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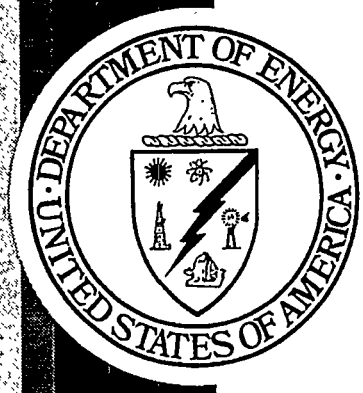

Office of Environmental Management

Office of Technology Development

Technology Catalogue

Second Edition

MASTER

April 1995

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Introduction

Section 1.0

1.0 INTRODUCTION

The Department of Energy's (DOE's) Office of Environmental Management (EM) is responsible for remediating DOE contaminated sites and managing the DOE waste inventory in a safe and efficient manner. EM's Office of Technology Development (OTD) supports applied research and demonstration efforts to develop and transfer innovative, cost-effective technologies to its site clean-up and waste-management programs within EM. The purpose of the Technology Catalogue is to: (a) provide performance data on OTD-developed technologies to scientists and engineers responsible for preparing Remedial Investigation/ Feasibility Studies (RI/FSs) and other compliance documents for the DOE's clean-up and waste-management programs; and (b) identify partnering and commercialization opportunities with industry, other federal and state agencies, and the academic community.

In January 1994, DOE announced "A New Approach to Environmental Research and Technology Development at the U.S. Department of Energy." The goal of DOE's new approach is to conduct a research and technology-development program that will overcome major obstacles in the cleanup of DOE sites. Areas were identified to focus Department-wide environmental research and technology-development activities on DOE's most pressing environmental-restoration and waste-management problems. These "Focus Areas" are targeted for action on the basis of risk, prevalence, or need for technology development to meet environmental regulations and requirements. DOE has established a framework and strategy for coordinating efforts among DOE organizations, Management and Operating (M&O) contractors, the national laboratories, other government agencies, the scientific community, academia, and stakeholders. The new strategy will build upon existing programs.

Many of the technologies have been successfully demonstrated in the field and now are sufficiently mature to be transferred to users throughout the DOE complex. The Technology Catalogue is a means for communicating the status of the development of these innovative technologies.

This Second Edition of the Technology Catalogue features 65 technology profiles. Forty-two (42) of the profiles were featured in the First Edition of the Technology Catalogue and have been revised to reflect the most current technical-performance information available. Of the 23 new technology profiles in this Second Edition, 9 are sponsored by the Waste-management Education & Research Consortium (WERC). WERC was funded with $425 million for five years beginning in 1989 by the DOE to expand U.S. capability and resources for managing waste and restoring the environment. The consortium members include New Mexico State University; New Mexico Institute of Mining and Technology; Navajo Community College at Shiprock, New Mexico; Sandia National Laboratories; and Los Alamos National Laboratory.

Several methodologies were employed to select and prepare technology profiles. Factors affecting the selection of technologies include the availability and quality of technical information and the maturity of each technology. DOE Program Managers made the final selection of technologies for which profiles were developed. The primary sources of information for the Second Edition of the Technology Catalogue were technical reports, published articles, and data supplied by the principal investigators (PIs).

Of the 65 technologies in the Second Edition, 28 are categorized as characterization/monitoring technologies, and 37 are remediation technologies. The technology profiles include the following topical areas:

- Technology title and description
- Technical performance and cost data
- Projected near-term performance (1 to 3 years)
- Applicable waste types and forms
- Development status
- Key regulatory considerations regarding the application of the technology
- Potential commercial applications
- Baseline comparison technology
- Intellectual property
- Points-of-contact and references for more information

The information in each category introduces the technology to the reader and provides a "snapshot" of its status with respect to performance and availability. More detailed information can be obtained from the sources cited in each profile.

The Technology Catalogue currently serves as a source of information on DOE's emerging technologies and is being provided periodically to the inter-agency Federal Remediation Technologies Screening Matrix as well as to other U.S. Environmental Protection Agency, U.S. Department of Defense, and commercially available databases. The information contained in the Technology Catalogue is also available via electronic access to the DOE EnviroTRADE® Information System. The Technology Catalogue will continue to be a valuable source of technical information to be used by the DOE International Technology Exchange Program to enhance the competitiveness of U.S. industry worldwide by communicating the merits of U.S. technologies. [Note: A catalogue dedicated to the technology transfer aspects of OTD-sponsored characterization, monitoring, and sensor technologies (CMST) is under preparation. The CMST Catalogue will be released in early fiscal year (FY) 1996.]

DOCUMENT ORGANIZATION

The Technology Catalogue attempts to match applications with specific technologies in addition to providing profiles on each technology. Section 2 describes the development process utilized to select and prepare technology profiles. Section 3 contains waste-applicability tables developed to aid the user in matching applications with each technology. Table A addresses Site Characterization and Monitoring Technologies, and Table B addresses Site Remediation Technologies. Section 4 contains Site Characterization and Monitoring Technology profiles, and Section 5 contains Site Remediation Technology profiles.

FOR MORE INFORMATION, PLEASE CONTACT:

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Development Process

Section 2.0

2.0 DEVELOPMENT PROCESS

Development of the Second Edition of the Technology Catalogue began by revising information contained in the original 41 profiles featured in the First Edition and drafting profiles for 15 technologies selected by DOE Program Managers. The nine (9) profiles sponsored by WERC were developed by principal investigators, underwent an internal peer-review, and were submitted for inclusion in the Second Edition.

The methodology utilized to develop and update the technology profiles featured in the Second Edition is illustrated in Figure 2. As shown, information originated from several sources such as technical reports, the open literature, technical task plans, DOE databases, and other databases. Once sufficient information was gathered, it was reviewed for clarity, consistency, and quality. A technology profile was then drafted and underwent internal review, at which time information gaps were identified. Once information and data gaps were filled-in, the draft profile was revised. As a final quality-assurance check, profiles were submitted to PIs to review for technical accuracy. The profiles were then revised and submitted to DOE-HQ for review, approval, and subsequent publication and distribution.

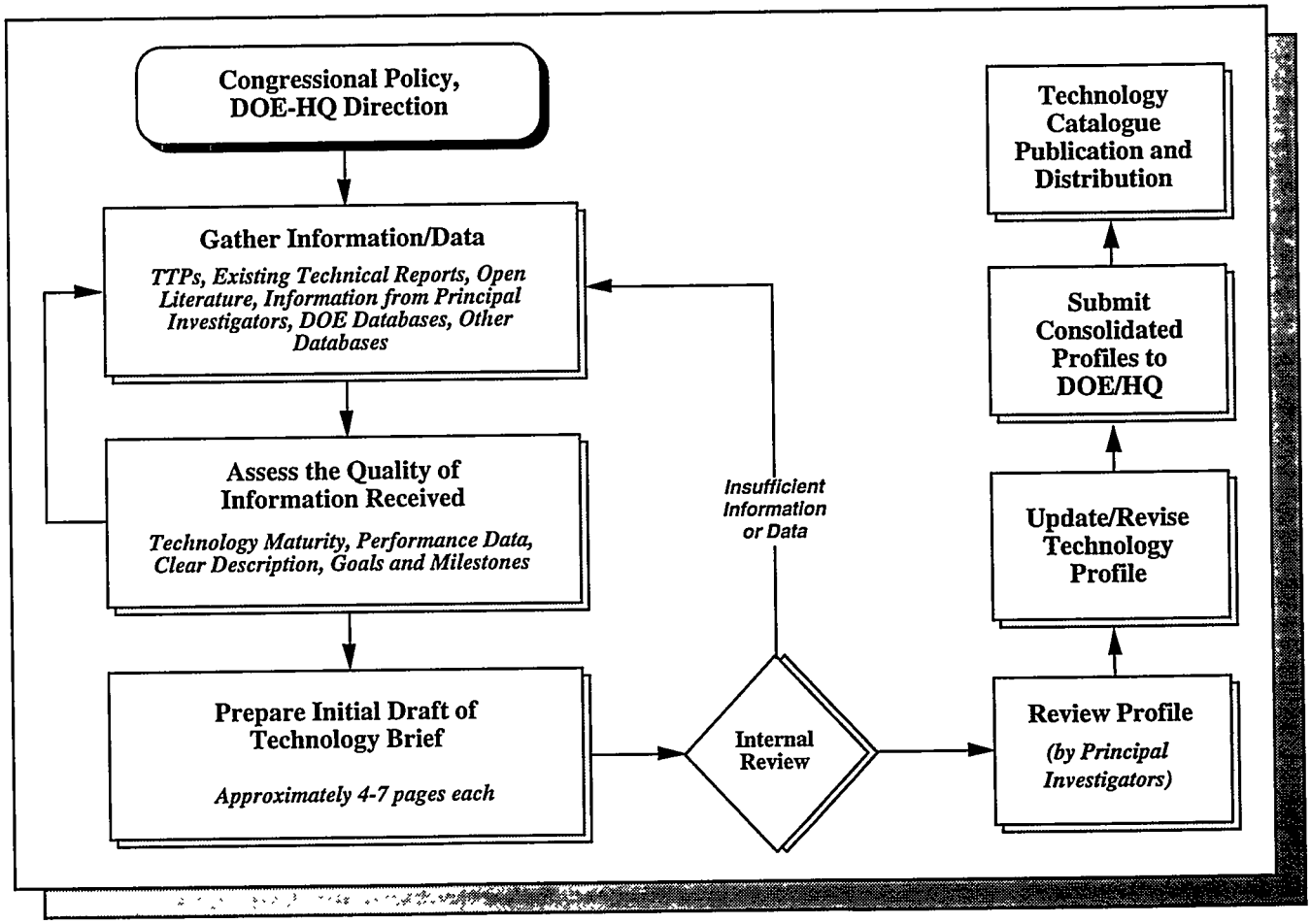


Figure 2. FY 1994 Technology Catalogue Development Process.

Waste Applicability Tables

Section 3.0

Table A. Site Characterization and Monitoring Technologies.

Technology	Description	Media	Speed	Applicable Wastes			Page No.
				Metals	Organics	Radionuclides	
Adaptive Sampling Program Support	Computer software that integrates, manages, and provides visualization of site data.	Soil, groundwater	PLUME™ analyses range from seconds to hours depending on analysis complexity. SitePlanner site creation depends on amount of data available.	Waste-independent.			23
Advanced In Situ Moisture Logging System	Measures moisture content and soil density around access tubing.	Arid soils, rock	Varies. Typically 15 min. per 100 ft. of tube.	Waste-independent.			27
Broadband Electromagnetics for Three Dimensional Site Characterization	Three-dimensional characterization of buried waste.	Soil	A survey requiring detailed coverage over 1/2 acre can be performed in one working day.	Waste-independent.			31
Colloidal Borescope	Direct observation of colloidal-sized particles and subsequent groundwater flow direction and rate.	Groundwater	30 min. to obtain a measurement.	Waste-independent.			35
Cone Penetrometer	A truck-mounted device that rapidly penetrates the ground to collect site data.	Soil	Pushes at a rate of 30-40 feet per half hour (except in mixed-waste environments).	Waste-independent.			41
Crosswell Seismic Imaging	Non-intrusive imaging of geology between boreholes.	Soil or rock	Data collection 1-3 wk. Interpretation 1-2 mo.	Waste-independent.			45
Electrical Resistance Tomography	Electrical currents are injected into the ground, and the potential distribution is measured.	Soil, rock, water	Approximately two hours to install electrodes in borehole. Data collection from 40 min. to 2 hr. Data processing 20 min. to several hours (depending on area of the measurement plane, etc.).	Waste-independent.			49

Table A. Site Characterization and Monitoring Technologies.

Technology	Description	Media	Speed	Applicable Wastes			Page No.
				Metals	Organics	Radionuclides	
Fiber-Optic Chemical Sensors	Optic fibers transmit probe signals to remotely located sensors to provide a real-time multipoint monitoring capability.	Groundwater, vadose zone, vapor extraction off-gases	Real time.	N/A	VOCs	N/A	55
Halosnif Fiber-Optic Spectrochemical Sensor	A real-time compound-class-specific sensor.	Air, gases	Real-time results.	N/A	Volatile chlorine-containing compounds TCE, PCE, CFCs	N/A	61
Hybrid Directional Boring and Horizontal Logging	Provides directional access in desired locations.	Wide range of geologies	Dependent on geology. Clays - 200 ft/d Alluvial fills - 100 ft/d.	Waste-independent.			65
In Situ Permeable Flow Sensor	Measures full three-dimensional flow velocity vector.	Saturated, permeable un-consolidated materials	Velocity measurements in 24-48 hr.	Waste-independent.			71
Integrated Geophysics Program	Integration of various geophysical techniques to characterize a site.	Soils, rock	Between 100-1000 samples per day and 1/4 -1 hectare (depending on sample intervals).	Waste-independent.			75
Integrated Spectroscopic System for Contaminant Speciation	Integrates four spectroscopic techniques to identify contaminants.	Soil, groundwater	Depends on level of characterization needed. Manpower and instrument-time limited, not sample-limited.	All toxic metals (e.g., Cr, Hg)	N/A	All radioactive metals (e.g., U, Pu)	79
Light Duty Utility Arm System for Remote Tank Access	Provides the capability to gather data on chemical and physical characteristics in under-ground storage tanks.	N/A	N/A	Underground storage tank wastes.			85

Table A. Site Characterization and Monitoring Technologies.

Technology	Description	Media	Speed	Applicable Wastes			Page No.
				Metals	Organics	Radionuclides	
Long Range Alpha Detector	High-voltage signal plane detects alpha particles.	Soil	10 -15 minutes for large monitor (shorter time for smaller monitor).	N/A	N/A	Alpha-emitting contaminants (not limited to U and Pu)	89
Magnetometer Towed Array	Magnetometers detect local disturbances in the earth's magnetic field. This indicates buried ferrous objects.	Soil	Can characterize more than 10 acres per day.	All metals	N/A	All metals	93
Microbial Monitoring	Monitors microbial population changes in soil and ground water samples.	Soil, ground-water bio-reactors	Analysis is complete in 2 days to 1 month (depending on the technique used).	Waste-independent.			97
On-Site Analysis of Metals in Soils Using Stripping Voltammetry	An in-field analytical method capable of measuring concentrations of selected trace metals.	Soils, Sediments	Total Cr analysis takes 8 minutes per sample. Other elements to be determined.	Al, Au, Ca, Cd, Co, Cr, Cu, Fe, Mo, Pb, Pd, Pt, Ni, Ru, Sn, Tc, Th, Ti, U, Va, Y, Zn	N/A	N/A	99
Portable Acoustic Wave Sensor	Monitors changes in the speed and power of a wave as it travels across the sensor.	Soil, vapor, water	Rapid (2 seconds) and continuous analysis possible.	N/A	VOCs, TCE, CCl_4	N/A	103
Prompt Fission Neutron Logging System	Provides a nearly continuous profile of contaminants as a function of position along a borehole.	Soil and rock surrounding a cased borehole	Approximately 3 hours are necessary to log and analyze a typical 100 ft. borehole.	N/A	N/A	Fissile materials, U-235, Pu-239	107
Rapid Geophysical Surveyor	Provides high-resolution geophysical data.	Soil	Can collect magnetic data at rates up to 25,000 data points per hour.	Ferrous contaminants	N/A	N/A	111

Table A. Site Characterization and Monitoring Technologies.

Technology	Description	Media	Speed	Applicable Wastes			Page No.
				Metals	Organics	Radionuclides	
Rapid Transuranic Monitoring Laboratory	Provides rapid in-field monitoring.	Soil, smears, fallout coupons, filters, air, liquids	Can analyze 100 samples per day.	N/A	N/A	Pu, Am, alpha emitters and entire gamma spectrum from X-rays to Co-60 and Cs-137	115
Remote Characterization System	Vehicle remotely delivers several geophysical sensors to a buried-waste site to obtain data.	Soil	Vehicle can travel 1 to 6 ft./sec.	Waste-independent.			121
ResonantSonic℠ Drilling	An advanced and improved drilling technology.	Vadose zone, groundwater	Drills holes at double the rate of a cable tool.	Waste-independent.			125
Seamist™ Borehole Instrumentation and Fluid Sampling System	Provides multiple vapor sampling/monitoring locations in a single borehole for unsaturated zone and air permeability measurements.	Soil, vapor	Up to 30 ft/min.	Waste-independent.			129
Slant Angle Sonic Drilling	A method of rapid access to the subsurface for installation of a sloped well using resonant drilling.	Soil, rock	Varies, depending on the type of formation. 1 ft./sec. to 0.5 ft/min. for loose to compact formations, respectively.	Waste-independent.			133
Unsaturated Flow Apparatus Centrifuge	Simulates migration of contaminants of subsurface environments of arid sites to obtain transport data.	Soil, vadose zone	Can achieve results in 3 days.	Waste-independent.			137
X-Ray Fluorescence Spectroscopy	Measures concentrations of heavy metals in soils.	Arid soils	Spectrum takes about 5 min. (depending on the contaminant of interest and device sensitivity requirements).	Heavy metals (e.g., Cr, Ni, Cu, Zn, Hg, Pb)	N/A	N/A	141

Table B. Site Remediation Technologies.

Technology	Description	Media	Applicable Wastes			Page No.
			Metals	Organics	Radionuclides	
Adsorption of BTEX Using Organozeolites	Adsorption of aromatic compounds.	Groundwater Surface water	N/A	Single-ring aromatics BTEX	N/A	147
Arc Melter Vitrification	Vitrification.	Soil	Toxic metals	Organics	N/A	151
Bio-Immobilization of Heavy Metals	Uses bacteria to transform heavy metal ions to an insoluble, less toxic form.	Groundwater Surface water aqueous streams	Toxic metals	N/A	N/A	155
Biological Destruction of Tank Waste	Biosorption.	Supernatants, aqueous streams	Toxic metals	Organics	Various radionuclides, TRU	159
Bioreactors for Bioremediation	Uses a bioreactor to biodegrade unwanted chlorinated chemicals.	Groundwater	N/A	TCE, PCE, Vinyl Chloride, DCE, TCA, and BTEX.		163
Bioremediation of High Explosives by Plants	Bioremediation.	Soil	N/A	Nitroaromatic compounds, TNT	N/A	169
Chelators for Application In Radioactive Actinide Waste Remediation	Selective removal of radioactive and highly toxic actinides with organic chelators.	Soil, Process waste streams	N/A	N/A	Pu	173
Compact Processing Units for Radioactive Waste Treatment	Biosorption.	Liquids, sludges, slurries	N/A	N/A	High-level, low-level, TRU	177
Cryogenic Retrieval of Buried Waste	Freezing/Retrieval Containment.	Soil, buried waste	N/A	N/A	TRU	181

Table B. Site Remediation Technologies.

Technology	Description	Media	Applicable Wastes			Page No.
			Metals	Organics	Radionuclides	
Decision Support System to Select Migration Barrier Cover Systems	Multi-objective decision making software system.	Arid and humid soils	Waste-independent.			185
Dry Barriers for Containment and Remediation at Waste Sites	Drying of horizontal soil layer to create a barrier.	Soil	N/A	VOCs, volatile solvents, petroleum fuels	N/A	191
Dynamic Under-ground Stripping of VOCs	Enhanced removal.	Soil, ground- water	N/A	VOCs	N/A	197
Electrokinetic Remediation of Heavy Metals and Radionuclides	Electrical current is supplied between two electrodes, ions of contaminant will be attracted to one of the electrodes.	Soil	Heavy Metals	N/A	Radionuclides	201
Encapsulation of Hazardous Wastes	Encapsulation of wastes.	Liquid, slurry, solid waste	Metals, inorganics	N/A	N/A	205
Engineered System for In Situ Bioremediation of Groundwater	Micro organisms biodegrade CCl_4 to harmless chemicals.	Groundwater	N/A	CCl_4	N/A	209
High-Energy Corona	Destruction of VOCs at room temperature.	Gas, aqueous liquids, non-aqueous liquids	N/A	VOCs, halogenated solvents (e.g., TCE, PCE, carbon tetrachloride, chloroform, diesel fuel, gasoline)	N/A	215
Hydraulic Impact End Effector	Fracturing of solid waste forms.	Hard waste forms in tanks	N/A	N/A	N/A	219

Table B. Site Remediation Technologies.

Technology	Description	Media	Applicable Wastes			Page No.
			Metals	Organics	Radionuclides	
In Situ Air Stripping of VOCs Using Horizontal Wells	Enhanced removal.	Permeable soils, groundwater	N/A	N/A	VOCs, light hydro-carbons, chlorinated solvents, TCE, PCE	223
In Situ Groundwater Remediation Using Colloid Technology	In situ colloid immobilization of contaminants.	Groundwater	Heavy metals absorbed on clay and silica	pesticides	Pu	227
In Situ Vitrification of Contaminated Soils	Destruction/immobilization.	Soil	Heavy metals	VOCs	Various radionuclides, TRU	231
In Well Vapor Stripping	Gas is bubbled through contaminated groundwater to liberate contaminants.	Groundwater	N/A	VOCs	N/A	235
Medium-Pressure Waterjet Dislodging and Conveyance End Effector Using Confined Sluicing	Confined sluicing.	Supernatant, sludge, saltcake in tanks	Waste-independent.			239
Methane Enhanced Bioremediation for the Destruction of Trichloroethylene Using Horizontal Wells	Co-metabolic destruction.	Soil, groundwater	N/A	N/A	Halogenated aliphatic organics, TCA, TCE, PCE	243
Migration Barrier Covers	Containment/treatment.	Arid soils	Soluble metals	VOCs, organics	N/A	247
Plasma Hearth Process	Waste form enhancement.	Soil, stored waste	N/A	Organics	N/A	255

Table B. Site Remediation Technologies.

Technology	Description	Media	Applicable Wastes			Page No.
			Metals	Organics	Radionuclides	
Polyethylene Encapsulation of Radionuclides and Heavy Metals	Encapsulation.	Aqueous salt and concentrate, saltcake, sludge, ash, ion exchange resin in tanks	Toxic metals (e.g., Cr, Pb, Cd)	N/A	Various radio-nuclides, TRU	259
Polymer Gel As A Barrier for Ground Spill Contaminants	Injection of a wall-forming fluid that gels in situ.	Soil	Applicable to many chemicals and radioactive contaminants (depending on the polymer barrier material selected).			263
Remediation of Metals Contaminated Soils Using Ligand-Based Extraction Technology	Density classification followed by extraction to remove metals from soil.	Soil	Pb, Hg, Cr	N/A	U	267
Remote Excavation System	Retrieval.	Soil	Waste-independent.			273
Resorcinol-Formaldehyde Ion Exchange Resin for Cesium Removal	Ion Exchange.	Cs supernate salt streams	N/A	N/A	Cs	277
Selective Extraction/Leaching of Uranium from Soil	Attrition scrubbing and carbonate leaching remove uranium from the soil.	Soil, sediment	N/A	N/A	U	281
Six-Phase Soil Heating	Extraction.	Soil	N/A	VOCs, SVOCs	N/A	285
Subsurface Barrier Emplacement Development	An impermeable grout barrier is placed beneath the waste to prevent further contamination.	Soil	Waste-independent			289

Table B. Site Remediation Technologies.

Technology	Description	Media	Applicable Wastes			Page No.
			Metals	Organics	Radionuclides	
Thermal Enhanced Vapor Extraction System	Extraction.	Arid soils	N/A	VOCs, SVOCs, VOC-oil mixtures, chemicals with vapor pressures <0.002 atm @ 20°C	N/A	295
Tunable Hybrid Plasma	Organic compounds are destroyed or oxidized with an electron beam.	Air	N/A	VOCs	N/A	299
VOC Off-Gas Membrane Separation	Membrane Separation.	Gas stream	N/A	VOCs, halogenated solvents carbon-tetrachloride, chloroform	N/A	303
VOC Recovery and Recycle	A Brayton cycle heat pump condenses an air stream and VOCs can be captured and re-used or disposed of.	Air	N/A	VOCs	N/A	305

Site Characterization and Monitoring Technology Profiles

Section 4.0

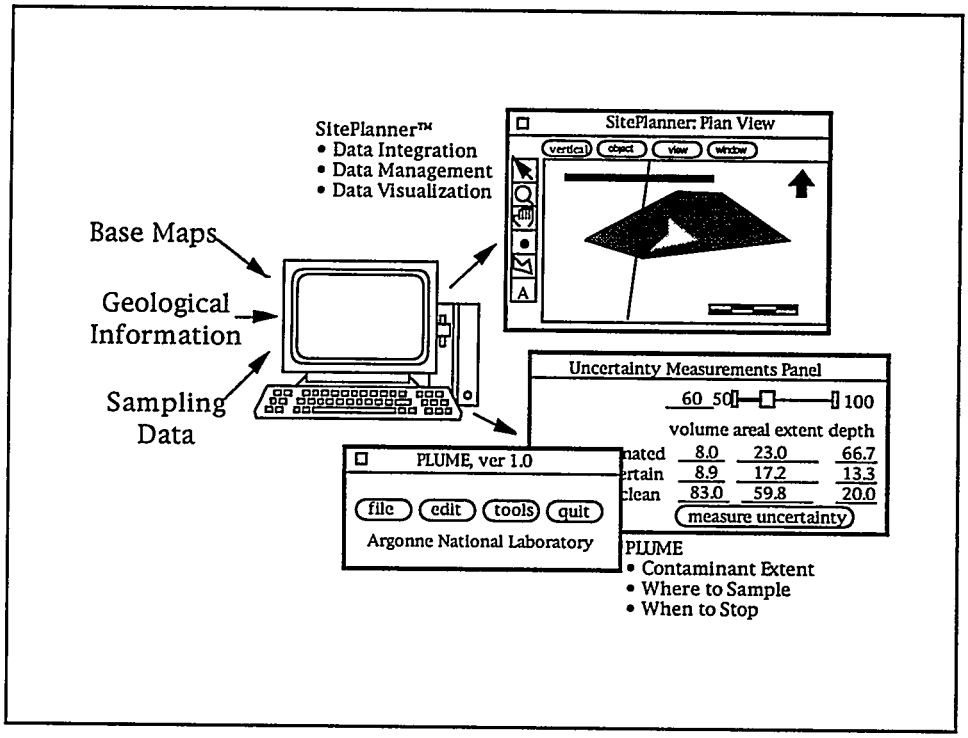
ADAPTIVE SAMPLING PROGRAM SUPPORT

Argonne National Laboratory

DESCRIPTION

Site characterization has traditionally been a very expensive process. Sampling programs to identify the presence and extent of contamination were built around pre-planned sampling grids and off-site analyses of samples. The result was an expensive and time-consuming process, with significant pressures to over-sample a site and frequent return site visits to clarify unexpected data. Recent advances in field-screening technologies that can provide "real time" results for a variety of contaminants allow for the application of adaptive sampling programs to site characterization. Adaptive sampling programs change to reflect information as it is generated in the field. Effective implementation of adaptive sampling programs requires a means for integrating, managing, and visualizing site data in the field, determining new sampling locations that provide the most information, and constructing estimates of contaminant extent based on available data.

Two technologies have been developed to address the particular demands of adaptive sampling programs. The first is called SitePlanner. SitePlanner provides qualitative support for adaptive sampling programs. SitePlanner is a graphical object-oriented database designed to support environmental site assessment work. SitePlanner organizes its data by object (such as monitoring wells, soil bores, landfills, etc.), not by table. Data objects are displayed visually as icons in a variety of graphics, including plan views, profile views, fence diagrams, and bore logs. All SitePlanner graphics are dynamically tied to the underlying data for a site and can be summoned interactively. SitePlanner is built around OpenWindows and is a completely mouse- and menu-driven package that is relatively easy to learn and use. In the context of adaptive sampling programs, SitePlanner provides a rapid and simple means of integrating, managing, and visualizing site data as they are being generated. SitePlanner provides field staff with the ability to understand their data as quickly and efficiently as possible.



Adaptive Sampling Programs

The second technology is called PLUME™. PLUME™ provides quantitative support for adaptive sampling pro-

grams. PLUME™ allows the integration of "soft" information regarding contaminant location with hard sampling data to form a conceptual image of contamination extent. Based on this conceptual image, PLUME™ uses a combination of Bayesian and spatial statistics to measure the potential impact of additional sampling points and to search for the next set of sampling points that contributes most to the contamination definition. PLUME™ includes statistical measures of contaminant extent, such as estimates of volumetric contamination and lateral extent. PLUME™ can be used to select new vertically and/or directionally drilled bores that would have the greatest impact on the uncertainty associated with contaminant extent. PLUME™ can estimate the value additional sampling data would have, allowing staff to weigh the benefits of collecting more samples with sampling and analysis costs. PLUME™ can be connected with SitePlanner, allowing the use of SitePlanner for data management, as well as the visualization of PLUME™ results.

