies will examine different waste compositions to target other specific analytes, such as benzidine, that pose particularly acute threats to human health.

5.2.2.6 References Cited

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5.2.3 Wet Air Oxidation

5.2.3.1 Background

Wet air oxidation is a high-temperature, high-pressure, liquid-phase oxidation process. The technology is used in municipal wastewater treatment, typically for treating dilute solutions of 5 to 10 percent solids or organic matter. Wet air oxidation also has been tested but not used on a large scale for treating explosives waste. In a typical wet air oxidation system, contaminated slurries are pumped into a heat exchanger, where they are heated to temperatures of 177 to 300°C, then into a reactor, where they are treated at pressures of 1,000 to 1,800 psi.

5.2.3.2 Laboratory-Scale Applications

In 1982, the Army conducted a series of laboratory-scale studies on technologies, including wet air oxidation, that formerly had been identified as technically or economically infeasible for treating explosives waste. Wet air oxidation was applied to lagoon slurries containing 10 percent explosive contamination with added chemical catalysts. Although the technology was found to be very effective for treating RDX, several disadvantages were noted. First, the treatment produced hazardous byproducts from TNT. Second, the technology had high capital costs. Third, lagoon slurries had to be diluted prior to treatment. Fourth, gaseous effluents from the oxidation process, such as carbon monoxide (CO), CO_2, and NO_x, needed to be treated by another technology. Finally, the laboratory-scale system was found to have a 5 to 10 percent down time, because clays blocked the pump system and heat exchange lines, and solids built

up in some of the reactors. The Army still is evaluating wet air oxidation treatment for TNT-contaminated red water (U.S. ATHAMA, 1992).

5.2.3.3 Reference Cited

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5.2.4 Low Temperature Thermal Desorption

Low temperature thermal desorption (LTTD) technology originally was developed for treating aqueous slurries contaminated with volatile organic compounds (VOCs). The technology also has been tested for treating explosives-contaminated slurries.

In LTTD, contaminated slurries are fed into the system, heated to 200 to 300°C by a hot oil heating chamber, and treated under elevated pressures. Emissions from the system are treated in an afterburner.

The Army conducted a laboratory-scale study on low temperature thermal desorption of explosives waste in 1982, as part of a series of studies on technologies that previously had been demonstrated as unsuccessful for treating explosives waste. LTTD was shown to achieve a 95 percent destruction and removal efficiency (DRE) in 20 minutes, but two degradation products—3,5-dinitroanaline and 3,5-dinitrophenol—were found to be recalcitrant regardless of treatment time and temperature. The reactivity and toxicity of these products were unknown at the time, meaning that the product of thermal desorption might have to be treated as a hazardous waste. Pilot-scale engineering and cost analyses of this technology have been delayed, pending further testing of the degradation products.

5.3 Physical/Chemical Treatment Technologies

5.3.1 Ultraviolet Oxidation

5.3.1.1 Background

Ultraviolet (UV) oxidation has not been used extensively for remediating water contaminated with explosives, because of the widespread use of granular activated carbon (GAC) treatment. Nevertheless, UV oxidation can be an effective treatment for explosives-contaminated water and, unlike carbon treatment, actually destroys target compounds, rather than just transferring them to a more easily disposable medium. This section discusses the types of explosives-contaminated water that can be treated by UV oxidation, examines some pilot-scale tests of UV oxidation, and provides a detailed discussion of a treatability study of UV oxidation recently conducted at Milan Army Ammunition Plant (AAP).

5.3.1.2 Treatable Wastes and Media

UV oxidation can be used to treat many types of organic explosives-contaminated water, including process waters from the demilitarization of munitions (pink water) and ground water contaminated from disposal of these process waters.

5.3.1.3 Pilot-Scale Applications

In 1981, the Army conducted a pilot-scale study of UV oxidation for treating waters from the Kansas AAP contaminated with RDX (U.S. AARRDC, 1982). RDX concentrations in the process water ranged from 0.8 to 21.0 mg/L. The UV oxidation system consisted of thirty 40-watt, UV lamps, and an ozone generator, which provided ozone to the treatment process. Treatment times in this system ranged from 37 to 375 minutes at flow rates of 0.2 to 2.0 gpm. Final RDX concentrations in the effluent ranged from 0.1 to 1.7 mg/L, which would not have met current regulatory criteria.

Similar studies have been conducted at Crane AAP, Iowa AAP, Holston AAP, and Picatinny Arsenal. It is difficult to compare performance data from these studies, however, because each study operated under different treatment conditions. Some used 40-watt, low pressure, UV bulbs; others used 65-watt, medium pressure, UV bulbs. Some amended the water with hydrogen peroxide (H_2O_2); others did not. The studies also used different concentrations and species of contaminant, different total residence times, and different concentrations of ozone. In addition, some of the studies used simulated pink water, which usually lacks many of the constituents of real pink water.

UV oxidation is being considered at Picatinny Arsenal for the treatment of ground water containing 6.0 ppb of RDX. The Waterways Experiment Station in Vicksburg, Mississippi, currently is running a pilot test on the proposed UV oxidation system and a parallel test of an activated carbon system to compare the economic feasibility of the two.

5.3.1.4 Treatability Study at Milan AAP

In the 1970s, Milan AAP was the site of munitions washout operations. Process waters from these operations were placed in lagoons until the early-1980s, when the waters were drained and the lagoons were capped. A contaminated ground water plume is migrating from the site. The Army has conducted a study to determine whether the contaminated ground

water could be treated by UV oxidation (U.S. ATHAMA, 1992). The treatability study focused on how to optimize the performance of a full-scale UV oxidation system, should UV oxidation be selected as the final remedial technology at the site. The treatability study consisted of bench- and pilot-scale tests.

Bench-Scale Tests

Bench-scale UV oxidation tests were conducted on 15 gallons of contaminated water from a site. The bench-scale system consisted of a 2.4-L reactor with a single 40-watt UV bulb. Ozone was diffused through the reactor at rates ranging from 2.8 to 15.0 (mg/L)/s, and a solution of 35 percent H_2O_2 by volume was used in the tests. The pH in the system ranged from 4.0 to 8.5, and the pH of the water was found to drop due to the production of organic acids during treatment. The concentration of all explosives in the influent was 57,500 µg/L, with TNT, RDX, HMX, and tetryl present in the highest concentrations. Residence times varied from 40 to 200 minutes per treatment batch. These tests indicated that UV radiation degraded explosive contaminants and that longer UV exposure times yielded better contaminant removals. H_2O_2 levels were found not to affect contaminant degradation, and UV oxidation was found to be most effective at pHs of 7 or greater. The level of 1,3,5-TNB, which is a product of the UV oxidation of TNT, was the rate-limiting factor in each test; 1,3,5-TNB concentrations actually increased after 40 minutes of UV exposure.

Pilot-Scale Tests

The pilot-scale tests had two purposes: (1) to obtain design data for a full-scale, 500-gpm, UV oxidation system; and (2) to estimate the cost of operating a full-scale UV oxidation system.

Pilot-scale UV oxidation tests were conducted in a 650-gallon Ultrox P-650 system, consisting of six reaction chambers, each containing twelve 65-watt, low-pressure, UV lamps, and a cooling system to prevent temperature increases during long exposure times. The treatment system was operated in recycle batch mode, meaning that each 650-gallon batch was recycled through the system seven or eight times. The total concentration of explosives in the influent was about 20,656 µg/L, and the pH of the water was maintained at 7 to 11 during treatment. Tests were conducted at ozone doses ranging from 1.11 to 3.33 (mg/L)/minute and with residence times ranging from 40 to 210 minutes. The pilot-scale study indicated that UV oxidation was most effective at a pH of 9 and an ozone dosage of 3.3 (mg/L)/minute. Residence times greater than 180 minutes coupled with high ozone doses destroyed all of the explosives, including 1,3,5-TNB. Biotoxicity tests indicated that the effluent from the UV oxidation system was toxic, due to leaching of metals from bronze impellers within the equipment.

5.3.1.5 References Cited

U.S. AARRDC. 1982. U.S. Army Armament Research and Development Command. Ultraviolet ozone treatment of RDX (cyclonite) contaminated wastewater. ARLCD-CR-83034. Dover, New Jersey.

U.S. ATHAMA. 1992. U.S. Army Toxic and Hazardous Materials Agency. Milan Army Ammunition Plant O-line ponds area treatability study report for ground water treatment alternatives. Draft final document. CETHA-IR-B. Aberdeen Proving Ground, Maryland.

5.3.2 Granular Activated Carbon

5.3.2.1 Background

In the 1980s, the Army discontinued the practice of disposing of untreated process waters from the production of munitions in open lagoons. Every Army ammunition plant currently employs some type of granular activated carbon system to treat process waters as they are generated. GAC is very effective at removing a wide range of explosive contaminants from water. GAC is a transfer technology only, however, and carbon adsorption media can only be partially regenerated. This section outlines the types of explosives-contaminated water that can be treated by GAC, discusses isotherm tests, and looks at two studies of continuous flow column GAC equipment conducted at Badger and Milan AAPs.

5.3.2.2 Treatable Wastes and Media

GAC can be used to treat explosives-contaminated water, including process waters from the manufacture and demilitarization of munitions (pink water) and ground water contaminated from disposal of these process waters. GAC is not used to treat red water produced during the manufacture of TNT.

5.3.2.3 Isotherm Tests

Isotherm testing is a simple laboratory technique for initial screening of a particular wastewater prior to GAC treatment. From 6 to 10 aliquots of wastewater are measured into containers that can be stirred or shaken for a period of time. Into each container is introduced a known quantity of pulverized carbon with a different amount of carbon for each container. After stirring the mixture for a period of time, the mixture is filtered and the filtrate analyzed. The results of the tests indicate the relative adsorbability of explosives, the adsorption capacity and exhaustion rate of the carbon, the maximum degree of removal achievable, and whether there is preferential adsorption of any explosives.

5.3.2.4 Continuous Flow Column Studies

The Army conducted pilot-scale studies of continuous flow column GAC equipment at Badger AAP and Milan AAP. At both sites, GAC treatment was found to be effective for removing every type of explosive from the water and removing 2,4- and 2,6-DNT to below detection levels.

Badger AAP

At Badger AAP, residues from the open burning of rocket paste contaminated ground water beneath the burning ground with 2,4- and 2,6-DNT. A pilot-scale GAC system consisting of eight, 4.25-in. diameter columns was tested at the site. The first column, which was the test column, operated in series with the second column, which was a back-up column used to remove contaminants when contaminant breakthrough occurred in the first column (i.e., when contaminants began to appear in the effluent from the first column). The fill depth in each column varied from 2 to 4 ft, a range that generally provides good data. Fill depths of greater than 4 ft require as much as 70,000 to 80,000 gallons of water to be pumped through the system to get breakthrough.

Based on the data obtained in an isotherm test, two types of commercially available carbon filters were selected for pilot-scale testing at Badger AAP: Calgon Filter Sorb 300 and Hydrodarco 4000. Flow rates were maintained at 0.3, 0.5, and 0.7 gpm, and a total of about 20,000 gallons of water were used in each test. Influent concentrations ranged from 200 to 600 µg/L of 2,4- and 2,6-DNT. A packed-column air stripper was used prior to GAC treatment to remove trichloroethylene from the water. All laboratory analyses were conducted using HPLC equipment, rather than GC.

The data obtained at Badger AAP were used to design a full-scale treatment system that currently is being implemented.

Milan AAP

Ground water at Milan AAP was contaminated with seven types of explosives. The GAC system tested at Milan AAP was similar to that tested at Badger AAP, except that Atakim 830 carbon was substituted for the Hydrodarco 4000. Tests were conducted at four flow rates ranging from 0.2 to 1.0 gpm, and as many as 56,000 gallons of water were used in each test. The concentration of total explosives in the influent ranged from 600 to 900 µg/L.

The data from the pilot-scale GAC study are being evaluated concurrently with data from a pilot-scale study of ultraviolet oxidation (see section 5.3.1.4).

5.3.3 Compressed Gas Cylinder Handling

5.3.3.1 Background

Compressed gas cylinders exhibit a wide range of hazardous characteristics. The chemicals contained within compressed gas cylinders may be flammable, corrosive, pyrophoric, or poisonous, or they may be oxidizers (definitions of these and other terms appear in Table 5-6). In addition, these chemicals are contained within the cylinders by valves that are relatively small and vulnerable. Left unattended, cylinders become more hazardous. Labels fall off and stenciling corrodes, making it difficult to identify the contents of the cylinders; valves fail due to corrosion; leaks develop; and emergency situations occur that demand immediate attention. Many of the serious injuries and deaths attributed to hazardous materials result from accidents involving liquefied or compressed gases.

Technologies now are available for safely managing compressed gas cylinders. New recycling and EPA-permitted treatment facilities are in operation, and antiquated disposal procedures have been replaced by sophisticated systems designed to protect the environment.

The Compressed Gas Association (CGA) advises EPA and the Department of Transportation (DOT) on technical matters directly affecting the compressed gas industry. CGA members include gas manufacturers, suppliers, and distributors; chemical manufacturers; valve and cylinder manufacturers; consultants; and environmental contractors. CGA provides to the public numerous pamphlets and videos that are useful as guidance and technical resources.

This section discusses criteria for inspecting compressed cylinders; systems for handling and transporting unstable cylinders; options for treating, disposing of, and recycling cylinders; and some methods that have proven unsuccessful for disposing of compressed cylinders. Appendix B presents a case study of compressed gas cylinder handling at a Superfund site.

5.3.3.2 Cylinder Inspections

Before a compressed cylinder can be transported or treated, a detailed inspection and evaluation of the cylinder, including its valve, must be conducted. Cylinders should be inspected for the following:

- *Leaks.* All valves and fittings must be tested for leaks with recognized CGA procedures, which might include the use of a soap or suitable solution to detect the escape of gas, or a hand-held direct reading instrument.

Table 5-6. Definitions of Compressed Gas Cylinder Terms

Gas	A formless fluid that fills the space of its enclosure and changes to the liquid or solid state under increased pressure or decreased temperature.
Gas Pressure	Gas pressure commonly is designated in pounds per square inch (psi); the analogous metric unit is the kilopascal (kPa); 1 psi equals 6.895 kPa. The term psia refers to absolute pressure. Absolute pressure is based on a zero reference point, a perfect vacuum. Measured from this reference point, atmospheric pressure at sea level is 14.7 psi. Gauge pressure (psig) has local atmospheric pressure as a reference point. As such, psia minus local atmospheric pressure equals psig.
Compressed Gas	Any material or mixture contained at an absolute pressure exceeding 40 psi at 70°F or exceeding 104 psi at 100°F; or any flammable liquid having a vapor pressure exceeding 40 psi at 100°F as determined by the American National Standard Method of Testing for Vapor Pressure of Petroleum Products, ANSI/ASTM D323-79.
High Pressure Gas	A gas contained at a pressure of 500 psig (3448 kPa) or higher at 70°F (21.1°C).
Liquefied Compressed Gas	A gas that, under the charged pressure, is partially liquid at a temperature of 70°F.
Nonliquefied Compressed Gas	A gas other than a gas in solution, that, under the charged pressure, is entirely gaseous at 70°F.
Inert Gases	Inert gases, which include argon, carbon dioxide, helium, krypton, neon, nitrogen, and xenon, are simple asphyxiates which can displace the oxygen in air necessary to sustain life and thus cause suffocation.
Corrosive Gas/Liquid	A liquid or gas that destroys living tissue by chemical action.
Irritant	A noncorrosive liquid or gas that, on immediate or prolonged contact, induces a local inflammatory reaction in living tissue.
Poison	A gas or liquid that creates an immediate hazard to health when inhaled, ingested, or absorbed through the skin, and can be fatal in low concentrations.
Pyrophoric Gas	A gas that will ignite spontaneously in dry or moist air at a temperature of 130°F or below.
Oxidizer	A gas or liquid that accelerates combustion and that, on contact with combustible material, may cause fire or explosion.
Pressure Relief Device	A temperature- or pressure-activated device that functions to prevent the rupturing of a charged cylinder by releasing pressure above a predetermined point.

Source: CGA, 1981.

- *Dents.* Guidelines mandate that a dent at a weld be no deeper than 0.64 cm. If a weld is not involved, dents may be no deeper than 10 percent of the cylinder's greatest dimension. Dents are measured using a ruler and a dial caliper.
- *Gouges and cuts.* Gouges and cuts reduce the thickness of cylinder walls. Thickness gauging is required to determine whether cylinders with gouges or cuts have structural weaknesses that constitute a safety hazard. Ultrasonic thickness gauges often are used to measure cylinder wall thickness.
- *Bulges.* Bulging weakens a cylinder. Cylinders with bulges must be evaluated by trained personnel to determine if the cylinders maintain their structural integrity.
- *Corrosion.* While corrosion may be limited to surface rust, corroded cylinders should be inspected using thickness gauging to evaluate the integrity of their walls and to ensure that continued handling and transportation of the cylinders will be safe.
- *Fire damage.* The following is evidence of fire damage: charring of paint or protective coatings; burning or melting of fuze plugs, valves, and pressure relief devices; scarring or burning of metal surfaces; and disfiguring of the cylinder. DOT regulations mandate that a cylinder showing evidence of fire damage may not be placed into service or transported until it has been reconditioned, unless a proper inspection reveals that the cylinder is only discolored or smudged and is in serviceable condition.
- *Improper backfilling.* Cylinders sometimes are backfilled with materials that they were not designed to contain. This can cause many problems, including corrosion of the interior walls.
- *Retrofitted valves.* Gas cylinders occasionally are retrofitted with valves or fittings that are not designed for the cylinder or its contents. Proper inspections should reveal if these conditions exist.

Cylinder labels and stenciling also should be inspected to determine the contents of the cylinder. A cylinder is considered to be "unknown" under any of the following circumstances:

- The cylinder has no original label or stenciling identifying its contents.

- The cylinder is labeled, but the inspection reveals that its fittings and/or pressure relief device is inconsistent with the labeled gas.
- The cylinder's contents are suspected to have been contaminated with other materials, which can alter the chemistry of the original contents.

The contents of an unknown cylinder must be identified through laboratory analytical procedures, not by examining the cylinder's color, valve outlet, or other markings. Applicable analytical procedures include mass spectrometry, as well as Fourier transform infrared (FTIR) and GC. An unknown cylinder cannot be shipped off site for disposal or recycling or treated on site until its contents have been identified. An unknown cylinder that is shipped off site for laboratory analysis must be given a tentative shipping description (Hazard Class) as defined in 49 CFR 172.101(c)(11).

5.3.3.3 Handling Techniques

DOT regulations and CGA guidelines ensure that safe handling and transportation procedures are being followed. Generators of compressed cylinders must use hazardous waste manifests and licensed waste transporters. Each generator also must have an EPA identification number as a small or large generator unless exempt.

Two handling procedures are available: hot tapping/controlled access and overpacking.

Hot Tapping/Controlled Access

The management of a cylinder with an inoperable valve requires state-of-the-art hot-tapping equipment, which performs one of three operations:

- Drilling into the cylinder at a predetermined location, thereby allowing the contents of the defective cylinder to flow into a primary containment vessel.
- Shearing the valve from the cylinder or shearing the cylinder in half and capturing the gas or liquid in a primary containment vessel.
- Drilling into the cylinder while maintaining a tight seal and introducing a new valve into the cylinder without releasing gas into a primary containment system. Secondary containment may be used during this procedure depending on the known or suspected gas involved.

The first two operations are followed either by onsite treatment of the gas in the primary containment vessel or the recontainerization of this gas into a DOT-approved cylinder for offsite treatment or recycling. All three operations are identified as the current BDATs for managing compressed cylinders with inoperable valves and essentially are the only methods in use today.

Overpacking

Salvage cylinder overpacks can be used to contain a compressed gas cylinder that is being transported to an offsite facility or is leaking. An overpack is an oversized cylinder fabricated to accept a smaller cylinder into itself. Once closed, the overpack contains any release from the defective cylinder. Valves and pressure gauges on the overpack allow its internal pressure to be monitored so that the defective cylinder can be removed safely. Cylinder overpacks are similar to the 85- or 110-gallon salvage overpacks used to transport 55-gallon drums.

5.3.3.4 Treatment, Disposal, and Recycling Options

Compressed cylinders may be sent to a treatment or recycling facility, or treated on site.

Offsite Treatment

Discarded and abandoned cylinders must be disposed of in EPA-permitted treatment, storage, and disposal facilities (TSDFs). TSDFs use two systems to treat the contents of cylinders. In one system, vapor or gas is drawn from the cylinder through a manifold directly into an incinerator. In the other system, vapor or gas is drawn from the cylinder into a chemical scrubbing medium. In both systems, the remaining empty cylinder then is purged, cleaned, devalved, and landfilled or recovered for scrap.

Recycling

If the contents of a cylinder are known, generators may send cylinders to a recycling facility. At the recycling facility, the cylinder's contents are removed from the cylinder through a manifold system and introduced back into the manufacturing process as a raw material. The empty cylinder then is either cleaned, devalved, and sent for steel scrap recycling, or, if in suitable condition, cleaned, painted, restamped, and hydrostatically tested for reentry into the market as a filled and usable cylinder.

Onsite Treatment

In onsite treatment, cylinders of liquified or compressed gases are treated, neutralized, or otherwise disposed of at their location, without the use of an offsite TSDF or recycling facility. Onsite treatment involves chemical scrubbing, incineration, flaring, or controlled atmospheric venting of cylinder contents. Onsite treatment may be used under any of the following conditions:

- There are no available offsite management options.
- The cylinder is in a non-DOT transportable condition and cannot be removed from the site or recontainerized into another vessel.

- The cylinder is leaking and must be treated expeditiously.
- Regulatory authorities mandate onsite treatment only.

Onsite treatment of cylinders containing RCRA hazardous substances requires permit approval by federal or local authorities.

5.3.3.5 Unsuccessful Treatment Approaches

Several techniques have been tested for the treatment and recycling of compressed gas cylinders. Most of these techniques are no longer used because they do not adequately protect human health or the environment. Nevertheless, these methods occasionally are used by contractors or regulators unaware of the current BDATs.

Detonation (Uncontrolled Release)

A pressurized cylinder can be destroyed by the detonation of a disposal charge that breaches the cylinder body or its valve. Chemicals contained in the cylinder also might be destroyed during the explosion. In the past, this practice was used to dispose of cylinders with inoperable valves, for which detonation was more cost effective than more sophisticated treatments or recycling. Today, detonation is considered to have several drawbacks, including fragmentation from the cylinder body. In addition, the cylinder can rocket away from the detonation site.

Projectile Method (Uncontrolled Release)

In the projectile method, a high-caliber projectile is fired from a rifle into a cylinder, releasing gas from the cylinder through the vent holes produced by the impact. As with detonation, this procedure releases untreated gases to the environment. In addition, the cylinder may rocket from the site or detonate.

Valve Release (Controlled or Uncontrolled Release)

In valve release, the cylinder's valve is opened, and the cylinder is allowed to vent until empty. Like detonation and the projectile method, this procedure releases potentially toxic or ozone-depleting substances untreated into the environment. Valve release should be used only for atmospheric gases and must be employed using both a regulator to control flow and a stack to prevent the formation of an oxygen-deficient work area for the operator.

5.3.3.6 Reference Cited

CGA. 1981. Compressed Gas Association. Handbook of Compressed Gases, Third Edition.

5.3.4 Reactive Chemical Handling

5.3.4.1 Picric Acid

Background

Picric acid is a yellow crystalline substance that was discovered in 1771 by the British chemist Peter Woulfe. Picric acid's name is derived from the Greek word *pikros,* meaning bitter, due to the intensely bitter and persistent taste of its yellow aqueous solution. In the past, this strong acid was used as a fast dye for silk and wool and in aqueous solutions to reduce the pain of burns and scalds.

When dry, picric acid has explosive characteristics similar to those of TNT. Table 5-7 summarizes the explosive characteristics of picric acid. The first experiments to use picric acid as an explosive bursting charge were conducted in the town of Lydd, England, in 1885, and picric acid was adopted by the British as a military explosive in 1888 under the name Lyddite. Since that time picric acid has been used by many countries as a bursting charge under the names Shimose (Japan), Granatfullung 88 (Germany), Pertite (Italy), Melinite (France), and trinitrophenol (United States). Today, the use of picric acid as a military explosive has been largely discontinued, because picric acid was found to have several disadvantages:

- It is prone to sympathetic detonation, wherein the detonation of a nearby charge would cause it to detonate without a priming charge.

Table 5-7. Explosive Properties of Picric Acid

Gross formula	$C_2H_3N_3O_7$
Melting point	122.5°C
Autoignition temperature	572°F
Molecular weight	229.1
Oxygen balance	-45.4%
Heat of explosion	1,080 kcal/kg
Density	1.767 g/cm^3
Lead block test	315 cm/10 g
Detonation velocity (when confined)	7350 m/s
Deflagration point	570°F (300°C)
CAS	88-89-1
United Nations (dry or wetted with less than 30 percent water by weight)	0154
United Nations (with 30 percent or more water, by weight)	1344

Source: Adapted from DOD, no date; Material Safety Data Sheet, 1985; Meyer, 1981; NSC, 1981.

- When it contacts metals, such as mercury, copper, lead, or zinc, it forms explosive salts that are sensitive to friction, heat, and impact. Special precautions also are required if picric acid falls on concrete floors, because this causes the formation of sensitive calcium salts.
- Metal and cement shells that contain picric acid must be sealed with a protective varnish to prevent contact between the picric acid and the shell lining.

In addition to its explosive properties, picric acid also is highly toxic. Like many trinitrocompounds, picric acid is absorbed through the skin and through inhalation. Acute picric acid exposure can depress the central nervous system and reduce the body's ability to carry oxygen through the blood stream. Prolonged exposure may result in chronic kidney and liver damage. Percutaneous absorption may cause vomiting, nausea, abdominal pain, staining of the skin, convulsions, or death. The Occupational Safety and Health Administration's (OSHA's) permissible exposure level (PEL) for picric acid is a time weighted average (TWA) of 100 $\mu g/m^3$, with a "skin" notation to indicate the possibility of dermal absorption, and the American Conference of Governmental Industrial Hygienists (ACGIH) recommends a threshold limit value (TLV)-TWA of 0.1 mg/m^3.

Proper personal protective equipment, such as gloves, respirators, and self-contained breathing apparatus (SCBA), including Level B attire, should be worn when handling picric acid outside of an established laboratory environment. The use of advanced personal protective equipment should be commensurate with the activity of the individual. Individuals responding to a spill of picric acid or handling spilled material, should wear SCBA, including Level B attire. On the other hand, chemists and technicians working in a laboratory setting should wear gloves and work under a fume hood to ensure safe handling of picric acid.

The following sections discuss handling procedures and disposal options for picric acid.

Handling Procedures

Picric acid is soluble in water and various solvents. When hydrated, picric acid becomes nonexplosive and is safe to transport and incinerate in offsite facilities. Nevertheless, dry picric acid residues on the outer surface of containers as well as in threaded container closures present a significant friction-sensitive hazard. This hazard prompts many generators to use remote handling equipment when opening containers of picric acid, a technique usually reserved for containers of dry (desiccated) material.

DOT classifies solutions of picric acid containing less than 10 percent water as explosive materials and solutions of picric acid containing greater than 10 percent water as flammable solids. This regulatory distinction dictates the mechanics of preparing picric acid for shipment, such as packaging, labeling, and adhering to manifest documentation requirements. It has little relevance to the facility receiving the picric acid for treatment.

Disposal Options

Incineration currently is the BDAT for the destruction of picric acid (40 CFR 261.23(a)(6)). Incineration facilities have varying acceptance criteria governing the concentrations of picric acid in water; some require picric acid concentrations to be as low as 1 percent, others will accept solutions with picric acid concentrations as high as 50 percent.

Because of picric acid's history as a commercial and military explosive, many civilian police bomb squads and military EOD units formerly accepted picric acid for disposal through controlled detonation. Detonation was the disposal method of choice until the mid-1980s, when it was discovered that picric acid was not, in fact, destroyed by open air detonation but simply dispersed by the explosion of the disposal charge. The resulting dispersal of picric acid over the detonation site caused finely divided particles of the substance to enter the surface strata. Testing of surface samples obtained from picric acid detonation sites often showed trace quantities of the compound unaffected by the detonation. In addition, slow motion video of several picric acid detonations clearly showed a heavy yellow smoke of finely divided picric acid particles, which negatively affected localized air quality.

5.3.4.2 Peroxides

Background

Peroxides are shock-sensitive compounds that can explode if subjected to mechanical shock, intense light, rapid changes in temperature, or heat. In some cases, peroxides also can explode through a spontaneous reaction. Peroxide structures are particularly dangerous when present in organic solvents, which often are highly flammable. In testing conducted in the mid-1980s, the detonation of a sample of a hard peroxide crystal destroyed a 4-lb lead Trauzl block, a test used to determine whether or not a substance is explosive. Similarly, a controlled detonation of pure peroxide crystals discovered in an evaporated bottle of isopropyl ether demonstrated that peroxide explosions produce high levels of destructive fragments.

The following sections discuss the formation of peroxide compounds, procedures for inspecting and testing for the presence of peroxides, and options for treating and disposing of peroxides.

Peroxide Formation/Inhibition

Peroxides form in organic solvents as a result of autoxidation. Common peroxide-forming solvents can be divided into the following groups:

- Ethers, including open chain and cyclic ethers, acetals, and ketals (e.g., ethyl ether, isopropyl ether).
- Hydrocarbons with allylic, benzylic, or proparglic hydrogen (e.g., cumene, cyclohexane).
- Conjugated dienes, eneynes, and diynes (e.g., butadiene, furans).

Most of these solvents are purchased from the manufacturer with an added inhibitor, such as hydroquinone or tert-butyl catechol, which chemically inhibits peroxide formation.

Autoxidation in solvents is facilitated by three factors:

- Exposure to oxygen
- Exposure to light, including sunlight
- Storage time

Oxygen is a necessary ingredient for peroxide formation. A cap or bung left off a container or drum, or a loose fitting seal, may supply sufficient oxygen to support peroxide formation by eliminating the inhibitor and supporting the initiation of the autoxidation process. Light, including sunlight, also promotes the elimination of inhibitors and stimulates the autoxidation process. Light, however, cannot promote the autoxidation process unless sufficient oxygen is present in the container. Once formed, peroxides can, in direct sunlight, undergo autodetonation. Storage time simply allows peroxides to develop and form structures. Since autoxidation is a self-sustaining reaction, the rate of peroxide formation increases with time.

More than a decade ago, the National Safety Council (NSC) published easy-to-follow laboratory guidelines (NSC, 1982) for preventing the formation of peroxides in solvents; unfortunately, although these guidelines can be obtained easily from the NSC, they seldom are followed. The formation of peroxides in an organic solvent can be inhibited in two ways: (1) by adding an inhibiting compound to the solvent, or (2) by purging the oxygen from the free space in the solvent container. Chemical manufacturers add inhibitors to almost all solvents, except those used for HPLC. These are specifically manufactured without inhibitors, because inhibitors interfere with the UV detection process. Inhibitors added by the manufacturer, however, are effective only during shipping and marketing of the product; once the solvent container is opened and exposed to oxygen, the autoxidation process begins. Oxygen is the rate-limiting factor in peroxide formation. Replacing oxygen in the free space of a solvent container with an inert gas, such as nitrogen or argon, prevents autoxidation of the solvent. This method has proven very successful in inhibiting peroxide formation.

Peroxide Detection

Visual Inspections. Solvents stored in glass bottles can be inspected for peroxides visually. Bottles containing organic solvents usually are made from amber or brown glass, so a soft light source, such as a flashlight, is helpful for lighting the interior of the bottle to allow a good view of the liquid. The light source should be placed behind or to the side of the bottle, because light shone directly on the glass creates reflections that obstruct inspection of the bottle's contents.

During the visual inspection, the investigator should look for two signs of peroxide contamination:

- *Gross contamination.* Hard crystal formations in the form of chips, ice-like structures, crystals, or solid masses, or an obscure cloudy medium.
- *Contamination.* Wisp-like structures floating in a clear liquid suspension.

Peroxide formation may be present anywhere in the container, including the bottom of the container, the side walls of the glass, the threaded cap, or even the outside of the container. Peroxide formation in ppm concentrations may not be visually observable and must be identified through appropriate testing procedures.

Metal cans and drums cannot be inspected visually and must be opened to allow appropriate testing. Opening containers is a delicate procedure due to the possibility of peroxide accumulation in the cap threads. While peroxide contamination tends to occur less frequently in the cap area than in other container areas, metal cans and drums should be opened only by trained individuals, and the application of remote opening equipment should be considered.

Metal containers are believed to accelerate the rate of peroxide formation. The scientific documentation supporting this belief, however, is largely anecdotal.

Laboratory Testing. Several methods are employed to test for the presence of peroxides. The following two tests are among the more common:

- *Commercially available peroxide test strips.* These test strips provide quantitative results and are simple to use. The test strip is saturated with a representative sample of the liquid in question. A section of the strip changes color if peroxides are present; this color then is compared to a graph, which indicates the peroxide concentration in ppm. Test strips typically register as high as 100 ppm.
- *Potassium iodide (KI) test.* In this test, 100 mg of potassium iodide is dissolved in 1 mL of glacial acetic

acid. Then 1 mL of suspect solvent is added. A pale yellow color indicates a low concentration of peroxides; a bright yellow or brown color indicates a higher concentration of peroxides. This is the preferred method for testing di-isopropyl ether.

