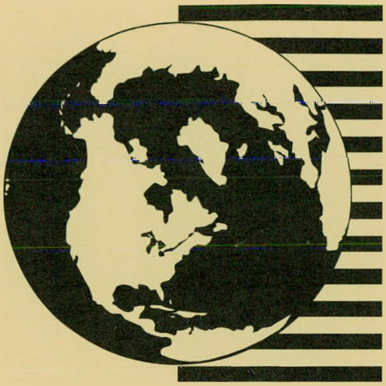

Environmental Technology Program

Annual Report

FY 90

Lawrence Livermore
National Laboratory

UCRL-LR-105199

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Environmental Technology Program

Annual Report

FY 90

Program Leader: Jesse L. Yow, Jr.

January 2, 1991

Lawrence Livermore
National Laboratory
UCRL-LR-105199

Contents

Overview of the Environmental Technology Program

Program Leader: Jesse L. Yow, Jr.

Introduction

Lawrence Livermore National Laboratory's Environmental Technology Program was organized in FY90 to research, develop, demonstrate, test, and evaluate innovative technologies for reducing the costs and increasing the effectiveness of environmental restoration and waste management. During FY90 the program was funded primarily by the Office of Technology Development of the U.S. Department of Energy's Office of Environmental Management, with supplemental funding from the LLNL Institutional Research and Development Program. The program works closely with environmental restoration and waste management projects funded by DOE's Office of Environmental Restoration and Office of Waste Operations. This report introduces the scope, participating organizations, and interfaces of the Environmental Technology Program, and describes a selection of its technical accomplishments in FY90.

Program Scope

The Environmental Technology Program is organized into the following main elements, each of which represents an integration of individual tasks and activities to meet program objectives:

- Hazard Assessment and Risk Management
- Characterization, Monitoring, and Analysis
- Subsurface (Groundwater and Soil) Remediation
- Waste Treatment
- Waste Minimization
- Education Initiatives

These areas of emphasis evolve with time according to the needs of sponsors. The general scope of each area is outlined below.

Hazard Assessment and Risk Management supports other areas of the program by comparing risks associated with existing and new alternative environmental technologies, and will develop and test capabilities with which to identify and prioritize environmental management needs. FY90 accomplishments included the preparation of methods by which the Office of Technology Development could prioritize research activities.

Characterization, Monitoring, and Analysis develops and tests tools with which to detect and measure contaminant compounds; monitor contaminant transport and fate; and simulate, evaluate, and extrapolate the effects of treatment alternatives. This element supports other areas of the program by providing quantified information about initial and limiting conditions, active processes, and anticipated trends for laboratory- and field-scale environmental assessments and remediations. FY90 accomplishments included underground imaging, numerical analysis of *in situ* air stripping through horizontal wells, fiber-optic sensor development, and preparation of methods for measuring retardation factors and distributions of subsurface contaminants.

Subsurface Remediation develops and tests new technologies (and new combinations of existing technologies) for removing, destroying, or containing subsurface contaminants. This element supports other areas of the program by generating and fostering state-of-the-art alternatives for treating subsurface contamination, and by defining needs for characterization, monitoring, analysis, and effluent treatment technologies. FY90 accomplishments included initial work with *in situ* microbial filters for treating underground volatile organic compound (VOC) contaminants, and two separate pilot-scale investigations of vacuum-induced soil venting for fuel hydrocarbon and VOC contaminants.

Waste Treatment develops and tests technologies for removing, destroying, or treating contaminants that are already under containment or are being generated by manufacturing, remediation, or experimental processes. This element supports other areas of the program by providing new alternatives for waste stream or effluent treatment, and by defining needs for characterization, monitoring, analysis, and waste minimization technologies. FY90 accomplishments included the development of approaches for the biodegradation of high-explosive wastes in processing waters, methods for molten salt destruction of mixed wastes, and methods for removing VOCs from groundwater and wastewater.

Waste Minimization develops and tests technologies for minimizing the generation of hazardous wastes or contaminants during manufacturing, remediation, or experimental processes. This element supports other areas of the program by generating and fostering system improvements to reduce the amount of resultant wastes. FY90 accomplishments included the development of plans for demonstration tests of reusable, cleanable steel high-efficiency particulate air (HEPA) filters.

Education Initiatives are aimed at strengthening the pool of technical talent available to the nation for work in environmental restoration and waste management. FY90 accomplishments included the formulation of collaborative programs with academic, industrial, and government specialists to encourage education and career training in key technical disciplines.

Program Participants

LLNL's matrix management structure allows maximum flexibility in building multidisciplinary teams for effectively conducting program assignments. More than 30 scientists, engineers, and technicians supported the Environmental Technology Program during FY90, either directly in technology development activities or indirectly by initiating concepts for new technologies. People from the following LLNL functional areas and organizations participated in the program:

- Chemistry & Materials Sciences
- Computations
- Earth Sciences
- Energy Program
- Engineering
- Environmental Protection
- Environmental Sciences
- Hazards Control
- Human Resources
- Institute for Geophysics & Planetary Physics
- Laser Program
- Nuclear Chemistry
- Physics
- Special Projects
- Weapons Program

Program Interfaces

The Environmental Technology Program draws from many national laboratory strengths and capabilities that were developed in the course of other DOE-sponsored programs. Relevant strengths and capabilities include the development, design, and analysis of large, complex engineered systems and field tests; advanced instrumentation, measurement, and calibration capabilities; sophisticated numerical simulation of systems and processes; and specialized material development and manufacture expertise. In turn, the Environmental Technology Program provides technologies to the defense complex and to other national and international users to support waste treatment and waste minimization activities and to expedite the resolution of subsurface contamination problems.

Program scientists and engineers are working in collaborative relationships with a number of industrial and academic establishments, effectively transferring technology into and out of the LLNL program as needed. Industrial connections include specialized consultants who help with technology development and companies that are interested in licensing technologies developed by the program. Academic connections include Stanford University and several campuses of the University of California (through the Institute for Geophysics & Planetary Physics and through other types of working agreements). As the Environmental Technology Program evolves, we will identify industrial partners for selected activities; we also expect to broaden our academic collaborations through subcontracts, visiting scholar arrangements, and education program activities.

In addition to vertical interfaces with sponsors and contractors and horizontal interfaces with industrial firms, academic institutions, and defense complex organizations, the Environmental Technology Program involves formal and informal lateral interfaces with other national laboratories; with organizations such as the National Institute of Standards and Technology, Solar Energy Research Institute, and United States Geological Survey; and with technical and professional organizations that represent potential users of technologies. Since many technologies from the program will be applied in regulatory compliance situations, interfaces are also being developed with regulatory agencies.

Lateral interfaces that develop in the context of DOE Integrated Demonstration Projects are particularly worthy of note. LLNL is extensively involved with the Westinghouse Savannah River Laboratory, Sandia National Laboratories, Idaho National Engineering Laboratory, Oak Ridge National Laboratory, Pacific Northwest Laboratory, and Martin Marietta's Hazardous Waste Remedial Actions Program in the context of the Integrated Demonstration Project at Savannah River. LLNL activities in this project during FY90 included underground imaging for process characterization and numerical analysis of *in situ* air stripping through horizontal wells.

Additional Information

Additional information about Environmental Technology Program activities and technologies is available from:

Dr. Jesse L. Yow, Jr., Program Leader
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Livermore, CA 94550

Prioritization of Research

Principal Investigator: Ronald P. Koopman

A simple, flexible, and easily understood methodology for evaluating research proposals has been developed for the Office of Technology Development. We have successfully used the methodology twice, each time for evaluating more than 200 proposals.

Introduction

As a first step in a program to prioritize research for the various Office of Technology Development (OTD) program areas, we developed criteria and a methodology for evaluating research proposals. This methodology was used first by teams of DOE Technical Program Officers to evaluate proposals from across the DOE complex. Approximately 260 proposals were evaluated, and recommendations were sent to DOE management. As a result of this exercise, technical teams formed in key program areas are evaluating proposals in those areas. The next application was directed at the waste minimization area, in which the teams of technical experts evaluated over 200 proposals. We also will evaluate the effect of uncertainty in the method and data and identify areas in which improved methods or better information are required.

This methodology could be extended to prioritize research in the overall OTD program to create an optimum program based on costs vs benefits. This would be done by developing performance curves and relative weights for each major program area within OTD.

Waste Minimization Prioritization

The waste minimization prioritization involved meeting with approximately 50 technical experts from the plants and labs that make up the DOE nuclear weapons complex. They and the proposals were divided among eight waste streams. These waste streams are actually materials-processing paths that produce waste such as plutonium, uranium, tritium, and solvents. The groups of experts spent three intensive days evaluating proposals and developing research programs for each of the waste streams.

Technical proposals for waste and hazard minimization were solicited from the plants and labs in the DOE weapons complex. We developed a methodology—DOE decision-makers specified it to be simple, easily understood, and highly flexible—that would allow knowledgeable technical people to evaluate and rank the proposals. The methodology in this case was intended to serve as a decision aid and to allow other priorities (e.g., regulatory requirements, site needs) to be considered equally in the decision-making process.

Criteria

For the Waste Minimization effort, Lawrence Livermore National Laboratory (LLNL) and Sandia National Laboratories (SNL) jointly developed the criteria, in consultation with DOE/DP, as an outgrowth of prior individual projects at both laboratories. The criteria are

- Primary Benefits—cost savings, occupational exposure risk reduction, environmental and public risk reduction, and improved operations.
- Likelihood of Technical Success.
- Usefulness—timeliness and leverage.
- Other Benefits—teaming, innovation, and national impact.

Scales and Weights

The scales and scoring guidance were also developed collaboratively by LLNL and SNL. The scales provided qualitative and quantitative guidelines by which the evaluators scored the proposals. The scales assisted the evaluators in their intra-group process and helped achieve scoring consistency across the groups. (See Table 1.) In addition, each of the criteria, except Likelihood of Technical Success, had an assigned weight, which was a measure of its importance to DOE

Table 1. Attributes of proposals vs likelihood of technical success.

Attributes of project	High likelihood	Medium likelihood	Low likelihood
Technical breakthrough	Not required	May be needed	One or more needed
Design of plan	Well-designed	Adequate	Inadequate
Key issues anticipated	Anticipated	Identified	Overlooked
Supporting technologies	Well-developed	Needs development	Undeveloped
Experience	Significant	Some	None
Work of others	Familiar	Some awareness	None

decision-makers. Likelihood of Technical Success was treated as a probability and the reviewers were asked to read the entire proposal before comparing it with the attributes listed in Table 1.

Aggregation Function and the Figure of Merit

The primary benefits and usefulness are dependent on technical success; consequently they were multiplied by their weights, summed, and multiplied by the Likelihood of Technical Success. The result was then added to the sum of the other benefits times their weights.

Training

The proposal evaluation process was explained to the evaluators who read and scored an example proposal. The reviewers who gave the high and the low scores were asked to discuss the reasons for their scores. A few misunderstandings about the process were uncovered, and a few modifications to the process were made as a result of these discussions.

Scoring

Each member of a waste-stream evaluation committee read each proposal assigned to his committee and scored each of them according to the criteria. The committee discussed each score and either reached consensus or arrived at a group average. The group average score was recorded along with the high and the low (if complete consensus was not reached). If necessary, proposal authors were called to supply more information and in some cases, proposals were combined to produce a stronger proposal.

Data Base Support

A data base for all the proposals was created with the following information: activity title, proposal number, site, cost, criteria scores (high, low, average), proposal score, waste stream, general priority, and waste-stream overall rank. This allows sorting by overall score, by score for each waste stream, by site, or by any of the other values listed above.

Proposal Prioritization

Each score is intended to be a measure of the proposal's inherent technical value. Scores are only one factor to be used by the technical evaluation teams to prioritize the proposals and to make funding decisions by the Waste Minimization Management Group (WMMG), and DOE decision-makers. The waste-stream evaluation committees were advised not to be constrained by the scores when ranking proposals and encouraged to consider other factors, such as how well a proposal fit into a DOE-wide plan to address high-priority issues.

The methodology is oriented toward short-term payoff and high certainty of success. High-risk/high-payoff proposals, however, should be encouraged, and a technique should be developed to encourage high-payoff proposals and fund the most promising ones, even if the risk is high.

High-Frequency Electromagnetic and Electrical Resistance Tomography of the Savannah River Integrated Demonstration Project

Principal Investigator: Abelardo L. Ramirez
Co-Investigators: William D. Daily and Earle W. Owen

We are using underground imaging (tomography) and both electrical and electromagnetic energy sources to monitor the changes in water content due to air injection and extraction as part of the Savannah River Integrated Demonstration Project. The objective of the experiment is to use electrical resistance tomography and high-frequency electromagnetic tomography to map the changes in water content in a plane between the tomography measurement boreholes. Different data sets are compared to examine the changes in spatial distribution of water content with time.

Introduction

To demonstrate a remedial cleanup of volatile organic compounds from saturated and unsaturated soil horizons at the Savannah River Site, the Savannah River Integrated Demonstration Project (SRIDP) is being undertaken by DOE. Phase 1 of this project consists of an *in situ* air-stripping process to remove trichloroethylene (TCE) from saturated and vadose-zone soil horizons. The process involves simultaneously injecting air and extracting air and vapor through lower and upper parallel horizontal wells that have been drilled in the contaminated region.

We are using underground imaging (tomography) with both electrical and electromagnetic energy sources to monitor the changes in water content due to air injection and extraction as part of the project. Our objectives are to use electrical resistance tomography (ERT) and high-frequency electromagnetic (HFEM) tomography to map the changes in water content in a plane between the tomography measurement boreholes. Different data sets are compared to examine the changes in spatial distribution of water content with time. The plane, or window, being monitored is roughly perpendicular to the horizontal injection and extraction boreholes. To produce a tomographic section using either technique, the medium must be probed by sending signals along many orientations. By making measurements with both the source and the receiver at a number of different positions in their respective holes, we can obtain data for a multitude of signal paths through the region.

Successful application of these underground imaging techniques provides a two-dimensional view of the effects of air injection/extraction on the groundwater regime. This information allows an understanding of the heterogeneous subsurface environment and of the induced flow processes that act upon the contaminant and the geologic environment. Groundwater flow strongly influences contaminant mobilization and transport, and geologic structure affects the flow of groundwater and vapor flow. Underground imaging techniques have several advantages: they reduce the need for the many boreholes that would be required to monitor the air injection/extraction process, prevent the potential spreading of contaminants from those boreholes, and save money and time.

High-Frequency Electromagnetic Measurements

HFEM tomography is conceptually similar to the medical tomography that inspired it. A region to be studied is sampled by transmitting energy through it along many paths of known orientations. From the transmission data, a cross-sectional image of the region of interest is constructed. This technique involves the measurement of phase change and signal attenuation in the frequency range of 34–38 MHz. For a given path length, the phase change is a function of the water content of the medium.

Electrical Resistance Tomography

ERT uses measurements of the resistivity of the soil mass to infer the quantity of water present. As in the case of the dielectric constant, the bulk resistivity is a strong function of water content: the resistivity decreases with increasing amounts of water. In the case of ERT, lines of electrodes (which can act as both sources and receivers) are strung out along boreholes. To determine the resistivity, current is passed between multiple pairs of electrodes. The electrical potential differences due to the presence of these dipoles are then measured at many locations. The values of these measured potential differences must reflect the distribution of current density within the medium and, thereby, the distribution of electrical resistivity.

Preliminary HFEM Results

High-frequency electromagnetic measurements have been made between boreholes MHM 3 and 4 and between boreholes MHM 4 and 5. The tomograph regions were chosen to define the changes in moisture content expected to occur from air injection/extraction. All measurements were made using an automatic network analyzer controlled by a computer. An electrical short-sleeve dipole antenna was used for a transmitter and an active monopole antenna was used as a receiver. At each antenna position, the signal amplitude was measured at 36 MHz, and the phase was measured as the frequency was swept from 34 to 38 MHz. Using this information, we obtained the line integral permittivity and attenuation rate. Image reconstruction is by an algorithm described by Dines and Lytle (1979).

Tomographs presented here are of electromagnetic permittivity. To be useful, these data must be able to be interpreted in terms of moisture content, which requires laboratory calibration of the electromagnetic properties of materials at the project site. Although calibration work is outside the scope of our current activities, we used volume-fraction mixing rules to develop estimates of parameters such as saturated porosity and percent saturation; this can be done only if certain assumptions for material properties are made. A preliminary interpretation of the HFEM results suggests that the estimated saturated porosity for sand near the injection well is 34%; this estimate assumes that the dielectric constant for the dry silicate minerals is 4 and that for water is 81. The changes in dielectric constant measured during the test suggest that air injection may have dropped the degree of bulk saturation below the water table from 100% to as low as 80%.

Tomographs in Fig. 1 illustrate some additional interpretations. The image to the left shows the distribution of permittivity before air injection/extraction started; approximately 170 rays and a pixel size of 6 ft by 6 ft were used to reconstruct this image. This image shows that regions of relatively high permittivity are found at depths between 98 and 118 ft and between 136 and 174 ft. The former corresponds to a clay layer recognized in lithologic logs of nearby wells; the latter corresponds to the saturated zone below the water table. Notice the significant contrast in permittivity between the sands above and below the water table. The center image shows the permittivity distribution for the

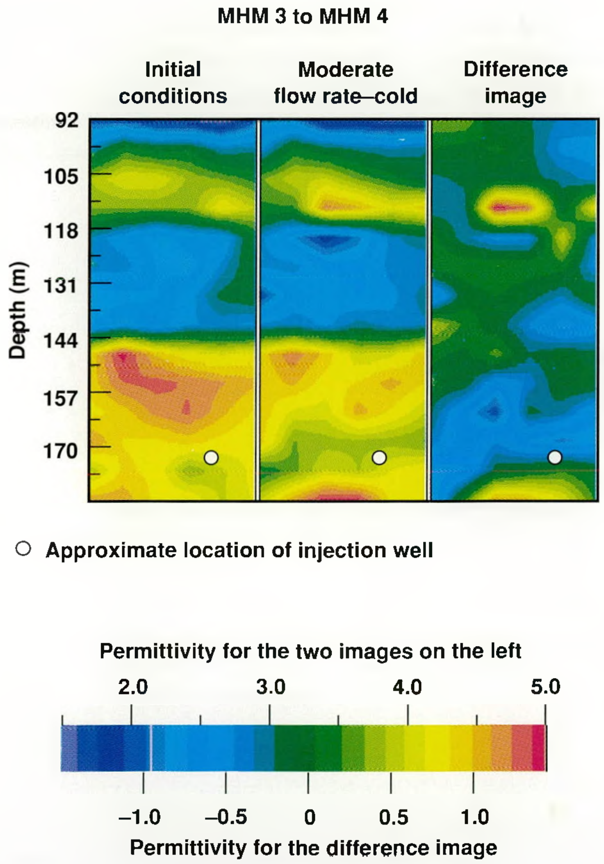

Fig. 1. HFEM tomographs showing the permittivity distributions before and during air injection and the differences between them.

same region after injection was started. The image to the right shows the differences in permittivity between the other two images. This image shows that the permittivity in the region between 151 and 167 ft has decreased significantly. Our preliminary interpretation is that this decrease corresponds to a decrease in moisture content from air injection. Other data suggest that the sands above the water table are also showing a decrease in permittivity, probably because of decreases in moisture content.