TECHNICAL PERFORMANCE

Field Demonstration. SitePlanner and PLUME™ have been demonstrated at the unlined chromic acid pit and the "60s" pits within Sandia National Laboratories' Chemical Waste Landfill. In both cases, SitePlanner and PLUME™ were used to manage and analyze site characterization data for these sites and to make recommendations for further sampling. In a retrospective study of subsurface chromium concentration at the unlined chromic acid pit, characterization savings of more than 50% were observed for an adaptive sampling program versus the traditional characterization approach originally used at the site.

Costs. Commercial implementation of SitePlanner and PLUME™ for adaptive sampling program support requires computer hardware that currently costs approximately $7,000 and associated software that currently costs approximately $15,000. Computer hardware and software costs, however, have been falling dramatically.

WASTE APPLICABILITY

The adaptive sampling program approach embodied in SitePlanner and PLUME™ is designed specifically for characterizing the presence and extent of contamination in groundwater and surface and subsurface soils.

STATUS

Both SitePlanner and PLUME™ are presently commercially available products. Both are available on Sun Sparcstations with Sun OS 4.1.x and OpenWindows, on PC compatibles with SCO Unix. Minimum hardware requirements are 32 Mbytes of RAM, and 75 Mbytes of swap space. Microsoft Windows-based versions are currently under development.

REGULATORY CONSIDERATIONS

There are no regulatory considerations directly associated with this technology.

POTENTIAL COMMERCIAL APPLICATIONS

Recent advances in field-screening analytical techniques provide a growing array of field-screening technologies applicable to different types of contaminants and media. The availability of these technologies enables the application of adaptive sampling programs to the problem of identifying the

presence and extent of contamination at hazardous waste sites. SitePlanner and PLUME™ together provide a cost-effective approach to supporting adaptive sampling programs in the field. For SitePlanner, this includes field-level data integration, data management, and data visualization. For PLUME™, this means directing the progress of the sampling program and providing estimates of contaminated volumes. Cost savings are realized by reducing the cost per sample analyzed, the number of samples taken, and the number of trips to the field required to bring characterization activities to closure. Given the large number of federal and private installations awaiting site characterization activity, the overall potential for cost savings is enormous.

BASELINE TECHNOLOGY

The alternative to adaptive sampling programs is a standard, pre-planned sampling program approach. These types of programs are typically based on a set grid super-imposed over the area of concern. Samples are collected from the grid and sent to off-site laboratories for analysis. The time required for off-site sample analyses precludes the use of data within the sampling program. Data from these programs ultimately reside in centralized data archiving systems and/or standard geographical information system (GIS) packages. The results are pressures to oversample initially, frequent return visits to the field to clarify the unexpected sample values, and long lag times before data become available to program managers.

INTELLECTUAL PROPERTY

Patents:	None.
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ADVANCED IN SITU MOISTURE LOGGING SYSTEM

Sandia National Laboratories

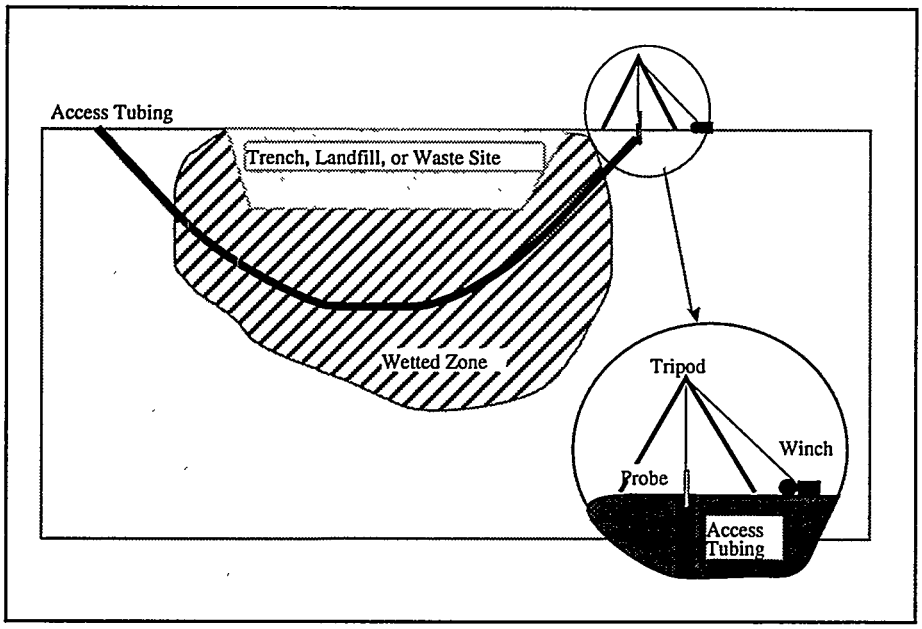
DESCRIPTION

The Advanced In Situ Moisture Logging System measures moisture content and soil density around access tubing within the soil/rock medium. These measurements determine the changes in fluid potential that, in turn, are indicative of leakage/contaminant movement from a waste site. The device is self-contained and programmable, making the application faster and easier, with longer access tubing capabilities than are available in conventional technology. The device provides an alternative for vadose-zone monitoring schemes, instead of costly monitor-well networks.

The conventional means of deploying such a probe is to lower a logging tool down an access tube to a depth of several meters or possibly tens of meters. The electronics to operate and process data from the probe are in a housing that sits at the top of the access casing. The cable used to lower the probe down the access tube serves to support the device and to provide electronic communications. The signal/noise ratio may be impaired with the increasing cable length. Therefore, a practical limitation on hole depth exists.

The new Troxler Probe, Model 4350, is self-contained. In other words, the electronics required to take a reading and to program subsequent readings of moisture content and soil density are contained within the housing of the device itself. The probe is drawn through an access tube via a support cable that requires no electronic communications to the top of the casing. Therefore, the length of the access tubing is not prohibitive, and long horizontal tubes may be used if a delivery system is properly engineered.

The proposed choice for a delivery system is to employ a constant-velocity winch or one that can be hooked up to a datalogger or laptop computer to record cable take-up rate and time and/or length. Two systems have recently become available: one from Mount Sopris Instrument Co., Inc., Golden, CO, and another winch system mounted in a trailer is available from Troxler Electronic Laboratory of Research Triangle Park, NC. Other devices exist to monitor in situ moisture content and soil density; however, they are general point source devices. The advantage of a downhole logging device is its continuous data collection along the length of the access tubing. Therefore, a greater spatial coverage is obtained.



Moisture Logging System

With the advent of the horizontal/directional drilling technologies, the applications of the downhole self-contained monitoring devices are significantly enhanced. One could envision a network of horizontally drilled access tubes beneath a facility that, coupled with the right monitoring technology, could provide an early-warning system for leak detection.

In addition, information from downhole logging devices is essential in evaluating the performance of such remedial alternatives as capping or soil venting strategies and serving as input to risk-assessment modeling methodologies. In deep vadose-zone regimes, this type of device/monitoring system may be used instead of expensive monitor-well installations.

TECHNICAL PERFORMANCE

In quantifying moisture content, the neutron source/detector in the Troxler 4350 consists of an americium/beryllium combination (10 mCi). The source and detector are in close proximity to each other, and the probe counts thermalized "slow" neutrons that have contacted hydrogen atoms. This technique is significantly different from those used in the mineral and oil industries, where the source and detector are widely spaced and the probe counts "fast" neutrons. This device's count ratio is generally linear with respect to percent moisture. Its configuration allows for quantification of the moisture content to within ± 2% volumetric water content when calibrated to a given soil and has an approximate radius of influence of about 30 cm. The mineral/oil industry probes integrate soil moisture over much larger volumes, with much less accuracy and precision. The gamma source for measuring soil density is an 8-mCi Cs-137 configuration.

The Troxler 4350 can be used in vertical as well as horizontal access tubes. Existing vertical and/or horizontal access tubes are necessary, but beyond that, the device is self-contained. Optimal velocities should be established for pulling the probe through an access tube with a constant-velocity winch. Guidance has been prepared on minimizing time while maximizing accuracy and precision in the logging process.

If the tool becomes stuck inside a hole, there are a number of options to dislodge it. If a surface-to-surface hole is being used, the tool may be dislodged by pulling it from either end. If that fails, the Ditchwitch technology may be employed to retrieve the tool. In the event that the Ditchwitch fails, the last resort would be to excavate the tool, assuming that there are not too many contaminants in the soil. The tool is typically about 30-40 ft below the surface.

The first trials found that the device needed to be more rugged for use in the field; however, subsequent testing showed it to work as intended. The tool is quite reliable and easy to use, but there is always a need for caution when using a device containing nuclear material. There are no user-serviceable parts, but the user can recalibrate the tool if needed.

Cost. The start-up costs are $30,000 for the Troxler 4350 probe and $16,000 for a Mount Sopris winch. Because of these high costs, Troxler Electronics Laboratories, Inc. will lease this tool. Troxler's winch trailer package can also be leased. The Mount Sopris winch is also leasable. No routine maintenance costs are expected.

PROJECTED PERFORMANCE

The major technical challenge to this technology is to define adequately the accuracy and precision of the method. Use of the Mount Sopris MGX winch system or the Troxler winch system is a great help in establishing reproducible results. Guidance has been prepared to aid users of this methodology in their applications to minimize time and maximize performance.

WASTE APPLICABILITY

Since this technology is specifically used to detect the change in fluid concentrations in arid soils attributed to leaks/contaminant migration from a waste site, the technology is waste-independent.

STATUS

The technology has been field demonstrated and tested. A completion report is being prepared. To date, there are no other logging tool manufacturers other than Troxler that have developed a similar tool.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and for the protection of occupational workers from electrical power, winch operation, and radiation exposure. In addition, permits may be required for drilling at hazardous-waste sites. Since the tool utilizes low-level radioactive materials, it must be stored in a shielded case with the proper security. Transportation of the device must meet Department of Transportation requirements for nuclear materials. Use of the tool outside DOE would require U.S. Nuclear Regulatory Commission licensing for nuclear materials. Troxler is aware of these requirements.

In addition, new guidance from the U.S. Environmental Protection Agency will make vadose-zone monitoring of new waste-disposal sites a requirement. This technology would meet the intent of that guidance.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be used at a wide variety of sites with several different remediation processes. It can be used at any site where monitoring of the vadose zone is needed to detect the potential for contaminant movement from waste sites. Such information is critical to the characterization of waste sites and the monitoring of waste remediation activities and post-closure performance of remediated waste sites. It offers an alternative vadose-zone monitoring scheme, instead of costly monitor-well networks.

BASELINE TECHNOLOGY

Since most cabled nuclear logging devices are not self-contained, they do not lend themselves to long horizontal access tube applications.

INTELLECTUAL PROPERTY

The patent owner is Troxler Electronics Laboratories, Inc., #5155356, "Apparatus and Method for Detecting Subterranean Leakage from a Large Storage Vessel."

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BROADBAND ELECTROMAGNETICS FOR THREE DIMENSIONAL SITE CHARACTERIZATION

RUST Geotech, Inc.

DESCRIPTION

Broadband Electromagnetic (BBEM) Induction is an advanced geophysical technique applied for three-dimensional characterization of a buried-waste site. BBEM uses measurements of a secondary magnetic field that is induced in the subsurface following the linear decay of a source magnetic field. Time-domain measurements are taken of the secondary magnetic field transient response at various time intervals over a broadband frequency range to locate, identify, and characterize buried-waste areas, buried-waste forms, buried-waste contaminants, underground utilities, and subsurface geology. This non-intrusive technique is a geophysical approach targeted at electrically conductive objects and media (such as metals, saline solutions, and subsurface geology). BBEM development has initially focused on the adaptation of existing hardware and software for shallow, high-resolution problems.

Another name for this measurement technique is Time Domain Electromagnetic (TDEM) Induction. A source signal is generated using an asymmetric two-coil induction system which has a large 5-m diameter transmitting loop. The BBEM system generates the equivalent of a three-decade frequency spectrum (40 Hz to 40 kHz). When the source current flow is interrupted, the current is allowed to decay at a linear ramp. Afterward, a secondary, transient magnetic field may be observed in the subsurface, and broadband (over a wide frequency range) measurements of frequency, amplitude, and time-domain signals can be detected. These measurements indicate the depth, the geologic features, and the apparent conductivity of buried conductors in the medium under excitation. The time-domain measurements are useful to delineate between the conductivity and penetration depth of a received signal. By using the system in various configurations (transverse, profile, or vertical electric expander), the BBEM system can be used to describe three-dimensional subsurface geometries. Collected numerical data are used to generate three-dimensional graphical descriptions of subsurface materials and buried waste.

TECHNICAL PERFORMANCE

Field Demonstration. The utility of this technique was demonstrated in 1992. BBEM has located vertical buried-waste pit boundaries within 1 m precision and pit depth extent within 2 m. BBEM will be useful to describe any waste environment where conductive targets are sought. A survey requiring detailed coverage over 1/2 acre can be performed in one working day. Only two people are required to take readings, to move coils, and to perform initial quality control readings in the field. It is estimated that approximately 5 h of maintenance is required to operate BBEM 50 h/wk. The electrical energy usage is minimal (less than 100 W). The presently available commercial systems may be purchased for approximately $75K. Other costs are associated with operator and geophysical analyst salaries.

PROJECTED PERFORMANCE

The major technical challenges to be addressed to improve the BBEM measurement system include: (1) selecting the best available hardware and software system for waste characterization; (2) developing field procedures to improve target definition; and (3) developing methods of analysis that optimize the interpretation capabilities of the operator/data interpreter. Another desired improvement is to develop data analysis methods to increase the definition of small conductors in a conductive host medium (i.e., component delineation and improved resolution).

WASTE APPLICABILITY

BBEM will be useful to describe any buried-waste environment where conductive targets are sought. Applicable wastes include electrically conductive objects, materials, geologic structures, and brine-liquid wastes. Examples include ferromagnetic buried material, metal objects, drums, and other containers with conductive contents (saline solutions and other high-ionic content liquids or solids) that may be buried in subsurface soils.

STATUS

The initial evaluation procedure was scheduled for completion on September 30, 1993. The components of the BBEM measurement system are currently available through commercial vendors, but 2 years will be required to complete the evaluation of the candidate hardware and software systems.

REGULATORY CONSIDERATIONS

The regulatory considerations are minimal. As BBEM represents a nonintrusive technique, the only input involves the momentary input of a transient electromagnetic field beneath the property surveyed. Nonintrusive BBEM surveys are totally benign and should be completely acceptable to the public.

POTENTIAL COMMERCIAL APPLICATIONS

Commercial applications include geotechnical mining applications and underground geological survey studies.

BASELINE TECHNOLOGY

BBEM is a superior method to measure earth conductivity because of its utilization and analysis of the full transient decay curve over a wide frequency range with one source and receiver. This provides, in effect, the equivalent of three frequency decades of information and, through a single station, scans a section of ground into the third dimension. An interpretation curve is firmly founded on 20 to 30 data points rather than the usual single point for each combination of frequency and coil separation associated with conventional, narrow-band, frequency-domain electromagnetic systems. Although BBEM is more sophisticated and gives a fuller, more accurate description of the subsurface, it also requires a greater investment for instrumentation and operator training.

INTELLECTUAL PROPERTY

Development of the TDEM method for applications in mineral exploration started in 1978 by Newmont Mining and CSIRO in Australia. It is not clear who owns the intellectual property rights.

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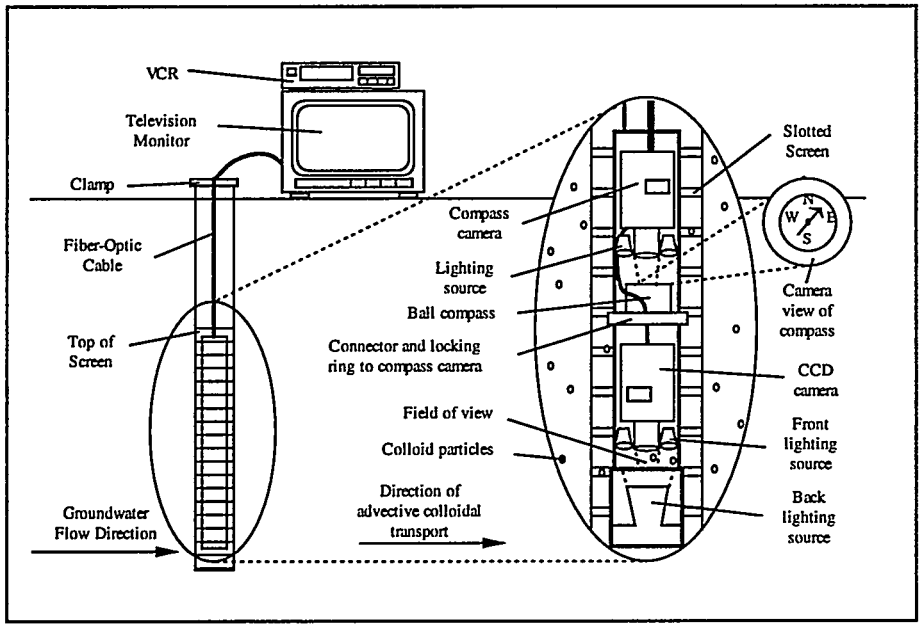
COLLOIDAL BORESCOPE

Oak Ridge National Laboratory

DESCRIPTION

The borescope is used as in situ instrumentation to directly observe colloidal-size particles and subsequent groundwater flow direction and rate. This instrument has demonstrated very important evidence that the traditional well-sampling methods are unnecessary and that micropurge sampling techniques are a possible replacement.



Cross-Section of a Borescope in a Well

The colloidal borescope is capable of determining the vertical and spatial distribution of local groundwater velocity, both in magnitude and in direction. The observational capabilities provide the potential for enhancing an understanding of porous flow at the most basic level. It is capable of measuring direction and velocities in low- and high-permeable material. The instrument could provide the basis for a stochastically based groundwater flow and transport model that more accurately describes the movements of contaminants in the subsurface. The instrument also provides the capability of observing flow processes at the pore scale. The instrument is capable of assessing local flow velocities ranging from 0-15 mm/s, which greatly exceeds even the fastest groundwater flow velocities in monitoring wells.

The borescope is inserted into a monitoring well and fixed at the surface with a clamp. The instrument consists of a charge-coupled device (CCD) camera, an optical magnification lens, an illumination source, a down-hole compass to assess direction of natural flow, and a water tight stainless steel housing. The instrument is approximately 60 cm long, with a diameter of 44 mm. The electronic image is transmitted to the surface by a 33-m fiber-optic cable. The image is viewed on a high-resolution, 25 cm monitor and recorded on VHS tape for further observation and analysis. The magnified image corresponds to a 1.0 x 0.4 x 0.1 mm field of view.

Current applications include:

- Site characterization by determining preferential flow paths and fractures;
- Assessing heterogeneities associated with porous media;

- Establishing the existence of immiscible contaminant layers and their associated flow properties;

- Assessing the efficiency of groundwater remediation programs by determining the effective radius of influence of groundwater extraction systems;

- Determining the amount of biological activity present in a bioremediation system; and

- Evaluating the effects of sampling on colloidal concentrations.

Potential applications include providing physical observation capabilities necessary to develop and confirm new, more accurate theoretical models of the porous-media flow process. It would also be useful for assessing the effects of water-sampling techniques on natural colloidal concentrations. The instrument could provide the basis for a stochastically based groundwater flow and transport mode, and it could also provide insight to heterogeneity, pore-size distribution, flow direction, effective radius of pumping, and pressure movement in aquifers.

TECHNICAL PERFORMANCE

Operation of the borescope is not complicated. The instrument is inserted into a well and the flow is observed on a surface video monitor. The instrument can be used in a well as small as 5-cm in diameter. A measurement is obtained in about 30 min. Local aquifer flow speeds up to 15 mm/s can be observed and assessed, which greatly exceeds the fastest groundwater flow. The stainless-steel construction allows for easy decontamination, and little maintenance is required. Integrity of the water-proof seals is checked periodically.

Studies with the colloidal borescope have revealed several very important issues related to groundwater sampling, including:

1) Water samples taken directly from the well screen (micropurge technique) are representative of groundwater in the surrounding formation; therefore, purging several well volumes prior to sample collection is unnecessary and wasteful.

2) There is a visually observable disruption and mobilization of colloidal particles when a sampling device is inserted into a well. Significant increases in particle sizes and numbers are observed during the insertion. The transient effects decrease with time and approach steady values in about 30 min. It is recommended that samples be collected using a dedicated sampling pump to prevent disturbing the well.

3) Observations with the colloidal borescope show that high sampling flow rates mobilize additional particles that are normally immobile under ambient conditions. Water sampling should be performed at low flow rates on the order of 100 ml/min to prevent additional colloidal mobilization and to prevent mixing with stagnant water in unscreened well volumes. Ambient groundwater flow is sufficient to supply water to the pump. The technique of micropurge sampling using dedicated pumps and low volume pumping (100 ml/min) was proposed by Kearl et al. (1992).

4) The borescope has observed mobile particles in the 1 to 10 mm size in several field sites. This result is significant since the traditional sampling practices use a 0.45-mm filter to remove larger particles with no consideration for their potential mobility. Sampling at low flow rates without filtering would give a representative quantification of the total "mobile" pollutant load. In other words, both the contamination that is moving in the dissolved phase and the

contamination that is sorbed to mobile particles can be appropriately measured based on the results and recommendations afforded by the colloidal borescope.

The use of micropurging is advocated by a certain equipment manufacturer (QED Inc.) and is being examined by the EPA (1993). There is a pausity of data demonstrating that analytical results are reliable for characterizing groundwater chemistry. Field testing was conducted at a site near Kansas City, Missouri, where comparative sampling was conducted using both micropurging and traditional techniques. Repetitive micropurge sampling and visual observations utilizing the colloidal borescope were preformed at a site near Paducah, Kentucky. Analysis of data using the nonparametric sign test indicates that within a statistical 95% confidence level, there was no significant difference between the two methods for the site contaminants and the majority of analytes. These analytical results were supported by visual observations with the colloidal borescope, which demonstrated impacts on the flow system (i.e., colloidal disturbance with instrument insertion, larger than filter-size colloidal particles observed in ambient groundwater flow, rapid-sampling flow rates disturb colloidal concentration) in the well when using traditional sampling methods. Under selected circumstances, the results suggest replacing traditional sampling with micropurging based on reliability, cost, and waste minimization.

Cost. The borescope is more cost-effective than conventional methodologies. The instrument presently costs approximately $20K, but costs should significantly decrease when production begins. The colloidal borescope provides a direct means of accurately determining groundwater flow direction and velocity in a more cost-effective manner than conventional methodologies. The borescope measurement technique uses existing monitoring wells for assessment and thus avoids the cost of additional well installation. (Conventional methods require about four wells to characterize aquifer flow.) Data are obtained in minutes, as opposed to the hours or days required to complete conventional groundwater flow measurements.

There are significant cost savings resulting from micropurge sampling compared to conventional well-purge sampling. Where there are a large number of wells and/or mixed waste is suspected, the costs associated with storing, testing, and disposing of purge water (from conventional well purge sampling) are considerable (e.g., $100,000/yr at ORNL). Shanklin et al. (1993) reported that micropurging would reduce annual sampling costs at a federal site by $115,000 by eliminating rinsate samples and decontamination of sampling equipment.

PROJECTED PERFORMANCE

Continued software development is necessary to address the variability of water flow, and additional work is currently under way to address the variability observed in well bores. The effects of subsurface magnetism on the compass is yet to be determined.

WASTE APPLICABILITY

Since this technology is specifically used for characterization and monitoring of aquifer flow and the aquifer matrix at problem sites, the technology is waste-independent.

STATUS

Prototypes are presently available. An advanced version with associated software is expected to be available in 1994.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous waste operations and protection of occupational workers from electrical power. Also, permits may be required for drilling at hazardous waste sites.

POTENTIAL COMMERCIAL APPLICATIONS

The Colloidal Borescope is potentially applicable for water-well installation and characterization, for municipal or community groundwater monitoring, and also applicable to mining industries which require the quantification of groundwater flow and aquifer characteristics. In addition, the Colloidal Borescope is applicable to any industry where information on colloidal size particles and subsequent groundwater flow velocity is necessary. The Colloidal Borescope can be used to determine preferential flow paths and fractures. It can also be used for assessing heterogeneities associated with porous media, establishing the existence of immiscible contaminated layers and their associated flow properties, assessing the efficiency of groundwater remediation programs by determining the effective radius of influence of groundwater extraction systems, determining the amount of biological activity present in a bioremediation system, and evaluating the effects of sampling on colloidal concentrations.

BASELINE TECHNOLOGY

The baseline technology is a standard technique used to measure hydraulic head gradients and hydraulic conductivities in boreholes to determine flow velocity. Four holes are required for a measurement using this standard technique as compared to using one hole with the Colloidal Borescope. With the standard technique, information about the hydraulic conductivity of the medium is required and is generally determined using a pump test in which large quantities of water are pumped from the well. Disposal of this purge water can be difficult and expensive.

INTELLECTUAL PROPERTY

The intellecual property rights are unknown or do not exist. Contact the principal investigator for further information.

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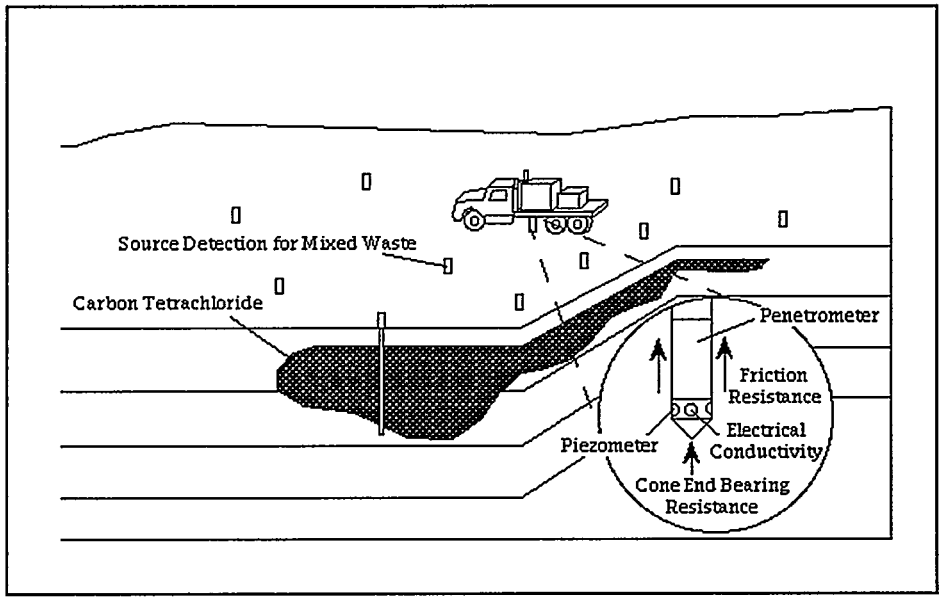
CONE PENETROMETER

Westinghouse Hanford Company

DESCRIPTION

The cone penetrometer is a truck-mounted device that rapidly penetrates the ground to collect site data. It has been used for approximately 50 years for geotechnical applications, but its use in environmental restoration is relatively new. The cone penetrometer rod has a conical tip of up to 2-in in diameter. It is pushed hydraulically into the ground with a maximum pressure of 64,000 lb. The hole generated by the cone penetrometer retains the outside diameter of the rod and can be grouted as the probe is withdrawn to seal the hole and prevent contamination of the groundwater. As the rod progresses into the ground, a computer reads data from sensors located in both the tip and the side of the probe (for soil characterization). The cone penetrometer can monitor for contaminants as the probe is advanced or can leave monitoring points in place as the rod is withdrawn. It can advance through coarse-grained soils at a rate of 40 to 50 ft/h. The cone penetrometer is used to install characterization and monitoring points and may be able to provide chemical and radiological readings from the subsurface. Successful development, demonstration, and deployment of the system as a source-detection tool will provide more cost-effective site characterization and remediation by reducing the number of drill holes required, minimizing secondary waste, and reducing potential worker exposure to contaminated materials.



Source Detection Screening Using Cone Penetrometer

TECHNICAL PERFORMANCE

The system requires a high level of understanding of soil and hydraulics. The cone penetrometer system functions well in a wide range of soils. It can advance through coarse-grained soil at a rate of 40 to 50 ft/h.