A peroxide test should be performed each time material is removed from a container. If the material is removed on a daily basis, tests should be done every other day. Containers of peroxide-forming compounds should be marked with the date the container was first received and first opened, the results of the first peroxide test, and the results of the last peroxide test before disposal. Tables 5-8, 5-9, and 5-10 show the testing requirements for common peroxidizable compounds during storage, as well as handling and testing requirements for these compounds while in use.

The results of peroxide testing dictate how the material should be handled. The following are the general levels of risk associated with various concentrations of peroxides:

- *Between 3 and 30 ppm.* Expired compounds testing within this range pose little or no threat of violent reaction on the given test date. For compounds testing in this range, the investigator should consider adding fresh inhibitor to retard the autoxidation process, and the container should be tightly sealed to prevent air and light exposure.
- *Between 30 and 80 ppm.* Expired or mismanaged compounds that test within this range may pose a threat to operations in the laboratory or facility. Several major exothermic reactions have occurred during the reduction of peroxides within this range.

Table 5-8. Compounds That May Form Peroxides During Storage[a]

Compound	Test Cycle in Storage	Special Handling and Tests While in Use
Isopropyl ether	Every 3 months	Consume or discard within 3 days of opening these containers.
Divinyl acetylene	Every 3 months	Consume or discard within 3 days of opening these containers.
Vinylidene chloride	Every 3 months	
Potassium metal	Every 3 months	Avoid oil/hydrocarbons, if KO_2 is present.
Sodium amide	Every 3 months	

[a] These compounds must be promptly consumed or properly discarded after exposure to air. (Peroxide accumulations in these containers may explode without even being concentrated!)
Source: National Safety Council, 1982.

- *Greater than 80 ppm.* Any solvent testing in excess of the maximum quantifiable limits of standard peroxide test strips must be considered potentially shock sensitive.

Treatment and Disposal Options

Deactivation. Most, if not all, peroxide-forming chemicals are regulated as hazardous wastes. The BDAT for peroxides is deactivation to eliminate the ignitability characteristic (55 FR 22546). Technologies that may be used to deactivate peroxide-formers (classified as D001 oxidizers) include chemical oxidation, chemical reduction, incineration, and recovery. Any of these technologies is acceptable, provided it eliminates the ignitability characteristic. To be accepted by an offsite, EPA-permitted, treatment and disposal facility, peroxide containers that no longer are in use must be peroxide free and present no explosive hazard.

Stabilization/Reduction. Peroxides within a container can be chemically stabilized. The following describes one chemical procedure that has been used successfully to stabilize peroxides. (The reader is cautioned that any procedure used to handle a sensitive chemical or eliminate peroxides should be undertaken only by very experienced personnel who understand the potential for uncontrolled exothermic reactions during the procedure.) The solvent container is accessed through its cap by a remotely operated titanium-coated drill. A Teflon catheter then is inserted through the access point to draw a 1-cm^3 sample of solvent for testing. Three standard peroxide test strips are used to measure the sample's peroxide concentration. All negative indications are verified by adding a drop of sample solvent to a 10 percent potassium iodide solution for colorimetric evaluation.

If the container is found to contain peroxides, a solution of ferrous ammonium sulfate is injected into the container. This produces an oxidation-reduction reaction that, while often very exothermic, has proven to be successful in eliminating peroxides. The container is retested continuously until all peroxides have been dissolved and peroxide tests are shown to be negative. Hydroquinone then is added to stabilize the container and guard against an immediate recurrence of peroxidation. Finally, the container is resealed with a silicone sealant and standard sealing tape and placed in a designated safe area pending offsite disposal.

Open Detonation. Open air detonation or burning of peroxide-forming compounds formerly was used by police bomb squads and government explosive technicians in an effort to assist the private sector. This practice was found to have two major disadvantages:

- Potentially shock-sensitive materials were subjected to movement prior to disposal.

Table 5-9. Compounds That Readily Form Peroxides in Storage Through Evaporation or Distillation[a]

Compound	Test Cycle in Storage	Special Handling and Tests While in Use
Diethyl ether	Every 12 months	HPLC grades of these compounds are normally packaged without peroxide inhibitors. These uninhibited containers should be stored in an inert (oxygen-free) atmosphere and tested at 3-month intervals. Limit these containers to sizes appropriate to the application in order to prevent repeated exposures.
Tetrahydrofuran	Every 12 months	Every 3 months, if uninhibited
Dioxane	Every 12 months	Every 3 months, if uninhibited
Acetal	Every 12 months	Every 3 months, if uninhibited
Methyl-isobutyl-ketone (Isopropylacetone)	Every 12 months	Every 3 months, if uninhibited
Ethylene glycol dimethyl ether	Every 12 months	Every 3 months, if uninhibited
Vinyl ethers	Every 12 months	Every 3 months, if uninhibited
Dicyclopentadiene	Every 12 months	Every 3 months, if uninhibited
Isoprene	Every 12 months	Every 3 months, if uninhibited
Organometallics (Grignard Reagents)	Every 12 months	Every 3 months, if uninhibited. Do not store in a cold room. These highly reactive compounds accumulate peroxide at low temperatures because the peroxide degradation rate is slowed relative to the peroxide formation rate.
Diacetylene	Every 12 months	Every 3 months, if uninhibited
Methyl acetylene	Every 12 months	Every 3 months, if uninhibited
Cumene	Every 12 months	Every 3 months, if uninhibited
Tetrahydronaphthalene	Every 3 months, if uninhibited	Every 12 months
Cyclohexene	Every 12 months	Every 3 months, if uninhibited
Methylcyclopentene	Every 3 months, if uninhibited	Every 12 months
t-Butyl alcohol	Every 12 months	Every 3 months, if uninhibited
Acetaldehyde	Every 12 months	Anhydrous acetaldehyde will autoxidize at 0°C or below under ultraviolet light catalysis to form peracetic acid, which may react with more acetaldehyde to produce the explosive acetaldehyde monoperacetate.

[a] Concentration processes (evaporation or distillation) defeat the action of most autoxidation inhibitors. Special handling and accountability are required of those compounds offered as HPLC grade, because HPLC-grade materials are packaged without autoxidation inhibitors.

- The compound in question was dispersed untreated into the surrounding air and soil.

5.3.4.3 Ethers

Ethers are organic compounds with common uses as both medical anesthesia and solvents. Simple ethers may be highly volatile and have flammable and potentially explosive characteristics. The most commonly used ether is diethyl ether—a clear, colorless liquid that vaporizes readily at room temperature and is highly flammable. Diethyl ether's flashpoint is –45°C and its flammable range extends from 1.85 to 48 percent by volume. Aside from their flammability, liquid ethers also can contain organic peroxides produced by a reaction between the ether and atmospheric oxygen (Meyer, 1989).

5.3.4.4 References Cited

DOD. No date. Department of Defense. Publication TM9-1300-214/TO 11A-1-34.

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Meyer, E. 1989. The Chemistry of Hazardous Materials, Second Edition. Prentice Hall, Inc. Englewood Cliffs, New Jersey. 394-395.

Meyer, R. 1981. Explosives, Second Revised and Expanded Edition. Weinheim Publications. Deerfield, Florida.

NSC. 1982. National Safety Council. Industrial Safety Data Sheet I-655-Rev.82, Stock No. 123.09. Chicago, Illinois.

Table 5-10. Compounds That Pose Hazards Due to Peroxide Initiation of Polymerization

Compound	Test Cycle in Storage	Special Handling and Tests While in Use[a]
Butadiene	Every 12 months	Every 3 months, if stored as liquid
Styrene	Every 12 months	Every 3 months, if stored as liquid
Tetrafluoroethylene	Every 12 months	Every 3 months, if stored as liquid
Vinyl acetylene	Every 12 months	Every 3 months, if stored as liquid
Chlorobutadiene (Chloroprene)	Every 12 months	Every 3 months, if stored as liquid
Vinyl pyridine	Every 12 months	Every 3 months, if stored as liquid
Vinyl chloride	Every 12 months	Every 3 months, if stored as liquid

[a] When stored in the liquid state, the peroxide-forming potential dramatically increases.
Source: Manufacturer warning labels.

NSC. 1979. National Safety Council. Data Sheet 10351-79.

5.3.5 *Reuse/Recycle Options for Propellants and Explosives*

5.3.5.1 Background

Recovery and reuse technologies for energetic materials, including both explosives and propellants, are available in production-scale facilities capable of handling quantities greater than 100,000 lb. Recovery/reuse options should be considered at explosives waste sites for several reasons. First, new recovery methods and potential uses for reclaimed explosive materials are rapidly developing. Second, recovery/reuse options reduce overall remediation costs by eliminating destruction costs and allowing the value of reclaimed materials to be recovered. Finally, EPA's treatment hierarchy, which is based on environmental considerations, favors recovery/reuse options over destruction technologies.

This section describes the types of explosives waste and media that can be recovered/reused, the available recovery/reuse technologies, some leading recovery/reuse companies and institutions, potential applications for recovered energetic materials, and advantages and limitations of recovery/reuse technologies.

5.3.5.2 Treatable Wastes and Media

A detailed knowledge of energetic materials is necessary to minimize the risks associated with recovery/reuse and to develop a suitable recovery/reuse plan. For a detailed description of energetic materials, refer to section 1.2.2. In addition to pure energetic materials, munitions and rocket motors and explosives-contaminated soils and sludges also can be recovered/reused.

Energetic Materials

Propellants that contain combustion modifiers, such as lead compounds, are difficult to reuse because of the stringent controls on lead emissions. Reuse of these propellants as commercial explosive additives is rarely an option. Primary explosives and initiating explosives, such as lead azide, generally are not candidates for recovery/reuse due to their high sensitivity. Very little has been done on recovering pyrotechnics, probably due to their highly variable compositions, their sensitivity, and the low value of their ingredients. This section does not discuss pyrotechnics in detail.

Munitions and Rocket Motors

Recovery/reuse methods generally are applied only to munitions and rocket motors that have documented histories, including documentation of how the item was manufactured, its energetic fill, and its inert parts. In addition, the recovered item must be present in sufficient quantities for the recovery/reuse process to be economical. These criteria limit the types of munitions for which recovery/reuse is feasible. Bunkered ordnance discovered during a remediation effort may have a documented history and sufficient quantity. Ordnance encountered during range cleanup often is in various stages of physical disrepair and does not meet the criteria for recovery/reuse.

Explosives-Contaminated Soils and Sludges

Soils and sludges contaminated with energetic materials present handling problems during recovery and reuse operations. AEC has established a guideline that soils containing greater than 10 percent energetic materials by weight should be considered explosive during handling and transportation. As a general rule, soils and sludges containing less than 10 percent energetic materials by weight pass AEC's nonreactivity tests. Reuse/recycle options are more feasible for contaminated soils and sludges meeting the nonreactivity criteria, because they can be removed, transported, and handled using conventional equipment, which could provide a substantial cost savings. Unless diluted with fuel, the material extracted from contaminated soils and sludges most likely must be treated as an energetic material.

5.3.5.3 Operation and Maintenance

Recovered munitions and rocket motors either can be reused "as is," or the energetic materials can be recovered from these items and reused or recycled. If an ordnance item is to be reused as is, it is inspected,

recrated, and sold as reconditioned ordnance. Energetic materials recovered from munitions can be reused in their original application, or specific ingredients can be extracted and recycled into energetic materials. Explosives-contaminated soils and sludges can be recovered for the fuel value of their contaminants. Table 5-11 provides an overview of the potential uses for recovered munitions and energetic materials.

Energetic Material Extraction

One of the more technically challenging aspects of energetic material recovery/reuse is the separation of energetic components from inert components. For Hazard Class 1.3 composite propellant rocket motors and items containing plastic-bonded explosives, high-pressure water washout (hydromining) and machining are the established separation methods. Other washout methods that have been demonstrated at bench scale include liquid nitrogen and liquid ammonia washout at high pressure. The latter two methods are scheduled to be demonstrated at prototype scale in the next year under DOD's Large Rocket Motor Demilitarization Program.

Thiokol Corporation's washout facility near Brigham City, Utah, which has been used mainly for rocket motor case and warhead body recovery, utilizes hydromining technology (see Figure 5-11). In operation since the mid-1960s, this facility has been used to remove over 17 million pounds of propellant and recover over 3,000 motor cases. Another major hydromining facility in the United States is the Aerojet Solid Propulsion Company facility in Sacramento, California.

Propellant machining is used in final grain shaping to provide desired ballistics (i.e., propellant burn back pattern) and recover missile motor cases. All of the propulsion companies have employed this method, in which a drill, boring mill, or special tooling is used to cut propellants from motors under carefully controlled conditions.

Recovery methods for TNT-based explosives are well established and involve melt and steam-out processes. These processes liquify TNT so that it can be poured out of the munition. TNT melt and steam-out facilities are located at several Army ammunition plants and depots, and at the Western Demilitarization Facility in Hawthorne, Nevada.

Table 5-11. Overview of Items and Uses[a]

Item	Energetic Material	Typical Ingredients	Potential Reuse	Comments
Rocket Motor	Hazard Class 1.3 Propellant	Binder/AP/Al	Original, CEA, IR (AP) Original, CEA, IR (HMX)	CEA & AP recovery have been demonstrated full scale, special additives such as lead oxide may require destruction methods
	Hazard Class 1.1 Propellant	NG/NC/HMX/AP/Al/ Binder		CEA & HMX recovery demonstrated prototype scale
Gun Propellant	Hazard Class 1.1 Propellant	NC/NG/NQ	Original, CEA, IR (NC)	CEA demonstrated full scale
Bombs	Explosive	TNT, Al, AN, RDX	Original, CEA	CEA & IR demonstrated full scale
Warheads	Explosive	Binder, HMX, RDX, Al	Original, CEA, IR (HMX)	CEA demonstrated prototype scale, IR (HMX) bench scale
Bomblets	Explosive	Binder, HMX, RDX, Al	Original, CEA, IR (HMX)	Recovery demonstrated bench scale
Illuminating Flare	Pyrotechnic	Binder, $NaNO_3$, Mg	Original	IR not demonstrated
Signal Flare	Pyrotechnic	Binder, Metal Nitrates, Mg	Original, IR ($MgNO_3$)	IR not demonstrated
Mfg. Waste	Propellants, Explosives, Pyrotechnics	Any of the above	CEA, IR (HMX, AP)	Composition and ingredient reuse demonstrated bench to full scale, sludges not demonstrated

[a]Key: Al = aluminum; AN = ammonium nitrate; AP = ammonium perchlorate; CEA = commercial explosive additive; HMX = high melting explosives; IR = ingredient recovery (most likely ingredient to be recovered); Mg = magnesium; $MgNO_3$ = magnesium nitrate; $NaNO_3$ = sodium nitrate; NC = nitrocellulose; NG = nitroglycerine; NQ = nitroguanidine; Original = original intended use; RDX = royal demolition explosives, or cyclonite; TNT = trinitrotoluene.

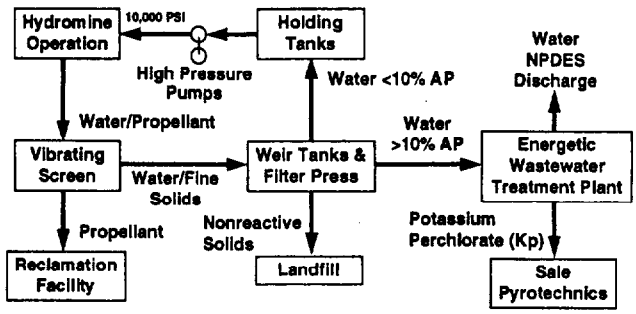

Figure 5-11. Flow diagram of hydromining process.

Another means of disassembly and separation of munitions components is called "reverse engineering." Several systems have been built to reverse engineer munitions. These systems, which are called ammunition peculiar equipment (APE), work well for specific munitions but do not adapt easily to varying configurations. Reverse engineering methods disassemble munitions down to the casing that contains the energetic material. Standard methods for further reducing the size of the munition include wet saw cutting and high pressure water jet.

A size reduction method called Cryofracture has been developed by General Atomics Corporation. It involves cooling munitions to liquid nitrogen temperatures and crushing them in a hydraulic press. After being processed in this manner, the ordnance can be fed to a specially designed incinerator. Several separation methods, including solvent, density, magnetic, and melt and steam-out separation processes, could be applied to recover the energetic material after fracturing. The types of items that have been successfully Cryofractured are shown in Table 5-12. Because Cryofracture can handle multiple versus individual munitions, the technology might be most useful in separating inert and live materials in smaller items, such as bomblets, for which reverse engineering is less practical.

Reuse of Energetic Materials

Once energetic materials have been separated from inert materials, reuse is more straightforward, and many large-scale reuse applications have been demonstrated. Ordnance items and rockets routinely are reinspected and used for training or similar applications. Surplus explosives also have been purchased from the government by commercial explosives companies since before World War II. In addition, the patent literature reveals many examples of smokeless powders, TNT, tetryl, HMX, and RDX being added as sensitizing agents and blast enhancers for slurry and emulsion explosives used in the mining and quarry industries. According to the Institute of Manufacturers of Explosives (IME), hundreds of millions of pounds of slurries and emulsion explosives are used annually. While the feasibility of using recovered propellants and explosives in slurries depends on their availability and cost, this potentially could be a significant market for recovered energetic materials. When used in slurries, explosive additives are generally in the range of 5 to 30 percent, and most major commercial explosive formulations can be altered to accommodate military propellants and explosives.

Other smaller scale applications for recovered energetic materials recently have been demonstrated. For example, Thiokol Corporation has made 2-lb booster charges, used to initiate ammonium nitrate/fuel oil (ANFO) or slurry explosives, from Hazard Class 1.1 rocket propellants. TPL, Inc., has demonstrated using reclaimed granulated plastic-bonded explosives (PBX) for explosive-metal bonding and forming applications. Requirements for this type of application, such as a detonation velocity of 2.2 km/s with a variation of ± 50 m/s, are fairly stringent. The TPL application was demonstrated under a small business innovative research (SBIR) contract from the Naval Surface Weapons Center in Crane, Indiana.

Ingredient Recovery

Ingredient recovery from propellant or explosive compositions is the least advanced reuse technology. In theory, ingredient recovery is not difficult, but, until recently, there has been no economic or environmental driving force to recover individual ingredients. Moreover, many military programs have a "no change" policy that prohibits changes in materials used in ordnance manufacture. This policy also would distinguish between recovered materials and virgin materials made from reactants. The "no change" policy is starting to change under environmental and economic pressures, but ingredient recovery probably will continue to meet resistance from risk-averse program managers.

Three significant efforts are being conducted in the area of ingredient recovery and reuse. In the first, AP is recovered from Hazard Class 1.3 composite rocket propellants. This technology involves leaching of the soluble AP from size-reduced propellants, recrystallization at an AP vendor, and reincorporation of AP into rocket propellant. Over 100,000 lb of AP have been recovered and recrystallized using this method, and the propellants made from the recovered AP cannot be distinguished from those made with virgin materials. A schematic of the reclamation process is shown in Figure 5-12. Two companies, Thiokol Corporation and Aerojet Solid Propulsion Company, are participating in this effort with support from two AP producers, WECCO & Kerr McGee, as well as the U.S. Air Force and the Large Rocket Motor Demilitarization Group.

Table 5-12. Types of Munitions That Have Been Cryofractured[a]

Munition Type	Tested Form	Explosive Elements	Explosive Items Cryofractured
M55 Rockets (155-mm)	Rocket in firing tube	Comp B burster 3.2 lb Doublebase cast propellant 19.3 lb	5
M23 Land Mines	Steel drum with three mines and packing material	Comp B burster 0.8 lb	126
M60 105-mm Cartridges	Wood box with two cartridges in fiber tubes	Tetrytol burster 0.3 lb Tetrytol booster 0.05 lb Singlebase grain propellant 2.8 lb	72
155-mm Projectiles	Projectile	M-110 and M21A1	1,204

[a] All explosives fractured without explosion.
Source: General Atomics, 3550 General Atomics Court, San Diego, CA 92121-1194.

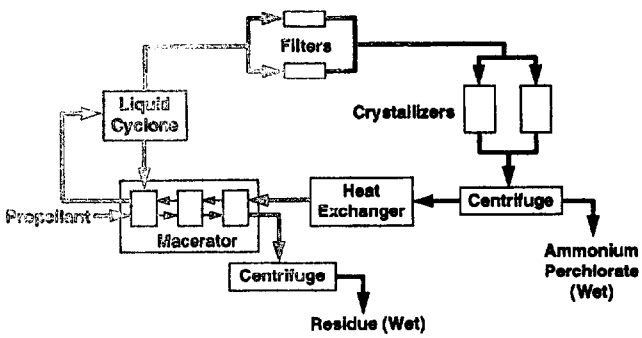

Figure 5-12. Flow diagram of ammonium perchlorate reclamation process.

Another ingredient drawing interest for recovery is HMX. The HMX recovery process involves separation by dissolving and subsequent recrystallization using solvents such as acetone or dimethyl sulfoxide (DMSO). At least two organizations have reported successfully meeting material specifications for recovered HMX: TPL, Inc., which recovers HMX from PBX; and the U.S. Army Missile Command (MICOM), which recovers HMX from Hazard Class 1.1 propellants. In addition to reuse in military applications, HMX might have commercial applications, such as serving as an oil well perforation charge.

The third ingredient that has been successfully recovered and recycled is white phosphorus. The Crane Army Ammunition Activity (CAAA) installation in Crane, Indiana, has an acid-conversion plant that converts white phosphorus into phosphoric acid. Using this plant, the CAAA installation can recover marketable scrap metal and phosphoric acid from white phosphorus munitions. The acid-conversion plant processes munitions from other Army facilities and has sold thousands of tons of phosphoric acid and scrap metal from its demilitarization operations.

Energy Recovery

One recovery/reuse approach proposed for energetic contaminants in soils and sludges is solvent extraction followed by burning of the extract with other fuels to provide energy. AEC has demonstrated that low levels of smokeless powder, RDX, or TNT can be used to supplement boiler fuel. This energy recovery approach also could be applied to extracted energetic materials, using the AEC studies as a guide to the sensitivity and fuel value of the materials.

5.3.5.4 Applications

Table 5-13 lists a variety of recovery and reuse applications. Some, such as the Louisiana Army Ammunition Plant's steam-out facility for TNT-based explosives, which has been operational for decades, are well established production-scale methods. These facilities normally have the infrastructure to handle wastewaters from the recovery process. Others, such as the Cryowash process, which uses 12,000 to 30,000 psi liquid nitrogen to remove energetic materials from cases, are emerging bench-scale technologies. The Cryowash process has been demonstrated on hundreds of pounds of energetic materials and is scheduled to undergo full-scale prototype testing within the year. Developmental status must be considered when selecting recovery/reuse technologies for particular applications.

5.3.5.5 Advantages and Limitations

Recovery and reuse of energetic materials should be a goal in every remediation effort. EPA places this option higher than destruction technologies on the preferred treatment scale. Each situation, however, requires a cost/risk/benefit assessment. At sites where rocket motors and ordnance are in sufficient quantity and have known materials and histories, recovery/reuse should be seriously considered. At sites where the pedigree and volume criteria cannot be met, cost/risk/benefit assessments probably will indicate that destruction technologies should be used. In each instance, the safety of the operating personnel must be the highest priority.

Table 5-13. Application Summary

Removal Method	Facility	Status	Most Likely Use	Status
Mechanical	Thiokol, Chemical Systems Division UTC, U.S. Army Facilities, other	Production	Commercial Explosive	Prototype
Melt/Steam-out	U.S. Army Facilities	Production	Military Explosive	Production
Cryofracture	General Atomics	Prototype	Commercial Explosive	Emerging
Cryocycle	Sandia National Labs	Bench	Commercial Explosive	Emerging
Reverse Engineering	U.S. Army Facilities	Production	Military Explosive	Production
Water Washout	Thiokol, Aerojet	Production	New Propellants	Prototype
Liquid Ammonia Washout	U.S. Army MICOM	Bench	New Explosive	Bench
Liquid Nitrogen Washout	General Atomics	Bench	Commercial Explosive	Emerging

5.3.6 Solvent Extraction

Solvent extraction is a technology that the Army originally determined to be infeasible for treating explosives-contaminated soils. The technology, however, might have potential for treating these soils if a few lingering technical issues can be resolved.

In 1982, the Army conducted laboratory-scale solvent extraction on explosives-contaminated lagoon samples from a number of sites. Each sample was washed with a solution of 90 percent acetone and 10 percent water. This process achieved greater than 99 percent contaminant removals.

In 1985, the Army conducted a pilot-scale engineering analysis to determine the feasibility of full-scale solvent extraction. This analysis indicated that, for solvent extraction to be economically feasible, the number of required washes would have to be reduced and acetone would have to be recovered and reused. Currently, the only available technology for recovering acetone is distillation, which exposes acetone to heat and pressure. Exposing a solvent that has been used to extract explosive contaminants to heat and pressure raises serious safety considerations. In fact, the distillation column used to recover acetone often is referred to as an "acetone rocket." Nevertheless, the Army believes that full-scale solvent extraction would be feasible if a safe, efficient, alternative recovery method were developed.

5.3.7 Volume Reduction for Explosives Waste

A soil washing procedure, termed the Lurgi Process, currently is being developed in Stadtalendorf, Germany. Although no data have been published on the effectiveness of this process, initial reports suggest that the process can reduce levels of explosive contamination in soils to low ppm levels. As with all soil washing technologies, the Lurgi Process produces secondary wastes, such as washwater and concentrated explosives.

In the Lurgi Process, contaminated soils are excavated and processed in an attrition reactor, which detaches the explosive material from the soil particles. The mixture of detached particles then undergoes a separation process to remove large rocks. These rocks are crushed and returned to the site. The remaining material undergoes a second separation process, which separates clean from contaminated particles. Clean particles are dewatered, separated into heavy and light materials, and returned to the site. Contaminated particles undergo a final series of washing, separation, and chemical extraction processes to remove any remaining clean particles. Finally, the contaminated material is clarified and concentrated before being disposed of or treated.

Chapter Six
Treatment Technologies for Radioactive Waste

6.1 Wet-Based Volume Reduction for Radioactive Soils

6.1.1 Background

Many sites with radioactive soils have large volumes of soil contaminated with low concentrations of radioactive waste. Volume reduction is a promising alternative to actions that remove and dispose of all the contaminated soils. Currently, there is no universally applicable volume reduction technology; the feasibility of volume reduction must be evaluated on a site-by-site basis. This section provides general guidelines for conducting treatability studies to determine the feasibility of reducing the volume of contaminated soils at radioactive waste sites.

6.1.2 Treatability Studies for Radioactive Soils

ORIA has conducted and is conducting treatability studies for the volume reduction of radioactive soils. Based on ORIA's experience to date, the recommended general steps for a treatability study for radioactive soils are as follows:

- Soil characterization
- Bench-scale testing
- Mini-pilot plant
- Pilot plant

6.1.2.1 Soil Characterization

Characterization of representative soil samples provides the initial information needed to determine if volume reduction is technically feasible. Soil characterization also is a valuable aid in planning the use of plant equipment and greatly enhances the overall planning and development process. The purpose of characterization is to identify physical differences in the soil constituents that can be exploited to separate contaminated soil particles from clean particles. Common exploitable differences between contaminated and clean particles include size, specific gravity, particle shape, magnetic properties, friability, solubility, wetability, and radioactivity.

6.1.2.2 Bench-Scale Testing

Bench-scale testing is designed to verify whether a volume reduction technology can meet the performance goals for a site. Bench-scale testing employs, on a small scale and in a batch sequence, the general techniques of particle liberation, particle separation, and dewatering. A general flow chart for the sequence of these techniques is shown in Figure 6-1.

Particle separation processes divide a mixture of soil particles into two or more volumes (see Table 6-1). During particle liberation, contaminated soil particles are released from clean particles, resulting in a mixture of unattached contaminated and clean particles (see Table 6-2). Dewatering the contaminated volume becomes an important unit operation since there are restrictions on the amount of free water in waste being disposed of (see Table 6-3).

The flow chart shown in Figure 6-1 is simple, but the actual volume reduction process grows in complexity and specificity as the bench-scale testing progresses toward the design of a pilot plant.

6.1.2.3 Mini-Pilot Plant

A mini-pilot plant can be developed to demonstrate volume reduction on site at a rate of about 10 kg/hr. The decision to develop a mini-pilot plant is based on favorable results from the bench-scale testing. From the

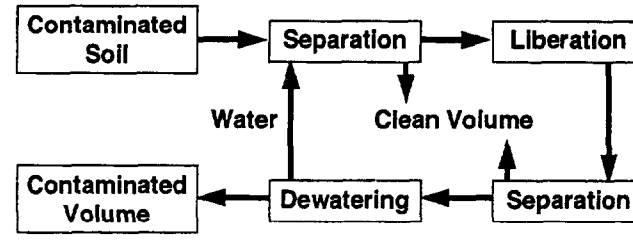

Figure 6-1. General flow diagram for bench-scale testing.

Table 6-1. Particle Separation Techniques

	Technique				
	Sizing	**Settling Velocity**	**Specific Gravity**	**Magnetic Properties**	**Flotation**
Common Name	Screening	Classification	Gravity separation	Magnetic	Flotation
Basic Principle	Various diameter openings and effective particle size	Faster vs. slower settling, particle density, size, shape of particles	Differences in density, size, shape, and weight of particles	Magnetic susceptibility	Suspend fines by air agitation, add promoter/collector agents, skim oil froth
Major Advantage	Inexpensive	Continuous processing, long history, reliable, inexpensive	Economical, simple to implement, long history	Simple to implement	Very effective for some particle sizes
Major Disadvantage	Screens can plug, fine screens are fragile, dry screens produce dust	Difficulty with clayey, sandy, and humus soils	Ineffective for fines	High operating costs	Contaminant must be small fraction of total volume
General Equipment	Screens, sieves	Mechanical, non-mechanical hydrodynamic classifiers	Jigs, shaking tables, troughs, sluices	Magnetic separators	Flotation machines
Lab Test Equipment	Vacuum sieve/screen, trommel screen	Elutriation columns	Jig, shaking table	Lab magnets	Agitair laboratory unit

Table 6-2. Particle Liberation Techniques

	Technique				
	Washing	**Scrubbing**	**Attrition**	**Crushing and Grinding**	**Surface De-Bonding**
Basic Principle	Water action	Moderate particle/particle action	Vigorous particle/particle action	Size reduction	Surfactant action
General Equipment	Trommel, washer, screw classifier	Trommel, screw classifier	Trommel, mill	Crushers, mill grinders	Trommel, mill
Lab Test Equipment	Stirring units, trommel, elutriation column	Trommel	Trommel	Crushers, mill grinders	Trommel

batch tests, a continuous process is developed that begins to simulate a field system. This process addresses many operational issues not addressed during bench-scale testing. The technical necessity of developing the mini-pilot plant is matched by its importance in helping to obtain the public's acceptance of onsite treatment as a viable alternative to complete removal of contaminated material.

6.1.2.4 Pilot Plant

A pilot plant, which typically processes about 200 kg/hr, should be developed to demonstrate volume reduction. The pilot plant is designed to provide detailed cost, design, and performance data on the volume reduction process. For example, the pilot plant developed for a radium-contaminated site in Montclair, New Jersey, effectively separated over 50 percent of the contaminated soil, producing a fraction with approximately 11 picocuries per gram (pCi/g) activity. Table 6-4 shows the performance goals and actual results obtained at the Montclair site.

6.1.3 Advantages of Volume Reduction

Physical liberation and separation methods are used widely in processing ore and coal. These processes are well characterized, and considerable information is available on their operation. These methods are excellent candidates for use in volume reduction of soils contaminated with low levels of radioactivity and have been demonstrated to be effective in tests with soil from

Table 6-3. Dewatering Techniques

	Technique			
	Filtration	Centrifugation	Sedimentation	Expression
Basic Principle	Passage of particles through porous medium: particle size	Artificial gravity settling: particle size, shape, density, and fluid density	Gravity settling: particle size, shape, density, and fluid density; flocculent aided	Compression with liquid escape through porous filter
Major Advantage	Simple operation, more selective separation	Fast, large capacity	Simple, less expensive equipment, large capacity	Handles slurries difficult to pump, drier product
Major Disadvantage	Batch nature of operation, washing may be poor	Expensive, more complicated equipment	Slow	High pressures required, high resistance to flow in cases
General Equipment	Drum, disk, horizontal (belt) filters	Solid bowl sedimentation and centrifugal, perforated basket	Cylindrical continuous clarifiers, rakes, overflow, lamella, deep cone thickeners	Batch and continuous pressure
Lab Test Equipment	Vacuum filters, filter press	Bench or floor centrifuge	Cylindrical tubes, beaker, flocculents	Filter press, pressure equipment

Table 6-4. Goals Versus Results for Volume Reduction Treatability Study at Radium-Contaminated Site in Montclair, New Jersey

Goal	Result
50 percent volume reduction	56 percent volume reduction
15 pCi/g in residual soil	11.3 pCi/g in residual soil
Minimal process water contamination	Less than 100 pCi/L

Source: U.S. EPA. Office of Radiation and Indoor Air. Unreported data.

the Montclair site. Physical separation can significantly lower the cost of remediating sites with radioactive soils by reducing the volume of soils that must be disposed of. For this reason, soil separation technologies should be considered during the feasibility studies for Superfund and other sites. Soil characterization will provide preliminary information on the feasibility of volume reduction, liberation, separation, and collection of clean and contaminated fractions. Bench-scale test results effectively lead to a preliminary design that will correlate well with field equipment. The equipment, commonly used in the coal and ore industries, is commercially available or relatively easy to manufacture and operate.