Preliminary ERT Results

Figure 2 shows the borehole layout used for ERT and HFEM during the SRIDP. Boreholes MHM 3 and MHM 5 were completed with alternating steel and plastic casing so that the steel sections, spaced 12 ft apart between a depth of 100 and 200 ft, are used for ERT electrodes. Current is injected and voltages are measured at these electrodes using a string of removable probes that make contact with each downhole electrode, but can also be connected to instrumentation at the surface. This arrangement allows the boreholes to be used for both HFEM and ERT. Various ERT data sets have been collected during the air injection/extraction process. Using an algorithm that iteratively fits the measurements (in a least-square sense) to those calculated from a finite-element model, we have constructed a tomograph of the resistivity distribution in the plane between the two boreholes.

Figure 3 shows a tomograph that depicts the electrical resistivity distribution based on data obtained during maximum flow injection. Note that the pixel size is 12 ft by 12 ft. The locations of various features sampled by the image plane are also shown. An anomaly having a relatively low resistivity is present between the depths of 100 and 110 ft. It is associated with a clay layer recognized

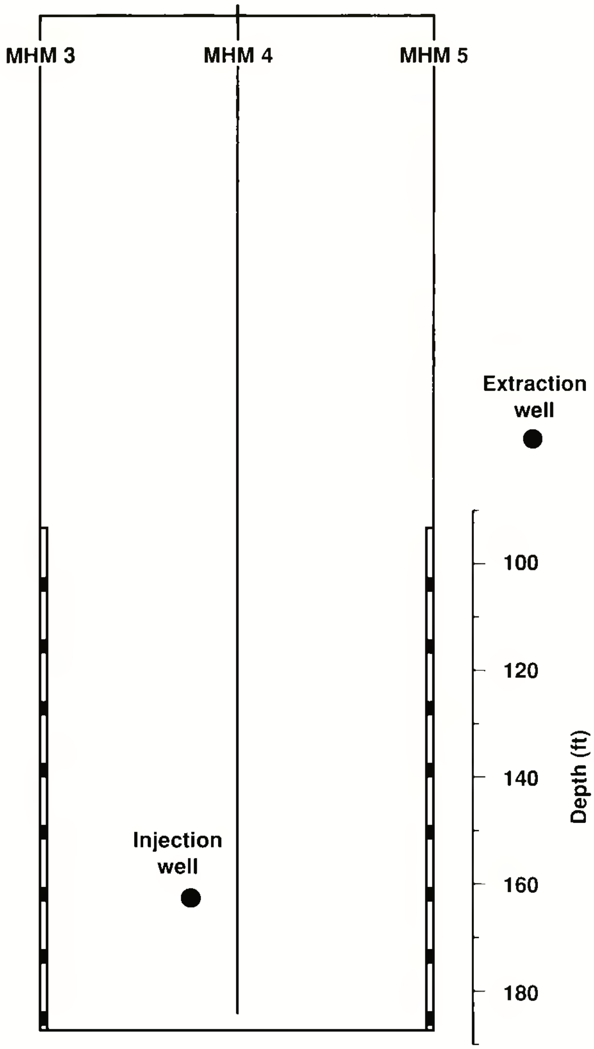

Fig. 2. Borehole layout used for ERT and HFEM imaging.

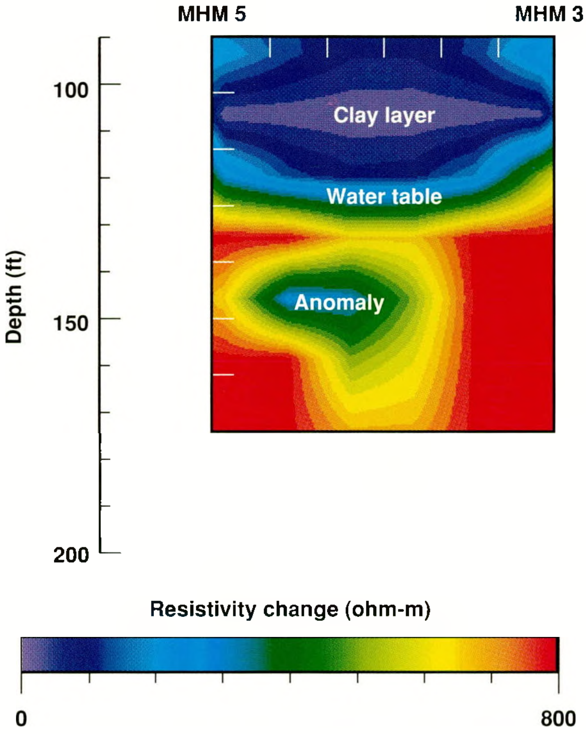

Fig. 3. ERT tomograph showing the resistivity distribution during air injection.

in the core collected in the near vicinity of the image plane. A change in resistance observed near the 130-ft depth is probably related to the presence of the water table. One other anomaly is observed below the water table centered at a depth of 150 ft. Our hypothesis is that it may be related to the air injection process going on at the time the data were collected. Additional analyses are planned to evaluate this hypothesis.

HFEM and ERT Water-Injection Experiment

Experiment

Information on the flow of groundwater through the unsaturated zone is required for validation of models for flow through this zone. Many contaminated sites are located above the water table, so key questions that must be answered during the characterization and assessment of such a site are how much water passes through the unsaturated zone and at what rate. Current techniques to do this involve the costly emplacement of multiple drill holes.

We are using HFEM and ERT to map the distribution and movement of water of an artificial recharge of the unsaturated zone at LLNL. This experiment is being conducted at LLNL's Extraction Well Discharge Facility (EWDF), an artificial recharge basin that is used to discharge decontaminated groundwater (originally contaminated with VOCs) after it has been treated.

The results of this field experiment will be compared with calculated infiltration profiles. The goal of the experiment is to demonstrate the usefulness of underground imaging techniques to define the flow behavior of fluids with localized sources (e.g., disposal trenches or tanks) in the unsaturated zone. The experiment is estimated to last approximately one year. A trench was constructed at the facility to direct the water flow from the pipeline outlet to the location of interest (Fig. 4), and boreholes were drilled to the water table depth. The boreholes were completed with

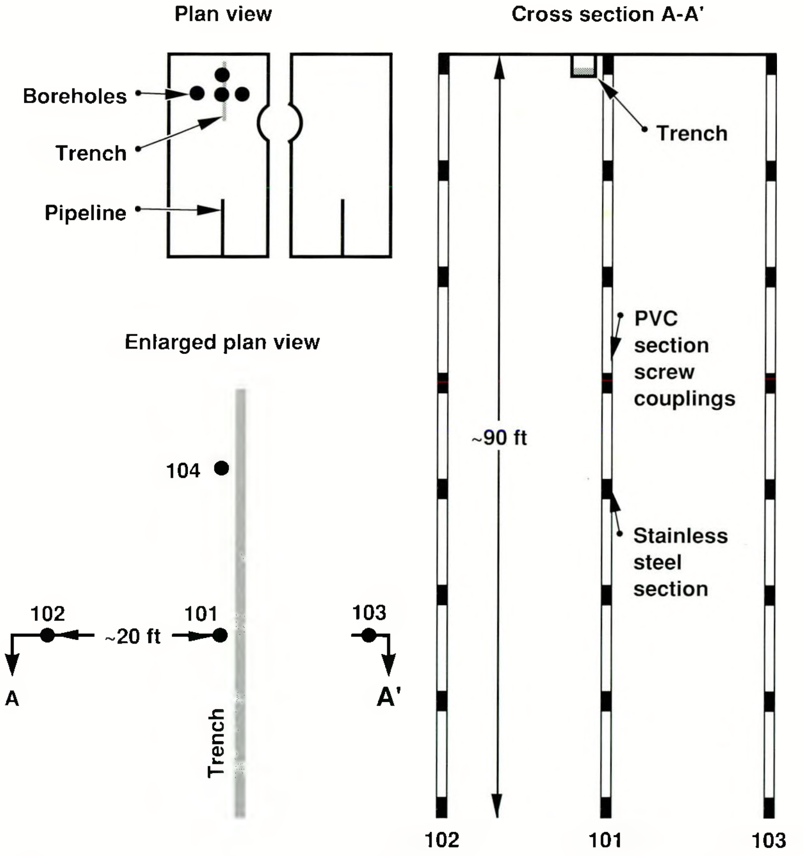

Fig. 4. Borehole layout used for ERT and HFEM imaging of the vadose zone beneath the Extraction Well Discharge Facility.

alternate sections of PVC and stainless steel casing sections as shown in cross section A–A′ of Fig. 4. The annular space between the casing and the borehole wall was grouted with a cement/bentonite grout (10% bentonite).

Prior to the test, hydrologic modeling of the infiltration region was performed and baseline HFEM and ERT data were collected. To begin the infiltration process, water discharge was diverted to the trench during the last month of FY90. Geophysical measurements that record wetting behavior will be made at frequent intervals as infiltration develops. Discharge at the test location will continue for a period of a few months. Measurements will continue at intervals for the next six months so that we can observe the drying behavior of the vadose zone. The geophysical results will be inverted using tomographic techniques and interpreted in terms of the change in moisture content (from baseline conditions). Finally, our interpretations will be compared with the numerical predictions of moisture content change.

Preliminary Results

Figure 5 shows the ERT image of data taken at the EWDF. Eight electrodes are evenly spaced from the surface to 85 ft depth along each of the two

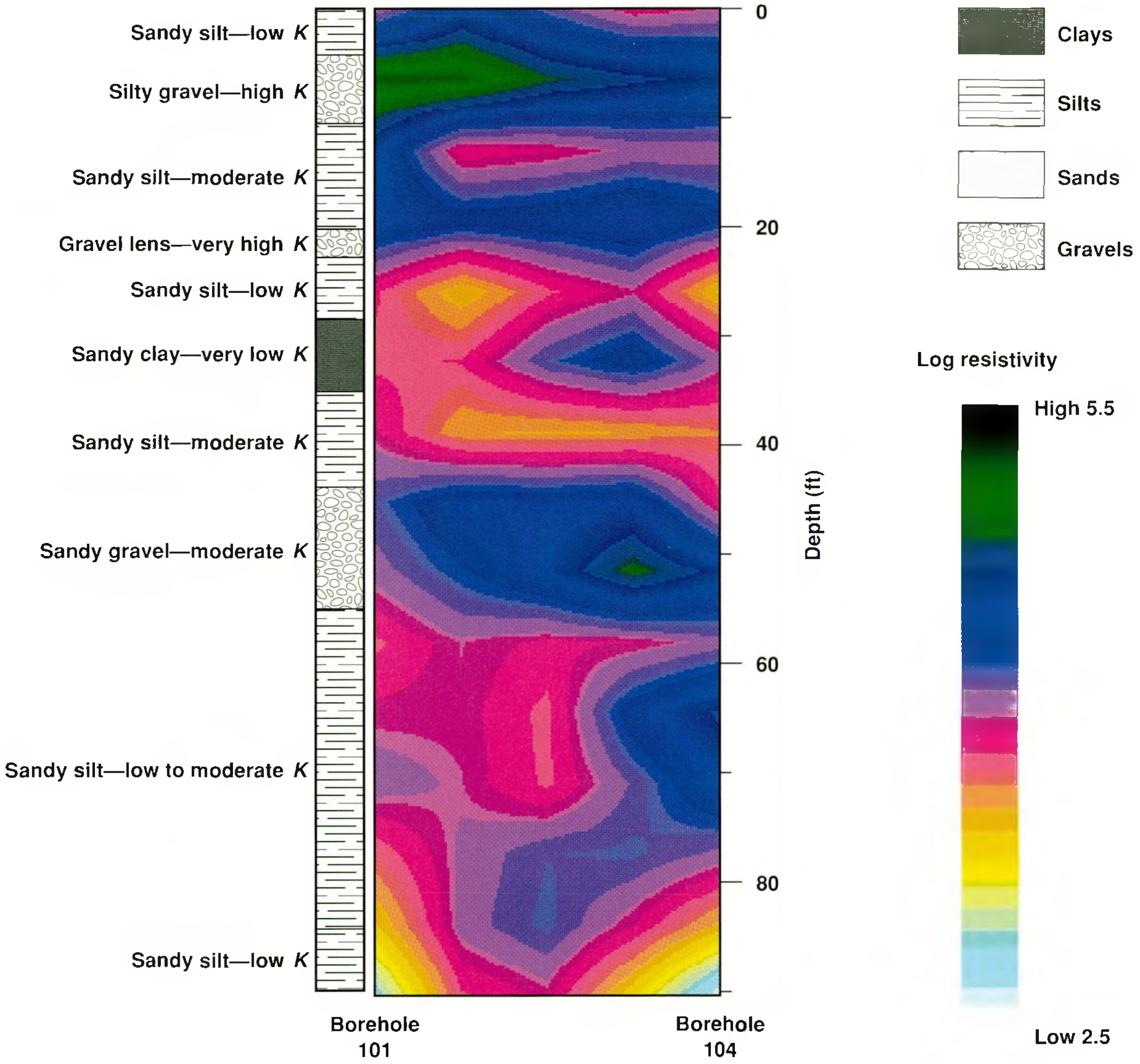

Fig. 5. ERT tomograph of the electrical resistivity distribution before the start of water infiltration.

boreholes as shown in Fig. 4. From these electrodes, 451 different combinations of current and voltage dipole measurements were collected. This image represents the electrical resistivity prior to any water being added to the trench.

Highly resistive parts of the ground are shown as darker colors and less resistive regions as lighter. Variations in resistivity of two-and-a-half orders of magnitude are observed between these boreholes. From the drilling logs of each borehole, we can see some correlation between the lithology and resistivity image. The most resistive regions are gravels, which also have the highest permeability (*K*). Conversely, the least resistive regions (with lowest permeability) correspond to the more silty material containing clay-sized particles.

Modeling and Analysis of Air Injection and Vapor Extraction Using a Pair of Horizontal Wells for *In Situ* Stripping of Volatile Organic Compounds

Principal Investigators: Thomas A. Buscheck and John J. Nitao

We are conducting a numerical modeling study in support of a pilot study of* in situ *stripping of volatile organic compounds. The purpose of our study is to assist in design and operation of the test, monitoring of pressure and saturation changes occurring during the test, and interpretation of field results.

Introduction

Two horizontal wells have been installed at the Savannah River Plant near Aiken, SC, to test the feasibility of *in situ* stripping of volatile organic compounds (VOCs) from the saturated and unsaturated zones. One is an air-injection well lying below the water table; the other is a vapor-extraction well screened in the vadose zone (Kaback et al., 1989a,b). We are conducting a numerical modeling study to assist in (1) the design and operation of the test, (2) the monitoring of pressure and saturation changes occurring during the test, and (3) the interpretation of field results. In FY90, we focused on the flow of air and water vapor between the wells, and considered the implications of the flow patterns on VOC stripping (Buscheck and Nitao, 1990). Emphasis is also placed on understanding the mechanisms affecting the effectiveness of *in situ* VOC stripping and how the operational parameters can be varied in order to enhance performance.

Calculations

The calculations were performed with the V-TOUGH code—LLNL's enhanced version of Lawrence Berkeley Laboratory's TOUGH code (Nitao, 1989; Pruess, 1987). V-TOUGH is a multidimensional numerical simulator capable of modeling coupled transport of water, air, and heat in heterogeneous, anisotropic, porous media. Assuming that the wells are horizontal, parallel, almost infinitely long, and that regional groundwater flow can be neglected, we constructed a two-dimensional cross-sectional model orientated orthogonally to the well axes and symmetrical about the vertical plane through the two wells (Fig. 1). The extraction and injection wells are perforated 16.5 m above and 9.1 m below the water table, respectively.

Using the detailed geologic descriptions and permeability data (which were based on sieve analysis) provided by Savannah River Laboratory, we identified 18 distinct hydrostratigraphic sub-

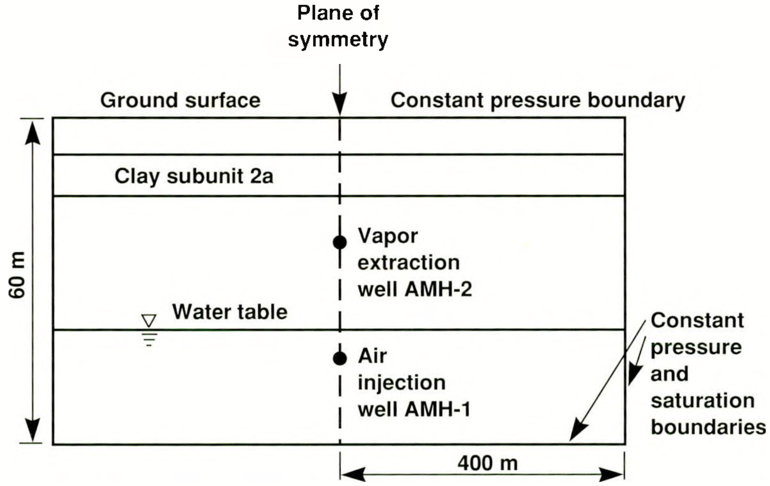

Fig. 1. Schematic of the conceptual model used in the simulation. The vertical scale is exaggerated by a factor of 10.

units that are discretely accounted for in our model. For this system, the most significant hydrostratigraphic feature is that most of the subunits are relatively permeable with the exception of an upper clay, which acts as an upper no-flow boundary located 10.7 m below the ground surface, and a relatively tight, silty, clayey sand subunit lying between the extraction well and the water table, with one-fifth to two-fifths the permeability of the adjacent subunits.

Three different cases were simulated in order to investigate the system response to a broad range of injection/extraction well flow-rate histories. For Case 1, the "nominal" case, the injection and extraction flow rates were equal ($\Delta Q = 0$) and constant throughout the 40-day test period. An examination of the pressure and saturation fields indicates that a steady-state flow field was established between day 2 and day 5. $\Delta Q = 0$ results in a narrow two-phase injection zone of buoyancy-driven flow between the injection well and the water table (Fig. 2). Because gas flow in this two-phase zone is primarily linear upward flow, gas-phase pressures are constrained to be close to hydrostatic (Fig. 3). Consequently, the gridblock pressure of the injection well does not deviate significantly from hydrostatic pressure.

Because $\Delta Q = 0$ results in little overpressuring of the vadose zone, the water table is depressed only 1.3 m at the plane of symmetry (Fig. 4). At the top of the two-phase zone, there is an abrupt transition to radial single-phase gas flow in the vadose zone, with the radial flow field centered at the top of the two-phase zone (Fig. 5). The effect of the leaky barrier is to partially pneumatically isolate the extraction and injection wells, thereby exaggerating the pressure drawdown and buildup and laterally distorting the doublet flow field.

Because *in situ* stripping of VOCs from the saturated zone is dependent on the contact between the injected air and water, these results indicate that injecting and extracting at equal mass rates will result in a limited sweep zone. Cases 2 and 3 were designed to better understand flow conditions that would allow better sweep geometry. Improved sweep effectiveness can be achieved by pulsing the system with periods of overinjection to broaden the sweep zone and periods of overextraction to "capture" gaseous VOCs that had been displaced laterally during periods of overinjection.

Before looking at pulsed flow rates, we decided to investigate overinjection with an extreme example of using only air injection (Case 2). In order to illustrate the extreme consequences of overinjection, a high mass injection rate was specified (0.03 $kg{\cdot}s^{-1}{\cdot}m^{-1}$).

