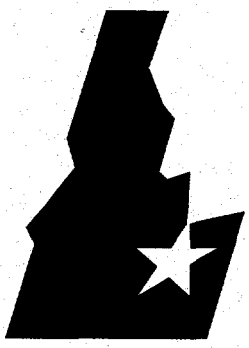

Idaho
National
Engineering
Laboratory

INEL-95/0411

August 1995

Innovative Technology Development Program Final Summary Report

John Beller

Lockheed
Idaho Technologies Company

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Final Summary Report

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Published August 1995

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Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223

ABSTRACT

Through the Office of Technology Development (OTD), the U.S. Department of Energy (DOE) has initiated a national applied research, development, demonstration, testing, and evaluation program, whose goal has been to resolve the major technical issues and rapidly advance technologies for environmental restoration and waste management.

The Innovative Technology Development (ITD) Program was established as a part of the DOE, Research, Development, Demonstration, Testing, and Evaluation (RDDT&E) Program. The plan is part of the DOE's program to restore sites impacted by weapons production and to upgrade future waste management operations.

On July 10, 1990, DOE issued a Program Research and Development Announcement (PRDA) through the Idaho Operations Office to solicit private sector help in developing innovative technologies to support DOE's clean-up goals. This report presents summaries of each of the seven projects, which developed and tested the technologies proposed by the seven private contractors selected through the PRDA process.

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TABLES

Innovative Technology Development Program Final Summary Report

1. BACKGROUND AND OBJECTIVES

The U.S. Department of Energy (DOE) Office of Environmental Management has pledged to work closely with the private sector to reduce the costs associated with cleaning up the DOE complex from 40 years of weapons production. Through the Office of Technology Development (OTD), DOE has initiated a national applied research, development, demonstration, testing, and evaluation program, whose goal has been to resolve the major technical issues and rapidly advance technologies for environmental restoration and waste management.

The Innovative Technology Development (ITD) Program was established as a part of the DOE, Research, Development, Demonstration, Testing, and Evaluation (RDDT&E) Program. The plan is part of the DOE's program to restore sites impacted by weapons production and to upgrade future waste management operations.

The ITD Program is based on the premise that conventional methods for many of the environmental and waste management problems are marginal, time consuming, costly, and may not reduce the possibility of future problems. ITD was charged with finding technologies that are presently beyond the frontiers of science and engineering. Traditional research is considered a relatively low risk, which results in a low probability for advancing the state-of-the-art. ITD evaluates technologies that are a much higher risk, substantially increasing the potential to advance the state-of-the-art. If successful, these visionary projects will make revolutionary changes in the practices of waste management and environmental restoration.

On July 10, 1990, DOE issued a Program Research and Development Announcement (PRDA) through the Idaho Operations Office to solicit private sector help in developing innovative technologies to support DOE's clean-up goals.

This report presents summaries of each of the seven projects, which developed and tested the technologies proposed by the seven private contractors selected through the PRDA process.

2. PROCUREMENT HISTORY

In FY 1990, several problems were identified for which innovative solutions were solicited. These problems were derived from the DOE predecisional draft document *Applied Research, Development, Demonstration, Testing, and Evaluation Plan*, dated November 1989. The areas requiring technology development were kept broad-based to enhance and support the concepts inherent in development of innovative technologies.

On April 25, 1990, an announcement of the procurement activity was issued in the Federal Register. In addition, an announcement was published in the Commerce Business Daily of May 25, 1990. Over 250 requests for the PRDA were received and sent to the private sector.

The DOE Idaho Operations Office issued the PRDA on July 11, 1990, soliciting technologies from a wide variety of areas. These included

1. Site characterization
2. Remediation
3. Decontamination and decommissioning
4. Waste treatment and disposal
5. Waste minimization.

The PRDA closed August 24, 1990 with the receipt of 120 proposals. These proposals were evaluated by a group of 37 technical evaluators from national laboratories, government agencies, and universities. Reviewers were screened for potential conflicts of interest and were required to sign conflict of interest and confidentiality forms. In September 1990, the group met in Idaho Falls, Idaho and was divided into subgroups of three to four people of similar technical background. Each group was assigned a set of proposals, which they reviewed independently and then met to reach a consensus.

The results of the technical evaluation were compiled and presented to the Source Evaluation Board (SEB). The SEB evaluated the business proposals provided with each technical proposal. From these two evaluations, the SEB provided a recommendation to the Source Selection Official. On March 1, 1991, DOE announced the selection of seven contractors.

In July 1991, the DOE Idaho Operations Office transferred the contracts to EG&G Idaho Inc. for award. Before the awards, it was determined that each of the contracts fell under the requirements of the National Environmental Policy Act (NEPA). The federal regulation in 1991 required that a short Environmental Assessment (EA) be prepared to fulfill the NEPA requirements. This delayed issuing all but one of the contracts until June 1992, when the regulations were revised.

3. PROCUREMENT RESULTS

Six of the seven contracts were awarded to private firms, while one contract was awarded to a university. The contracts are listed in Table 1. Each of these contractors was awarded fixed price contracts, which were monitored by EG&G Idaho for both performance and technical validity of the tasks undertaken. EG&G Idaho technical personnel supported researchers where appropriate, providing recommendations and suggestions.

Table 1. Innovative Technology Development Program FY 1990 procurement.