6.2 Dry-Based Volume Reduction for Radioactive Soils

6.2.1 Background

This section discusses a volume reduction system being operated at Johnston Atoll, a site with large volumes of plutonium-contaminated soil. The system combines wet and dry volume reduction. The latter method is very successful because contamination at Johnston Atoll is not uniformly distributed—a condition common for most contaminated soils. Contaminated and uncontaminated soils are interspersed as a result of nonuniform initial disposition, weather, vegetation, traffic, or previous cleanup efforts. Excavating only the contaminated soils from a site is difficult because excavation equipment, such as bulldozers, is not able to remove just the contaminated spots, and operators of the equipment have little experience in soil cleanup. Site managers also are inclined to excavate large soil quantities to ensure that all contaminants have been captured. As a result, large volumes of clean soil typically are excavated along with contaminated soil. Volume reduction procedures, which separate or sort clean soils and contaminated soils to different paths, reduce the volume of soil requiring wet corrective action.

6.2.2 Treatable Wastes and Media

Although the volume reduction plant at Johnston Atoll is set up to process radioactive soils, the technology theoretically could be applied to soils contaminated with other heavy metals or organic chemicals, such as explosives. For example, X-ray fluorescence detectors, which identify heavy metals, could be substituted for the radiation detectors used in the process. Similarly, an organic vapor detector could be used to identify volatile organic compounds. The key volume reduction will occur when the large volume of clean soil is removed from the smaller volume of contaminated soil.

6.2.3 Operation and Maintenance

6.2.3.1 Analyzing Soils

Two methods typically are used to analyze soils at sites contaminated with radionuclides: (1) the removal method, in which samples are drawn at various locations across the site and analyzed in a laboratory; and (2) the in situ method, in which a radiation detector is used to estimate an average contaminant concentration for an area much larger than the size of removal samples. The Johnston Atoll cleanup plant employs a third method, which combines the best features of the other two methods. This method, known as the conveyor method, conveys all suspect soil beneath detectors under well-defined conditions and automatically sorts clean soil from contaminated soil.

6.2.3.2 Separating Soils

Figure 6-2 is a flow diagram of the separation process used at the Johnston Atoll cleanup plant. First, excavated soil is screened to remove large rocks. These rocks, which have a relatively large volume with respect to their contaminated surface area, typically are cleaner than the sand and soil fines. As a result, their presence lowers the average radioactivity concentration of the soil. Removal of oversize rocks by screening is an effective volume reduction technique. The rocks must be crushed, however, to ensure that they are clean. Once separated out, large rocks pass through a crusher, which reduces their size and allows radionuclides on their surfaces to be detected more easily.

After the screening process, several devices are used to sort soils based on their levels of radioactivity. These sorters have an array of radiation detectors on 3-ft wide conveyors that analyze batches of soil. Each batch is approximately 4 in. wide, 1 ft long, and ¾ in. deep, and is counted for 2 seconds. The detectors trigger gates that direct each batch of soil either to a contaminated path or to a clean path.

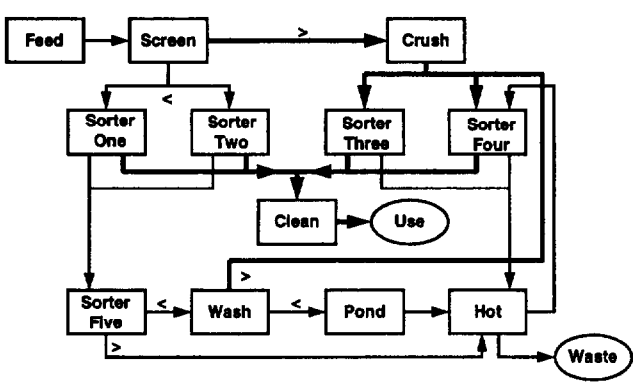

Figure 6-2. General flow diagram of the soil separation process.

After soils are separated into clean and contaminated paths, soils on the contaminated path are subdivided further to separate uniformly contaminated soil fines from contaminated particles. Contaminated particles are defined as those having more than 5,000 becquerels (Bq) of radioactivity, which is equivalent to a pure plutonium oxide particle about 70 microns in diameter. As soon as a contaminated particle is identified, it is diverted to a drum. Contaminated fines continue on to a washing system, which includes a spiral classifier and a settling pond. This system separates the very finest, highly contaminated, soils from the larger, less-contaminated, fines.

6.2.3.3 Monitoring Plant Performance

The cleanup plant at Johnston Atoll is equipped with several diagnostic instruments that monitor the performance of the plant. These instruments include weigh scales, density gauges, and flow meters, which assess various properties of the clean and contaminated soils. The computer equipment used to operate the plant also generates detailed data on plant performance, including both daily and weekly summaries. These data are important for establishing that soil emerging from the plant actually is clean and determining contaminant levels in waste soil.

Figures 6-3 through 6-6 show some of the performance results of the Johnston Atoll cleanup plant over its first 40 weeks of operation. Figure 6-3 shows the percent of oversize rocks removed and crushed. These materials, which represent 25 to 30 percent of the soil by weight, are over 99 percent clean. Figure 6-4 shows the recovery of clean soils by weight (including oversize rock), typically around 98 percent from one pass through the sorters. Figure 6-5 shows the average specific activity levels of clean soils recovered from the cleanup plant. These levels generally are 5 times less than the cleanup standard of 500 Bq/kg. A total of about 25,000 tons of soil met this standard. Figure 6-6 shows the amount of radioactivity captured by the plant—almost 2 GBq (equivalent to 0.8 g of plutonium) after 40 weeks. This activity is concentrated in about 500 tons of soil.

The computer monitoring data can be verified by conventional analyses, including laboratory analysis of discrete samples and in situ analysis of the clean pile. In addition, Johnston Atoll uses an in situ pan method, in which clean soils from the plant are placed in a 1-m^2 pan to a depth of 1 cm and analyzed by a radiation detector. This method is fast and very accurate, because particles of contamination have been removed and the remaining contamination is uniformly distributed.

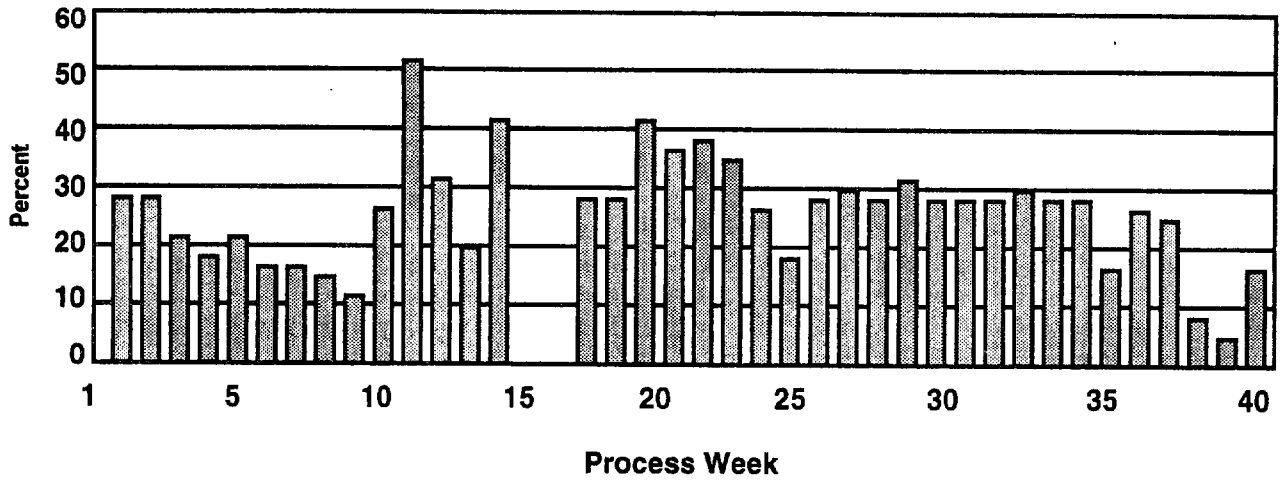

Figure 6-3. Percent of feed soil recovered as oversize rocks.

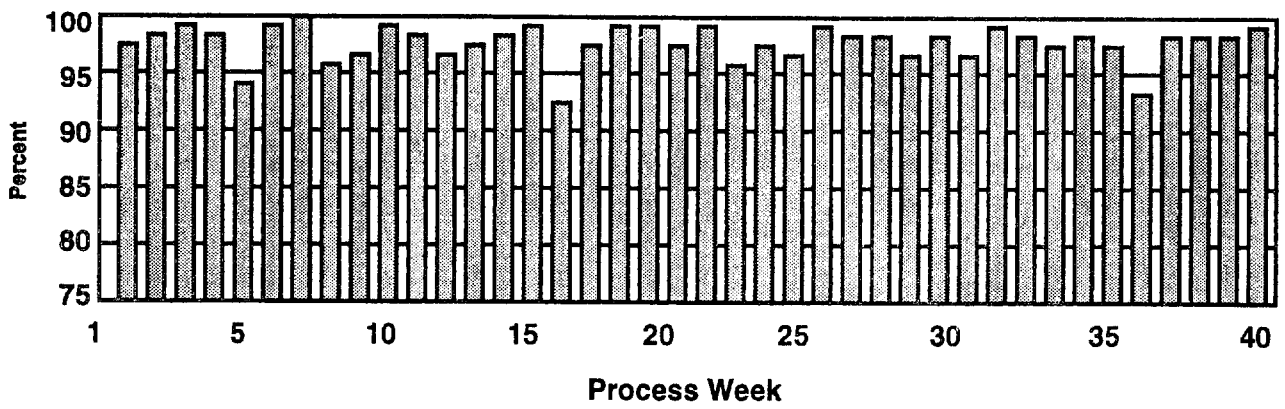

Figure 6-4. Percent of feed soil recovered as clean soil.

The computer monitoring data can be used not only to determine the actual contaminant levels achieved by the plant but also to monitor the performance of the plant in terms of startup time, down time, productivity, and estimated date of cleanup completion. Extrapolating from current productivity rates, the Johnston Atoll project should be finished in a total of 140 weeks.

6.2.4 Advantages and Limitations

Soil that emerges from the cleanup plant could be a valuable commodity for construction purposes, because it has been processed to a uniform size. Over 98 percent of the soils excavated from radioactive waste sites at Johnston Atoll can be recovered as clean soils to avoid importing soil at much greater expense than the cleanup process.

This technology eliminates the cost of conducting a detailed site characterization. Once the general boundaries of the contamination have been established, the soil can be excavated and processed in the cleanup plant. Similarly, the technology eliminates the need to conduct additional assays after the cleanup is completed, because the detectors on the conveyors continuously monitor contaminant levels of the waste stream. The 500 Bq/kg guideline allows sites to average radioactivity over 1 acre, but the cleanup plant actually accounts for every kilogram of excavated soil.

Compared to stabilizing large volumes of radioactive soils, the volume reduction process used at Johnston Atoll is very inexpensive. The cost for the entire volume reduction project is estimated at $15 million, with a plant cost of $2.4 million.

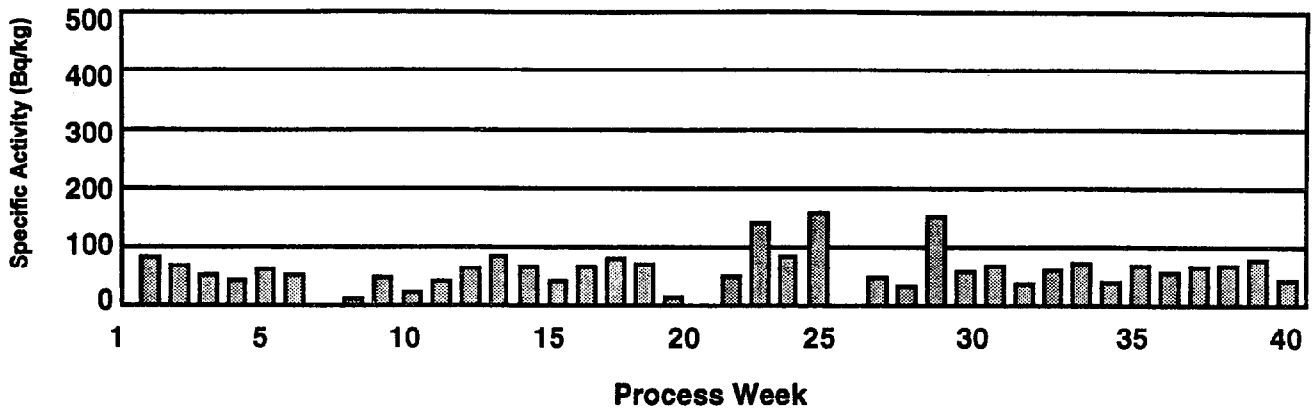

Figure 6-5. Specific activity of clean soil recovered on a weekly basis.

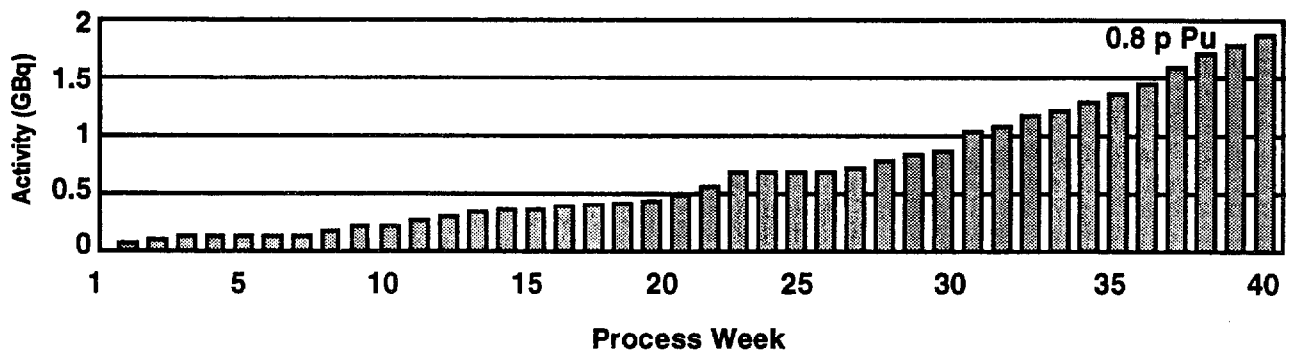

Figure 6-6. Cumulative radioactivity recovered over first 40 weeks of operation.

Many of the potential limitations of the technology can be eliminated through careful planning. Site managers must keep track of in-line performance data to verify that contractors are living up to their claims. This is especially important since the process combines technologies from several fields, including computer programming, mining, and waste disposal. Plant performance should be evaluated in terms of soil mass, rather than volume, because density can be highly variable at various stages of the process. Extensive computer records should be generated as evidence to regulators that the process is effective.

6.3 Treatment of Radioactive Compounds in Water

6.3.1 Background

Radioactive compounds, such as radium, uranium, and radon, occur naturally in drinking water sources, particularly in ground water. On July 18, 1991, EPA proposed final regulations (56 FR 33050) specifying the limits on radioactive compounds in drinking water. This section discusses the final regulations; the treatment of radium, uranium, and radon; the available treatment methods; and the factors that influence the selection of particular treatments.

Drinking water treatments fall roughly into five groups:

- Precipitation, which includes both coagulation/ filtration and lime softening.
- Ion exchange, which includes both anion and cation exchange processes.
- Membrane treatment, which includes reverse osmosis (RO) and electrodialysis (ED).
- Adsorption by various media, such as GAC, which is a common medium for drinking water treatment; activated alumina (AA), which can be used for the treatment of some radioactive compounds; and selective complexers, which essentially complex the contaminant and are not regenerable.
- Aeration, which is used to remove volatile compounds, including radon.

6.3.2 Treatment Selection

The factors that influence treatment selection include removal requirements, best available technologies

(BATs), water quality, water source, cost of treatment, and the type and quantity of residual wastes.

6.3.2.1 Removal Requirements

The Safe Drinking Water Act (SDWA) requires that EPA establish primary and secondary drinking water standards. Primary standards consist of two parts: (1) a non-enforceable maximum contaminant level goal (MCLG), and (2) an enforceable maximum contaminant level (MCL). The MCLG, which is based on health criteria alone, is zero for all radioactive contaminants regulated. Because this goal cannot always be achieved, the SDWA also specifies a companion enforceable MCL, which is based on health criteria, available technology, and treatment cost. Secondary standards (SMCLs) are similar to primary MCLs except that these regulations set limits for contaminants that affect aesthetic qualities of drinking water, such as taste, odor, color, and appearance. These secondary levels represent reasonable goals for drinking water quality and are not federally enforceable.

Currently, the MCL for radium-226 and -228 is 5 pCi/L. Under the proposed regulation, radium-226 and -228 have separate limits, each equal to 20 pCi/L. The proposed limit for uranium is 20 µg/L, which corresponds roughly to 30 pCi/L, and the proposed limit for radon is 300 pCi/L. Table 6-5 presents these current and proposed limits.

The proposed regulation also has two general restrictions, which establish MCLs for compounds that emit alpha particles, beta particles, and photons. These restrictions are summarized in Table 6-6. The proposed MCL for alpha emitters (excluding radon, uranium, and radium) is 15 pCi/L. The proposed MCL for emitters of beta particles and photons is based on specific radiation doses. These contaminants cannot exceed levels that result in a 4 millirem per year dose to an individual who drinks 2 liters of water per day. The proposed regulation lists two pages of specific radionuclides with the drinking water concentrations that yield 4 millirem annual doses. These vary considerably for different contaminants; for example, the limit for tritium is 20,000 pCi/L, while the limit for barium-140 is only 90 pCi/L.

6.3.2.2 Best Available Technologies

Under the SDWA, whenever EPA sets an MCL, it also must identify one or more BATs for achieving that level. Utilities are free to select any technology that can meet the MCL. If a non-BAT treatment fails to achieve the MCL, however, the utility is required to use the BAT. The proposed regulation (56 FR 33050) identifies the following BATs for radioactive contaminants:

- Radium-226 and -228—cation exchange, lime softening, and reverse osmosis.

Table 6-5. Current and Proposed MCLs for Radium, Uranium, and Radon

Radionuclide	Current Limit	Proposed limit (July 1991)
Combined Ra-226 and Ra-228	5 pCi/L	
Ra-226		20 pCi/L
Ra-228		20 pCi/L
Rn-222		300 pCi/L
U (total)		20 µg/L (30 pCi/L)

Table 6-6. Current and Proposed MCLs for Emitters of Alpha Particles, Beta Particles, and Photons

Radionuclide	Current Limit	Proposed Limit (July 1991)
Gross Alpha	15 pCi/L (including Ra-226, but not U, nor Rn-222)	15 pCi/L (excluding Ra-226, U, and Rn-222)
Beta particle and photon emitters (manmade radionuclides)	4 mrem/year (dose to body or any internal organ)	4 mrem/year (dose to body or any internal organ)

- Uranium—coagulation/filtration, ion exchange, lime softening, and reverse osmosis.
- Radon—aeration.
- Alpha emitters—reverse osmosis.
- Beta particle and photon emitters—ion exchange and reverse osmosis.

GAC also is used to treat radon in drinking water, and EPA evaluated it as a potential BAT. It is not listed as a BAT, however, because it requires a long empty bed contact time, which renders it economically infeasible for large systems. Similarly, adsorption by selected complexers and activated alumina have proven successful for treating radium and uranium, but adsorption is not a BAT because these media are not regenerable—once they become saturated with contaminant, they must be disposed of. In addition, although certain beta emitters, such as cesium-137, strontium-89, and iodine-131, are not specifically regulated, the regulation identifies reverse osmosis and ion exchange as effective treatments for these contaminants (see Table 6-7).

EPA's proposed regulation (56 FR 33050) lists a range of expected removal rates for each BAT-contaminant combination (see Table 6-8). For example, coagulation/filtration typically removes 85 to 95 percent of uranium from drinking water. The range of removal rates listed for each BAT depends on the chemistry, concentration,

and solubility of particular contaminants, and on variation in the quality of the water being treated.

6.3.2.3 Water Quality

Important aspects of water quality include pH and the presence of anions, cations, and other radioactive contaminants.

Uranium can be a cation, neutral, or an anion depending on the pH of the water. In water with a pH less than 5, uranium is a cation; in water with a pH between 5 and 7, uranium is neutral; in water with a pH greater than 7, uranium is an anion. As a result, ion exchange for uranium may involve either cation exchange or anion exchange. The pH of the water also affects the uranium removal efficiency of iron coagulation. Iron coagulation is very efficient at pHs near 6 and near 9; the treatment is not efficient, however, at pHs between 7 and 8 or below 5 (see Figure 6-7). When alum is used as a coagulant, the removal pattern is similar to that of iron coagulation. The uranium removal efficiency of lime softening and anion exchange depends on the presence of naturally occurring elements in the water. Table 6-9 illustrates the impact of magnesium levels on the effectiveness of lime softening for uranium removal. Table 6-10 shows the effect of sulfate levels on uranium removal by ion exchange.

As with uranium, the effectiveness of ion exchange for radium removal depends on the presence of other elements, such as barium, calcium, and magnesium, in the water being treated. These elements may be preferred to radium in the resin's selectivity sequence, shown below:

$$Ra^{+2} > Ba^{+2} > Ca^{+2} > Mg^{+2} > Na^{+} > H^{+}$$

Even if radium is highly preferred by a particular cation resin, the final percentage of radium removed will depend on the selectivity sequence of the resin and other elements present in the water.

Water with more than one radioactive contaminant may require more than one treatment process. For example, radium usually is treated by cation exchange with sodium, and uranium usually is treated by anion exchange with chloride. Water contaminated with radium *and* uranium can be treated by a mixture of cation resin and anion resin.

6.3.2.4 Water Source

Treatment efficacy can depend on the source of the water being treated. A treatment appropriate for contaminated ground water often will not be appropriate for contaminated surface water. Surface waters that are high in turbidity will foul ion exchange media, reverse osmosis membranes, or GAC. These methods can be used only if surface water is pretreated to achieve ground water turbidity levels. Lime softening can be used for both ground and surface waters without pretreatment, though it might be more costly for surface water. Coagulation/filtration treatment is designed to remove turbidity and therefore is used only on surface waters.

6.3.2.5 Cost of Treatment

Cost often is a determining factor at large water utilities that treat enormous quantities of water over extended periods of time. Cost might not be as important at cleanup sites, however, where the total volume of water

Table 6-7. Range of Removal of Cesium-137, Iodine-131, and Strontium-89 by Reverse Osmosis and Ion Exchange

	Beta Emitters—% Removal		
Treatment Method	**Cesium 137**	**Iodine 131**	**Strontium 89**
Reverse osmosis	90-99	90-99	90-99
Ion exchange	95-99		95-99

Table 6-8. Range of Removal Rates for Each BAT-Contaminant Combination

	Contaminant—% Removal		
Treatment Method	**Radium**	**Uranium**	**Radon**
Coagulation/Filtration		85-95	
Lime softening	75-97	85-99	
Ion exchange	65-97	65-99	
Reverse osmosis	87-98	98-99	
Aeration			Up to 99

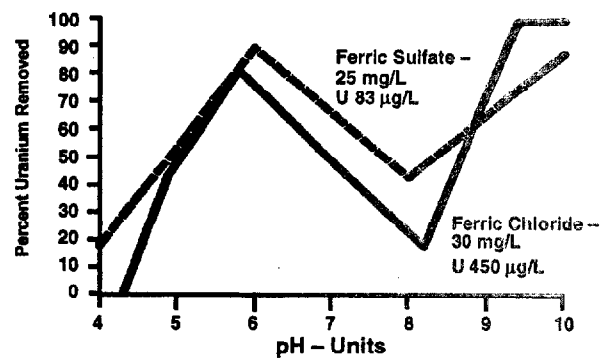

Figure 6-7. Effect of pH on removal of uranium by iron coagulation.

Table 6-9. Effect of Magnesium and Lime Dose on Uranium Removal by Lime Softening (Percent Removal)

	Lime Dose -$Ca(OH)_2$ - mg/L		
$MgCO_3$ mg/L	50	150	250
10	32	90	89
40	9	95	94
80	24	93	98
120	15	99	99

Table 6-10. Effect of Sulfate on Uranium Removal by Anion Exchange

	Influent			
Field Site[a]	U - µg/L	SO_4 - mg/L	Bed Volume Treated at Termination (x 1,000)	Percent Uranium Removal (total)
1(I)	22		9.4	99.8
2(I)	30	320	25	99.8
3(I)	104	9	7.9	99.8
4(C)	52	390	34.5	73.1
5(C)	35	400	11.9	29.8
6(C)	28	3	62.9	99.6

[a] (I) Intermittent flow; (C) continuous flow.

to be treated is limited. Adsorption by GAC, for example, is a relatively expensive technique. While GAC would be impractical for a large utility, it might be an appropriate option for a smaller scale cleanup.

6.3.2.6 Residual Wastes

Different treatments generate different quantities of residual waste. Uranium treatment by coagulation/filtration produces 2,100 gallons of waste per million gallons of treated water; lime softening produces 5,000 gallons; anion exchange produces 340 gallons; and reverse osmosis produces 333,000 gallons, assuming two-thirds treated water and one-third reject water.

Table 6-11 delineates the types of residuals produced by each drinking water treatment method. Coagulation/filtration produces a sludge from the settling basins and a filter backwash water that both contain the contaminant. Lime softening also produces a sludge from the settling basins and filter backwash water wastes. Ion exchange normally creates a brine waste, but, depending on the type of regeneration material used, it could produce a caustic or acid solution. In addition, ion exchange resins themselves contain residual radionuclides. Adsorption media, such as GAC, activated alumina, and specific complexers,

Table 6-11. Types of Residual Waste Produced by Drinking Water Treatments

Treatment Method	Residual (Waste)
Coagulation/Filtration	Backwash water Sludge (alum or iron)
Lime softening	Backwash water Sludge (lime)
Ion exchange	Brine Caustic solution Acid solution Resin
Adsorption (GAC/AA)	GAC Activated alumina
Membrane processes (RO/ED)	Reject water
Aeration	Air Adsorption media

accumulate contaminants that must be safely disposed of. If aeration is used to strip radon, the resulting gas must be passed through an adsorption system, such as GAC, from which the adsorption medium will become contaminated. The type and quantity of waste generated ultimately may drive the selection of treatments at cleanup sites.

6.4 Incineration of Radioactive and Mixed Waste

6.4.1 Background

Incineration serves several purposes as a management strategy for mixed waste: (1) it destroys some hazardous materials by breaking them down into simpler chemical forms, (2) it eliminates liquids in waste that otherwise complicate waste management, (3) it decreases the volume of waste, and (4) it may generate usable energy. Incineration currently is a critical component in DOE's strategy for managing low level radioactive and mixed wastes.

Table 6-12 lists all of the DOE and commercial incinerators that handle radioactive and mixed wastes in the United States. This section focuses on two of these incinerators: (1) the incinerator operated by Scientific Ecology Group, Inc. (SEG), in Oak Ridge, Tennessee; and (2) the incinerator operated at the Oak Ridge Gaseous Diffusion Plant. This section also discusses advantages and limitations of incinerating radioactive and mixed wastes.

6.4.2 SEG's Incinerator, Oak Ridge, Tennessee

6.4.2.1 Background

SEG operates the world's largest radioactive waste incinerator and the only incinerator licensed to burn

Table 6-12. Radioactive and Mixed Waste Incinerators in the United States

	Unit	Location	Current Status	Comments
DOE Incinerators	Toxic Substances Control Act (TSCA) Incinerator	Oak Ridge Gaseous Diffusion Plant	In full-scale operation since 1991.	EPA Region 4 responsible for compliance and enforcement.
	Waste Experiment Reduction Facility (WERF)	Idaho National Engineering Laboratory	Facility closed since Feb. 1991. Planned restart in 1993.	Facility closed to update Operational Safety Requirements.
	Controlled Air Incinerator (CAI)	Los Alamos National Laboratory	On stand-by since 1987.	Facility closed to upgrade. Announced restart in 1993, likely restart in 1995.
	Glass Melter	Mound Laboratory	On stand-by. Planned restart in 1993.	Awaiting RCRA part B permit from Ohio EPA.
	CIF	Savannah River Site	Under construction. Planned operation in Jan. 1996.	Startup deferred 2 to 3 years while RCRA part B permit is negotiated.
Commercial Incinerators	Scientific Ecology Group (SEG)	Oak Ridge, TN	Full-scale operation began in fourth quarter of 1989.	RCRA part B permit pending.
	DSSI	Kingston, TN	In full-scale operation.	System modified to meet new BIF regulations.

Source: U.S. EPA, 1993.

commercial radioactive waste in the United States. SEG's incinerator is an automated, controlled-air incinerator capable of burning 1,000 lb of waste per hour.

6.4.2.2 Treatable Wastes

The following radioactive materials are incinerated at the SEG operation:

- Dry active wastes, such as paper, plastic, wood, cloth, rubber, canvas, fiberglass, and charcoal.
- Ion exchange resins used to polish condensate from nuclear power plants.
- Animal carcasses from scientific—but not medical—research.
- Sewer sludges and lubricating oils that have become contaminated with radioactive materials.
- High efficiency particulate air (HEPA) filters

Other materials, including metals, explosives, flammable liquids, shock-sensitive materials, or polyvinyl chloride (PVC), might not be suitable for incineration at SEG. In addition, large pieces of metal, such as sections of pipe, cannot be incinerated, because they can jam the augers that slowly propel ashes from the charging area to the discharge area of the incinerator. Items smaller than a 10-in. crescent wrench do not interfere with the action of the augers.

6.4.2.3 Operation and Maintenance

In addition to the actual burning of waste, the incineration process involves sorting of waste, packaging of waste, and treatment of incinerator flue gas emissions to control air pollution. The incinerator also has several redundant features to ensure safe operation.

Sorting Waste

Since many materials cannot be incinerated, materials must be sorted before being fed to the incinerator. Waste arrives at SEG in sealand containers loaded atop flatbed trailers. The containers house large plastic bags of low level dry active waste materials. The bags are removed from the sealand containers and placed on a revolving carousel, from which SEG operators manually sort waste materials. Metals are sent to a metal melt facility, unidentifiable liquids are sent to be analyzed, and PVC-bearing materials are shredded and compacted.

Waste Packaging

Before any waste is burned, it must be packaged properly. Typically, waste is packaged in plastic bags that line large feed boxes. The feed boxes, which can hold up to 300 lb of waste, have bar codes and tracking sheets that identify the type of waste they contain, the customer, the date, and the manifest number. The bar codes allow waste to be monitored at every stage of the incineration process. Feed boxes are placed on a

conveyor, which carries them to the incinerator. Each box has anchors on the bottom so that the contents of the box can be dumped mechanically through a feeding sluice and into the primary chamber of the incinerator.

Burning Waste

The incinerator has three chambers—the primary combustion chamber, secondary combustion chamber, and retention chamber—each with its own burner and thermostat. The total residence time for gases, from the dumping of waste materials into the primary combustion chamber to the emission of flue gases from the retention chamber, is about 3 seconds.

Primary Combustion Chamber. Waste feeds into the primary chamber in batches, usually 200 to 300 lb every 15 minutes. The feed rate is limited by the Btu content of the waste, the resultant temperatures in the three chambers, and the quality of the flue gas leaving the incinerator. Flue gas quality factors include oxygen concentration, CO concentration, and opacity caused by particulates in the flue gas line. No waste is fed to the incinerator while these quality factors exceed certain limits. Once the flue gas factors return to normal, waste can be charged again.

The primary combustion chamber operates at about 1,000°C. At this temperature, volatile and partially volatile metals are released as gases or aerosols. Operating the chamber at too low a temperature results in elevated concentrations of lead and cadmium in the hearth ash, requiring costly stabilization of the ash prior to disposal. Operating the chamber at a higher temperature ensures that these compounds are completely volatilized and thus removed from the hearth ash. Primary chamber temperature is maintained by a mechanism that sprays water into the chamber at a desired upper temperature limit. This mechanism not only cools the chamber, but also can provide an inexpensive way to dispose of contaminated water. Contaminated water otherwise would require costly solidification processes, which would result in increased burial volumes.

Hearth ash from the primary chamber drops onto two rotary screw augers located in the bottom of the chamber. These augers rotate forward for 10 seconds, pause, then rotate backward for 8 seconds. The net effect is a slow forward motion. Over a period of 14 hours, the augers turn over the burning waste to promote even and complete combustion, then grind the ash into a fine powder and convey it to the end of the chamber, where it is cooled and dropped into the hearth ash collection boxes. A typical ash box weighs approximately 1,200 lb when full.

Secondary Combustion Chamber. Flue gases and particulate matter from the primary chamber pass into a secondary combustion chamber. The temperature in this chamber ranges from 1,000 to 1,200°C, depending on the amount of CO gas and aerosols emitted from the primary combustion chamber. There is not enough oxygen in the primary chamber to allow these gases and aerosols to burn. As the gases pass from the primary chamber into the secondary chamber, however, they are mixed with fresh air and they combust quickly, heating the secondary chamber. Secondary chamber temperature usually peaks shortly after each waste charge and then gradually declines until waste is charged again.