We found that steady-state flow was effectively established between day 2 and day 10. Because of the high overinjection rate, the resulting high vadose-zone pressures quickly depress the water table downward. Within two days, the water table is displaced 9.1 m (to the depth of the injection well), thereby replacing the two-phase injection zone with a zone of complete desaturation. The

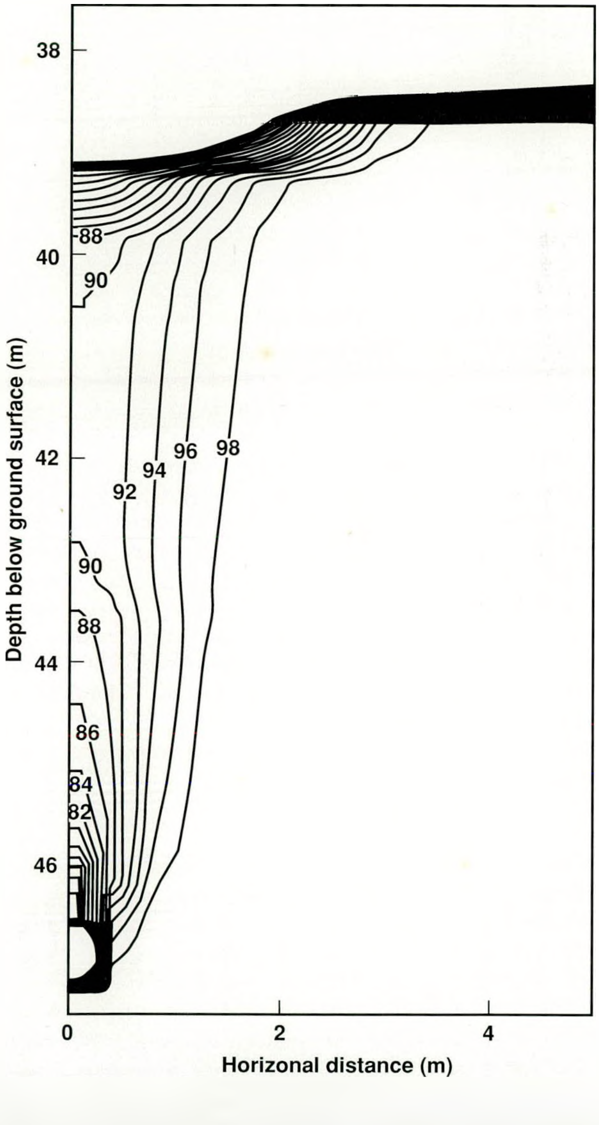

Fig. 2. Near-field contour plot of percent liquid saturation at 10 days for Case 1. Only the saturation contours between 60 and 100% are plotted. The saturation contour interval is 2%.

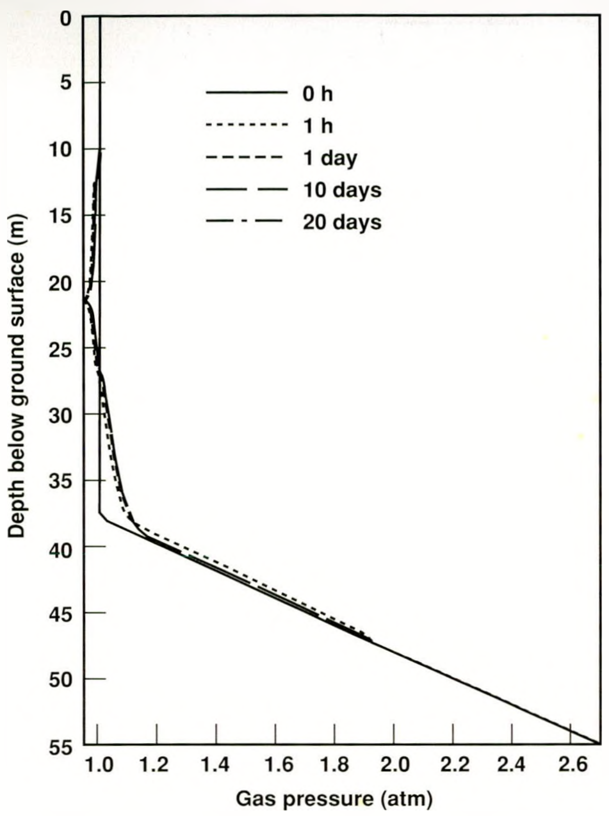

Fig. 3. Vertical pressure profile along the plane of symmetry for Case 1 at various times.

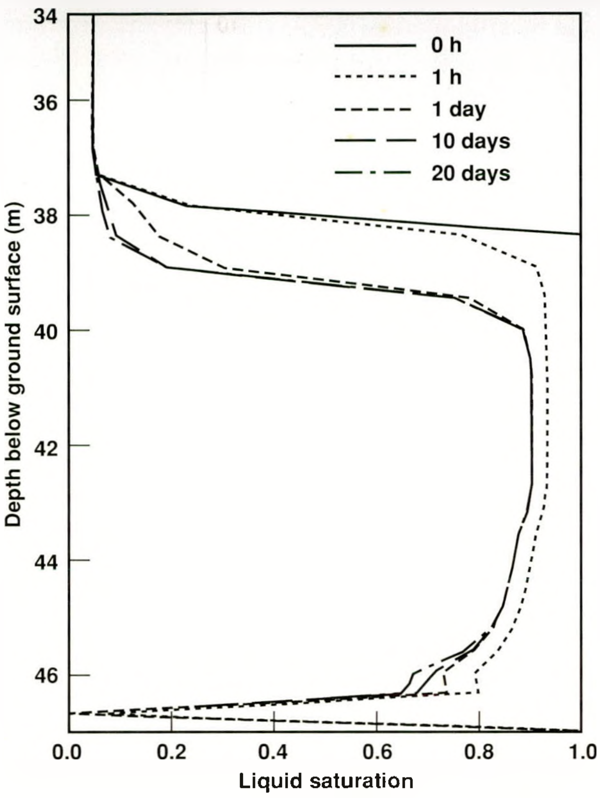

Fig. 4. Vertical liquid saturation profile along the plane of symmetry for Case 1 at various times.

radial single-phase gas flow region is now centered at the injection well itself. Because radial flow allows horizontal pressure gradients around the injection well, injection pressures are no longer constrained by hydrostatic pressure and two-phase flow effects.

In Case 3, various combinations of flow rates were employed to obtain successive periods of $\Delta Q = 0$ and $\Delta Q > 0$. Insofar as $\Delta Q = 0$ results in a relatively narrow sweep zone (thereby limiting its VOC sweep effectiveness), the focus in Case 3 continued to be on cycles where $\Delta Q \geq 0$. The insight gained from studying the system response to a wide range of overinjection conditions will provide a theoretical foundation for the design of optimized VOC recovery cycles. At the same time, it will be necessary to capture the gaseous VOCs that have been laterally dispersed during overinjection cycles, which will be best achieved through the use of extraction-only cycles.

Case 3 employs eight five-day cycles, alternating between $\Delta Q = 0$ and $0.015\ \mathrm{kg{\cdot}s^{-1}{\cdot}m^{-1}}$. Three different base flow rates, Q0, were also investigated. While the $\Delta Q = 0$ cycles again had a relatively narrow two-phase injection zone, the width of this zone increased with Q0. For the overinjection cycles, we found that employing one-half the ΔQ used in Case 2 resulted in the two-phase injection zone remaining throughout all of the four overinjection cycles. Consequently, injection gridblock pressures were always close to hydrostatic.

Changing flow conditions at the beginning of any given cycle always results in an abrupt transient period, with steady-state flow established by the end of the cycle. At the injection well, this initial transient period always indicated two-phase flow

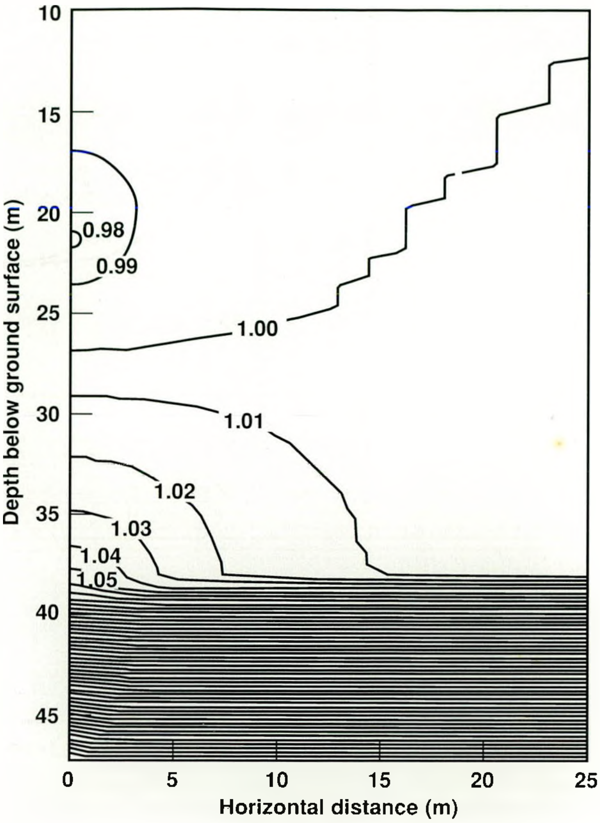

Fig. 5. Near-field contour plot of pressure (atm) for Case 1 at 10 days. The pressure contour interval is 0.01 atm.

effects, as saturations in the two-phase injection zone adjusted to attain the combination of gas-phase pore volume and a balance between hydrostatic pressure, gas-phase pressure, and capillary pressure.

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A Fiber-Optic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons

Principal Investigator: Fred P. Milanovich
Other Investigators: Paul F. Daley, S. Michael Angel, Kevin C. Langry,
William Colston, Jr., and Steven B. Brown

For use in groundwater and vadose-zone monitoring, we have developed a fiber-optic chemical sensor that is a modification of our previously developed fluorescence-based sensor that identifies various volatile hydrocarbons. It works on the principle of detecting quantitative, irreversible chemical reactions that form visible, light-absorbing products. The fiber-optic sensor, evaluated against gas-chromatographic standard measurements, has demonstrated accuracy and sensitivity sufficient for environmental monitoring of trace levels of the contaminants trichloroethylene and chloroform.

Introduction

The fiber-optic chemical sensor technology is an outgrowth of research initially sponsored by the U.S. Environmental Protection Agency, for whom a fluorescence-based probe for the remote detection of chloroform was conceived, developed, and demonstrated in the mid-1980s (Milanovich et al., 1986). When the sensitivity and accuracy of the probe proved insufficient for many monitoring applications, research was discontinued. However, in other DOE-sponsored research, we invented a new-concept sensor that has demonstrated significantly improved sensitivity and accuracy for both TCE (trichloroethylene) and chloroform (Angel et al., 1989). This sensor is currently under evaluation for monitoring well and vadose-zone applications.

Principles of Operation

The basic components of the sensor technology are the chemical reagent, the sensors, and the electro-optic measurement device. We have developed two types of sensors, one for single and one for continuous measurements.

The chemical basis of this technology is an irreversible development of color in specific reagents upon their exposure to various target molecules. The primary reagent is an outgrowth of the work of Fujiwara (1916), who first demonstrated that basic pyridine, when exposed to certain chlorinated compounds, developed products with an intense red color. We and others have since demonstrated that this and closely related reactions can be used to detect trace amounts of these same compounds (Angel et al., 1987).

The single-measurement sensor is composed of the terminus of two optical fibers and an aliquot (20 µL) of reagent in a small capillary tube. The fibers are sealed into one end of the capillary tube, and reagent is placed into this capillary to a length of approximately 5 mm. A porous Teflon membrane is placed over the open end of the capillary to prevent loss of the reagent. Target molecules, TCE for example, readily pass through the membrane and produce color in the reagent. This color results in decreased transmission of light at 540 nm. The measurement of the time history of the color development provides a quantitative measure of the target molecule's concentration. Since the reaction is nonreversible, the reagent must be replenished for every measurement, which is readily accomplished through the use of replaceable, disposable capillaries.

Figure 1 shows a sensor that has been designed for continuous operation (Berman et al., 1990). It is essentially identical to the single-measurement version, except that two microcapillary tubes have been added. These tubes supply new reagent to the sensor either continuously or on demand.

The readout device is shown schematically in Fig. 2. The emission of a miniature tungsten–halogen lamp is collected by suitable optics,

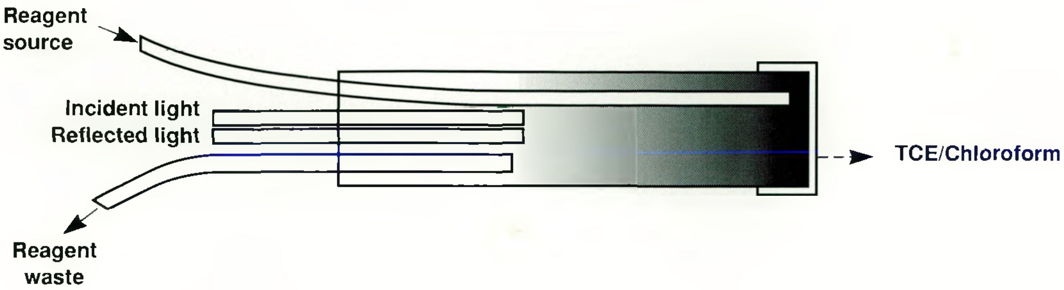

Fig. 1. Schematic of continuous-measurement sensor.

chopped with a tuning fork, and directed into an optical fiber. The fiber transmits this light with high efficiency to the sensor, where the light passes through the chemical reagent, reflects off the Teflon membrane, and is collected by a second optical fiber. This latter fiber transmits the reflected light to an optical block, where it is divided into two beams by a long-pass dichroic mirror. These resulting beams are optically filtered at 540 and 640 nm, and their intensity is ultimately measured with silicon photodiodes using phase-sensitive detection techniques.

Because the colored product absorbs strongly at 540 nm and is virtually transparent at 640 nm, the ratio of 540 to 640 gives a nearly drift-free measure of 540-nm absorption. The sensors are calibrated in two ways: in the headspace above standard TCE solutions of known weight/weight concentration, or in vapor phase using calibrated dilutions (volume/volume) of dry TCE vapor. Figure 3 shows the time-dependent transmission of sensors exposed to TCE standard solutions every 10 min and a resulting calibration curve.

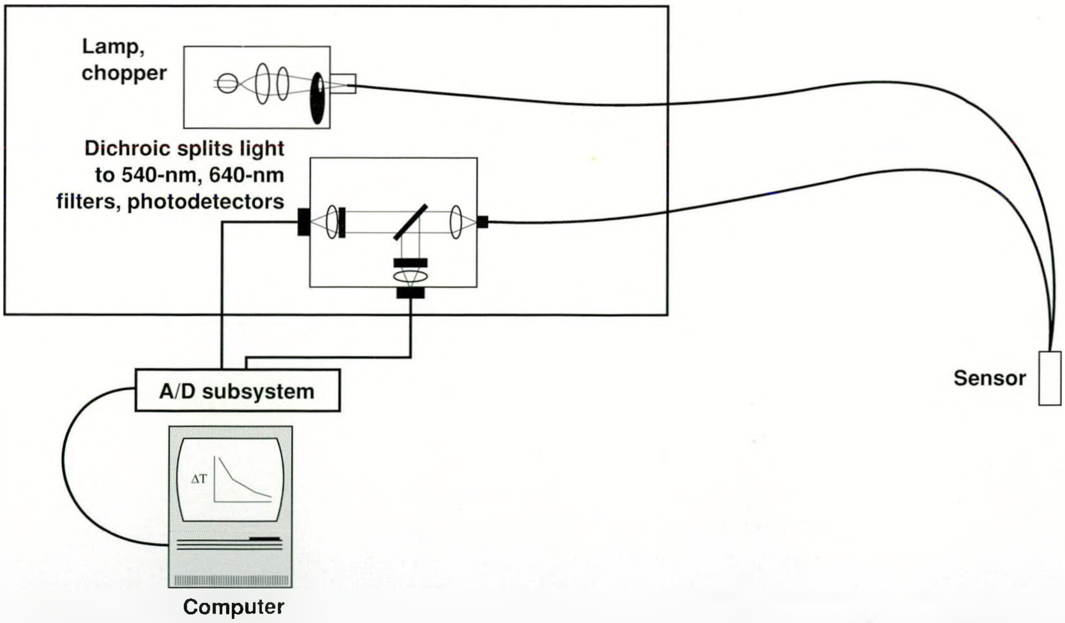

Fig. 2. Sensor readout device.

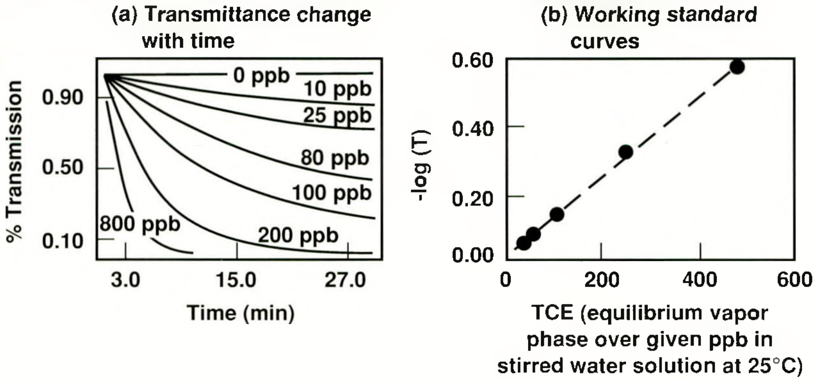

Fig. 3. Sample transmission and working curve for absorption sensor.

Results and Discussion

For groundwater monitoring, the single-measurement sensor has been evaluated against a contractor sample and analysis of 40 monitoring wells located within the boundary of LLNL. These wells are sampled quarterly and chemically analyzed according to EPA Standard 624 purge and trap gas chromatography. We obtained concurrent samples during the quarterly contractor sampling and used our fiber sensor to make duplicate TCE concentration determinations. Samples were sequestered with no headspace into 250-mL Pyrex bottles. These were immediately returned to the laboratory and divided in half. The fiber sensor was then introduced into the resulting headspace through a gas-tight valve, and a measurement was initiated after stirring the sample for 5 min.

Table 1 shows a comparison of some of the contractor measurements (using a gas chromatograph [GC]) with measurements using the fiber sensor. All fiber-sensor values are the average of the duplicate samples. There is excellent agreement between the GC and the fiber-sensor determinations, since nearly all values fall within the variance of the GC.

Table 1. Comparison of TCE measurements from monitoring wells at LLNL.

		TCE (ppb)	
Well	Date	Fiber-optic sensor	Gas chromatograph
MW142[a]	3/06/90	94	140
MW217	3/05/90	106	86
MW271	3/07/90	86	160
MW352	2/13/90	44	58
MW357	2/13/90	78	84
MW364	3/07/90	59	74
MW365	3/06/90	27	22
MW458	3/06/90	33	20
P418[b]	2/13/90	54	72
P419	2/13/90	61	66

[a] MW = monitoring well.
[b] P = piezometer.

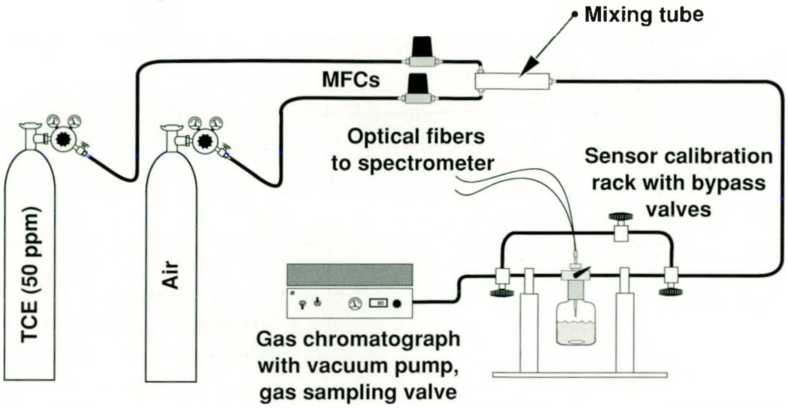

Fig. 4. Schematic of vadose-zone calibration and measurement scheme.