ABB Environmental Services, Inc.	
	A Methanotropic Biofilter for the Treatment of Airstreams Contaminated with Chlorinated Hydrocarbons
	Principal Investigator: Margaret Findlay
Science Applications International Corporation	
	Application of Neural Networks to Site Characterization
	Principal Investigator: Ali Dabiri
International Sensor Technology, Inc.	
	Remote Fiber-Optic TLD Monitoring System
	Principal Investigator: Dr. P. (Peter) F. Braunlich
Research Triangle Institute	
	Novel Technique for Invasive Subsurface Barriers
	Principal Investigator: C. C. (Clark) Allen
University of Idaho	
	Selective Chelation and Extraction of Lanthanides and Actinides with Lariat Crown Ethers in Supercritical Fluids
	Principal Investigator: C. (Chien) M. Wai
SRI International	
	Sonochemical Waste Treatment
	Principal Investigator: Allan J. Johnson, Sr.
Membrane Technology & Research, Inc.	
	Improved Membranes for Water Remediation Projects
	Principal Investigator: Dr. J.(Johnnas [Hauns]) G. Wijmans

4. RESEARCH SUMMARIES

This section presents a summary of each research project and its accomplishments. A final technical report on each project gives full details of the technologies and methods used. Table 2 lists these reports, which are available from John Beller, Environmental and Life Sciences Products Directorate, P.O. Box 1625, Lockheed Idaho Technologies Company, Idaho Falls, ID 83415; telephone (208) 526-1205 (until supply is exhausted).

Table2 . Innovative Technology Development Program reports grouped by project.

Project	Report number	Report title
Methanotrophic Biofilter Treatment of Airstreams Contaminated with Chlorinated Hydrocarbons	EGG-WTD-11387	A Methanotrophic Biofilter for the Treatment of Air-streams Contaminated with Chlorinated Hydrocarbons
Application of Neural Networks to Site Characterization	EGG-WTD-10677	Application of Neural Networks to Waste Site Screening
Remote Fiber-Optic TLD Monitoring System	INEL-95/0226	Remote Fiber Optic Radiation Monitoring System Final Technical Report
Novel Technique for Invasive Subsurface Barriers	RTI Report No. 5481-O1F	Final Technical Report for Proof-of-Concept Coagulated Latex: Novel Use In Modifying Groundwater Flow
Selective Chelation and Extraction of Lanthanides and Actinides with Lariat Crown Ethers in Supercritical Fluids	EGG-WTD-10993	Selective Chelation and Extraction of Lanthanides and Actinides with Supercritical Fluids
Sonochemical Waste Treatment	EGG-WTD-10966	Sonochemical Waste Treatment
Improved Membranes for Water Remediation Projects	EGG-WTD-11384	Improved Membranes for Water Remediation Projects

Project:	Methanotrophic Biofilter for the Treatment of Airstreams Contaminated with Chlorinated Hydrocarbons
Report No.:	EGG-WTD-11387
Organization:	ABB Environmental Services
Contact:	Jaret Johnson ABB Environmental Services, Inc. Corporate Place 128 107 Aububon Road Wakefield, MA 01880 (617) 245-6606

Description

The object of this project was to undertake a laboratory investigation into the feasibility of using a fixed film methanotrophic biofilter for the treatment of trichloroethylene (TCE) in an air stream. Biofiltration is a process in which organic vapors are passed though a porous medium that supports a microbial community, resulting in the continuous biodegradation of the unwanted chemicals. Biodegradation of TCE by methanotrophic cultures has been well documented by a number of authors, and this process is an area of active research due to the ubiquitous nature of this environmental contaminant.

To make this evaluation, a series of bench-scale continuous flow experiments were performed with a prototype biofilter. A 26-L (empty volume) biofilter was constructed and operated with influent TCE concentrations between 400 mg/m^3 to 2,000 mg/m^3 in air at retention times between 15 and 60 minutes. A second identical biofilter was constructed to test a strategy with which the TCE airstream was treated by a single reactor while the second reactor was operated in semibatch mode without TCE but with methane and oxygen additions to regenerate biomass. The reactors were switched periodically to maintain continuous TCE degradation and biomass replenishment. This approach was taken for the following reasons:

- TCE degradation is a co-metabolic side effect of methane oxidizing enzymes, and therefore, bacteria processes cannot be maintained with TCE and without methane
- TCE degradation is competitively inhibited in the presence of higher methane concentrations, and therefore, the biofilter cannot be operated with the addition of both substrates
- TCE degradation capacity of a methanotrophic culture capacity decays over time because of product toxicity and biochemical changes in the bacterial metabolism.

To elucidate the growth conditions necessary to optimize TCE degradation and to determine the best operating parameters in the biofilters, a series of semibatch studies were conducted on a smaller scale using a 3-L reactor. These experiments included tests to compare a pure strain

methanotroph with a mixed culture to select the best biofilm, determination of growth rate, TCE degradation as low methane concentrations, and amendments to the growth medium to optimize TCE degradation.

Research Conclusions

The suspended growth and small-scale biofilter batch studies provided significant data for understanding the methanotrophic system and maximizing its potential. These results seem to confirm much of what has been recently reported on this subject and help to elucidate the limits of this process. The methanotrophic bacteria produced extracellular polysaccarides that result in a thick biofilm suitable for fixed film reactors. However, this characteristic prevents the use of less porous support media (i.e., sand), which becomes clogged. The polysaccarides are also responsible for the clumping of the culture in suspension and its susceptibility to protozoan grazing. The small-scale biofilter, experiments showed that a maximum of 15 mg of biomass (dry weight) could be measured on a single supporting ring. In the large-scale biofilter, approximately 5,000 rings filled the 30-L reactor or 75 g of biomass. Optimistically, if the surface area were increased by a factor of two, 105 g of biomass might be maintained in the reactor.

Other significant results and observations are summarized below:

- The maximum observed biodegradation capacity in the 26-L biofilter column was 2 g/m^3 hour. After 6 hours of operation, biodegradation capacity decayed by 20 to 80%.
- The maximum observed first-order TCE degradation rate constant was 0.6 $g_{vss}^{-1}hour^{-1}$. Initial TCE degradation rate constant is roughly equal to the methane degradation rate constant under ideal conditions and never exceeded the methane rate.
- Preliminary experiments with vinyl chloride (chloroethylene) indicate that this compound will be degraded at three times the rate of TCE, and the degradation rate decays equally.
- The addition of 20 mL sodium formate to the growth media and incubation under nitrate limiting conditions had a positive effect on TCE degradation capacity.
- Operation of the reactor with a low concentration of methane (1 to 2%) did not significantly improve the performance of the reactor.
- The dual column configuration did not overcome the limits encountered in the TCE degradation mechanics; continuous TCE degradation in a biofilter was not feasible.