Demonstration. The CPT was tested at the Hanford site, Washington, from July 16 through August 6, 1992 to demonstrate the effectiveness of the CPT system in gravelly-cobblely materials while addressing the site's characterization needs. The CPT was successful in penetrating the Hanford soils. Depths ranged from 40 ft to 147 ft. Additional information acquired included measurement of radiation contamination and soil gas organic-vapor concentrations.

Cost. Start-up costs are $500K, Operations and Maintenance costs are $3000/day, and life-cycle depreciation is approximately 10 years.

PROJECTED PERFORMANCE

The cone penetrometer has been adapted for full use in the gravel/cobble subsurface common to arid sites. This required increasing the weight capacity of the truck, reinforcing tools associated with the penetrometer to withstand the additional force, and evaluating the use of vibration to facilitate penetration through gravel.

WASTE APPLICABILITY

The cone penetrometer is used to install characterization and monitoring probes and is waste-independent.

Standard Penetrometer Probe	
0-40,000 lb Tip Load Cell	AV
0-20,000 lb Sleeve Load Cell	AV
0-500 psi Pore Pressure Transducer	AV
Equal-End-Area Friction Sleeve	AV
Pore Pressures Sensed Behind Tip	AV
Pore Pressures Sensed on Surface of Tip	AV
Two-Axis Tilt Sensor (±15°)	AV
Calibrated Seismic Transducers in Triaxial Configuration	AV

AV = Available
PT = Prototype Tested
CD = Conceptual Design

STATUS

The status of several different cone penetrometer sensors is given in the tables below.

REGULATORY CONSIDERATIONS

Regulatory issues vary, depending on the type of waste to be characterized. In general, regulations concerning subsurface access characterization well drilling will apply. Ecological impacts are minimal.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is very applicable for any commercial environmental characterization need. Industries such as power, fuel storage and distribution, chemical,

Specialty Penetrometer Probe	
Electrical Resistivity	AV
Ground Penetrating Radar (10ft range)	PT
Active Hydrolic Conductivity	PT
Grouting Capability After Probe Withdrawal	AV
Gamma Radiation Detector	PT
Temperature Measurements	AV
In Situ Soil Density	CD
Self-Grouting	AV
Downhole Laser Induced Fluorescence	PT

refineries, and many others that may have soil or groundwater contamination could benefit by this rapid, extensive, and visually and economically attractive contamination site characterization technology.

BASELINE TECHNOLOGY

The baseline technology for site characterization is conventional drilling (auger or mud rotary) and laboratory characterization. The traditional approach lacks detail and precision, is slow in requiring laboratory analysis of contamination, risks cross-contamination, and is potentially hazardous (drilling in waste site). The CPT integrated technique for site characterization is faster, using less costly procedures; has minimum invasiveness, reduced cross-contamination risk; gives greater detail information, except in geophysical logging; and has field analytical ability and real-time data processing.

INTELLECTUAL PROPERTY

There is no patent on this technology, which has been used for the past 50 years for geotechnical applications.

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CROSSWELL SEISMIC IMAGING

Sandia National Laboratories

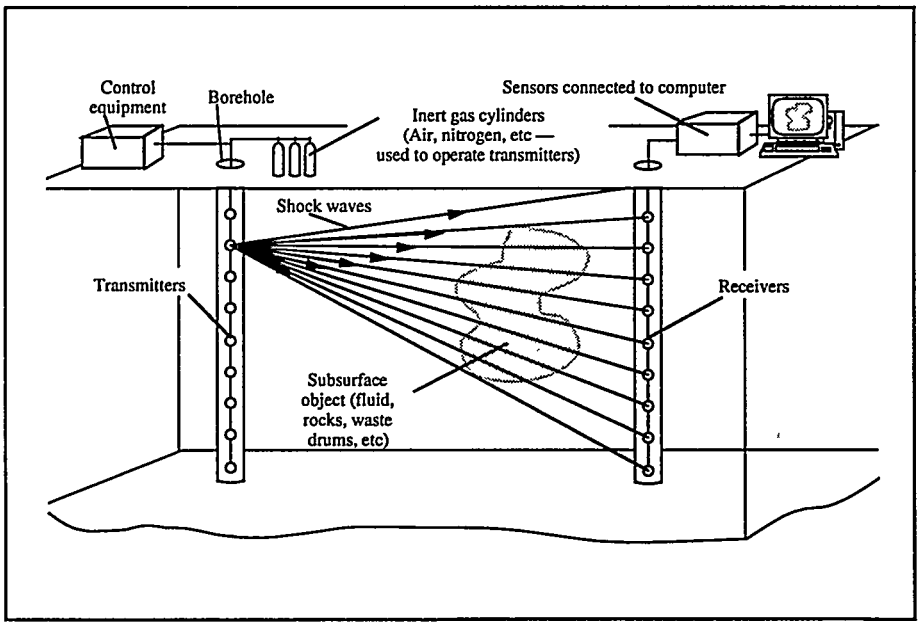
DESCRIPTION

For many remediation technologies, a good understanding of the subsurface geology must be obtained to understand contaminant transport and to best devise the proper remediation scheme. Much of this geologic input is presently derived from well log data, which may be scarce, especially in contaminated areas where drilling must be kept to a minimum. Seismic imaging provides a means to image the geology between boreholes nonintrusively.

Crosshole seismic imaging involves the fielding of a downhole source and a downhole receiver in two boreholes, one on each side of the region to be imaged. Seismic travel times are measured between a great number (>300) of source and receiver locations in the two boreholes. These travel times are then inverted into a map of the two-dimensional velocity structure through a method known as tomography. Some of this imaging can be done with surface seismics. However, placing both the source and receiver downhole results in shorter travel paths that preserve higher seismic frequencies and result in better resolution.

For remediation processes where the properties of the subsurface are changed, comparing seismic velocity images before and during the process can provide needed information on where the technology is being effective and to what degree changes are being implemented in the subsurface. The seismic sources used generate primarily shear or primarily compressional waves, depending on the source used. The shear-wave source is a controlled vibrator, while the compressional-wave source is an impulse source. Comparing the velocity structures for both the compressional and shear waves provides additional information about rock properties and fluid content.

The system is reliable and functions well with only general maintenance. Operation of sources requires training of personnel in both source operation and operation of winches for fielding tools. The seismic sources are pneumatic and require compressed gas (usually air, argon, or nitrogen) that is supplied from tanks at the surface. The only physical output will be the vented gas. Effects of failure are restricted to high-pressure hazards and are easily controlled. Components must be periodically pressure tested for continued integrity. Electrical power for running direct-current motors



Crosswell Seismic Imaging

and computer control and recording equipment is also required. Some additional site power may be required for winch operation and for appropriately sizing and casing the boreholes that are needed.

TECHNICAL PERFORMANCE

Field Demonstration. Field demonstrations have shown good correlation of imaged velocities with geology interpreted from well logs. Changes in saturation caused by injected air during an air sparging experiment have also been modeled. Resolution of the present system is approximately 1m in size and 5% in saturation variation.

The seismic method will not provide the spot resolution that well logging can. Also, some a priori knowledge of the geology is needed to interpret the velocity models in terms of geology. The expense of crosshole seismics is greater than surface seismics, although this may change as crosshole seismics become more routine.

Cost. Initial one-time expenditures for equipment needed to field the system include costs for sources and receiver, winches, tripods, PCs for source control, and the seismic recording system. Estimated cost for this full system is $400K. Much of this system may be available for rent or lease at a much lower cost. Field operations have been running on the order of 1 to 3 weeks (depending on survey size) for a three-man crew. Processing and interpretation presently take on the order of 1 month, but will probably decrease significantly as software is streamlined. Life-cycle costs should not exceed start-up and operations costs, except when additional wells need to be drilled. Data collection takes about 1 to 3 weeks, depending on survey requirements. The interpretation of the data takes about 1 to 2 months.

PROJECTED PERFORMANCE

The major technical challenges are: increasing the frequency and power output of the sources to increase resolution, improving imaging and inversion codes to handle such things as anisotropy, and decreasing the survey time through development of more rapid fielding sources and multistation receiver strings. Times for fielding and interpretation should decrease significantly as the method develops further.

WASTE APPLICABILITY

Since this technology is specifically used for characterization and monitoring of the ground media at problem sites, the technology is waste-independent.

STATUS

Although all sources are not commercially available at this time, steps are being taken to transfer the technology. There are several commercially available compressional-wave sources (such as the airgun) that are used primarily for oil and gas exploration, but can be readily modified for use in the environmental arena. No shear-wave sources are commercially available, though there is a poorer quality shear wave generated by the compressional-wave sources. The complete fielding system and interpretation software are currently available, though not commercially.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and protection of occupational

workers from electrical power, pressurized gas, and mechanical hazards associated with operating winches and working under overhead tripods. Personnel should be trained in operating pressurized systems. In addition, permits may be required for drilling at hazardous-waste sites.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be of use at a wide variety of sites and in conjunction with several different remediation processes. Seismic imaging can be used at any site where information on geology between boreholes is necessary. This is especially useful when the number of boreholes that can be drilled is restricted. It can also be used for monitoring any remediation technology that significantly changes the seismic properties of the subsurface such as air sparging, steam flooding, and water flooding.

BASELINE TECHNOLOGY

Although several companies are currently working on downhole seismic sources for oil and gas exploration, no one else is applying these techniques to environmental remediation sites.

For characterization, well logging and surface seismics offer alternatives. Drilling and logging require a large number of wells to be drilled to obtain a continuous picture of the subsurface. This makes this technology relatively more expensive and provides only isolated point information. Surface seismics are relatively limited in resolution. For monitoring imaging, only crosshole electromagnetic techniques being developed are a viable alternative.

INTELLECTUAL PROPERTY

The patent owners are DOE, Sandia National Laboratories, and Richard Hills. Patent Number: 504,317,171 "Advanced Downhole Periodic Seismic Generator."

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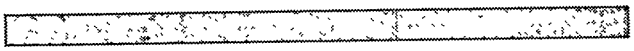

ELECTRICAL RESISTANCE TOMOGRAPHY

Lawrence Livermore National Laboratory

DESCRIPTION

Electrical Resistance Tomography (ERT) is used to create 2-D or 3-D visualizations of in situ remediation processes such as air stripping, bio-remediation, and subsurface heating. There are no alternative methods currently available to image the fluid saturation distributions in true two-dimensional and three-dimensional cross-sections of the subsurface.

ERT is done by injecting electrical currents into the ground and measuring the potential distribution that results from these currents flowing in the conductive subsurface. For the work reported here, arrays of electrodes were buried in two boreholes, with some pairs acting as current-source electric dipoles and other pairs acting as potential-measuring dipoles (Fig. 1). Several boreholes can also be used to produce a 3-D subsurface image.

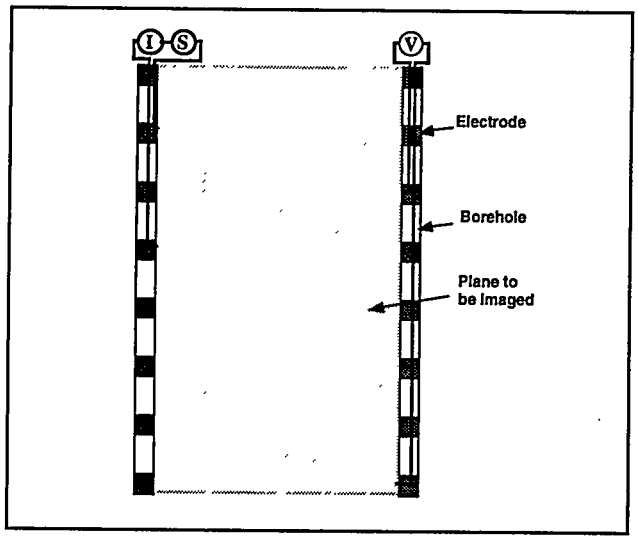

Figure 1. Schematic diagram showing the data collection approach for ERT measurements, where: I = source current, S = signal source, and V = voltage.

The series of electrodes in each borehole is grouted in place to give quality electrical contact with the formation. Current is driven through the formation from an electrode pair, and the potential difference is measured between other electrode pairs (termed an electrode dipole) in the electrode array. The procedure is repeated for many combinations of source and receiver electrode dipoles. The data collection process can be automated since there are no probes to move within the boreholes (in contrast to other logging techniques).

Calculating the distribution of resistivity in the vicinity of the boreholes based on the measured transfer resistances is a highly nonlinear problem. The nonlinearity results because the current paths are dependent on the resistivity distribution. The ERT inversion process involves solving both the forward and inverse problems. The solution to the forward problem uses the finite element method (FEM) to compute the potential electrical response in the soil due to the current source. The reverse problem is solved by a transfer resistivity data inversion routine to approximate the current path. The final products of the process are images (tomographs) showing the distribution of resistivity in the plane between the two boreholes used. By interconnecting a network of boreholes, a three dimensional representation of the area being investigated can be developed. By analyzing the resistivity images before, during, and after a remediation process, useful 3-D subsurface images (e.g., as of saturation images) can be inferred.

The inputs for this technology are switched-polarity, D.C. electric currents that are injected into the formation to measure electrical resistivity. Voltage used depends primarily on the electrical properties of the formation. The voltage used may be as low as 24 V or as high as 200 V. The outputs of the data collection process are measurements of resistance. The outputs

of the data inversion process are images (tomographs) showing the distribution of resistivity in the plane between the two boreholes used.

The data acquisition rate is sufficiently rapid to allow detailed sampling of large subsurface regions in reasonable amounts of time; for example, at the Savannah River Project one cross borehole data set could be obtained in approximately one hour. ERT is advanced enough to monitor remedial process in almost real-time; at present the tomograph images are available for inspection a few hours after the data are collected. Sensors are cheap and robust—pieces of stainless steel buried in the ground to depths of hundreds of feet; sensors can be placed in boreholes (alternatively they can be pushed into the ground, thereby reducing the need for drilling) and/or at the ground surface. True 3-dimensional imaging is possible—not just a series of 2-D planes.

ERT was originally developed for medical diagnostics during the 1980s; this new technique is just a few years old as a geophysical technique. Even though ERT is a young technology and it is yet in the research and development phase, it is being used by the LLNL in a number of applications. ERT is a unique cross-cutting technology that can be used for a wide range of applications. Currently, there are four or five companies and universities around the world involved in this type of research.

TECHNICAL PERFORMANCE

General. The data acquisition system is computer-controlled and can be operated by personnel with minimal training. Operation requires a technician to interact with the data collection system on a periodic basis to start the automatic program that performs data collection and to connect electrodes in other boreholes to the acquisition systems. Further development of the data collection system will allow unattended data collection and unattended connect/disconnect of electrodes in other boreholes. The data inversion algorithms need to be operated by professionals (such as engineers and physicists) proficient in the use of complex mathematical algorithms. The electrodes used are generally permanently grouted within the boreholes. These stainless-steel electrodes and attached wires can be left in the ground without harm to the environment. If electrodes are placed in radioactive soil or along a contaminated ground surface, they may need to be decontaminated upon removal.

Field Demonstrations. Several field demonstrations of the technology show that the ERT tomographs effectively map the subsurface structures and processes relevant to environmental restoration. This technology has been demonstrated at the Dynamic Underground Stripping Project at LLNL during FY91-92 (see profile on Dynamic Underground Stripping). The objective was to evaluate the capabilities of the technology to map the penetration of the steam flood as a function of space and time. Measurements were made over a 4-week period (before and during steam injection). Twelve vertical planes were monitored during the course of the test. Data from nine planes are considered reliable; three of the planes yielded unreliable data which resulted in tomographs which are very different from all others obtained at the site and do not match lithologic columns or induction-well logs obtained in the same wells. These results were probably caused by loss of insulation on the wires connecting these electrodes to the ground surface.

The ERT was also used at LLNL to monitor and evaluate subsurface-heating technologies such as the six-phase electrical heating and the in-situ radio-frequency heating technology.

The ERT was used to monitor a radio-frequency heating process used for the in situ remediation of volatile organic compounds from subsurface water and soil at the Savannah River Site near Aiken, SC. A dipole antenna located in a horizontal well in the unsaturated zone was used to heat a contaminated

clay layer. The heat-induced changes were tomographically imaged by their effects on the formation's electrical resistivity.

Cost. The hardware costs for data acquisition are approximately $50K. The cost for an engineering workstation to perform data inversions ranges between $10K and $20K. The cost of licensing the data inversion algorithm is negotiated by the DOE and the interested party. The life-cycle costs will depend on several factors, including the application of interest, frequency of use, the degree of resolution desired, and the flexibility to install electrodes in boreholes used for other types of measurements.

ERT tomographs used in conjunction with core samples information and well logging can be used to spatially extend borehole information much beyond the local area around the boreholes. When used in this manner, ERT can result in a net reduction in borehole drilling costs of at least 50%. This estimate accounts for costs of obtaining and collecting ERT data. The analysis conservatively assumes that the unprecedented level of detail offered by ERT could be obtained from the conventional technology by drilling a few additional coreholes and interpolating/ extrapolating the information beyond the borehole walls.

Time. It takes approximately two hours to install electrodes in each borehole. Data collection times generally range between 40 minutes and two hours per measurement plane; this time depends on the number of electrodes installed in each borehole. Data-processing times range generally from 20 minutes to several hours on a modern engineering work station; this time depends on several factors, including the area of the measurement plane being sampled, the number of measurements collected, and the presence of data noise.

PROJECTED PERFORMANCE

It is projected that the 3-D algorithm will be successfully demonstrated by FY96.

WASTE APPLICABILITY

ERT can be used to monitor the subsurface progress of subsurface environmental clean-up processes (e.g., air injection, steam injection, water flush, and radio-frequency and low-frequency heating) so that the processes can be adjusted and optimized in almost real time. ERT can also be used to map the movement of liquids in the subsurface so that it can verify the emplacement and performance of surface and subsurface barriers such as grout curtains. It can also be used to detect leakage from holding tanks and liquid-waste ponds.

STATUS

The technology is near full development. The 2-1/2 D inversion algorithm was tested in several field demonstrations and is available for licensing. A prototype 3-D data inversion algorithm is available but is under evaluation. Complete development will require three years at full funding to field demonstrate the 3-D algorithm and to demonstrate capacity to detect leaks under leaking structures with the 2 1/ 2 D algorithm.

REGULATORY CONSIDERATIONS

Currently EPA has no system-certifying sensor technology for site characterization or monitoring. Potential worker health and safety hazards are associated with electrical, physical, and chemical hazards of

electrode installation. A potential exists for worker exposure to contaminant venting from the well head during electrode emplacement.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications could include subsurface geologic mapping for mining and petroleum industries. It is also commercially applicable for the environmental applications discussed previously, such as monitoring soil heating, soil moisture during steam or gas injection/vacuum extraction, and aquifer perturbations during remediation activities. The technology is also applicable to the medical industry for tomographical imaging for various diagnostic techniques. It can also be used for non-destructive evaluation of large-scale structures such as dams.

BASELINE TECHNOLOGY

This imaging technique minimizes the need for drilling monitoring wells while providing unprecedented detail of subsurface structures and processes. The baseline logging technology is line measurement of fluid saturation along boreholes performed by using a number of well established geophysical well-logging techniques (e.g., neutron and resistivity logs); on the other hand, at least twice the number of boreholes at a closer spacing would be required to be able to observe the same level of detail. ERT directly measures a formation's electrical properties between boreholes using mathematical data reduction techniques. Therefore, the tomographical method produces true 2-D and 3-D images, but the conventional method of geophysical well logging requires that the measured values be interpolated between the boreholes. The ERT technology is ideally suited for field operations requiring minimal field personnel because once the electrodes are installed, the data collection system can be designed to run automatically with minimal personnel intervention. In contrast, conventional well logging requires field personnel intervention since a physical probe must be moved vertically within a borehole for those techniques.

A limitation of the technology is that ERT requires the use of complex data inversion algorithms that need to be operated by highly-trained professionals. Data inversions require the use of fast engineering workstations, whereas workstations are generally not needed to analyze well-logging data. Data collection times are longer than for the baseline technology (well logging) because more data are required. Finally, the results are relatively more sensitive to the presence of data noise than the baseline technology. Major challenges include: 1) the development of fully three-dimensional data inversion algorithms; and 2) minimizing or eliminating image artifacts that develop due to sensitivity and resolution gradients within the image plane.

INTELLECTUAL PROPERTY

Several disclosures have been submitted on various applications of this technology. No patents have been awarded at this time. LLNL is currently negotiating a Cooperative Research and Development Agreement with a geophysical services company. Several other companies are negotiating with LLNL to obtain rights to use the technology and to cooperate in further development.

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FIBER-OPTIC CHEMICAL SENSORS

Lawrence Livermore National Laboratory

DESCRIPTION

Current U. S. Department of Energy policy requires characterization of sites where trichloroethylene (TCE), carbon tetrachloride (CCl_4), and other species have been discharged into the soil and groundwater. Currently, contaminated samples are collected and analyzed by an outside laboratory. This is an expensive and time-consuming process. An alternative is to use a fiber-optic chemical sensor that can be put down an existing monitoring well or punched into the soil using a penetrometer-type device. Accordingly, measurements can be made continuously and at a relatively low cost.

Generally, the chemical species of interest in environmental analysis do not absorb visible light or produce fluorescent emissions even when the contaminants are highly concentrated. Therefore, detecting analytes at the relatively low concentrations (e.g., ppm levels) that exist in many contaminated environments requires an indirect method. In this regard, there are three phenomena useful to chemical sensing with fiber-optics which may be appropriate in various contaminant-detection applications. These include the following :

- Incident monochromatic light producing Raman or fluorescent scattering (i.e., direct spectroscopy).
- Chemical-reaction-inhibited light transmission. Reaction between trace contaminant and optrode dye reagent induces wavelength-dependent light absorption.
- Chemical-reaction-modulated fluorescence. Reaction between trace contaminant and organic fluorescing dye modulates the fluorescence properties of the dye.

It is the last two phenomena which will be discussed in this profile. An optical device is being developed which incorporates fused quartz optical fibers as a wave guide to conduct light to and from a downhole probe. A chemical reagent in the fiber-optic tip of the optrode reacts with trace chemical contaminants to effect a change in the light transmissibility or fluorescing properties of the fluid in the optrode. The chemical reagent in the probe is an "organic transducer" since its photophysical properties change with contaminant concentration, thereby enabling detection. The chemical fluorescence probe will be slightly different than the light transmission probe due to the different types of organic transducers. In fact, the specificity of the probes is a function of the reagent used. For example, the light transmission optrode uses a pyridine reagent to detect TCE, but the chemical fluorescence optrode uses different organic fluorescing dyes to detect CCl_4. Each type of probe could be inserted into existing monitoring wells or pushed into the ground with a penetrometer device.

The light transmission optrode is being developed by the Lawrence Livermore National Laboratory (Fred Milanovich, Principal Investigator) with cooperation from the University of California which has a patent pending. The target application is TCE detection. The light transmission optrode is being demonstrated in two different configurations at the Savannah River Site in Aiken, SC.

This device works by absorbing a small amount of TCE-contaminated vapor into the optrode tip where it reacts quantitatively with the pyradine reagent (see Figure 1). The principle of detection is that fluid in the optrode (chemical reagent) becomes increasingly red (absorbs light) when reacted with specific chlorinated compounds. The pyradine reagent is specific to detection of trichloroethylene (TCE), chloroform, bromoform, bromodichloromethane and

chlorodibromoethane. The unknown concentration level of these compounds can be measured because absorption of light relative to the reaction time is directly proportional to contaminant concentration.

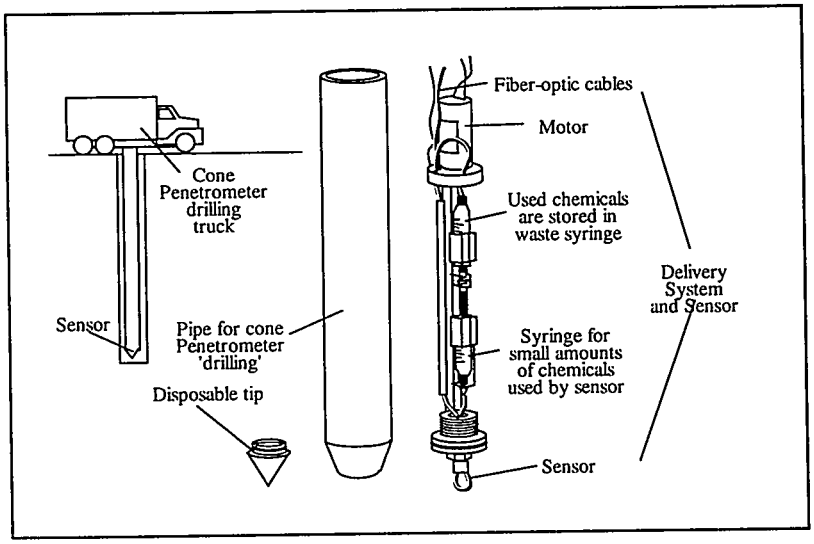

Figure 1. Light Transmission Optrode

This light-absorbing sensor has demonstrated dramatically improved performances over previously reported fluorescence-based sensors (light-producing chemical reaction). The input of the device is a small amount of sampled contaminated vapor, and the physical output involves a small amount of contaminated pyridine reagent (<50 ml/measurement). Vapor can be sampled from groundwater or unsaturated soils zones, but groundwater monitoring requires groundwater isolation in a headspace. The sensitivity of groundwater analysis is related to the Henry's law constant for equilibrium vapor concentrations. Sensitivity to 5 ppb has been demonstrated for vapor-phase TCE and chloroform detection.

The ***chemical reaction-fluorescence optrode*** is being developed at LLNL (Kevin C. Langry, Principal Investigator) to be demonstrated at the Hanford Site in Richland, WA. A license to use the technology has been extended to Purus, Inc. The target contaminant is carbon tetrachloride, but this technology would also be applicable to other contaminants. Similar to the light transmission optrode, the reaction fluorescence optrode uses a chemical reagent to induce a change in the photophysical characteristics of an organic dye (see Figure 2). Whereas the light transmission optrode utilizes reaction induced photo-attenuation, the fluorescence optrode utilizes a reaction between the contaminant (e.g., CCl_4) and the organic dye to cause a change in the fluorescence properties of the organic dye. In this way, the dye may be considered to be an organic transducer which modulates the source light beam with a combination of wavelength-dependent optical attenuation and the production of fluorescence emission in the regions of the optical spectrum that are distinct from the probe's frequency. In this case, the organic-dye molecules react reversibly and specifically with the chemical-contaminant species of interest. The physical-chemical reaction between the analyte (contaminant) and the organic transducer dye produces a

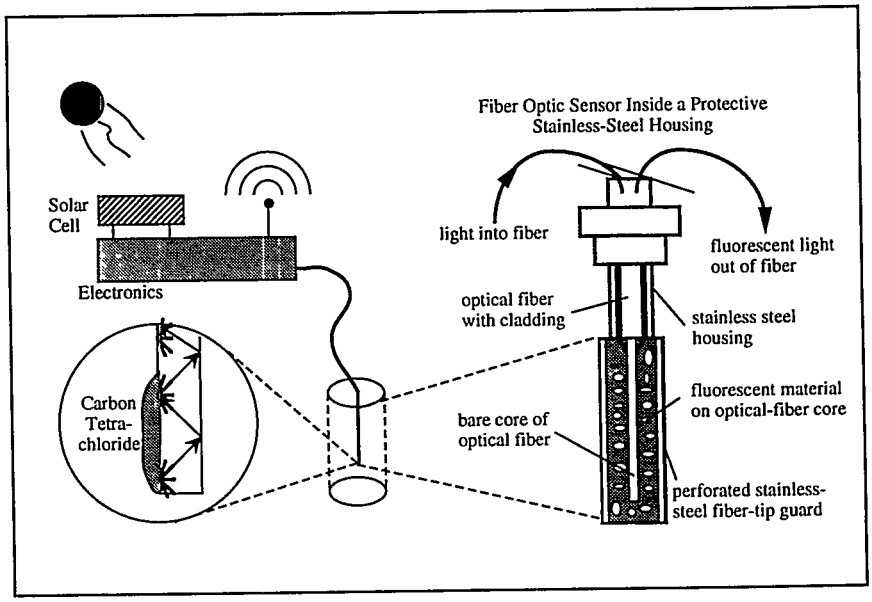

Figure 2. Reversible Fiber-Optic CCl_4 Sensor

change in the photophysical characteristics of the dye that modulates the probe beam. The magnitude of the optical response is correlated to the concentration of the analyte. When the nature of the analyte-dye interaction is known, specific dye molecules can be selected to detect a narrow range of chemical species.

