WORK PLAN for

Environmental Restoration at the Pantex Plant

Submitted to the
Higher Education Consortium/Pantex Research Laboratory

for

Environmental Research

by

Randall J. Charbeneau
Principal Investigator
Center for Research in Water Resources
University of Texas at Austin

June 19, 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
TABLE OF CONTENTS

SUMMARY

BACKGROUND

Site Hydrogeology
Subsurface Contamination at the Pantex Plant
Remediation Objectives

CONSORTIUM STUDY PLANS

TASK ONE: AQUIFER TESTING, TRACER TEST, AND PRODUCED WATER TREATABILITY

Background
Aquifer Testing
Treatment of Produced Water
Purpose
Background - Adsorption
Background - Biodegradation
Background - Chemical Oxidation
Adsorption Treatability Studies - FY95
Biodegradation Treatability Studies - FY95
Adsorption Treatability Studies - FY96
Biodegradation Treatability Studies - FY96
Treatability Studies - FY97

TASK TWO: BIOREMEDIATION OF GROUNDWATER AND CONTAMINATED SOIL

Background
Bioremediation and Sorption of Perched Aquifer High Explosives
Background
Research Program Subtasks
Future Activities
Bioremediation of Contaminated Soils
Objectives
Bioremediation Processes
Treatability Studies
Scope of Work - Overview
Laboratory Screening
Bench Scale Testing
Pilot Scale Testing
Chlorinated Solvent In Situ Bioremediation
Purpose and Scope
Laboratory Studies
Biostimulation Studies
Microcosm Biodegradation Studies
Column Studies/Continuous Flow
Additional Investigations

TASK THREE: VADOSE ZONE REMEDIATION
Background
Air Permeability Measurements
VOC Adsorption Isotherms
Modeling of Soil Vapor Extraction Systems
Future Activities

TASK FOUR: CHROMIUM REMEDIATION
Background
Develop and Validate Analytical Procedures and Quality Control Programs
Develop Chemical Models for Chromium in the Vadose Zone and Perched Aquifer
Ion Exchange Studies
Redox Chemistry of Chromium
Identify Sources and Speciation of Chromium
Evaluate Sorption of Chromium on Soils

CONTINUING ACTIVITIES
SUMMARY

This report summarizes the Work Plans for activities associated with Environmental Restoration of the perched aquifer and contaminated soils at the Pantex Plant. The Higher Education Consortium/Pantex Research Laboratory is participating in the Consortium Grant to evaluate subsurface remediation alternatives for the perched aquifer at the Pantex Plant. Research activities will develop site characterization data and evaluate remediation alternatives for the perched aquifer and the overlying vadose zone. This report provides a summary of the study plans for research activities in the following four (4) task areas:

Task 1. Aquifer Testing, Tracer Tests, and Produced Water Treatment
Task 2. Bioremediation of Contaminated Soil and Groundwater
Task 3. Vadose Zone Remediation
Task 4. Chromium Remediation

The work plans cover research activities for the remainder of FY95, and proposed activities for FY96 and thereafter. A separate document will present more detailed plans for FY96 activities and budget requirements.

BACKGROUND

The Pantex Plant is located in the Texas Panhandle in Carson County, about 17 miles northeast of downtown Amarillo. The Pantex Plant facility consists of about 9,000 acres in the main Plant area, with an additional 5,900 acres leased from Texas Tech University for use as a safety and security buffer zone. The topography at the Plant is relatively flat, characterized by rolling grassy plains and numerous natural playa basins. The region is a semiarid farming and ranching area, with the Plant surrounded by agricultural land. Several significant industrial facilities are located in the general area.

The Pantex Plant was first used during World War II from 1942 to 1945 by the U.S. Army for loading conventional ammunition shells and bombs. The Plant was deactivated after the war and was vacant until 1949. In 1949 Texas Technological College (now Texas Tech University) in Lubbock, Texas purchased the full site for $1 for use in agricultural experimentation. The sale contained a recapture clause. In 1951, the Atomic Energy Commission began rehabilitating portions of the original Plant and constructing new facilities for nuclear weapons operations. Actual plant operations occur on approximately 3,000 acres in several widely separated zones. The operating zones and the land surrounding them required for the security buffer zones utilize approximately 30% of the plant’s total area. The remainder is used by Texas Tech Agricultural Research Operations for farming and grazing.

The principal operations presently performed at the Pantex Plant are the assembly and disassembly of nuclear weapons in the active stockpile using components received from other DOE plants and with chemical high explosive (HE) components fabricated at the Plant; operation of an experimental HE synthesis and characterization group;
surveillance testing of nuclear weapon components; obsolete nuclear weapons
disassembly; open controlled burning of the HE components and HE-contaminated
materials; and the storage, maintenance, modification, repair, and nonexplosive testing of
nuclear weapons components. Weapons assembly, disassembly, and stockpile
surveillance activities involve short-term handling (but not processing) of encapsulated
uranium, plutonium, and tritium, as well as a variety of nonradioactive toxic chemicals.
(Groundwater Protection Management Program Plan, DOE, 1994; 1993 Environmental
Report for Pantex Plant, DOE, 1994)

Site Hydrogeology

The primary surface deposits at the Pantex Plant are the Pullman and Randall soil
series. Beneath these soils is the Blackwater Draw Formation, consisting of a sequence
of buried soils with an upper unit of mostly silty clay and caliche, and a 20-foot thick
lower unit of silty sand with caliche. The Ogallala Formation, consisting of sand, silt,
clay, gravel, and some caliche, underlies the Blackwater Draw Formation. The base of
the Ogallala is an irregular surface that represents the pre-Ogallala topography. The depth
to the base of the Ogallala varies from 300 feet at the southwest corner of the Plant to 720
feet at the northeast corner of the Plant. Underlying the Ogallala Formation are the
sedimentary rocks of the Lower Dockum Group, consisting of shale, clayey siltstone, and
sandstone. The Lower Dockum Group is less than 100 feet thick beneath the Plant, and is
underlain by Permian rocks.

The principal groundwater units beneath the Pantex Plant are the Ogallala
and the underlying Dockum Group aquifers. The depth to groundwater consists of up to 460 feet
of unsaturated sediments that lie between the land surface and the Ogallala aquifer.
Within the Ogallala Formation there are two water-bearing units beneath part of the
Pantex Plant. On the eastern side of the Plant at a depth of about 300 feet there exists a
25- to 40-foot thick fine-grained zone (FGZ) which acts as a vertical barrier to infiltrating
water. Recharge appears to be focused through Playa 1 (from stormwater runoff and
Plant wastewater treatment effluent), the surface water drainage system, and possibly
diffuse non-playa recharge infiltration. This recharge moves downward through the
vadose zone and accumulates on the FGZ. As a result, overlying the FGZ is a perched
water zone with a saturated thickness varying from 0 to 100 feet. The lateral extent of the
perched water zone is unknown.

The main Ogallala aquifer lies below this perched water zone, and is the principal
water supply on the High Plains. At the Pantex Plant, the Ogallala saturated zone is
thickest to the northeast, where the Plant’s five production wells are located. Further to
the north and northeast of the Plant is the City of Amarillo’s Carson County Well Field.
The groundwater gradient beneath the Plant is to the northeast, toward the city’s well
field.

Subsurface Contamination at the Pantex Plant

Overall, the air, surface water, and groundwater quality near the Pantex Plant is
good. There is no evidence that contamination from the Plant has reached the main
Ogallala aquifer. Nor is there any evidence of recurrent releases of contamination to the
atmosphere. However, past waste management practices have resulted in contamination
of near-surface soils at some Plant locations, and the perched water zone beneath Zone 12 is contaminated with high explosives, solvents, and chromium.

Nearly 150 solid waste management units have been identified within 14 Plant areas where past releases of hazardous materials may have impacted the environment. These areas include the burning ground, high priority release sites, the Zone 12 groundwater assessment area, landfills, ditches and playas, leaking underground storage tanks, and other locations. The known contaminants and areas at the Pantex Plant where contaminants have been identified include:

- Trichloroethene (TCE), dichloroethane (DCA), chromium, hexavalent chromium, and high explosives (HE) species [Cyclotetramethylene (HMX), Cyclonite (RDX), 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT)] in the perched groundwater under Zone 12;
- TCE, DCA, and RDX in the perched groundwater under Zone 11;
- High explosives HMX, RDX and TNB in the perched groundwater under the south side of Playa 1; and
- Petroleum products from leaking underground storage tanks in the vadose zone.

Evaluation of the extent of the groundwater contamination is currently under way as part of the site characterization studies being performed by the University of Texas Bureau of Economic Geology, the U.S. Corps of Engineers, and Argonne National Laboratory. The leaking underground storage tanks have been removed or replaced. Evaluation of the extent of vadose zone contamination is pending. Potential problem areas which have not been fully investigated include:

- Chemicals (solvents and metals) from past operations in the vadose zone;
- Infiltration of contaminated perched groundwater through the perching layer and the lower unsaturated zone into the uncontaminated Ogallala aquifer below; and
- Migration of contaminated groundwater offsite.