Status

ABB provided the following recommendations for the methanotrophic biofilter prior to implementation:

- More research needs to be conducted on the microbiological level with regards to sustaining the expression of the soluble methane monooxygenase enzyme before a fixed film methanotrophic biofilter can be considered feasible

- TCE degradation capacity may be increased by a more efficient nutrient delivery system, heating the air stream (e.g., 35°C), and increasing the biofilter surface area. However, it is improbable that such modifications would make this process cost-competitive with activated carbon for treatment of TCE

- A methanotrophic biofilter might be cost competitive for treatment of vinyl chloride due to this compound's lower affinity for activated carbon and the higher methanotrophic biodegradation rate (compared with TCE).

Project:	Application of Neural Networks to Site Characterization
Report No.:	EGG-WTD-10677
Organization:	Science Applications International Corporation (SAIC)
Contact:	Ali Dabiri SAIC 4161 Campus Point Court San Diego, CA 92121 (619) 458-3700

Description

This project investigated the feasibility of using neural network techniques to reduce the cost of waste site screening. The successful technique would reduce the number of boreholes and the samples analyzed from each borehole to properly screen the waste site. The analytic tool development described is in expensive because it makes use of neural network techniques that can interpolate rapidly and can learn how to analyze data rather than having to be explicitly programmed.

A neural network is an interconnected collection of units that behave like neurons in the brain. Each unit receives multiple normalized input signals and generates a single output signal. The output from each unit is typically connected as input to other units in the network. The connections are weighted so that the output of a unit is the weighted sum of the activation signals passed through a nonlinear threshold function. A subset of the units receives input from external sources, and another subset of units generates output for the network, so that the entire neural network can be viewed as a nonlinear mapping between a vector of input activations to a vector of output values.

The connection weights among the units represent the nonlinear mapping function for the neural network. The weights are determined through training where the weights are incrementally adjusted over multiple training cycles. Once the neural network is trained, it is capable of recalling the mapping by feeding the input activation forward through the network to the output. The types of units, connection topology among the units, propagation of signals through the network and learning algorithm are defined by the selected neural network paradigm: back propagation and fully recurrent neural networks. Back propagation is an effective mapping function if the relationship between the input activation vector and output activation vector is a continuous nonlinear mapping. The fully recurrent network effectively maps multiple time series sequences at the input to one or more output sequences at the output.

The neural network approach has two advantages over analytical models. First, the neural network attempts to capture the large-scale behavior of the process and progresses to the fine-scale behavior if the information is available. Analytical models are typically constructed from the bottom up, extending the micro model in steps to a macro model description of the site.

The second advantage is that once a neural network has successfully been applied at one site, the same process can be used to screen other sites. The neural network approach is adaptable and can be tuned to a specific site.

Research Conclusions

The differences between the neural network prediction and actual measurement, referred to as innovations, represent information not captured by the neural network during training. The innovations or deviations from modeled behavior can be due to a number of causes, including systematic measurement error, such as under-sampling and measurement calibration or bias errors; particular soil conditions, such as rock stratification or soil moisture conduits; or processes not observed in the original training samples. Because the neural network has been derived independent of the mathematical model, the network in this configuration can be used to validate the original data measurements or suggest novelty from normal learned behavior.

The connection weights for a fully connected, recurrent back propagation network have several features that differentiate it from normal back propagation. The connection weights represent the correlation strength or codependency among the input and output measurements. Unlike back propagation networks, the weights are well ordered so that the same weights can be derived from different initial states and even different training data for the same process. Therefore, the weights represent the combination of the nominal model for the site independent of specific soil conditions and a local model, which changes the weights to account for conditions specific to the cell neighborhood being predicted. This suggests that there is a relationship between soil conditions and the connection weights and that it may be possible to change the weights to adapt the recurrent network to the new site without extensive training for the new site. This observation is the basis for a general adaptive tool for waste site screening.

The results of the application of the fully recurrent neural network to site data are promising for a general-purpose site screening tool. To date, recurrent neural networks have been developed that are able to capture the dynamics at different depths and radii from the injection site; to generalize to different radials; to account for local variations in soil conditions; and are independent of injection time and rate. In its current configuration, the recurrent network reduces the number of test bore sites by extending the accuracy of the predictions over more widely spaced test sites.

Applications

There are a variety of applications of this technique in environmental site screening and remediation to reduce the cost of drilling and sampling. Following are some examples that demonstrate how this technique could be applied to some of the present environmental problems.

1. Optimum Well Siting. A major factor in the success or failure of a site characterization and cleanup is the effectiveness of the well siting and the sampling procedures used. While the need is obvious, the cost entailed in doing extensive drilling and sampling is prohibitive and will force the position of seeking the most information from the fewest samples.

Traditional methods of drilling and sampling are based on classical statistical methodology where the points are selected randomly in the hope that the contaminated positions will be effectively characterized by the sampling.

Sampling design can be substantially improved by one of the following methods:

- A model that takes into account the underlying physical process, such as transport, flow, reaction, etc. This model-aided sampling approach is an improvement over the more traditional approaches because it uses a model of the actual process driving the contaminants to their current and future states. The problem of this method is that it can also be costly, both in labor and computer time. In addition, the spatial and temporal variations in data describing the subsurface, flow, and other physical parameters place further demands on these modelings.