For vadose-zone monitoring, LLNL's Site 300 was chosen as the location for initial evaluation of the fiber sensor. The vadose zone was accessed at several locations through existing dedicated, soil-vapor monitoring points. The samples were drawn at nominally 450 cm^3/min through copper tubing to a remote mobile laboratory. The lab contained both the fiber-optic sensor apparatus and a portable GC. The instruments were connected to the sample stream in series as depicted in Fig. 4. Both devices were calibrated for TCE measurements with precision gas mixtures prior to sampling. The fiber-optic sensor tracked the GC very well through a wide range of concentrations. Results from both instruments demonstrate that the GC was at its limit of detection, whereas the fiber sensor readily made a successful measurement. Estimates of TCE concentration for this location were less than 10 ppb.

The single-measurement sensor demonstrates adequate sensitivity and accuracy for this viable new environmental monitoring technology. However, because the current design requires the sensor to be refurbished after each measurement, its application is somewhat limited in environmental monitoring. Preliminary results with prototypes of a continuous-measurement sensor are very promising. Figure 5 shows typical on-demand measurements obtained with this sensor in laboratory testing. We anticipate that this sensor will become an integral component in a down-well monitoring instrument currently being developed at LLNL.

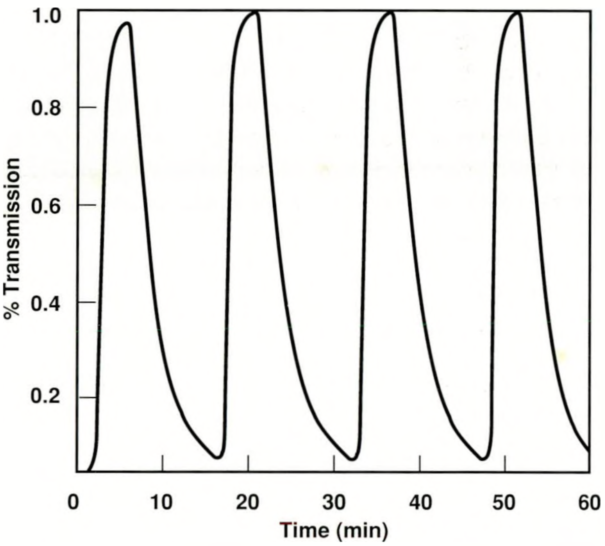

Fig. 5. On-demand measurement of 10 ppm of TCE with continuous sensor.

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Field-Based Measurement of Contaminant Distribution Coefficients and Retardation Factors

Principal Investigator: David W. Rice

Better site-characterization methods are needed for determining cleanup strategies for contaminated groundwater aquifers. We are developing a sampling approach that promises to yield an accurate prediction of contaminant movement based on field determinations.

Introduction

For efficient remediation of contamination in saturated media, assessing the total amounts of contaminants is vital. However, current methods of measuring the distribution coefficients (K_d) of contaminants between solid and liquid phases can be problematical. We are developing and demonstrating field-based measurement techniques that accurately reflect the distribution of volatile organic compounds (VOCs) between solid and liquid phases and the derived retardation factors (R) in saturated media. Though the project is limited to the study of VOCs (especially perchloroethylene, PCE) present in alluvial sedimentary materials, the techniques can be applied to other types of contaminants such as metals and radionuclides, and to other geologic settings.

These new techniques will lead to more realistic cleanup strategies and cost projections. Based on innovative methods for geologic characterization, they do not introduce tracers that would further contaminate the site. Our work has three areas of focus:

1. Development and validation of innovative techniques for sediment characterization.
2. Development of an algorithm to calculate field-based K_d and R.
3. Comparison of field-based determinations of K_d and R with laboratory results, modeling scenarios, and site-history matching.

This demonstration project is partially supported by the DOE Office of Environmental Restoration and is part of the Remedial Investigation/Feasibility Study activities at the Livermore site, which are being conducted in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act. All of these activities are guided by terms of a Federal Facility Agreement negotiated on behalf of LLNL by DOE, the U.S. Environmental Protection Agency, the California Regional Water Quality Control Board – San Francisco Bay Region, and the Department of Health Services.

The results of our project will be used to address the needs of LLNL and other DOE sites in:

- Understanding contaminant distribution and migration in the subsurface.
- Demonstrating better strategies for site characterization and sampling.
- Providing input to models that assess transport and transformation of contaminants.
- Comparing groundwater remediation alternatives.

Spatial Characterization

Field-based distribution coefficents are being used in predictive models to assess contaminant plume migration, extent of site contamination, and effectiveness of remedial processes. By establishing and validating a sampling approach that yields an accurate prediction of contaminant movement, we can

- Estimate more accurately the time required to clean up a VOC plume.
- Use more effectively the boreholes constructed during remedial investigations.
- Design remediation systems that maximize efficient cleanup.

A thorough understanding of the subsurface environment is critical in evaluating the effectiveness of our methods. We must be able to distinguish between geologic, measurement, and/or sampling uncertainties. To this end, we have chosen an area above a PCE plume on the LLNL site and conducted a detailed spatial characterization of the chemical, physical, and hydraulic parameters necessary to determine a field-based R (Figs. 1(a) and (b)).

The characterization of permeable materials shows what appears to be a series of buried stream channels, probably deposited by the ancestral Arroyo Seco. A reconstructed idealized cross section of a buried stream channel through boreholes 518, 520, and 521 at depths between 80 and 105 ft is shown in Fig. 1(c). This figure is based on interpretations of the geophysical logs, geologists' lithologic description, and PCE distribution.

Within a permeable zone, changes in PCE concentrations occur on a vertical scale of 1 to 3 ft. A sharp gradient of PCE concentrations in the confining sediments is observed declining away from the permeable sediments. The spatial distribution of PCE is significantly related to the distribution of permeable materials. We conclude that hydraulic conductivity is a major controlling factor in the distribution of PCE in this area.

An important implication of the spatial distribution is that, because a monitor well's screened interval covers an entire permeable zone, groundwater collected as representative of aquifer pore water is extracted from sediments with a variety of PCE concentrations. Therefore, the groundwater sample is an integrated vertical and horizontal average of the PCE concentrations in the pore water of the screened zone. Care should be taken to ensure that data representing the same spatial scales are used during the calculation of partitioning coefficients. For example, saturated sediments within a monitor well completion zone should be sampled frequently enough to adequately represent the variability of total PCE present in saturated sediments. In this way, an average of the total PCE concentrations in saturated sediments within the zone of interest will represent the same vertical spatial scale as does the groundwater extracted from the well.

Calculations and Sample Analysis

Because of this concern over spatial scale, we investigated two calculation approaches to determine field-based K_d and R: (1) a spatially averaged approach using average VOC concentrations from saturated sediments collected across a permeable zone and from monitor well water screened in the same permeable zone, and (2) a spatially discrete approach using data collected from a discrete sampling depth using specially designed and constructed bulk thermal desorption and pore water extraction chambers. Concentrations of PCE in the pore water centrifuged from aquifer samples (approach 2) were averaged and compared with average PCE concentrations in groundwater from the screened interval (approach 1). The values differ by an approximate factor of 10 (Table 1). One possible explanation for the difference may be that pore water within the aquifer sample is displaced by drilling fluids during the drilling and depth-sampling process. These field-based determinations of K_d and R compared well to laboratory-derived values and values determined from solute transport modeling, such as site-history matching determinations.

We analyzed three samples for inorganic ions to identify possible ion signatures that might be used to quantify pore water displacements by drilling fluids. These samples were (1) pore water extracted from a saturated aquifer sample from borehole 602, using the pore water extraction chamber; (2) pumped groundwater collected from monitor well 602; and (3) drilling fluids. Drilling fluid prepared using pure bentonite clay was found to have higher concentrations of sodium and lower concentrations of calcium than LLNL groundwater. By comparing the measured sodium, calcium, and PCE concentrations in aquifer sample pore water with the concentrations in groundwater from monitor well 602, we calculate pore water displacement at 60–80%. Although these data are based on a single determination, the information is important in calculating field-based K_d and R. Analysis of centrifuged pore water samples is continuing, and additional data points will soon be available.

During the final phase of this project in FY91, we will develop methods to incorporate the subsurface spatial variability of field-measured K_d into predictive modeling of the rate of plume movement, the extent of site contamination, and the effectiveness of remedial processes.

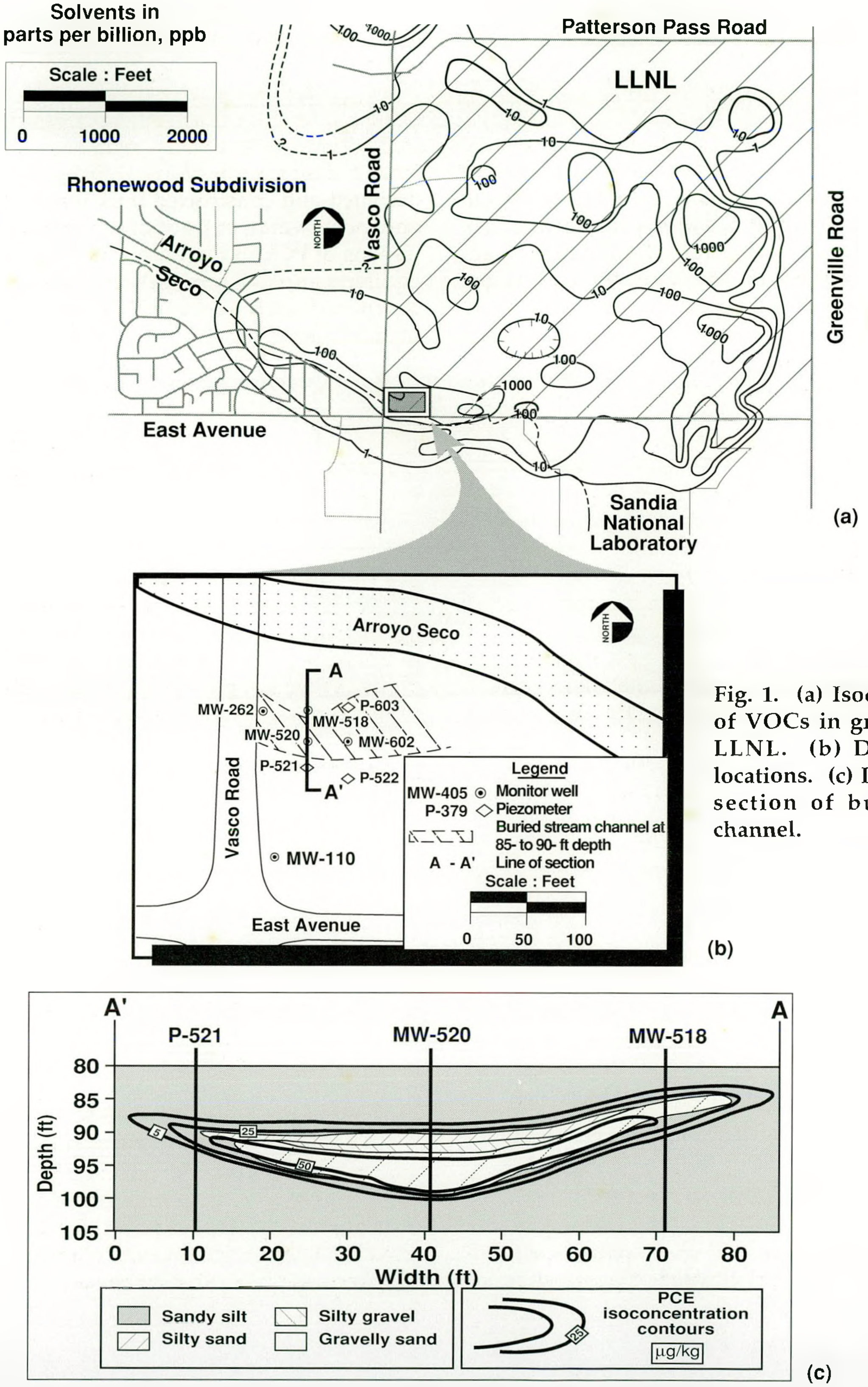


Fig. 1. (a) Isoconcentrations of VOCs in groundwater at LLNL. (b) Detailed well locations. (c) Idealized cross section of buried stream channel.

Table 1. Comparison of K_d values from field-based and laboratory analyses for PCE.

		K_d method		
Monitor well	Depth (ft)	Spatially averaged	Spatially discrete	Laboratory batch
MW-518	131–139	0.516	—[a]	
	136			0.52
MW-520	94–101.5	0.126	—	
	95.3			1.20
MW-521	86–95	0.11	—	
	90.0			2.02
MW-602	90–100	0.21		
	88.5–88.8		0.57	
	90.8–91.0		0.52	
	97.3–97.8		0.83	
	93.8–94		0.6	
	93.5			1.07
	95.5			1.00
	97.5			0.41

[a] Measurements in progress.

In Situ Microbial Filters

Principal Investigators: Richard B. Knapp, Alfred G. Duba, Kenneth J. Jackson,
John P. Knezovich, Robert T. Taylor, and Ananda M. Wijesinghe

We are integrating studies in five disciplines to develop subsurface microbial filters to clean contaminated groundwater; this unique integrated approach has potential to provide significant advances in subsurface bioremediation. A large-scale two-dimensional model will be used as a test bed. The concept has the potential to realize significant cost savings over the standard pump-and-treat method.

Introduction

Many of the hazardous or toxic organic compounds that contaminate subsurface soils of many DOE sites can be biotransformed to nontoxic substances by *in situ* microorganisms. This remediation method is currently of great interest because of its minimal adverse impact on the environment and human health. However, there is a poor understanding of how the process operates and how it can be optimized.

Subsurface contamination often occurs as large three-dimensional plumes that expand over time. Current thinking is that it is unrealistic to consider bioremediation of an entire large, moving plume; difficulties include the ability to supply nutrients as well as the possible adverse consequences of nutrient injection on groundwater flow. We plan to develop and evaluate a microbial-filter strategy (Fig. 1). In this strategy, microbes or nutrients would be injected at the expanding boundaries of a plume, say the downstream edge, and microbial metabolic rates would be enhanced such that biotransformation of the hazardous chemicals would occur as fast as the flowing groundwater delivers the contaminants to the microbial filter.

It is also feasible to attempt remediation of small portions of large, moving plumes—portions near or around the contaminant source, where the contaminant concentrations are relatively large. Bioremediation over these small volumes together with microbial filters at the boundaries of the plume could eventually clean up the entire plume.

Current remediation efforts often rely upon pump-and-treat methods; groundwater is pumped and treated at the surface and then disposed. This approach is expensive since the entire plume is treated at once, which requires a high density of withdrawal wells. In addition, the process has to be repeated for several pore volumes of the plume, because of the continual desorption of hazardous chemicals caused by dilution of groundwater during the treatment process.

Approach

Subsurface bioremediation combines physical, chemical, and microbiological processes. Physical processes involve flow and transport in heterogeneous media, chemical processes involve changes in the *in situ* aqueous environment that result from microbiologic and anthropogenic activities, and microbiologic processes involve population changes as well as metabolic processes that consume nutrients and transform the hazardous chemicals. The technology has been successful when applied to shallow petroleum hydrocarbon contamination, but has had only limited effect in treatment of halogenated hydrocarbons such as trichloroethylene (TCE), a class of contaminants common at DOE sites. A recent attempt at the Moffet Field site by Stanford University remediated only ~20% of the available TCE.

We believe that three steps must be taken to increase these low remediation rates: more systematic research of the basic processes, an integrated interdisciplinary team approach, and intermediate-scale modeling to account for the effects of a complex and heterogeneous subsurface. We have formed a team of microbiologists, geochemists, hydrologists, hydrogeologists, engineers, and physicists to attack problems related to microbial enzymology (the biochemistry of microbial metabolism), microbial ecology (microbial processes in the environment), chemical ecology (the interaction of microbial processes, aqueous chemical processes, and water–soil interactions),

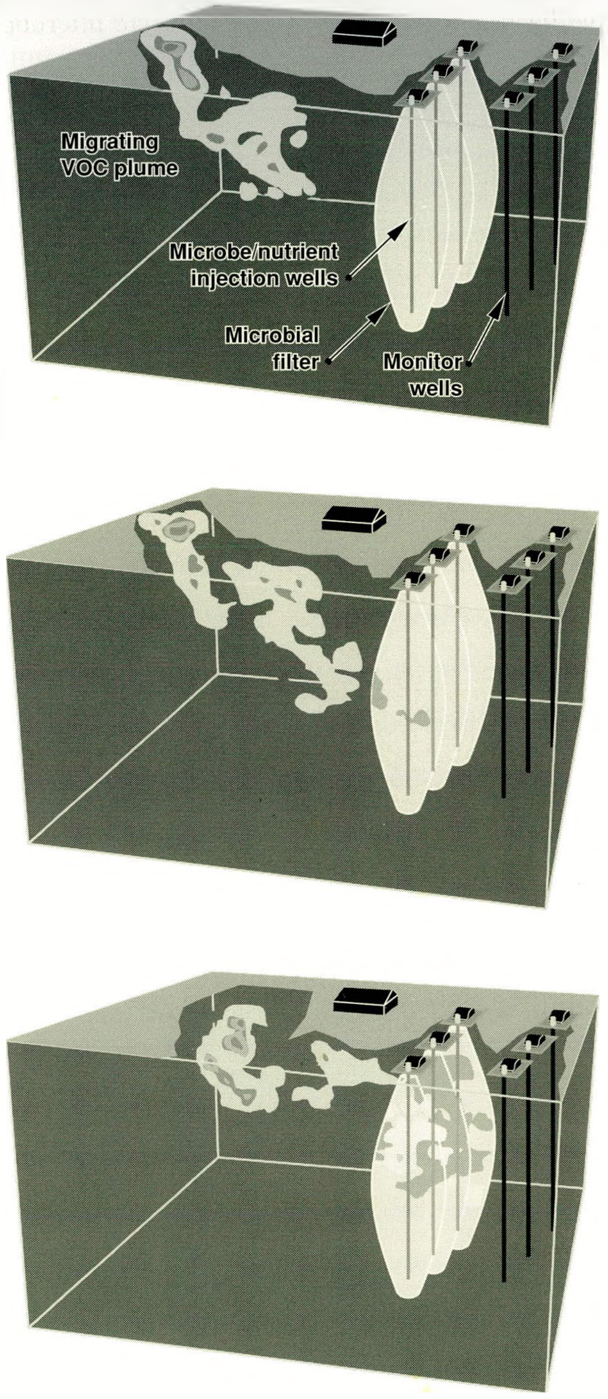


Fig. 1. The *in situ* microbial filter concept. Microbial activity is enhanced downstream from a migrating contaminant plume; microbes degrade the contaminants as groundwater flow transports them through this region. Groundwater enters the filter contaminated and leaves clean.

hydrology (modeling of coupled flow and transport of solutes with microbial population dynamics), and intermediate-scale experiments (to investigate effects of a heterogeneous medium).

The following are brief synopses of work in FY90. Our initial efforts are directed at the *in situ* remediation of two representative subsurface-contaminant volatile organic compounds (VOCs), TCE and chloroform.