**Remediation Objectives**

Personnel at the Pantex Plant have made a commitment to remediate subsurface contamination by the year 2000. For the most part, the extent of contamination has been identified through site characterization investigations. In addition, ongoing activities include two field investigations looking at bioventing of diesel fuel which was released from underground storage tanks, laboratory treatability studies (at PNL) for biodegradation of HE, and planned field investigations for biodegradation of HE beneath Zone 12. Basic plans for a comprehensive remediation program have not been developed.
CONSORTIUM STUDY PLANS

The primary objective of the Consortium's environmental research is to work with Pantex Plant personnel to investigate remediation options for HE, solvents and chromium in the subsurface environment. In addition, field testing will be performed to supplement ongoing site characterization studies with single and multiple-well aquifer tests to identify perched aquifer hydraulic characteristics. Given the relatively short time frame for remediation, these research activities will include the conjunctive use of laboratory and field experiments, with much testing done on the pilot scale of field experiments rather than the bench scale of laboratory experiments.

The Consortium's proposal for “Environmental Restoration at the Pantex Plant” (April 1995) identified four (4) major research tasks. The first of these involves aquifer testing, tracer tests, and produced water treatment studies. Task Two addresses bioremediation. Under bioremediation, three sets of activities are identified. These include bioremediation of high explosives, bioremediation of contaminated soils, and chlorinated solvent in-situ bioremediation. Tasks Three and Four address vadose zone and chromium remediation, respectively. Summary study plans for the four task areas are presented in the following sections.

TASK ONE: AQUIFER TESTING, TRACER TESTS, AND PRODUCED WATER TREATMENT

Background

Activities associated with this task include aquifer pumping tests and tracer tests to evaluate aquifer characteristics, and treatability investigations for groundwater which will be produced during pump-and-treat remediation efforts. Detailed work plans for aquifer and tracer tests will be provided in separate documents. In the following discussion, activities associated with the field tests are reviewed, and work plans for the treatability studies are presented. Proposed treatability studies for produced water overlap with other investigations for bioremediation and remediation of chromium contaminated waters. Research activities and expenditures will be coordinated between researchers associated with these investigations.

A number of monitoring wells have been completed in the perched water zone by the U.S. Corps of Engineers (COE) and other investigators as part of the site characterization studies. Many of these wells have had slug tests performed, which give rough estimates of local hydraulic conductivity of the formation. As an alternative to slug tests, single and multiple well aquifer tests involve production of groundwater over a longer time period. In particular, multiple well tests have the advantage of providing better and more representative estimates of the field hydraulic conductivity than slug tests. Future plans for aquifer testing by Consortium researchers is described.

One option for perched aquifer remediation is pump-and-treat. Contaminated groundwater is recovered through production wells. At the surface the water is treated using air stripping, carbon adsorption, biological treatment, or other methods. The treated
water may be returned to the aquifer via injection wells, or disposed of through surface drainage. Plans for treatment of produced water are described.

Aquifer Testing

Consortium investigators have performed two multiple well aquifer tests. The results from the first of these were presented in a TBEG Milestone Report. The second test was performed during the week of May 22, 1995, utilizing wells PTX10-1008, PTX10-1007, and PM-44. The work plan for that test was presented in a separate document, and results from the test are currently being analyzed and will be reported in the near future.

Two additional multiple well aquifer tests are currently scheduled. During July 1995 a piezometer will be placed near well PTX06-1014, located near the southeast corner of the Plant. At this location, a long-term aquifer test will be performed, starting in mid- to late-July. A second aquifer test will be performed as part of the development of the groundwater treatability system which will be located near well PTX06-1004. After one of the groundwater extraction wells is drilled and completed near PTX06-1004, the aquifer test will be performed using the two adjacent wells. Information from this aquifer test will be used to site the two additional groundwater extraction wells in the treatability system. This second test is currently scheduled for the second week in August. Separate detailed work plans will be presented for each of these aquifer tests.

In addition to the multiple well tests, single well recovery tests will be performed on a number of wells to correlate hydraulic conductivity estimates with those obtained using slug tests. These tests will be performed during the summer and fall 1995, and separate work plans will be provided for these tests. All of the hydraulic conductivity estimates will be very important for the groundwater model being developed by Argonne, and will provide important information for ultimate design of a perched water zone remediation system.

The saturated thickness of the perched water zone is small enough so that application of conventional pump-and-treat technology might be difficult. However, a remediation scheme where the produced water is treated at the surface and then injected to recirculate through the perched aquifer may be possible. Such a two-well tracer test will be performed and evaluated as part of this task during FY96. This test will investigate the possibility of groundwater recirculation with surface treatment as a remediation option. The test will provide information on the ability to control flow through the perched water zone, the significance of aquifer heterogeneities, and information that can be used to estimate remediation times using groundwater recirculation. This tracer test may use the wells completed as part of the groundwater treatability system. A separate work plan will be provided for the groundwater tracer test.

Personnel: These field studies will be planned, performed and analyzed under the direction of Randall Charbeneau (UT) and Ken Rainwater (TTU).
Treatment of Produced Water

Purpose
This research task will determine the treatability of produced groundwater that is contaminated with relatively low concentrations of mixtures of high explosives. The initial emphasis will be on granular activated carbon (GAC) adsorption to support the current Pantex plan for treating the produced groundwater. Biodegradation also will be evaluated in depth from several perspectives: as a separate treatment process prior to GAC, as a process occurring simultaneously with adsorption in GAC columns, and as a technique for off-line bioregeneration of exhausted GAC. Depending upon the relative biodegradability and adsorbability of the high explosives, an initial chemical oxidation process may be attractive, primarily to improve biodegradability. Chemical oxidants could include ozone or pair-wise combinations of ozone, ultraviolet irradiation and hydrogen peroxide.

Background - Adsorption
Treatability on granular activated carbon (GAC) can be characterized in several related ways for a given GAC: GAC usage rates (lb/1000 gal treated), GAC service life versus empty bed contact time (EBCT) and bed volumes fed versus EBCT. Once the treatability is determined, economic analyses and treatment system design can be performed.

Adsorption of mixtures of chemicals is very complicated because chemicals compete with each other for adsorption sites on the GAC. Therefore, a change in the influent concentration of one chemical can affect both its removal and the removal of the other chemicals in the mixture. A variety of experimental and computer modeling approaches can be used to characterize adsorbability and to predict how changes in concentration will impact treatment performance. These include:
- single and multi-component adsorption isotherm (equilibrium) experiments,
- batch adsorption kinetic experiments,
- rapid small-scale column tests (RSSCTs), and
- multi-component equilibrium and kinetic computer simulation models.

For a defined mixture, rapid small-scale column tests are a quick and accurate technique for defining treatability. These are continuous-flow column tests conducted at small scale in the laboratory. Using scaling relationships from mass transfer fundamentals, the laboratory results are then scaled to the anticipated performance of a full scale unit. The tests can be conducted quickly and require only a small volume of water. By running a series of three to five such tests, the treatability generally can be defined accurately enough for design and cost estimating purposes.

RSSCTs have limitations and, if possible, should be supported by other experimental and analytical approaches. In particular, RSSCTs provide no information from which to generalize the results. Each experiment defines treatability for one condition of influent concentrations and EBCT. Thus, if one or more of the influent concentrations change, the resulting effect on treatability can only be predicted by running an RSSCT under the new conditions. RSSCT data from other conditions are, at best, of very limited use in predicting performance for a new condition. Furthermore, more than
one set of scaling relationships exists for scaling RSSCT performance to larger scale performance. In the absence of supporting experiments, the selection of the appropriate scaling relationship is not always obvious.

RSSCT experiments should be complimented by other approaches in several ways. First, batch kinetic tests should be conducted to help define the appropriate scaling relationships. Second, single and multi-component isotherm experiments should be run to provide more basic information on adsorbability. Third, the isotherm, kinetic and RSSCT data should be used in combination with computer simulation models to provide a more effective tool for predicting how changes in operating conditions, especially influent concentrations, will affect performance. Once confidence in the computer models is established for a given contaminant stream, the models permit extension of the experimental results to other conditions without having to run experiments for all conditions of interest.

Background - Biodegradation

High explosives are generally considered to be resistant to biodegradation (or recalcitrant), but nevertheless subject to biodegradation under appropriate conditions. For such chemicals, development of microbial cultures that are adapted to the specific chemicals of interest is an important initial step. Further study of appropriate environmental conditions is important to ensure the success of biological treatment processes in dealing with these chemicals. Laboratory treatability studies are essential for resistant chemicals to establish that biological processes can achieve the treatment goals.

Investigation of biodegradation of high explosives will consist of a three-step approach:
- development of a microbial culture,
- delineation of appropriate growth conditions (nutrients, other environmental conditions) that maximize the rate of biodegradation, and
- performance testing of a variety of biological reactors.