- A neural network model that could be training for the existing sampling data obtained from existing bore sites. This trained network could be used to decide where the next well should be drilled. The neural network can predict the waste contaminants in locations near the wells that have already been characterized. The waste level map obtained for this exercise will determine the optimum location of the next hole to be drilled. Obviously, there is no need to drill at the locations where there is not any major change of contaminants with respect to other characterized locations.

*2. **Reduction in Number of Samplings.*** The results indicate that the fully recurrent network approach has the potential to predict waste contamination levels at a certain depth from the waste contamination levels measured at more shallow depths. The three- to six-setup configuration of a fully recurrent network can be utilized for this purpose. The neural network will be trained from the existing sampling data obtained from the existing neighboring bore sites. Assuming minor variations in geology of neighboring bore sites, one could use the trained network and three- to six-setup configuration to predict the waste contamination levels at the next two levels down. (If the geology of the two sites are different, it is possible to change the connection weights of the fully recurrent network to adapt it to the new site without extensive training for the new site.) The new values could be utilized to predict the waste levels at an even lower depth, and this process could continue. At some point in the process, the waste contamination level can be measured at a certain depth to check the accuracy of the predictions. This process can substantially reduce the number of samplings.

*3. **Reduction in Number of Bore Sites.*** The trained network mentioned above could also predict the contamination levels at the next two bore sites out in the radial direction with the three- to six-setup configuration. These new values could be used to predict the contamination levels at even larger radii. At some point, the contamination levels can be measured to check the accuracy of the predictions. This process can substantially reduce the number of bore sites.

Project:	Remote Fiber-Optic TLD Monitoring System
Report No.:	INEL-95/0226
Organization:	International Sensor Technology, Inc. (IST)
Contact:	Scott Jones IST NE 1425 Terre View Drive Pullman, WA 99163 (509) 332-3328

Description

This project focused on the development of a passive, fiber-optic based system for monitoring belowground radioactive contamination in soils and ground water. Remote laser heating via optical fiber is the principle used to read a small thermoluminescent dosimeter (TLD). The thermoluminescent emission is returned to the reader by the same optical fiber. The fiber optic probes monitor for the presence of beta and gamma emitting radionuclides. Since the probes are evaluated in situ, analysis is accomplished without any sample or detector retrieval. The probes are immersible, and therefore can measure activity in ground water via test monitor wells or bore holes without retrieving either the dosimeters or water samples. Probes up to 500 ft long are intended for permanent deployment to provide a long-term monitoring capability. The portable reader, operable from a 12V automotive electrical system, is used to periodically read out the probes, which can be deployed at remote sites lacking electric power. The reading cycle resets the probes for the beginning of the next exposure period. A single reader can monitor hundreds of permanently emplaced probes, providing for an economical portable radiation measurement system.

The principal intention of this project was to develop a capability for passively measuring gamma and beta radiation emitted by nuclides associated with environmental contamination at DOE facilities. Measurement of the time evolution of radioactive groundwater plumes was the original concept for this development project, but many more potential applications came to light during the conduct of the program. The system is potentially a very versatile tool for application to DOE radiation measurement problems. The specific isotopes considered were ^{90}Sr, ^{137}Cs and ^{60}Co, but were not intended to be exclusive.

Radiation Sensitivity

The lower limit of radiation dose measurement with the conventional TLD method is nominally a few millirad for routine dosimetry, where relatively massive (28 mg) TLD chips are heated directly in front of the light measuring photomultiplier tube (PMT). Using high sensitivity phosphors, this figure may fall to 0.1 mrad or so. The overall sensitivity of a TLD scales with the phosphor mass for gamma dosimetry.

In the present system, small phosphor masses, on the order of 100–300 μg, are heated at distances of perhaps hundreds of feet from the PMT, with a number of optical components in the

light path, the most obvious being the optical fiber, that contribute to significant attenuation of the TL emission. Nevertheless, using high sensitivity phosphor, this system is capable of detecting gamma radiation doses of a few mrad using probes that are about 200 ft long. The rapid heating rates achievable with Laser TLD is the reason for the relatively high sensitivity attainable with small TLDs. Dosimeter readout time are measured in milliseconds instead of seconds.

The measurement of radioactivity can be made in terms of absorbed dose (rads or mrad), or exposure in terms of (activity/mass or activity/volume) $\times$ time, e.g., pCi-hrs/ml or μCi-hrs/gram. The measurement is made relative to a specific calibration condition, e.g., ^{137}Cs gammas or ^{90}Sr activity. No specific isotopic identification is currently possible, but with a number of differentially filtered probes, some indication of radiation quality is achievable, e.g., beta only, gamma only, or mixed beta/gamma.

Currently, measurement sensitivity (the lower limit of detection) is equivalent to about 3.5 mrad ^{137}Cs gamma dose, or 25 pCi/ml for a 168 hour (1 week) exposure for ^{90}Sr dissolved in water (it is assumed that ^{90}Sr is in equilibrium with its daughter ^{90}Y).

Physical Description of System

The system consists of a reader unit about the size of a home stereo receiver that is operable from 12V dc automotive electrical system (or 120 V ac), which is capable of reading up to 10 detachable probes at a time, although any number of probes may be used with the system. The reader is operated via a laptop or notebook IBM-compatible personal computer (PC).

A probe consists of a single large-core optical fiber with a small (0.6 mm diameter) TLD element at the distal end. A standard fiber optic connector connects the probe to the reader. The probe tip must be enclosed by an opaque, sealed cap, and the entire length of the probe is covered by opaque tubing. The tip enclosure, consisting of a sealed Teflon (FEP) catheter of 0.28-mm wall thickness (62 mg/cm^2), does not have a substantial effect on gamma radiation sensitivity. However, it does affect the sensitivity to beta radiation, and therefore beta-emitting radionuclides, and completely eliminates the possibility of measuring alpha radiation, at least in a rugged configuration. The overall diameter of a single probe is about 2 mm, and is very flexible.