Retention Chamber. Flue gases from the secondary chamber pass into a retention chamber, which is a large thermal fly wheel that provides time for any remaining hazardous materials to be destroyed. The chamber is sized to provide an adequate delay or retention time for the gases. The temperature in this chamber tends to be very stable due to the volume and mass of refractory in the chamber. A propane burner in this chamber maintains a temperature range from 1,000 to 1,300°C to ensure complete combustion of flue gas components.

Treatment of Incinerator Flue Gas Emissions

From the retention chamber, flue gases pass into a steam boiler, where they are cooled to about 200°C. The boiler generates 70 lb of saturated steam pressure, which can be used to dry contaminated resin, evaporate wastewater from sludge, heat stack gases for plume suppression, or heat the facility. Flue gases then pass through a baghouse filter, which removes the particulate entrained in the gas stream; a HEPA filter and wet scrubber, which remove nonvolatile radionuclides and acid gas; and an ID fan, which maintains the entire system under a negative pressure for contamination control. Emission gases are monitored at the stack for radioactive materials. Should such materials be detected, various notification alarms sound.

Safety Features

Draft fans, air supply fans, gas monitors, opacity detectors, HEPA filters, negative air-pressure controllers, and an emergency power source are among the redundant features that can improve the safety of an incinerator. The most important feature is an emergency power source. SEG has a 300-kilowatt diesel backup generator, capable of carrying the entire incinerator load when outside power is lost.

Since SEG's incinerator is used to process radioactive wastes, it must be operated under a vacuum. SEG's primary combustion chamber is operated at –0.5 in. H_2O, while the vacuum at the suction of the ID fan is –30.0 in. H_2O. The difference between these is the differential pressure that occurs across the scrubber, baghouse, boiler, and HEPA systems.

6.4.3 *Incinerator at the Oak Ridge Gaseous Diffusion Plant*

6.4.3.1 Background

The incinerator located at the Oak Ridge Gaseous Diffusion Plant is a 6-ft diameter by 25-ft long rotary kiln unit rated at 10 million Btu per hour with a secondary combustion chamber rated at about 22 million Btu per hour and a total system maximum heat release of 28 million Btu per hour. The unit, which currently processes primarily liquid wastes, processed 2.2 million lb of waste in fiscal year (FY) 1991 and 2.8 million lb in FY 1992. The system is permitted to handle both Toxic Substances Control Act (TSCA) and RCRA wastes.

6.4.3.2 Treatable Wastes and Media

Although the incinerator is capable of handling a variety of waste types and forms, the near-term processing plan is to burn primarily liquid low-level mixed wastes, because of the concern about the handling and ultimate disposition of incinerator residuals derived from offsite wastes. The following restrictions limit the types of wastes that can be fed to the incinerator:

- Waste must be free of dioxin wastes as defined in 40 CFR 268.31 and listed as waste codes F020 through F023 and F026 through F028 in 40 CFR 261.
- Waste must be free of cyanide wastes as defined in waste codes F007 through F011 listed in 40 CFR 261.
- Waste must be free of explosive material that detonates on heating or percussion, ignites spontaneously in dry or moist air, or meets the definition of reactive waste as defined in 40 CFR 261 or as designated by EPA hazardous waste code D003.
- Waste containing uranium with U-235 enrichment of less than 1 percent must not exceed 0.08 Ci per shipment (i.e., per truckload).
- Waste containing uranium with U-235 enrichment of more than 1 percent must have a total uranium content of less than or equal to 5 ppm.
- In general, the waste form must be nonvolatile, such that it does not rapidly evaporate when the waste container is opened.
- If the boiling point of the waste is less than 100°F, acceptance will be on a case-by-case evaluation.
- For liquid organic wastes, the corrosivity must be limited to less than 6.35 mm/yr.
- For aqueous wastes, the pH must be greater than 6 for drummed liquids or between 8 and 10 for bulk liquids.

The incinerator has metals contamination limits in the feed waste (see Table 6-13). In addition, the incinerator has the following restrictions on specific elements:

- Total chloride: <89 percent by weight.
- Total sulfur: <6 percent by weight (drums); <3 percent by weight (bulk).
- Total fluoride: <85 percent by weight (drums); <25 percent by weight (bulk).

To be fed to the incinerator, solid materials in drums must be shreddable, which limits rebar, pipe, and concrete pieces larger than 2 in. in diameter. Wastes received for processing must be identified by radionuclide content. Prior to processing, the incinerator staff analyzes the waste to determine whether incineration of the waste, along with other wastes, will exceed the annual committed effective dose equivalent limits. Required lower limits of detection for specific radionuclides are listed in Table 6-14. Waste shipping containers must meet the following requirements:

- Maximum dose equivalent rate at contact: 50 mrem/hr.
- Maximum dose equivalent rate at 2 ft: 5 mrem/hr.
- Transferrable beta/gamma surface contamination: 1,000 disintegrations per minute (dpm)/100 cm^2.
- Transferrable alpha surface contamination: 200 dpm/100 cm^2.

6.4.3.3 Operation and Maintenance

The incinerator uses a wet off-gas treatment system composed of a quench tower, venturi scrubber, demister, packed-bed scrubber, two-stage ionizing wet scrubber, ID fan, and a 100-ft stack. The facility's maintenance procedures typically include two planned outages every year—one in the spring for a few weeks

Table 6-13. Metals Contamination Limits for Oak Ridge Gaseous Diffusion Plant Incinerator

Metal	Liquid (Drums)	Liquid (Bulk)	Solids	Sludge
Aluminum	20,000	11,000	80,000	80,000
Beryllium	10	5	5	5
Cadmium	1,500	500	800	800
Chromium	6,000	3,300	6,000	6,000
Lead	2,500	2,000	1,000	1,000
Mercury	200	60	120	120
Zinc	65,000	65,000	65,000	65,000
Plutonium	0.004[a]	0.004[a]	0.004[a]	0.004[a]

[a] Or 246 pCi/g.
Source: U.S. EPA, 1993.

Table 6-14. Required Lower Limits of Detection (LLD) for Radionuclides in the Oak Ridge Gaseous Diffusion Plant Incinerator

Radionuclide	Required LLD (pCi/g)	Radionuclide	Required LLD (pCi/g)
H-3	60	Pb-210	1
C-14	60	Th-228	1
P-32	5	Th-230	1
Co-57	0.1	Th-232	1
Co-60	0.5	Th-234	1
Kr-85	5	Pa-234	1
Sr-90	5	U-alpha	1
Tc-99	20	Np-237	1
I-131[a]	0.7	Pu-238	1
Cs-137	1	Pu-239	1

[a] Analysis for I-131 is not required if waste has been stored more than 6 months.
Source: U.S. EPA, 1993.

and a major one in the fall for 1 to 2 months, depending on maintenance requirements. Maintenance activities during these outages include fiberglass repair and replacement of pumps and deteriorating equipment.

6.4.4 Advantages and Limitations

6.4.4.1 Advantages

Incineration produces a waste form that is dense and easy to transport, and takes up relatively little space when buried. Incineration has been shown to yield varying volume reduction factors (VRFs): commonly 4 to 40 for most types of compressible dry active wastes and combustible solids, and greater than 100 for liquids and most plastics. SEG also operates a supercompactor, which exerts up to 10 million lb of pressure on the filled ash box and can produce further VRFs of 2 to 5.

The annual permissible dose equivalent release limit from the SEG site is 10 mrem, but actual releases tend to be much lower. In 1991, the SEG incinerator processed 5.3 million lb of radioactive wastes, exposing the nearest resident to an estimated dose of 0.027 mrem for the year, compared to natural background levels of approximately 150 mrem/year.

6.4.4.2 Limitations

The primary disadvantage of incineration is that it can produce toxic ash that requires further processing prior to disposal. This is a particular concern for incineration of radioactive waste, which yields waste residues that have much higher radionuclide concentrations than does the original waste stream. As a result, containers or bins of ash from the incineration of radioactive waste may have high external radiation exposure rates. When radiation exposure levels are expected to be high, personnel interaction with equipment and ash bins should be minimized. Ash collection bins and other ash handling equipment also might need to be shielded.

Incineration produces three types of ash: hearth ash, which is discharged from the primary chamber during combustion; fly ash, which gets stripped from the flue gas in the baghouse; and boiler ash, which gets stripped from the flue gas in the boiler. Hearth ash from an incinerator operated at the proper temperature usually passes EPA's Toxicity Characteristic Leaching Procedure (TCLP). Fly and boiler ash always are characteristic because of the presence of lead which emanates from the primary chamber and passes from the incinerator in fine aerosol form.

Ash that passes TCLP testing can be compacted immediately and shipped for burial, while ash that fails TCLP testing must be solidified by concrete or epoxy into a monolithic waste form by mixing it with a hardener and fixer base material and allowing it to harden. Once hardened, the waste form is sampled and retested. If the sample passes, the waste form may be buried; if it fails, the waste must be reprocessed. To date, SEG has not experienced a TCLP failure of its stabilized fly ash waste form.

Another disadvantage to incineration is that the operation of wet scrubbers generates salt that must be removed. SEG uses a quick dry dewatering system in which salt drums are decanted into larger drums that contain filtering systems. A vacuum then is applied to draw the water out of the salt mixture. The remaining salt is not hazardous and can be disposed of accordingly. SEG currently is developing a spray dryer to provide a one-step drying process for the salt slurry.

6.5 In Situ Vitrification

6.5.1 Background

Vitrification is the process of converting materials into glass or glass-like substances at high temperatures. Vitrification is an attractive option for stabilizing high-level radioactive contaminants, because vitrified materials are very durable and exhibit low radionuclide leachability. In addition, vitrification is applicable to mixtures of organic and inorganic wastes, because the technology pyrolyzes organics and immobilizes inorganics.

Thermally formed glasses are produced by fusing or melting crystalline materials or previously formed glasses, which form a network of interlocking silicate tetrahedra upon cooling. During vitrification, inorganic contaminants become immobilized in the glass matrix

in three ways: (1) as network formers, by replacing silicon and forming covalent bonds with oxygen atoms in the network; (2) as network modifiers, by forming ionic bonds with oxygen atoms that do not bridge between tetrahedra; or (3) by becoming encapsulated in vitrified material.

The ability of a vitrification process to immobilize a particular contaminant is known as the retention efficiency for that contaminant. Retention efficiencies vary from metal to metal, because different metal oxides have different solubility limits in glass. Table 6-15 shows the retention efficiencies for a number of semivolatile and nonvolatile metals. The retention efficiency for any metal also depends on the operating parameters of the vitrification process. Retention efficiencies can be increased by reducing the gases generated during vitrification, allowing a cold cap to increase contact time between metals and the melt, recycling volatilized metals, decreasing the melt temperature, or modifying the melt composition with additives.

Contaminants that are not immobilized in the vitrified waste form either are destroyed through pyrolysis or combustion or removed during off-gas treatment. In general, only organics and asbestos are destroyed during vitrification. The ability of a vitrification process to destroy an organic contaminant is known as the destruction efficiency for that contaminant. Tables 6-16 and 6-17 list the destruction efficiencies of in situ vitrification (ISV) for common organic contaminants. Destruction efficiencies can be increased by allowing a cold cap to increase contact time with the melt, adding oxygen to enhance secondary combustion of organics in the area above the melt, or recycling organics back to the melt.

There are two types of vitrification technologies: electric process heating and thermal process heating. Electric process heating includes joule heating, plasma heating, and microwave heating. Of these processes, only joule heating, in which a high-voltage electric current is used to heat soils, can be operated in situ. ISV eliminates the risk of exposing site workers to excavated contaminants and thus is potentially the most useful technique for treating radioactive contaminants. This section focuses on ISV, examining treatable wastes and media, the operation of ISV by joule heating, treatment of off-gases, and advantages and limitations of the technology.

6.5.2 Treatable Wastes and Media

ISV can be applied to a wide variety of wastes, including radioactive wastes and sludges, contaminated soils, contaminated sediments, industrial wastes and sludges, underground storage tanks, drummed wastes, and asbestos wastes. Organic contaminants, which are destroyed during the heating process, and inorganic contaminants, which are immobilized in the vitrified waste form, both can be treated by ISV. ISV is relatively expensive to operate, however, so it should be used primarily to treat highly concentrated hazardous wastes, wastes with complex mixtures of contaminants, and wastes that require a high-quality product.

Table 6-15 Metals Retention Efficiencies for ISV

Class	Metal	Retention Efficiency, %[a]	Scale[b]
Volatile	Mercury(Hg)	0	Engineering
Semivolatile	Arsenic(As)	70-85	Engineering
	Cadmium(Cd)	67-75	Pilot
	Cesium(Cs)	99-99.9	Pilot
	Lead(Pb)	90-99	Pilot
	Ruthenium(Ru)	99.8	Pilot
	Antimony(Sb)	96.7-99.9	Pilot
	Tellerium(Te)	50-99	Pilot
Nonvolatile	Americium(Am)	99.99	Pilot
	Barium(Ba)	99.9	Engineering
	Cerium(Ce)	98.9-99.9	Pilot
	Cobalt(Co)	98.7-99.8	Pilot
	Copper(Cu)	90-99	Engineering
	Chromium(Cr)	99.9	Engineering
	Lanthanum(La)	98.9-99.98	Pilot
	Molybdenum(Mo)	99.9-99.999	Pilot
	Neodymium(Nd)	99-99.98	Pilot
	Nickel(Ni)	99.9	Engineering
	Plutonium(Pu)	99.99	Pilot
	Radium(Ra)	99.9	Engineering
	Strontium(Sr)	99.9-99.998	Pilot
	Thorium(Th)	99.99	Engineering
	Uranium(Th)	99.99	Engineering
	Zinc(Zn)	90-99	Engineering

[a] Percentage of original amount remaining in the melt.
[b] Engineering-scale tests involve a melt depth of 1 to 2 ft. Pilot-scale tests involve a melt depth of 3 to 7 ft.
Source: Hansen, 1991.

Characteristics of the soil and waste that can affect the ISV process include:

- *Moisture content.* Moisture content does not necessarily limit the technical applicability of ISV, but it does affect the technology's economic feasibility, because soils with high moisture content require more energy to drive off excess water. Limits of 20 to 25 percent moisture content by weight have been identified for some ISV processes (U.S. EPA, 1987; U.S. EPA, 1988).

Table 6-16. ISV Organic Destruction and Removal Efficiencies

Contaminant	Initial Concentration (ppb)	Percent Destruction	Total DRE (including off-gas removal)
Aldrin	113	>97	>99.99
Chlordane	535,000	99.95	>99.999
Dichlorodiphenyl dichloroethane (DDD), Dichlorodiphenyl dichloroethylene (DDE), Dichlorodiphenyl trichloroethylene (DDT)	21-240,000	99.9-99.99	>99.999
Dieldrin	24,000	98.0-99.9	>99.99
Dioxins	>47,000	99.9-99.99	>99.9999
Fuel oils	230-11,000	>99	>99.999
Furans	>9,400	99.9-99.99	>99.9999
Glycol	NA	>90	>99.99
Heptachlor	61	98.7	>99.99
Methylethyl ketone (MEK)	NA	>99	>99.999
Polychlorinated biphenyls (PCBs)	19,4000,000	99.9-99.99	>99.9999
Pentachlorophenol	>4,000,000	99.995	>99.99999
Toluene	203,000	99.996	>99.99999
Trichloroethane	106,000	99.995	>99.99999
Xylenes	3,533,000	99.998	>99.99999

Source: In Situ Vitrification Update, 1990.

- *Soil composition.* In order for ISV to be effective, the soil must contain adequate quantities of glass-forming materials, such as SiO_2 and Al_2O_3; and current-carrying alkaline flux agents, such as Na_2O, K_2O, and CaO. These materials can be added to soils to improve the effectiveness of ISV.
- *Buried debris.* ISV might not be appropriate for soils with substantial buried debris, which can interfere with current between the electrodes.
- *Combustible materials.* Combustible materials produce large volumes of off-gas, which must be treated and can provide a pathway for inorganics to escape the melt.
- *Volatile contaminants.* ISV of soils with high levels of volatile contaminants, such as mercury, lead, and cadmium, can produce secondary contamination.
- *Metals.* High concentrations of metals can short the electrodes. The effects of shorts can be minimized by employing an electrode feed system, which temporarily raises electrodes when a short begins to occur.

6.5.3 Operation and Maintenance

6.5.3.1 Heating

A schematic of ISV is shown in Figure 6-8. Four electrodes are inserted into the contaminated soil by an electrode feed system, which automatically controls the height of the electrodes. Because unsaturated soil is not electrically conductive, a conductive mixture of flaked graphite and glass frit is placed between the electrodes as a starter path. A current is established between the electrodes to heat the starter path and surrounding soil to 2,000°C—well above the 1,100 to 1,400°C required to melt the soil. Gradually, the starter path is oxidized, and the molten soil, which is electrically conductive, begins to carry the current. As the molten vitrified mass grows, it incorporates radionuclides and nonvolatile metals and pyrolyzes organic components. Byproducts of pyrolysis migrate to the surface where they combust in the presence of oxygen. A hood placed over the vitrified area directs the gaseous effluent to an off-gas treatment system. A full-scale system typically processes waste at the rate of 3 to 5 tons per hour. The average processing time required for one setting of the electrodes is 150 to 200 hours, depending on soil depth and electrode spacing (Buelt et al., 1989).

6.5.3.2 Off-Gas Control

Off-gas constituents of particular concern include:

- Volatile and semivolatile metals and organics, which are the very contaminants vitrification is designed to immobilize and destroy.
- Inleakage air, which creates convection currents in the area above the melt that can entrain particles and contaminants from the cold cap.

Table 6-17. Organic Destruction Efficiencies for Vitrification Systems

Compound	°C for 99% Destruction in 2 Seconds	Measured DE (%)
Hydrocyanic acid	482-866	NA
Chlorobenzene	482-866	99.99986
Formic acid	318-368	NA
Phosgene	427-479	NA
Methylene chloride	427-479	>99.9995
Phenol	374-421	99.99992
Acetone	374-421	>99.9995
Isodrin	374-421	>99.9998
Ethanol	374-421	>99.9995
Mustard gas	318-368	NA
Nitrogen mustard	318-368	NA
Carbon tetrachloride	318-368	99.99988
Aldrin	318-368	99.99994
Dieldrin	318-368	>99.9995
Sulfoxide	218-316	>99.99
Endrin	38-160	>99.998
Dithiane	182-213	>99.96
Sulfone	NA	>99.995
Xylenes	NA	99.99817
DIMP	NA	>99.8
DMMP	NA	>99.8
ACN	NA	99.99996
AN	NA	99.9994

Sources: Armstrong and Klingler, 1985; U.S. ATHAMA, 1988; Klingler and Abellera, 1989.

- Byproducts of the combustion of organics, which provide a pathway for inorganics to escape the melt.
- Entrained particles produced by the feed dust or volatilization of glass components, which also can serve as carriers for inorganics.

Off-gases are controlled by two mechanisms: emission reduction and off-gas treatment. Many of the methods discussed in section 6.5.3.1 for increasing retention of waste constituents also apply to reducing emissions. These include allowing a cold cap to increase contact time between metals and the melt and recycling contaminants captured in the off-gas system. Other methods include modifying the soil with additives to reduce its level of volatile constituents and adding oxygen to enhance secondary combustion of organics and products of incomplete combustion. Emission reduction methods cannot completely eliminate evolved off-gases, however, and gases that escape the melt

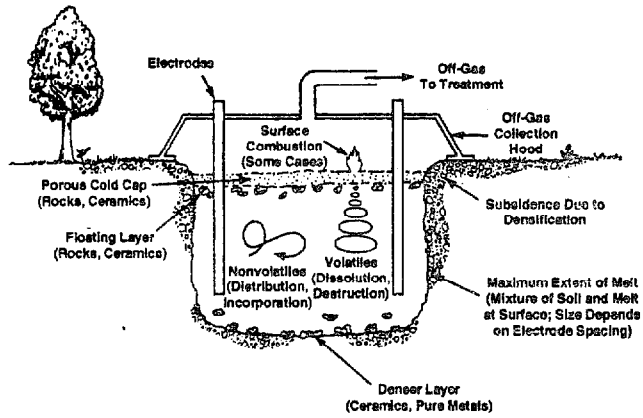

Figure 6-8. Schematic of ISV by joule heating (from U.S. EPA, 1989).

must be captured and treated. Components of the off-gas treatment system include HEPA filters, which perform the initial and final filtering to remove particulates; scrubbers, which cool gases and remove particulates; a condenser, which removes water vapor; and a heater, which reheats gases above dewpoint. To ensure containment of off-gases, the entire vitrification system is operated at a negative pressure. This precaution protects against the possibility of pressure surges caused by temperature fluctuations or the rapid release of large volumes of combustion gases.

6.5.4 Advantages and Limitations

6.5.4.1 Advantages

The advantages of ISV include the technology's ability to destroy organics, solidify a wide variety of waste streams, and avoid excavation and reburial of hazardous contaminants. In addition, the vitrified waste form resists leaching, has high strength and impact resistance, exhibits long-term durability, and reduces the volume and increases the density of solidified waste.

Chemical Immobilization

Chemical immobilization, or the resistance to leaching of hazardous constituents, is the most important feature of vitrified waste. Vitrified waste forms have undergone numerous tests for leaching of toxics and radionuclides. These tests generally indicate that vitrified wastes have leach rates below levels accepted by EPA. Table 6-18 shows the TCLP data for various in situ and ex situ vitrification processes. Results for partially vitrified or crystalline waste forms indicate only slightly higher leachability (Spalding and Jacobs, 1989).

Strength and Impact Resistance

Waste forms produced by ISV have high compressive and tensile strengths—up to 5 to 20 times those of

Table 6-18. TCLP Leach Data for Selected Processes and Selected Metals[a]

Metal	Glass Melter[b] (ppm)	Kiln/Vitrification Process[c] (mg/L)	ISV Glass[d] (mg/L)	ISV Metal3 (mg/L)	TCLP Limits (mg/L)
Arsenic	<0.02	<0.01	<5	<5	5.0
Barium	<0.05	0.175	0.05	<1	100.0
Cadmium	0.007	0.015	<1	<1	1.0
Chromium	0.03	0.825	<1	2.7	5.0
Lead	<0.05	0.15	<1	<1	5.0
Mercury	<0.0002	0.00035	<0.03	<0.03	0.2
Silver	<0.01	0.01	<0.1	<0.1	5.0

[a] As original contaminant concentrations and process DREs were not always supplied, these leach data are not directly comparable. The data are presented to show that, in general, vitrification products pass TCLP limits.
[b] Penberthy Electromelt International, Inc., vendor information.
[c] Harlow et al., 1989.
[d] Farnsworth, Oma, and Bigelow, 1990.

unreinforced concrete. Table 6-19 compares the compressive and tensile strengths of concrete to those of ISV and joule-heated ceramic melter (JHCM) products. The impact resistance of glassy and partially devitrified waste forms produced by ex situ processes also has been tested. In these tests, vitrified waste forms shattered only under extreme conditions, such as an impact of 80 mph. In addition, shattering increased the surface area of the waste forms by a factor of only about 40 and produced few particles smaller than 10 µm, which could potentially disperse in air currents (Wicks, 1985).

Table 6-19. Compressive and Tensile Strengths of Unreinforced Concrete and Glasses Produced by ISV

Source of Waste Glass	Compressive Strength (psi)	Tensile Strength (psi)
ISV (50% sludge/50% soil)	59,350	4,410
ISV (20% sludge/10% soil/70% liner)	43,210	4,309
JHCM	43,210	4,300
Unreinforced concrete	3,000 - 8,000	400 - 600

Source: Koegler et al., 1989.

Long-Term Durability

Natural glasses, such as obsidian and basalt, last millions of years. It is impossible to measure directly the long-term durability of a synthetic waste form, but kinetic and thermodynamic modeling can be used to estimate long-term durability. Kinetic models mathematically describe the processes, such as ion exchange, diffusion, and the formation of protective layers, that affect the leaching behavior of a glass. Kinetic models indicate that waste glasses should be very durable but cannot predict which types of glass will be most durable. The thermodynamic model estimates a glass's leachability and loss of thickness based on its free energy of hydration. This model predicts that the durability of glasses produced by ISV ranges from 1,000 to 1 million years (Jantzen, 1988).

Volume Reduction and Density Increase

During vitrification, void gases and water are evaporated, and organic materials are destroyed. These processes decrease the volume and increase the density of the vitrified waste. Volume reductions depend on the type of waste and the technology used. For example, ISV of soil produces a 25 to 45 percent volume reduction, while microwave melter vitrification of liquid and sludge wastes produces a 98 to 99.5 percent reduction. The density of vitrified products ranges from 2.3 to 2.65 g/cm^3 (Buelt et al., 1987), compared to 0.7 to 2.2 g/cm^3 for products of conventional stabilization technologies (Stegman et al., 1988).

6.5.4.2 Limitations

The effectiveness of ISV can be limited by characteristics of the soil, such as high moisture content and inadequate quantities of glass-forming constituents. In addition, ISV is limited by depth constraints, susceptibility to chemical attack, and relatively high cost.

Depth Constraints

ISV has not been demonstrated to be effective at depths of over 5 meters, and currently, 60 percent of all DOD sites extend deeper than 5 meters. If ISV capability could be extended to 9 meters, the technology could be applied at 90 percent of the existing DOD sites. Depth limitations result primarily from heterogeneous power distribution within the melt. During field applications of ISV, almost half of the power has been delivered to the upper third of the melt, and less power has been dissipated in the lower regions of the melt.

Several potential methods for increasing the depth of ISV have been identified, including using hot-tipped electrodes, passive electrodes, or thermal barriers, and starting the melt at the bottom of the contaminated area. Hot-tipped electrodes would have tips made from highly conductive material, such as molybdenum, or have insulation covering the upper portion of their shafts. Passive electrodes would be conductive iron-based materials placed in the startup layer. When these iron-based materials melted, they would settle to the bottom of the system, directing current downward. Thermal barriers placed next to the site would prevent lateral dissipation of power and reflect heat downward. The last option, starting the melt at the lower regions, might be possible with the use of the electrode feed system, which could mechanically raise and lower the electrodes as necessary. The drawback to this method would be that it could create a subsurface cavity that might collapse and splash molten glass on the off-gas treatment hood.

Potential for Devitrification

Devitrification, which is the formation of a nonglassy crystalline structure in the waste form, can increase the leachability of hazardous constituents from the waste form (Spalding and Jacobs, 1989). Devitrification usually occurs during cooling of the molten glass or after the glass has cooled if, for some reason, the amorphous glass structure crystallizes. If a waste form is reheated, devitrification can occur as the waste form cools for a second time. This is a concern because certain radionuclides produce heat as they decay.

Chemical Attack

Vitrified waste forms are highly resistant to chemical attack, but they can be broken down through matrix dissolution and interdiffusion. Matrix dissolution is a form of alkaline attack that begins with hydration of the silica network and can proceed to dissolution of the vitreous material. Interdiffusion, which is the primary mechanism by which contaminants leach from a waste form, is a form of acid attack. It is an ion exchange process that preferentially extracts elements present as network modifiers, leaving the silica structure almost intact.

A waste form's resistance to chemical attack is influenced by several factors:

- *Chemical composition.* Waste forms with lower ratios of oxygen to network formers have more bridging oxygens and are more durable.
- *Waste loading.* Higher waste loadings can increase the durability of waste forms, due to the formation of protective surface layers of waste constituents.
- *Time.* Leachability generally decreases with time.
- *Temperature.* Leachability is lower at lower temperatures. The mechanism of attack also varies with temperature: interdiffusion predominates at ambient temperatures, and matrix dissolution predominates at temperatures above 100°C.
- *pH.* Acid attack decreases at high pHs; alkaline attack decreases at low pHs.

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6.6 Polymer Solidification and Encapsulation

6.6.1 Background

Many radioactive, hazardous, and mixed wastes are considered to be "problem" wastes, because they are difficult to solidify and encapsulate with conventional technologies. This section describes two processes conducted at the Brookhaven National Laboratory (BNL) in Upton, New York, that encapsulate problem wastes in thermoplastic materials: polyethylene (PE) encapsulation and modified sulfur cement encapsulation. Both methods have advantages over conventional hydraulic cement solidification, which currently is used to solidify the majority of the problem wastes generated by DOE and the commercial sector. Waste solidification and encapsulation methods involving thermoplastic materials produce durable waste forms that minimize the release of toxic contaminants to the environment, comply with all applicable regulatory criteria, and maintain these characteristics under long-term storage or disposal conditions. These methods also are simple to operate, easy to maintain, and cost effective.

6.6.2 Treatable Wastes and Media

Because thermoplastic materials are inert, they do not react with waste constituents during the solidification process. As a result, solidification technologies involving thermoplastic materials can be applied to a wide range of waste types, including many radioactive wastes, such as sodium nitrate, sodium sulfate, boric acid, incinerator ash, and ion exchange resins.

Modified sulfur cement readily encapsulates certain wastes that are particularly problematic for hydraulic cement. Mixed waste incinerator fly ash, for example, typically has relatively high concentrations of metals, such as zinc and lead, in the chloride form. While the chemistry of hydraulic cement inhibits the encapsulation of large quantities of this type of waste, sulfur cement achieves relatively high waste loadings of these compounds. Figure 6-9 compares the waste loadings of several waste streams achieved by modified sulfur cement and Portland cement.

6.6.3 Operation and Maintenance

During PE encapsulation, PE is mixed with waste material, heated, and extruded into a waste drum by a single screw extruder. Figure 6-10 is a drawing of a

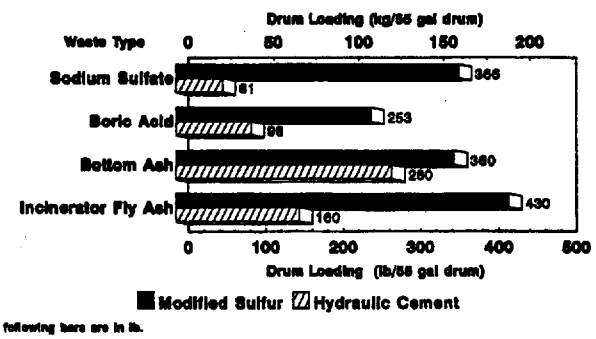


Figure 6-9. Maximum waste loading of sodium sulfate, boric acid, bottom ash, and incinerator fly ash in modified sulfur cement and Portland cement waste forms.

full-scale PE extruder. The extruder is similar to extruders used in the plastics industry, with one modification: it has two dynamic feeders rather than a single feed hopper. Figure 6-11 is a schematic of the PE encapsulation process, showing the two hoppers that feed the extruder. The two feeders allow waste and PE to be extruded simultaneously. Each feeder can be calibrated individually, however, to precisely monitor the proportions of waste and binder. A full-scale extruder can process 900 kilograms of mixed material per hour. Once the material cools, the contaminants are immobilized in a stable, homogenous, monolithic waste form (see Figure 6-12).

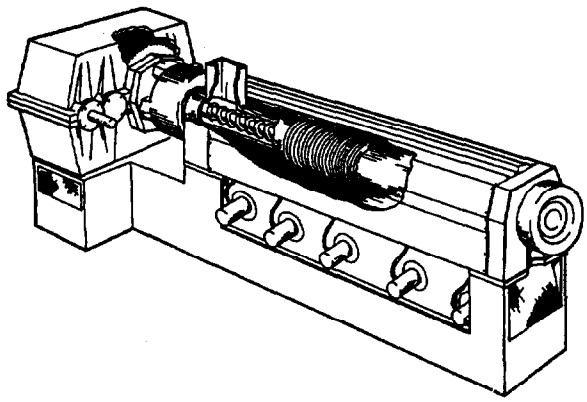


Figure 6-10. Drawing of full-scale extruder with 4.5-in. diameter screw.

Modified sulfur cement, developed by the U.S. Bureau of Mines, is not a hydraulic cement but a thermoplastic material composed of 95 percent elemental sulfur. The sulfur cement encapsulation process is similar to that for PE encapsulation. Unlike PE, however, sulfur cement is not viscous when melted, so it is not necessary to run the cement through an extruder to mix it with the waste. Instead, a double planetary orbital mixer is used. Sulfur cement and waste are added to the mixer, heated by oil bath circulation, mixed by rotating blades, and drained by gravity into a waste drum or mold. A hydraulic platen can be used to push waste mixtures that resist gravity draining into the mold. Upon cooling, the mixture forms a stable, monolithic waste form.

6.6.4 Laboratory-Scale Applications

BNL has conducted full-scale feasibility testing to predict the long-term integrity of waste forms produced by PE encapsulation. These tests examined the effects of water immersion and thermal cycling on the compressive strength of PE waste forms and determined the radiation stability, radionuclide leachability, toxic leachability, and biodegradability of PE waste forms. The following sections describe the results of this testing.