Consortium researchers at Texas A&M have a culture established for TNT degradation, and will use this culture as a starting point for developing organisms to biodegrade other high explosives. The culture will be supplemented with organisms from a variety of sources, in particular organisms from Pantex soils contaminated with high explosives.

Several biological treatment process configurations will be evaluated as noted above. Consideration of separate biological treatment processes will be limited to attached growth processes because the relatively low concentrations and the potential for intermittent operation of the treatment facility lend themselves to such processes. Typical attached growth processes included packed or fluidized beds and rotating biological contactors (RBCs).

Background - Chemical Oxidation

An alternative approach to treating recalcitrant chemicals is to carry out a chemical oxidation step prior to biological treatment. The objective of the chemical oxidation step is conversion of the starting materials (high explosives) to a more biodegradable form, as opposed to complete destruction of the chemicals. Partial oxidation through chemical means can greatly enhance the biodegradability of recalcitrant
chemicals. Partial chemical oxidation in combination with biodegradation also retains a large part of the economic attractiveness of biological processes. Ozone, ultraviolet (UV) irradiation, and hydrogen peroxide are candidate chemical oxidants. Ozone might be used alone, but the other two would only be considered in pair-wise combinations. The combination of UV and hydrogen peroxide probably is most attractive for ease and simplicity of operation. The need for chemical oxidation is largely dependent on the success of testing program for biodegradation alone. If all the high explosives prove to be readily biodegradable after acclimated cultures are developed, chemical oxidation will be tested only to a limited extent. If the biodegradation rates are slow or complete biodegradation is difficult, a more extensive chemical oxidation test program will be conducted.

Adsorption Treatability Studies - Fiscal Year 1995

The treatability studies will focus on two goals:

- laboratory screening of a variety of GACs to provide data for selection of the best GAC for the Pantex site.
- a preliminary characterization of adsorption in support of pumping tests planned for the summer and fall of 1995.

Because of the short time frame, only RSSCT experiments will be conducted to support the selection of the appropriate GAC and to define the adsorbability. Furthermore, only the groundwater now available will be used in the testing; therefore, only a single mixture of high explosives will be evaluated, instead of a broad range of mixtures.

A variety of GACs (5 to 10) will be selected for study after consultation with Pantex personnel. An initial RSSCT will be run for each GAC at a common EBCT. The initial screening test should eliminate most GACs. Additional screening tests at several EBCTs will be conducted for the two or three most attractive GACs. The results will then be scaled to anticipated full scale performance using the scaling relationship that is most likely to apply. A plot of GAC service life versus EBCT will be developed. Concentrations of the applicable explosives, as well as total organic carbon (TOC) will be measured. These tests should identify the best GAC, establish the order in which the chemicals will breakthrough the bed, and estimate the expected service life of the GAC. The results, especially for service life will be specific to the influent concentrations tested. Additional testing is needed to study other concentrations.

Personnel: The experiments will be conducted at the University of Texas under the direction of Gerald Speitel Jr.

Biodegradation Treatability Studies - Fiscal Year 1995

Biodegradation treatability studies will focus on developing a culture that is capable of aerobically biodegrading the mixture of high explosives encountered at Pantex. Organisms from various sources will be combined in batch reactors and exposed to high explosives to develop a stable culture that is adapted to the biodegradation of high explosives. Once an adapted culture is developed, further characterization of the culture will be performed. The dominant organisms in the culture will be identified and
favorable growth and environmental conditions will be characterized in support of fiscal year 1996 biological treatment process studies. The biodegradation treatability studies are described in more detail under Task Two.

Personnel: Culture development will be undertaken at Texas A&M University under the direction of Robin Autenrieth. Culture identification and characterization will be performed at Texas Tech University under the direction of Caryl Heintz.

Adsorption Treatability Studies - Fiscal Year 1996
The primary goal of these adsorption treatability studies is a broader characterization of adsorption to cover the full range of conditions anticipated during the remediation operations at Pantex. This portion of the work will include a multi-step experimental and computer modeling effort, as outlined below.

1. Single component adsorption isotherms will be developed for each explosive of interest over the applicable concentration range, using uncontaminated Pantex groundwater as the background matrix. These experiments provide fundamental information on the adsorbability of the chemicals, and provide essential information for the computer modeling.
2. Multi-component adsorption isotherm experiments will be conducted on selected mixtures to assess the degree to which the theoretical model of competitive adsorption matches the actual data. This issue is important in assessing the accuracy of computer simulation of GAC column performance.
3. Single component batch kinetic experiments will be conducted on one or more of the explosives to generate adsorption kinetic parameters needed by the computer models. These experiments will also provide insight into the appropriate scaling relationships for the RSSCT data analysis.
4. A set of three to five mixtures will be defined for further study through RSSCT experiments. The mixtures will span the range of concern at the Pantex site. Three to five RSSCT experiments will be conducted on each mixture to define the service life versus EBCT relationship for each.
5. Computer simulations will be run independently for each of the mixtures and compared to the RSSCT results as a confirmation step in determining the utility of computer models in predicting GAC performance for these chemicals.

Personnel: The experiments will be conducted at the University of Texas under the direction of Gerald Speitel Jr.

Biodegradation Treatability Studies - Fiscal Year 1996
The primary goal of this research is the demonstration of successful operation of one or more biological treatment processes. Three approaches to biological treatment will be evaluated. First, biological treatment as a separate step prior to GAC polishing will be considered. Attached growth processes, such as packed bed, fluidized beds or RBCs will be tested. Second, biological growth will be established within GAC columns so that biodegradation and adsorption occur simultaneously in a single reactor, which may be economically attractive. Third, off-line bioregeneration of exhausted GAC will
be studied. In this approach, exhausted GAC is contacted with a recirculating stream of acclimated organisms to promote desorption and biodegradation of adsorbed chemicals. In this way, the GAC is regenerated and the high explosives are destroyed.

This work will involve a multi-step experimental and computer modeling effort as outlined below:

1. Measurement of biodegradation rate constants for the chemicals of interest.
2. Laboratory scale bioreactor experiments with the candidate treatment processes to determine the degree of treatment that can be accomplished as a function of influent concentrations, detention time and other operating conditions.
3. Testing of the applicability of computer simulation models for the purpose of extending the results to other influent concentrations.
4. Measurement of desorption rates off the GAC to determine the rate and possible extent of GAC regeneration for the off-line bioregeneration process.

Personnel: The work with separate biological treatment processes and simultaneous biodegradation and adsorption in GAC columns will be conducted at the University of Texas under the direction of Gerald Speitel Jr. and can be completed over a period of 18 to 24 months. Off-line bioregeneration, including the desorption experiments, will be studied at Texas A&M University under the direction of Robin Autenrieth.

Treatability Studies - Fiscal Year 1997

The biological treatment studies started during fiscal year 1996 would be completed during this year. Also, chemical oxidation studies would be undertaken during this year. The extent of these studies will be largely determined by the success of the biological treatment work. If some of the high explosives prove to be especially recalcitrant, an extensive evaluation of chemical oxidation will be undertaken. Otherwise, a limited tested program is envisioned. This work will be carried out at the University of Texas or jointly at the University of Texas and Texas A&M University.
TASK TWO: BIOREMEDIATION OF GROUNDWATER AND CONTAMINATED SOIL

Background

Bioremediation of unsaturated soil and groundwater involves the use of microorganisms to convert contaminants to less harmful species in order to remediate contaminated sites. Bioremediation of organics in the saturated and unsaturated zones is an attractive remediation technology because of its low cost and high level of public acceptance. Research as part of this task will investigate the application of bioremediation technology at the Pantex Plant for HE, solvents, and petroleum hydrocarbon fuels. The initial efforts will focus on HE.

Three areas of investigation will be pursued. The first involves bioremediation and sorption of perched aquifer high explosives. These investigations are coordinated with the bioremediation treatability studies outlined under Task One. The second area of investigation concerns remediation of contaminated soils. This work will evaluate biodegradation for contaminated soils, and identify treatment technologies and engineering requirements. The third investigation area will address in-situ biodegradation of chlorinated solvents. While initial investigations are underway, concentrated efforts on chlorinated solvents will start in FY96.

Bioremediation and Sorption of Perched Aquifer High Explosives

Background

Several high explosive contaminants, including RDX (Research Development Explosive), HMX (High Melting Explosive), and other nitroaromatic explosives including TNT (trinitrotoluene) and TNB (trinitrobenzene), have been detected in the soil and groundwater at the Pantex Plant. As organic compounds, the potential for natural and artificial biodegradation of the HEs is of great interest. Natural bioattenuation may be affecting the transport of the HEs in the perched aquifer, and might be stimulated artificially for in-situ treatment. More immediately, the Battelle/Pantex Environmental Restoration group will install a traditional pump-and-treat system that includes removal of HE by adsorption onto granular activated carbon (GAC). Once the HE is sorbed to the GAC, the GAC may not be acceptable for typical regeneration or disposal, so on-site treatment of the GAC to separate or degrade the HE on the GAC will likely be necessary. In this task, the research team will combine its previous experience with microbial biodegradation of TNT with investigation of potential HE degraders in subsurface soils and groundwater from the Pantex site. The results will be useful in development of GAC treatment in a biofilm reactor, as well as in description of the biotransformations possible with the indigenous microbes.