System Operation

Operation of the reader is very simple. One or more probes are connected to the reader and the Read Probes selection is chosen from the menu on the PC. The probe is identified by scanning an attached barcode label (or entered from the PC keyboard). The operator may annotate any information about the reading or can simply initiate the reading. The reading is performed in a few moments and a data file (with annotation) is recorded on the computer hard drive. The probe is reset by the reading operation and the next measurement period commences. The file format is compatible for importing to a database, and all readings can be downloaded to the database at convenient intervals. The database, which must be established for a particular measurement program, will contain all the pertinent information about any probe, with the current probe reading file(s) containing the reading data (measured radiation dose or exposure,

time, date, etc.). With the database, a complete history of the radiation parameters for the point location of the probe tip is maintained, for example, average dose rate, time evolution of the dose rate or radioactivity, etc.

Research Conclusions

This development project exceeded the basic goals set forth in the program proposal, namely probe sensitivity, length, and survival, and reader portability. Some deviations from the envisioned final configuration of the system have occurred between the date of proposal submission (August 1990), project funding (July 1992), and completion (April 1995). These deviations are in detail and not in function.

The capabilities of the system closely approach what is physically possible for a TLD radiation measurement system, given the size constraint on the dosimeter element. This achievement is entirely due to the high signal-to-noise ratio obtainable with Laser TLD.

Potential Applications

Potential applications of this system are quite broad, which is a result of the high sensitivity we attained during this project. Implementation of this system for the measurement of the isotopes $^{90}Sr + {}^{90}Y$, ^{137}Cs, ^{60}Co and other radiations may be very useful in the following scenarios:

- Long-term monitoring of groundwater via test wells, such as those monitoring the belowground radioactivity at the ICPP. Contamination level increases and movement can be obtained on a long-term, continuous measurement basis, without sample or detector retrieval. Measurement at locations lacking electrical power is possible.

- Monitoring the occurrence of leaks or changes in leak rates around waste storage tanks and tank farms, or storage pond perimeters can be monitored at and below the ground surface for leaks and seepage. Different length probes can be measured from a single point in the tank facility.

- Measurement for the presence or movement of contamination around known spill- or dump-sites or cribs. Soil emplacement is possible. In loose soils, contamination may be carried a significant distance by precipitation runoff.

- Site characterization by measuring contaminant distribution in the soil profile.

- Measurement for radioactivity in all types of piping; effluent and sewer drains; probing for contamination leaks to building exteriors in spill situations, etc.

- Continuous monitoring in ventilation or exhaust ducts, filters, and plumbing without repeated detector emplacement or retrieval.

- Site perimeter environmental gamma dosimetry for site perimeter monitoring, providing near real-time readout of environmental TLDs in emergency situations. This application, as well as effluent, sewer, or runoff monitoring, may be of interest to public health and environmental protection agencies as well as DOE.

- Monitoring of personnel working in hot zones. Probes could be incorporated in the life support umbilical of rad workers working in hot zones, to provide remote measurement of dose and dose-rate from a safe location.

Project:	Novel Technique for Invasive Subsurface Barriers
Report No.:	RTI Report No. 5481-O1F
Organization:	Research Triangle Institute (RTI)
Contract:	W. Joseph Alexander Post Office Box 12194 Research Triangle Park, NC 27709 (919) 541-5929

Description

This project focused on the proof-of-concept for a novel invasive barrier technology. The petroleum industry has been developing and using polymer technologies for approximately 30 years to enhance oil recovery operations by reducing formation permeability. High-molecular-weight polymer solutions are injected into oil reservoirs to reduce formation permeability and improve the water-oil mobility ration. The use of polymer technology in the petroleum industry demonstrates the feasibility of injecting polymers into the subsurface as a means of reducing formation permeability.

This project evaluated injecting a latex polymer emulsion and a reactant coagulant solution into an simulated aquifer. The latex and coagulant react in the aquifer to form a low-permeability barrier that is not limited in its application to sites characterized by shallow groundwater contamination. In fact, the latex and coagulant can be injected so that an impermeable barrier is formed around and/or under a contaminated site.

For this research effort, RTI proposed to develop an improved polymer system for application to environmental problems. Due to its application in the environment, the proposed polymer system had to be nonreversible, noncorrosive, and nontoxic under a variety of environmental conditions. In addition, the polymer system had to demonstrate long-term stability and good rheological properties as well as be economically feasible.

The major activities in this project included the following:

- Performing synthesis experiments to evaluate coagulation properties of different commercially available polymer emulsions with different coagulating agents
- Performing grain size analysis of the three test sands used in the laboratory experiments
- Designing and constructing a flow chamber to simulate various aquifer conditions
- Evaluating methods of polymer introduction into sand-packed burets, columns, and the flow chambers
- Evaluating the retention and flow characteristics of the polymer within porous media of various grain sizes using sand-packed burets columns and flow chamber

- Measuring hydraulic conductivity in columns packed with porous test media following introduction of the polymer/coagulant mixture

- Evaluating the effects of time and flow rate on polymer-treated sand columns

- Evaluating the impact of latex barrier on groundwater flow in a flow chamber using stratified porous media with inherent heterogeneities

- Conducting a technical reference review to identify potential problems/solutions associated with polymer applications in future field studies.

There are several potential advantages of using the latex barrier concept as an environmental remedy:

- Latex coagulum is expected to form a strong barrier by combining with existing aquifer materials

- Latex emulsion can contain high concentrations of high-molecular-weight polymeric particles and remain sufficiently fluid to penetrate porous media

- Latex coagulates under controlled conditions to form a low-permeability material

- In contrast to downhole grouting techniques that seal a limited area around the wellbore, the fellation time of latex polymer emulsions can be controlled to allow coagulation to occur at extended distances from the point of injection, thereby decreasing the injection well spacing requirements

- Injected latex emulsion has the ability to flow into and through the zones of greatest permeability and to coagulate within these zones, thus sealing zones of greatest fluid transmission.