6.6.4.1 Compressive Strength

Compressive strength, which indicates the mechanical integrity of a waste form, may be compromised by

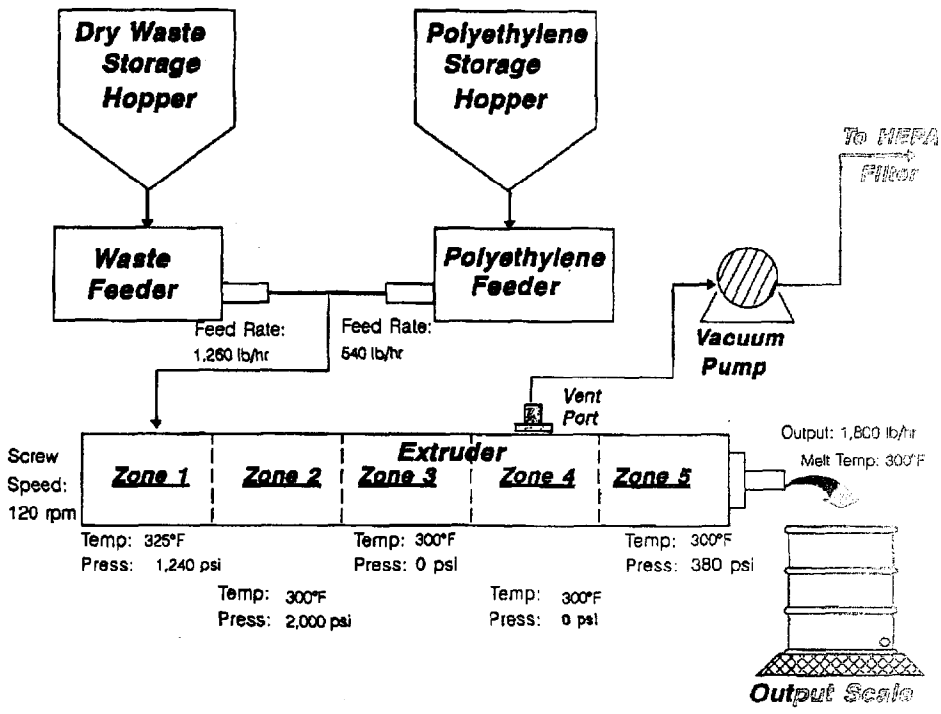


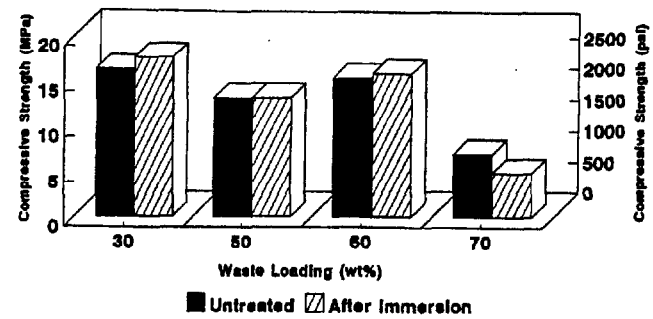
Figure 6-11. Schematic of PE encapsulation process showing two feed hoppers.

Figure 6-12. Photograph of PE waste form.

water immersion and temperature fluctuations. In tests conducted before and after a 90-day water immersion, however, PE waste forms showed no significant changes in compressive strength (see Figure 6-13). In addition, temperature cycles between −40°C and 60°C over a course of 150 hours did not significantly alter the compressive strength of PE waste forms.

6.6.4.2 Radiation Stability

Exposure to ionizing radiation breaks down the hydrocarbon chains in many thermoplastic materials, weakening polymer structures and liberating hydrogen gas. This is an obvious concern for a technology developed to encapsulate radioactive wastes. In testing at the BNL, exposure to radiation doses of up to 10^8 rad *increased* cross linking of the hydrocarbon chains in PE



* 90-Day Water Immersion Test;
ASTM D-695 Compressive Strength Test.

Figure 6-13. Effect of water immersion on compressive strength of PE waste forms.

waste forms. The cross linking produced waste forms that were stronger (see Figure 6-14), more stable under thermal cycling, and more resistant to solvents, and had lower leachability.

6.6.4.3 Toxic and Radionuclide Leachability

Leaching is the primary mechanism by which contaminants are released to the environment from material encapsulated in a waste form. The American Nuclear Society's dynamic 90-day test (ANS 16.1) in distilled water measures the relative radionuclide leachability of different materials. The ANS 16.1 generates an index of leachability based on the negative log of the waste form's effective diffusion coefficient. PE waste forms have leachability indices ranging from 7.8 to 11 on the ANS 16.1 scale (see Figure 6-15). These indices are two to five orders of magnitude higher than the minimum index suggested by the Nuclear Regulatory Commission. Preliminary data from EPA's 18-hour TCLP in acetic acid suggest that PE waste forms have low toxic leachability as well. (Because the leachability index [LI] is a negative logarithm, the higher the LI, the better the performance of the waste form.)

6.6.4.4 Biodegradability

PE is an organic material, so biodegradation under microbial conditions is a logical concern. Attempts by engineers to stimulate the biodegradation of PE in landfills, however, have been largely unsuccessful. In a 3-week test for bacterial and fungal growth under ideal conditions—temperatures of 35 to 37°C, humidity greater than 85 percent, and an abundance of nutrients—PE waste forms showed no microbial growth. Since the conditions of this test were extremely conservative, researchers expect that PE waste forms will not biodegrade under ordinary disposal conditions.

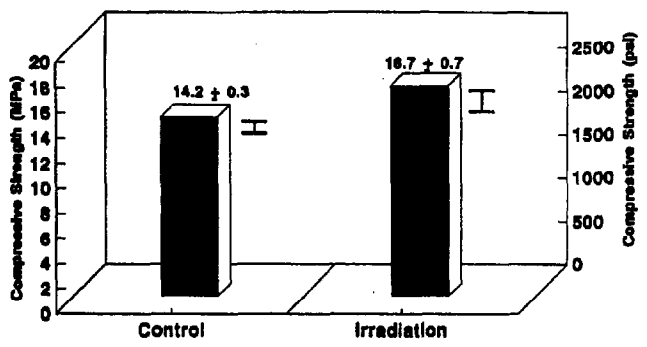
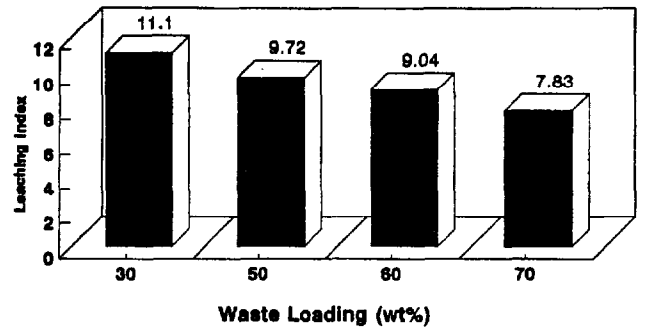


Figure 6-14. Effect of exposure to 10^8 rad on compressive strength of PE waste forms.



* Sodium leachability determined using ANS 16.1 Leach Test.

Figure 6-15. ANS 16.1 leachability indices of PE waste forms containing sodium nitrate.

6.6.5 Advantages and Limitations

The advantages of using a solidification and encapsulation process involving a thermoplastic material rather than a hydraulic cement derive primarily from the processes by which the two binder materials solidify. Thermoplastic materials solidify as they cool, usually in a matter of hours. Furthermore, thermoplastic materials are inert, so they cannot react with waste of any kind. By contrast, hydraulic cement takes days to cure and solidify through a series of hydration and chemical reactions. These reactions increase the chance of chemical interaction between the waste and the cement, which limits the amount and types of waste that can be solidified and can compromise the integrity of the final waste form.

Since PE melts at a fairly low temperature (120°C), there is little risk of volatilizing contaminants or radionuclides during mixing of the waste and binder. PE has a relatively low density, making PE waste forms significantly lighter than those made from hydraulic cement. In addition, PE waste forms achieve waste loadings as high as 70 percent by weight and 550 lb per drum for some waste streams, compared to just 20 percent and 200 lb for Portland cement forms (see Figure 6-16). This difference in loading can translate to substantial cost savings. For example, the Rocky Flats Plant in Golden, Colorado, which generates up to 1 million kg of sodium nitrate per year, could save between $1.5 and $2.7 million by using PE encapsulation instead of conventional technologies. Figure 6-17 is an economic analysis for treatment of nitrate salts at the Rocky Flats Plant, comparing the expected costs of using PE and conventional encapsulation.

The advantages of sulfur cement encapsulation over hydraulic cement encapsulation are similar to those of PE encapsulation. Like PE, sulfur cement does not require a chemical reaction to set and attains full strength within hours rather than days. In general, sulfur cement waste forms have much higher waste loadings than those of hydraulic cement waste forms, although these loadings vary with the type of waste being encapsulated. Sulfur cement waste forms have greater compressive and tensile strengths and are highly resistant to corrosion by acids and salt. Figure 6-18 shows Portland cement concrete and modified sulfur cement concrete specimens after a 2-week exposure to a solution of 10 percent hydrochloric acid. The Portland cement sample was severely attacked, exposing the quartz aggregate, whereas the sulfur cement sample was unaffected.

An additional advantage of sulfur cement encapsulation is that waste sulfur is in abundant supply from the desulfurization of incinerator flue gas and the cleanup of petroleum products. Currently, most of this supply, which is expected to increase to 30 million tons per year by 2000, is disposed of as waste. Therefore, sulfur cement encapsulation essentially uses one type of waste to encapsulate another. The price of sulfur is about 13 cents/lb, but this is expected to drop as supply increases.

6.7 In Situ Grout Injection

6.7.1 Background

In situ grout injection contains waste material in a solid monolith by mixing it with cement grout, thereby increasing the waste's physical stability and compressive strength, decreasing water intrusion to the waste, and decreasing the leachability of waste constituents. This section discusses the applicability of in situ grout injection for radionuclides, describes the grout injection process and the mechanisms by which grouts contain waste, and discusses the advantages and limitations of the technology.

6.7.2 Treatable Wastes and Media

In general, in situ grout injection can be considered at any site from which wastes cannot be removed, but

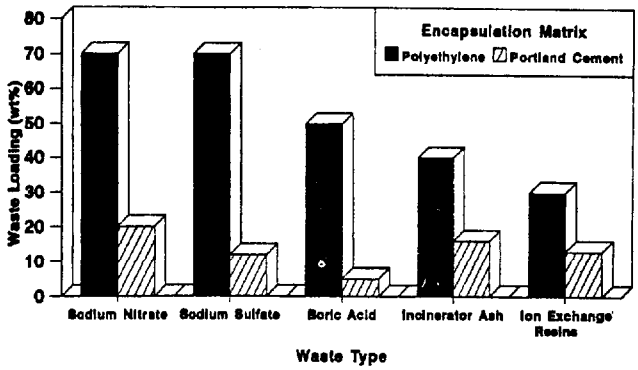


Figure 6-16. **Maximum percent waste loadings of sodium nitrate, sodium sulfate, boric acid, incinerator ash, and ion exchange resins in PE and Portland cement waste forms.**

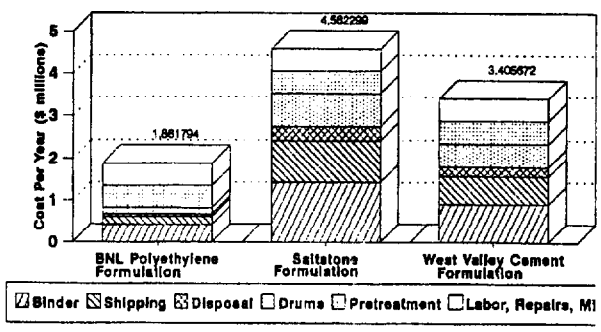


Figure 6-17. **Economic analysis of encapsulating sodium nitrate at Rocky Flats Plant. (Based on RFP production of 1.0 million kg of nitrate salt pe year.)**

several characteristics of the soil influence whether the technology will be able to contain waste effectively. These characteristics include void volume, which determines how much grout can be injected into the site; soil pore size, which determines the size of the cement particles that can be injected; and permeability, which determines whether water will flow preferentially around the monolith. Soil with the appropriate characteristics can be treated using a very simple in situ grout injection system.

Before in situ grout injection is applied at any site, extensive laboratory feasibility studies should be conducted. These studies should incorporate performance criteria, process criteria, and site-specific criteria, and consider the constraints of real processing equipment. For example, while feasibility tests may call for a formula of 40 percent cement by weight, the processing plant may be precise enough to produce formulas only within a certain range, such as 35 to 45 percent, and the impact of this variability must be assessed in the laboratory. Laboratory studies also can address other design issues, such as achieving a

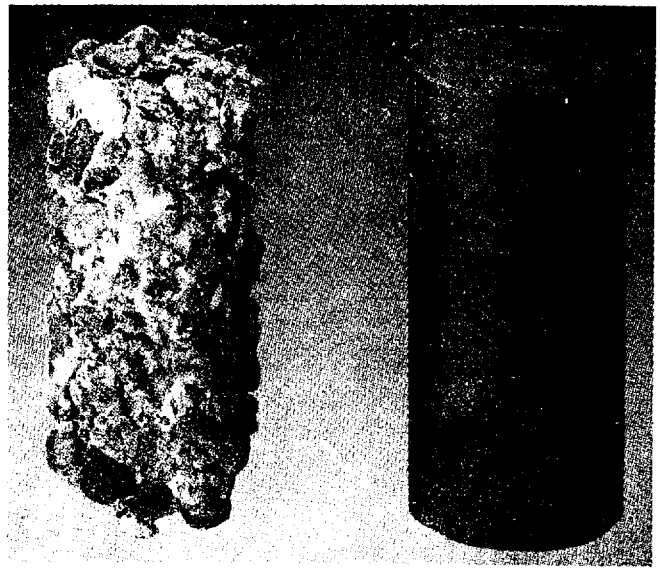


Figure 6-18. **Portland cement (left) and modified sulfur cement (right) waste forms after 2-week exposure to a solution of 10 percent hydrochloric acid.**

specific permeability, minimizing volume increase, or eliminating surface berm.

6.7.3 Operation and Maintenance

6.7.3.1 Injection

Figures 6-19 and 6-20 illustrate the in situ grout injection process. A pipe is drilled or hammered into the ground where the waste is located. A grout consisting of cement and other dry materials, which can include fly ash or blast furnace slag, then is injected to the waste through the pipe by a pump, conveyor belt, or pneumatically controlled blower. Once all of the voids at a particular depth become saturated, the pipe is raised and more grout is injected. This process continues until the grout forms a rough column extending to the surface from as far as 50 to 60 ft below the surface. A variation on the basic design involves using a pipe with a mixing apparatus that rotates as the grout is injected (see Figure 6-21). This apparatus mixes soil with the grout, creating a distinctly recognizable column of mixed grout and soil. If necessary, a hood can be placed over the system to capture volatile contaminants released during the injection process.

Whichever system is used, the object is to create a solid monolith of adjacent columns that contains the waste (see Figure 6-22). If the permeability of such a monolith is at least two orders of magnitude less than that of the host soil, water flows preferentially around the monolith and through the soil. This decreases both water intrusion to the waste and leaching of hazardous constituents from the monolith.

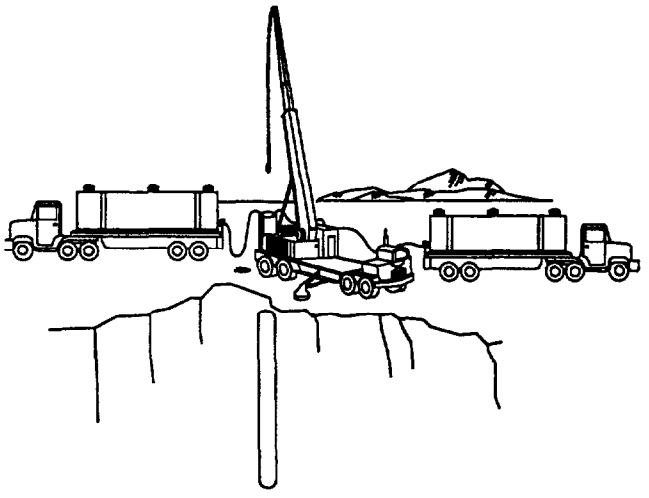


Figure 6-19. Grout injection apparatus.

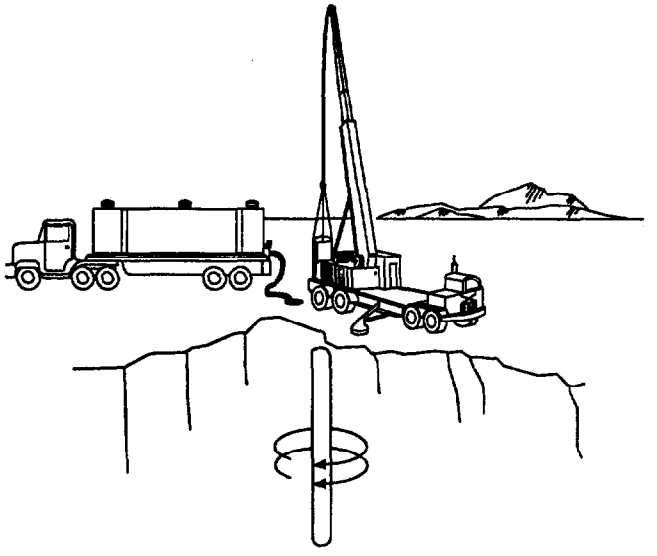


Figure 6-21. Grout injection system with in situ mixer.

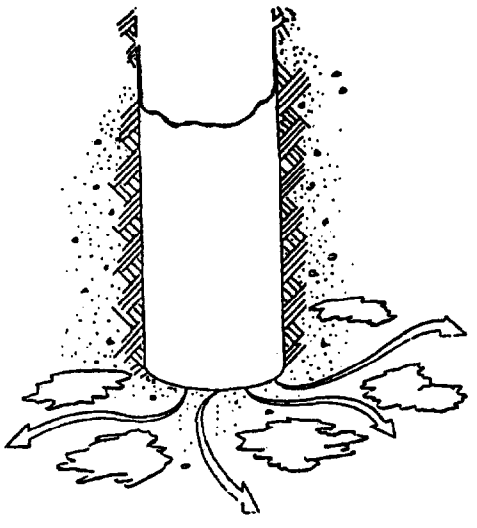


Figure 6-20. Flow of grout from bottom of grout injection pipe.

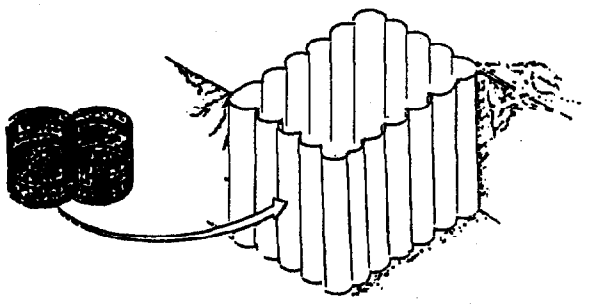


Figure 6-22. Monolith formed by overlapping grout columns.

Of the many types of grout available, cement-based grouts are the most common, for several reasons. First, materials for cement-based grouts, such as cement, fly ash, and blast furnace slag, usually are available within 150 miles of any site, making cement-based grouts relatively inexpensive. Second, cement-based grout is a proven material. The construction industry has extensive experience with in situ grouting and has shown that cement-based grouts can withstand extreme natural forces.

6.7.3.2 Containment Mechanisms

The mechanisms by which grouts contain hazardous wastes are not fully understood, because the crystalline structure of the cement-waste matrix is morphologically complex and incorporates a diverse array of elements. As a result, modern instruments have difficulty locating trace concentrations of waste constituents within the matrix. Nevertheless, some mechanisms of containment have been identified. These include adsorption, particularly of organics and gamma pellet clays; precipitation, especially of metals as hydroxide in cements with pHs between 9.5 and 11; encapsulation, whereby wastes are physically coated and surrounded by cement; and ion exchange, passivation, and diadochy. The ability of these mechanisms to contain a contaminant species depends on the contaminant's pH, solubility constant, equilibrium constant, and redox potential in the pore water. In some cases, contaminants may need to be reduced to less soluble states prior to grout injection.

Figure 6-23 shows the general chemistry of cement formation. A series of reactions leads to the formation and collapse of an ettringite structure, followed by the formation of a concrete-like calcium silica hydrate (CSH) structure. The grouted waste is not identical to concrete, because waste constituents affect the set and phase structure of the cement. Due to the similarity

between concrete and grouted wastes, however, the flow of grouted waste is very predictable and can be modeled. Figure 6-24 shows flow behavior of grout at two different densities.

6.7.4 Advantages and Limitations

6.7.4.1 Advantages

The ability of the monolith to resist leaching is its most important feature. The ANS's 16.1 test assigns a leachability index to a structure based on the negative log of its effective diffusion coefficient. Figure 6-25 shows the total releases over time, and Figure 6-26 shows the annual rates of release, from two hypothetical structures with leachability indices of 11 and 13. These indices are typical for metals; organics tend to leach at rates four to seven orders of magnitude higher.

Cost is another advantage of in situ grout injection. Although the initial capital costs for batch or surface processes often are less than those for in situ processes, the total costs for batch and surface processes, including transportation and disposal, tend to be greater.

Grouts can be formulated to set very quickly. This is an advantage at sites, such as solar ponds, that essentially are open pits. Within a day, previously grouted areas become a platform for further grout injection operations. The injection apparatus also is fairly small and portable, so it can be maneuvered into sites with tight space constraints.

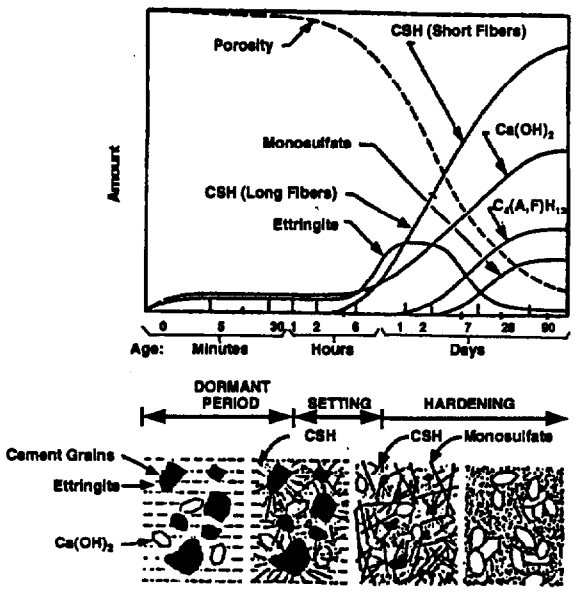


Figure 6-23. General chemistry of cement formation, showing growth and collapse of ettringite structure, followed by growth of CSH structure.

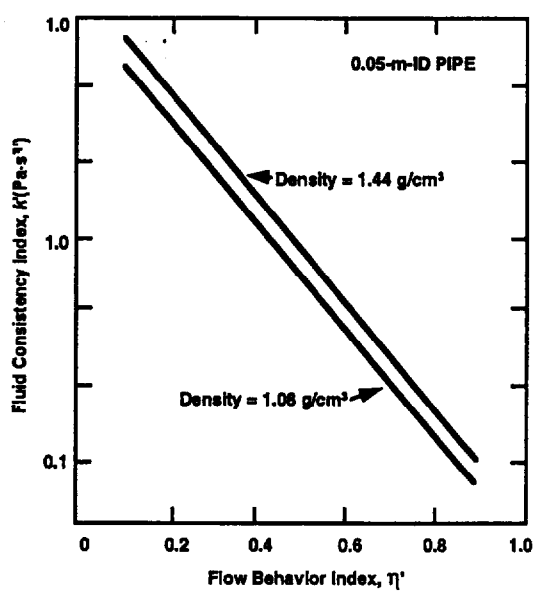


Figure 6-24. Flow behavior of grout at two different densities.

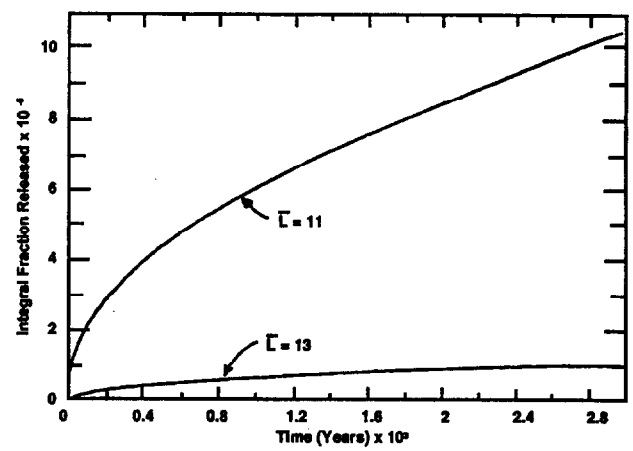


Figure 6-25. Releases over time from structures with ANS 16.1 leachability indices of 11 and 13.

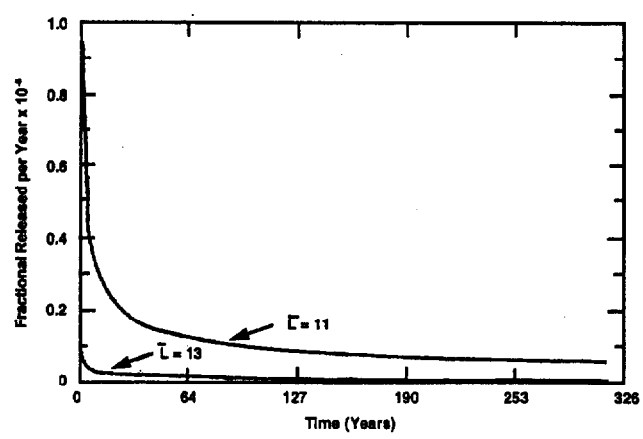


Figure 6-26. Releases per year from structures with ANS 16.1 leachability indices of 11 and 13.

6.7.4.2 Limitations

Because the technology operates in situ, process control is relatively poor and it is difficult to verify that the grout actually contained the waste. Rigorous verification involves digging up the perimeter of the grouted area. In addition, in situ grouting does not lend itself to waste retrieval, so it is not a good choice for DOE sites from which wastes may have to be retrieved after 30 or 40 years.

Cement-based grouts have some specific disadvantages. First, injection of a cement grout creates a volume increase—once the grout fills the available voids, it returns to the surface as berm. Second, since cement is particulate, it can flow only to soil pores of sufficient size. The first two or three injection holes at any site usually are test holes to determine how much grout the soil uptakes. Third, cement-based grouts have limited application. Cement-based grouting is a BDAT for a variety of metals but not for organic wastes.

6.8 Electrokinetic Soil Processing

6.8.1 Background

Electrokinetic soil processing (variably known as electrokinetic remediation, electromigration, or electrochemical decontamination) uses electric current to decontaminate soils and slurries that contain radionuclides, heavy metals, certain organic compounds, or mixed organic and inorganic wastes (Acar, 1992; Acar and Hamed, 1991; Acar et al., 1993c; Banarjee et al., 1990; Bruel et al., 1990; Hamed et al., 1991; Kelsh, 1992; Lageman, 1989; Pamukcu and Wittle, 1992; Probstein and Hicks, 1993; Runnels and Wahli, 1993; Renauld and Probstein, 1987; Runnels and Larsen, 1986; Shapiro and Probstein, 1993; Shapiro et al., 1989; Wittle and Pamukcu, 1993). The application of electric current has several effects: (1) it produces an acid in the anode compartment that sweeps across the soil and desorbs contaminants from the surface of soil particles (Acar et al., 1991; Alshawabkeh and Acar, 1992), (2) it initiates electromigration of different species toward the respective electrodes (Acar and Alshawabkeh, 1993), and (3) it generates an electric potential difference that can lead to electroosmosis-generated flushing of different species (Acar et al., 1993b; Acar et al., 1989; Alshawabkeh and Acar, 1992). This section provides an overview of electrokinetic phenomena in soils, outlines the types of waste and media to which electrokinetic soil processing can be applied, examines some potential environmental uses of electrokinetic soil processing, discusses bench- and pilot-scale testing of the technology, and looks at current research on different techniques that may improve the technology's effectiveness.

Electrokinetic soil processing is a controlled application of electroosmosis and electrical migration together with electrolysis reactions. Electroosmosis is one of several transport processes induced in soils by an electric current. Electroosmosis and electrophoresis are defined as the mass flux of pore fluid and charged particles, respectively, under an electric field. Figure 6-27 depicts electroosmosis. The fluid in the anode compartment flows across the soil mass to the cathode compartment under an electric field. This flow ceases when the counteracting flux under the hydraulic gradient becomes equal to the electroosmotic fluid flux. Figure 6-28 depicts electrophoresis through transport of negatively charged particles toward an anode under an electric field.

Pore fluid between soil grains moves toward the cathode, because most soils have a negative charge on their surface. This charge is due mostly to imperfections in the mineral produced during its formation as elements of similar size and kind replace the ones in the mineral lattice. The charge deficiency also may be caused by broken edges or the existence of natural organic species in the soil mass. The excess negative charge exists in all soils, and the total electrical charge per unit surface area (surface charge density) increases as the specific surface of the soil mineral increases. The surface charge density increases in the following order: sand < silt < kaolinite < monmorillonite.

The interaction of the pore fluid ions with the negatively charged soil surface results in alignment of the ionic species as depicted in Figure 6-29. The excess negative charge on the soil surface attracts and clusters excess cations close to the surface, while a neutrality of charge in the pore fluid is maintained by a corresponding concentration of negative species away from the soil surface. When an electric field is established along the capillary, cations close to the surface move towards the cathode, thereby imparting a strain on the pore fluid surrounding their shells,

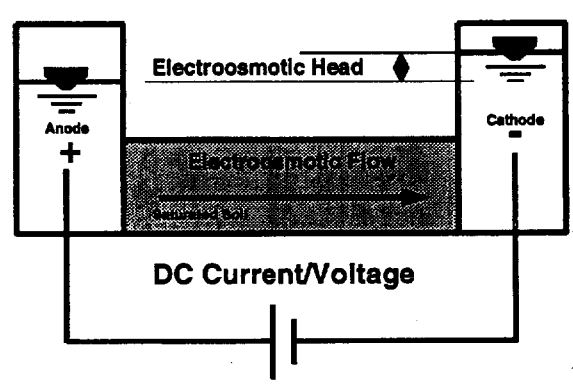


Figure 6-27. Electroosmotic flow of pore fluid in saturated soil.

which results in a pore fluid flux towards this electrode. The thicker the zone with the excess cations, the greater the electroosmotic flow will be. The thickness of this zone, however, depends upon the electronegativity of the soil surface, the concentration of ions in the pore fluid, the valence of the cation, and the dielectric properties of the pore fluid. When the ionic concentration increases, the thickness of this layer decreases, and the net momentum imparted by the migrating cations and anions decreases. As a result, electroosmotic advection substantially decreases or ceases.

Ionic species in the pore fluid are transported across the soil mass even when electroosomotic transport ceases (Acar, 1992; Acar and Alshawabkeh, 1994; Acar et al., 1993c). This movement of ionic species is at least an order of magnitude faster than transport of species by diffusion or electroosmotic advection and is one of the reasons why electrokinetic soil processing is a cost-effective means of extracting species from soils.

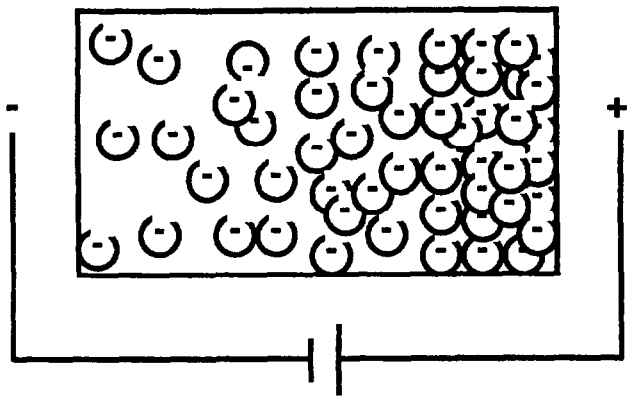


Figure 6-28. Electrophoresis of negatively charged particles toward the anode.

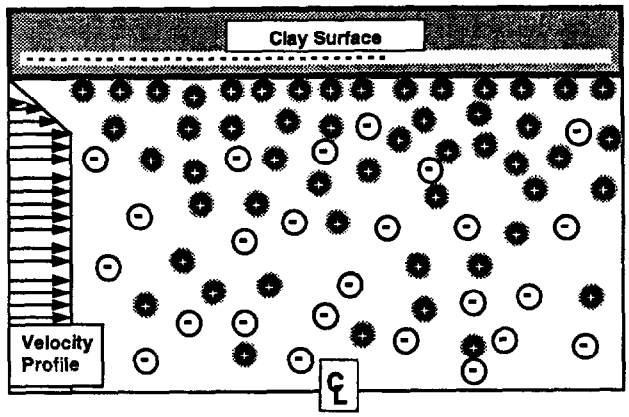


Figure 6-29. Diagram of advection by electroosmosis, depicting the excess cations at the clay surface and the resulting velocity profile across the soil capillary.

Electrokinetic soil processing involves not only ionic migration and electroosmotic advection but also electrolysis reactions generated at the electrodes (Acar et al., 1990; Acar et al., 1991; Alshawabkeh and Acar, 1992). Figure 6-30 shows the transport of the hydronium (protons) and hydroxyl ions generated at the electrodes by the electrolysis reactions. In unenhanced electrokinetic soil processing, the protons migrate across the soil mass and meet the hydroxyl ions close to the cathode compartment, generating water within that zone and decreasing ionic conductivity. The sweep of this acid front across the soil mass also assists in desorption of the cationic species concentrated close to the soil surface. Figure 6-31 depicts the removal of lead from a soil capillary and its electrodeposition on the cathode and precipitation close to the cathode at its hydroxide solubility value. The hydrogen ion generation and transport can be used as an acid washing process in electrokinetic soil processing, if desired.