Remediation of the organic compounds at the Pantex facility will likely require the incorporation of several treatment technologies for complete restoration. Bioremediation offers either an alternative treatment technology or a complimentary process to a treatment train that is typically cost effective and complete. Overall
remediation of contaminated sites have benefited from the incorporation of biological processes as a primary component or a complimentary component at numerous sites. Microorganisms and abiotic processes can sometimes transform target compounds to undesirable intermediates if the biodegradation or abiotic processes are not well understood. The purpose of the research studies is to elucidate the biodegradation process for the identified HEs (RDX and HMX primarily) through a series of bench and field scale experiments. The cooperative efforts of the investigators at the three institutions provides an excellent collection of expertise. This team of researchers provides the overall breadth and depth needed for the contamination complexities at this site.

**Research Program Subtasks**

Sorption and bioremediation are not separate issues since the bioavailability of contaminants is largely governed by their affinity for the solid phase. The study program for bioremediation and sorption of perched aquifer HEs includes a number of related subtasks. The benefits from the sorption studies include determination of the mass of HEs sorbable to mass of activated carbon, expected partitioning to biomass, sorptive capacity of soil, desorption from soil, and information on polymerization concerns. The bioremediation studies will provide a characterization of microorganisms, an understanding of the ability to use HEs as a C or N source, nutrient requirements for microbes, substrate utilization rates (feed rate for reactors), primary degraders (need for bioaugmentation), toxicity to microbes, rate and extent of biodegradability, transformation of HEs and formation of intermediates, and intermediate by-product characterization.

The subtasks are identified and described in the following:

- **Subtask 1:** Application of TNT-degraders to HMX and RDX. In previous research at Texas A&M University, eight different bacteria have been isolated that have demonstrated the capability of degrading TNT. These bacteria will also be evaluated individually and in combination to determine their potential for degradation of HMX and RDX. Activities in this subtask will be centered at TAMU and could be completed by August 31, 1995, if HMX and RDX are made available quickly.

- **Subtask 2:** Characterization and Optimization Study. Samples of the known TNT-degrading bacteria will be sent to TTU for evaluation of their phenotypic metabolic properties using the Biolog apparatus. In addition, optimum growth conditions for individual organisms will be evaluated at different combinations of carbon and nitrogen sources. Evaluation of the known TNT-degraders will be carried out at TTU and should be completed by August 31, 1995. After HMX- and RDX-degraders are isolated from Pantex soil and/or water samples, those microbes will also be evaluated for phenotypic metabolic properties and optimum growth conditions. If HMX and RDX are made available quickly, as stated in subtask 1, this part of subtask 2 should be completed by October 31, 1995.

- **Subtask 3:** Development of Support Culture Media. With the information from the work on the known TNT-degraders that are also found to degrade HMX and/or RDX, a culture medium will be devised that can support the microbial population and sustain the HE-degrading capability. This work will be centered at TAMU and
should be complete by October 31, 1995. If HE degraders are isolated from soil and groundwater from the Pantex site, a similar effort will be spent on those microbes. This second effort should be completed in fiscal year 1996 by December 31, 1995.

- Subtask 4: Sorption of High Explosives. The sorption experiments will be conducted at both UT and TAMU. Experiments at UT are considering the extent of sorption and desorption of high explosives HMX and RDX on activated carbon. Additional studies will also evaluate the rate and extent of sorption and desorption on soils. In conjunction with these efforts, the rate and extent of partitioning of HEs to biomass will be investigated at TAMU where similar studies are currently being conducted on TNT.

Personnel: These studies will be directed at Texas A&M University by Robin Autenrieth and Jim Bonner, at Texas Tech University by Caryl Heintz, and at the University of Texas by Gerald Speitel Jr.

Future Activities

Several additional subtasks are anticipated for fiscal year 1996. It should be recognized that HE-contaminated GAC will likely be generated both in pumping tests planned by the Higher Education Consortium during July and August 1995 and by the Battelle/Pantex ER group's treatability study starting in the fall of 1995. First, experiments are needed to establish the best combination of TNT- and HE-degrading bacteria for biofilm construction on GAC. Next, the actual performance of the biofilm in HE biotransformation must be quantified under actual remediation conditions, using a pilot system. The pilot system will then be scaled up for actual field application. Operational field data on variables, such as pH and temperature, that affect system performance will also be evaluated and used to modify the system. In addition, this research team will cooperate with the Vadose Zone Remediation team to evaluate the potential for in-situ processes in the saturated and/or unsaturated zone.

Bioremediation of Contaminated Soils

Objectives

The purpose of this part of the work plan is to describe the treatability studies that will be used to determine: a) the extent to which bioremediation can be used to remove quantities of high explosives and volatile organics in excavatable soils at the Pantex Plant, particularly those at Zone 12, b) the extent that bioremediation can immobilize the metals that exist in these soils, and c) the parameters that affect the use and performance of large scale bioremediation processes for these soils.

Based on the results of these treatability studies it will be possible to: a) determine the technical and economic viability of in-situ or ex-situ bioremediation processes for the site soils and b) develop general design criteria for a pilot scale bioremediation unit that can establish actual costs and operating criteria for a potential full scale bioremediation unit.
Bioremediation is a candidate technology for these soils because:

a) the process has been shown to be effective with soils containing high explosives and volatile organics
b) the process has been shown to result in immobilization of residual organics and metals in soils
c) the process has been shown to reduce eco-toxicity concerns associated with chemicals in soils
d) the soils at the site contain chemicals that can leach to the groundwater, thus bioremediation will reduce the source of chemicals contaminating the site groundwater, and
e) the soils at the site (clayey silts) are of a type that are amenable to bioremediation processes.

Thus, the overall objectives of these studies are to:

- Develop sound scientific information, obtained through laboratory and field studies, to provide a solid basis for site specific technical and regulatory decisions,
- Demonstrate an innovative regulatory approach, based on reduced mobility and eco-toxicity of remediated waste constituents and on decreased relative risk, that may be considered for other soils at the Pantex Plant,
- Demonstrate that the Department of Energy (DOE), working in a cooperative effort with an experienced university research program, can develop appropriate, innovative, environmentally sound solutions to a major waste management problem.

**Bioremediation Processes**

For existing conditions at the Pantex Plant, DOE has identified the need for a remediation and groundwater contaminant system that effectively controls the migration and concentration of contaminants to and within the perched aquifer beneath the plant. Bioremediation can be an effective remediation for the soils at the site thus controlling the migration of chemicals to the perched aquifer.

Bioremediation involves the microbial degradation of relatively complex substances into less complex end products, often carbon dioxide and water. Bioremediation processes accomplish biodegradation, immobilization, and detoxification. Bioremediation processes have been recognized as an environmentally sound, relatively inexpensive, and efficient method to treat industrial and other man-made chemicals.

Bioremediation, particularly ex-situ land treatment and composting type processes, has been demonstrated to degrade soils containing chemicals from high explosives. In addition, the director for these studies, Raymond Loehr, has had experience with the bioremediation of RDX, HMX, and TNT as part of treatability studies conducted for the U.S. Environmental Protection Agency.

Despite the application of biological processes to many waste treatment and remediation situations, the use of bioremediation for contaminated soils continues to suffer from poor understanding and acceptance. This is particularly true for the immobilization and detoxification performance achieved by bioremediation processes. Available data indicates that the residues from bioremediation processes pose little risk to
human health and the environment. Additional data are needed to show the limited risk associated with the bioremediation process residues and to develop relative risk "clean-up" standards or criteria.

There are many bioremediation processes that can be used. These include: a) passive, natural bioremediation in which natural consortia of microorganisms at a site are able to degrade hydrocarbons and other chemicals, b) in-situ processes such bioventing which can be used for sorbed, volatile and semi-volatile chemicals in unsaturated soils, and c) ex-situ processes such as prepared bed land treatment, slurry reactor, or pile composting type methods that can be used for excavated impoundment sludges and contaminated soils.

The proposed treatability studies will identify the fundamental factors to determine: a) if bioremediation is likely to be an effective process for remediation of the Pantex soils, b) which bioremediation processes may be the most effective, and c) design and operating parameters that can be used to estimate the cost-effectiveness of bioremediation processes for these soils.

**Treatability Studies**

The assessment of the feasibility of bioremediation for a specific site requires a thorough understanding of the fundamentals, mechanisms, and processes of bioremediation. For each situation, the mix of contaminants and environmental conditions are unique. Thus, to evaluate the feasibility of bioremediation for a situation, both detailed characterization and treatability studies are needed.