The configuration of both types of sensors is essentially the same and is not complicated. It requires a simple light source (a light bulb or light-emitting diode), a photodetector (silicon photodiode), and simple optics (lens, filter, and mirrors) to focus and guide light into and out of the fiber-optic conduit. The same fiber can be used to transmit the probe beam to the sensor, as well as to carry the modulated signal back to the detector. Consequently, at the proximal end of the fiber is a small calculator-size box of optics and electronics that contains both the light source and the signal-detection equipment. The electronics box is configured to a small central processing unit (CPU) or a lap-top computer that collects and analyzes the sensor signals and provides useful information on the analyte concentration. At the distal and working end of the fiber is the sensor, normally encased in a protective metal shield to prevent damage.

TECHNICAL PERFORMANCE

General. Technologies using chemical fiber-optic sensors have been in existence for over 10 years. The foundations for developing the TCE (light transmission) optrode originated 3-4 years ago at LLNL. The light transmission optrode is unique in that the chemistry remains in solvent form rather than being bound in a matrix. The sensor can thus be used continuously despite the irreversible nature of the chemical reaction. The chemical fluorescent optrode has a chemical fluorescence dye inside the optrode, and the reaction is reversible. Specifications of the light transmission chemical sensors are shown in Table 1.

Field Tests. Field-test and demonstration results are available in the literature.[2-5] The sensor's detection limit for TCE is about 150 ppb (v/v) in vapor and 5 ppb (w/w) in groundwater. The level of detection of this sensor is within OSHA permissible-exposure limits. Less than one hour is required to emplace a probe using a cone penetrometer. The probe has been placed to a depth of over 100 ft. in under one hour using a cone penetrometer. For use in a vadose zone well, the implementation is even faster.

Table 2 contains a list of field tests and descriptions of the tests or developmental accomplishments.

Table1. Specifications for Chemical Sensors.

Aspect	Specification
Medium	vapor phase VOC's
Range	5-1000 ppb Low Range Reagent 1-100 ppm High Range Reagent
Sensitivity	5 ppb
Contaminants	TCE, chloroform, other chlorinated hydrocarbons
Sampling frequency	Three minutes per measurement
Repeatability	±5%
Accuracy	±10% (Compared to Gas Chromatograph / ECD)
Calibration	Recommended once per week
Reagent Usage	20 microliters/sample
Power required	110 V, 5 amps

Cost. The start-up cost for this monitoring system is $10K. Operation should require less than one hr/wk with minimal maintenance necessary to replenish the reagent every several months. The life-cycle cost depends largely on the frequency with which measurements are made. The individual sensors will be comparatively inexpensive and should cost less than $100. The costs associated with fiber-optic sensors will depend on the protocols and application for which the technology will be used. The life-cycle costs are estimated at $25K/yr (5 yr) and $1.25K/yr (10 yr).

PROJECTED PERFORMANCE

Future developments include developing alternative reagents specific to other VOCs and developing a downhole device for isolating head space in groundwater applications. As yet, direct measurement of VOCs dissolved in water has not been accomplished, and all measurements have been made in the vapor phase above contaminated aqueous solutions. (Therefore, sensitivity to measurement in aqueous solutions is dependent on the Henry's law constant for vapor/aqueous equilibrium as well as the measurement sensitivity in the vapor phase.) However, the issue of direct measurement of VOCs in water will be addressed in future development.

WASTE APPLICABILITY

The fiber-optic chemical sensors are generally applicable to volatile organic chemicals (VOCs) in soil and groundwater. Application to groundwater sensing is indirect by measuring the vapor phase above the contaminated aqueous phase. A pyridine reagent has been developed for the light transmission optrode which is applicable for selective TCE detection. The pyridine is also applicable to a narrow range of compounds including chloroform, bromoform, chlorodibromoethane, and bromodichloromethane. The reaction fluorescence sensors are applicable to carbon tetrachloride, toluene, xylene, and similar compounds in unsaturated soils.

The initial sensors are not intended to be general analytical instruments. Rather, the initial products are designed to be used as real-time continuous monitors during site screening or remediation. Other uses are long-term well monitoring, industrial processing, or laboratory screening. The sensor also can be used in conjunction with remediation technologies either in situ in the soil column or above ground as a process-tracking aid.

Table 2. Field Test Information

Test Date	Location	Description
Sept. '91	Westinghouse, SRS, Aiken, SC.	Measurement of TCE in a soil-vapor well.
Mar. '92	Westinghouse, SRS, Aiken, SC.	Measurement of TCE in a soil-vapor well and two groundwater wells.
April '92	Westinghouse, SRS, Aiken, SC.	Penetrometer placement of TCE sensor.
April '92	LLNL Site 300, Livermore, CA.	Measurement of TCE in conjunction with an above-ground soil-gas treatment process.
Aug. '92	Ft. Lewis, WA.	Measurement of TCE in three groundwater wells.
April '93	Westinghouse, SRS, Aiken, SC.	Delivery of complete stand-alone monitoring system for long-term evaluation.
Oct. '93	LLNL Site 300, Livermore, CA.	Measurement of TCE in a groundwater well using Burge Instrument Company-developed in situ water sampler and head-space sensor.

STATUS

Above-ground and penetrometer application is available now. The light-transmission chemical sensor technology is fully developed and ready for commercialization. A fully operational in situ device for long-term monitoring of vadose zone wells was transferred to the SRS in FY93. Packaging and software for long-term monitoring was made available in June 1993. The reaction-fluorescence optrode is also currently available.

REGULATORY CONSIDERATIONS

Interconnection to an aquifer could occur during probe placement, leading to environmental impact (i.e., if a penetrometer is used for probe insertion, the borehole that is produced could provide access for contamination to spread vertically from the aquifer). The detection level of the sensor is compatible with regulatory cleanup milestones. Currently, EPA has no system for certifying sensor technology for site characterization.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include cost effective site characterization and monitoring for any industry which may have TCE, CCl_4, or other applicable contamination (other VOCs are detectable with further reagent development). LLNL has reached agreement with Burge Instrument Company and Purus, Inc. for the commercialization of the light transmission-based chemical-sensor technology. Plans are underway by both companies to introduce commercially available environmental-monitoring instrumentation for the detection of chlorinated hydrocarbons using the fiber-optic sensor.

BASELINE TECHNOLOGY

The baseline technology is purge and trap gas chromatography of grab samples. In contrast, this fiber-optic chemical sensor technology allows trace quantities of TCE (for example) to be measured on a continuous in situ basis. The sensor can be automated to provide a database of fluctuating contaminant concentration over time to aid in ongoing remediation efforts. It is as selective and sensitive as GC (the baseline, gas chromatography) and is faster and cheaper. The TCE optrode (light transmission measurement) does not provide as much information as GC in situations where multiple volatile organic compounds are present.

INTELLECTUAL PROPERTY

The University of California has a patent pending for the light-transmission optrode for TCE detection. The Department of Energy owns the patent for the reaction-fluorescence optrode: 4,834,497 (May 30, 1989). Purus has been licensed to market this technology.

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Reaction Fluorescence: None at present.

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HALOSNIF FIBER-OPTIC SPECTROCHEMICAL SENSOR

Pacific Northwest Laboratory

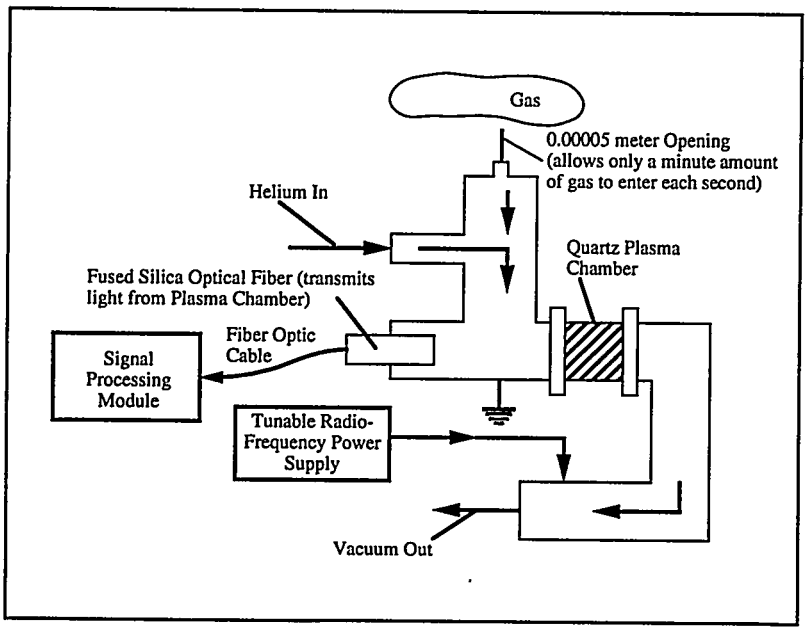
DESCRIPTION

HaloSnif is a fiber-optic spectrochemical sensor capable of detecting any volatile chlorinated compound in air or gas. During operation, HaloSnif operating at subambient pressure (40 torr) continuously draws an air sample through a critical orifice into the plasma-excitation chamber where it is mixed with helium and excited with a radio-frequency signal inductively coupled to the plasma chamber. The plasma chamber is coupled via a fused silica optical fiber to the signal-processor unit. The optical emission of the plasma is filtered with a narrow-band-pass filter designed to monitor the 837.6 nm emission line from the excited chlorine atom. The intensity of the chlorine emission is directly proportional to the concentration of chlorine-containing species in the sample gas. The detection sensitivity for carbon tetrachloride is 5 ppmv. The response of the system is linear from the detection limit to 10,000 ppmv. The detection limit for other chlorine-containing compounds can be estimated by calculating the ratio of the percent of chlorine in the compound of interest to that of carbon tetrachloride.

Data acquisition is achieved using a LabView™ data acquisition software package mounted on a Macintosh computer system. The data-acquisition system is interfaced to the electro-optical signal-processing module via a 1 to 10 V analog output. Real-time concentrations of total chlorinated compounds are displayed on the monitor for observation by on-site personnel. All data are stored in computer memory for post-run processing and analysis.

TECHNICAL PERFORMANCE

HaloSnif's response to chlorinated species is linear from its lower detection limit of 1 to 5 ppmv (for most compounds) in air to approximately 10,000 ppmv. In addition, HaloSnif is not sensitive to moisture or other nonchlorinated compounds present in the sample gas. HaloSnif operates at 40 torr. Equilibration times are normally less than 1 min to reach 90% of full scale. The total weight of the HaloSnif system is 50 lb. HaloSnif also features real-time multipoint environmental field monitoring, small probe size, and the ability to use multiple probes with one central detection and data acquisition system. HaloSnif requires 5 A of 110 VAC power to operate.



HaloSnif Fiber-Optic Sensor

HaloSnif can be reconfigured as an element-specific detector for gas chromatography effluents containing chlorine- and fluorine-containing compounds. By simply replacing the critical orifice inlet with an open-face membrane material, HaloSnif is capable of measuring the concentration of total organic chlorine in water samples.

Cost. It is estimated that the final unit will be approximately $15K for the base system and approximately $250 per sensor assembly. Operations and maintenance costs are expected to be minimal.

PROJECTED PERFORMANCE

HaloSnif has the potential to detect gas-phase compounds containing bromine, mercury, fluorine, and possibly phosphorus by simply modifying the analytical-emission wavelength monitored by the detector.

WASTE APPLICABILITY

HaloSnif is applicable to the detection of any volatile chlorine-containing compound including carbon tetrachloride, trichloroethylene, tetrachloroethylene, and chlorofluorocarbons in air or gases.

STATUS

All components of HaloSnif are commercially available. Field testing of the new compact unit will be conducted to determine its short-term and long-term maintenance requirements.

REGULATORY CONSIDERATIONS

HaloSnif is considered intrinsically safe, and no environmental impacts are anticipated.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications of HaloSnif include monitoring at waste sites, chemical storage areas, and process-based manufacturing plants using CFCs.

BASELINE TECHNOLOGY

The baseline technology is the photo ionization detector (PID), or conventional gas chromatography equipped with an electron-capture or electrolytic-conductivity detector.

INTELLECTUAL PROPERTY

HaloSnif was developed at Pacific Northwest Laboratory (PNL). The patent has been assigned to PNL and the Department of Energy (DOE).

Patent No. 5,085,499, "Fiber Optics Spectrochemical Emission Sensors."

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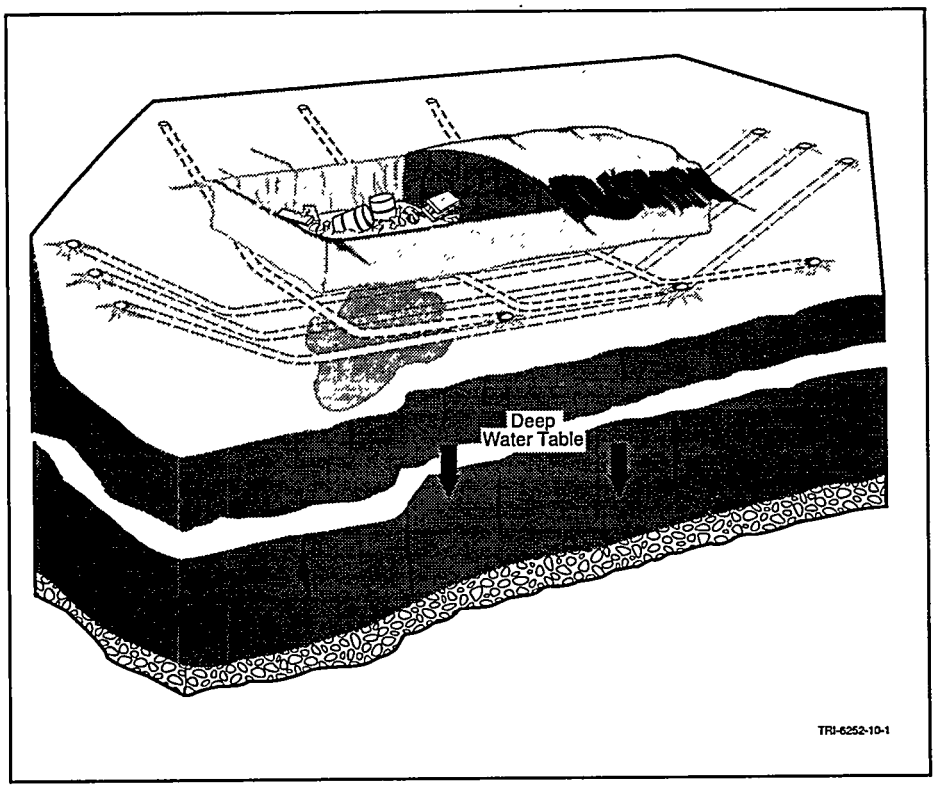
HYBRID DIRECTIONAL BORING AND HORIZONTAL LOGGING

Sandia National Laboratories

DESCRIPTION

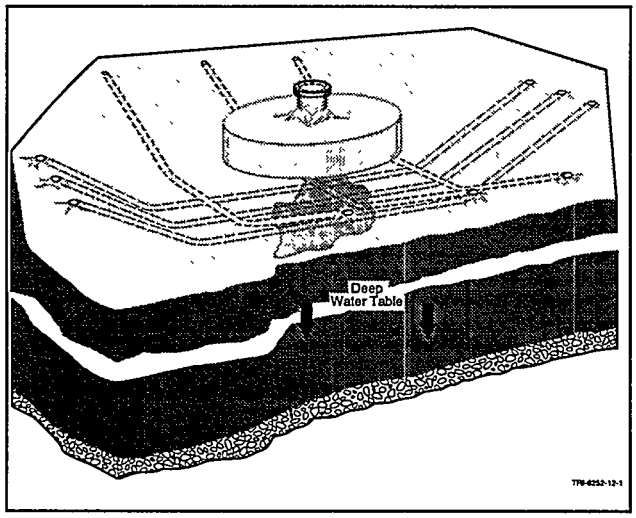
The main application of the Hybrid Directional Boring and Logging (HDBL) system is for cost-effective, high-quality access to an otherwise inaccessible contaminated subsurface (see figure below) for site characterization and sensor emplacement. The directional boring technology is an adaptation of existing hardware from various underground industries, primarily from the underground utilities industry. In the short-term development plans, the depths of the boreholes are somewhat shallow (50 ft), but long-term goals include greater well depths (80-100 ft), diameters (~6 in.) and lateral (horizontal) extents suitable for remediation purposes (400-1,000 ft).



Horizontal/Directional Drilling Concept

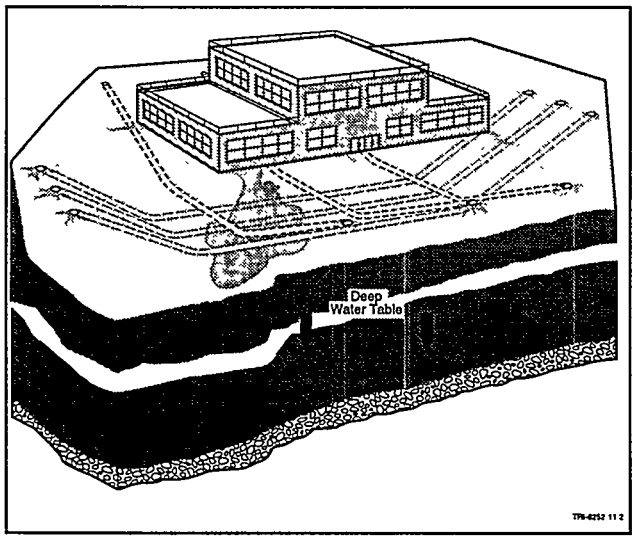
Hardware integrated for the directional-boring facet of this technology includes wireline coring rigs, hydraulic thrust systems, electric cone penetrometers, steering-tracking hardware, and push-coring systems. Hydraulically activated thrust equipment capable of exerting more than 40 tons of thrust is used to push the directional boring heads into the earth. Directional control is obtained by proper positioning of the face of the nonsymmetric boring head. Slow rotation of the boring head will cut and compact the geologic material into the borehole wall. Thrusting a boring head that is not rotating will cause a directional change. The machinery is capable of initiating a borehole, steering down to a desired horizontal depth, continuing at that depth, and then steering back to the surface at a downrange location. This directional boring technology is desirable for environmental applications because the access method requires very minimal addition of fluids and very little soil removal during the drilling process.

Various logging and sampling technologies could be adapted, such as gamma and spectral gamma sensors, resistivity, mass spectrometry, fiber-optic fluorescence, pore pressure, soil moisture, temperature, volatiles sampling (contaminant vapors), and a sidewall coring/soil sampling apparatus (second generation). In addition, various



Horizontal Wells Beneath A Buried Tank

methods to emplace monitoring equipment could be developed including a pneumatic hammer technology for sleeve emplacement. A key function of the sampling hybrid concept is to provide multiple discrete samples per run. It has the potential to recover



Horizontal Wells Beneath A Building

pristine samples; moreover, it can be used to develop inexpensively a grid of horizontal wells in an otherwise inaccessible subsurface (as shown in the figures) for contamination characterization, plume monitoring, and remediation verification.

The following are important technical considerations for users of the technology.

Geology Dependency. Cutting and compacting the cuttings works best in soils that are most uniform, but will work in many nonhomogeneous soils.

Onboard Position Tracking. A low-cost 2-axis magnetometer-accelerometer type wireline guidance package used in the river-crossing industry was used. This equipment is less sophisticated than systems used on larger rigs, but was adequate for development testing. The guidance system used was subjected to the severe environments of frictional and torsional/longitudinal vibration caused by the drilling process. Improved tracking equipment is in development.

Bits and Reamer Configurations. Cutting and successfully compacting the cuttings occurs over a short horizontal distance, and mechanical wear is severe. A key improvement in the drilling process was obtained by adding 2-10 gal/min of potable water to cool and lubricate the drill bits and reamers. After the wellbore is drilled at some nominal diameter, reamers are used to enlarge the borehole and then compact the cuttings in the borehole wall. Several reamer passes may be needed in certain soils and the casing pullback hardware can vary with casing/diameter and soil conditions. Small-diameter completions may not require reaming, thus significantly reducing installation costs.

Casing Materials. The material choice can be critical to installation success or failure. Site geology is again a controlling factor. Higher-strength fiberglass casing has been used most successfully in this project.

TECHNICAL PERFORMANCE

The Utilities Industry Rod Pusher is capable of exerting hydraulic, bidirectional thrust in excess of 80,000 lb and can be used in most soils with the

standard solid rod and some soils with the Hogentogler cone penetrometer hollow rod. Rod diameters are 1.75 in. for both types.

Core Sampler. This equipment provides a core 8-in long and 1-in in diameter.

Prototype Boring Machine. Performance characteristics of this machine include hydraulic bi-directional thrust in excess of 80,000-lb and dry-bore compaction cutting for location/directional control. The first test of the X-810 boring machine was performed at the Savannah River site in South Carolina.

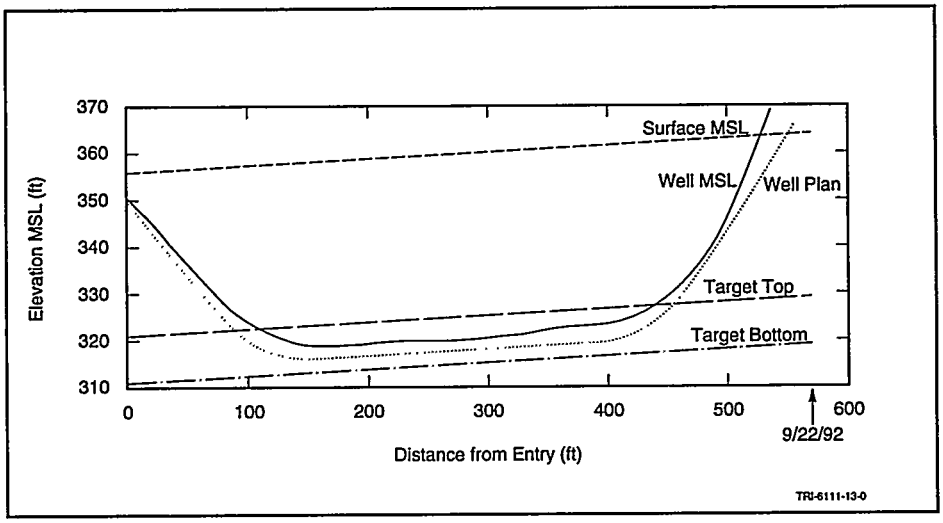
Testing of directional boring for monitoring-equipment installation was performed at the Savannah River Site (SRS) in an actual contamination zone during the summer of 1992. This test used onboard electronics from the river-crossing industry, new-generation bits/reamers/casing pulling plugs, and several new types of environmental casing/screening materials and was highly successful. The test provided preliminary data, hardware confirmation, and a 570-ft long, 40-ft deep, 3-in diameter (see graph below), fiberglass-cased environmental well for Savannah River Radio Frequency soil heating tests.

The soils at the site are coastal-plain sediments consisting mostly of dense clays and sands.

The limits of the X-810 boring machine were tested as part of the Hanford site in Washington. This test provided additional thrust data and evaluated steering control in loose cobbles and gravels of the glacial till. Additional testing at another Hanford location using the standard P-80™ rod pusher with soil samples was successful from the standpoint of steering control and the ability to collect interstitial uncemented sand samples. A Pierce-Airrow™ 4-in diameter pneumatic piercing tool was also relatively successful in penetrating the Hanford formation in a very qualitative test.

The prototype was again used in FY 1993 to emplace a 410-ft well at a depth of 33 ft at Sandia National Laboratories (SNL), Albuquerque, NM. The test provided additional data on machinery capabilities and hardware designs.

Costs. Drilling costs in the range of $25-$75/ft (excluding the cost of casing/screen materials) have been obtained in developmental testing.



Savannah River Site M-Area

PROJECTED PERFORMANCE

The project goal is to drill to a maximum depth of 80 ft and to obtain a maximum horizontal reach of 1,000 ft. Other goals are to log multiple discrete soil samples per run and to integrate various instrumentation and sensing packages into the boring hardware.

WASTE APPLICABILITY

This technology is waste-independent.

Several geophysical monitoring, fluid characteristics, and contamination analysis tools can be incorporated with the hybrid drilling hardware. Developers state that the drilling method is amenable to a range of soil geologies. The developers have also noted that this method may ultimately be limited to compactible soils, although hardrock air drilling may be a future option for more difficult media.

STATUS

The hybrid directional drilling system is being developed from modified hardware for existing drilling equipment used in the underground utility industry. The first-generation hybrid equipment may be available from the developer/ manufacturer in 1994. The availability of more advanced, second-generation equipment may follow the first-generation, according to demand.

REGULATORY CONSIDERATIONS

The secondary process waste of this drilling technology is kept to a minimum by using only a small amount of water for drilling and electronics cooling. Cuttings are compacted into the formation with very little returned to the surface. Various drilling and safety regulations apply, depending on the type of contaminant in the soil.

POTENTIAL COMMERCIAL APPLICATIONS

This technology was developed from existing underground utility installation technologies, so it could be returned and approved for use in these industries. In addition, the environmental monitoring, sensing, and characterization applications are useful to many industries (i.e., steel, aluminum, petrochemical refining, fertilizer, plastics, heavy and light manufacturing, etc.) that may have a shallow contaminant plume. The hybrid technology can be used economically by many industries to characterize, remediate, or monitor the contamination.

This technology could contribute to cost-effective characterization and remediation/ventilation beneath occupied buildings in regions where natural radon gas infiltration has occurred.

BASELINE TECHNOLOGY

A baseline technology might be any larger directional-boring and drilling rigs adapted from the oil, gas, and river-crossing industries. The larger-equipment technologies are much more expensive ($300/ft of well bore compared to $20 to $75/ft) with HDBL for larger directional drilling applications and may not be appropriate for use at shallow depths.

INTELLECTUAL PROPERTY

Both Department of Energy (DOE) and Charles Machine Works, Inc., have patents pending.

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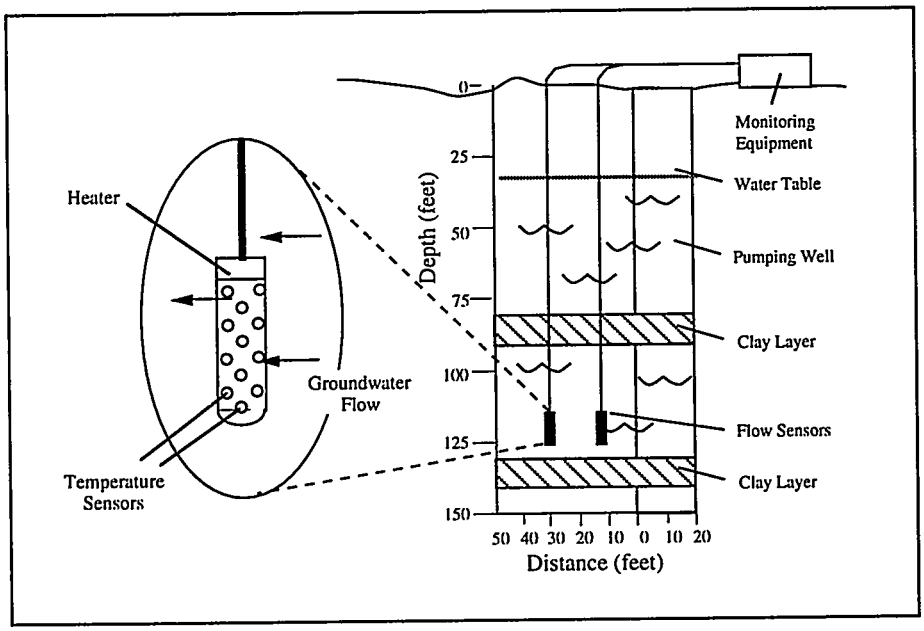
IN SITU PERMEABLE FLOW SENSOR

Sandia National Laboratories

DESCRIPTION

Groundwater flow is perhaps the most important mechanism for the dispersal of many types of toxic waste once they have been released into the subsurface. Accurate information about the groundwater flow field is critical to the characterization of waste sites, the monitoring of waste-remediation activities, and the monitoring of the post-closure performance of remediated waste sites. In situ permeable flow sensors can measure the full three-dimensional groundwater flow-velocity vector at a point in a saturated, permeable, unconsolidated medium using only one hole. In Situ Permeable Flow Sensors require only very crude estimates of the hydraulic conductivity, thus eliminating costly testing to determine hydraulic conductivity. The flow sensors measure the velocity characteristic of a very small volume of material, on the order of 1 m^3. The sensors are simple to install and can be monitored remotely for extended periods of time without requiring personnel in the field. Use of this technology at a site does not preclude using any other technology at the same time or at some future date. Shown below is a schematic of the In Situ Permeable Flow Sensor.