6.8.2 Treatable Wastes and Media

Electrokinetic soil processing can be used to treat soils contaminated with the following species: lead (Hamed et al., 1991); cadmium (Acar et al., 1993c); radionuclides (Acar et al., 1993b), such as uranium, thorium, and radium; polar organic species, such as phenol (Acar et al., 1992) and nitrophenol (Wittle and Pamukcu, 1993); and nonpolar organic species, such as BTEX compounds below the solubility values (Bruel et al., 1990). The applicability of the technique to nonpolar organic species by different surfactant enhancements is under investigation (Acar et al., 1993b). This application requires the introduction of a conditioning fluid at the electrodes and relies upon conductance of current across the electrodes through the pore fluid. Electroosmotic flow is shown to saturate a soil mass in case partially saturated conditions are encountered.

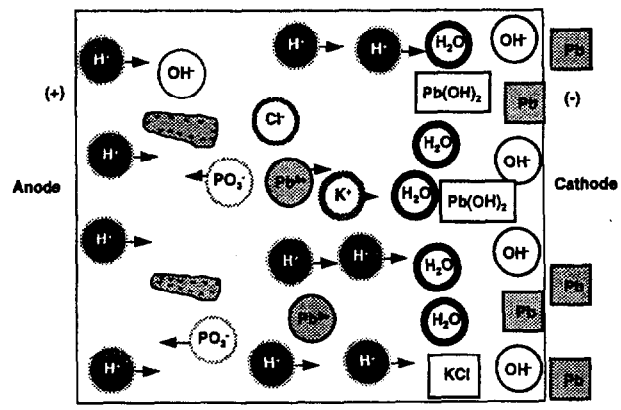


Figure 6-30. Migration of ionic species and colloids under an electric field.

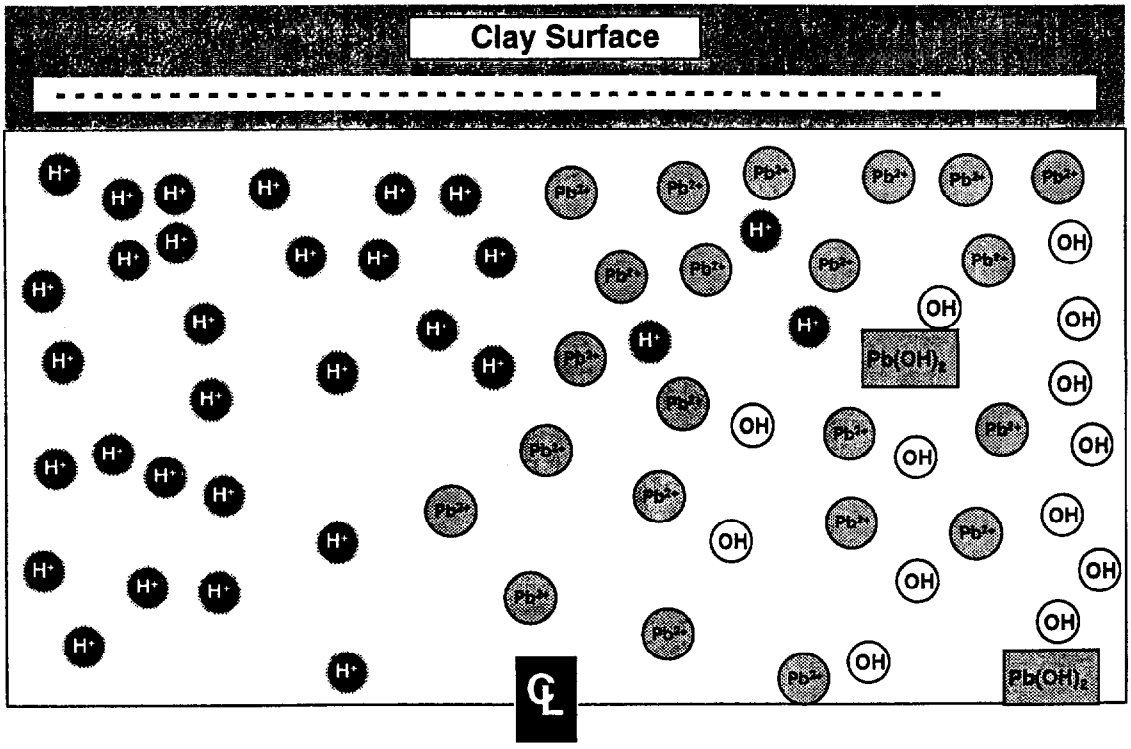


Figure 6-31. Schematic of protons displacing lead from the soil surface and the transport of both protons and lead toward the anode compartment.

6.8.3 Operation and Maintenance

A diagram of electrokinetic soil processing is shown in Figure 6-32. Anode and cathode series are inserted or laid on the ground, and a current is established across the electrodes. A conditioning fluid is circulated at the electrodes, serving both as a conducting medium and as a means to extract and exchange the species. Another use of this conditioning fluid is to control and/or depolarize the cathode reaction so that the base generated does not lead to premature precipitation of the incoming species at their hydroxide solubility values. The movement of the acid and/or the conditioning fluid across the electrodes assists in desorption of species, as well as dissolution of carbonates and hydroxides. Electroosmotic advection together with ionic migration assists in the transport and removal of contaminant species. Some species electrodeposit on the electrodes; others are extracted through the use of chemical processes or ion exchange systems within the process control container.

6.8.4 Bench- and Pilot-Scale Applications

6.8.4.1 Bench-Scale Studies

The following is a brief summary of the results of some of the bench-scale work using electrokinetic soil processing to treat specimens containing lead, cadmium, uranium, and phenol.

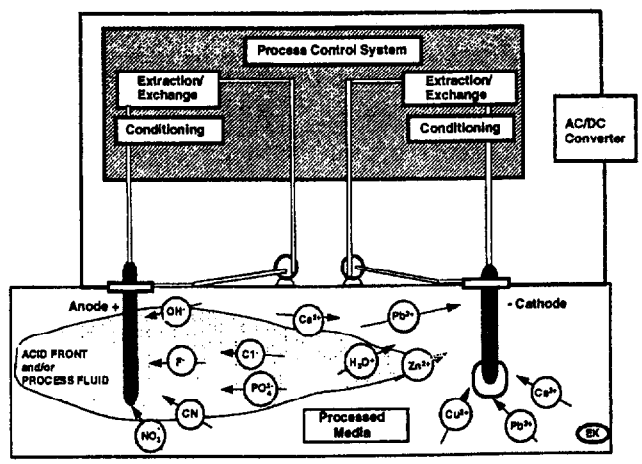


Figure 6-32. Schematic of electrokinetic soil processing, showing the migration of ionic species and the transport of the acid front and/or pore fluid across the processed medium.

Lead

Figure 6-33 presents the lead profile in lead-spiked kaolinite specimens after electrokinetic soil processing. Lead is redistributed across the specimen in shorter duration tests mainly due to the desorption in the anode compartment by the advancing acid front and reprecipitation close to the cathode. In longer duration tests, however, the lead is removed from the cell due to the sweep of the acid across the specimen and the prevailing electromigration of lead. The energy

expended to decontaminate the specimen in these tests varied from 30 to 60 kilowatt hours per cubic meter (kWh/m^3). This translates to an electrical cost of roughly $1.50 to $3.00 per m^3. Lead is efficiently removed from spiked kaolinite specimens at concentrations of up to 1,500 µg/g (Hamed et al., 1991). In all the tests, most of the lead precipitates on the cathode.

Cadmium

Figure 6-34 shows the results of experiments conducted in investigating cadmium removal at a concentration of about 100 µg/g from spiked kaolinite specimens. The cadmium was found to electrodeposit on the cathode or precipitate on the cathode as cadmium hydroxide (Acar et al., 1993c).

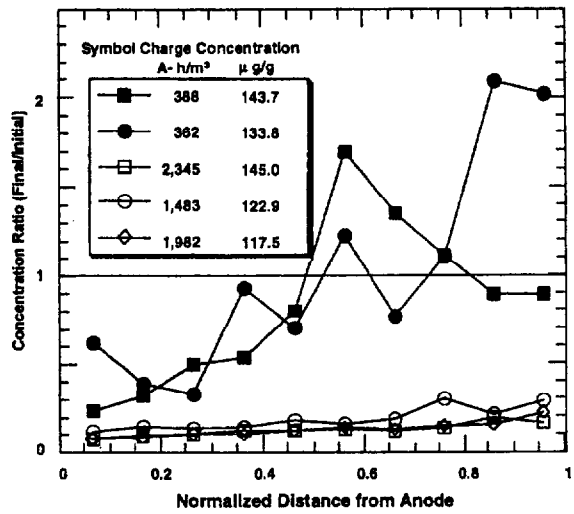


Figure 6-33. Lead removal across the specimens. Closed symbols represent shorter duration tests with lower charge input to specimens (Hamed et al., 1991).

Uranium

Uranium removal has been investigated by running unenhanced remediation tests in uranyl nitrate-spiked kaolinite specimens. The results are presented in Figure 6-35. The precipitate close to the cathode compartment is uranium hydroxide. This premature precipitation of the migrating ions when confronted with the hydroxide ions generated at the cathode is one reason why a conditioning fluid is needed (Acar et al., 1993b).

Phenol

Phenol removal also has been investigated after spiking kaolinite specimens with 500 µg/g of phenol (Acar et al., 1992). The results are presented in Figure 6-36. The effluent concentration is presented as a function of pore volumes of flow. Most of the phenol in the kaolinite specimens is removed in two pore volumes of flow. Phenol is one of the easier organics to remove by electrokinetic soil processing because it is miscible and it protonates in an acid to produce positively charged species. Thus, phenol functions just as any other cationic species, in its removal by electroosmotic advection, electromigration, and the protonation generated by the acid front. An energy expenditure of only 10 to 30 kWh/m^3 was sufficient to remove 95 percent of the phenol in the specimen.

6.8.4.2 Pilot-Scale Studies

In collaboration with the U.S. EPA Risk Reduction Engineering Laboratory (RREL), the Louisiana State University group is conducting pilot-scale studies of electrokinetic soil processing both in the laboratory and at a site in Baton Rouge, Louisiana. Laboratory studies indicate that lead is removed from specimens of kaolinite at an energy cost of about $15 per m^3 within a period of 3 months. At the site, lead concentrations at

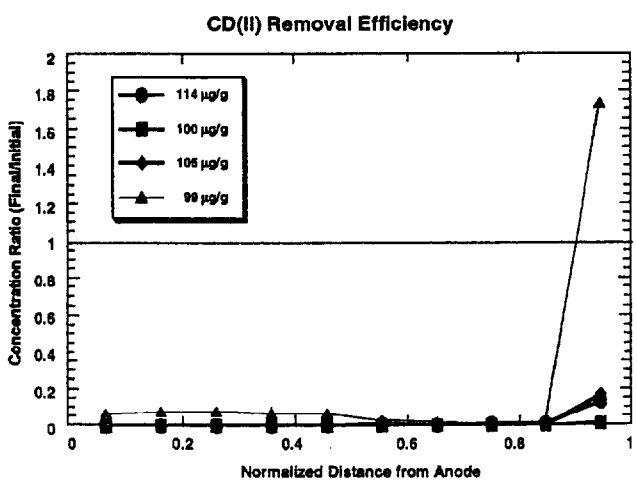


Figure 6-34. Cadmium removal in spiked kaolinite specimens (Acar et al., 1993c).

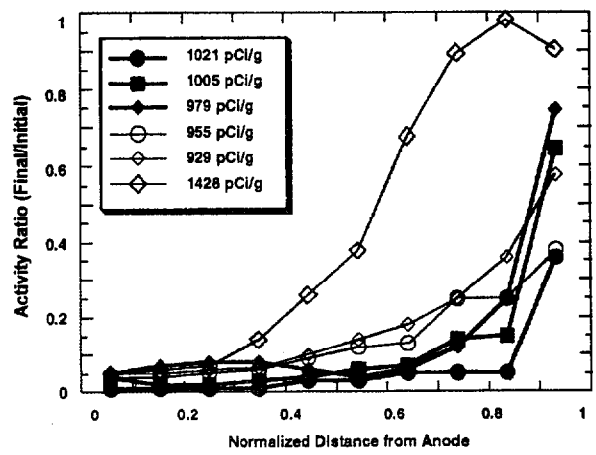


Figure 6-35. Uranyl removal in uranyl nitrate-spiked kaolinite specimens. Open symbols represent shorter duration tests (Acar et al., 1993b).

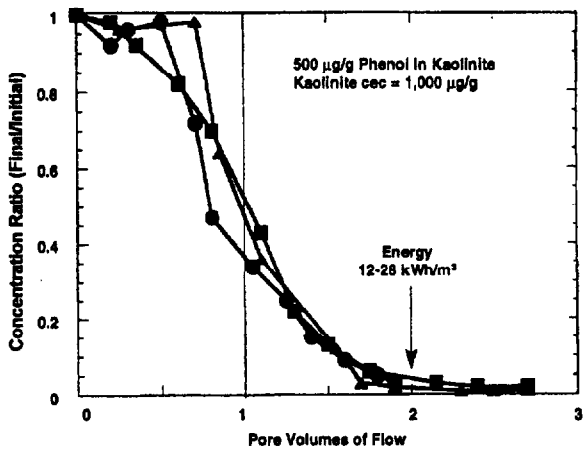


Figure 6-36. Phenol concentration profile in the effluent in spiked kaolinite specimens (Acar et al., 1992).

one location are as high as 100,000 µg/g. These high concentrations, together with the presence of shells rendering calcium concentrations of up to 90,000 µg/g, are the major obstacles to the efficiency of electrokinetic processing of the soil at the site. Migration and precipitation of calcium as bicarbonates and hydroxides clog the soil pores and prevent the transport of lead. The presence of calcium increases by 10 times the amount of acid necessary to remove the lead. At locations where calcium concentrations are lower (10,000 µg/g) and shells are not encountered, bench-scale studies demonstrate that lead can be successfully removed by unenhanced and enhanced remediation (Acar et al., 1993a). The pilot-scale studies are run at a current of up to 800 $\mu A/cm^2$ across electrodes placed 2- to 4-m apart.

Pilot-scale field studies also have been reported in the Netherlands on soils contaminated with lead, arsenic, nickel, mercury, copper, and zinc (Lageman et al., 1989). In one study, the process removed 75 percent of the lead from fine sand with an initial concentration of 9,000 ppm. Another study achieved a 90 percent removal of arsenic from clay with an initial concentration of 300 ppm. Both of these studies used energy levels of 60 to 200 kWh/m^3 and involved chemical conditioning of the anolyte and the catholyte.

6.8.4.3 Studies on Chemical Conditioners

The effects of injecting chemical conditioners at the anode and the cathode currently are being investigated (Acar et al., 1993a). These conditioners can modify the chemical reactions that take place at the electrodes and enhance the effectiveness of the system. For example, acetic acid depolarizes the reaction at the cathode and prevents base formation. When acetic acid is added, the main reaction becomes the reduction of proton and the evolution of hydrogen. Acetate anions also migrate into the system, solubilizing contaminant species. In one test, acetic acid successfully solubilized uranium at 1,000 ppm. Instead of collecting at the cathode as a solid precipitate, uranium was solubilized and removed in the effluent.

Similar studies are being conducted on clays contaminated with thorium at concentrations of 1,500 to 2,000 µg/g. Thorium has four charges and adsorbs very strongly onto clay. Researchers expect that conditioning the cathode with acetic acid will allow thorium to be removed at high levels by preventing the formation of upstream base, which blocks the pores of the clay.

Chelating agents are another type of chemical conditioner used to solubilize specific contaminants. Currently, researchers are trying to identify a chelating agent to solubilize radium, which ordinarily forms a highly insoluble sulfate that intercalates with the clay structure. As a result, radium resists electrokinetic removal in bench-scale studies, even at 1 ppb and as many as 3 pore volumes of acid flow. To remove radium, a chelating agent also could be used to process the media with mixed radionuclides, such as radium, strontium, and thorium. Alternatively, radium-contaminated media could be flushed with ammonium ions instead of with acid.

The impact of micelles on the removal of polar organic compounds, such as hexachlorobutadiene is being studied (Acar et al., 1993b). A micelle is a charged particle that is nonpolar on the inside. These particles desorb polar organic contaminants, allowing them to be flushed from the soil. Preliminary results suggest that injecting positively charged micelles at the cathode increases electrokinetic removal of such organic wastes.

6.8.5 Advantages and Limitations

The primary advantage of this technology is the potential for many in situ applications. Electrokinetics has several potential applications in waste management. Besides enhancing chemical migration, the technique can be employed in implementing electrokinetic flow barriers; diverting plumes; detecting leaks; and injecting chemicals, grouts, microorganisms, and nutrients to subsurface deposits.

The fact that the technique requires a conducting pore fluid in a soil mass could be considered a shortcoming, particularly at sites where there are concerns about introducing an external fluid into the soil. In addition, the technique has been demonstrated to be successful at electrode spacings of only 6 to 10 m. Large-scale applications will require that several electrodes be placed across a site.

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Appendix A

SEARCH FOR A WHITE PHOSPHORUS MUNITIONS DISPOSAL SITE IN CHESAPEAKE BAY[1]

Gary Buchanan, International Technology Corporation, Edison, New Jersey
Harry Compton, Environmental Response Team, U.S. EPA, Edison, New Jersey
John Wrobel, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

EXECUTIVE SUMMARY

The White Phosphorus Munitions Burial Area (WPMBA) is located in the Chesapeake Bay within the confines of the restricted waters of the U.S. Army Base at Aberdeen Proving Ground (APG). This investigation was designed to determine the exact location of the WPMBA and determine the impacts upon the surrounding ecosystem. The lack of any records from the period of disposal (1922-1925) has exacerbated the problem of locating the site. The present assumed location of the site is based on information obtained from former employees, and the designation of this area as the "Phosphorus Area Unit" by President Roosevelt in 1940 as part of the Migratory Bird Treaty Act. The exact number of munitions, the volume of white phosphorus, and the exact location of the original disposal site are all unknown.

Several techniques have been used during this investigation to determine the location of the WPMBA. A search was conducted to locate related information concerning the disposal, storage, and handling of white phosphorus. Aberdeen Proving Ground records, historical maps and aerial photos were reviewed. Manufacturers, former employees, and historians (National Archives, Library of Congress, U.S. Army Archives) were also contacted for relevant information. A geophysical investigation at the site was also conducted.

An initial geophysical survey was conducted during October of 1988 within the WPMBA. A coarse grid was developed to screen the area with an underwater proton magnetometer. Discrete areas exhibiting numerous or extremely large gamma changes were investigated in a second survey. Based on a review of the data, the area adjacent to Black Point was selected for a more intensive study during June of 1989.

Based on the geophysical data four areas were selected for sediment core analysis to determine if a burial site existed. A fifth area, the channel adjacent to the WPMBA, was selected for coring due to maintenance dredging concerns. A reference area was also selected north of the site in Spesutie Narrows. The coring was conducted during August of 1989 in each of the five areas. Due to the safety concerns in dealing with the burial area and the known presence of unexploded ordnance on APG, a remote coring operation was necessary. An EPA work barge was retrofit to perform the remote coring.

A total of 60 cores were obtained, ranging in depth from 1 to approximately 9 feet. Cores were screened on-site for high explosives using a Scan X Jr. portable gas chromatograph and composite samples were collected for analysis. All samples were analyzed for elemental phosphorus, high explosives, and RCRA analyses. Select samples were analyzed for total organic carbon, grain size, and toxicity testing.

Water samples were also collected at each of the areas cored and analyzed for elemental phosphorus and high explosives. Water quality measurements were recorded in each area and included temperature, pH, conductivity, salinity, oxidation-reduction potential, and dissolved oxygen.

Gull Island which is located along the eastern border of the WPMBA was examined as a potential disposal site. A proton magnetometer and metal detectors were used to survey the island for ferrous metals. Several test pits were excavated to examine the stratigraphy and soils of the island. Soil cores were collected from two locations on the island and analyzed for elemental phosphorus, high explosives, and grain size.

The results of the investigation indicate that white phosphorus was detected in 11 of the 60 core samples at concentrations less than 5 ug/kg. No white phosphorus was detected in the water column. No high explosive

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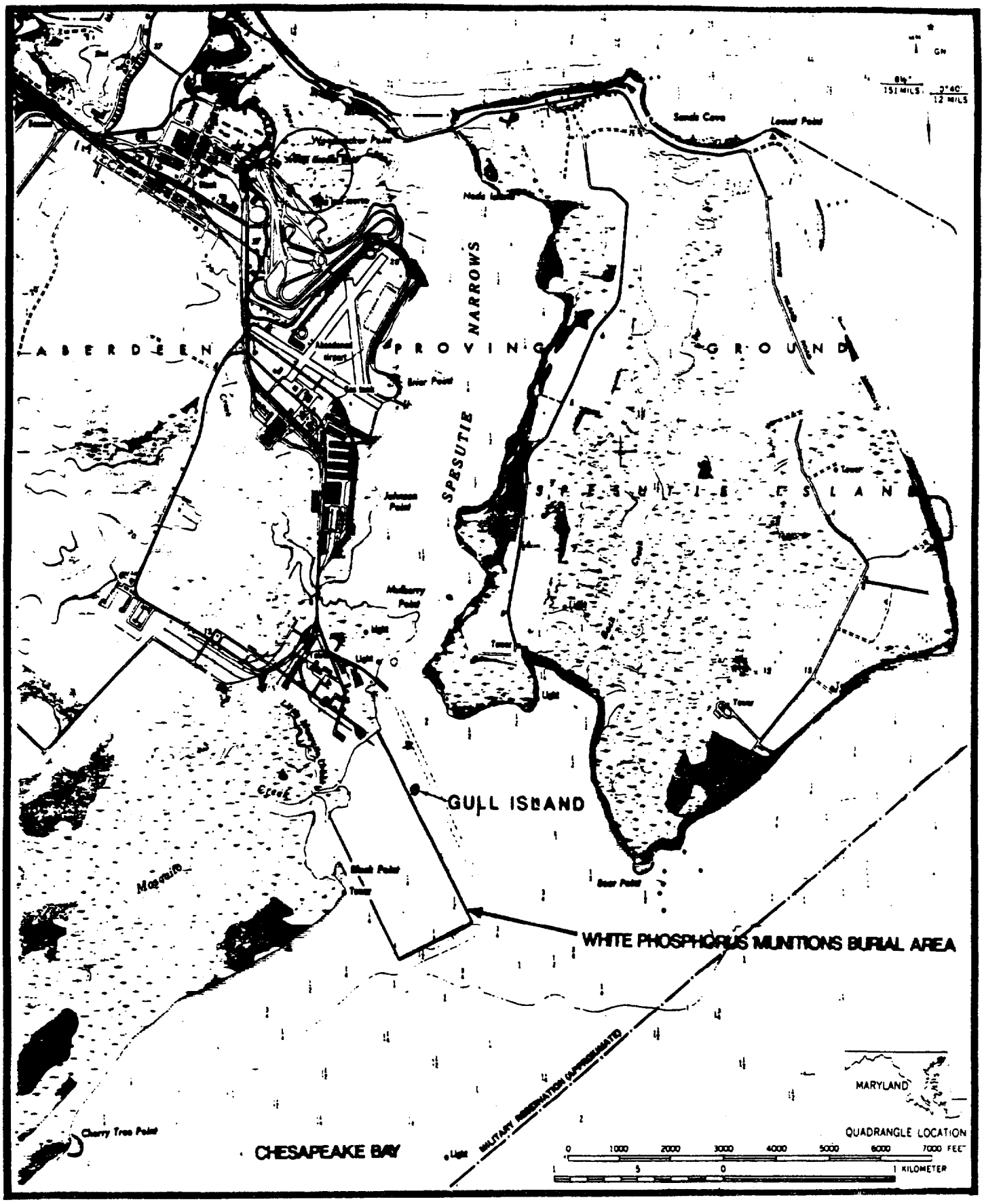
[1]Reprinted from the Proceedings of the U.S. EPA Forum on Remediation of Superfund Sites Where Explosives Are Present, December 1989, San Antonio, Texas.


GULL ISLAND
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
CHESAPEAKE BAY
SPESUTIE NARROWS
ABERDEEN PROVING GROUND
SPESUTIE ISLAND
MARYLAND
QUADRANGLE LOCATION
0 1000 2000 3000 4000 5000 6000 7000 FEET
1 KILOMETER

compounds were detected in the water or sediment samples. RCRA analyses indicate that the sediment cores would not be considered a hazardous waste. Definitive boundaries for the WPMBA could not be determined due to the diffuse and isolated nature of the contamination. No impacts upon the aquatic ecosystem are expected. Release of White Phosphorus are not expected unless the sediments are disturbed.

1.0 INTRODUCTION

This investigation concentrated on determining the presence, location and characteristics of the White Phosphorus Munitions Burial Area (WPMBA). The WPMBA is located in the Chesapeake Bay (Figure 1) within the confines of the restricted waters of the U.S. Army Base at Aberdeen Proving Ground (APG), Maryland.

This investigation was conducted as part of a Resource Conservation and Recovery Act (RCRA) Corrective Action Permit Condition. This Permit Condition required that the Permittee (APG) conduct a RCRA Facility Assessment (RFA). The primary purpose of the RFA is to insure the burial area is studied and any released wastes are identified and evaluated.

The Aberdeen area of this base was established in 1917 as the Ordnance Proving Ground. It became a permanent military post in 1919 and was designated Aberdeen Proving Ground. Testing of ammunition was begun in January of 1918 (Weston, 1978). Two other major additions to the base occurred. Spesutie Island was acquired in 1945 and the Edgewood portion of the facility merged with APG in 1971.

The open water areas of APG total approximately 37,000 acres (15,000 hectares). Large segments have been used as ordnance impact areas since 1917. There are an estimated four million unexploded and sixteen million inert projectiles of all calibers in these restricted waters (USATHAMA, 1980).

The WPMBA is located on the western side of the Upper Chesapeake Bay. The area is situated in the shallow waters off the mouth of Mosquito Creek, between Black Point and Gull Island. Spesutie Narrows and Spesutie Island lie to the north and northeast, respectively. The WPMBA is adjacent to and offshore of the Main Front Land Range Area which has been active since 1917. An estimated one million rounds of all calibers up to 16 inches have been fired at this range. The types of rounds fired included high explosives, anti-personnel, armor defeating, incendiary, smoke, and illuminating (USATHAMA, 1980). Although the WPMBA is adjacent to this range, discussions with APG personnel have indicated that there are no records of the open water areas of the WPMBA having been used as an impact area. The closest active range is the Ballistics Workshop located just north of the WPMBA. The WPMBA lies partially within the 1800 ft (550 m) safety clearance of this range. The Fuze Range, another active range, is located to the east of the WPMBA.

Based on interviews of former employees who worked on the base following World War I (WWI) the existence of the WPMBA was discovered in the late 1970's. Reportedly, an unknown amount of WWI white phosphorus (WP) munitions were buried in Chesapeake Bay in the area of Black Point during the period 1922-1925. The ordnance supposedly consisted of U.S., British, and French land mines, grenades, and artillery shells. Bulk phosphorus may also have been disposed of here. It is possible that this disposal event involved a single barge load of munitions; however it may have involved considerably more.

The site is located within Chesapeake Bay, a major estuarine ecosystem. Numerous species of fish utilize the bay during various stages of their life cycle. Up to 65 species of fish have been identified in the waters at APG and the adjacent Upper Chesapeake Bay waters (Miller, Wihry, & Lee, Inc., 1980). Several commercially and recreationally important species utilize the area, including striped bass (Morone saxatilis) and the blue crab (Callinectes sapidus) (USATHAMA, 1980). Aberdeen Proving Ground also lies in the pathway of the Atlantic Flyway, resulting in an abundance of migratory waterfowl. Due to the toxicity of white phosphorus, releases from the WPMBA could impact these resources within Chesapeake Bay. Fish are especially sensitive to concentrations of WP in the water column. It is important, therefore, to determine whether aquatic organisms and other wildlife are being exposed to WP.

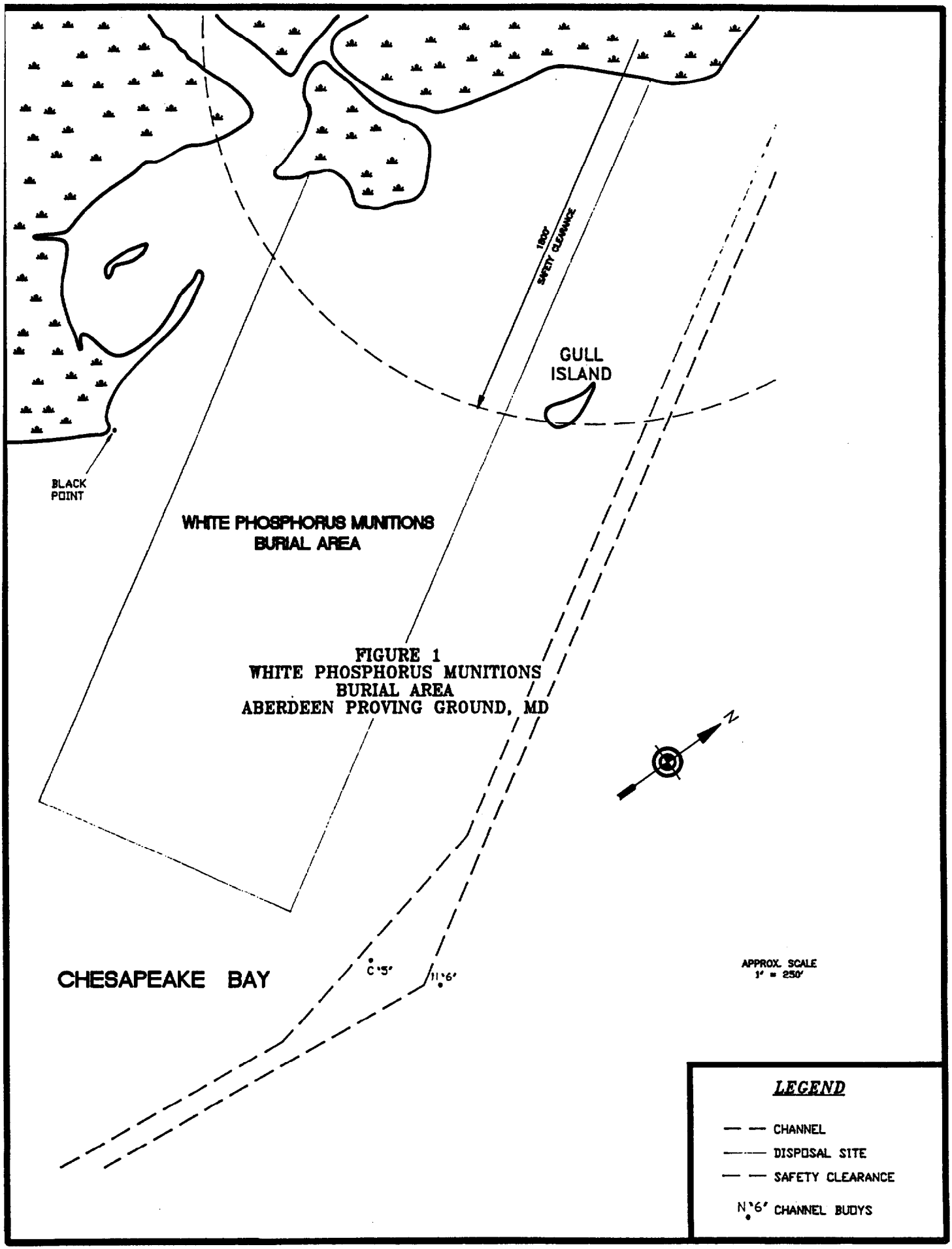


FIGURE 1
WHITE PHOSPHORUS MUNITIONS
BURIAL AREA
ABERDEEN PROVING GROUND, MD

2.0 MATERIALS AND METHODS

Due to the complex nature of this project, several methods were employed to investigate the WPMBA. A historical and information search was conducted to obtain more data concerning the site. Geophysical surveys were completed to define the boundaries of the WPMBA. Finally, physical, chemical and biological analyses were performed on the sediments and waters to determine the characteristics of the WPMBA. The results of initial surveys were used to modify the investigation in an ongoing fashion.

2.1 Historical/Information Search

Aberdeen Proving Ground records, historical maps, and aerial photographs were reviewed and analyzed. The Library of Congress, National Archives, the Ordnance Museum at APG, and several white phosphorus manufacturing companies were contacted for relevant information.

Previous environmental impact assessment documents produced for the installation were also reviewed. Attempts were made by APG to locate and interview former employees. Two former employees were contacted and questioned by APG.

Historical aerial photographs and bathymetric maps were reviewed to determine if indications of the disposal site were evident. In addition, a USGS Aeromagnetic map of the area was reviewed for indications of magnetic field anomalies.

2.2 Geophysical Surveys

On October 14-15, 1988, an in-depth geophysical investigation was conducted in the WPMBA. Transects were completed in two phases due to safety considerations and constraints of the nearby firing range. A Fisher Proton 2 Marine Magnetometer was used to screen the entire WPMBA. A proton magnetometer was deemed the most effective survey instrument based on field tests comparing various remote sensing instrumentation. A proton magnetometer is an electronic instrument which measures the strength of the earth's magnetic field in gammas. Ferromagnetic materials (containing iron) will alter the magnetic field and result in changes in the gamma readings. This instrument has a sensitivity of 1 gamma and can detect a large ferromagnetic object (several tons) from approximately 200 feet.