- **Characterization.** Characterization of a contaminated soil includes an assessment of organic and inorganic chemical compositions, chemical form, (free, aqueous, sorbed), biological activity, toxicity, soil chemistry (pH, permeability, exchange capacity, etc.), nutrient content, and moisture content. These data help determine the potential for bioremediation and indicate possible alternatives.

- **Treatability Studies.** Laboratory treatability studies typically are done in multiple steps. The first, initial screening, confirms that biological treatment is viable and identifies the conditions required to stimulate the available biomass and make the system function (e.g., nutritional amendments, dilution effects, need for pH control.) A bench-scale study then determines the fate of contaminants and defines the process in greater detail. It also provides information about: the kinetics of contaminant disappearance; contaminant fate; volatilization of organics; aeration rate; and disposition of metals. Evaluation of this information allows an estimate of the ultimate removal efficiency and a determination of the appropriate bioprocess to use. The data from the characterization and treatability studies then are used to estimate process design and economics. Operating parameters, monitoring and control requirements, and implementation milestones can be defined as the operation proceeds.

Treatability studies provide valuable site-specific data for a given situation and serve two primary purposes: a) to aid in the selection of the remedy, and b) to aid in the implementation of the selected remedy. Treatability studies indicate whether a given
technology, in this case bioremediation, can meet the expected cleanup goals for the site and can establish the design and operating parameters to achieve desired performance.

As indicated, a multi-phase or tier approach is considered for treatability studies: a) laboratory screening, b) bench-scale testing, and c) pilot-scale testing. Under some conditions, a fourth tier, field scale testing of a technology also may be a part of treatability studies.

Treatability studies provide critical performance and cost information needed to evaluate and select treatment process or system alternatives. The selection of the most appropriate process or system is based on achieving the criteria noted in Table 1. Regulatory acceptance as well as community acceptance are other criteria that may affect decisions about using a particular process or system.

Table 1: Criteria For Selection of a Site Specific Treatment Process or System

- overall protection of human health and the environment
- ability to achieve identified performance or clean-up goals
- short and long-term effectiveness
- implementability, including meeting space and time constraints
- cost

Scope of Work - Overview

Little is known about degradability of the chemicals in the Pantex soil or about the more feasible bioremediation processes, if the chemicals are able to be biodegraded. Therefore, a multi-phase approach will be used to evaluate the feasibility of bioremediation processes for the Pantex soils. In addition, the treatability studies will identify the extent that immobilization of metals may occur and any eco-toxicity problems are reduced.

The treatability phases that will be involved include: a) laboratory screening studies, b) bench-scale testing, and c) possibly pilot scale testing at the site. Laboratory screening is used to establish the validity of a technology. These small scale screening studies yield data that can indicate the potential of a technology to meet performance goals and can identify parameters for investigation during bench- or pilot-scale testing. They generate little, if any, design or cost data and rarely are used as the sole basis for the selection of a remedy.

Bench-scale testing is intended to determine the larger scale performance for the technology. Such testing can verify that the technology can meet expected cleanup goals and can provide information that relates to the criteria in Table 1. Bench-scale testing may also provide cost and design information.

Pilot-scale testing is a larger scale testing intended to provide quantitative performance, cost, and design information and can produce data required to optimize performance. Pilot scale testing can occur in the field with large scale units.
Laboratory Screening

This first step is designed to establish the general feasibility of bioremediation quickly and inexpensively. In this case, it will be used to answer the question: Can bioremediation remove the organic chemicals in the Pantex soils and to what levels?

Laboratory screening provides qualitative data used to evaluate the validity of bioremediation as a treatment process for the Pantex soils. No cost or design information is generated. This step requires minimum sample replication. In addition, a low level of QA/QC is sufficient because a remedy that is found to be valid generally will undergo bench-scale testing.

For this Pantex effort, several soils representative of the site characteristics, chemicals, and concentrations representative of the conditions at Zone 12 will be obtained. These soils will be used in the laboratory screening and subsequent studies.

The screening studies will be batch slurry studies set up to determine: a) if natural organisms in the soil are capable of degrading the high explosive and other chemicals, b) if amendments are necessary to assist the bioremediation of these chemicals - possible amendments include pH adjustment, nutrients, or acclimated organisms, and c) the degree of chemical removal that will occur. It is recognized that slurry systems are not representative of soil based bioremediation systems. However, slurry treatability studies do provide general feasibility data rapidly.

Parameters to be measured to assess performance will include: a) oxygen uptake rates, b) the concentration of specific chemicals such as TNT, RDX and HMX, e) nutrient concentrations, and d) pH. At the beginning and end of the study, the toxicity of the slurry and the mobility of the metals in the solids will be measured.

The laboratory screening studies are expected to require three months: one month to acquire the soils, organize and set up the equipment, and perfect the analytical methods; one month to conduct the slurry screening studies; and one month to analyze the data and to prepare a draft report for review and evaluation.

Bench Scale Testing

This step is designed to verify that bioremediation can achieve satisfactory performance goals. These studies provide a quantitative evaluation of the performance of a technology as well as some cost and design information. Bench-scale tests are performed to focus on the critical parameters that have an impact on performance.

The operational and performance information resulting from bench-scale testing permits more accurate full-scale cost and schedule estimates than can be obtained from laboratory screening. Bench-scale tests provide information needed to size unit operations and to estimate treatment train considerations such as mixing and materials handling. A moderate to high level of QA/QC generally is needed to increase the confidence in the decision that the remedy selected can meet the performance goals for the site.

Assuming that the laboratory slurry screening studies show that bioremediation is feasible with the Pantex Zone 12 soils, bench scale testing would be initiated to provide the necessary more detailed process information. For the Pantex soils, in-situ or ex-situ solid phase bioremediation processes are likely to be the more feasible. Therefore, these will be evaluated in the bench-scale testing.
Pan and large scale container solid phase studies will be conducted. The purpose will be to determine the rates of chemical removal, the immobilization of metals and other chemicals that results from bioremediation, and the reduction in relative toxicity that will occur. Optimum process conditions - such as adequate moisture content and constant pH - will be maintained. Process variables that will be evaluated will be the need for nutrients, the addition of acclimated organisms, the time needed for the available chemicals to be degraded, and temperature variations expected to occur at Pantex.

Parameters that will be measured to assess performance will include: a) the change in concentration of specific chemicals, such as TNT, RDX, HMX, and TNB, as well as other chemicals that may be in the soil, b) the mobility of metals, and c) the change in relative toxicity. All of these factors are needed to determine risk based remediation process decisions.

These bench scale testing studies are expected to require at least 8-12 months to set up the testing and analytical equipment, conduct the studies, and evaluate the results.

Pilot Scale Testing

This can be the final scale of treatability evaluation needed to select the appropriate bioremediation process. These studies are designed to provide detailed size, cost, and performance data, especially that data needed to optimize the design and operational schedule.

A few critical performance, design, and cost parameters are investigated during pilot-scale testing. These parameters are evaluated over a narrow range of values to optimize process operation. A moderate to high level of QA/AC is needed to increase confidence in the decision that the remedy selected can meet the performance goals for the site.

Pilot-scale testing typically involves using large scale equipment with a configuration similar to that of the full-scale operating unit being considered. For the Pantex soils, it may be that a small scale on-site bioremediation unit can be constructed and operated. Such a unit will demonstrate actual performance, materials handling, costs and impact of site temperature, precipitation, and other environmental conditions.

At this preliminary stage, it is impossible to predict what such pilot scale units might look like for the Pantex site. However, experience with such units at other sites in Texas and Oklahoma indicate that they could be one-quarter to one-half acre in size, would require on-site equipment and personnel to operate them, and would have to be conducted through a year to evaluate site conditions (temperature, rain, etc.). Typical studies have covered about 15-18 months, with perhaps 3-6 months needed to prepare the site and construct facilities for the pilot scale evaluation, and 12 months to conduct the evaluation. In addition, there will be several months needed to analyze the data, and to prepare the needed evaluative reports.

Summary—Treatability studies should continue until sufficient information has been collected to evaluate all relevant treatment alternatives and the design of the selected alternative. Treatability studies will reduce the uncertainties associated with the selection and application of a technology, but they cannot guarantee that the chosen alternative will be completely successful. However, better data on the performance of a technology with
site specific wastes expand the overall confidence in the final technology selection and design.

Personnel: The laboratory and bench-scale treatability studies for contaminated soils will be conducted at the University of Texas and directed by Raymond Loehr. The laboratory studies should be completed in FY95, with the bench-scale studies starting in FY96.

Chlorinated Solvent In Situ Bioremediation

Purpose and Scope

This project will determine whether or not bioremediation is a feasible approach for remediating TCE-contaminated groundwater at Pantex. The perched aquifer in Zones 11 and 12 is contaminated with chlorinated solvents (particularly TCE), which could potentially migrate to and contaminate the underlying Ogallala aquifer. The initial laboratory studies will determine if bioremediation is potentially viable and will provide information for larger scale testing.