The basic operating principle of this technology is to bury a thin cylindrical heater vertically in the ground at the point where the groundwater flow velocity is to be measured. If the heat flux out of the cylinder is uniform over the surface of the cylinder, then the temperature distribution on the surface of the cylinder will vary as a function of the direction and magnitude of the groundwater flow velocity past the cylinder. In the absence of any flow past the device, the temperature on the surface of the probe will be independent of the azimuth and symmetric about the vertical midpoint of the probe. The vertical midpoint will be warmer than the ends of the probe because heat transfer away from the ends of a finite length cylinder is more efficient than from the midsection of the cylinder. Groundwater flow past the device perturbs the surface temperature distribution, with the pattern and magnitude of the temperature variations reflecting the direction and magnitude of the groundwater flow velocity. In essence, relatively warm temperatures will be observed on the downstream side and relatively cool temperatures on the upstream side of the instrument as the heat introduced into the formation by the heater is advected around the probe.



In Situ Permeable Flow Sensor

If the groundwater flow has a vertical component, the vertical temperature distribution on the surface of the probe will

no longer be symmetric about the vertical midpoint of the probe, but will be skewed in the direction of the flow. The surface of the downstream end of the probe will be warmer than the upstream end. If there is a significant horizontal component to the flow velocity, the surface temperature distribution will not be independent of the azimuth, but rather the surface temperature will vary approximately as the cosine of the azimuth, with the downstream side of the probe being warmer than the upstream side. The magnitude and direction of the three-dimensional flow velocity vector are determined from the magnitude and the pattern of the temperature variations on the surface of the probe, respectively.

Electric power, either from line power or a generator, is required. For remote monitoring, access to a telephone line or cellular phone service is also desirable (data transfer by radio frequency transmission is presumably possible).

TECHNICAL PERFORMANCE

Field Demonstration. Field tests conducted at the Savannah River Site indicate that flow velocities as low as a few meters per year are resolvable. The probes are simple to install and monitor. Data from a number of probes at the same site can be collected and sent via modem to computers at a remote site. Other than for installation and occasional maintenance, the system can be operated remotely for extended periods of time. Once the heater on the probe is activated, a flow-velocity measurement can be obtained after about 24 to 48 h. Current prototype sensors last for approximately one year.

Failure occurs when the waterproof coatings ultimately leak, allowing water into the probe where it shorts out the electronics. Failure of the probe does not present any serious consequences other than the fact that useful flow-velocity measurements will no longer be available from the probes.

The sensor measures the velocity at essentially a point. Sometimes the average velocity over a wider area is desirable. The standard technique measures a velocity that is an average of the velocity over a much broader region, one whose dimensions are characterized by the separation of the boreholes.

Cost. Purchase of a calibration facility, data acquisition system, and computer for data analysis is estimated at approximately $25K. Each flow sensor is estimated to cost between $500 and $700. In remote-monitoring applications, approximately one-tenth of a person's time is required to collect and analyze the data.

PROJECTED PERFORMANCE

The detailed and relatively inexpensive information gained by this technology will enable a greater utilization of time and resources for characterizing, monitoring, and remediating the ground media at problem sites. This technology, used in conjunction with a cone penetrometer technique would greatly reduce the disturbance to the hydraulic properties of the formation compared to the emplacement technique used in the field tests.

WASTE APPLICABILITY

Since this technology is specifically used for obtaining groundwater flow-velocity information at problem sites, the technology is waste-independent.

STATUS

Virtually all of the components for the sensors and the data acquisition system are available commercially. Currently, temperature differences of about

0.01°C can be measured. At this level, flow velocities as low as a few meters per year can be resolved. The probe design needs to be improved to ensure long-term reliability of electronics and sensors in groundwater conditions. Flow sensors can monitor groundwater flow until they leak (approximately 1 yr).

On-going activities include the use of the technology to monitor an air-stripping/bioremediation experiment at the Savannah River Site in South Carolina and a study of the interaction between groundwater and Columbia River water at the Hanford Site in Washington State.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and protection of occupational workers from electrical power. In addition, permits may be required for drilling at hazardous-waste sites.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be useful at a wide variety of sites and with several different remediation processes. The In Situ Permeable Flow Sensors can be used at any site where information on groundwater flow velocity is necessary. Such information is critical to the characterization of waste sites, the monitoring of waste-remediation activities, and the monitoring of post-closure performance of remediated waste sites. Commercialization of this technology is underway.

BASELINE TECHNOLOGY

The baseline technology is a standard technique used to measure hydraulic head gradients and hydraulic conductivities in boreholes to determine flow velocity. Four holes are required for a measurement using this standard technique in comparison to only one hole with the In Situ Permeable Flow Sensors. Information about the hydraulic conductivity of the medium is required in the standard technique. This is generally determined using a pump test in which large quantities of water are pumped from the well. At contaminated sites, disposal of this purge water can be difficult and expensive. The flow sensors measure the velocity characteristic of a very small volume of material, on the order of 1 m^3. The standard technique measures a velocity that is an average of the velocity over a much broader region, one whose dimensions are characterized by the separation of the boreholes.

INTELLECTUAL PROPERTY

There is no patent on this technology; it is in the public domain. Sandia National Laboratories has applied for copyrights on engineering drawings and on the software that interprets flow-sensor data.

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INTEGRATED GEOPHYSICS PROGRAM

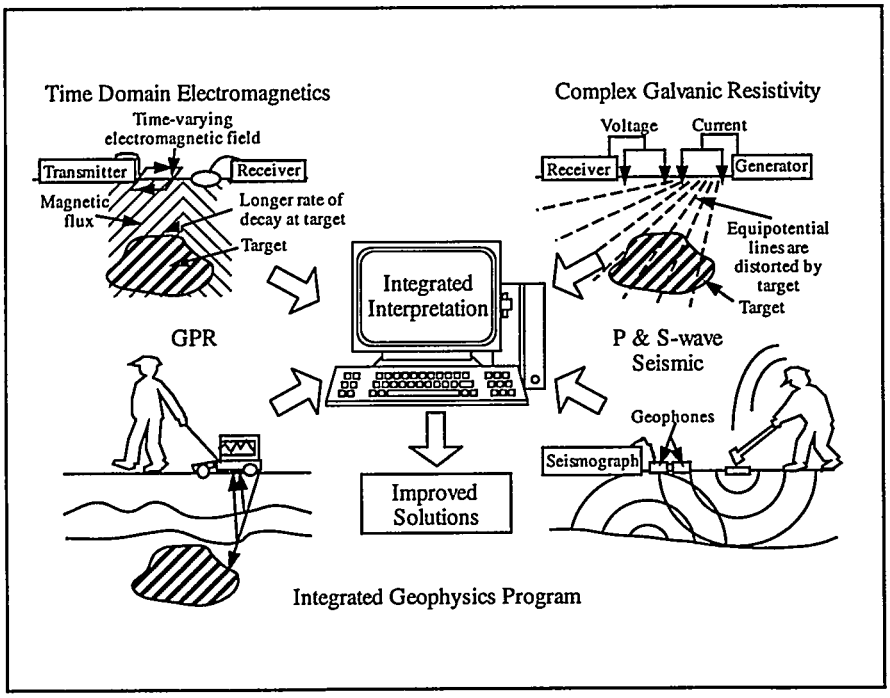
Sandia National Laboratories

DESCRIPTION

The program demonstrates the effectiveness of integrating several surface-geophysical techniques to non-intrusively characterize mixed-waste landfill sites. The use of a particular geophysical technique primarily depends on the target of interest, the geology of the survey area, and the possible interference from surrounding cultural objects. Because each technique measures different situations, an integrated approach offers data and interpretation not attainable by using a single technique. In addition, an integrated approach enables an area to be possibly characterized faster and cheaper because repeated access is not necessary. A brief description of the various characterization techniques used in the field demonstrations is listed below.

Certain chemicals react with clays to produce substances that provide a characteristic response to the complex galvanic resistivity method, as described by King and Olhoeft (1991) and Olhoeft (1986). In addition to possibly identifying broad classes of wastes in the pits, the complex resistivity response may delineate the chemical interaction boundary and, thus, the waste pit boundaries.

Naturally occurring voltage, generally termed a spontaneous potential (SP), frequently builds up at the boundaries of a waste pit due to the difference in chemical composition and solution pressure of the material on each side of the boundary. A simple map of the voltage measured over disturbed and undisturbed areas can be used to define pit boundaries.



Integrated Geophysics Program

Under favorable transmissivity circumstances, ground penetrating radar (GPR) profiles may indicate pit boundaries because of a propagation contrast in the disturbed area compared with undisturbed soil. This may be attributed to a moisture contrast or mechanical factors related to soil disturbance. In this manner, GPR measurements may yield information on the volume of wastes within a pit.

The waste materials within the pit (such as metals, metal salts, and other chemicals) have a profound effect on the conductivity of the pit in contrast to that of undisturbed ground. Time domain electromagnetic (TDEM)

methods can be used to map conductivity/resistivity contrasts. In addition to delimiting the pit area, the conductivity data will provide insights to the type and quantity of material in the pits. A conductive plume that is migrating beyond the pit boundary toward a borehole would be readily detected with this technique.

Shear wave (S-wave) refraction and compression wave (P-wave) reflection seismic surveys can detect seismic-wave transmission differences expected between disturbed and undisturbed material. Variations in the phase, amplitude, frequency, and velocity of horizontally polarized shear waves are indicative of changes within the subsurface. The locations of these seismic differences can help differentiate pit boundaries and also can help determine the volume of waste within a particular pit.

TECHNICAL PERFORMANCE

Data were acquired in two areas that have both known and unknown attributes at SNL. The locations of the known Chromic Acid and Organic Pits were interpreted at or near their historical boundaries, unknown pits were identified, areas of disturbance possibly related to contaminants were interpreted outside the boundaries of both known and unknown pits, rudimentary waste types were identified and modeled where appropriate, and anomalies from recent activities were identified and discounted from further analysis. Pit boundaries and basic geometries (horizontal and vertical extent) were identified to less than 3 feet through integrated interpretation of complex galvanic resistivity, GPR, and S-wave seismic data. Indications of metallic debris within the identified pits were obtained through combined interpretation of all the data sets. Contaminant migration was suggested from interpretation of the data, but no identification of discrete contaminants or assignment of concentrations was possible.

The principal disadvantages of an integrated approach are time and expense. If, for instance, one chooses to use only a single technique to characterize a hazardous waste site, it can represent a considerable savings, but assumes one method will be successful in completely describing the problem area.

Cost. The cost to implement this method of site characterization depends on the size of the site and the instrumentation/data needed.

PROJECTED PERFORMANCE

Future improvements in performance will result from higher-quality instrumentation being commercially available and improvements in the interpretation of the data obtained. The major technical challenges are increasing the frequency and power output of the sources to increase resolution, improving imaging and inversion codes, and decreasing the survey time through development of more rapidly fielding instrumentation. Times for both fielding and especially interpretation should decrease significantly as various methods develop further.

WASTE APPLICABILITY

Since this technology is specifically used for characterization and monitoring of the ground media at problem sites, the technology is waste-independent.

STATUS

All instruments used in the program are available from commercial sources. The instruments are of field-worthy design and have been adequately tested. Operation of instrumentation and interpretation of data must be performed by knowledgeable and fully-trained workers.

REGULATORY CONSIDERATIONS

Although non-intrusive geophysical surveys are, in general, benign, handling of 50 pound instrument packages and sensors is required. Compliance with the Occupational Safety and Health Act is required for hazardous-waste operations, handling of heavy loads, and protection of occupational workers from electrical power.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include the use of the technology by various industries to non-intrusively characterize the subsurface of various sites where physical contrasts with the surrounding media are expected (e.g., chemical companies' waste landfill sites). This technology can be of use at a wide variety of sites and in conjunction with several different remediation processes.

BASELINE TECHNOLOGY

Characterization of hazardous waste sites can be performed with a single technique to minimize time and expense. This can be an efficient approach but assumes that one method can provide a complete description of the site and waste target. An integrated approach using pertinent geophysical techniques offers data and interpretations not attainable by a single technique. To successfully integrate the data from various geophysical techniques, considerable experience is necessary to ensure that the highest quality data are acquired at suitable spacings. Once sufficient high-quality data are acquired, modeling and an integrated interpretation of the data can be conducted. This integrated approach offers solutions that encompass numerous physical-property contrasts and, thus, are more reliable than interpretation from a single geophysical technique.

INTELLECTUAL PROPERTY

None.

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None.

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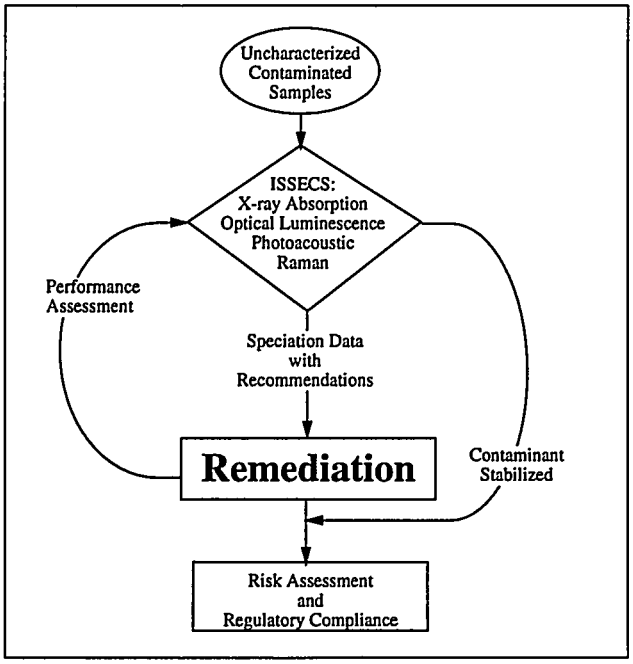
INTEGRATED SPECTROSCOPIC SYSTEM FOR CONTAMINANT SPECIATION

Los Alamos National Laboratory

DESCRIPTION

The Integrated Spectroscopic System for Contaminant Speciation (ISSECS) is a new approach for characterization of soils, sludges, and groundwater. The approach is both sensitive and adaptable to different contaminant media and can be applied over a broad spatial range. The principal application of ISSECS is to soils contaminated with radioactive and/or toxic metals such as uranium, plutonium, and chromium. The key feature is that the technique provides contaminant speciation information in broad spatial ranges from sub-micron size to the bulk-sample size (like a zoom lens). Speciation information indicates the distribution of a particular contaminant moiety within a particular contaminant type, for example, the speciation of uranium in a particular region of soil may be described as 80% hexavalent uranium (in the form UO_2^{2+}) and further quantified as 10 ppb hexavalent uranium and 2.5 ppb tetravalent uranium (IV).



Integrated Spectroscopic System

When new remediation technologies are being developed, analytical data are generally available giving contaminant concentrations and the spatial extent of contaminant plumes. On the other hand, the contaminant plumes often exist in many different chemical forms or species. It is asserted that when chemical contaminants exist in several different species (e.g., toxic and radioactive metals which have many accessible oxidation states), adequate performance monitoring and suitable application of specific remediation technologies will require knowledge of the type, concentration, and heterogeneity of molecular species. Unless speciation information is factored into the characterization need early on, remediation development and testing strategies are strictly by trial and error, which is both costly and inefficient. It is noted that some routine analytical approaches are currently used such as electron microscopies, X-ray, and electron diffraction. In principle, these methods can provide some contaminant speciation information but in actuality are limited because they cannot easily address sample and contaminant heterogeneity over spatial ranges from <1 micron to >1 cm.

To adequately specify uranium speciation, techniques that probe the structure at the molecular level are required. Elemental specificity (e.g., as provided by ICP-AES), while important, is insufficient by itself. Techniques are also needed that are applicable to opaque samples such as solids (e.g., soils and mineral assemblages), because these frequently possess challenging optical properties. One approach that satisfies these criteria is based on molecular spectroscopic methods that probe the vibrational and electronic properties of the system. This is the approach taken by the ISSECS methodology.

No single molecular spectroscopic method is readily available to provide a detailed description for uranium or other species of interest. To achieve a detailed description, a combination of spectroscopic techniques is generally required. ISSECS involves the combination of four state-of-the-science spectroscopic techniques to directly probe molecular structure. Four core spectroscopic methods are identified which, when used in combinations of two or more, are sufficient for contaminant speciation studies in subsurface matricies. The laboratory-based approach consists of: (1) x-ray absorption spectroscopy, (2) pulsed-laser photoacoustic spectroscopy, (3) laser-induced luminescence spectroscopy (time resolved pulsed-laser and continuous-wave), and (4) laser Raman vibrational spectroscopy. Applying these techniques in combination provides a greater level of information on contaminant speciation than do the techniques separately. The spectroscopies can determine average speciation at the bulk scale (~1-2 cm) as well as more precise speciation at the microscopic scale (~1-10 microns). The methods span an analyte concentration range from 1% to 0.1 ppb and below (i.e., the relevant regime for the U.S. Department of Energy sites). By contrast, more conventional approaches rely on microscopic methods only, which can provide very accurate speciation data for small populations but not for bulk samples.

ISSECS not only addresses all relevant spatial scales for contaminant heterogeneity, but because the characterization tools are all optically based, their application is noninvasive. The contaminated samples can be studied in the exact same form as they existed in the environment without having to alter the samples. Once the samples representing the contaminated plume are collected, they are characterized in the laboratory. These data are provided to the site remediation personnel along with recommendations for candidate remediation strategies based on the contaminant speciation. ISSECS also provides feedback on how well the remediation treatments perform, as well as post-treatment analyses.

TECHNICAL PERFORMANCE

General. The ISSECS method has been applied at the Fernald Environmental Management Project in Ohio. A wide variety of source terms for uranium contamination have been identified reflecting the diversity of operations at the facility. Most of the uranium contamination is contained in the top 1/2-m of the soil, but uranium has also been found in perched waters indicating substantial migration. The uranium species in the perched waters is likely to be hexavalent (e.g., UO_2^{2+}).

Cost Data. The costs of using ISSECS to do a complete environmental sample are projected to be $5,000-$7,000/sample. This cost is comparable to EPA sample-analysis costs at the National Atmospheric and Radiation Emission Lab (NAREL) in Alabama. Assuming a reasonably homogeneous matrix (e.g., the shallow subsurface of a field surrounding a process plant), the sampling density required to obtain meaningful results would be 1-10% of that required to map the contamination. Representative analysis of an entire plume would typically require 2 to 20 samples. The estimated capital cost to develop a complete laser lab facility is $650,000 (not including physical plant). The X-ray absorption spectroscopy technique requires access to a synchrotron radiation facility (such as the Stanford Synchrotron Radiation Laboratory in California), but subcontracting costs are factored into the per sample costs. Turn-around time for the ISSECS analysis is estimated to be only 2 days (with samples running concurrently).

X-ray absorption spectroscopy. Of the four core methods, X-ray absorption is the most incisive. It provides oxidation-state information [e.g., U(IV) vs. U(VI)] directly. It also provides a "snap shot" of the local coordination environment about the target (uranium) ion. Thus, the identity and number of coordinating atoms (from ligands and/or surfaces) and their bond lengths can be quantified.

Optical luminescence. Laser-induced optical luminescence spectroscopy is a very valuable probe for

the speciation of hexavalent uranium moieties and other emissive species. This method has excellent sensitivity. Furthermore, the often distinct, species-specific nature of the hexavalent uranium emission spectrum allows optical luminescence to be used as a "finger print" for speciation.

Photoacoustic spectroscopy. This method is the ideal complement to optical luminescence because species that are not emissive tend to yield excellent photoacoustic spectra. Thus, the speciation of uranium in the non-emissive or weakly emissive oxidation states (i.e., 0, +3, +4, and +5) can be probed by measuring the electronic spectra using photoacoustic spectroscopy. Of the four core methods, photoacoustic spectroscopy is the most sensitive. Dissolved species concentrations of 10^{-8} mol/liter can be probed routinely.

Raman vibrational spectroscopy. This final core method provides molecular structure information explicitly via the number, energy, and intensity of the observed vibrational transitions. This method can also be used as a "finger print" for species identification because of the distinctive nature of the Raman spectrum. However, of the four methods, this one is generally the least sensitive.

Results from untreated soils. Untreated soils from five discrete soil locations at the Fernald site have been analyzed. Based on X-ray absorption analyses, the uranium in the untreated samples exists principally (80-90%) in the hexavalent oxidation state (UO_2^{2+}). This result is interesting because many source terms consisted of the tetravalent uranium species UO_2. It is concluded that soil and groundwater chemistry are as important as the source term in defining uranium speciation. This bulk microscopic finding could only be obtained using X-ray absorption spectroscopy. Later investigations of these same samples using laser-induced luminescence and Raman spectroscopies could identify the uranyl moieties, principally as microcrystalline-mineral phases of uranyl hydroxides, silicates, phosphates, and carbonates.

Hexavalent uranium has a greater solubility than uranium in other oxidation states; thus strong oxidizing agents may not be necessary as part of a chemical remediation scheme. In fact, the remediation strategy based on selective chelators for U(IV) was revised in accordance with this result to incorporate reducing agents. Therefore, remediation of soil having a high speciation of U(VI) requires only mild chemical conditions and conventional extractants such as carbonate and citrate washes. Note, however, that this result implies that the uranium is less stable in the soils than would be a tetravalent uranium species. Since hexavalent uranium is potentially more mobile, the remediation timelines are more important. In addition, because hexavalent uranium (as uranyl species) has a very small magnetic moment, remediation based on magnetic separation technologies will be of limited value unless the uranium is associated with some other paramagnetic phase (e.g., iron oxides). In contrast, if the uranium is primarily the tetravalent moiety (e.g., UO_2), then remediation strategies based on soil washing require more potent complexing (iron-oxide chelators) and/or oxidation reduction reagents to dissolve the material.

Results from treated soils. The characterization of treated soils from two Fernald sites has focused on material that has undergone leaching using conventional extractants or novel chelators such as Tiron. Redox agents have also been used to facilitate the leaching process. In general, the effective treatments decrease the total uranium while increasing the ratio of U(IV) to U(VI). Observation of different X-ray absorption spectra in the A-series soils suggests that there are several uranium species left in the soils following treatment (rather than a single intransigent species), and the treatment chemistry may be dictating the difference in the remnant species.

The optical luminescence data for the treated soils demonstrate that there is a decrease in size and probably quantity of the particulate hexavalent uranium that gives rise to the green emission. In

particular, the highly structured emissive phase seen in the untreated SP2 and SP9 soils was never seen in treated samples. Thus, all treatment technologies do seem to lead to a more dispersed, finer grained contamination. Some instances of particulate green emission still exist in these samples, and the spectral band structure indicates that this is attributable to a schoepite phase. An orange emissive phase is also seen in many samples that is probably attributable to a hexavalent species.

PROJECTED PERFORMANCE

Future work consists of testing the ISSECS methods to other contaminants. Demonstration, Testing, and Evaluation is being conducted on thorium-contaminated soils in conjunction with Bectel, Inc. and the EPA's National Air and Radiation Environment Lab.

WASTE APPLICABILITY

The principal application of the ISSECS method is characterization and remediation performance monitoring in soils contaminated with radioactive and/or toxic metals such as uranium, plutonium, and chromium. The ISSECS method can also be adapted to characterize groundwater and sludges. The key feature of ISSECS is that it provides contaminant speciation information.

STATUS

The technology is developed and tested for uranium in soils. It was demonstrated at the Fernald Site.

REGULATORY CONSIDERATIONS

This technology is very sensitive (spanning an analyte concentration range from 1% to 100 parts-per-trillion) and will therefore be useful in verifying regulatory compliance. This is a laboratory technology so it will have negligible environmental impact when it is used (other than the impact of the soil sampling).

POTENTIAL COMMERCIAL APPLICATIONS

Although federal and state governments are the principal customers, this technology is potentially applicable to industries having toxic-metal (chromium, etc.) or radioactive contamination in soils (or groundwater and sludges). Possible industries include steel-production facilities, nuclear-medicine facilities and support industries, nuclear-fuel manufacturers, and chemical industries.

BASELINE TECHNOLOGY

The baseline technology for contaminant speciation includes some routine analytical approaches. The speciation technologies currently used are electron microscopies, X-ray spectroscopy, and X-ray diffraction. In principle, these methods can provide some contaminant speciation information, but in actuality are limited because they cannot easily address sample and contaminant heterogeneity over spatial ranges from <1 micron to >1 cm.

INTELLECTUAL PROPERTY

Los Alamos National Laboratory has initiated the patent process for this technology.

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Industrial/University Partners
None.

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LIGHT DUTY UTILITY ARM SYSTEM FOR REMOTE TANK ACCESS

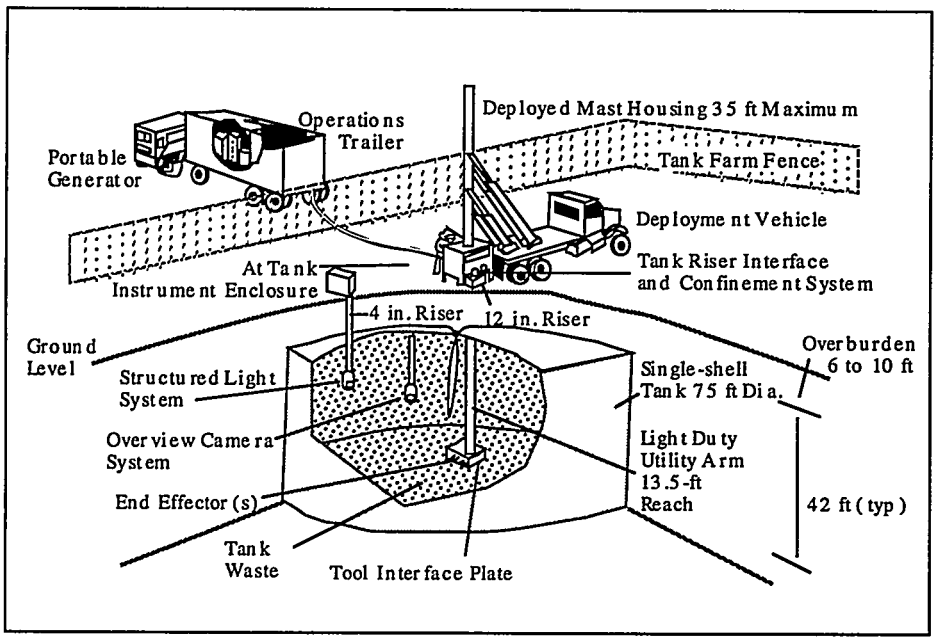
Westinghouse Hanford Company

DESCRIPTION

The Light Duty Utility Arm (LDUA) System provides a remotely operated, mobile system to deploy end effectors (robotic tools) for waste tank surveillance and inspection. This technology will enhance existing capabilities that are limited to single-axis instrument deployment. The current means for performing tank inspection and waste analysis consists of vertical deployment of cameras, sensors, and sampling instruments through risers (openings) on fixed supports. These systems are limited to operation directly below the tank penetration riser.

In contrast, the LDUA provides a robotic arm with seven degrees of freedom that can position itself at any point within a 13.5-ft radius hemisphere of the penetration riser. The robotic arm system is designed for deployment through a 12-in diameter tank riser and reachs to a depth of over 48-ft below the ground's surface. The robotic arm system will be able to maneuver and position equipment weighing 75 lb. The LDUA enables certain waste analysis, in-tank surveys, and waste topography activities to be performed in situ to gather data on chemical and physical properties of the waste and information on the structural condition of the tanks. This will not replace laboratory analysis; however, it will provide the capability to gather data in multiple locations within a tank much faster than is currently possible.

The LDUA consists of various interfaces including a human/machine-graphical user interface; a standardized utility-arm/end-effector interface (called the Tool Interface Plate); and a utility-arm/tank-riser interface for confinement. The tank deployment process would begin by installing the tank-riser interface, which includes a confinement enclosure. The LDUA mast would then be lowered into the confinement enclosure and an appropriate end effector installed. At this point, the mast would be lowered into the tank. The robotic manipulator would be subsequently deployed out of the mast to initiate the in-tank campaign. Data would then be transmitted to data acquisition stations, analyzed, and archived.



Light Duty Utility Arm System

Upon completion of data collection, the mast and arm would be retracted out of the tank through a decontami-

nation spray (a pelletized carbon dioxide blast or H_2O system) that removes surface contamination from the mast, manipulator, and end effectors. The pressurized spray decontamination system is mounted just above the tank riser inside the confinement enclosure.

The LDUA graphical user interface can be operated by a single specially trained technician. The graphical control interface includes supervisory control of the robotic system to ease operator fatigue. The LDUA also provides a Quick Disconnect Tool Interface Plate for operation of a variety of end effectors.