Microbial Enzymology

This effort has two purposes:

(1) Define the culture conditions for optimizing the efficacies and intracellular metabolic lifetimes of certain oxygenases within select isolated bacteria.

(2) Quantify the biocatalytic TCE and chloroform degradation rates and conversion potentials of small samples of such cells.

Efforts are also being made to determine the effects that select methanotrophs have on their aqueous environment and to measure their population changes and movements through porous media in response to hydraulic and other driving forces. We are currently using select strains of methanotrophic bacteria that produce methane monooxygenase (MMO) enzyme systems.

To establish how the disappearance of TCE and chloroform correlates with bacterial transformations, we have developed simple micro-scale radioactive assays for the conversion of TCE to radiolabeled water-soluble products and the oxidation of chloroform to CO_2. Both of these VOC conversions are catalyzed by the soluble form of MMO present in typical Type II methanotrophic bacteria. Using these assays we can now easily measure the MMO-dependent VOC-conversion activity of 1 μg of methanotroph biomass (about one million cells), using an incubation time of only 20 minutes.

An important discovery during the development of these assays was the finding that both TCE and chloroform degradation are catalyzed only by Type II methanotrophs that produce the soluble intracellular form of MMO (sMMO), not the particulate (membrane) intracellular form of MMO (pMMO). We found that the presence of a very small amount of copper in the culture medium results in undesirable and significant intracellular pMMO activity. Stimulating the growth of indigenous mixtures of methanotrophs by pumping

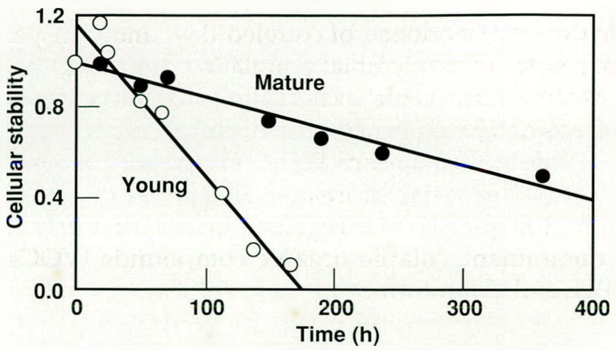


Fig. 2. Relative cellular stability of biocatalyst as a function of time for two populations of the methanotroph *Methylosinus*. The two populations were cultured for different durations in a bioreactor: the young population was cultured for 49 hours and the mature population was cultured for 191 hours.

methane and air into the subsurface may increase their biomass, but it may not yield MMO intracellular biocatalysts that are effective for the organic contaminant of interest.

We conducted experiments to establish growth conditions for obtaining high densities of methanotrophic bacteria that contain exclusively TCE-active and chloroform-active sMMO. They indicate a marked difference between young and mature populations in the cellular stability of this biocatalyst (Fig. 2); this has important implications for the microbial-filter or containment-source-treatment strategy of periodically injecting pregrown methanotrophs for *in situ* bioremediation. We have also measured the biodegradation rates of TCE and chloroform. For TCE, the rate constant is 12/hr/(g/L); this is the fastest degradation yet reported in the literature.

In order to examine the diffusion, motility, and possible chemotactic responses of select methanotrophic bacteria, we have made considerable progress in developing optical techniques for measuring accurately and reproducibly rather small numbers of cells (1000–100,000). To our knowledge, such determinations have not been reported for VOC-degrading bacteria such as methanotrophs. Both of our methods, one based on the microbes' absorbance of optical light and the other on their scattering of laser light, seem to provide the necessary sensitivity and should be useful for experiments in which the aqueous samples to be analyzed are rather clean or essentially free of particles other than the bacteria. These techniques have been successfully used to calibrate microbe population size down to the 10^3–10^4 microbes/mL range (scattering and absorption, respectively), which is 3.5 to 4.5 orders of magnitude below that available using standard spectrophotometric techniques.

Microbial Ecology

The development of a biofilter may require the use of microorganisms that are native to the contaminated site, because microorganisms that have had long-term exposure to contaminants often acquire the ability to degrade these compounds. Furthermore, VOCs such as perchlorethylene (PCE) and carbon tetrachloride (CT) cannot be degraded by methanotrophic organisms and will require treatment by alternate species. Because each contaminated site requiring remediation will have its own unique chemical and biological profile, we have begun field investigations to define the capabilities and nutrient requirements of microorganisms that are present at contaminated sites.

Chemical and geological data from a number of contaminated areas at LLNL and Site 300 have been examined. Highest priority was given to obtaining samples from areas that contain a wide range of TCE concentrations within a relatively small area; microorganisms in such areas have the greatest likelihood of having been selected for their ability to survive in the presence of this contaminant. Samples from a TCE-contaminated shallow aquifer at Site 300 were brought into the laboratory and were held under aerobic and anaerobic conditions. A variety of carbon sources and nutrient solutions were added to these cultures to stimulate the growth of heterotrophic microorganisms; this type of microorganism is of particular interest because its growth and metabolic activity are not limited to the presence of a single carbon source and it may also have the ability to degrade VOCs.

Our initial results indicate that the microorganisms present at this site were able to degrade TCE, PCE, and CT under fermentative (i.e., anaerobic) conditions utilizing glucose as a carbon source. Under aerobic conditions, few microorganisms were cultivated and none possessed the ability to degrade these VOCs. These results indicate that the native population of microorganisms at this site would be best stimulated for VOC remediation by providing conditions that enhance fermentative processes. Such information will ultimately help us tailor the biofilter approach to individual remediation sites.

Chemical Ecology

Microbial population growth and biotransformation of contaminated groundwater may be accompanied by chemical reactions involving both inorganic and organic components. The evolution of the chemical composition of the aqueous system may determine whether conditions are favorable for the microorganisms to thrive in the subsurface, and chemical factors may impact the ability of the microbes to biotransform pollutants. Changes in the solution chemistry caused by enhanced microbial activity may also be reflected in perturbations of the various chemical equilibria or metastabilities previously governing the inorganic fraction of the system. Many chemical reactions between solutions and mineral phases are influenced strongly by subtle changes in the composition of the aqueous phase.

A quantitative description of the chemical effects of the growth or injection of a microbial community and the results of aerobic metabolism of a carbon source in a porous medium is prerequisite to predicting the performance of a bioremediation effort in a physical model or in the field. Therefore we have modified the EQ3/6 geochemical modeling codes to make calculations involving the evolution of the aqueous organic components: thermodynamic data for these species have been incorporated into the data base for the codes, and coding allowing EQ3/6 to use these data has been completed. An important aspect of this task is the capability to model partial equilibria among possible aqueous species in the system. In order to be able to rapidly test a variety of models a data base preprocessor has been written that allows the EQ3/6 user to choose from options that define alternate and parallel sets of partial equilibria.

We have monitored the chemical evolution accompanying the growth of a colony of methanotrophic bacteria in a series of experiments. The focus of these experiments is to document the inorganic chemical changes that occur as a function of microbial growth in sealed flasks and to determine the systematics of chemical change caused by the bacteria. Additional experiments in continuous bioreactors have begun that will allow tracking of the chemical evolution as cell densities increase beyond those obtained in the flasks.

Flow and Transport

The subsurface is characterized by processes that include fluid flow, contaminant transport, solute–media chemical interactions, microbial population dynamics, and microbe–solute interactions. To predict the performance of bioremediation and to interpret test results, we must be able to mathematically model these coupled processes. We have begun to develop computational models for calculating chemical mass balance and microbial population dynamics. This will integrate the various tasks in the project.

Progress has been made in modeling of stochastic population dynamics. We have successfully implemented a stochastic simulation of microbial population dynamics in a computer model that already was able to model the transport of noninteracting reactive solutes in heterogeneous media. This software uses the particle tracking technique; to our knowledge, this is the only effort using this approach.

Commercial computer software capable of being modified to incorporate coupled microbial–solute processes has been identified and has been purchased. We expect to begin the modification in the last quarter of this fiscal year. This software takes the more traditional deterministic, finite-difference approach. It is not presently clear which approach will be more advantageous.

Two-Dimensional Physical Model

Perhaps the greatest uncertainty in developing the *in situ* microbial filter is in taking the concept from the lab to the field. Experience in engineered subsurface processes in the petroleum industry has shown that an interim physical modeling step is necessary to increase the likelihood of success. This step permits the details of process interactions and, most importantly, media heterogeneities to be worked out in a controlled environment. We are developing a large-scale two-dimensional physical model as a test bed for our concept.

During the fiscal year, we visited laboratories at Stanford, Lawrence Berkeley, and the R. S. Kerr Laboratory of the Environmental Protection Agency at Ada, OK, which had functioning physical models. We then designed a 1-m prototype of our anticipated full-scale physical model for testing the biofilter concept. A rudimentary version of the prototype was also built to allow testing of sand-

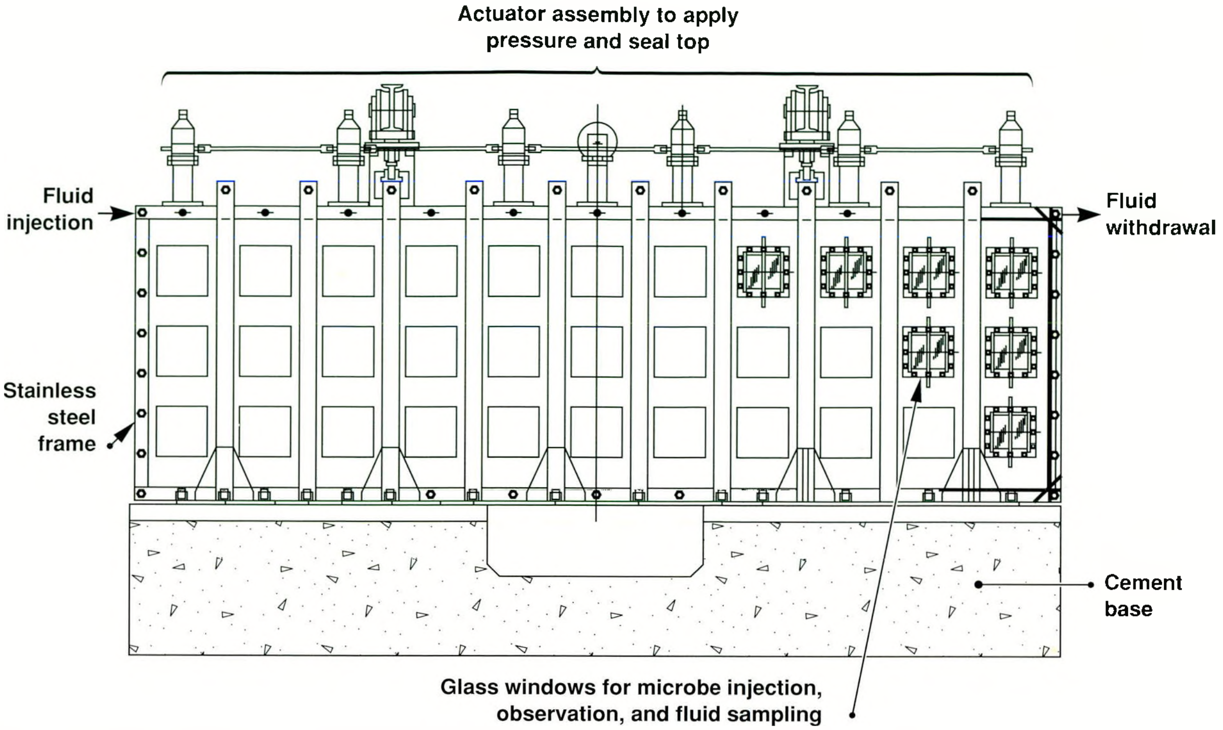


Fig. 3. Diagram of the planned large-scale two-dimensional physical model.

packing methods and tracer testing. Tests on this model have shown that the basic two-dimensional design does not create excessively large flow boundary layers at the sides. Lab-bench-scale tests have determined the most efficient means to achieve reproducible packing of sand in a rectangular model. The one-fifth-scale prototype two-dimensional physical model has been designed, fabricated, and delivered. Fabrication of the full-scale model awaits testing of the prototype (Fig. 3).

Permeability measurements were made on several candidate sands in a standard cylindrical test cell and in our rudimentary version of the prototype. Agreement of the values of permeability of the various sands was excellent, increasing our confidence that the design we've chosen will provide accurate predictable permeability values for testing biofilter performance.

Cost Comparisons

A preliminary estimate of the cost to apply the microbial filter concept in the field and a comparison between this method and the standard pump-and-treat approach was completed using the LLNL site as an example. Key to this analysis is the development of the unit cell concept (Fig. 4). The unit cell is the drainage volume around pump-and-treat extraction wells; it defines a common, normalized basis upon which alternative strategies can be compared. The analysis shows that the *in situ* microbial filter concept is competitive with the pump-and-treat method (Fig. 5). The microbial filter method appears to have higher front-end costs ($7.2M vs $4.1M) but lower annual operations and maintenance costs ($187K vs $371K). Two remediation durations are chosen for comparison, 30 years and 60 years. The microbial filter provides a 16% savings for the 30-year period and a 30% savings for the 60-year period.

Our cost estimates for the microbial filter appear to be most sensitive to the cost of electricity, used mainly for pumping, and the cost of drilling closely spaced wells to establish the thin filter. This latter variable appears to be the most challenging aspect of the concept. The rate of TCE degradation catalyzed by the enzyme is so fast that we only need to get the enzyme (the microbes are really just carriers for the enzyme) to the TCE in the subsurface; neither the thickness of the filter nor the microbial population density is the issue. The practical problem is in establishing a relatively thin filter in the subsurface. The cost savings over the

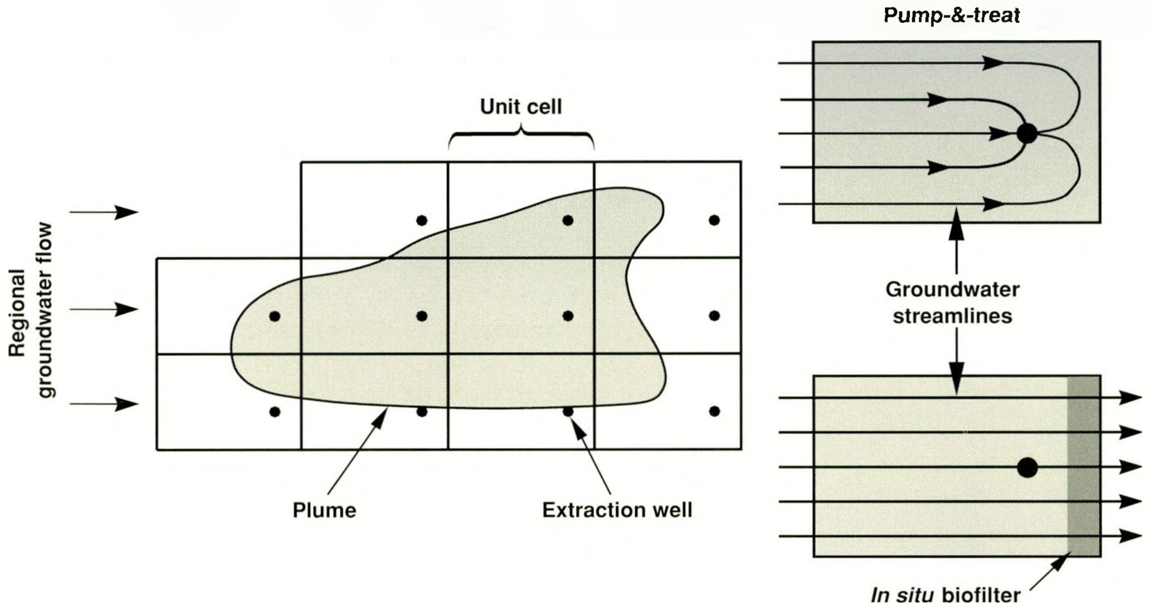
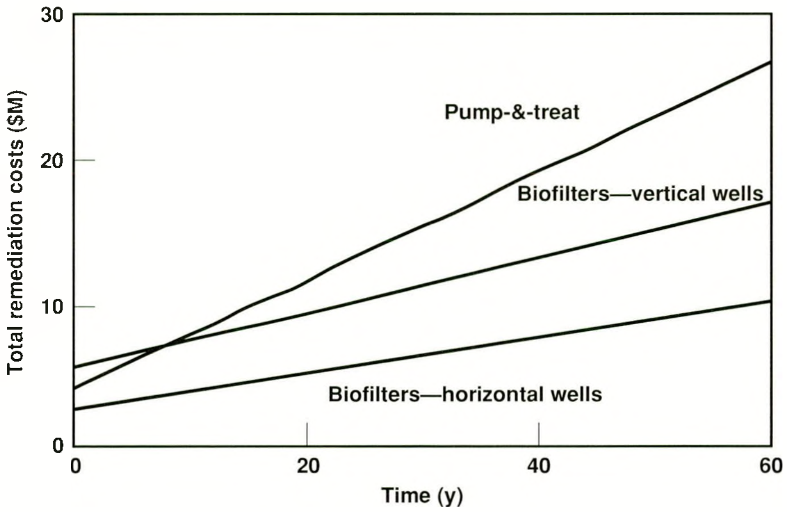


Fig. 4. Diagram of the unit cell concept. The unit cell represents the *capture zone,* the volume influenced by pumping at an extraction well; its size is a function of natural variables, such as permeability and groundwater velocity, and pumping variables, such as extraction rate. It defines the smallest subvolume that can be viewed independently of other subvolumes in a remediation field.

pump-and-treat method result from the fact that we are really processing a much smaller volume of the plume at any one time and the basic treatment costs are very low.

The LLNL site is used just as an example and probably does not represent the optimal location for applying the concept. A site that has a greater natural groundwater velocity, a greater concentration of hazardous chemicals, or a narrower contaminant plume than the LLNL site would provide even greater cost savings. In addition, the estimates use present-day technology; with expected advances in drilling technology an even greater savings, perhaps as high as 50%, could be realized in the very near future.

Fig. 5. Financial comparison of the pump-and-treat method vs two *in situ* microbial filter strategies based on the LLNL site. The two microbial filter strategies use 13 vertical wells per unit cell or 2 horizontal wells per unit cell to emplace and sustain the zone of enhanced microbial activity. Either bioremediation strategy becomes favorable after approximately 8 years of remediation. The microbial filter strategy reduces fluid pumping and disposal costs.



Pilot Demonstration of Vacuum-Induced Venting in Gasoline-Contaminated Soils

Principal Investigator: Anthony J. Boegel

The vacuum-induced venting process has shown success in cleaning up subsurface gasoline contamination. Later phases of this pilot study will employ dewatering and steam flooding, which shows potential for faster and more cost-effective remediation.

Introduction

In the first phase of the remediation of the area of a gasoline spill at the LLNL site, we are using vacuum-induced extraction technology. Fuel hydrocarbons are extracted from the vadose zone (the subsurface unsaturated zone) by vacuum-induced venting. The implementation of this technology began in late 1988 and early 1989.

Vacuum-Induced Venting

In this pilot process, the extraction well is a multiply screened well. The liquid-ring vacuum pump at the surface generates a vacuum of 20–25 inches of mercury and a flow rate of about 50 cubic feet per minute (cfm). The extracted vapors are processed in a thermal oxidizer that destroys more than 99.8% of the hydrocarbons before discharge to the atmosphere.