The specific goals of the laboratory testing include the following:

- determine if viable methanotrophic and/or aromatic-degrading bacterial populations exist in the perched aquifer and if these populations can be stimulated to degrade TCE;
- determine to what extent TCE can be completely degraded by indigenous bacteria;
- maximize and compare the degradation rates that are attainable with methane oxidizers and aromatic degraders, and determine what variables (nutrients, dissolved oxygen, and substrate concentrations) affect degradation of TCE; and
- determine how biotransformation of TCE is inhibited or affected due to the presence of chromium, explosives, and/or chlorinated solvent degradation products.

Laboratory Studies

The potential for in-situ bioremediation of chlorinated solvents in groundwater will be assessed with a series of laboratory studies. These experiments will yield information about the presence of indigenous microorganisms and their ability to cometabolize TCE. The specific tests that will be conducted include biostimulation studies to determine what bacterial populations exist and how best to increase these populations; biodegradation tests to determine how well TCE can be biodegraded; and similar tests to determine the effects of varying oxygen, substrate, and nutrient concentrations.

Biostimulation Studies: Biostimulation tests will determine if aerobic methane-oxidizing or aromatic-degrading bacteria are present in the aquifer. Biostimulation will also increase populations of these bacteria. Initial biostimulation studies will not include determination of the ability to biodegrade TCE, but will be used to determine if bacteria that can potentially cometabolize TCE are present in the aquifer.

Setup. Crimp-top or screw-top vials with Teflon-lined Mininert sampling valves will be used as the test containers. Each vial will contain a measured amount of sediment
and groundwater (without contaminants), as well as varying amounts of nutrients and primary substrate (methane or phenol). Vials will be incubated at conditions that are as close as possible to ambient aquifer conditions (i.e., in the dark and at the same temperature as the perched aquifer groundwater). Headspace in the vials will be sampled over time and analyzed to detect changes in the headspace gas composition. In particular, the relative amounts of oxygen, methane, and carbon dioxide will be analyzed to determine trends. Increasing CO$_2$ and decreasing O$_2$ (and methane) concentrations indicate utilization of substrates and stimulation of the bacteria of interest. Phenol has low volatility and cannot be easily measured in headspace; thus, loss of O$_2$ and increases of CO$_2$ would signify utilization of phenol. Changes in methane concentrations can be measured directly.

**Substrates.** Methane-oxidizing bacteria will be of primary interest, but bacteria that utilize other substrates will be examined. Phenol degraders will be studied in addition to methane. Bacteria that utilize other substrates have been found to cometabolize TCE, but studies at other sites have found that methane- and phenol-utilizing bacteria achieve the highest TCE biodegradation rates.

**Controls.** Control vials will be used to determine the substrate losses that are attributable to abiotic mechanisms such as sorption to experimental apparatus or aquifer solids, equipment leaks, and/or volatilization. Water controls will test the integrity of the test vials and determine losses from the vials, and killed controls will be used to measure additional losses due to sorption to aquifer sediments or vials.

**Microcosm Biodegradation Studies:** Microcosms will simulate ambient conditions and determine the extent to which TCE can be biodegraded in the perched aquifer at Pantex. Microcosms will be used to study how nutrients, substrates, inhibitors, and environmental conditions may affect the biotransformation of TCE.

Radiolabeled TCE will be used in biodegradation experiments because of the ease of quantifying end products and the certainty of recovery and analysis of radiolabeled compounds. Experiments with radiolabeled compounds will indicate biodegradation of contaminants by loss of TCE and by generation of $^{14}$CO$_2$, thus allowing precise determination of the extent of TCE biotransformation and the fate of contaminants under a variety of test conditions.

**Setup.** For biotransformation experiments, vials containing sediment and groundwater will be used. Uncontaminated groundwater will be used for microcosm construction, allowing better control over TCE input, better accounting for TCE degradation, and better simulation of ambient conditions. Solids that are used in microcosms will be from the saturated zone of the perched aquifer. TCE, nutrients, substrates, and oxygen will be added, and microcosms will be incubated in the dark at ambient temperatures. Variables for microcosms include nutrient (nitrogen and phosphorous) concentrations and compositions (from none added to reasonable levels that could be applied in situ), different substrates and concentrations (phenol and methane; one study with phenol has shown increasing TCE degradation with increased phenol addition), and different oxygen concentrations and methods of application (atmospheric oxygen, pure oxygen, hydrogen peroxide, and solid peroxides). For each test condition, multiple vials will be prepared to allow sacrificing of vials over time.
Liquid scintillation counting will be used to determine the fate of $^{14}$C, as non-degraded $^{14}$C-TCE, as $^{14}$CO$_2$, or as $^{14}$C-nonvolatiles. The main questions that will be answered with these data is whether or not TCE can be potentially degraded under *in situ* conditions. Measurement of $^{14}$CO$_2$ produced by breakdown of radiolabeled TCE will indicate the extent of TCE mineralization, if indigenous organisms are capable of completely degrading TCE. Nonvolatile $^{14}$C byproducts will indicate partial breakdown of $^{14}$C-TCE and must be quantified to calculate mass balances for $^{14}$C in each vial.

**Contaminants and Concentrations.** TCE is the primary contaminant of concern. In 1993, TCE concentrations ranged from <0.005 mg/L to 0.093 mg/L in samples taken from Zone 12 monitoring wells. Average TCE concentration was 0.036 mg/L in samples from well PM-20. To simulate the upper bounds of the concentration range, microcosms will be prepared with an initial aqueous TCE concentration of 100 $\mu$g/L.

**Substrates.** Methane and phenol are the primary substrates of interest. Methane will be delivered by dissolving it into water (if headspace-free microcosms are used) or by supplying a headspace that includes methane. Phenol will be used because other studies have found that phenol degrading bacteria efficiently degrade TCE. Phenol is relatively easy to handle and will be added as a liquid. In general, field studies have shown that phenol degraders grow faster than methanotrophs. The larger quantity of stimulated biomass can degrade TCE faster than slower-growing methanotrophs, although methanotrophs generally have higher normalized TCE degradation rates (work by McCarty and others -- in situ and column studies at Moffett Field, CA and column studies for St. Joseph, MI).

**Inhibition/Toxicity Testing.** Microcosms may be used to study the inhibitory effects of chromium, high explosives, chlorinated solvent breakdown products, or other factors which may be detrimental to biodegradation. Because microcosms will be constructed using aquifer material, contaminants in addition to TCE will likely be present in the test vials.

**Controls.** Control microcosms will be used to determine contaminant losses due to mechanisms other than biodegradation of contaminants, including sorption to aquifer material, sorption to test vessels, and volatilization and leakage from the microcosms. Abiotic control microcosms will contain autoclaved aquifer material or use a chemical that is inhibitory or toxic to microorganisms, such as sodium azide, mercuric chloride, or formaldehyde. One control microcosm will be set up for sampling at each time step. Sampling and analysis of the control microcosm at each sample time will be sufficient to determine the stability of the microcosms and the losses due to abiotic mechanisms.

**Column Studies/Continuous Flow:** Several researchers have used continuous flow column studies to determine several factors that are important to *in situ* bioremediation. These additional determinations may be made using column studies: sorptive properties of the aquifer material; oxygen transfer efficiency and oxygenation methods, methane transfer efficiency; methods for cycling substrate and oxygen injections to efficiently distribute biomass throughout the treatment zone; and nutrient interactions with aquifer sediments. Column testing can be used as a closer replication of non-static conditions found in the aquifer. Several researchers have described the setup and operation of columns for these determinations. Most of these researchers are colleagues of Perry.
McCarty at Stanford and have utilized these techniques for studies at Moffett Field, CA and St. Joseph, MI.

**Additional Investigations:** These additional studies may be out of the scope of this portion of the Pantex research project, but may be necessary to answer additional questions for achievement of the ultimate goal of remediating the perched aquifer.

**Inoculation of Aerobic Microcosms:** Injection of TCE-degrading bacteria into an aquifer to achieve *in situ* remediation of groundwater may be effective in achieving remedial goals. This method has many complicating factors (e.g., survival of non-indigenous organisms, transport of bacteria throughout an aquifer), but may be studied as an alternate to biostimulation of indigenous organisms. If methane oxidizers and phenol degraders do not exist in the perched aquifer, or if these indigenous organisms cannot efficiently degrade TCE, this technique will become more appealing and may warrant testing.

**Field Studies:** Field studies would apply laboratory findings to the site and determine the effectiveness of this technique as applied to a pilot scale treatment unit. This step would be the most important step in proving that TCE can be degraded *in situ* in the perched aquifer at Pantex, and may be necessary prior to full-scale implementation. Successful results of an *in situ* pilot-scale study would show that this method is appropriate for remediating groundwater at Pantex, and provide additional performance and cost data for scale-up.