An area larger (approximately 285 acres) than that reported for the WPMBA was screened to get maximum coverage. Transects were approximately 200 ft apart. The distance between transects was selected based on the reported size of the actual burial area (6 hectares, or 15 acres). A Lowrance X-16 fathometer and a Sitex EZ-97 LORAN C (Long Range Navigation) receiver were used throughout the sampling periods for bathymetric and navigational purposes, respectively.

Transects were run in an approximately north-west direction and then repeated in a south-east direction. The magnetometer was towed at an average speed of 2-3 knots (1.0-1.5 m/sec) approximately 50 feet (15 m) behind the boat at a depth of approximately 2-2.5 feet (0.6-0.8 m). Ten transects were run in duplicate for a total of 20 passes over the near-shore area. Seven additional transects were run in duplicate in the off-shore area. A graphical representation of the transects is shown in Figures 2 and 3. The path of the transects shown deviates from a straight line; this is a function of the LORAN coordinates and the plotting techniques utilized.

Buoys were set and surveyed at those sites where large fluctuations were recorded, indicating a target or anomaly, and which were deemed significant. During this investigation, the magnetometer was "walked" over Gull Island to determine its potential as a dump site.

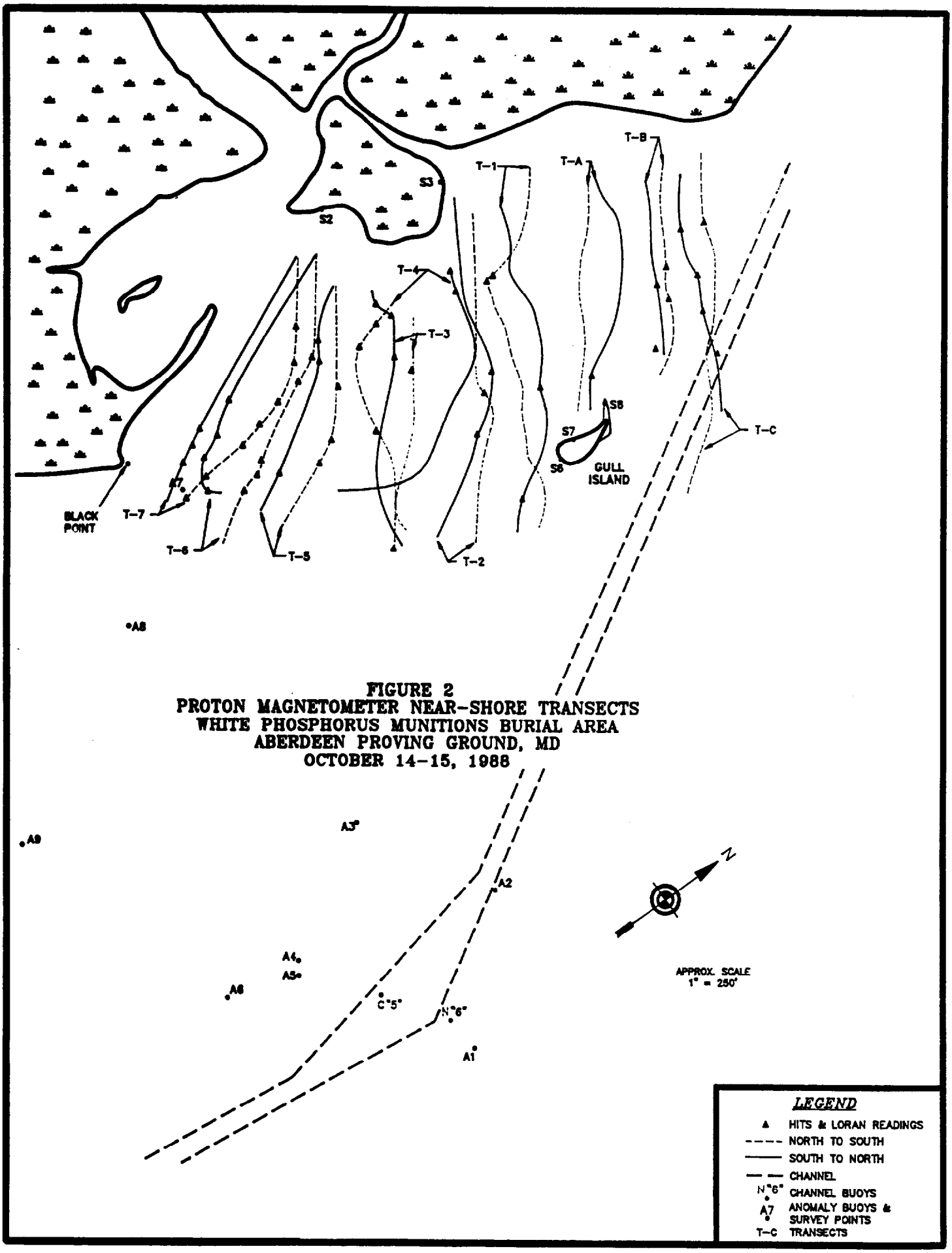


FIGURE 2
PROTON MAGNETOMETER NEAR-SHORE TRANSECTS
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD
OCTOBER 14-15, 1988

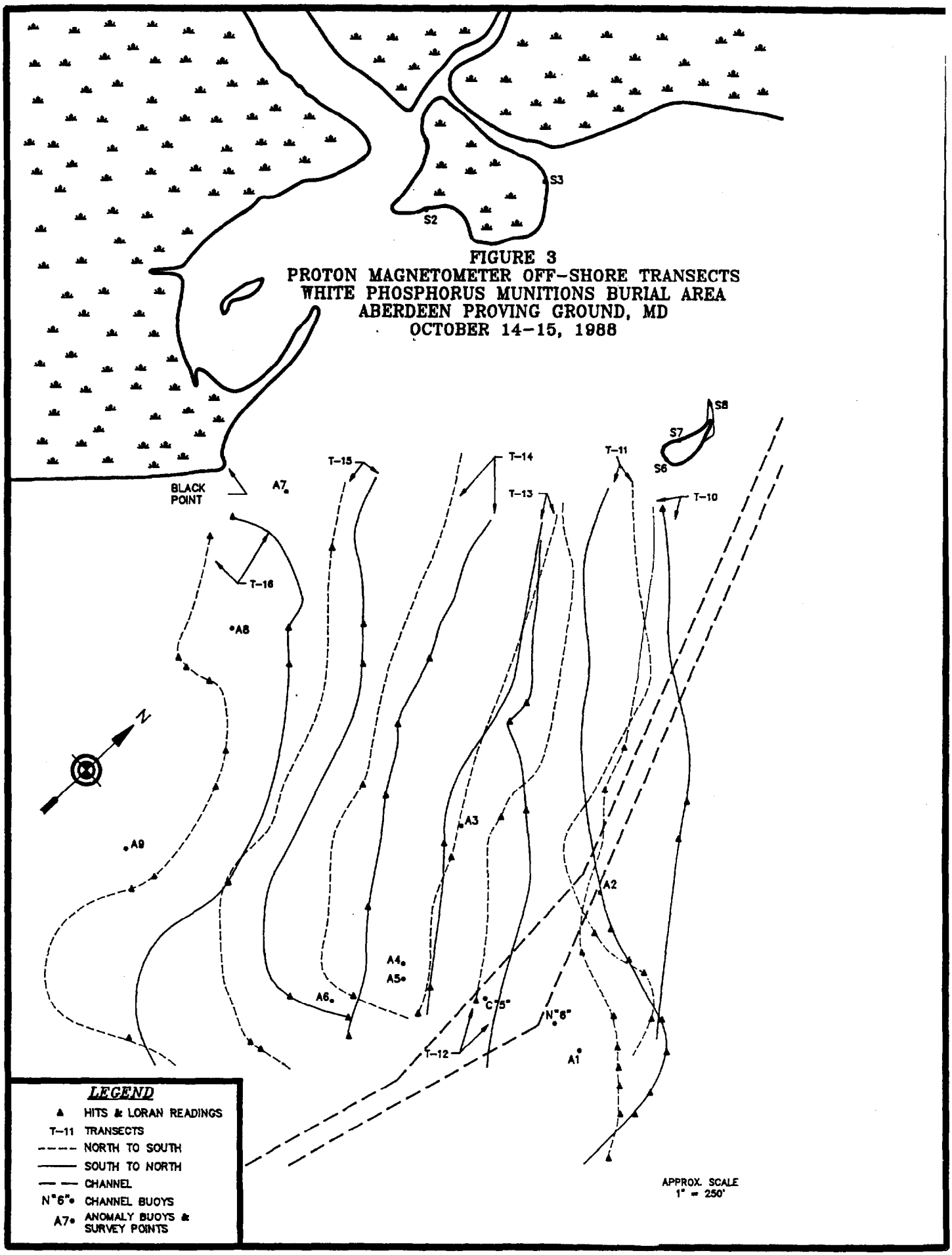


FIGURE 3
PROTON MAGNETOMETER OFF-SHORE TRANSECTS
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD
OCTOBER 14-15, 1988

Based on a review of the data in conjunction with the U.S EPA Environmental Monitoring Services Lab (EMSL-Las Vegas), the area adjacent to Black Point was selected for a more intensive survey in June of 1989. Transects lines were set up every 20 feet (6 m) to more accurately define the magnetic field and the associated anomalies. The even numbered transects (i.e., T-2, T-4) are depicted in Figure 4, while the odd numbered are shown in Figure 5. Additional transects were run perpendicular to the north and south transects in an east-to-west or a west-to-east direction at select points. These were titled 'tie lines' and functioned to tie in the data from adjacent transects for data interpretation. All data from the magnetometer was passed through a digital-to-analog converter and then to a portable strip chart recorder. Concurrently, LORAN coordinates were recorded through an interface onto the fathometer chart paper at select time intervals and at buoy markers.

2.3 Remote Sediment Coring

Coring activities occurred August 7-17, 1989 and involved the remote collection of 60 sediment cores within the WPMBA. Due to the inability to confidently define the boundaries of the WPMBA, a systematic search sampling method was employed in five areas. A square grid size of 273 feet (83 m) was utilized assuming a circular target size of 150 ft (46 m) with a 0.9 probability (90% chance) of finding the target. Based on this method, a total of 50 cores would be required to cover those areas with numerous or large magnetic field anomalies.

Cores were collected off Black Point, in the channel, north of Gull Island (Area I), east of the channel (Area II), and west of the channel (Area III). In addition, ten cores were collected in the adjacent APG channel to assist in future dredging decisions. Sediment coring was utilized to secure samples for white phosphorus and high explosives analysis.

Core liners (6 ft butyrate plastic tubes) were utilized throughout the WPMBA investigation to collect, transport, store and maintain the integrity of the cores. Four reference samples from two cores were collected in Spesutie Narrows.

All core samples were screened at the staging area for high explosives using a Scan X Jr. Portable Gas Chromatograph, inspected for white phosphorus, and examined for stratigraphy. The Scan X Jr., a portable GC with an Electron Capture Detector (ECD), was configured to detect the presence of Nitroglycerine (NG) and trinitrotoluene (TNT).

If the stratigraphy of the core was relatively homogeneous, a composite sample of the core was collected. The core composite was collected by using a clean scoop to obtain equal amounts of sediment at six inch intervals throughout the length of the core. If a discrete strata was observed, a separate sample of that strata was collected. All sampling equipment was decontaminated between samples following ERT/REAC procedures, and all notes were logged on field data sheets or log notebooks. Each sample was assigned a unique sample number which corresponded to a field data sheet.

To determine whether Gull Island was the location of the WPMBA, core samples were collected in September of 1989. Soil cores were collected from the south end and the north end of the island. Samples were collected at one foot intervals from a depth of 5-8 ft and composited for WP and high explosive analyses. A listing of the physical/chemical analyses performed on the sediment samples is depicted in Table 1.

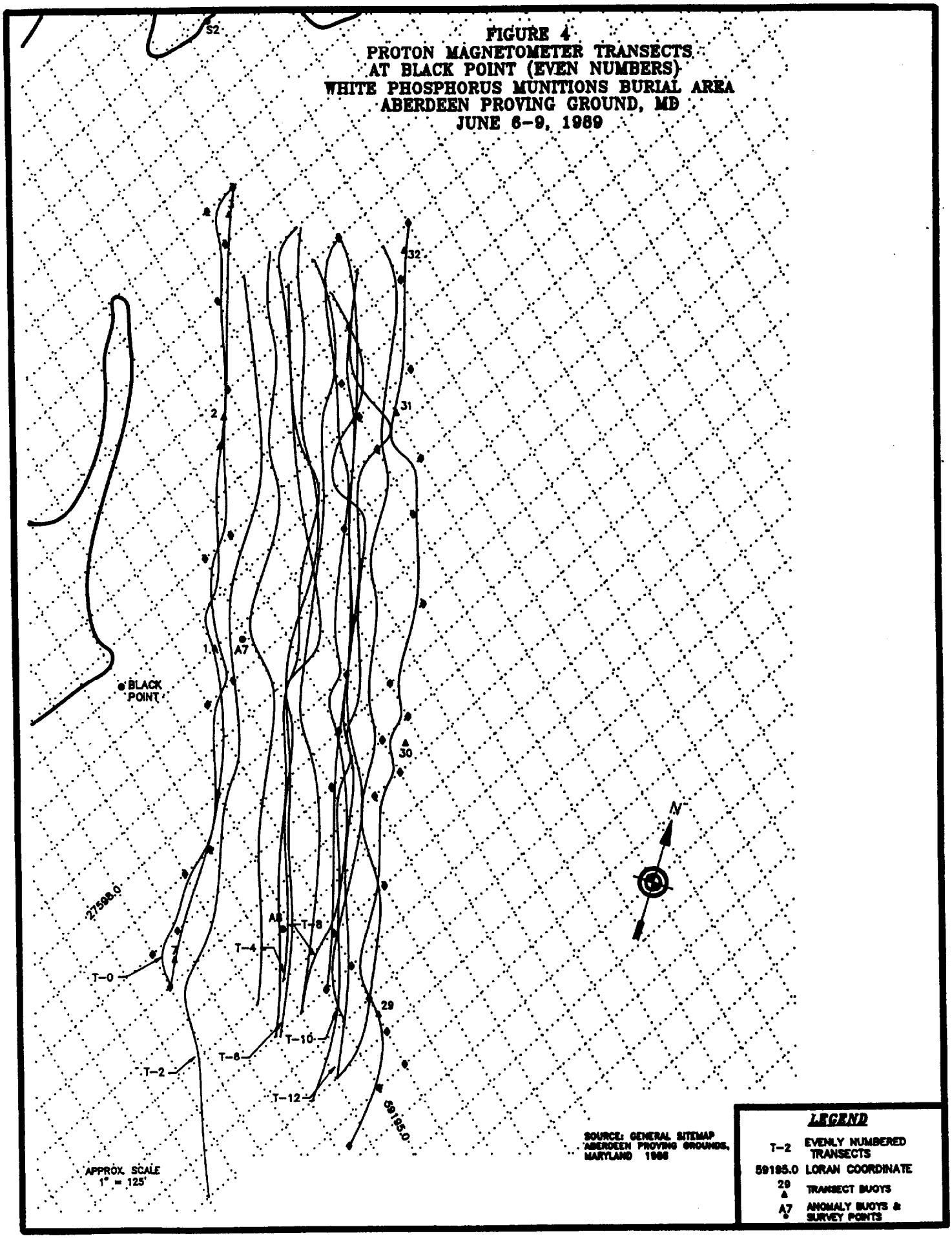


FIGURE 4
PROTON MAGNETOMETER TRANSECTS
AT BLACK POINT (EVEN NUMBERS)
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD
JUNE 6-9, 1989

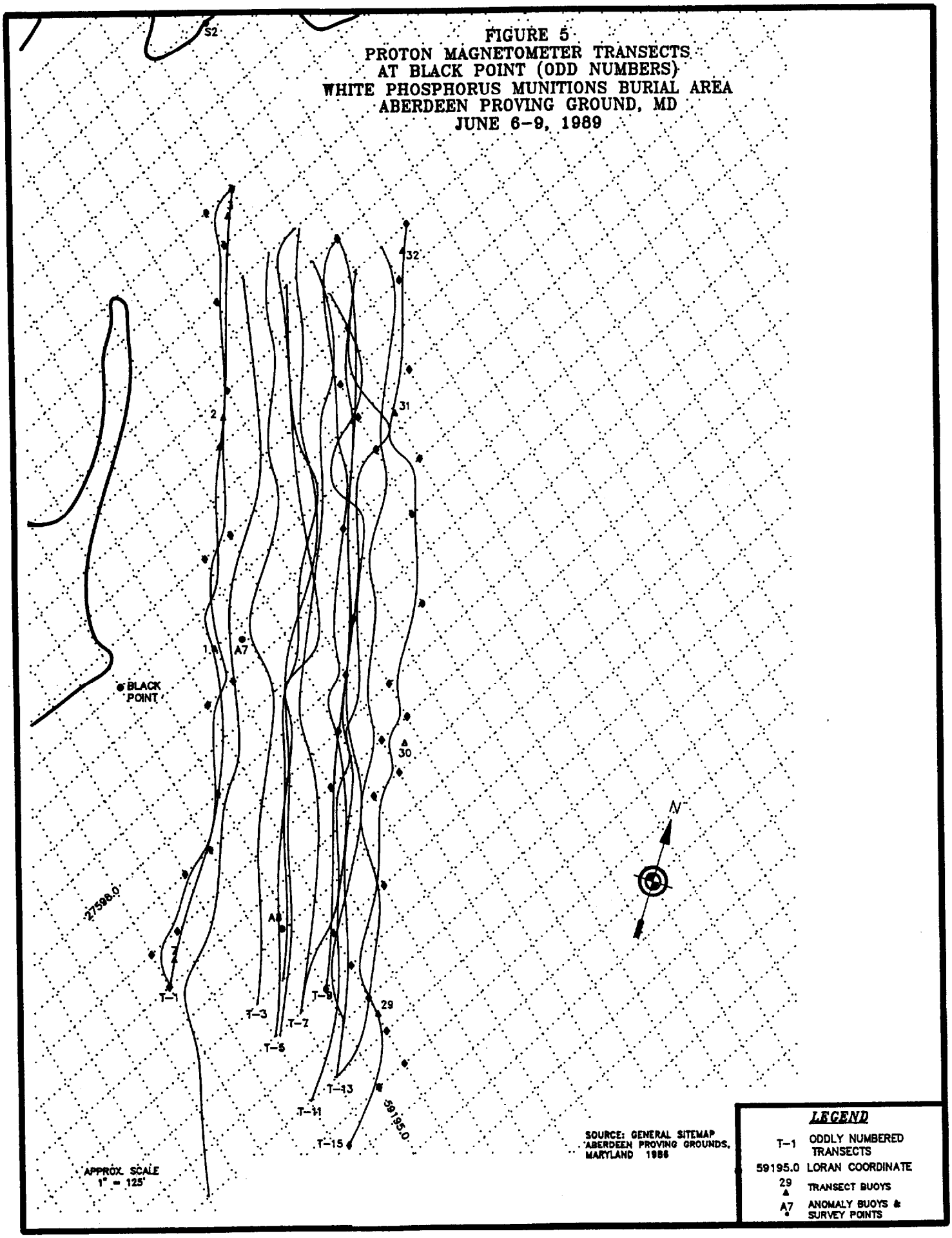


FIGURE 5
PROTON MAGNETOMETER TRANSECTS
AT BLACK POINT (ODD NUMBERS)
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD
JUNE 6-9, 1989

TABLE 1. LIST OF ANALYSES PERFORMED
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD

ANALYSIS	MATRIX
White Phosphorus	S,W
High Explosives	S,W
RCRA	S
EP Toxicity for Metals	S
EP Toxicity for Herbicides/ Pesticides	S
Reactive Cyanide	S
Reactive Sulfide	S
Ignitability (Flash Point)	S
Corrosivity	S
Total Organic Carbon	S
Grain Size	S
Metals	W
Base/Neutral/Acid Extractables	W
Pesticides/PCBs	W

S - SEDIMENT
W - WATER

The following water quality parameters were collected in-situ: pH, temp., dissolved oxygen, conductivity, salinity, oxidation-reduction potential.

2.4 Water Analysis

During the remote coring operation, water samples were collected for white phosphorus and high explosives analysis. Water samples were collected at the surface and 0.5 m off the bottom of each coring area. This included the reference area by Brier Point, the channel north of Gull Island, Black Point, and Areas I, II, and III. Water samples were collected with a Kemmerer bottle for bottom depths, and for surface samples by immersing the sample containers under the water surface.

In-situ water quality data was collected at each site using a Hydrolab Surveyor II. Parameters measured were dissolved oxygen, temperature, pH, conductivity, oxidation-reduction potential and salinity. Readings were taken at 0.5 m above the bottom and 0.5 m below the surface at all sites.

2.5 Analytical Methods

Elemental phosphorus was extracted and analyzed using the methods and techniques outlined in the method "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography" by R.F. Addison and R.G. Ackman (1970). Sediment and water samples were extracted with toluene and analyzed by gas chromatography/mass spectrometry. The mass spectrometer was selected as the detector because it can be programed to scan specifically for the P_4 molecule of elemental phosphorus. This eliminates the misidentification of phosphorus due to coeluting peaks or any interferences in the matrix.

Matrix spike and matrix spike duplicate samples were analyzed for each batch of ten samples for each matrix. Blanks were analyzed on each analysis day. The method detection limit using GC/MS was 1.0 ug/L for water samples, and 5.0 ug/kg for sediment samples.

The high explosives (Table 2) in water and soil were extracted and analyzed using Method No. UW01, Explosives in Water, and Method No. LW02, Explosives in Soil (Roy F. Weston, Lionville Lab).

Water samples were not extracted and were analyzed by injecting 10 ml of sample onto a sample loop and then analyzing by High Pressure Liquid Chromatography (HPLC). Soil samples were analyzed by extracting the sediment with acetonitrile, filtering the extract, and analyzing by HPLC. The HPLC was equipped with a diode array detector so wavelengths could be set for specific peaks to enhance sensitivity. Traditionally the wavelength is set at 250 nm.

Matrix spike and matrix spike duplicate samples were analyzed for each batch of 10 samples for each matrix. Blanks were analyzed on each analysis day. The method detection limit for nitroexplosives was 5.0 ug/L for water samples, and 1.0 mg/kg for sediment samples.

TABLE 2. LIST OF EXPLOSIVES ANALYZED
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD

HMX - Cyclotetramethylenetetranitramine
RDX - Cyclotrimethylenetrinitramine
1,3,5 TNB - 1,3,5 Trinitrobenzene
1,3 DNB - 1,3 Dinitrobenzene
Tetryl - Trinitrophenolmethylnitramine
2,4,6 TNT - 2,4,6 Trinitrotoluene
2,6 DNT - 2,6 Dinitrotoluene
2,4 DNT - 2,4 Dinitrotoluene

TABLE 3. LIST OF EP TOXICITY HERBICIDES/PESTICIDES ANALYZED
IN SEDIMENTS WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD

2,4 - Dichlorophenoxyacetic Acid (2,4 - D)
2,4,5-Trichlorophenoxypropionic Acid (2,4,5 - TP)
gamma-Benzenehexachloride (gamma-BHC)
Endrin
Methoxychlor
Toxaphene

2.6 Health and Safety

The risk of encountering UXO's in the area, in conjunction with the U.S. Army's safety procedures, required that coring activities be conducted remotely. The sampling procedure established a series of step-by-step standing orders for positioning the barge, readying it for sampling, evacuating the barge, remotely coring and retrieving, screening of the cores, transporting the cores, and sampling the core material. A 200-foot safety zone was established during all coring and retrieval activities. The remote operation of the vibracore was conducted from the tow vessel, and sampling personnel evacuated the barge using a motorized Zodiac inflatable boat.
Reactive Materials Management, Inc., was secured to provide assistance with standard UXO safety procedures. Their primary role was to survey and inspect the core for metal objects after retrieval and prior to handling, and assist sampling personnel in the event that munitions were found.

The maximum credible event (MCE) was discussed as well as procedures for such an event. The MCE for this investigation involved determining what was the most dangerous ordnance that would be encountered or entrained within the core tube. The MCE for this investigation was determined to be a 40 mm grenade; it was improbable that larger munitions would be entrained by the core.

The other major risk to personnel involved the potential contact with white phosphorus and WP munitions. The hazards posed to sampling personnel from WP included the potential for fire and explosion, and the inhalation of toxic fumes produced during its burning.

Several contingencies were put in place in order to minimize the WP hazard. A 55-gallon drum, filled with water and placed in close proximity to all core handling operations (i.e., on the barge, near the sample prep table), was to be used to submerge a core with an isolated flare-up. A pressurized hose was also available on the barge (via pump) and at the sample prep area to douse any core which could not be isolated and submerged. In the event of an incipient fire, personnel were instructed to don emergency respiratory equipment (self contained breathing apparatus) and evacuate the area immediately. As a back-up to the water systems available, a ten gallon pail filled with wet mud was placed on the barge and in the sample prep area.

In order to control incidental skin contact with WP or other contaminants which may have been contained in sediments, personnel involved with sample handling wore butyl aprons, rubber boots, nomex coveralls, and long sleeve butyl gloves. Hard hats equipped with face shields prevented sediments or contaminants from splashing into eyes. The use of protective clothing increases the potential for heat stress related injuries. Frequent breaks between sampling events, construction of shaded areas, and resupply of fluids eliminated the hazards associated with the sun and hot weather conditions.

3.0 RESULTS

3.1 Historical/Information Search

The results of the historical and information search led only to clues as to the location and contents of the WPMBA. The review of the Aberdeen Proving Ground records did not reveal the exact location or the contents of the WPMBA. A review of previous environmental impact assessment documents revealed that no documentation of the actual dumping location was found. It was stated in one of these reports that generally, records on the manufacturing and disposal operations prior to World War II did not exist or were largely incomplete (USATHAMA, 1980). Reportedly, the existence of the disposal site was based on interviews of former installation employees. One reference stated ..."the phosphorus disposal area, was established nearly 55 years ago to dispose of deteriorated World War I white phosphorus projectiles of various calibers. After disposal in 5 feet of water, this area was backfilled with earth. An additional two feet of fill was then placed over the area" (USATHAMA, 1980). Another references stated the following: "Area 12, just off Spesutie Island, was the site of a 1922 to 1925 dumping operation for World War I munitions containing WP. The site is about 6 ha (hectare)

in area. The WP is buried under about 0.6 m of fill, covered with 0.9 m of water. The amount of WP buried at this site is unknown" (ESE, 1981). Another excerpt stated: "The burial reportedly occurred in the waterfront region near Black's Point [sic], encompassing an area of 6 hectares (15 acres). When disposed, the munitions were placed in the tidal flats and covered with 0.6 m of sediment".

No evidence of a disposal site was observed in any of the historical aerial photographs reviewed. The most pertinent observation was the presence of what appears to be dredge spoils on Gull Island in the 1944 photo. The size of the island was greatly increased compared to earlier photos. Evidence of shoaling and exposed dredge spoils is also evident inshore, northwest of the island. The dredge spoils are not visible in the 1951 and 1956 photos, indicating the rapid dispersal of these sediments by winds, tides, and storms. The most obvious shoreline change is evident at Black Point. The photos indicate the shoreline is growing due to an accretion of sand in a northern direction towards the mouth of Mosquito Creek. The most recent aerial photo, from 1981, shows that this accretion has extended approximately half way to the mouth. Based on field observations, this process seems to have accelerated in recent years. At present, this peninsula has formed a protected cove across the mouth of Mosquito Creek and only an entrance way of approximately 10 meters is present.

A review of the NOAA historical bathymetric maps indicated: there was no indication of Gull Island on any of the maps dated prior to the dumping, Black Point was rounded with no visible peninsula, and the bathymetry of the area was similar.

The 1971 aeromagnetic map (USGS) that was examined did not indicate the location of the WPMBA. The map indicated that the intensity contours were bent towards Black Point and Mosquito Creek to the northwest, however, no maximum or minimum intensities were recorded in the WPMBA.

No direct information concerning the disposal site was available from the Library of Congress, the National Archives, or several white phosphorus manufacturers, including E.I. Dupont a manufacturer of WP during WWI.

Through the examination of U.S. Army bulletins and other federal regulations it was determined that bulk white phosphorus was transported in iron or steel containers. The significance of this is that if bulk white phosphorus was disposed at this site, it should have been contained in ferrous metal containers. Therefore, if still present, these containers would be detected by a proton magnetometer.

One major piece of information comes from Proclamation 2383, signed by President Franklin D. Roosevelt on January 24, 1940. Previously, two areas were designated as Migratory Waterfowl Closed Areas under a regulation adopted by the Acting Secretary of the Interior on December 12, 1939, under the authority of the Migratory Bird Act of July 3, 1918 (40 Stat. 755, 16 U.S.C. 704). One of the areas approved by the proclamation was entitled the "Phosphorus Area Unit".

Reportedly a large migratory waterfowl kill had occurred during the 1930's due to a release of white phosphorus from this area. Speculation is that this proclamation was a result of this kill.

This proclamation was the only written document found that specifically mentions phosphorus and delineates the boundary of the area. The size of this area encompasses approximately 130 acres (53 hectares). It was assumed that the area described incorporated the WPMBA.

One former employee of the base was contacted by APG (J. Wrobel, APG, Personal communication). He reported that a hurricane in the 1930's uncovered the WPMBA which led to a large waterfowl kill. He stated that "the ducks turned pink and died". The Army then placed a flood light on the area to discourage waterfowl use. No other persons with knowledge of the site were identified.

Several storms occurred during the 1930's which could have been responsible for eroding the sediment cap on the WPMBA, with the August 23, 1933 hurricane the most likely of these. This storm was actually termed a gale in the vicinity of APG with winds reaching 42 miles per hour (mph). The storm reportedly caused the greatest statewide damage of all time. Waves and tides caused the majority of damage and considerable erosion of the western shore of Chesapeake Bay was reported (Truitt, undated; USDA, 1933). Winds in the vicinity of APG were reported to be out of the northeast shifting to the southeast during the storm. Waves impacting the Black Point area from the southeast could have caused considerable erosion and led to the uncovering of the WP munitions. Two other hurricanes occurred, in 1936 and 1938, and both passed by the coast of Maryland and caused high winds inland.

Aberdeen Proving Ground supplied information concerning World War I munitions. In addition, several reference books were reviewed to determine the types of munitions that may have been disposed at the site. Three types of rounds which contained WP were listed by one reference (Prentifs, 1937). All rounds were constructed of steel. One, a Livens Projectile, contained up to 30 pounds (lbs) of fill (WP). Two sizes were in use, a 2 foot 9 inch, and a 4 foot projectile. The second type of round listed was a four inch Stokes mortar shell. The fill in this shell was 6.3 to 9.5 lbs of WP. The third type mentioned in this reference was a 4.2 inch mortar shell which contained approximately 8 lbs of WP.

Another undated reference, entitled "Chemical Techniques and Practices of Artillery", contained information on two other types of ordnance. The first was a 75-mm gun that used a shell containing 1.81 lbs of WP. The bursting charge contained 1.6 lbs of TNT. The second ordnance was a 155-mm howitzer that used shells containing 15.4 lbs of WP.

The APG records also included a more recent investigation involving samples collected from the channel east of the WPMBA (USACOE, 1982). Approximately eight sediment samples were collected in the channel between the Mulberry Point dock and buoy number 2. Additional samples were collected from Spesutie Narrows and disposal areas (presumable dredge spoils) northeast and southwest of the WPMBA. These samples were analyzed for metals, volatile solids, hexane extractables, chemical oxygen demand, total kjeldahl nitrogen, total phosphate, phosphorus, and grain size. No phosphorus was detected in any of the samples at a detection limit of <30 ppb.

3.2 Geophysical Surveys

The geophysical surveys were initially set up to screen the entire WPMBA with subsequent surveys focusing in on particular areas. A preliminary review of the first survey results indicated that no large (i.e. several acres) homogeneous burial area was evident. What was evident was the fact that numerous isolated magnetic field anomalies were present within the entire WPMBA. Some of these anomalies were outside of the WPMBA boundaries. A total of approximately 110 major anomalies were detected during these surveys (Figures 2 and 3). Transects T-6, T-7, T-10, T-11, T-14, T-15, and T-16 contained the majority of the anomalies and some of the largest in magnitude. These magnetic field anomalies indicate the presence of ferrous objects. This could include munitions from the WPMBA, UXO's from the firing ranges, construction debris, or any other object containing iron which may have been dumped in the area.

During the October, 1988 survey the proton magnetometer was utilized to screen Gull Island. This survey did not detect any major anomalies on the island.

The Black Point survey also detected numerous magnetic anomalies. Anomalies greater than 400 gammas were observed throughout the transects. Many of these anomalies were probably caused by single containers (cannon shells). However, no homogeneous areas were detected which would indicate the exact boundaries of the WPMBA. What was detected was a heterogeneous zone with the majority of anomalies concentrated in the near-shore transects (T-0 - T-9). Three areas were identified as containing clusters and the largest anomalies. One area was located directly off Black Point along transects 3 and 5; one was located approximately 600 feet north of Black Point along transects 5 and 7; and one was located approximately 400 feet south of Black Point along transects 5 through 9. In these areas, a significant number of anomalies occurred on at least four to six adjacent survey lines (approximately 80 to 120 feet across).

3.3 Remote Sediment Coring

The screening results indicated that none of the cores analyzed with the Scan X Jr. had nitroglycerine present at a detection limit ranging from 1 to 10 ppm NG.