TECHNICAL PERFORMANCE

Design. Spar Advanced Technology Systems has been contracted to design, fabricate, and deliver the LDUA arm and deployment system. The Spar design comprises a 13.5 ft, seven degree of freedom robotic arm mounted on a 63 ft telescoping mast. This provides multi-directional reach to the full tank depth. These components are transported in a sealed mast house on a truck base, which makes the system mobile for use in multiple tanks. The mast, arm, and end effectors are designed for deployment through a 12-in diameter access riser. The LDUA will support instrumentation end effectors that weigh up to 75 lbs. As low as reasonably achievable (ALARA) principles were applied to LDUA design to minimize human exposure to hazardous environments. The design includes a pelletized carbon-dioxide blast system for high-pressure spray decontamination during retraction. The CO_2 system is being developed through a Cooperative Research and Development Agreement with Non-Destructive Cleaning, Inc.

Laboratory Testing. Detailed reliability analysis is part of the design verification process.

Costs. Start-up, operations, and maintenance costs are currently being determined and are not available at this time.

PROJECTED PERFORMANCE

The system is planned for cold testing in FY95 and for a hot-testing demonstration in FY96 in the actual radioactive waste environment of a Hanford Underground Storage Tank. Detailed performance information will be available after the cold test in FY95.

WASTE APPLICABILITY

The LDUA System technology is applicable for remote visual inspection of underground storage tank structural conditions. It is also applicable to extract multiple small-waste samples in multiple locations inside a tank. The penetration depth would be limited to surface samples, and the depth of penetration would depend on the waste hardness. The robotic arm can support other chemical and physical property instrumentation tools for in situ waste analysis of hazardous and radioactive wastes, provided that the total weight of the end effector instrument is less than 75 lbs.

STATUS

The LDUA is currently in the design evaluation and refinement phase of development. Hazards, operability, and regulatory studies were scheduled for FY94. Completion of design and initiation of fabrication activities are scheduled for FY95. A demonstration of the LDUA System is scheduled for the final quarter of FY95. The system consists of a mix of off-the-shelf and Office of Technology Development-developed hardware and software. Development of a remotely controlled complex robotic system capable of operating in a hostile environment is part of this effort.

REGULATORY CONSIDERATIONS

To meet potential regulatory considerations, the LDUA includes the pelletized carbon-dioxide blast decontamination system and a confinement enclosure mounted above the access riser. Clean Air Act requirements are applicable to the confinement enclosure and ventilation system. Minimal environmental impacts are anticipated from the use of this remote access technology. A detailed regulatory and worker-safety analysis will be completed in mid-FY95.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications are in the nuclear power industry for Nuclear Regulatory Commission compliance reactor safety inspections, for hot storage tank and spent fuel rod inspection, and for reactor decontamination and decommissioning.

BASELINE TECHNOLOGY

The baseline technology is deployment of cameras, instruments, and waste samplers through risers on fixed supports with their operation limited to vertical-axis motion directly below the riser.

INTELLECTUAL PROPERTY

Patents: None

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Oceaneering Space Systems
Mechanical Technology, Inc.
Perceptron, Inc.
Bristlecone Technologies, Inc.

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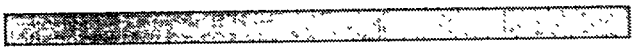

LONG RANGE ALPHA DETECTOR

Los Alamos National Laboratory

DESCRIPTION

The Long-Range Alpha Detector (LRAD) soil-surface monitor is essentially a large, flat box whose open end is placed on top of the soil to be measured (Fig. 1). Inside the box, a signal plane of either copper of aluminum sheet is biased at 300 V and creates an electric field between itself and the soil. Radiation coming from the soil ionizes the air in the box. Ions created above the soil are collected by the electric field, resulting in an electrical current which is measured by the electrometer. Readings can be obtained directly from the electrometer or from an attached computer which averages the readings over thirty seconds and graphically displays the results. The entire unit, including computer, is powered in the field by its own car battery and DC to AC inverter.

TECHNICAL PERFORMANCE

These new monitors use the LRAD technology. Alpha radiation, which is a good indicator of uranium, plutonium, and many transuranic elements, is particularly difficult to measure using traditional technologies. An LRAD monitor detects the ions generated by the passage of alpha particles through the air, rather than the alpha particles themselves. In a soil-surface monitor, all of the ions generated over a large area (1 m by 1 m) are collected in a single detector. Soil with only natural background activity gives a signal in the LRAD soil-surface monitor twenty times higher than the intrinsic detector background. With 5% to 10% measurement precision, the LRAD soil-surface monitors are ideally sited to distinguish areas with natural background radiation levels from areas with radioactive contamination. Using such a detector, as many as 30 locations can be monitored in a day (with a sensitivity as good as 5 dpm/100 cm^2) without disturbing the soil or generating waste byproducts.

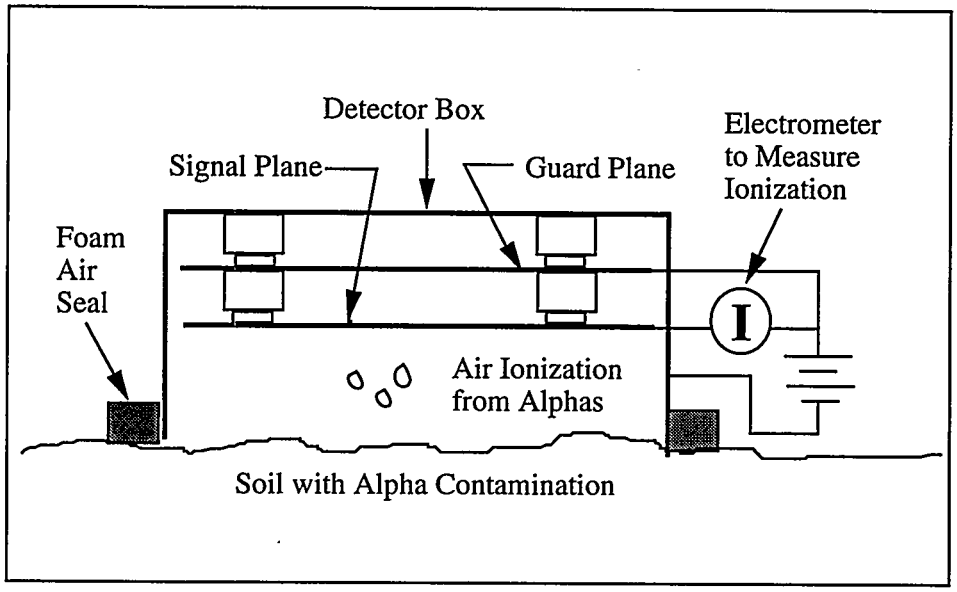

Figure 1. Schematic of the LRAD Soil-Surface Monitor

PROJECTED PERFORMANCE

The detectors are already near their optimum in alpha-detection performance. There is a low-priority effort underway to convert from commercial electronics and computers to cheaper, smaller and longer-battery-life custom electronics in weatherproof cases. Three

advances - segmenting the large monitors so that smaller hotspots can be isolated, providing simultaneous radon emission measurements, and integrating with other types of detectors for broader radiation coverage - are in the conceptual stages but have not yet been funded.

WASTE APPLICABILITY

The soil-surface monitors are ideally suited to monitoring low-level widespread alpha contamination, such as from uranium, plutonium, or thorium. Even sites last used 20 years ago have been shown to present measurable surface contamination.

STATUS

Two one-square-meter, tractor-mounted LRAD soil-surface monitors exist. A hand-cart-mounted 50 cm x 50 cm monitor and a handheld 25 cm x 50 cm monitor also exist. More handheld detectors are under construction. In the two years since the creation of the first detector in the summer of 1992, the soil-surface monitors have been used to characterize ten sites for six customers at three DOE facilities. The tractor-mounted monitors have proven field ruggedness.

REGULATORY CONSIDERATIONS

The LRAD soil surface monitor is both passive and non-intrusive. It generates no waste or by-products.

POTENTIAL COMMERCIAL APPLICATIONS

TMA/Eberline of Albuquerque, NM is the laboratory's technology transfer partner for this technology and will soon be ready to perform monitoring on a commercial basis. Eberline Instruments of Santa Fe, NM owns exclusive licenses to the technology and can either build detectors for users or sublicense the technology to other companies.

BASELINE TECHNOLOGY

The LRAD soil-surface monitoring is a cheaper and faster alternative to core sampling. While the LRADs do not give isotopic information, the gross alpha-activity readings they give are often all that is necessary to map contamination at a site. Handheld alpha detectors have relatively fragile probes and are less sensitive than the LRAD soil-surface monitors.

INTELLECTUAL PROPERTY

The University of California owns the patents on this technology. Eberline Instruments, Santa Fe, NM, has exclusive licenses to commercialize the technology, but may grant sublicenses.

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MAGNETOMETER TOWED ARRAY

Sandia National Laboratories

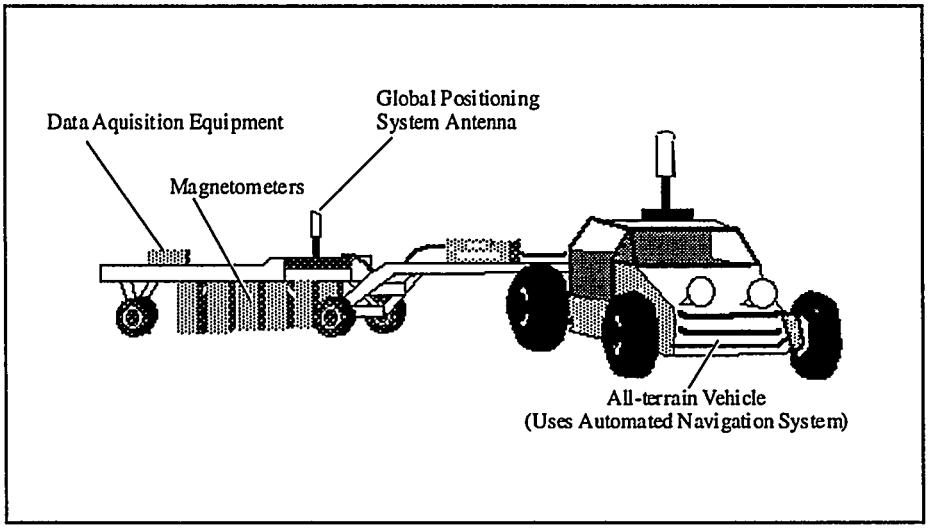
DESCRIPTION

The Magnetometer Towed Array (MTA) is a non-intrusive system for the detection and quantification of buried wastes. MTA, also known as the Surface Towed Ordnance Locator System (STOLS®) was developed by the Department of Defense with lead engineering provided by Geo-Centers, Inc. of Boston. STOLS® was built to detect ordinance and is being adapted to help characterize buried hazardous-waste sites.

The vehicle-based system deploys a non-intrusive sensor platform containing seven total-field magnetometers with precise satellite positioning for locating the magnetic data. These alkali-vapor magnetometers are spaced at 0.5 meter intervals perpendicular to the direction of travel. The magnetometers measure the total field strength at any given point at a rate of twenty measurements per second. This rate yields a total density of data points of 70,000 data points per acre at 5 mph (1.6 data points/ft^2). The vehicle which tows the sensor platform is rugged for handling the terrain variations in diverse field conditions. It enables the system to rapidly cover the survey area at an average rate of fifteen acres per day.

TECHNICAL PERFORMANCE

The strength of the Earth's natural magnetic field at any point is determined by the sum of the Earth's field plus any local variations caused by the presence of ferrous materials. To isolate the magnetic field caused by buried ferrous objects, an eighth magnetometer, placed in an area close to the survey site that is known to be free of ferrous material, is used to measure the Earth's magnetic field. Data from this reference magnetometer are used to remove the diurnal variation effects of Earth's field from the sensor platform data. This step leaves behind only the variations due to local ferrous objects.



Magnetometer Towed Array

The tow vehicle is a Chenowth Baja dune buggy (modified for a low magnetic self-signature) equipped with electronic computerized recording systems.

Precise positioning data are acquired once per second using a differential global positioning system. After interpolating the positioned magnetic data to a regularly-spaced grid, magnetic maps

of the survey area are readily produced. On these maps, the magnetic variations due to local ferrous objects are readily located through the use of data analysis software. In addition, areas missed are clearly seen and can be located and surveyed subsequently. Local landmarks can be recorded and plotted.

Displayed on a video monitor, the magnetic images of a surveyed area provide the user interface to semi-automated target-analysis software. Using a mouse, the user boxes a magnetic image. The software then performs an iterative least-squares fit to determine the best fit of magnetic moment and depth to the selected anomaly. The resulting output yields an estimate of size (based on correlating magnetic moments to small, medium, or large ferrous objects), depth, and the location in latitude/longitude state plane or local grid coordinates (in meters). A target report listing all targets in a given survey is printed as well as a site map showing all targets' and landmark locations in the surveyed area. Detection depths to 6.5 m are possible, with maximum depths being target size dependent.

Described below are three elements of the existing STOLS® that are being or have been modified to meet the needs at Sandia National Laboratories (SNL).

- The integration of a differential Global Positioning System (GPS)-Based Locator System. The GPS replaces the microwave-based navigation position recording system, allowing positioning to sub-meter accuracy (within 0.5 m in real time) and updated at 1 Hz. This integration is now complete.

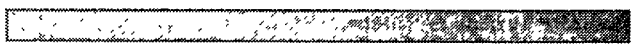
- Improvement of interpretation algorithms to characterize extended and clustered targets (i.e., trenches) which cannot be interpreted using the single-point dipole model of the existing STOLS® interpretation algorithms.

- Determine the feasibility of towed-array surveys utilizing other sensors (i.e., chemical and radiation sensors). This concept is named the Multi-Sensor Towed Array Detection System (MTADS).

Field test of STOLS®. In FY 92, the prototype STOLS® was used to characterize buried wastes at three Sandia National Laboratories Landfills (Radioactive Waste Landfill, Technical Area 2 Classified Waste Landfill, and the Chemical Waste Landfill). With a 0.5-m spacing between magnetometers and each magnetometer taking 20 measurements per second, the effective survey grid (per sensor) at 5 mph is 0.12-m by 0.5-m (i.e., STOLS® maps provide outstanding resolution). The automated nature of STOLS® should allow characterization of more than 10 acres per day.

Field test of STOLS®. During the week of September 7, 1993, the commercially available STOLS® was successfully demonstrated at the RB-11 Landfill. Less than 2 hours was required to actually survey the 4.5 acre site. STOLS® average rate is 15 acres/day. Among the findings were: (a) previously unidentified, large (1-in diameter) electrical cables buried across some of the pits at a depth of about 3 feet, (b) the collapsing trench was found to contain almost no metal, and (c) one of the northern pits was found to extend much further north than previously believed.

Cost. This technology is commercially available from Geo-Centers. Costs vary, depending on the site access; site size; health and safety requirements; and topographical characteristics, etc. Operations costs are competitive with conventional technology on larger sites and provide same-day, high-resolution data. Cost data may be obtained from Geo-Centers, Inc.



PROJECTED PERFORMANCE

STOLS® is commercially available. Ongoing activities include:

- Research of the utility of multiple sensors (e.g., ground conductivity, radiation detectors); and
- Development of software algorithms to interpret large extended targets (e.g., trenches filled with waste).

WASTE APPLICABILITY

This technology is applicable for any burial site (e.g., landfills) that the vehicle can traverse, providing ferrous metals were used at the burial site.

STATUS

The technology is available for commercial surveys. Field demonstrations took place during the fourth quarter of FY94.

REGULATORY CONSIDERATIONS

This technology is non-intrusive and passive. STOLS® is driven across the site and measures the Earth's natural magnetic field. As with any operation at a hazardous waste site, health and safety protocol must be followed. No specific permits are required to use STOLS®.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be used for any site needing characterization and for buried hazardous wastes or ordnance.

BASELINE TECHNOLOGY

Current technology requires a person to walk a grid and take measurements by hand. The data are then transferred to a contouring package for plotting. The resulting plots are then visually interpreted. A typical survey grid is 5 ft by 5 ft or 10 ft by 10 ft, with survey rates of an acre or two per day. The time-consuming nature of the survey usually prevents large areas from being surveyed (e.g., outlying burials are missed). Further, the coarse grid does not allow the boundaries of burials to be adequately determined and may miss small, isolated targets. The 1-in cable detected by STOLS® was not found by the previous conventional survey of RB-11.

INTELLECTUAL PROPERTY

Geo-Centers, Inc. has several patent applications in process. This technology is being developed and commercialized by Geo-Centers, Inc. and is commercially available. U. S. Naval Research Laboratory and Sandia National Laboratories' work are both public domain.

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MICROBIAL MONITORING

Oak Ridge National Laboratory

DESCRIPTION

Many technologies designed to remediate organic contamination either directly depend on increasing populations of bacteria that can degrade the compounds, such as the methane injection, or lead to increases in degradative populations as a secondary result of nonbiological remediation, such as the biological benefits of venting-bioventing. Microbial monitoring is needed to demonstrate the effectiveness of bioremediation and to demonstrate additional bioremediation benefits from other technologies (e.g., bioventing benefits from soil venting). The various advanced-monitoring techniques, developed and applied, (e.g., DNA probe analysis, lipid analysis, activity and biomass measurements) all contribute to documenting the necessary changes in microbial populations. In addition, these techniques permit feedback during operation so that procedures may be changed (e.g., changing nutrients) to increase effectiveness of the remediation.

TECHNICAL PERFORMANCE

Microbial population changes were monitored in soil and groundwater samples from the Savannah River Site (SRS). Microbial biomass was evaluated using measurements of colony-forming units, MPN techniques for methanotroph and methylotroph population, and PFLA analysis. Microbial activity was assessed using the acetate-incorporation techniques and by measurement of trichloroethylene (TCE) degradation in enrichments. DNA probes are used to enumerate specific groups of bacteria such as methanotrophs, toluene degraders, and others. Several new probes have been developed as part of this work.

The monitoring has been very effective in documenting significant changes in the microbial community in response to the remediation. The results of this effort indicate that there have been substantial changes in biological activity and biomass with increasingly aggressive measures to promote TCE degradation in the subsurface. However, there are some indications of a leveling off or a decrease in some of these measures as the 4% methane injection proceeds. Thus, the data indicate the success in stimulating TCE degrading populations in the subsurface and now may be indicating a limitation of further increases or the potential for decreases in critical populations. Other nutrients may be becoming limiting, and a further phase (methane injection with nutrient addition) may be necessary to increase critical population levels and degradative activity further.

Analysis can be completed in 2 days to 1 month, depending on the techniques used.

Cost. Costs will vary with the intensity of the sampling techniques used. Costs at SRS were high because of the redundancy built into the sampling that was needed to develop the data on the reliability of individual monitoring techniques. Costs for a more focused effort would be lower. Sample costs vary from less than $100 to greater than $500.

PROJECTED PERFORMANCE

This technology is expected to demonstrate the effectiveness of bioremediation and give feedback during operations to increase the effectiveness of bioremediation technologies.

WASTE APPLICABILITY

This technology is applicable to the monitoring of populations that can degrade organic compounds.

STATUS

Materials and equipment are off-the-shelf, except for the DNA probes that are not commercially available.

REGULATORY CONSIDERATIONS

Ecological impacts are not anticipated from users of this technology. The potential exists for exposure to solvents and low-levels of radionuclides.

POTENTIAL COMMERCIAL APPLICATIONS

This technology has potential commercial applications at any site undergoing bioremediation.

BASELINE TECHNOLOGY

The baseline technology is mass-balance measurements that are limited in monitoring critical changes in the microbial populations.

INTELECTUAL PROPERTY

Patent Ownership: None

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ON-SITE ANALYSIS OF METALS IN SOILS USING STRIPPING VOLTAMMETRY

Pacific Northwest Laboratory

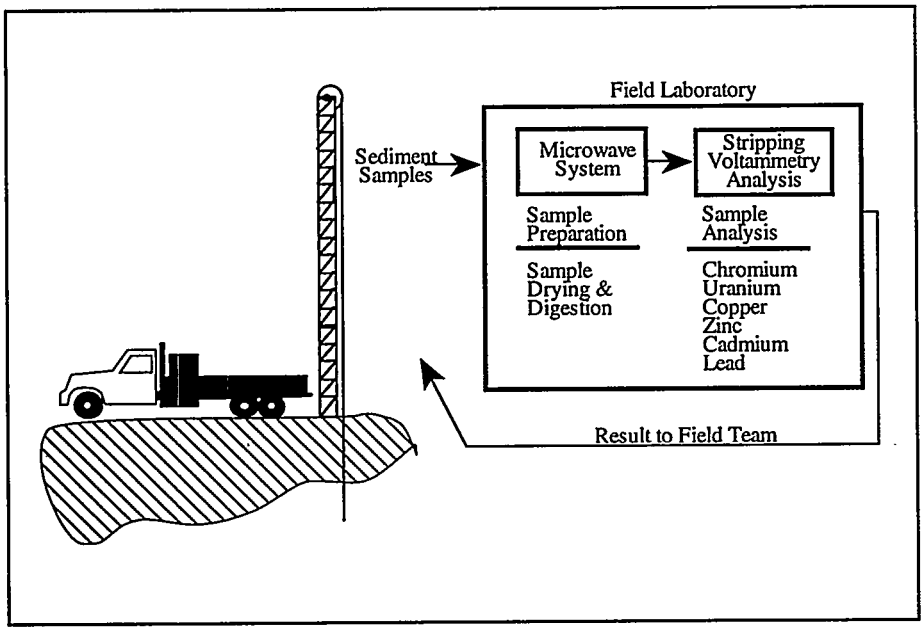
DESCRIPTION

Stripping Analysis (SA) has been demonstrated in the field to measure the concentrations of leachable chromium (Cr), lead, calcium, copper, nickel, zinc, and cobalt in soils and sediments. The demonstration is being done at the Chemical Waste Landfill (CWL) at Sandia National Laboratories (SNL) in Albuquerque, NM. Samples are taken from beneath the CWL during drilling operations and analyzed in a portable laboratory at the site. If successful, this technique will allow decisions to be made in the field during characterization and remedial activities by determining the areal and vertical extent of contamination within hours of the sampling.

Stripping voltammetry has been used for several decades in the laboratory. Recent advances associated with nonelectrolyte (i.e., adsorptive) pre-concentration schemes and the development of miniaturized electrodes have increased the potential for practical use of the technique in the field.

In this program, the samples are dried with a microwave system and digested with a nitric acid leachate. The resulting solution is diluted with distilled or deionized water and analyzed by the SA technique. For a particular analysis, an electrode(s) is immersed in the solution. The voltammetric response (potential change) of the adsorbed species during the stripping is a function of the concentration of the specie on the electrode. This, in turn, is directly related to the bulk concentration of the specie in the solution through the adsorption isotherm.

The SA equipment uses 10 A at 120 VAC (120 W). Ten square feet of bench space and a vent hood are also required for operations in the field. Since a different coating procedure must be used on the electrode for a particular specie, SA is not suitable for pre-screening a site to identify the contaminants, but it is capable of measuring the concentration of select contaminants after they have been identified by other techniques or from a prior knowledge.



Adsorptive Stripping Voltammetry

TECHNICAL PERFORMANCE

The SA system has a detection limit of 10^{-10} to 10^{-11} moles/l. Concentrations of chromium

and uranium have been measured in solution to 1 ppb in both laboratory and field testing.

The concentrations of two or three trace metals may be measured simultaneously from a single analysis. A four-hour test is typical for obtaining the results in the field for 12 samples. However, the time required for a single analysis is very test-specific. For example, 20 to 30 minutes were required to determine the concentrations of Cr(III) and Cr(VI) from a single sample in a field test. However, when only Cr(VI) is measured, only eight minutes were required to measure the total concentration of chromium.

Cost. Start-up cost depends on the analytical requirements for the specific task. The cost for the stripping voltammetry equipment would range from $5K for single-element to $37K for multi-element, multi-sampling capability. A microwave digestion unit is approximately $12K. The operations and maintenance costs are dominated by the need for two operators, one of whom may be a technician. The annual cost for chemicals and supplies ranges from $1K to $2K. Life-cycle costs without labor would vary from $20K to $50K for a single ASV system.

PROJECTED PERFORMANCE

The ASV technique has the potential to measure trace concentrations of approximately 14 metals in addition to those associated with the CWL as shown in the table below. Improvements in the detection limits for some metals may be anticipated.

Modifications to the electrodes and processes have also resulted in demonstrated capability of measuring trace levels of electroactive drugs (anti-cancer antibiotics, cardiac glycosides, etc.) and large macromolecules such as insulin and ferritin.

The following table shows trace metals measured in laboratory and field tests.

Field Tests at CWL	**Laboratory Testing[1,2]**	
Chromium (Cr)[3]	Aluminum (Al)	Technetium (Tc)
Cadmium (Cd)[4]	Iron (Fe)	Thorium (Th)
Copper (Cu)[4]	Gold (Au)	Tin (Sn)
Lead (Pb)[4]	Molybdenum (Mo)	Titanium (Ti)
Nickel (Ni)[4]	Palladium (Pd)	Uranium (U)
Zinc (Zn)[4]	Platinum (Pt)	Vanadium (Va)
-	Ruthenium (Ru)	Yttrium (Y)

1. Reference 4.
2. Includes metals tested in the field.
3. Measured at CWL in 1992.
4. Measured at CWL in 1993.

WASTE APPLICABILITY

The ASV technique is being developed specifically to measure trace concentrations of metals in soils and sediments. However, it will probably be extended to make contaminant measurements of radioactive mixed-waste materials in the Mixed Waste Landfill (MWL) at SNL. It could also be used to analyze the contaminants in ground and reactor cooling water and in rain.

STATUS

The concentration of chromium was measured to the 1 ppb level, and the ability to distinguish between Cr(III) and Cr(VI) was demonstrated during the field tests in June 1992 at the CWL site. During FY 93, the ASV technique was scheduled for extension to the other four trace metals listed in the table. Shortly thereafter, the technology should be ready for transfer to a commercial contractor.

REGULATORY CONSIDERATIONS

Dilute (1%) nitric acid and very small amounts of elemental mercury (50 ml) are contained in the 100 ml sample used for each analysis. Because of these small quantities, no environmental impacts or risks to the public are anticipated for the ASV process.

POTENTIAL COMMERCIAL APPLICATIONS

All the equipment used for the ASV analysis is "off-the-shelf," and at the conclusion of the demonstration it is planned to transfer the technology for an operational system. Thus, the ASV technique should soon be available to the commercial sector for use in measuring the concentration of metals in water, soils, and sediments.

The capabilities of the ASV system could also be extended to the metals that have been laboratory tested and are listed in the table. Additional applications in the fields of medicine and pharmacology are possible.

BASELINE TECHNOLOGY

The baseline technologies are acid digestion plus inductively coupled argon plasma (ICAP) or atomic adsorption (AA) analyses; both require the use of an off-site laboratory. In addition to being less convenient for field work than ASV, they are slower. Furthermore, they are less sensitive. For example, experiments with chromium indicated that the detection limit for the ICAP technique was an order of magnitude greater than that for ASV.

INTELLECTUAL PROPERTY

Patent Ownership: None

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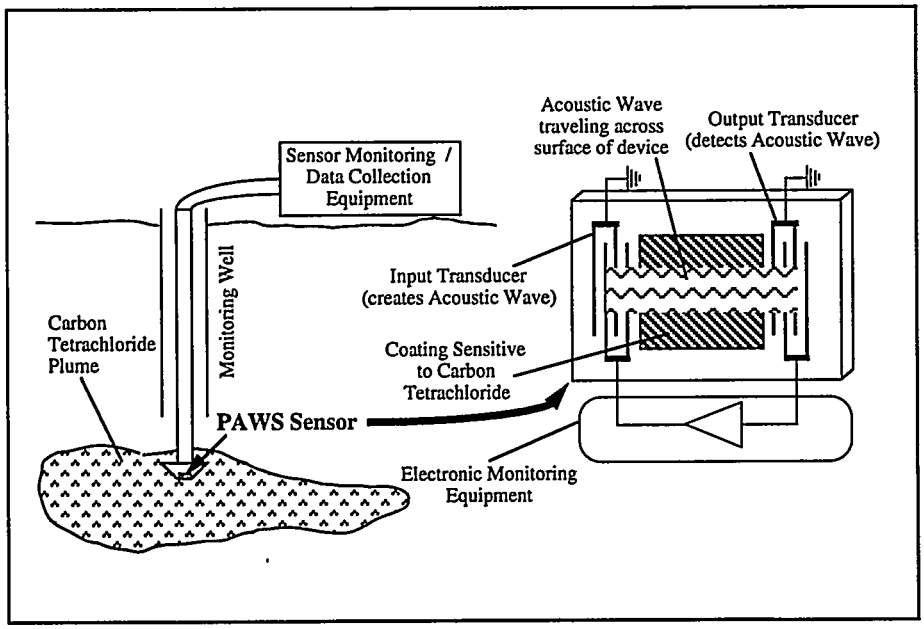
PORTABLE ACOUSTIC WAVE SENSOR

Sandia National Laboratories

DESCRIPTION

The Portable Acoustic Wave Sensor (PAWS) system is designed to provide continuous, real-time monitoring of sites for levels of chlorinated hydrocarbons and other volatile organic compounds (VOCs). Prototypes have been developed for both above-ground and down-hole applications. Future down-hole probes may be permanently placed using a technology such as a cone penetrometer. Down-hole systems are presently being used with on-site monitoring wells. Present systems monitor vapor concentrations in air or from soil samples, while future systems will be configured to monitor groundwater as well.