**Personnel:** The investigations for chlorinated solvent in-situ bioremediation will be performed at the University of Texas and directed by Gerald Speitel Jr.
TASK THREE: VADOSE ZONE REMEDIATION

Background

A primary method for vadose zone remediation involves soil vapor extraction (SVE) technology where volatile organic contaminants (VOCs) are removed from the soil above the water table by circulating air through the soil. When used in combination with bioventing and air sparging, soil vapor extraction may prove to be a useful remediation technology for saturated and unsaturated zone organic contaminants at the Pantex Plant. The applicability of vadose zone technologies depend on the soil permeability, porosity and water content, well spacing and suction pressures. The potential application of soil vapor technologies in the deep vadose zone beneath the Pantex Plant will be investigated using mathematical modeling, laboratory studies, and pilot plant testing. The model for the perched aquifer and its quantitative framework will be used as the basis for modeling of soil vapor extraction systems.

During the current fiscal year, the research group will be working in three primary subtask areas. The subtasks are intended to cooperate with and benefit the new treatability study by the Battelle/Pantex ER group that is currently underway. The site selected for the current treatability study east of Zone 12 is not located near a potential source of VOCs, but the installation will be used to demonstrate soil vapor extraction apparatus. The proposed subtask areas for fiscal year 1996 include field investigation near possible source locations in Zone 11 or 12. It is anticipated that the treatability system will not be ready for operation until fiscal year 1996.

Air Permeability Measurements

To date, core samples have been received from three new perched aquifer monitoring well installations and one soil boring in Zone 12. Laboratory measurements of the air permeabilities for selected important lithogical units are being performed in the geotechnical facilities. The tests are being done on repacked samples, since the soil texture for most of the core materials received thus far are quite sandy. Porosity estimates are also being done for each sample. Additional core samples are anticipated from at least two more new monitoring well locations as selected by the Corps of Engineers. These samples will be analyzed similarly.

Personnel: These investigations will be performed at the University of Texas and directed by Daene McKinney.

VOC Adsorption Isotherms

Previous sampling of existing monitoring wells in and near Zones 11 and 12 have demonstrated the presence of several VOCs as dissolved in groundwater, including TCE, DCA, PCE, and benzene. These VOCs are likely present in the vapor phase in the vadose zone, and the source solvents may still be exist as residual liquids. Soil vapor extraction techniques move the vapors and volatilize the VOC liquids. Vapor movement to the extraction wells may be affected by adsorption to the soil matrix. In this subtask, laboratory vapor sorption experiments will be performed using samples of the recently
collected core materials. As additional core materials become available, these will also be tested.

Personnel: These investigations will be performed at Texas A&M University and directed by Aydin Akgerman.

Modeling of Soil Vapor Extraction Systems

Prediction and maintenance of SVE system performance can be supported through proper use of numerical models. A small number of commercial or public domain models are now available to simulate air flow only or air and vapor transport in axisymmetric or two-dimensional systems. Each of these models require significant assumptions to allow solution of the partial differential equations that describe the air flow, volatilization, and vapor transport processes. Two efforts will take place in this subtask. In the first effort, a two-dimensional finite difference model for SVE previously under development by the research team will be completed. This model is unusual in that it accounts for the changes in air permeability that occur as the residual liquids, whether water or VOCs, are evaporated from the pore space. This capability allows the model to demonstrate the preferential flow that takes place as SVE progresses. The model will allow specification of extraction and vent wells, initial VOC and moisture content, mass transfer and dispersion coefficients, and choices of boundary conditions. The model output will provide transient descriptions of vapor effluent and residual saturations for the liquids. In the second effort, several available commercial or public domain SVE models will be quickly collected and evaluated for immediate use by the research team or the Battelle ER group. The models will be compared for basic assumptions, input requirements, output capability, and utility for application to the Pantex problems. It is recognized that consultants to the Battelle ER group in the treatability study will likely perform modeling as part of their scope. It is not clear, however, whether the model used by the selected contractor will be made available to the ER group for its own use in the near term.

Personnel: These investigations will be coordinated through Texas Tech University and directed by Ken Rainwater.

Future Activities

For fiscal year 1996, the research team will continue subtasks 1 and 2 as necessary due to production of additional subsurface materials. The development of the 2-D finite difference model should be completed. In addition, several additional concerns will be studied. The presence of the treatability system with its SVE and vent wells affords an excellent venue for a tracer test to determine the zone of influence of the system. Movement of a conservative tracer, such as argon gas, can be used to establish breakthrough and calibrate an SVE model in concert with observed operational parameters such as flow rate and pressure. If vapor sorption is found to be significant in subtask 2, a sorbing vapor may be used to demonstrate the field effects of sorption. Another major concern is the lack of existing data on the distribution of VOCs, especially
TCE, in the vadose zone. It is not known at this time whether the Battelle ER group or the Corps of Engineers' contractors plan to do deep soil borings at locations in Zones 11 and 12 beneath former historical sources of TCE. If those groups do not do such testing, the Consortium will develop a sampling program (possibly using a cone penetrometer with the drilling rig purchased by DOE for use by TBEG) for DOE review and consideration.

TASK FOUR: CHROMIUM REMEDIATION

Background

Chromium has been found at concentrations above background levels in several wells in the perched aquifer below the Pantex Plant, particularly in those beneath Zone 12. In some wells, the concentrations of total chromium exceed levels used to define hazardous wastes by the toxicity characteristic and approach being two orders of magnitude higher than drinking water standards. Concentrations in at least one of these wells (PM-20) shows marked increases in total chromium concentrations from 1991 through 1994. This may represent the initial front of a chromium plume reaching this well. Some samples from the perched aquifer show elevated levels of chromium and iron, which is not expected and may represent unusual chemical behavior. Chromium in the perched aquifer is assumed to result from release at the surface, therefore there may be significant amounts of chromium in the vadose zone moving towards the perched aquifer. However, zones of high chromium concentrations have yet to be located in any soils.

Understanding the chemistry of chromium is critical to developing methods for remediating it. Chromium typically exists in the environment in one of two oxidation states. The form typically used for industrial purposes is hexavalent chromium and this is the form believed to have been released to the environment at the Pantex Plant. It is relatively mobile because it does not sorb strongly to soil components nor does it readily form insoluble precipitates. However, it is not totally non-reactive. Chromium has been observed to move in the subsurface at a speed only 10% of the groundwater at one site. A barium chromate solid phase is believed to control chromium concentrations in groundwater at another site. An important reaction for understanding the movement of chromium (VI) in the subsurface is reduction to trivalent chromium. This reaction can be brought about by soil organic matter, ferrous iron, sulfide or thiol groups. Conversion to the trivalent form is important because chromium is much less mobile in this oxidation state because it tends to sorb to soil components and to form hydroxide precipitates. This means that chromium in the trivalent state would be more difficult to remove by groundwater extraction. However, trivalent chromium would have less environmental risk, particularly if it could be shown that it remains in the trivalent form.

Several methods exist of remediating chrome at the Pantex Plant. One option for which plans are currently being developed is to pump contaminated water from the perched aquifer and treat it above ground. Several methods could be used for treating this water, but they have not been evaluated at Pantex. Hexavalent chromium can be removed
by anion exchange, adsorption onto activated carbon, or after oxidation to the trivalent
form, chromium can be removed by precipitation as chromium hydroxide, cation
exchange, or sorption. Effectiveness of these different methods for treatment of
chromium in groundwater from the perched aquifer is unknown.

Although high levels of chromium have been found in several wells in the
perched aquifer, the source of contamination has not been identified. Potential sources
of chromium in Zone 12 include plating operations, a cooling tower and other
unidentified industrial uses. Locating the source of chromium and identifying its
chemical state is important to developing remedial plans for the site. Identifying the
source or sources of chromium will enable plans to be made to remove chromium from
contaminated soils or immobilize it so that it will not continue to contaminate
groundwater. Deciding to remove or immobilize chromium will depend in large part on
whether the chromium is in a mobile (hexavalent) or immobile (trivalent) form in the soil.

Develop and validate analytical procedures and quality control programs

Analytical procedures for total chromium, trivalent chromium, and hexavalent
chromium will be developed by each of the research teams. At TTU and UT, atomic
absorption spectrophotometry (flame and graphite furnace) techniques will be used to
measure total chromium and a colorimetric procedure will be used for hexavalent
chromium. Trivalent chromium will be calculated by difference. At TAMU, an
inductively coupled plasma-mass spectrometer (ICP-MS) will be used to measure total
chromium. A special ion exchange column will be attached to the inlet of the ICP-MS to
separate trivalent and hexavalent chromium species before analysis when speciation is
desired. The research team at TTU will develop either field analysis techniques for
individual chromium species or sampling and preservation techniques that preserve
chromium speciation for later laboratory analysis.

Each research team will develop appropriate quality control programs. Regular
inter-laboratory round robin testing will be done to insure that all laboratories are
producing reliable data. The Environmental Science Laboratory at TTU already
participates in the Environmental Protection Agency's laboratory procedure validation
program, and will continue to do so through this project.