Research Conclusions

Of the polymer formulations developed and tested for this project, one formulation clearly demonstrated proof-of-concept and meets the original objectives of the proposed research effort. Formulation No. 1 (Tylac 68323/$FeCl_3$) provided consistent results in terms of reductions in hydraulic conductivity of two orders of magnitude due to its very cohesive characteristics and ability to adhere to the solid matrix. Formulation No. 2 (Tylac 40705/$Na_2B_4O_7$-$10H_2O$) had an apparent reduction in the hydraulic conductivity of the test medium by five to six orders of magnitude, but not for long periods of time or by the desired physical mechanisms (the apparent reduction in hydraulic conductivity may be attributed to increased head loss in the test apparatus rather than in the test medium). For these reasons, Formulation No. 1 is the preferred polymer/coagulant mixture developed during this phase of research.

Formulation No. 1 exhibits other desirable characteristics such as controlled setup time (coagulation can occur in less than 30 seconds following introduction of the $FeCl_3$) and apparent

strength characteristics (the coagulum is dense, rubbery, and extremely resistant to tearing). Chemical compatibility testing further indicates that this formulation has the ability to coagulate even in the presence of concentrated trichloroethylene and still maintain its ability to reduce hydraulic conductivity.

Based on these findings, RTI subjected Formulation No. 1 to further testing in a flow chamber to demonstrate that latex could be successfully emplaced in a simulated aquifer system and could form an effective barrier to groundwater flow. RTI determined that the formulation was most effectively emplaced using a simulated injection well where multiple treatments of alternating injections of coagulating agent and polymer emulsion were introduced into the aquifer. Tracers injected in the test chamber indicated that the groundwater flow was diverted and that the groundwater discharge was reduced. Tests using a simulated recovery well demonstrated that "contaminants" introduced into the aquifer would be recovered effectively upgradient of the barrier in both coarse- and fine-grained materials.

Status

The fact that proof-of-concept has been successfully demonstrated suggests the technical feasibility of the latex concept as an invasive barrier technology.

Based on the results of the column experiments, future phases of research should focus on the potential effectiveness of the coagulum as a subsurface barrier. First, manometers should be used to measure the pressure difference across the region of interest in the column apparatus (i.e., that region affected by the coagulum). This would eliminate the problems associated with computing the head loss attributed to the column apparatus itself. Second, the polymer and coagulant should be injected directly into the fully saturated porous medium, possibly through manometer-like ports. In this way, the problems associated with air in the porous medium are alleviated. Third, since natural soils have heterogeneous particle size distribution, organic content, and mineralogy, experiments should be conducted to determine the influence of such heterogeneity on the behavior of the coagulum in porous media.

Additionally, based on the results of these experiments and the findings of the literature search, the potential gains from developing a polymer/coagulant combination with a delayed set time are considered exceptional. Such a combination would facilitate the field application of this technology because it would allow coagulation to occur farther from the well, simplifying the injection process and possibly reducing the number of required wells.

Some of these ideas for future research may best be executed through use of a larger-scale (i.e., on the order of meters) flow chamber with manometers and injection ports at appropriate locations along its length. Such a chamber should be sufficiently large so that regions of different permeability, pore size distribution, organic content, etc., could be prepared to reflect the heterogeneity of an actual sample of aquifer material. In addition, by orienting the chamber appropriately and including horizontal flow, any difficulties with the $FeCl_3$ diffusing downward and not mixing with polymer could be observed.

Pilot Field Testing at Candidate Site (Phase II, Stage 3)

A potential candidate site has been identified that is sufficiently close to RTI to allow for interactive field and laboratory experiments. This is an important consideration for future phases of research because RTI expects that many issues will arise in the initial field work that require additional problem solving in the laboratory. The hydrogeology and contamination distribution at the site are complex, but well understood and documented. The hydrogeologic conditions have already been modeled and integrated in a geographic information system. Opportunities exist for shallow injection and excavation of latex formulations to determine the effectiveness of the emplacement. A pilot field study would also facilitate a cost analysis and allow preliminary determination of applicability, feasibility, and limitations of the latex barrier concept.

Project:	Selective Chelation and Extraction of Lanthanides and Actinides with Lariat Crown Ethers in Supercritical Fluids
Report No.:	EGG-WTD-10993
Organization:	University of Idaho
Contract:	C. M. Wai University of Idaho Department of Chemistry Moscow, ID 83843 (208) 885-6787

Description

This project focused on developing a method for the remediation of metal ions such as lanthanides (rare earth elements) and actinides (transuranic elements) that are a major concern in the treatment of industrial and nuclear wastes. The method is based on the combination of two advanced technologies: selective chelation and supercritical fluids extraction (SFE). The proposed process involves the formation of organometallic chelates from lanthanide and actinide metals. These organic chelated complexes can then be removed from waste materials by solubilization in supercritical fluids. A supercritical fluid is any fluid that has been raised simultaneously above both its critical temperature and critical pressure. In this region, the fluid is incapable of being liquified under any conditions; the material exists as a single homogeneous phase that is essentially a dense gas. Since supercritical fluids such as CO_2 are stable, nontoxic gases at ambient conditions, the metals can be easily recovered from the supercritical fluid by simply depressurizing the fluid and precipitating the metal. The chelated complex is reversible with respect to pH, allowing for the recovery and reuse of the ligand.

Organic chelation has long been used for selective separation of metal ions from aqueous solutions. Recent modifications to the structure of some chelating agents has resulted in the development of a new generation of highly selective chelating agents that can be used for more efficient separation of metal ions. Supercritical fluids technology has been shown to be industrially useful for the extraction of organic compounds from solid material.