To date, we estimate that about 5000 gallons equivalent of hydrocarbons have been removed from the vadose zone by this process and about 100 gallons of free product from the top of the water table by skimming. Recent chemical analyses indicate that the top 45 feet of the spill area have been cleaned up with the vacuum extraction process. Beneath 45 feet, it appears that the concentrations of fuel hydrocarbons are about one-fourth (~2000 ppm, volume/volume) of what they were when this work began (~8000 ppm).

Dewatering and Steam Flooding

The next phase of remediation will involve dewatering the saturated zone that contains both entrapped free product and dissolved fuel hydrocarbons. Dewatering is necessary because fuel hydrocarbons were trapped below the present water table at greater-than-saturation concentrations by rising groundwater. As the saturated zone is dewatered, we will use vacuum-induced venting of the newly dewatered zone to remove the fuel hydrocarbons.

Since this is a pilot study, we are considering a field trial of steam injection in the gasoline spill area, beginning in fall of 1991. After several months of steam injection, we will evaluate and compare this technology with vacuum-induced venting.

Steam injection will force saturated steam at about 75 psia and 310 °F into the saturated and unsaturated zones. As the steam front propagates, a condensation zone is formed in front of the steam containing the contaminants. This condensed front is removed via a groundwater extraction and vacuum-induced venting well. The condensate is then treated at the surface. This technology promises to be even faster than "conventional" vacuum extraction and could reduce the overall cost of remediation.

Pilot Demonstration of Vacuum-Induced Venting for Volatile Organic Compounds in Low-Permeability Soils

Principal Investigator: Paul F. Daley

Low permeability of soils in a contaminated site renders some cleanup methods unusable. We are using vacuum-induced venting with specialized pumps and a modified water-treatment system to overcome the problems of remediation in saturated sediments.

Introduction

Trichloroethylene (TCE) leakage over an extended period from the temperature-control system at LLNL's Site 300 Bldg. 834, an environmental testing facility, contaminated a soil interval approximately 14 feet thick lying about 25 feet below the surface. The lateral extent of the contamination covers an area about 300 feet in diameter, with the lower portion of the contaminated soil lying in a shallow, perched water-bearing zone that is bounded underneath by a dense clay layer. Beneath that layer is a more porous sandstone formation extending down several hundred feet that contains a regional aquifer. Extensive sampling in monitoring wells completed in the uppermost portion of this formation does not show evidence of TCE migration through the clay layer.

Groundwater extraction and treatment alone is not a viable means of remediating the shallow contamination because the saturated sediments are sparingly permeable and high concentrations of TCE occur in the unsaturated (vadose) zone. The objective of this project is to demonstrate the usefulness of induced-venting technology to clean up volatile organic compounds in sediments of low relative permeability. We are installing and evaluating equipment that applies vacuum to a series of wells screened in the affected soil interval. The induced gas flow through the soil created by the partial vacuum causes the volatile TCE to move toward the extraction well bores in a volumetric sweep process. During preliminary testing TCE entrained in the effluent air was discharged to the air; however, in future continuous operation, emission controls will be required by the regional air pollution control district.

Vacuum Extraction Systems

The first two vacuum extraction systems were installed in 1989; they utilized liquid-ring pumps capable of pulling a strong vacuum (>25 in. mercury at the pump) but with limited capacity for flow, at about 50 cubic feet per minute (cfm). Vacuum-induced venting on three extraction wells with these systems near the source area of the spill removed from 10 to 28 lb of TCE per day, and despite the low permeability of the site, vacuum was measurable more than 75 ft from the extraction wells. However, the high vacuum induced by the liquid pumps caused "mounding" or upward movement of the water table, which required that water be simultaneously pumped and treated to avoid water being pumped into the vacuum extraction manifold.

Operation of the vapor and water extraction system identified additional problems: (1) water extraction during vapor extraction was necessary because of the shallow water table; this water was difficult to treat by simple aeration, because oily co-contaminants formed emulsions that retained TCE; (2) thermo-formed polyethylene tanks used for aeration were found to take up TCE, and this uptake apparently became more efficient as the tanks "weathered" through continued exposure to the solvent.

Specialized pump testing was proposed to examine the possibility of greatly increasing the area of influence of the vacuum system by manifolding a greater number of wells together, and using a higher-capacity blower operating at lower vacuum. These tests were performed in August 1990. Using a portable blower modified for vapor-phase flow testing, we developed flows of greater than 300 cfm while pumping on an extended manifold that connected nine wells at the core of the site. We also found that at the lower vacuum of this system (about 11 in. mercury at the extraction well heads), water was not drawn into the extraction manifold. This means that water extraction can be separated from episodes of vapor extraction. We are procuring a similar blower system to replace the liquid ring pump at this part of the complex, for extended test and evaluation.

Water-Treatment System

We are modifying the water treatment system in the following ways:

(1) Turbine pumps in the extraction wells are being replaced with low-turbulence, positive-displacement pneumatic pumps to reduce emulsification of the floating oil.

(2) An oil separator will receive the water stream, skimming the oily material and any remaining emulsions from the well water.

(3) The water stream will be pumped through spray nozzles into the aeration tanks, reducing the TCE concentration before the water contacts the plastic tanks.

(4) Aeration of the water will start immediately upon entry into the tanks, with air pumped by low-pressure, high-volume centrifugal blowers.

Air-Treatment Systems

Two candidate systems for air treatment that emerge from fuel hydrocarbon spill remediation technologies are being evaluated for testing. The first (Continental Recovery Systems, Wellesley, MA) incorporates *in situ* regeneration of adsorbant carbon by steam distillation—co-condensation of TCE and steam—with TCE recovery from a phase separator. A system of this type may be used during the early, high-yield phase of the extraction, to be followed by carbon canisters that would be regenerated off-site. These would be installed when TCE extraction rates were low enough that frequent change-out would not be required. A second, more speculative, system uses pulsed high-energy ultraviolet light to photolize the TCE in vapor phase. This would destroy the contaminant, and avoid creation of tertiary wastes. However, this technology is as yet unproven at the scale required for our site. We are actively pursuing installation of a pilot-scale pyrolysis unit for testing. Either of these systems would be high-cost procurements that would be cost-shared with the Site 300 Environmental Restoration Project.

We have obtained a low-cost dual-detector gas chromatograph (SRI Instruments, Torrance, CA) for monitoring vented vapor levels and effluent from the air-scrubbing system. This instrument has already been used in the field for soil gas analysis and has proven to be both rugged and sensitive, with detectability limits for TCE in gas phase of about 200 ppb, volume/volume (based on 1-mL samples). The instrument will be housed in an instrument shack at the site and will be operated by computer, so that unattended monitoring of the system will be possible.

Biodegradation of High-Explosive Wastes

Principal Investigator: John P. Knezovich
Co-Investigator: Jeffrey I. Daniels

To develop methods for the treatment of high-explosive (HE) wastes in soil and water, we have defined conditions under which microorganisms can degrade two common HE compounds, RDX and HMX, to harmless byproducts. We are designing a flow reactor for the treatment of HEcontaminated water.

Introduction

Research and development activities involving HE at federal facilities, including U.S. Department of Energy laboratories, have resulted in the contamination of soils and groundwaters. Unfortunately, no currently available technologies can address the elimination of such HE residues. Bioremediation (the application of biodegradation technology to the transformation of hazardous waste to harmless byproducts) represents a promising strategy that offers the versatility needed to treat HE in environmental media. Our objective is to develop a biological system for the remediation of HE-contaminated groundwater and wastewater so that environmental quality can be preserved.

This research consists of two parts: (1) isolation and adaptation of a microbial population (consortium) optimized for the degradation of RDX and HMX; and (2) demonstration of a flow reactor for the continuous treatment of HE-contaminated wastewaters and aquifers.

Microbial Population

Microorganisms obtained from HE waste streams were cultured in batch reactors that received low concentrations of HE compounds along with a variety of nutrient preparations. This approach was used to stimulate the growth of diverse microbial populations in such a way that natural selection operated to enhance the metabolic capabilities of microorganisms that favored HE degradation.

In our initial feasibility study, which was supported by LLNL's Institutional Research & Development Program, we discovered that the degradation of RDX required the presence of a separate carbon source for the maintenance of a viable microbial population. This process, which is known as cometabolism, occurs when the compound of interest (e.g., RDX) is degraded but does not provide the energy required to sustain microbial metabolic activity. This phenomenon makes the degradation of HE contaminants to environmentally acceptable concentrations (e.g., <100 µg/L; Etnier, 1989) difficult because the microorganisms tend to metabolize the most readily available carbon source rather than the contaminant of interest. As a result of screening studies, we found that peptone (a mixture of protein derivatives) is a superior carbon source for supporting the cometabolism of HE compounds.

Using the approach outlined above, we successfully demonstrated the biodegradation of RDX and HMX under aerobic conditions (Knezovich and Daniels, 1990). Using ^{14}C-labeled compounds, we verified that these explosives can be degraded to concentrations less than 100 µg/L; carbon dioxide is the principal transformation product. The occurrence of this transformation under aerobic conditions is significant because this process does not lead to the formation of hazardous byproducts (e.g., hydrazines), which are known to arise from the anaerobic degradation of these compounds.

Flow Reactor

We are now in the process of defining a strategy for the treatment of waters contaminated with HE compounds. In collaboration with scientists at UCLA (Stenstrom et al., 1989), we are developing bench-scale flow reactors to define the optimum conditions for the continuous treatment of HE-contaminated water. The results of these studies will be used to design an upflow treatment system that will subsequently be tested in the field (Fig. 1).

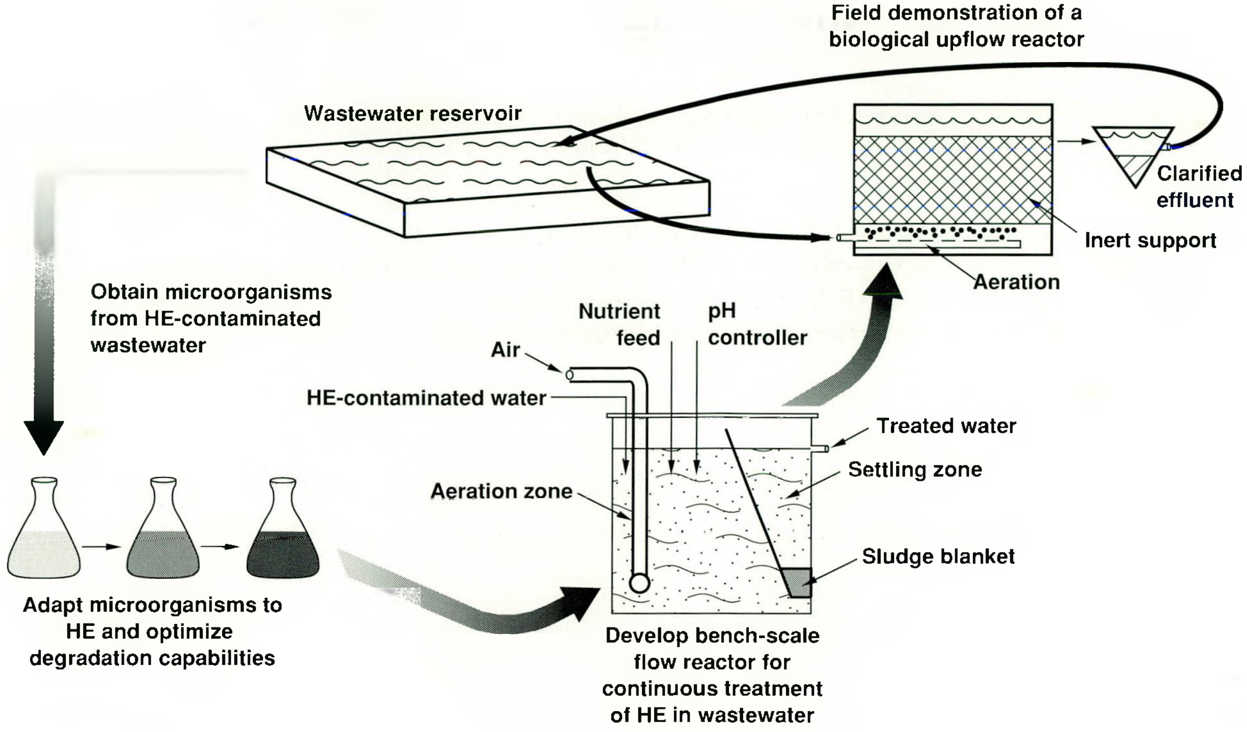


Fig. 1. Diagram of our strategy for developing and demonstrating a biological process for the remediation of high-explosive wastes.

By establishing a system for the biological degradation of RDX we will be in a position to rapidly develop treatment strategies for other conventional explosives, as well as for HE compounds currently under development.

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Destruction of Mixed and Hazardous Wastes in Molten Salt Media

Principal Investigator: John F. Cooper
Co-Investigators: Oscar H. Krikorian, Clarence L. Hoenig, and Joseph C. Farmer

We are developing a process for the rapid, safe, and economical destruction of radioactive, toxic wastes by oxidation within beds of molten salts. Because accidental emissions are prevented and gases are assayed before release, it eliminates the dangers perceived by the public to be inherent in incineration processes.

Introduction

In a joint undertaking, LLNL and Rockwell International have begun development of a process for the rapid, safe, and economical destruction of radioactive toxic wastes (i.e., "mixed wastes") by controlled oxidation within beds of molten salts. Intended as an alternative to incineration, this process reduces large volumes of combustible solids and liquids to small inorganic residuals that can be immobilized in cement for burial or processed for actinide recovery.

Molten salts (carbonate/halide eutectics) provide the heat transfer and reaction medium, catalyze oxidation of organics, and prevent formation of acidic gases (e.g., HCl) by forming solutions of their stable salts (e.g., NaCl). The waste is introduced into a pyrolysis vessel containing molten salt; pyrolysis gases evolved are completely oxidized in a second vessel operating at about 700°C (Fig. 1). The

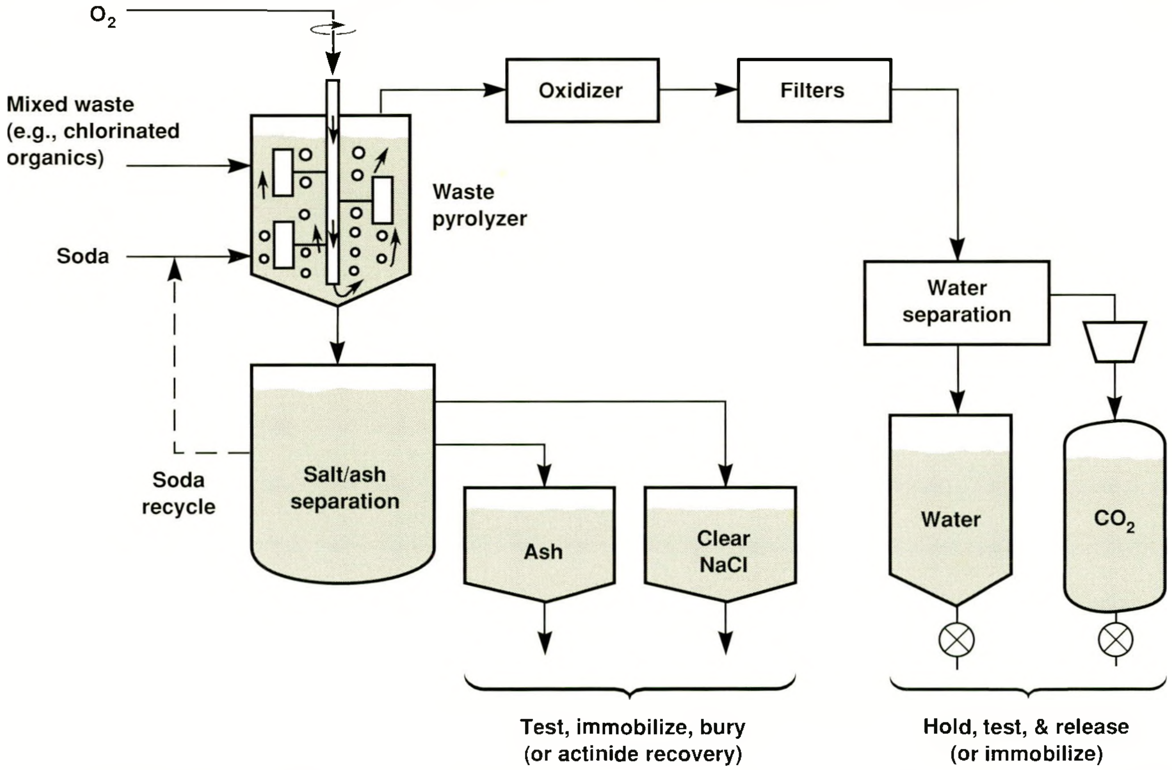

Fig. 1. The molten salt process provides for oxidation of the combustible fractions of mixed waste with temporary retention of of the product gases as liquids pending assay. The solid products (immobilized ash and a nontoxic salt) are analogous to those of incineration.

wastes are reduced to form inorganic mixtures of "ash" and sodium chloride, which are separated into disposable products by an aqueous process. (Unreacted carbonate is recycled to the pyrolysis unit.)

The melt avoids formation of potentially fugitive radioactive particulates and molecular species by a combination of particle wetting, encapsulation, and dissolution. The process will be operated as an oxygen-fed, electrically ignited "closed" system, with temporary retention of the gas products (water and carbon dioxide) until they are determined to be safe for discharge. This "hold, test, and release" option decouples the treatment of wastes from the discharge of the products and thereby prevents accidental emissions resulting from limitations of dynamic assay, operator or feeding error, or system mechanical upset. By avoiding potentially fugitive inventories and by assaying all gas products prior to release, we eliminate the publically perceived dangers of incineration of mixed wastes.

Our partner, Rockwell International, has three decades of experience in the use of molten salts to destroy combustible wastes or to pyrolyze coal. In air-breathing coal- or gas-fueled systems operating at about 900°C in single brick-lined vessels, they have demonstrated destruction efficiencies of 99.999% or more for hazardous organohalogens and solid wastes typical of the nuclear industry (Table 1). The challenges of this program are (1) to develop a two-stage pyrolysis/oxidation process in order to broaden the range of treatable wastes and to lower the operating temperatures to help retain actinides, and (2) to re-engineer the process for closed-system, oxygen-fed operation. We have made progress in both areas.

Development of a Bench-Scale Processor

While waste destruction can be achieved in a single-stage process, it is advantageous to destroy the waste in two steps: pyrolysis under oxygen-deficient conditons, followed by complete oxidation of the pyrolysis gases. By introduction of wastes into an oxygen-lean medium, we avoid the oxygen-catalyzed polymerization of alumina and silica components that may freeze the melt and clog the

Table 1. Destruction efficiencies demonstrated by existing technology.

Waste class	Substance	Temp. (°C)	Destruction efficiency (%)
Halogenated organics	PCB	754–912	99.99995+
	Chlordane	900	99.99999+
	HCB	900	99.9999999+
Chemical warfare	VX	930	99.99999+
	GB	925	99.999999+
	Mustard	925	99.99998+
Pesticides	DDT	900	99.998
	Malathion	900	99.9998
Mixed solids	33% paper	900	HCl ND,[a] <5 ppm
	20% kimwipe		SO_2 ND, <2 ppm
	32% PE		CO <0.1%
	15% PVC, rubber		HC <0.1%
Aqueous slurries	96.6% aq. solution ($NaNO_3$, NaOH, 3.4% TBP, PVC resins)	900	99.99% (organics)

[a] Not detected.

tubing. This allows treatment of wastes rich in both alumina and silica such as clays, glossy papers, and sorbent beds.