Personnel: This research will be performed at all three universities over a period from
June 1995 to August 1995. The chromium remediation program is directed by Bill
Batchelor (TAMU) with participation of Desmond Lawler (UT), Howard Liljestrand
(UT), and Ken Rainwater (TTU).

Develop Chemical Models for Chromium in the Vadose Zone and Perched Aquifer

The behavior of chromium in the subsurface and in surface treatment systems
depends in large part on its chemical form, which is determined by the chemical
environment. A first step in understanding this chemical environment will be to develop
chemical models for chromium, based on the assumption of chemical equilibrium. These
models describe the ultimate conditions expected, but may not describe conditions that
are observed if kinetics of the reactions are slow. Equilibrium models will be developed
using generic tools such as MINTEQA2. These models will examine the effects of pH, pe, solid phases, and sorption sites on the chemical form and concentrations of chromium expected in the subsurface and in treatment systems. They will provide the framework for interpreting field data and directing studies for development of remediation technologies. As data are made available for chemical behavior of chromium under conditions found at the Pantex Plant, the models will be appropriately modified. In particular, models incorporating kinetics of chromium transformations can be developed later (FY 1996) when data is made available from laboratory tests.

Personnel: This work will be performed at TAMU under the direction of Bill Batchelor and at UT under the direction of Desmond Lawler and Howard Liljestrand over the period from June 1995 to October 1995.

**Ion Exchange Studies**

Ion exchange will be the first treatment method to be investigated for chromium in water from the perched aquifer at the Pantex Plant. A few assumptions underlie this choice. First, chromium is assumed to be primarily present as hexavalent chromium. Second, with near neutral pH and concentrations of total chromium in the range of 10 mg/L or less, hexavalent chromium would be present primarily as chromate ($\text{CrO}_4^{2-}$). Third, it is desirable to segregate the treatment for chromium from that of high explosives. Fourth, it is desirable to concentrate the chromium so that ultimate disposal could be done with much smaller volumes. With these assumptions, ion (i.e., anion) exchange is an excellent choice. If a resin that is highly selective for chromium (relative to common anions in natural waters) is found, ion exchange will concentrate the chromium onto the resin. Removing the chromium with a reducing agent will then remove the chromium from the resin as Chromium III at low pH. Raising the pH will lead to the precipitation of chromium hydroxide, $\text{Cr(OH)}_3$. With this understanding as background, the following studies will be undertaken at UT in the next few months:

- Literature review and product search to identify possible ion exchange resins for this application. Samples of possible resins that are identified will be obtained for use in laboratory studies.
- Preliminary ion exchange laboratory studies will be performed. Water to be treated will be water taken from one of the wells on the Pantex site. Water will be spiked with additional chromium if needed (likely in batch studies to determine capacity and selectivity). Batch studies will be undertaken to determine equilibrium description of ion exchange. Column studies will be performed to check for interferences, kinetic description, and breakthrough of any undesirable constituents. A sensitivity analysis of chromate exchange to pH variation will be undertaken by using the pH of the water as obtained from the Pantex site and one pH unit above and below that pH to determine whether small changes in pH could be used to enhance the exchange selectivity.
- Regeneration of the exchange resin will be studied as well. It is envisioned that a reductive regeneration will be utilized—to use, for example, sulfite or bisulfite at low
pH in the regeneration step should increase the driving force by maintaining a zero concentration of hexavalent chromium in the solution adjacent to the resin. Only one bed volume (or perhaps slightly more as a safety factor) is expected to be used, leaving a high concentration of chromium in the wash water. A second regeneration solution to raise the pH and replace the anions on the bed with a desirable anion for the exchange is then expected and will be investigated. This solution could contain a substance (e.g., iodide) that could be used as a tracer if the full-scale treatment at Pantex is to include recycling the water back into the groundwater. Again, only one (or slightly more) bed volume of regenerant solution is expected to be utilized in this step.

- Precipitation of the chromium as chromium hydroxide will be studied for the first regenerant solution. Raising the pH to the pH of minimum solubility of Cr(OH)$_3$ and allowing flocculation and sedimentation to occur should result in a low concentration of chromium in solution, acceptable for disposal (or reintroduction to the ion exchange column), and a sludge that needs to be disposed properly. Laboratory studies will be used to confirm this treatment technology.

In the longer term (FY 1996), two directions are expected at this time. First, refinement of the ion exchange treatment can be expected to be necessary. Design of such experiments will depend on results from those described above. Second, using activated carbon for joint treatment of chromium and high explosives is an option that must be investigated. Even if ion exchange is successful, some chromium is likely to get through to an activated carbon treatment for high explosives. The competitive adsorption of chromium and high explosives will be studied in subsequent laboratory studies. These studies will be undertaken in a matter similar to those described above for ion exchange.

Personnel: These investigations will be conducted at UT under the direction of Desmond Lawler and Howard Liljestrand over the period from June 1995 to October 1995.

Redox chemistry of chromium

Redox chemistry of chromium is important in understanding the movement of chromium in the environment and in developing remediation technologies. Hexavalent chromium is the form of chromium originally released to the environment and it is relatively mobile. It can be reduced by natural soil organic matter to the trivalent state which is relatively immobile. It can also be reduced by ferrous iron, sulfide and organic compounds with thiol groups that are naturally available or added as part of a treatment approach. Trivalent chromium can be oxidized to the mobile hexavalent form by manganese dioxide naturally present in the soil and by strong oxidants applied to the soil.

The initial work in this task will be to develop data on the reduction of hexavalent chromium by ferrous iron. These data can be used to understand the behavior of chromium in the subsurface, since some wells show high iron concentrations, and to understand the behavior of chromium in engineered treatment systems, since ferrous iron can be supplied relatively economically and is non-toxic. Experiments with ferrous iron will also be directed towards understanding the reasons for the high levels of chromium
and iron found in some perched aquifer samples. Batch slurry experiments will be conducted to evaluate the effect of pH on the rate and extent of reduction of hexavalent chromium to trivalent chromium.

Further studies (FY 1996 and later) will investigate effects of concentrations of ferrous iron and soils surfaces on reduction of hexavalent chromium; the rate and extent of hexavalent chromium reduction by natural organic matter as affected by pH, pe, and soil surfaces; oxidation of trivalent chromium by manganese oxide and strong oxidants; and microbial facilitated oxidation/reduction of chromium. Understanding oxidation reactions could be very important in developing risk assessments, because the hexavalent form is not only more mobile but is also more toxic than the trivalent form. Microbial facilitated redox reactions could be important if in-situ bioremediation is chosen as a remedial option. It could be applied generally throughout the perched aquifer or in a specific area identified as a "gate" treatment zone.

Personnel: This work will be conducted at TAMU under the direction of Bill Batchelor over the period from August 1995 to October 1995.

Identify sources and speciation of chromium

Identifying the sources of chromium contamination and the chemical forms in which it exists at the Pantex Plant are essential for developing optimum remediation strategies. An initial study is being completed at TTU to estimate industrial sources of contamination at the Pantex plant and field studies are being conducted by contractors to measure chromium contamination in different soils. These studies will be integrated to identify where the chromium now exists in the vadose zone above the perched aquifer.

Effective speciation of chromium requires effective sampling and preservation or rapid analysis. Samples will be obtained from chromium-contaminated wells at the Pantex Plant and immediately analyzed in the field for pH, temperature, oxidation-reduction potential, conductivity and dissolved oxygen. Chromium will be analyzed immediately using field techniques or preserved for later laboratory analysis. Samples will also be provided to the other research teams as needed. Analyses of major ions as well as chromium will be accomplished to support chemical modeling and understanding possible chemical interactions.

Later (FY 1996) work will identify the forms of chromium present in contaminated soils through application of sequential extractions with increasing ability to remove chromium. These studies would help define the limits of chromium remediation and characterize the mobility of chromium for risk assessments.

Personnel: This work will be conducted at TTU under the direction of Ken Rainwater over the period from June 1995 to October 1995.

Evaluate Sorption of Chromium on Soils

Sorption is a potential major factor affecting the movement of chromium in the subsurface. Experiments will be conducted to characterize soils in terms of their
potential to act as sorbents (grain size, cation exchange capacity) and to determine their performance as sorbents in batch equilibrium tests and column experiments. As additional core materials are to be made available from ongoing drilling at the site, this work will continue into FY 1996.

Personnel: This research will be conducted at TTU under the direction of Ken Rainwater over the period from June 1995 to October 1995.

CONTINUING ACTIVITIES

The basic goal for the Consortium’s Environmental Restoration research is to support DOE’s Pantex Plant remediation efforts. This Work Plan addresses the activities which are scheduled at the present time. As is the nature of research, the Work Plan will evolve based on research findings and changing Plant conditions and activities. The Consortium hopes to actively participate in the planned perched groundwater treatability studies, both in terms as contributors to the study efforts and in terms of analysis and diagnosis of system performance. As conditions and activities at the Plant progress, the Consortium Work Plan will evolve in measure to continue to support Site remediation efforts, and the Work Plan will be amended accordingly.