Research Conclusions

The following five beta-diketones were tested as ligands for the extraction of TH^4 and $(UO_2)^2+$ in supercritical carbon dioxide: acetylacetone (AA), trifluoroacetylacetone (TAA), hexafluoroacetylacetone (HFA), thenoyltrifluoroacetylacetone (TTA), and fluorinated beta-diketone 2, 2 dimiethyl-6, 6, 7, 7, 8, 8, 8,-heptafluoro-3, 5-octanedione (FOD).

From filter paper, free Th^{4+} and $(UO_2)^2+$ ions cannot be extracted ($<2\%$) by neat CO_2 or by methanol (5% by mole) modified CO_2. When the nonfluorinated beta-diketone AA was used as the extractant, only 5% of the spiked uranyl ions can be removed by neat CO_2 under the specified conditions. With fluorinated beta-diketone ligands (80 μmole) present in the fluid phase, significant amounts of the spiked uranyl ions can be extracted by supercritical CO_2. The

percent extraction of the spiked uranyl ions varies from 15% for TAA to 51% for FOD. It is apparent from the data the fluorine substitution in beta-diketone can significantly increase the extraction efficiency of the ligand for uranyl ions in supercritical CO_2. The percent extraction of Th^{4+} by supercritical CO_2 from the cellulose-based matrix varies from 68% for TAA to 80% for FOD. The extraction efficiencies of the fluorinated beta-diketones for Th^{4+} are higher than those found for $(UO_2)^{2+}$ in supercritical CO_2 at 60°C and 150 atm. Using the non-fluorinated betadiketone AA, only 6% of the spiked Th^{4+} can be extracted under the same conditions. FOD appears to be the most effective fluorinated beta-diketone for the extraction of Th^{4+} and $(UO_2)^{2+}$ in supercritical CO_2.

For the extraction of Th^{4+} and $(UO_2)^{2+}$ ions from water, TTA was chosen as the extractant because as a solid it is easier than the other betadiketones to handle experimentally. The ligand was loaded in a cylinder placed upstream from the liquid extraction cell. The pH of the aqueous solution was controlled at 6.0 using an acetate buffer. The extraction was performed dynamically at 150 atm and 60°C for 20 minutes. In the absence of a ligand, free uranyl and thorium ions cannot be extracted (<2%) by supercritical CO_2 even with 5% methanol in the fluid phase. With TAA present in CO_2, extraction efficiencies for $(UO_2)^{2+}$ and Th^{4+} are 62% and 75%, respectively, at 60°C and 150 atm after 20 minutes of dynamic extraction. When 5% methanol modified CO_2 was used as the fluid, extraction efficiencies increase to about 82% and 91% for $(UO_2)^{2+}$ and Th^{4+}, respectively, under the same T,P, and extraction time.

This study has demonstrated that thorium and uranyl ions either dissolved in aqueous solution or adsorbed on the cellulose based filter paper can be effectively extracted by methanol modified CO_2, containing any one of the fluorinated beta-diketones (TAA, HFA, TTA, and FOD) tested in this study. TBP can also extract uranyl ions in supercritical CO_2 to about the same degree as the fluorinated beta-diketones. The extraction efficiency of the mixed ligands (TBP + TTA or TBP + FOD) for uranyl ions was significantly higher than the individual ligands. This new SFE technique offers a host of potential applications for separation of actinides from solid and liquid materials.

Project:	Sonochemical Waste Treatment
Report No.:	EGG-WTD-10966
Organization:	SRI International
Contract:	T. Mill SRI International 333 Ravenswood Avenue Menlo Park, CA 94025 (415) 859-4245

Description

This research involved the use of high-intensity ultrasonic irradiation in conjunction with photoreactive semiconductors, such as TiO_2, to destroy aqueous organic pollutants. Metal chalcogenide semiconductors, such as TiO_2, ZnO, CdS, and $W0_3$, have been widely investigated as materials for the degradation of aqueous organics in light-induced redox reactions. The primary innovative aspect of the technology is the application of "power" ultrasound to the TiO_2-mediated photodegradation. The technology relies on the unique sonochemical effects of ultrasound in accelerating and improving some heterogeneous catalytic processes.

The primary objective of this research was to demonstrate the feasibility of the proposed treatment process, leading to eventual implementation. This required a systematic evaluation of the effects of variables such as ultraviolet (UV) intensity, ultrasound intensity, and catalyst loading on the enhancement in degradation rates for model substrates.

The project evaluated the unique effects of this ultrasonic energy on accelerating and improving the catalytic processes. The initiating step in this photocatalytic process involves the illumination of the semiconductor with light energy sufficient to generate conduction band electrons and valence band holes. The hydroxyl and hydrogen radicals, created by the reaction of adsorbed water with the electrons and holes, are generally considered to be the primary cause for the oxidative degradation of organics. SRI coupled this catalytic process with ultrasonic irradiation to further enhance the photocatalytic process. Ultrasonic irradiation provides a form of energy that can modify the chemical reactivity of some chemical processes. Power ultrasound produces its effects via cavitation bubbles. Transient cavities, produced using ultrasonic irradiation, exist briefly, expanding to at least double their initial size before violently collapsing into smaller bubbles. The collapse of these bubbles can yield local pressures of hundreds of atmospheres and temperatures of thousands of degrees. Dramatic enhancements in reactivity and rates of chemical processes can arise from the process of cavitational collapse.

Preliminary experiments suggested that ultrasonic irradiation of the reaction mixture concurrent with UV photolysis has the potential to increase the degradation rate and efficiency in cost-effective manner by allowing an increase in throughput for an optimum light intensity, eliminating potential catalyst poisoning, and allowing use of cheaper forms of TiO_2. The primary innovative aspect of this proposed treatment technology is the application of power ultrasound to heterogeneous photocatalysis, resulting in reaction enhancement.