Moreover, we believe separate units for pyrolysis and oxidation allow a lowering of the exit temperature from 900°C to about 700°C. The lower temperature broadens the options for materials of construction to include many metals and retards evaporation of actinides and salt (see below), simplifying offgas cleanup. We have begun the development of a two-vessel, two-stage bench-scale apparatus for testing these concepts through destruction of surrogates of common waste materials (Fig. 2). The apparatus consists of two 15-cm-diameter 1-m-long stainless steel vessels that are externally heated. The engineering work included design of injection nozzles, thermal expansion units and connecting plumbing, heat exchangers for cooling offgas, and diagnostics for temperature, pressure drops, and gas composition. The system will be fabricated and assembled in 1991.

Modeling of Salt Evaporation and Steam-Enhanced Volatilization of Actinides

We have applied thermodynamic methods to analyze the volatilities of uranium and plutonium under conditions of molten salt or other thermal

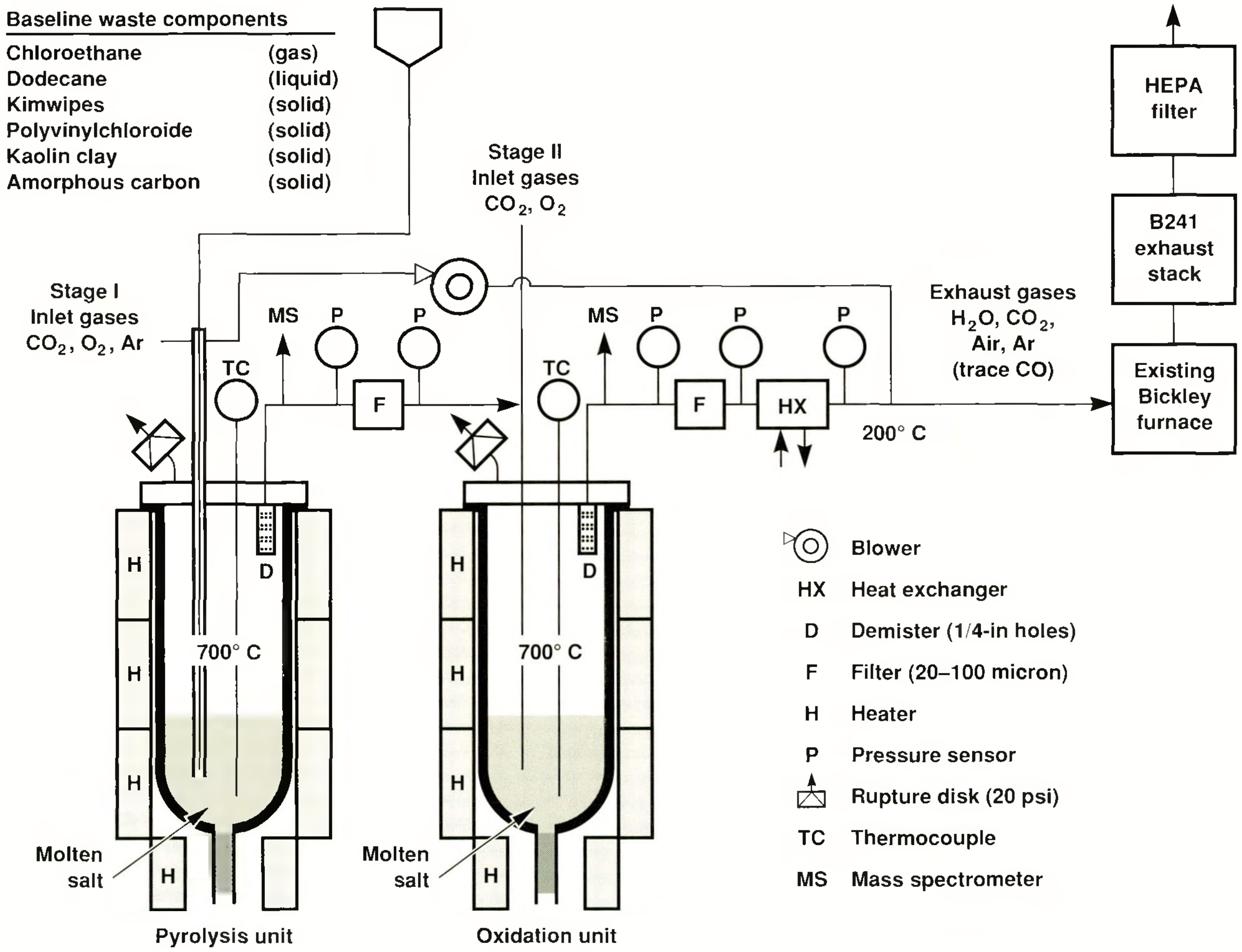

Fig. 2. The bench-scale two-vessel system allows separate optimization of the salt compositions and operating conditions of the pyrolysis and oxidation processes, with the objective of minimizing operating temperature, allowing treatment of wastes rich in alumina/silica ash and minimizing losses of volatile actinides.

oxidation processes, and have determined the reactions by which gaseous species evolve. Our estimates of the free energies of formation of gaseous uranium and plutonium oxyhydroxides, from correlations of bond energy and entropy for related species, are in reasonable accord with experimental data on uranium oxyhydroxides. Under typical thermal process conditions of 0.08 atm for both steam and oxygen, the volatilities of plutonium fall from 2.9×10^{-8} atm at 1200°C to 1.3×10^{-12} atm at 600°C. Good agreement is obtained between experimental values for plutonium losses from high-temperature molten salt process beds and these estimates (Krikorian, 1990). Loss of plutonium by steam-enhanced volatilization can be reduced by waste pyrolysis programmed to minimize oxidation potential, steam pressures, and temperatures and conducted with maximum melt contacting of the waste.

The offgas of the molten salt processor is found to contain particulates arising from two sources: condensation of evaporated NaCl and physical entrainment of droplets into the sparge gas. At temperatures from 750 to 950°C, carryover of 0.1–3 g/m^3 is primarily due to evaporation. Below 750°C sparge droplets predominate. At low temperatures, this sparging loss may be minimized by use of an orifice plate rather than a sparging nozzle, for which correlations indicate 10–100 ppm-wt. particulate loading of the offgas.

Compilation of Molten Salt Process Data and Development of a Baseline Design

Under subcontract to LLNL, Rockwell has compiled relevant molten salt oxidation and pyrolysis experience since 1975 into a single document, and developed a baseline design for an oxygen-fed, 1-ton/day waste treatment system including offgas retention as water and liquified carbon dioxide (–20°C, 20 atm) (Stewart et al., 1990). This exercise establishes a reference design that depends only on existing or demonstrated molten-salt- and gas-handling technologies. The molten salt unit is configured as a single vessel that supports waste pyrolysis within the salt phase (under oxygen-deficient conditions—40% stoichiometric O_2 in CO_2), followed by oxidation of the evolved pyrolysis gases immediately about the melt. The unit is 1 m in diameter by 6 m high and is lined with dense alumina bricks of high mechanical and chemical stability. Solids and liquids are entrained in the incoming gas steam tangentially at the base of the vertical vessel. Although this process attempts to maintain pyrolysis and oxidation conditions in the same vessel, isothermal operation is required (850–950°C). The same vessel could be used as a pyrolysis unit, optimized for pyrolysis alone, in a two-vessel system.

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Method to Remove Chloroform and Trichloroethylene from Groundwater and Wastewater

Principal Investigator: Kevin C. Langry
Co-Investigators: Derek Gragson and Hallie Whitfield

We are developing an efficient, low-cost, low-maintenance method for removing organohalides from groundwater, wastewater, and gaseous waste streams. We have determined the necessary diffusivity and solubility constants, evaluated commercially available membrane materials, and constructed a test device to demonstrate the effectiveness of the technique.

Introduction

Our method involves the passive separation of chloroform ($CHCl_3$) and trichloroethylene (TCE) dissolved in water by diffusion into chambers where these contaminants are degraded. The contaminated waste stream is in contact with a membrane permeable only to the volatile organohalide contaminants. The membrane permits rapid diffusion of the contaminants dissolved in the waste stream into a concentr and prevents the reagent solution from mixing with the contaminated water.

The initial work on this "sponge" project has been to evaluate the use of membranes to facilitate the removal of trichloroethylene (TCE) and chloroform ($CHCl_3$) from liquid and gaseous waste streams. A conceptual diagram of the proposed process, shown in Fig. 1, depicts contaminants diffusing out of a waste stream as the fluid flows down a tube with membrane-like walls. We also proposed to develop a process that degrades the contaminants as they pass through the membranes. The degradation is accomplished as the organohalide contaminants diffuse through the membrane directly into a solution that chemically decomposes the pollutants to innocuous oxides of carbon. Our feasibility study addressed several issues crucial to the development of a membrane-based separation system, including (1) evaluation of commercial membranes to permeate TCE and $CHCl_3$, (2) measurement of diffusion parameters for membranes found most permeable to TCE and $CHCl_3$, (3) selection of chemical reagents that most effectively decompose organohalides, and (4) the stability of the membranes to the chemical reagents employed to decompose the organohalides.

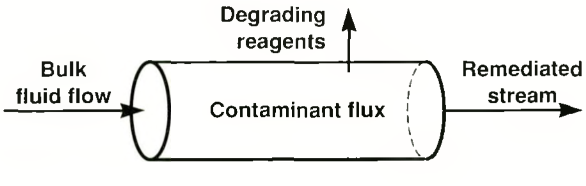

Fig. 1. Conceptual diagram of the proposed process.

The ability of a membrane-based filtering device to remove organohalides from a waste stream depends on several parameters, the most important being the rates at which the contaminants pass through the polymer membrane. This rate, the permeability, is a function of three separate processes. The contaminant must be adsorbed into the membrane, it must diffuse through the polymer matrix, and then it must desorb into the solution on opposite side of the membrane. The permeability is equal to the product of the diffusivity and the solubility coefficient. The diffusivity is related to the segmental mobility of the individual chains that comprise the polymer, and the solubility is a function of penetrant–polymer interactions.

To develop a mathematical model that will describe the processes involved in a membrane-based separation system, it is necessary to know the diffusivities and solubilities of the penetrants in the polymeric materials selected for use as membranes. In recent years there has been an increasing interest in the permeation parameters of toxic and hazardous materials in plastics, but there has been very limited data collected about TCE and $CHCl_3$. Therefore, much of our initial work has been directed at obtaining the numerical values of these constants and at characterizing the factors that affect the diffusion and degradation processes of the proposed technique.

Experimental Approach

The procedures used to evaluate the diffusion parameters of several synthetic membranes were designed to simulate conditions and contaminant concentrations that would likely be encountered in an actual groundwater remediation activity. In these experiments, we spiked normal reagent grades of TCE and $CHCl_3$ with small samples of ^{14}C-radiolabeled TCE and $CHCl_3$, respectively, and used dilute aqueous solutions that contained 10 ppm (wt/wt) of the organohalide. The concentrations of TCE and $CHCl_3$ were then measured by counting the radioactivity of the solutions with a scintillation counter.

Because some of the polymeric materials that we wanted to evaluate were either available only as thin-walled tubes or as thin sheets, the determination of membrane permeability was based on two types of experiments. For the tubes, lengths of tubing were placed into the spiked organohalide solutions in well-sealed gas-tight vials. Data were collected by measuring the activity of ^{14}C-labeled TCE or $CHCl_3$ dissolved in water into which was placed a standard length of plastic tube. The tube, sealed at each end with glass caps, contained an aqueous solution of tetrabutylammonium hydroxide (TBAH). In experiments that compared the fluxes of TCE into sinks of water, air, TBAH, and sodium hydroxide, we found that the base TBAH reacts rapidly with TCE and $CHCl_3$ to maintain an assumed zero-molar concentration of organohalide on the inside of the tube. The products of the base-promoted decomposition are ionized and very polar and are not permeable in the membrane. This precludes ^{14}C-labeled material from diffusing from the basic solution back through the tube to the bulk solution. For the sheets, we used specially constructed gas-tight permeation chambers that held the membrane to be evaluated between them. To measure the concentrations of the organohalides, small aliquots of solution were removed periodically and placed into a standard scintillation cocktail for counting.

Membrane Evaluation

Our initial evaluation of membranes was simply to assess the relative permeabilities of commercially available polymeric materials to TCE and $CHCl_3$. The materials were restricted to those that would most likely be stable to the strongly basic solutions that would be used to degrade the organohalide contaminants. On this basis, we examined low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polytetrafluoroethylene (PTFE), heat-shrinkable polytetrafluoroethylene (PTFE-HS), fluorinated ethylene–propylene copolymer (FEP), and heat-shrinkable fluorinated ethylene–propylene copolymer (FEP-HS). The PTFE-HS and FEP-HS (tubes) were evaluated in addition to their normal counterparts because the heat-shrinkable materials possess large voids within the gross structure. Scanning electron micrographs also show large holes on the surfaces of the tubes; it was thought that this porous structure might enhance the flow of organic compounds through the material.

Our results for the dependence of contaminant flux on membrane composition are shown in Fig. 2. An accounting of the total activity of labeled

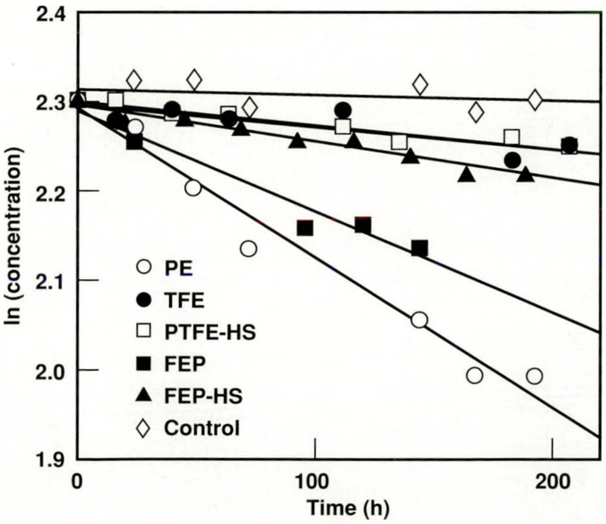

Fig. 2. Relative flux of $CHCl_3$ as a function of time through thin-walled tubes of different chemical compositions.

organohalide after completion of the experiments with polyethylene membranes yields 80–90% total recovery. The activity lost from the bulk solution is distributed in a 2:1 ratio between the base solution and the polymer. For the fluoropolymers PTFE and FEP, the total recovery was only about 50% of the initial activity, but the amount remaining in the polymer matrix was about three times greater than the activity of the base solution. The low recovery of ^{14}C activity in the fluoropolymer experiments may result from the inability of the radiolabeled analyte to completely diffuse out of the polymer to be counted. The relative slopes indicate that polyethylene is by far the most permeable membrane to TCE or $CHCl_3$. The results from similar experiments with sheets of polymers in the permeation cells were analogous to those obtained with the tubes.

The permeability of a penetrant is a function of the both the membrane composition and the structure of the penetrant. As shown in Fig. 3, TCE exhibits a substantially higher permeability in polyethylene than does $CHCl_3$. These results are in agreement with the generality that asymmetric molecules diffuse more rapidly through a substrate than do molecules with higher symmetry.

The linear dependence of flux on membrane thickness is seen in Fig. 4. The lack of complete linearity may be due to nonuniform membrane thicknesses in the thinner membranes.

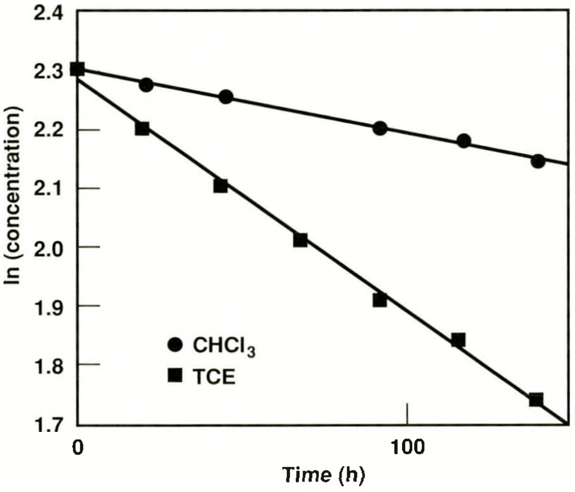

Fig. 3. Relative fluxes of TCE and $CHCl_3$ through 4-mil polyethylene.

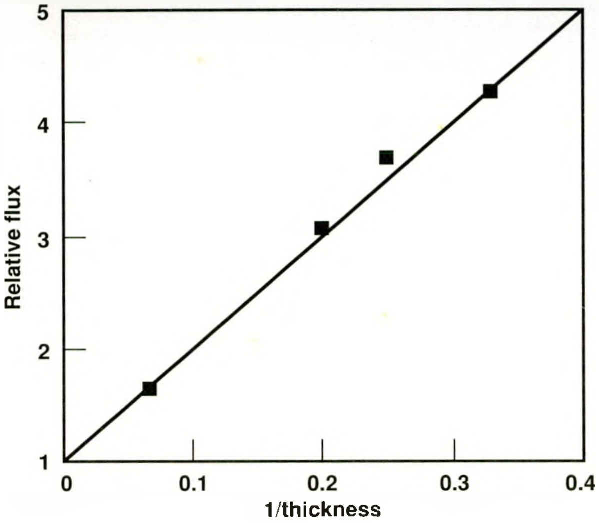

Fig. 4. Relative flux of TCE vs thickness of polyethylene film.

Experimental Filter for Removing TCE and $CHCl_3$ from Gaseous Waste Streams

We have constructed a small test device to provide a crude demonstration of the effectiveness of a membrane-based sponge for TCE and $CHCl_3$. The apparatus consists of a length of glass tubing fixed at each end with a high-density threaded Teflon plug. The glass tube was packed with approximately 500 polyethylene tubes filled with a 40% aqueous solution of TBAH. Each tube was sealed by heat-welding the ends of the polyethylene tubing. The influent end of the packed glass tube was connected via the Teflon plug to a gas cylinder containing TCE in air. The effluent end of the glass tube was connected to a multichannel mass spectrometer gas analyzer. The gas analyzer was employed as a detector to monitor effluent from the polyethylene-based filter. Two standard gas samples that contained 53 or 496 ppm of TCE in air were passed through the filter. Because of the different concentrations of TCE in the gas standards,

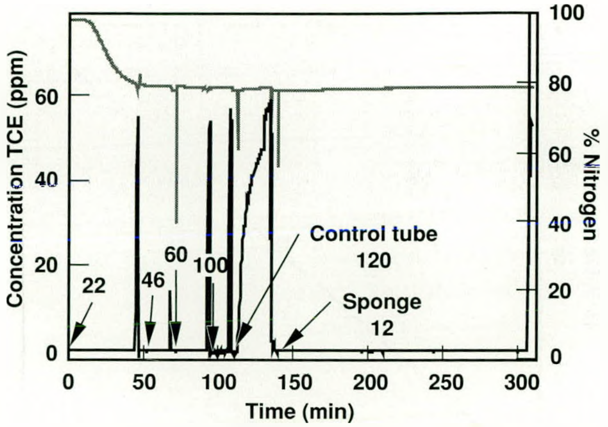

Fig. 5. Two-channel output of mass analyzer when 53 ppm TCE was flushed through filter. (Numbers indicate flow in cm^3/min.) The upper trace is nitrogen in the filter effluent as contaminant gas is passed through the device. The lower trace is TCE in the effluent. Calibration points are seen as spikes when the gas supply was shunted directly to the gas analyzer.

the concentrations of oxygen, nitrogen, and argon in the sample gases were different from the concentrations of these gases in air (for example, see Fig. 5). These differences allowed us to pass gas through the model air scrubber and monitor the rate at which the air was flushed out of the scrubber as well as the ability of the scrubber to remove the TCE from the flowing gas stream. A shunt line leading from the gas cylinder directly to the mass spectrometer was used to ensure continuous calibration of the detector.