The PAWS systems are built around surface acoustic wave (SAW) devices coated with visco-elastic polymers. Two independent responses of the SAW sensor (wave velocity and attenuation) are measured to provide information about the chemical species absorbed by the coating. The changes in the wave velocity and attenuation occur because the film coating the sensor softens and becomes heavier when it absorbs the contaminant. Sensing is rapid and reversible, and coatings can be optimized for particular chemical selectivity and sensitivity. The complete PAWS system consists of the following: (1) two SAW devices (a sensor and a reference); (2) RF oscillator electronics to drive the devices; (3) digital interface/communications electronics; (4) gas-handling hardware to sample the environment; and (5) a notebook computer to control the hardware and display responses in real-time. For down-hole applications, a tripod and winch are used to lower the sensor system into the well, while packers above and below the sensing section are used to isolate a region of the monitoring well. A purge pump can be added to extract the contaminant out of the soil for analysis.



Schematic of a Portable Acoustic Wave Sensor

TECHNICAL PERFORMANCE

The PAWS technology has capabilities for determining both molecular species and concentration of isolated chemicals. Depending on various factors, the PAWS systems can detect and measure, in a continuous mode, certain isolated VOCs in the vapor phase down to a few parts-per-million (ppm). Accurate analysis has been demonstrated with rapid (few seconds) and reversible responses. PAWS has a wide dynamical range and

can handle high concentrations (e.g., parts per thousand) observed at some sites. Although an array of sensors is needed to characterize a mixture of chemical vapors, the PAWS systems are very accurate when monitoring isolated species; agreement with baseline instruments within 2% has been obtained. The systems maintain a very stable calibration (within 3% over 50 days) and do not require any maintenance, which makes them easy to operate and maintain. During in situ monitoring, down-hole sensors can be automated to provide chemical information on the distribution and concentration of contaminants to site-remediation workers.

Although PAWS is faster, cheaper, and as safe as a gas chromatograph (GC) or infrared (IR) analyzer, for analysis of chemical mixtures, PAWS will not provide all of the information that can currently be acquired with a GC or IR analyzer. When used for real-time analysis, the sensitivity is not as good as in some of the alternative techniques. Like most of the alternatives, calibration of PAWS is compound-specific.

Cost. Expected cost of a single sensor system is $1K to $2K, while cost for array systems for mixture analysis are expected to range from $3K to $5K. Operation of the unit requires about 1 h/wk, and anticipated maintenance is estimated to be less than 1h/mo. Life-cycle costs will depend upon use, frequency, and volume of data required.

PROJECTED PERFORMANCE

Future developments include hardware miniaturization, development of coatings and pattern recognition for simultaneous characterization of multiple-chemical species, decreasing in the detection levels based upon improved coatings and environmental-sampling techniques, and the development and evaluation of semipermeable membranes and preconcentrators for corrosive environments and soil and groundwater analysis.

WASTE APPLICABILITY

This field-monitoring system is applicable to the quantitative detection of volatile organic compounds in soil, vapor, and water. Targeted contaminants include carbon tetrachloride (CCl_4) (at Hanford) and trichloroethylene (TCE) (at Savannah River Site).

STATUS

PAWS prototypes for above-ground and in situ vadose zone for a single contaminant are currently available. Above-ground mixture analysis prototypes based on sensor arrays will be available in 1 to 2 years.

REGULATORY CONSIDERATIONS

In some situations, the sensor may not be sensitive enough. For example, the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for CCl_4 may be lowered to 2 ppm (the current PAWS detection level for CCl_4 is 10 ppm).

POTENTIAL COMMERCIAL APPLICATIONS

This technology has the potential for many industrial applications for real-time, on-line monitoring of exhaust stacks or work-place environments. Sensors can also be integrated into on-line process control systems to optimize process operations.

BASELINE TECHNOLOGY

Grab samples and subsequent laboratory or field analysis with a GC or IR analyzer are the baseline technologies.

INTELLECTUAL PROPERTY

Patent Ownership: DOE and Sandia National Laboratories

Patent Nos.: 5,076,094 and 5,224,972

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PROMPT FISSION NEUTRON LOGGING SYSTEM

RUST Geotech, Incorporated

DESCRIPTION

The Prompt Fission Neutron (PFN) Logging System is also termed Integrated Borehole Geophysical System for Contaminant Identification. This technology is applied for in situ detection of fissile materials, principally U-235 and Pu-239, in soil and rock media surrounding the borehole. It has been reported that PFN probes can also be used as porosity devices or moisture gages. This technology addresses the need for better methods to characterize subsurface geohydraulic features, for in situ methods of characterizing contaminants, and for understanding subsurface contaminant behavior.

The logging system is self-contained and operates as a stand-alone instrument. During field operations, the probe is lowered into a borehole and data are collected. These data are stored digitally, processed rudimentarily, and displayed to permit quality assurance and initial interpretation. At a later time, the data are processed in detail and interpreted. To generate PFN data, the instrument generates a short burst of neutrons using a linear accelerator in a sealed tube within the probe. The neutrons penetrate the soil and rock surrounding the borehole but are slowed down and eventually captured by other atoms. The atoms that capture neutrons, U-235 and Pu-239 (and other elements with comparable fission cross sections), spontaneously undergo fission, producing additional neutrons. These additional neutrons are counted by a detector that is shielded so that it detects only the energetic neutrons from fission. The observed count-rate, which varies as a function of time after each neutron burst, is related to the partial density of fissionable elements in the soil. Epithermal neutrons detected after 200 microseconds are from fission reactions.

An advantage of PFN technology is that it provides a near-continuous profile of contaminants as a function of position along the borehole. Another advantage is that it analyzes some three orders of magnitude larger volume of material than an individual borehole sample. Furthermore, PFN logging provides the opportunity to repeat measurements in the same borehole, year after year, for monitoring purposes. PFN logging can produce in situ assay data in a fraction of the time it takes to submit all of the samples from a borehole to an analytical laboratory and obtain results. With the PFN Logging System, the time needed to log the hole is a few hours, and results are available instantly. On the other hand, the PFN system is not as sensitive in providing assays for waste concentrations as is possible in the laboratory.

TECHNICAL PERFORMANCE

Design. The PFN probe is approximately 11-ft long and is designed to bombard a 2-ft radius immediately around the borehole with a burst of 14 MeV neutrons at a repetition rate of 100/s. A 100-ft borehole could be logged in about 3 hours. PFN logging requires a cased borehole with a minimum inner diameter of 5 in. Vertical-direction data-point spacings are typically 0.1-0.2 ft. PFN would analyze 1,000 times greater volume than borehole sampling. The lower detection limit of the system is about 1 nCi/g Pu-239. (However, some regulatory limits are in the range of pCi/g.)

Cost. It is estimated that a cased, 100-ft deep borehole with an uncontaminated interior could be logged for $1,000 as part of a multiple-hole program. (This is compared to $100,000 for borehole sampling

and laboratory analysis of a 100-ft borehole with 20 samples taken at 5-ft intervals.)

PROJECTED PERFORMANCE

A field demonstration was completed in September 1993. The system performed within specifications. Performance is not expected to improve significantly.

WASTE APPLICABILITY

This measurement technique is applicable for in situ detection and quantification of fissile materials, principally U-235 and Pu-239, in soil and rock surrounding a cased borehole.

STATUS

Funding for further development of this system is not available in FY94. Further enhancements will be made contingent on the availability of funding.

REGULATORY CONSIDERATIONS

Of concern is the potential for human exposure to neutron bursts. Appropriate field procedures eliminate this risk because no radiation is generated until power is applied to the probe. The use of this tool in and around aquifers would be of concern if the tool with the neutron source were lost in the borehole and abandoned.

POTENTIAL COMMERCIAL APPLICATIONS

This technology could be used in mining and exploration activities to log and assay potential uranium deposits.

BASELINE TECHNOLOGY

The baseline technology is borehole sampling and laboratory analysis. While the laboratory analysis could detect fissile materials present in smaller concentrations than the PFN lower detection limit and give a full radiologic spectrum assay, laboratory analysis is much more expensive per datum point and analyzes a smaller volume per borehole. PFN logging is not intended to replace requisite sampling and analysis but to reduce the amount of sampling needed. PFN provides an in situ technique that would be useful to provide more datum point details to a borehole sampling program. It also provides a relatively inexpensive method for borehole monitoring.

INTELLECTUAL PROPERTY

The Department of Energy owns the intellectual property.

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Industrial/University Partners
None at present.

REFERENCES

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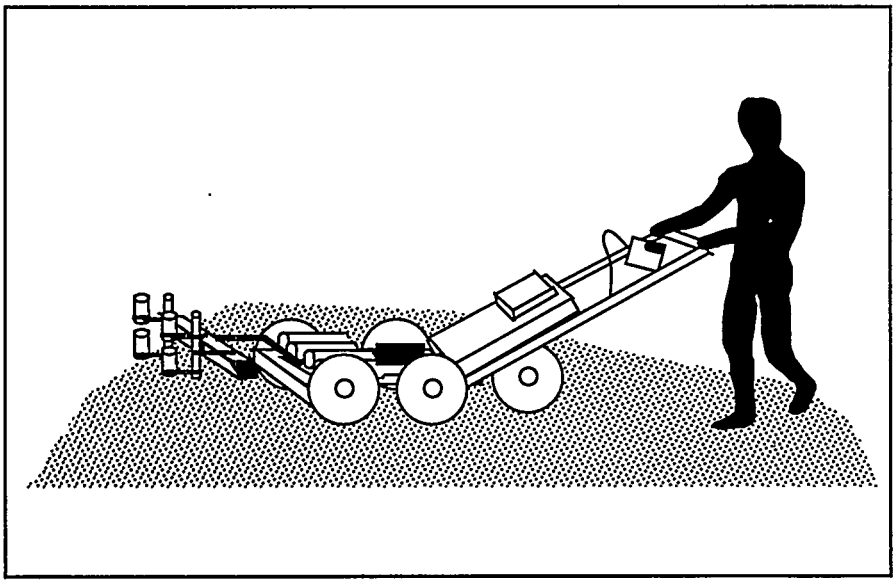
RAPID GEOPHYSICAL SURVEYOR

Idaho National Engineering Laboratory

DESCRIPTION

The Rapid Geophysical Surveyor (RGS) is a passive, nonintrusive measurement system that automates the collection of high-spatial-resolution geophysical data. Closely spaced data are required to adequately characterize complex buried-waste areas commonly found in the Department of Energy, Department of Defense, and private sectors. The system measures and associates the local magnetic field with precision positioning in a systematic fashion. Variations in the Earth's local magnetic field are indicative of subsurface ferromagnetic material which is a common component of buried wastes.

The RGS consists of magnetic-field sensors, a calibrated measuring wheel, and a microprocessor-based data logger mounted on a hand-pushed, non-ferrous vehicle. The data logger utilizes menu-driven software so that the key field survey parameters can be configured by the user. The user is required to push a 20-lb cart to collect magnetic data. Magnetic data are automatically collected and stored at user-specified intervals as close as 2-in. apart along survey profile lines. These data form a high-resolution database capable of locating individual objects and potentially determining object orientation, shape, and depth to burial. There is no input required for this passive system, and the output of the RGS is a set of spatially correlated magnetic data.



Rapid Geophysical Surveyor

TECHNICAL PERFORMANCE

Field Demonstration. The RGS was initially field tested in September of 1992 at the Subsurface Disposal Area (SDA) on the Idaho National Engineering Laboratory (INEL). The system functioned so well that a production survey of the Pit 9 area within the SDA was performed in October of 1992 with the prototype RGS. Since then, the RGS has been used on a number of sites within the INEL and for outside agencies, including the Department of Defense and the Environmental Protection Agency. The objectives of the magnetic surveys done with the RGS have varied in each case. The RGS has been successfully used to locate waste trenches and pits, underground storage tanks, and underground utilities. The RGS has been used with success in isolated areas and in the proximity of buildings and above-ground utilities where magnetic noise is a concern for conventional magnetic instruments and surveys.

The RGS has demonstrated data-collection rates of up to 30,000 data points per hour compared to a maximum of about 200 data points per hour for baseline, hand-held magnetometer technologies. Also, since the RGS automates data collection as compared to the tedious nature of manual data-collection techniques, errors caused by human fatigue are greatly reduced, improving field efficiency and overall accuracy. The RGS is a self-contained unit, drawing all power from a single 12-volt, 7 amp-hour gel cell battery that supports 8 hours of continuous operation before a battery recharge is required.

Cost. Survey cost with the RGS is proportional to site size and is essentially the man-hours required to perform the survey, as the capital investment in the equipment is very small. The initial development cost of the RGS was $80K. It is anticipated that the cost of a commercial version of the RGS would be well under $10K.

PROJECTED PERFORMANCE

Potential RGS enhancements within the DOE complex include the addition of a remote absolute positioning system that would preclude the use of the measuring wheel to track relative distance travelled by the RGS. A number of technologies have potential application, such as microwave interferometry, ultrasonics, optical techniques, and global-positioning systems.

WASTE APPLICABILITY

The RGS is applicable to all problems where ferromagnetic material is included in the waste search target. This includes waste pits and trenches in landfill scenarios and underwater applications. This concept can also be expanded to include other nonintrusive geophysical instruments such as electromagnetic devices.

STATUS

The RGS has been commercialized and is available to the private sector as a service. The system may be available for purchase at some time in the future, depending on commercial demand.

REGULATORY CONSIDERATIONS

Regulatory issues are expected to be minimal. Because this is a nonintrusive characterization technique, there is no subsurface disturbance or process waste, and little or no decontamination of equipment is anticipated by using RGS. There are no health hazards originating from the RGS itself; however, exposure to hazardous materials is possible directly from survey sites. The RGS concept sets a new standard for geophysical surveys, and it is conceivable that this new standard may be incorporated into the EPA standard practices for environmental surveys.

POTENTIAL COMMERCIAL APPLICATIONS

The RGS has been commercialized. Expected commercial applications for the RGS include underground storage-tank detection and location, pre-transaction real-estate environmental surveys, underground-utility location, and industrial-site environmental surveys.

BASELINE TECHNOLOGY

Hand-held instrumentation represents the current method for collecting magnetic and electromagnetic geophysical data. A hand-positioned magnetometer system is labor-intensive to use. In contrast, the RGS

can perform geophysical magnetic surveys more quickly (30 to 300 times faster) and more economically ($.25 versus $5 per datum point) than can handheld instruments. The RGS raises the standard for environmental surveys by providing the ability to collect spatially dense data sets at an affordable cost. To date, cost has been the primary concern and limitation when planning and budgeting environmental surveys, especially in the private sector.

INTELLECTUAL PROPERTY

A patent disclosure has been made.

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None at present.

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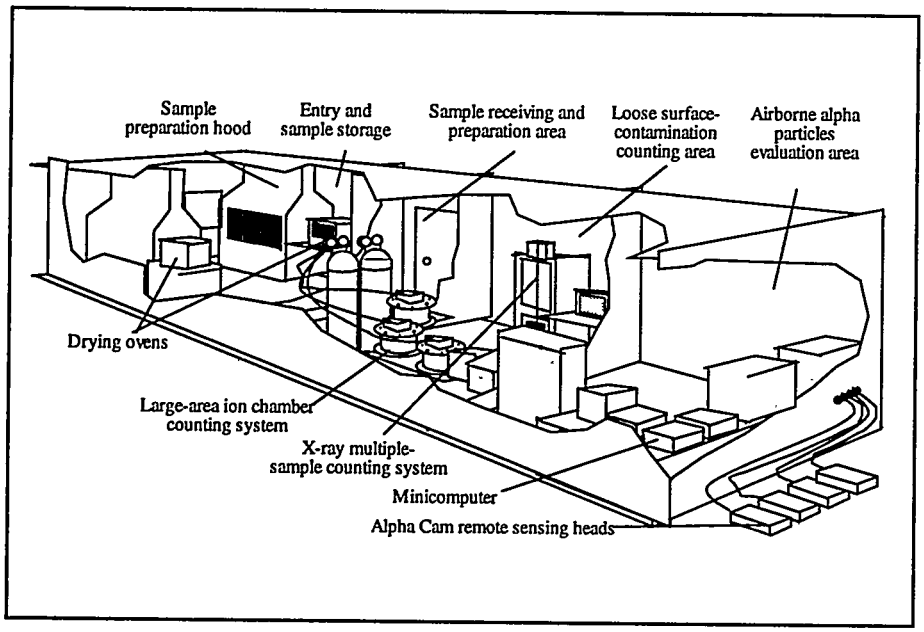
RAPID TRANSURANIC MONITORING LABORATORY

Idaho National Engineering Laboratory

DESCRIPTION

At the Idaho National Engineering Laboratory (INEL), there are 2M ft^3 of transuranic waste commingled with 8 to 10M ft^3 of soil. Retrieval and treatment of this material is one of the final disposition options being considered. The transuranic contaminants, such as oxides of plutonium and americium, can become attached to small soil particles during the excavation process or during internment because of deterioration of the original waste containers, subsidence, and backfill. Since retrieval at INEL and other arid sites would generate considerable dust, control of the potentially contaminated dust spread is mandatory, primarily because of the extremely low levels of uptake allowed (tenths of mg.). A contamination-control strategy involves ventilation, dust control, naturally occurring moisture control in the soil/waste mixture, and rapid monitoring to assess the success of the scheme.

The Rapid Transuranic Monitoring Laboratory (RTML) is a mobile laboratory developed at INEL for use in characterizing low-level radiological source terms at buried radioactive waste remediation sites. The RTML consists of two separate trailers that are powered from portable 30 and 50 kW diesel generators. One trailer houses the sample preparation laboratory that is equipped with a Class A fume hood, a drying oven, sieving equipment, two analytical balances, and sample containers. The second trailer houses the germanium photon spectrometer equipped with an automatic sample changer, two ionization-chamber alpha spectrometers, and a VAX 4000-series computer that controls operation, analyzes spectral data acquired by the spectrometers, and displays and generates the analysis results reports. The RTML is also equipped with four alpha continuous air monitors (CAMs). The alpha CAMs can be operated up to 200m from the trailer.



Rapid Transuranic Monitoring Laboratory

TECHNICAL PERFORMANCE

During June 1993, the RTML trailers were moved to a location adjacent to the Cold Test Pit (CTP) at INEL's Radioactive Waste Management Complex (RWMC). Four alpha CAMs were installed inside the tent enclosing the CTP. Before the field demonstration, 20 soil standards containing known activities of ^{239}Pu, ^{241}Am, ^{60}Co, and/or ^{137}Cs were prepared for the photon and alpha spectrom-

eters. Soil, smear, and air filter samples were collected from the pit, prepared for analysis in the sample preparation trailer, and analyzed using the RTML photon and alpha spectrometers. Air inside the tent enclosing the pit was monitored using the four RTML alpha CAMs. During the field test, these prepared blind soil standards were randomly distributed among prepared CTP soil samples before delivery to the RTML analysis trailer. Soil samples collected from the CTP were prepared for analysis by laboratory technicians who had no previous experience with the present sample preparation procedures. The same individuals also became proficient in operating the photon and ionization-chamber spectrometers after only one day of training. Over 300 samples were analyzed by photon spectrometry, and 136 samples were analyzed by ionization chamber spectrometry during the field test. Seventy-nine samples were analyzed during a 24-hour period with the photon spectrometer. In a 5-hour period of continuous work, 33 prepared samples were analyzed with the two ionization-chamber alpha spectrometers for an average rate of 6 samples per hour. All spectral analyses of the photon data were performed automatically with no input from the operator beyond basic simple parameters. No positive results were obtained for either the 143 CTP soil samples analyzed by photon spectrometry or for the 96 CTP soil samples analyzed by ionization chamber alpha spectrometry. Each of the 96 analyses of the 20 blind soil standards performed by photon spectrometry identified and quantified one or more of the four radionuclides present in the standards. The concentration of ^{239}Pu was quantified by all photon spectrometry analyses but two, and the concentration of ^{241}Am was quantified in all cases by both types of spectrometry. Concentrations of ^{239}Pu measured by ionization-chamber alpha spectrometry showed excellent agreement with the known values within the statistics of the measurements for 10-minute counts on 100-mg samples. Of the 40 measurements made on the blind soil standards, 33 measurements (83%) agreed with the known values within two standard deviations of the difference, and the remaining seven measurements were within three standard deviations. The demonstration showed that powering the RTML with portable generators did not introduce noticeable electrical or microphonic noise. Spectral resolution, instrument background count rates, and lower limit of detection (LLD) concentrations for the analytical instruments remained the same as when the RTML was powered from plant power. Under field conditions, LLD concentrations for ^{239}Pu, ^{241}Am, ^{60}Co, and ^{137}Cs by both types of spectrometry, using a 15-minute count time, were confirmed to be 40, 1, 5, and 5 pCi/g, respectively. LLD concentrations for ^{239}Pu and ^{241}Am by ionization chamber alpha spectrometry were both 40 pCi/g for a 10-minute count.

Analyzed samples can be characterized to tens of pCi/g for soils, smears, and filters, and to 1-DAC (a DAC h refers to the maximum permissible concentration of plutonium in air that can be measured in a one-hour sampling time) for continuous air monitoring. The RTM unit can measure isotopic plutonium at 20 pCi/g for 15 min. counts. This rapid in-field measurement allows up to 100 samples of soils/filters/smears to be analyzed per day per trailer. For an environmental restoration project such as a pit retrieval, 100 samples per day should be adequate to track contamination levels, thereby supplying an essentially on-line tracking capability. A true "on-line" tracking of ^{239}Pu content is presently not possible.

Cost. RTMLs can be procured for $500K. Operations and maintenance costs include four technicians and 10% time assistance from scientists. Life-cycle costs have not been estimated.

PROJECTED PERFORMANCE

In order to augment RTML analysis capabilities, document RTML instrumentation and analysis methodologies, and prepare the RTML for routine use by Environmental Management, the following work has been recommended for FY-94:

- A Beta detector for ^{90}Sr
- Alpha Spectral Analysis
- Photon Spectrum Analysis Code
- Peer-Reviewed Journal Articles
- Bar Code-Based Sample Analysis and Logging Database Code
- Software Configuration and Management Plan
- Quality Assurance/Quality Control Program
- Sample Containers for Photon Analysis Spectrometer
- Spare Equipment

WASTE APPLICABILITY

The RTM unit monitors plutonium, americium, any alpha emitter, and the entire gamma spectrum from X-rays to CO-60 and Cs-137 in soils, fallout coupons, filters, air, and liquids.

STATUS

The RTM unit was field deployable in 1994.

REGULATORY CONSIDERATIONS

Ecological impacts are not anticipated from use of the RTM unit. Samples for the RTM unit will be standard health-physics wrapped and will be prepared under a Class A hood.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include monitoring of radioactive contaminated retrieval areas and separation, processing, and storage systems. The RTML could also be applied in accident mitigation.

BASELINE TECHNOLOGY

The baseline for rapid monitoring during retrieval is "in laboratory" analysis and health-physics hand-held instruments. Hand-held instruments can provide gross alpha measurements on surface soils at the 5,000 - 10,000 pCi/g levels in minutes. Laboratory measurements can provide 4 samples per radiochemist per day at the 0.2 pCi/g level. Alpha CAMs "off the shelf" currently provide about 80 DAC - h sensitivities.

INTELLECTUAL PROPERTY

Patent Ownership: EG&G Idaho, Inc.

Patent Number: S-71-122, "A System to Control Contamination During Retrieval of Buried TRU Waste."

A Cooperative Research and Development Agreement and a licensing agreement were signed in May 1994 with Enseco, Inc. of Kirkland, WA.

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Industrial Partners
Ordella; Oak Ridge, TN
Enseco; Kirkland, WA

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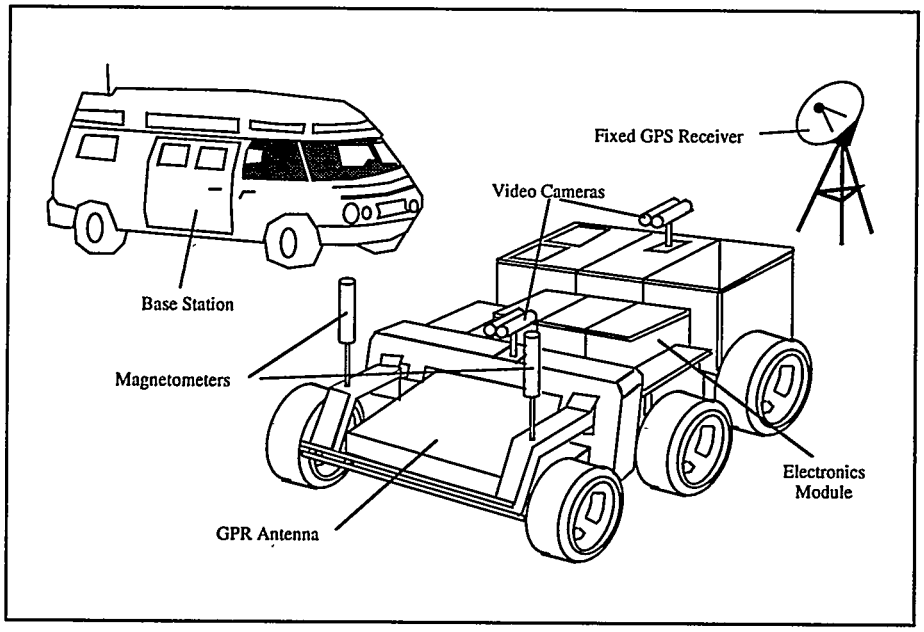
REMOTE CHARACTERIZATION SYSTEM

Idaho National Engineering Laboratory and
Pacific Northwest Laboratory

DESCRIPTION

The Department of Energy (DOE) has developed a Remote Characterization System (RCS) to address hazardous operational problems by using unmanned vehicles and remotely controlled instruments in site characterization surveys. The RCS, which is a hardware system developed under the Buried Waste Robotics Program (BWRP), includes a unique low-signature (nonferrous) survey vehicle, a high-level control station, a satellite-based (navigational/tracking) Global Positioning System (GPS), and a suite of geophysical sensors.



Remote Characterization System

The purpose of the RCS is to deliver several geophysical sensors remotely to a buried-waste site on one platform, obtain data from these sensors via a radio-frequency telemetry link, and provide accurate subsurface maps of the waste deposits and pit and trench boundaries. The targeted contaminants are metallic and nonmetallic waste, volatile organic compounds (VOCs), radionuclides, and other constituents. Initial nonintrusive characterization of buried waste is vital to determine the exact location of pit and trench boundaries, hot spots, radiation levels, and depths to the waste level and the underlying geological layers. This RCS presents an alternative characterization technique to allow improved data quality through automated data acquisition, improved data display for interpretation, and increased safety to personnel.

The Low-Signature Vehicle (LSV) is constructed largely of non-metallic and nonferrous materials to minimize its interference with the on-board geophysical sensors. The vehicle is self-propelled and guided by a remote base station. The high-level control station includes three 19-in. monitors that provide stereo visual display to the vehicle operator and keyboard- or joystick-operated controls. The full range of sensors to be supported by this vehicle and its instrument package has not yet been defined, but it will include ground penetrating radar (GPR), a metal detector, a magnetometer, an induction-type ground conductivity sensor, and a radiological sensor.

A differential, kinematic, GPS-based subsystem has been developed as a primary means of tracking the vehicle. The subsystem uses a fixed-reference antenna and an LSV-mounted antenna. It uses signals

from four or more earth-orbiting satellites to produce real-time position coordinates of the LSV at an update rate of 5/s and with an absolute accuracy of ±50 cm.