The results of the elemental phosphorus (WP) analysis of the sediment cores are listed in Table 4. A total of 11 samples out of 71 contained elemental phosphorus. The concentrations ranged from 0.62 - 4.64 ug/kg dry weight, and 0.28 - 1.90 ug/kg wet weight. All concentrations are reported as below the quantitation limit and are approximate. Seventeen of the 60 cores collected were located directly in the assumed boundaries of the WPMBA (Figure 6). Four of these cores contained WP. Thirty-three cores were adjacent to or outside of the WPMBA. Six of these cores contained WP. Ten cores were located in the boat channel and one contained WP. The locations of the cores were distributed throughout the study area. One core contained elemental phosphorus in Areas I, II and the channel; three cores contained phosphorus in Area III; and five cores contained elemental phosphorus in the Black Point area. The core lengths ranged from less than one foot to nine feet. Three of the samples (17, 18, and 20) at Black Point were adjacent to one another. The three cores in Area III were also in close proximity, as were cores 3 and 31 of Area I and the channel, respectively. The remaining three cores were solitary. No elemental phosphorus was detected in the samples collected on Gull Island.

An examination of the core locations in conjunction with the target locations at Black Point reported by EMSL indicated that seven cores (9, 13, 14, 18, 19, 37, and 38) were within this target area. Only core 18 had detectable concentrations of WP. It appears that cores 14 and 37 were collected almost directly on top of two of the areas with major anomalies, neither detected WP. Cores 17, 20, and 25 with concentrations of WP were adjacent to this target zone. Nine other cores were adjacent to the areas outlined by EMSL, none detected WP. Core 11, which also contained WP, was outside of the EMSL survey area.

No high explosives were detected in any of the core samples.

Four of the eight metals tested for in the RCRA EP toxicity analysis were detected in the sediments in very low quantities. Arsenic (As) was detected in fifty-four samples tested. Arsenic levels ranged from 0.002 mg/l, core 36, in the Black Point Area to 0.18 mg/l, cores 11 and 56, in the Black Point Area and Area III, respectively. Barium (Ba) was detected in fourteen locations in each of four areas: Black Point - cores 15 and 36; Area II - core 49; Area III - cores 51 and 52; Channel - cores 26-31 and 33-35. Detected barium levels ranged from 0.08 mg/l, core 33, to 0.29 mg/l, core 30.

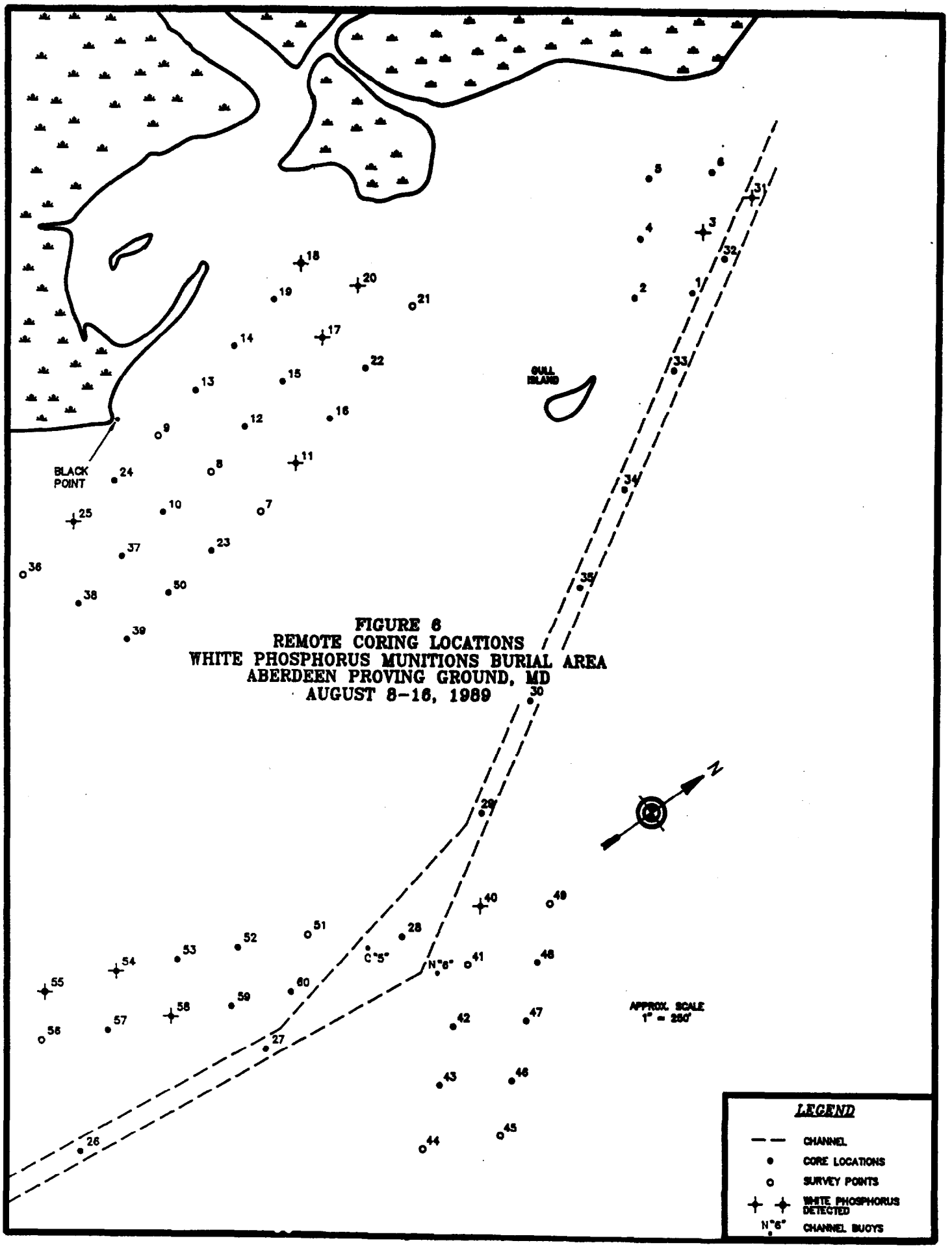


FIGURE 6
REMOTE CORING LOCATIONS
WHITE PHOSPHORUS MUNITIONS BURIAL AREA
ABERDEEN PROVING GROUND, MD
AUGUST 8-16, 1989

TABLE 4. RESULTS OF ELEMENTAL PHOSPHORUS ANALYSIS IN SEDIMENTS
ABERDEEN PROVING GROUND, MD
AUGUST 1989

Location	Core	Sample #	Phosphorus (ug/kg) Dry Weight	Phosphorus (ug/kg) Wet Weight	Core Length (ft)
Area I	3	4356	0.78J	0.42J	4.5
Black Point	11	4427	2.22J	1.00J	4
Black Point	17	4433	0.72J	0.30J	4.5
Black Point	18	4434	0.62J	0.28J	4.5
Black Point	20	4436	2.22J	0.71J	5.5
Black Point	25	4441	1.16J	0.94J	<1
Channel	31	4448	0.74J	0.34J	6
Area II	40	4457	2.41J	1.04J	8.5
Area III	54	4475	4.64J	1.90J	6
Area III	55	4476	3.38J	1.55J	6
Area III	58	4480	3.84J	1.80J	9

J = Analyte detected but below quantitation limit.

Cadmium (Cd) was detected only in the Channel Area, core 30, at 0.0087 mg/l. Mercury (Hg) also was detected only in the Channel Area, core 32, at 0.0014 mg/l. Silver (Ag), chromium (Cr), lead (Pb), and selenium (Se) were not detected in any of the EP Toxicity samples. All detected metal levels fell below cited maximum contaminant concentrations for EP toxicity (40 CFR Ch. 1 Sec. 261.24).

Herbicides and pesticides in the EP toxicity tests were undetected in all samples. Additional RCRA inorganic analysis included ignitability, corrosivity and reactivity for cyanide and sulfide. Cyanide reactivity was below the detection limit for all samples analyzed. Reactive sulfide was detected in 24 samples and ranged from 13.6 to 157.0 mg/kg. The flash point for all samples was greater than the limit of 200°F indicating the lack of highly combustible material. The corrosivity was also below the detection limit of 6.35 millimeters per year (mm/year) for all samples tested.

Sediment grain size analyses were performed to examine the composition and characteristics of the cores. Based on these analysis results and field observations the majority of cores exhibited a similar grain size composition. Most cores were predominantly silt with lesser amounts of clay and sand. This pattern was evident for Areas I, II, III, and the channel. Black Point sediments were similar offshore and north of the point. Close to Black Point the sediments were predominantly sand with increasing amounts of fines with depth. Peat and organic matter were common in the cores closer to shore and at a shallower core depth. Cores 44 and 45 in Area III contained peat at depths of 6.5 to 9 ft.

Total organic carbon concentrations in the sediments ranged from 34,000 - 340,000 mg/kg (3.4 -34 %). The majority of the cores contained less than 10 % organic carbon.

3.4 Water Analysis

Fourteen water samples were secured in representative areas during the coring operation in August, 1989. Samples were analyzed for elemental phosphorus and high explosives. There was no elemental phosphorus detected in any of the water samples at a minimum detection limit of 1.0 ug/L. The analysis for high explosives failed to reveal the presence of any of the nine explosive compounds tested for at the 5.0 ug/L minimum detection limit.

In-situ water quality parameters were consistent with seasonal variations common for this estuarine water body.

4.0 DISCUSSION

The purpose of this investigation was to answer questions related to a RCRA Facility Assessment. The primary purpose was to insure that the burial area was studied and any released wastes were identified and evaluated in subsequent study phases. The only waste for which there is evidence of a release is white phosphorus. The presence of WP in low concentrations in 11 cores indicates sediment contamination. The source may or may not be the WPMBA.

Other purposes of this investigation were to identify the boundaries of the WPMBA. Based on the results of this investigation it appears that boundaries for this burial area no longer exist. Due to the extended burial period and the dynamic nature of the bay, it appears that the material buried has been dispersed over a large area. It is also possible that isolated dumping episodes occurred over the general area, or that the WP detected is from more recent testing of munitions (UXO's). Another purpose of the RFA was to determine if releases of hazardous waste are occurring or have occurred. RCRA analyses indicated that the core samples would not be characterized as a hazardous waste. The historical information would lend credence to the reported uncovering of the WPMBA in the 1930's and subsequent release. The presence of trace concentrations of WP in the sediment indicate that releases have most likely occurred. However, the magnitude of past releases, and the present mass of WP remaining are unknown.

The results of the historical and information search revealed that no records were found which would identify the exact location and content of the WPMBA. The general area was determined based on references which were based on interviews of former base employees and the delineation of the area by the Migratory Bird Treaty Act. Relevant information indicated that white phosphorus was stored in ferrous metal containers and therefore should be detectable by proton magnetometers. An initial assumption that the shells were intact to a sufficient degree was found to be accurate since many targets were detected. In addition, the presence of WP in the areas where magnetic anomalies were found indicated that this was a correct assumption. A second important piece of information was the 1933 hurricane which was reported to have uncovered the WPMBA. Records indicating extensive erosion of the western side of Chesapeake Bay during this storm were located. This is further substantiating evidence that a release of WP occurred during the 1930's.

The fate of WP in the environment is an important issue at this site. "White phosphorus enters the aquatic environment as phossy water which is generated wherever WP is manufactured, stored under water, or spilled. Phossy water contains dissolved and colloidal WP as well as larger suspended particles. Data from manufacturing and munitions loading plants indicate that much of the WP in phossy water is dispersed or colloidal rather than dissolved. The mixture, whether dissolved, dispersed, or colloidal, reacts with dissolved oxygen and hydroxide ion to form various oxides, acids, and phosphine. In high concentrations as a suspension, it results in low to zero dissolved oxygen in the surrounding water; unreacted particles settle out and can be incorporated into aquatic sediments. These particles, when buried in anoxic sediments, are stable for long periods of time." (Environment Canada, 1984).

The lack of detectable quantities of WP in the water column indicates the stability of the WP in the sediments. However, it is possible that WP could be released to the water column during disruption of the substrate. Based on the low concentrations of WP that cause toxicity and the detection limit of 1 ug/l used in this study, it is important to look at concentrations that are potentially present. The current US EPA criteria (1986) for marine or estuarine waters is 0.10 ug/L of elemental phosphorus. An examination of the water chemistry of WP will lend some additional insight, however, data on reaction kinetics and decomposition products of WP in water are poorly defined (Environment Canada, 1984). Oxidation rates vary widely and appear to depend on pH, dissolved oxygen, temperature, metal ions, and the degree of dispersion of colloidal or suspended material. Half-lives of WP in seawater and freshwater were 240 and 150 hours, respectively, for an initial concentration of 1-50 ppm at $0^{o}C$ (Environment Canada, 1984).

A major factor controlling the rate of disappearance of white phosphorus apparently is whether it is suspended or dissolved. At concentrations below the solubility limit, and where a majority of the material is dissolved, it initially oxidizes in aerated water via a first order reaction to concentrations below 0.01 ppm. The material continues to slowly oxidize to equilibrium levels of 0.04 to 0.10 ppb. Other preliminary results, however, suggest that white phosphorus at low concentrations rapidly oxidizes to below 0.01 ppb. The disappearance rate from more concentrated suspensions apparently is controlled by diffusion and the protection of the phosphorus from the dissolved oxygen. It has been shown that saline water may influence the reaction rate. The authors suggested that perhaps salts coagulate the colloidal particles and make them less accessible to oxygen. It is suggested that WP may oxidize in a single step or react stepwise to form several oxides that are ultimately converted to phosphate as phosphoric acid. (Environment Canada, 1984)

It is possible that the WP sediment concentrations observed in the various areas are remnants of the disposal site. The dispersed nature of the WP may indicate that the exposure of the site in the 1930's spread WP over a wide area. Due to the assumed heavy sediment load in the water column during the 1933 storm, the WP may have been dispersed and then quickly covered by sediment. The anaerobic conditions observed in most of the cores would indicate that the WP would be stable for a long period of time.

Another explanation could be that the WP detected in each area was the result of isolated shells from prior testing which have deteriorated and released WP. If WP was tested at the adjacent ranges, the munitions could also have ended up in Mosquito Creek. Subsequently, contaminated sediment could have been transported downstream to the mouth of Mosquito Creek and the Black Point area. The lack of information on the life of WP in sediments, whether aerobic or anaerobic, makes it difficult to determine the source of this WP.

Low concentrations of elemental phosphorus in the water column have been documented as causing acute effects on aquatic organisms. Existing toxicity test data of WP on aquatic organisms was summarized by Sullivan et al. (1979). They report that freshwater and marine invertebrates are less sensitive to WP than fish. Various species of invertebrates were tested, with results for Chironomus tentans reported as a 48-hour EC_{50} ov 140 ug/l WP. EC_{50} is defined as the concentration of a contaminant that affects 50 % of the test population in a sublethal manner, such as immobilization. The lowest 48-hour EC_{50} was 30 ug/l for the freshwater cladoceran, Daphnia magna. Limited data was reported for marine invertebrates and included a 24-hour EC_{50} of 6500 ug/l for Gammarus oceanicus and a 168-hour EC_{50} of between 20 and 40 ug/l of WP for the lobster (Homarus americanus).

Fish are much more sensitive to the effects of WP. Of the freshwater fish studied, the bluegill (Lepomis macrochirus) was the most sensitive to WP with a static 96-hour LC_{50} of 2 ug/L (Sullivan et al., 1979). Marine and euryhaline fish are also very sensitive to WP. Atlantic salmon (Salmo salar) had a reported 96-hour LC_{50} of 2.3 ug/L whereas the strictly marine fish Atlantic cod (Gadus morhua) had a reported value of 2.5 ug/L WP (Sullivan et al., 1979).

Rapid bioaccumulation of WP has been documented and is related to the lipid content of the organism. Bioconcentration factors of between 20 and 100 have been reported for aquatic organism tissues, and in an extreme case up to several thousand in the Atlantic cod liver. Rapid removal from the tissues has also been reported if the organism is transferred to clean water (Sullivan et al., 1979).
The mechanism of toxicity of white phosphorus is reported to be related to its potent reducing powers. WP enters via the gills or intestinal tract, circulates in the blood and damages all tissues that it contacts. Damage appears to be related to exposure time and concentration (Sullivan et al., 1979). Gross effects of WP toxicity on fish include hemolysis with symptomatic reddening of the skin, jaundiced liver, and/or green intestines. In mammals, shock and cardiovascular system damage result in rapid death due to acute poisoning (Craig et al., 1978). Lower dosed deaths have been attributed to renal or liver failure and digestive tract damage. The reported threshold dietary level for retarding growth in rats is in the range of 0.003-0.07 mg P_4/kg/d, while the lethal dose is 7 mg/kg. Humans are about five times more sensitive than rats to the lethal effects of WP (NRCC, 1981; Sullivan et al., 1979).

Another concern is the impacts of contamination through the food chain. White phosphorus contamination in various fish tissues has been shown to be toxic or lethal if ingested by other fish or mammals including humans (NRCC, 1981; Sullivan, 1979). However, due to the reactivity of WP, the transfer of this element through the food chain would not be expected to last. In terms of long term food chain contamination, the potential from WP is considered nil (Environment Canada, 1984).

Based on previous investigations, the "no effect level" for WP in sediment probably lies below 2 ug/kg (wet weight). This value was the minimum sediment concentration found at which adverse impacts occurred to the benthic community in a freshwater system (Sullivan, 1979; Environment Canada, 1984). All WP wet weight concentrations were below 2 ug/kg for the WPMBA investigation. This would indicate "no effect" concentrations. The fact that these samples were composite samples may indicate that higher concentrations were present in distinct layers. However, the relative position in the core is important. If WP is close to the surface it will probably impact the benthic organisms; if WP is buried several feet under the surface it will not impact the benthic biota, unless uncovered.

Examining the data for marine environments indicates that sediment concentrations of WP above 70 ug/kg and water concentrations of 3 ug/L have been associated with impacts on the invertebrate community in the form of selected mortalities (Environment Canada, 1984). Furthermore, it is stated that concentrations of WP greater than 1 ug/L do not persist for appreciable periods of time, although resuspension of sediments may maintain a concentration of 0.5-1.0 ug/L in overlying water. Marine sediment concentrations of WP are also reported as stable (Environment Canada, 1984).

The threat of exposure of migratory waterfowl to WP is considered minimal. Eleven species of waterfowl associated with the Atlantic Flyway have been identified within the confines of APG. Dabbling ducks [mallard, black duck (Anas rubripes), wood duck (Aix sponsa)], diving ducks [canvasback, goldeneye (Bucephala clangula)], Canada geese, whistling swan, loon (Gavia inner), merganser (Mergus merganser), gallinule (Gallinula chloropus), and the American Coot (Eulica americana) have all been observed (Miller, etal. 1980). APG waters and wetlands are primarily utilized as winter habitat for all species cited. Wood duck have been observed during the summer breeding season. The diving ducks, loons, and mergansers are the species most apt to be of concern in relation to WP. Since these are all subsurface foragers, particularly feeding in the sediment, WP exposure is possible. Vegetative root stock, benthic invertebrates, mussels, and soft shell crabs are preferred sources for the associated species. Dabbling ducks feeding in shallow surface water on preferred aquatic vegetation may also be exposed to bottom sediments. Ingestion of WP could result during acquisition of the food source or directly from the food source itself. The observed waterfowl kill from 1933 is suspected to have occurred through actual consumption of available WP in the food and sediment. No additional waterfowl kills in the WPMBA have been cited since that time.

The absence or low levels of WP detected in the sediments of the WPMBA suggests a low probability of WP toxicity to lower food chain organisms. However, bioaccumulation to an upper level consumer, such as waterfowl, should be considered. Bioaccumulation of WP is manifested through its lipophilic tendency (Environment Canada, 1984). Waterfowl do exhibit high lipid levels due to their insulation requirements, therefore WP accumulation may be more pronounced. Avian toxicity data is minimal but the lethal dose has been cited as 3 mg/kg (NRCC, 1981). Several factors, however, suggest that bioaccumulation may be negligible. Waterfowl are utilizing the WPMBA waters during a few months in the winter season. Therefore, exposure to the small quantities of WP detected should be minimal. Additionally, waterfowl lipid content during the winter is elevated. This may serve to isolate any WP ingested and prevent manifestation of acute WP symptoms until metabolism can occur. Furthermore, large birds rather than more sensitive precocial young would be utilizing the food resource. For these reasons, sub-lethal effects on waterfowl should be isolated or of a low probability.

Previously cited references stated that the WPMBA was located in 0.9 m (3 ft) of water. Assuming this was low water, an examination of the bathymetry of the WPMBA (Figure 7) and the core locations indicate that 5 of the cores where WP was detected were in waters deeper than 4 feet (at low water). The remaining six cores were located in water depths of between 2 ft and 4 ft. The tidal range for this area of the Chesapeake Bay is approximately 0.8 to 2.4 feet depending on the tidal period. Even taking the tidal range into account, the former five cores are located in deeper water. These were the cores located in Areas II and III, and the channel. Changes in bathymetry have also most likely occurred due to storms, tides, and the closing of the Spesutie Narrows causeway in the 1960's. A comparison with historical bathymetric maps indicate that depth contours have changed in the WPMBA due to the accretion of sand in the Black Point area, the addition of Gull Island, and the dredging of the channel to Mulberry Point dock. The majority of the WPMDA's bathymetry is similar to historical maps, including Areas II and III.

The physical processes which occur within the WPMBA also need examination. Shorelines can be altered due to erosion and accretion. Erosion occurs due to the refraction of waves, with the wave energy concentrated on lands that extend into open water (Thurman, 1975). Storm waves can cause more erosion in one day than by average waves in one year. The rate of erosion is affected by the exposure of the shoreline, by the tidal range, and by the composition of the shoreline. A smaller tidal range results in greater erosion since there is less area to spread the wave energy (Thurman, 1975). A longshore current is established when waves strike the coast at an angle. This current of water carries sediment and is called longshore drift. The deposition of this sediment is a form of accretion. An example of this is Black Point, which can be termed a spit - a linear ridge of sediment attached at one end to land with the other end pointing in the direction of longshore drift (Thurman, 1975). Sand eroding from the coast south of the WPMBA is being transported along the coast and deposited on the spit at Black Point. This will occur when the wind and waves are out of the south, southwest, or south/southeast. Waves from the east/northeast to the east/southeast will reverse the longshore drift to the south/southwest. Winds out of the west, north, or northeast would probably not cause a drift due to the sheltered position of the area and the small fetch.

Periodic storms and shifts in winds and waves are the cause for changes in the geomorphometric processes at Black Point and the WPMBA. Accretion will occur when the longshore current and drift are in a northern direction. Erosion of the spit may occur when the direction is reversed to the south. An examination of the wind rose at APG (APG, 1988) indicates that winds which may cause accretion occur approximately 26 % of the time. Winds which may cause erosion occur approximately 16 % of the time, and the WPMBA is sheltered from winds approximately 58 % of the time. Wave of sufficient height and energy are needed to cause significant geomorphometric charges and only occur with high winds. Waves of sufficient height and energy are required to cause significant geomorphometric changes and only occur with high winds (i.e. 1933 hurricane). Winds greater than 17 knots in the erosional or accreting directions only occurred about 1 % of the time. This would indicate that significant erosion or accretion would only occur during high winds and the occasional severe storms.

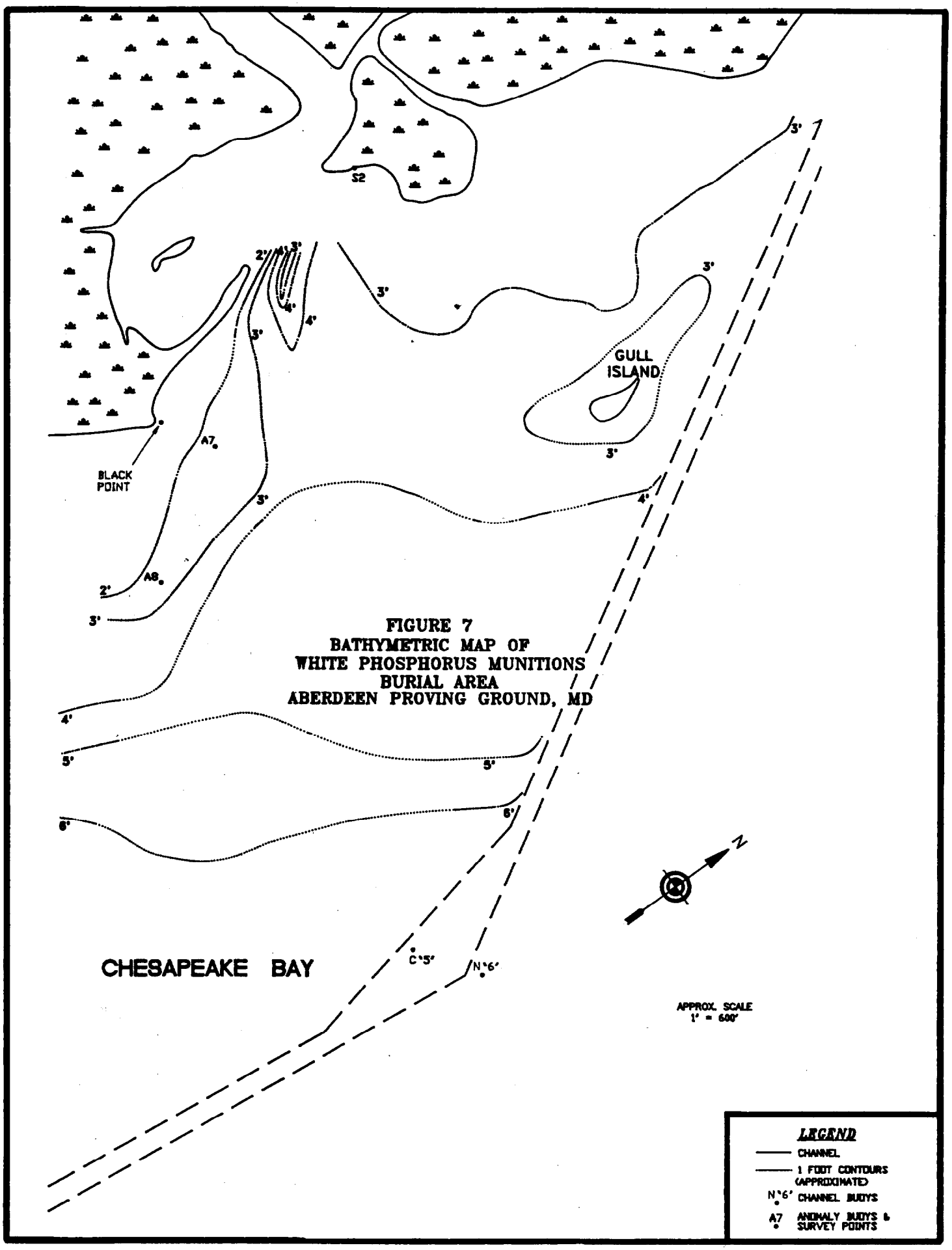


FIGURE 7
BATHYMETRIC MAP OF
WHITE PHOSPHORUS MUNITIONS
BURIAL AREA
ABERDEEN PROVING GROUND, MD

5.0 CONCLUSIONS

The lack of detectable quantities of WP in the water column, combined with the relatively low concentrations of WP in the sediments and the depth which they were found, indicates that WP is probably not being released into the water column. Based on the presence of WP in the sediments after such a long burial, it seems unlikely that large quantities are being released to the water. WP could be released when the sediments are disturbed due to severe storms or if dredging is conducted in the WPMBA. Without knowing the amount of WP originally buried it is impossible to determine how much WP has been released to the environment. It is possible that these detectable quantities of WP are the last remnants of the WPMBA, and the vast majority of the WP has already been released. Conversely, pockets of high concentrations of WP could be present in areas between core locations. Another possibility is that the observed WP concentrations reflect isolated shells fired from nearby ranges.

The following conclusions are listed to summarize the findings of this investigation:

1) Numerous metallic objects were detected surrounding and within the boundaries of the WPMBA. These objects may be ordnance from the WPMBA or from nearby firing ranges, or from other disposal activities.

2) No definitive boundaries for the WPMBA could be determined, although the largest concentration of magnetic anomalies (ferrous objects) was detected in the Black Point region.

3) No high explosives were detected in the sediments or waters of the WPMBA. Therefore no impacts upon the ecosystem are expected from high explosive contamination.

4) RCRA analyses indicated that the sediment cores would not be considered a hazardous waste.

5) No white phosphorus was detected in the water column of the WPMBA, therefore no impacts are expected upon the aquatic ecosystem. Releases of WP are not expected unless the WPMBA is disturbed.

6) White phosphorus was detected in trace concentrations (<5 ug/kg) in 11 of the 60 sediment cores. Concentrations which would indicate a large scale release or contamination problem were not detected.

7) White phosphorus was detected in all five areas sampled. These areas were widely spaced in the general WPMBA and no discernable contaminant pattern or trend was evident.

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Appendix B

Case Study: Remedial Action Implementation, Elizabeth, New Jersey

Following a fire at the Chemical Control Corporation Superfund site, Elizabeth, New Jersey, in August 1980, EPA and the U.S. Army Corps of Engineers cleaned up and removed waste gas cylinders from the site. Initially, the cylinders had been blanketed in sand and encased in overpacking. Most of the cylinders contained an explosive mixture. This explosive gas was treated and rendered inert before the cylinders were removed from the overpacks.

Remedial engineers sampled the 188 unmarked cylinders using a cylinder recovery vessel (CRV), which is a pressure vessel that remotely samples and evacuates cylinders with inoperable valves. The cylinders were stored in a vapor containment area (VCA) during this operation, and sampled and analyzed remotely from a laboratory 200 ft away. Analysis was performed using mass spectroscopy and Fourier transform infrared spectroscopy. The atmosphere in the VCA was monitored continuously and precautions were taken to protect against detonation.

Following analysis, the cylinder contents were treated using four principal methods:

- Flare stack, which allowed combustibles to be vented and ignited.
- Activated carbon adsorption.
- Liquid impinger scrubber, which reacted various gases with appropriate reagents in a packed column.
- Molecular sieve, which used ion exchange to bind chemicals for disposal.

Cylinder contents that could not be treated by one of the above methods were re-encapsulated for offsite treatment. The entire cylinder cleanup operation took approximately 8 weeks.

Figure B-1 is a schematic of a later generation system for waste gas cylinder management. This equipment was used to decommission approximately 2,000 cylinders from the Groce Laboratories Superfund site in

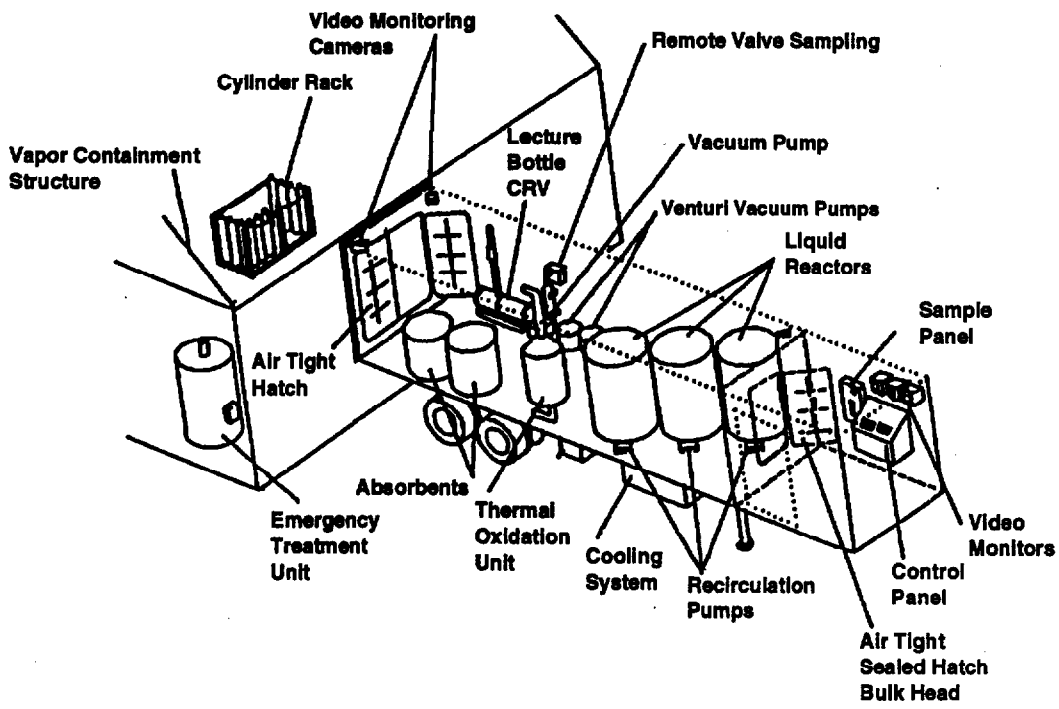

Figure B-1. Schematic of waste cylinder management system.

Greer, South Carolina. The system, which is enclosed in a mobile trailer, provided several separate treatment features:

- Three liquid reactors that treat reactive gases, including a caustic, acidic, and oxidizing unit, which can treat even class A poison dopant gases.
- A unit designed to thermally destroy flammable gases.
- Equipment for removal of oxidation products from the thermal oxidation system.
- Adsorption/absorption systems, which transfer gases to solid media.

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