Research Conclusions

The foregoing experimental program has established that 24D is rapidly photooxidized in the presence of UV light, $>0.005\%$ TiO_2, and oxygen to release chloride ion and (probably) form simple nonaromatic organics and CO_2. Added oxygen accelerates the rate, but H_2O_2 and HCO_3 ion have no effect. Changes in pH from 1.5 to 9 affect the rate only slightly, and changes in TiO_2 loadings have no effect once all UV light is absorbed ($>0.005\%$).

Acetophenone (AcP) is oxidized in a very similar manner with TiO_2, oxygen, and UV light. The rate of oxidation of AcP alone is about three times faster than that of 24D alone, even though cooxidation shows they have about the same reactivity with 0.2% TiO_2.

Both of these oxidations are very similar to oxidations of many other aromatic compounds reported in the literature. Therefore, the important finding, that ultrasound imposed on the UV/TiO_2 oxidation of 24D has little or no effect on the rate of the process, almost certainly applies generally to photooxidations with TiO_2 and oxygen.

Earlier reports indicating enhanced rates with ultrasound were found to be due to inadequate stirring and oxygen starvation in unsonicated experiments. We did find what appear to be small but real rate enhancements of oxidations of 24D by ultrasound when using solutions cooled initially to 15°C, where cavitation effects are enhanced, and when using 0.005% TiO_2 with 0.011 mL 24D At 25°C.

However, these rate enhancements are less than a factor of 2; accordingly, the use of ultrasound is not warranted in these oxidations as a means of speeding up the process, given the added cost of sonicators and the wear on the sonicator tips with even limited use.

Project:	Improved Membranes for Water Remediation Projects
Report No.:	EGG-WTD-11384
Organization:	Membrane Technology & Research, Inc.
Contract:	J. H. Wijmans Membrane Technology & Research, Inc. 1360 Willow Road Menlo Park, CA 94025 (415) 328-2228

Description

This project evaluated pervaporization technology to remove volatile organic compounds (VOCs) from contaminated groundwater. Pervaporization is a process in which liquid organic materials are vaporized through a membrane, collected by condensation, and removed as a concentrated permeate.

The pervaporization system developed by MTR would treat contaminated wastewater streams containing VOCs at concentrations as low as 1 ppm. Membranes and membrane modules that make up this system must have the selectivity characteristics necessary to remove the low-level organics, and they must be able to handle the high flow rates necessary to remediate groundwater. Thin-film composite membranes, composed of microporous support film coated with the thin (0.5 μm thick or less) permieselective membrane layer, are interwoven with spacers and wrapped around a central perforated tube to form a cylindric module. A dilute aqueous feed containing dissolved organic solvents enters the outer layers of the module and passes inward across the surfaces of the membrane as a vapor. The organics are separated from the water by preferentially passing through the membrane. The permeate fraction containing the organics then spirals inward to the central collection tube while the remainder of the feed flows across the membrane surface and exits as pure water. Transport through the membrane is induced by maintaining a lower vapor pressure on the permeate side of the membrane than on the side of the feed liquid. This vapor pressure differential is achieved by cooling the permeate vapor to a temperature below that of the feed vapor.

The three specific objectives of the project were (1) to develop high flux microporous support membranes, (2) to develop thin-film composite membranes with better VOC/water selectivity than currently available commercial membranes, and (3) to develop spiral-wound modules that minimize parasitic pressure drop and concentration polarization effects. All objectives were met.

Research Conclusions

A novel support membrane made from polyvinylidene fluoride was developed. This membrane provide two important improvements over the polysulfone membrane used previously:

- *Increased chemical stability.* The new membrane is stable with respect to chlorinated hydrocarbon liquids and aromatic hydrocarbon liquids, compounds that are commonly found in contaminated surface water and groundwater

- *Reduced resistance to flow.* The new support membrane will not impede permeating of organic compounds, even if the support membrane is coated with a very thin, highly-selective layer.

A novel composite membrane was developed, consisting of an ethylene-propylene copolymer selective layer coated onto a polyvinylidene fluoride support membrane. In pervaporization experiments with TCE/water and toluene/water mixtures, this membrane demonstrated organic enrichments that are 2- to 5-fold better than those obtained with MTR's current commercially available membrane, which is based on polydimethlsiloxane. However, in experiments with ethyl acetate/water and methyl ethyl ketone/water mixtures, MTR's current membrane performed better. The newly developed ethylene-propylene membrane is particularly suitable for water remediation applications involving removal of chlorinated hydrocarbons and aromatic hydrocarbons with low solubility in water.

The excellent separation that can be achieved in the removal of organics from water make the pervaporization process very sensitive to concentration polarization. This phenomenon results from the stagnant boundary layer that develops adjacent to the membrane surface on the feed side. We found that the negative effects of concentration polarization can be minimized by optimizing the spacer materials used in the spiral-wound modules and by optimizing the conditions under which the modules are operated. A most significant finding is that concentration polarization can be reduced; that is, separation factors can be increased by reducing the driving force for permeation across the membrane. From an energy standpoint, reducing the driving force is preferred over increasing the membrane thickness, which is one of the traditional methods used to counter concentration polarization.

The combination of improved membranes (improved chemical stability and reduced resistance to VOC transport, and improved separation factors for hydrocarbons and chlorinated hydrocarbons) with improved system operating conditions makes it possible to use pervaporization in remediation projects were VOCs are to be removed from contaminated ground or surface waters. An economic analysis shows that pervaporization treatment costs are approximately $3.00/1,000 gallon treated, and that pervaporization competes successfully with the combined air stripping/carbon adsorption process at VOC concentrations of 5 ppmw and higher.

The experimental results reported here were obtained with laboratory scale modules. Follow-on work would consist of preparing commercial-scale, spiral-wound modules containing the newly developed ethylene-propylene membrane, and of operating these modules under the improved operating conditions.