Figure 5 shows the output from two channels of the mass spectrometer when the 53-ppm TCE gas sample was flushed through the tube at flow rates up to 100 cm^3/min. The mass spectrometer detected no TCE exiting the scrubber. The tube was initially filled with nitrogen gas so that the time required to completely exchange gas in the filter with the TCE-contaminated air could be monitored. The top curve in the figure represents the concentration of molecular nitrogen in the filter effluent (right-hand scale). After about 50 min, the 100% nitrogen atmosphere has been flushed completely and replaced with the contaminated gas stream. The dips and spikes in the upper curve are periods when the filter effluent flow to the mass analyzer was replaced with gas coming directly from the supply of contaminated gas. This provided a means to calibrate the spectrometer and verify the detector output. The lower trace shows the level of TCE in the filter effluent stream. Even after completely flushing the filter tube, no TCE is observed in the effluent. The upward spikes in the TCE trace resulted when the supply of contaminated air was shunted directly to the mass analyzer for detector calibration. The lowest level of detectability of the spectrometer was about 0.5 ppm TCE. This experiment was repeated with the 496-ppm TCE sample with similar results. Again, no TCE was observed to exit the model scrubber.

This experiment, though far from a large-scale filter, demonstrates the feasibility of membrane-based remediation technology.

Cleanable Steel HEPA Filters

Principal Investigator: Werner Bergman

The high-efficiency particulate air (HEPA) filters used in air-cleaning systems cause significant disposal costs because of their fragility. We are developing a high-strength steel HEPA filter that can be cleaned and reused repeatedly; it promises to save DOE as much as $100 million per year. A field demonstration test will be conducted this fiscal year.

Introduction

HEPA filters are used in all DOE air-cleaning systems to remove radioactive, toxic, or carcinogenic airborne particles before the air is discharged into the work environment or the atmosphere. These air filters remove 99.97% of all airborne particles and have an air resistance less than one inch of water. Figure 1 shows the typical construction of a HEPA filter; glass-fiber paper is pleated into an accordion-shaped pack and the pack is glued into a square frame. The pleats are separated by corrugated aluminum spacers.

Although the HEPA filters are generally effective, they are fragile and can be destroyed when they become wet, hot, or overpressurized, thereby creating environmental and contamination problems. HEPA filters are also a significant part of DOE's radioactive-waste disposal costs. Of DOE's estimated $122M total annual HEPA filtration costs, $120M is due to handling and disposal.

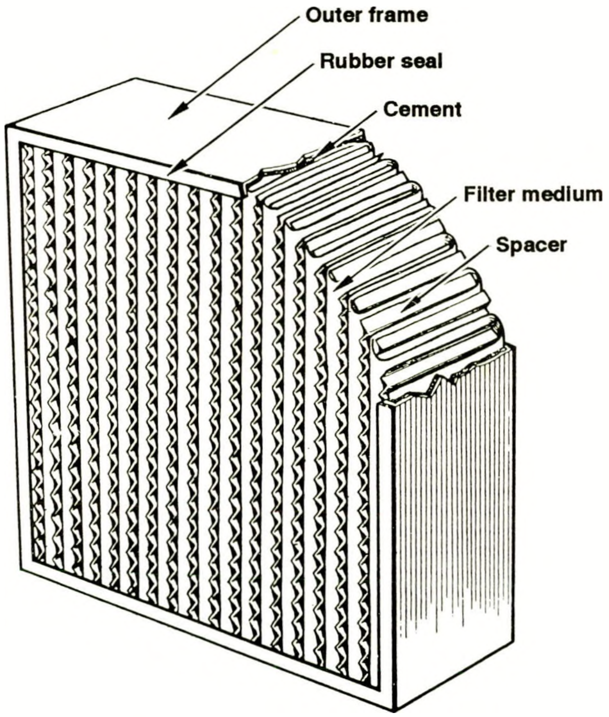

Fig. 1. Typical HEPA filter made of glass-fiber paper.

Initial Work on Steel HEPA Filter

The need for a high-strength HEPA filter led to a project more than a year ago to investigate making an all-steel HEPA filter. All-steel filters have been commercially available for many years, but none came close to the performance of the glass HEPA filter. An experimental evaluation of the commercially available steel filter media showed that none were acceptable for use in fabricating a steel HEPA filter. However, in cooperation with industry, we developed a steel filter medium that approached the performance of the standard glass fiber medium that is used in HEPA filters. This accomplishment validated the concept of a steel HEPA filter.

Figure 2 shows that the penetration of particles (fraction of particles passing through the filter) for the new steel fiber medium is similar to that for the glass HEPA media, although the steel medium has 3.4 times the pressure drop. An electron micrograph of the new steel fiber medium is shown in Fig. 3.

The new medium was then used to fabricate a prototype two-stage high-efficiency steel filter for an application as a vent filter. Figure 4 shows the two stages of pleated cylindrical filters. Penetration

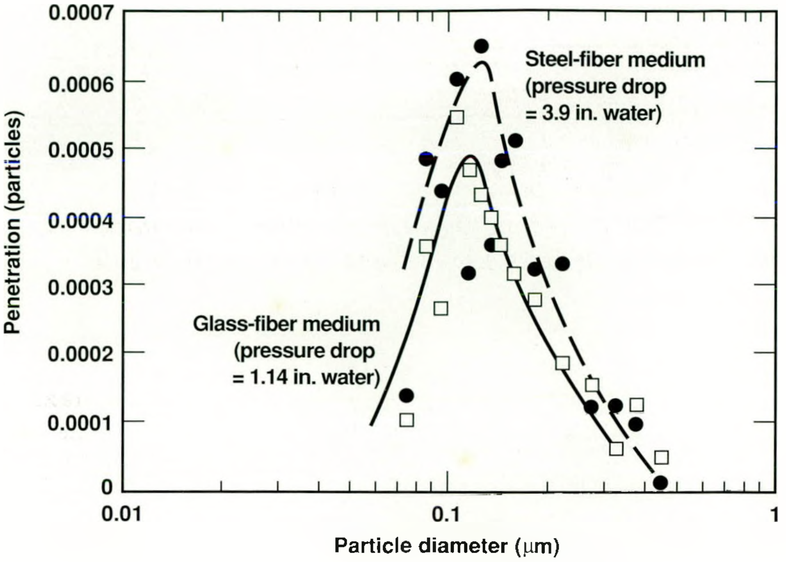

Fig. 2. Steel filter medium has similar penetration, but 3.4 times the pressure drop of glass-fiber-paper HEPA medium.

measurements on this filter using our automated filter test apparatus showed a maximum penetration of 3×10^{-8} for 0.1-mm-diameter particles, i.e., three particles out of one hundred million. The small vent filter represented a major achievement, not only because the project was successfully completed, but also because it is now reasonable to expect that a steel HEPA filter can be developed to replace the glass HEPA filter.

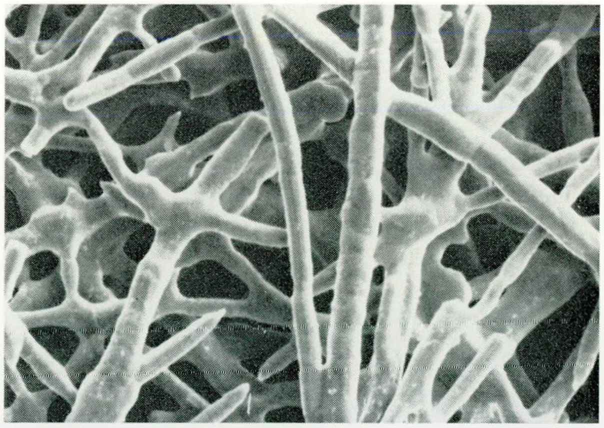

Fig. 3. Electron micrograph of the new stainless steel filter medium.

Development of a Cleanable Steel HEPA Filter

The success of the steel vent filter project, coupled with the significant problems associated with the glass HEPA filters, led to a new project to develop cleanable steel HEPA filters. This project is supported by DOE's Office of Environmental Restoration and Waste Management. The objective of this task is to develop stainless steel HEPA filters that can be repeatedly cleaned and reused. These filters will be used in all DOE air-cleaning applications presently using HEPA filters made from glass paper and will save approximately $100 million per year in filtration costs.

Overview of Plans

The project involves a series of tasks to be completed over five years. The primary development task consists of fiber size reduction, filter media optimization, filter design and fabrication, development of filter cleaning techniques, and field evaluations. The diameter of the steel fibers must be reduced from the present 2.0 mm to 0.3 mm to make the efficiency and pressure drop of the steel filter medium comparable to those of the present glass fiber medium. Secondary tasks include developing theoretical models, filter certification test procedures, and alternative fabrication methods and materials;

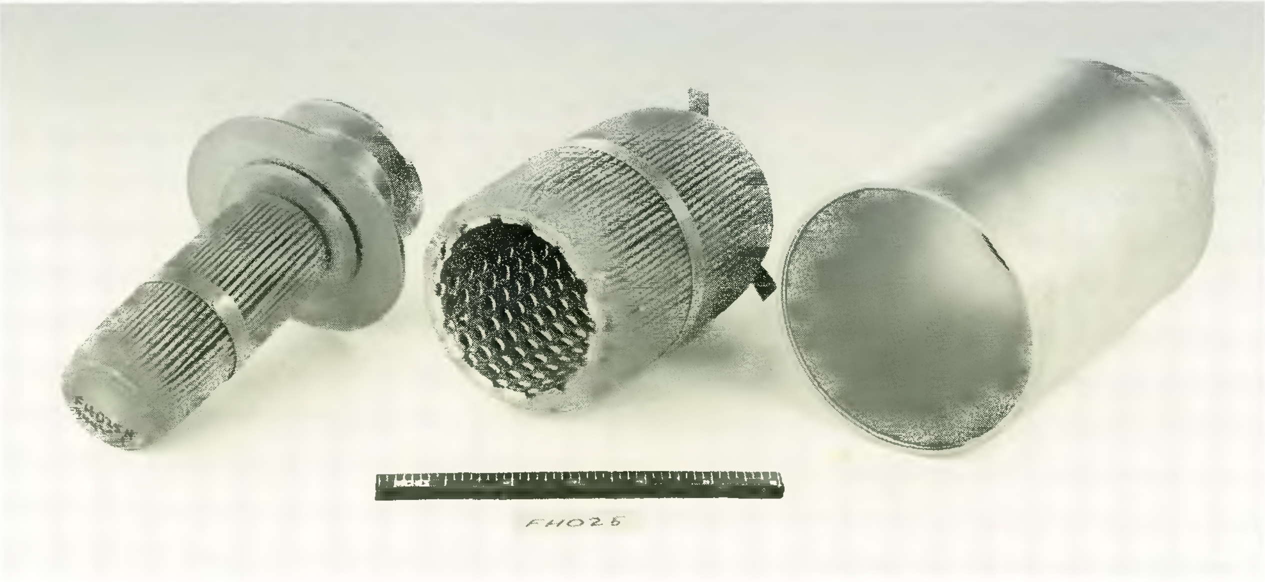

Fig. 4. Prototype steel vent filter with two cylindrical filter stages, shown disassembled.

identifying additional applications; and transferring the technology to the filter industry and to DOE facilities.

Before proceeding with these tasks, we will conduct a field demonstration test to establish the feasibility of the cleanable steel HEPA filter by September 1991. This test will be an extension of the vent filter project. The steel HEPA filter will be fabricated using the newly developed steel filter medium and commercially available materials and filter designs. A number of single-element filters will be fastened together to form a cleanable steel HEPA filter. A blow-back cleaning process will allow the filter to be repeatedly cleaned and reused. The proposed filter demonstration unit with blower and supporting equipment is shown in Fig. 5. This unit will be installed and evaluated in the exhaust system of a uranium grit blaster at the Y-12 Plant (Oak Ridge, Tenn.).

Highlights of FY90 Activities

During FY90 (July–September), we

- Prepared a preliminary project plan for FY90 and FY91 and assembled the project team.
- Evaluated potential demonstration sites at Y-12 and Idaho National Engineering Laboratory (INEL). The best site at INEL was the exhaust system of the Waste Experimental Reduction Facility radioactive waste incinerator. However, particle size measurements at this site showed that the particles are smaller than 0.3 mm diameter and are difficult to remove. Since there was not enough time to develop the proper filter medium, we canceled the INEL site. The best Y-12 site was a grit blaster to clean the surface of uranium parts. Since the particles from this operation are much larger, and therefore easier to clean, we selected this site for the field demonstration.
- Completed the conceptual design of the steel HEPA filter and of the field demonstration unit.
- Began the design and fabrication of the filter test apparatus for evaluating the performance of the steel filter elements and the steel HEPA filter.
- Initiated a study to determine the life-cycle costs of the present glass HEPA filters.

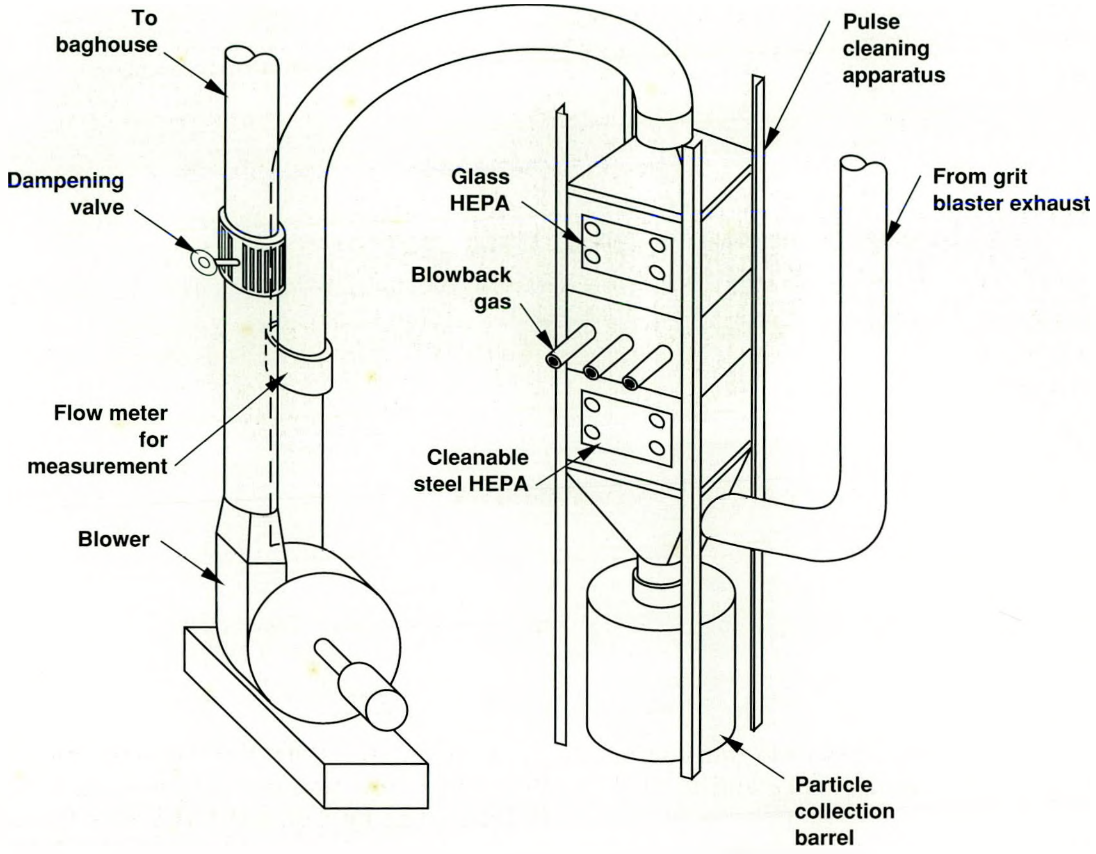

Fig. 5. Initial design of demonstration unit for field test at the Y-12 plant.

Education Initiatives in Environmental Restoration and Waste Management

Principal Investigator: Paul R. Dickinson

We are collaborating with education, industry, and government specialists to develop programs to encourage more students to pursue careers in environmental restoration and waste management disciplines. The initiatives are aimed at elementary and middle school teachers, middle and high school girls, and community college students.

Introduction

The draft DOE Research, Development, Demonstration, Test, and Evaluation (RDDT&E) Plan establishes as an important programmatic element education intervention programs focused on helping to ensure the availability of appropriately trained scientists, engineers, and technicians to support DOE's long-term Environmental Restoration/Waste Management (ER/WM) agenda. Given historical patterns and changing demographics, it is clear that a successful program must be geared toward encouraging more students, particularly women and minorities, to pursue college studies and later careers in science and technology areas relevant to ER/WM, and to provide direct assistance where appropriate. LLNL has responded to this need with the development of several ER/WM education initiatives.

Career Conferences for Young Women

The Laboratory initiated and co-sponsored a one-day career conference in November for young women in grades 6–12; the theme was environmental protection/restoration and waste management. Other sponsors included Mills College (Oakland), the Pacific Telesis Foundation, and The Math Science Network (Berkeley), which developed and conducted the program. Approximately 300 girls and 60 adults attended. This initial conference was a pilot for a western regional program intended to reach 2000 girls annually and eventually expand on a national scale. Funding support will be sought from EM/EPDD sources and private industry.

Teacher Training

A second initiative involves a plan for a broad regional implementation of a teacher-training methodology developed at LLNL called Project HOPES (Helping Our Partners Enhance Science). This program, developed with the assistance of the National Science Foundation, involves a 4-week summer program for teachers of grades K–8 (later K–12); it is designed to improve their knowledge and self-confidence in teaching the physical sciences. The program includes the direct participation of resource specialists (such as Laboratory or private industry scientists and engineers), the presentation of an integrated, multidisciplinary example of science in society (i.e., environmental protection/restoration), and the development and testing of lessons that the teachers take back to their classrooms. LLNL has taken the initiative to develop a HOPES curriculum based on an ER/WM theme with the intent of eventually implementing this program on a continuous basis in five western states. An application for a 3-year grant has been submitted to the California State Department of Education as the first step in the process.

Community College Curriculum

Finally, a major initiative has been developed with the California Community College system and Clark County Community College in Las Vegas, NV, which includes the collaboration of Lawrence Berkeley Laboratory, Sandia National Laboratories–Livermore, and the Nevada Test Site (NTS), to support the development and presentation of an

Environmental Hazardous Materials Technician curriculum. This effort was undertaken at the request of the community colleges and has evolved into a proposal for a national community college program.

The first step will be implementation of a pilot program in five western states in collaboration with the Environmental Protection Agency (EPA). This comprehensive program will involve direct Laboratory/NTS assistance to the colleges for accelerating the rate at which this badly needed curriculum can be introduced onto new campuses and for strengthening the technical content. We estimate that, if fully supported, this initiative could result in an increase of 550 new technician graduates or transfers to 4-year institutions by the end of its fifth year of operation. Minimal start-up funding will be sought from DOE and the EPA; the bulk of the annual operating budget will be sought from private industry.

Once the western states pilot is in place, we propose to expand this program to other parts of the country through a series of workshops for the other DOE and EPA laboratories and regional community colleges. The American Association of Community and Junior Colleges and the National Environmental Training Association are participating in this proposal.