TECHNICAL PERFORMANCE

Field Demonstration. A field demonstration of the prototype RCS was performed in June 1993 at an Idaho National Engineering Laboratory (INEL) buried-waste test site. The LSV has a 20-hp, gasoline-powered, two-cylinder engine with an average fuel consumption of 1 gal/hr, and there is a 12-V, 40-A alternator mounted on the rear section of the chassis. The vehicle has a six-wheel design with modified skid steering such that it can turn in place; however, in its normal operating mode, it traverses the survey area in both the forward and reverse directions, thereby eliminating the need to make frequent turns. The vehicle's ground clearance is 8 in., but the clearable obstacle height is approximately 4 in. when the current skid-mounted GPR antenna is used. The LSV operates at speeds of up to 6 ft/s (4 mph). The base station requires 12-kW of electrical power to operate the equipment and to heat or cool the van. The GPS navigation/tracking subsystem provides position coordinates with an accuracy of ±15 cm with post processing of the recorded data. The INEL demonstration and other field tests have included the successful operation of a ground-penetrating radar sensor, magnetometers, an electromagnetic induction sensor [EM31], a radiation detector, and a chemical sensor. At a typical site with a moderately rough ground surface, the prototype system can perform a site characterization survey at a rate of approximately .5 acre/hr with 100% coverage. This survey rate can be doubled if the ground surface is smooth, and can be substantially increased if 100% coverage is not required.

Cost. The prototype system is valued at approximately $550K.

PROJECTED PERFORMANCE

The prototype RCS has proven the concept of a low-signature vehicle as a remotely controlled platform for geophysical, radiological, and chemical sensors. An operational version of the LSV will provide a reliable, rugged, and relatively low-cost means of performing site characterization surveys safely, efficiently, and accurately. Sensors designed for vehicle mounting and remote operation will provide sensitivity and target-detection capabilities that are equal to or better than those of man-operated systems. New GPS technology will provide real-time navigation/tracking accuracy of a few centimeters. Software to implement automated or semi-automated operation will make the system more efficient and will permit 8-hr. survey missions.

WASTE APPLICABILITY

RCS is applicable to metallic and nonmetallic wastes, VOCs, radionuclides, and other types of contamination; a wide variety of sensors could be mounted on the Remote Characterization System.

STATUS

Work is continuing in FY94 to upgrade and test mechanical, electronic, and sensor components of the prototype RCS. A new ground-penetrating radar system that has been designed specifically for remotely controlled operations will be mounted on the LSV. Field tests will be performed at several sites. Transfer of this technology to private industry is proposed for FY95.

REGULATORY CONSIDERATIONS

No environmental or ecological impacts are anticipated from the use of this nonintrusive survey ve-

hicle. This characterization system is remotely operated and eliminates worker exposure to hazardous environments.

POTENTIAL COMMERCIAL APPLICATIONS

The potential applications are very broad. It is proposed that this survey vehicle could be incorporated into all stages of a remedial operation. Potential applications include remote support of domestic or foreign hazardous and radioactive cleanup operations (e.g., buried-waste landfills, nuclear-reactor accidents, and hazardous or physically unstable mine-tunnel investigations), rapid property survey, terrestrial topography, and lunar or Mars logging and exploration.

BASELINE TECHNOLOGY

The baseline technologies are hand-held instrumentation techniques. The use of remotely controlled devices removes operators from hazardous environments and increases the speed of operations, thus reducing overall characterization and remediation costs.

INTELLECTUAL PROPERTY

The patent is owned by DOE and the Department of Defense.

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Industrial/University Partners
None at present.

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RESONANTSONIC℠ DRILLING

Westinghouse Hanford Company

DESCRIPTION

ResonantSonic℠ drilling is being used in the environmental industry to drill faster, cheaper, and safer that conventional drilling methodologies. ResonantSonic℠ is a registered service mark of the Water Development Corporation, Woodland, California. The ResonantSonic℠ drilling method requires no mud, air, or water for rapid penetration through geologic materials ranging from rock and clay to sand and boulders. The specialized drill head imparts high-frequency vibrations into a steel drill pipe, creating a drilling action which allows the retrieval of continuous, undisturbed cores. An added benefit is that the method can be used for angle drilling.

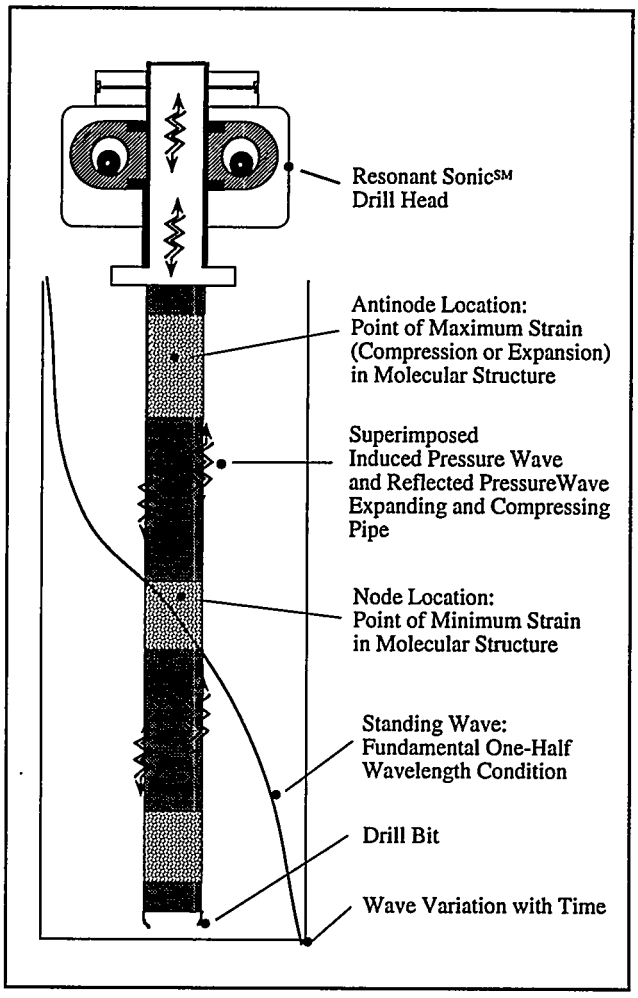

Figure 1. ResonantSonic℠ Energy

The ResonantSonic℠ drilling method uses a hydraulic drill head that transmits high-frequency sinusoidal pressure waves through a steel drill pipe to create a cutting action at the bit face. The pressure waves are created by counter-rotating, offset-balance roller weights located in the sonic drill head as shown in Figure 1. The drill head is designed to operate at frequencies close to the natural frequency of the steel drill column, causing the column to vibrate elastically along its longitudinal axis (see Figure 2.). In the resonant condition, the drill pipe acts like a flywheel, storing energy for its intermittent release at many times the input level. Operating frequencies exceeding 150 Hz and forces ranging up to 1,112kN (250,000 lbs-force) per cycle are reliably generated by WDC's newly designed ResonantSonic℠ drill heads.

There are several ways to perform the sonic drilling activity. The method which yields the coolest core and a representation of near in situ quality core is the dual-rod approach. By coupling the sonic drill head to the drill pipe, the cutting action developed at the bit face yields a continuous core of formation material moving into the core barrel. One drill stem affixes to the core barrel, and the other drill rod encapsulates the core barrel. Both drill rods can be resonated simultaneously or independently, one ahead of the other rod, depending upon formation conditions. ResonantSonic℠ drilling proceeds in five-foot, ten-foot, twenty-foot, or longer core runs as dictated by sampling requirements. Once the desired amount of core is in the barrel, the inner rod and core barrel are removed in sections from the borehole, and the core

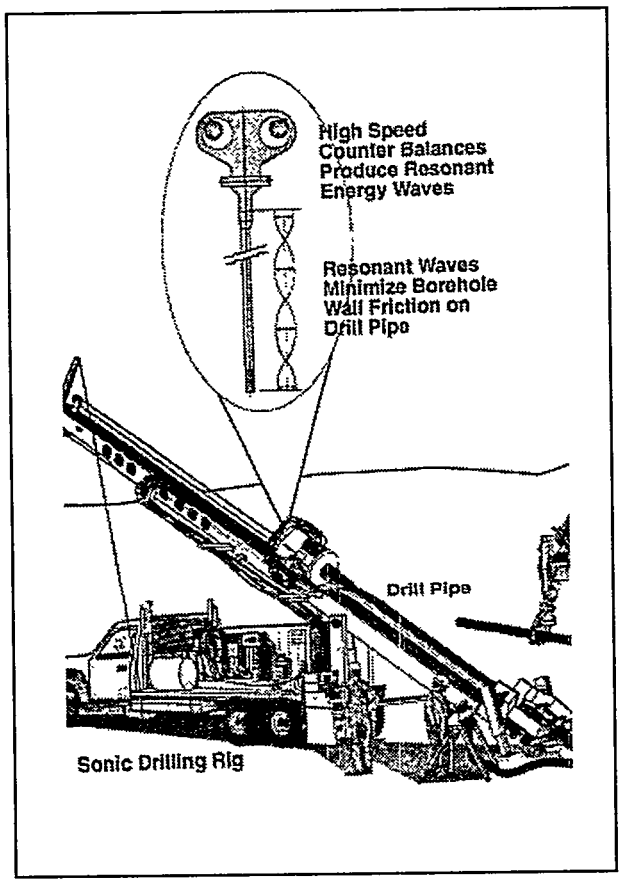

Figure 2. Schematic of ResonantSonic℠ Drilling

is retrieved. The outer drill pipe remains in place to support the borehole while the core is being removed.

Because of the high forces developed by the resonant drill head and the external flush nature of the drill pipe, formation material displaced by the cutting face of the bit is forced either into the borehole wall or into the core barrel, resulting in no cuttings generated in the drilling process. In order to enhance core quality, little, if any, rotation of the drill rods is used in this method.

TECHNICAL PERFORMANCE

Sonic drilling generally produces only the cored sample, and holes are drilled at double the baseline rate. Preliminary testing of sonic drilling at the Hanford site resulted in a cost reduction of approximately 15 to 25 percent over 11 holes, even though downtime from equipment failures was over 45 percent.

This technology has been successfully applied to continuous coring, monitoring well construction, and horizontal drilling activities. A demonstration of the improved system, with feedback control and component redesign for improved reliability and more rapid access, is planned.

Drill Head. Depending on the size of the sonic head, dynamic force output is 30,000 lb at 120 Hz. Power input ranges from 150 to 800HP. Rotational torque ranges from 25,500 to 40,000 in.-lb. Rotational speed is variable from 0-60 rpm.

Drill Rig. Vertical (90°) to horizontal (0°) drilling capabilities are available.

Speed of Drilling. The penetration rate of the sonic drill varies, depending on the type of formation being cut. Speeds from 1 ft/s to 0.5 ft/min are encountered when drilling loose to compact formations.

Formations. It drills any type of formation: alluvium, sands, clays, cobbles, boulders, bedrock, permafrost, caliche, and other types of formations including landfills. It is able to drill through metals, garbage, tires, wood, and concrete.

Cost/Benefits. Cost studies are currently in progress. Initial tests during 1991-92 resulted in a 20 percent cost reduction per foot.

PROJECTED PERFORMANCE

With the refinement of the sonic head, drill pipe, sampling tools, and core catchers, it is projected that the downtime can be reduced to less than 10 percent, which results in a substantial reduction in drilling costs.

WASTE APPLICABILITY

This technology is applicable for monitoring wells, vadose-zone soil-gas sampling, neutron-probe pipe installation, core sampling, and injection and extraction wells for bioremediation and/or air stripping/ vacuum extraction remediation projects. Additionally, in most conditions, closed-end tubes can be resonated into the ground to significant depths to yield no cuttings or core and to take discrete water samples or in situ cores.

STATUS

The ResonantSonic℠ method has been used in the past for projects ranging from pile driving to horizontal drilling. Current programs are utilizing the technique as a valuable tool for obtaining in situ, pristine environmental samples. In the future, this drilling technology could be used for remote, automated sampling at hazardous waste sites.

The ResonantSonic℠ technology was first developed in the 1905s by Albert Bodine, Jr. Mr. Bodine discovered how to design and build a machine that would generate high-frequency vibrations with very high-force output that would not self-destruct while passing the vibrations on to the object being resonated. In the 1970s and 1980s, Hawker Siddeley, Ltd., in Canada, made further advances to the patented drilling head and built several rigs for field application. In the forty years since its invention, traditional sonic drilling equipment has been underused, suffered reliability problems as a system, and had difficulty being accepted in the marketplace.

The Department of Energy (DOE) Office of Technology Development (OTD) and its contractors Westinghouse Hanford Company (Westinghouse Hanford) and Pacific Northwest Laboratory (PNL) and industry partner Water Development Corporation (WDC), through a cooperative research and development agreement (CRADA), are developing improvements to the ResonantSonic℠ drilling technology to enhance environmental cleanup efforts at DOE sites.

REGULATORY CONSIDERATIONS

Drilling and subsurface access regulations may vary, depending on the waste-site characteristics. Ecological impacts are minimized or eliminated by the absence of secondary waste streams. Occupational Safety and Health Administration (OSHA) regulations apply for drilling equipment operation, high noise levels, and potential contaminant exposure.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be applied to water well, natural-gas well, geothermal well, and oil well drilling. It is also useful to industries that may have soil or groundwater contamination problems. Rapid access to the subsurface, without excess soil removal or secondary waste streams, is economically desirable for such industries to determine the scope of the problem and to remediate the contamination. This method of continuous core removal is useful for other geologic studies and to the mining industry.

BASELINE TECHNOLOGY

This technology is compared to other baseline drilling methods such as hollow-stem auger and cable-tool methods which are commonly used for environmental characterization at Hanford-Test. Results indicate a 3-fold increase in penetration rates.

INTELLECTUAL PROPERTY

U.S. Patents for Resonant Sonic Drilling technologies are held by the Water Development Corporation (WDC). Patent numbers are available from the technology developer, WDC.

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SEAMIST™ BOREHOLE INSTRUMENTATION AND FLUID SAMPLING SYSTEM

Sandia National Laboratories

DESCRIPTION

SEAMIST™ is an instrumentation and fluid sampler emplacement technique designed for in situ characterization and monitoring. It uses an inverting, pneumatically deployed tubular membrane (impermeable material) to install sampling devices and instruments in boreholes.

The membrane is forced into a drilled or punched well by air pressure. The membrane descends, everts, and presses against the hole wall, providing wall support and the effect of a continuous packer. After emplacement, the entire hole wall is sealed, thus preventing ventilation of the pore space or circulation of pore water in the well. The membrane can be retrieved from the hole.

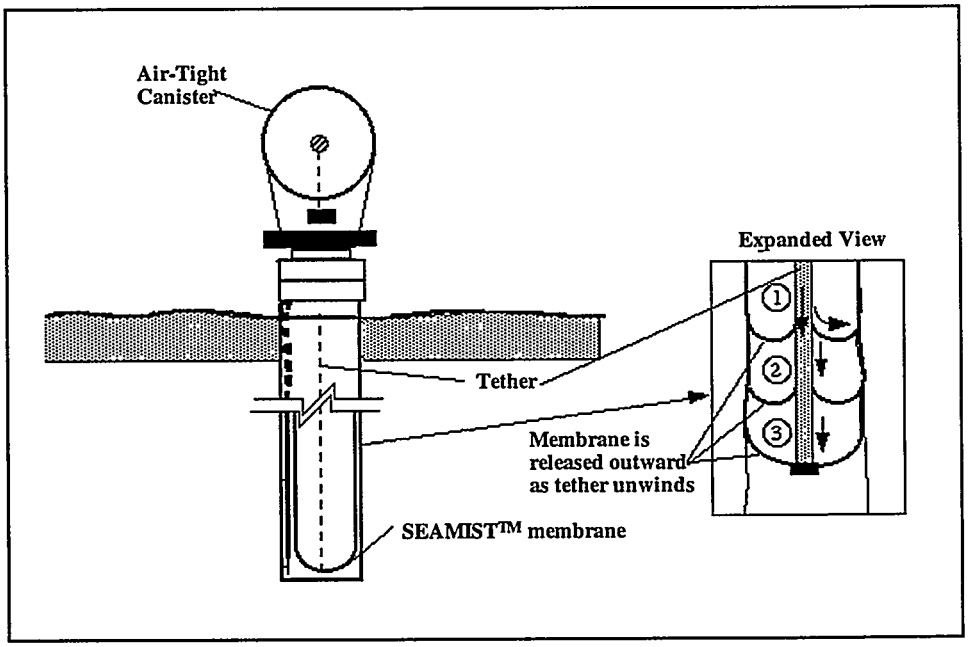
Monitoring instruments and pore fluid sampling devices are placed on the outer surface of the membrane, where they will be in contact with the hole wall. The membrane isolates each measurement location. Emplacement has been demonstrated for vertical, horizontal, and crooked or partially obstructed holes. Instruments or samplers are not dragged along the hole wall at any time.

Permanent installation of the membrane is possible by filling the membrane with grout after emplacement. Semi-permanent installation can be accomplished by filling the membrane with sand after emplacement.

The membrane can be applied to perform vadose-zone pore and fracture liquid sampling through the use of absorbent pads. Electrical resistance measurements inside the pads indicate moisture uptake. By attaching an array of absorbent pads to the membrane, high spatial resolution of the contaminant distribution is possible.

Extraction of soil-gas samples from a hole can be accomplished via tubes to surface sample collectors or Getters, such as activated-charcoal absorbers, can be attached to the membrane surface to absorb contaminants. A hybrid concept is to pull a gas sample through a charcoal filter positioned at the sampling point.

Air-permeability distribution within a soil matrix can be measured by emplacement of a membrane with



SEAMIST™ Emplacement System

several gas-sampling ports. As the gas is pulled from one port to the surface, its flow rate and measured pressure response at the adjacent ports imply a local permeability distribution.

Additional instruments can be applied, such as temperature sensors, thermocouple psychrometers, and fiber-optic sensors. Colorimetric materials can be used for visual indications of contaminant distribution.

TECHNICAL PERFORMANCE

Tritium Plume Monitoring. Two systems installed at Lawrence Livermore National Laboratory (LLNL) in 1991 are tracking the movement/concentrations of a tritiated water plume (vapor and liquid-water sampling) to 40-ft depths.

Carbon Tetrachloride Monitoring. Two emplacement systems with disposable membrane liners are in use at Hanford for carbon tetrachloride plume monitoring.

Fracture Flow Mapping and Rate Measurement. Membranes coated with liquid-indicating and wicking layers were used to map and measure brine flows underground at the Waste Isolation Pilot Plant (WIPP).

Tritium and VOC Sampling. The SEAMIST™ system transported vapor-sampling tubes and absorbent collectors 230 ft horizontally beneath an old radioactive-waste landfill at Los Alamos National Laboratory (LANL).

SNL Chemical Waste Landfill (CWL). The SEAMIST™ system transported logging tools and cameras in horizontal boreholes of up to 230 ft length and 1.75 to 4.0 in. diameters. It performed gas-sampling and permeability measurements in two boreholes of 11.5 in. diameter and 110 ft depth immediately after augering in SNL's CWL. It installed three borehole liners 110 ft long for continuous soil-gas pressure monitoring.

Vapor Sampling/Permeability Measurements. Three membranes were instrumented and installed at SRS in July 1992 for soil-vapor, vapor-pressure, and permeability measurements. Maximum depth was 130 ft, with ten sampling elevations per membrane.

Neutron Logging Tool Transport. The membrane towed a 3-lb neutron moisture-logging tool in horizontal boreholes at Los Alamos, New Mexico. Typically, four 4.5-in.-diameter holes (200-250 ft) were logged in one day, with data taken every 2 ft.

Vapor Sampling. A vapor-sampling system was installed to 90-ft depth for long-term monitoring at a commercial site in Tucson, Arizona.

Vapor Sampling in Long Horizontal Well. A SEAMIST™ membrane was installed in a 450-ft long, 4-in diameter screened well emplaced under a radiological/biological area. Seven soil-gas monitoring points were used to sense the presence of organic vapors.

Sensor Integration. Two SEAMIST™ membranes were integrated with a variety of chemical, temperature, pressure, and hydrologic sensors in a demonstration at the Chemical Waste Landfill.

Contaminant Transport Monitoring. Three SEAMIST™ membranes with vapor-sampling ports were used with an automated soil gas pressure and vapor-analysis system to monitor contaminant and tracer plume movement in the Chemical Waste Landfill. Both diffusion and barometric transport mechanisms were monitored.

Vapor Monitoring near Radioactive Waste Landfill (Los Alamos). Five vapor-sampling SEAMIST™ membranes were installed in 8-in diameter boreholes, 250 to 310 ft deep. These will provide continuous monitoring of VOCs and soil-matric potential at twelve discrete elevations per membrane.

Cost. Membrane - $500 to $10K, depending on complexity; emplacement canisters and support systems - $1K to $5K.

PROJECTED PERFORMANCE

Key performance parameters are listed below, including projections of near-term (1-3 yrs) performance.

WASTE APPLICABILITY

Demonstrated measurement/monitoring of soils contaminated with tritium, carbon tetrachloride, and volatile organic compounds (VOCs).

REGULATORY CONSIDERATIONS

Regulatory considerations are a function of where the technology will be used, the nature of contamination, and the intended application of the technology.

POTENTIAL COMMERCIAL APPLICATIONS

SEAMIST™ is commercially available for borehole lining, liquid/vapor sampling, and permeability measurements. Potential near-term applications include water sampling below the water table and large-scale vapor-plume movement experiments/monitoring. These applications would be useful to: the chemical, mining, oil, and natural gas industries; Environmental Protection Agency (EPA) and Department of Defense (DoD) cleanup operations; and various federal programs.

Performance Parameter	Demonstrated	Projected
Hole Diameter (in)	1.75 - 11.5	1.0
Hole Vertical Depth (ft)	310	>300
Hole Horizontal Length (ft)	450	>300
Vertical Deployment Speed (ft/min)	30	30
Horizontal Deployment Speed (ft/min)	30	30
No. Vapor Sampling Points/Membrane	12	30

STATUS

- Demonstrated capability to tow logging devices and cameras up to 250-ft in horizontal boreholes.
- Performed depth-discrete soil-gas sampling with up to 12 measurement ports, down to 310 ft.
- Blank membranes up to 500-ft long have been employed to seal and stabilize boreholes.
- Membranes have served as vehicles for a variety of chemical, temperature, matric-potential, and pressure sensors.

BASELINE TECHNOLOGY

SEAMIST™ is a new technology. It replaces the need for ex situ soil-sample analysis and multipoint, permanently installed vapor-sampling wells. The membrane minimizes the likelihood of contamination release from sampling and monitoring boreholes.

INTELLECTUAL PROPERTY

Patent and Trademark Ownership: Eastman Cherrington Environmental, Houston, TX; Patent No. 5176207.

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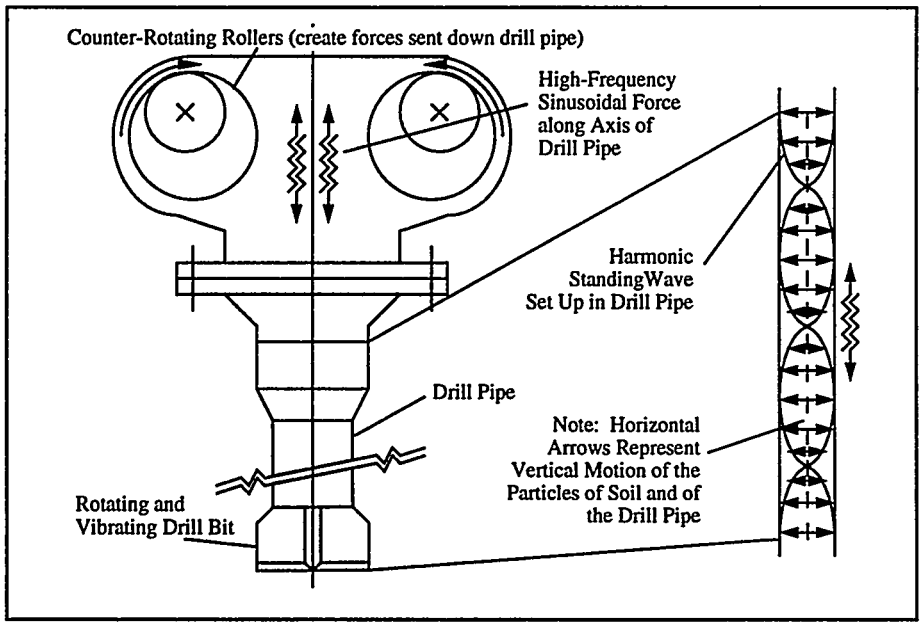
SLANT ANGLE SONIC DRILLING

Sandia National Laboratories

DESCRIPTION

Slant Angle Sonic Drilling (SASD) is a method of rapid access to the subsurface for installation of a sloped well using resonant-drilling methods. A high-power hydraulic oscillator head containing eccentric, counter-rotating rollers utilizes inertia to effect a high-frequency, sinusoidal standing-wave pattern in the drill pipe and drill head. In addition to vibration, the resonant drill bit also rotates, creating a very efficient cutting action in any geologic formation. Penetration rates are geology-dependent, but the sonic drilling method can be used for any formation including landfills since it affords penetration through boulders, metals, tires, wood, and concrete. The slant angle rig allows a well to be drilled at any angle from vertical to nearly horizontal. A hydraulically activated pull-down mechanism advances the drill and pipe into the formation. Below is a schematic of a sonic drill.

Various benefits arise from this drilling technique such as rapid penetration (speed), waste minimization, and high-quality core removal (including alluvial soils). The cutting action of the drill head forces a continuous core of the formation up into the drill string. Moreover, because of the high forces developed and the externally flushed nature of the specialized drill string, excess geologic material is forced into the borehole wall. The result is that no additional cuttings are generated or removed from the subsurface other than the continuous core. This has great economic advantage when applied to an environmental application, such as sampling below a chemical-waste landfill or an application with radioactive-soil contamination. The resonant-drilling method requires little or no drilling fluids for lubrication or cutting removal; this contributes to the production of a high-quality continuous core that is useful for both geologic and contaminant analysis of the subsurface formation.



Basic Principles of a Sonic Drill

Technology developments in the form of feedback control and advanced hardware design will improve both the speed of this technique and its component reliability. The advancement of this technology will include an analog or digital feedback control circuit, as well as laboratory and field analysis of bit temperature, bit design, and downhole drill-rod temperatures. The developers are in the conceptual stages of incorporating a method of downhole steering into this drilling technology to vary the drill angle during well drilling.

TECHNICAL PERFORMANCE

This technology has been successfully applied to continuous-coring, monitor well construction, and horizontal-drilling activities. A demonstration of the improved system, with feedback control and component redesign for improved reliability and more rapid access, is planned.

Drill Head. Dynamic force output is 30,000 lbs at 120 Hz. Power input is 150 hp. Rotational torque is 25,500 in-lb; rotational speed is 60 rpm.

Drill Rig. Pull-down force is 10,000 lb; the pull-down rate is 100 ft/min. Angle capacity is 45° to 90° off the truck, and 5° to 45° off standing mounting plates.

Speed of Drilling. The penetration rate of the sonic drill varies depending on the type of formation being cut. Speeds from 1 ft/s to 0.5 ft/min are encountered when drilling loose to compact formations.

Formations. The sonic rig drills any type of formation: alluvium, sands, clays, cobbles, boulders, bedrock, permafrost, caliche, and other types of formations including landfills. It is able to drill through metals, garbage, tires, wood, and concrete.

Cost/Benefits. The cost is approximately $100/ft for a cased, angled hole with continuous core. Drilling requires little or no fluid, and no cuttings are generated, which eliminates several waste streams and disposal costs. The result is savings of support staffing and cost savings for management of excess contaminated drill cuttings. There is a 95 to 100 percent core return in alluvial soil versus 60 percent for conventional drilling. Core sizes range from 2 to 12 in. in diameter, depending on the dictates of the drilling program.

PROJECTED PERFORMANCE

The drilling speed and component reliability are expected to improve with the inclusion of feedback control and component redesign.

WASTE APPLICABILITY

This technology is applicable for monitoring wells, vadose-zone soil-gas sampling, neutron-probe pipe installation, core sampling, and injection and extraction wells for bioremediation and/or air-stripping/vacuum-extraction remediation projects. Additionally, in most conditions, closed-end tubes can be resonated into the ground to significant depths to yield no cuttings or core and to take discrete water samples or in situ cores.

STATUS

Resonant sonic drilling has existed for over thirty years, originating from the work of its inventor, A. G. Bodine. The application of this technology has been demonstrated by various developers, including the Water Development Corporation. Ten of the U.S.-based sonic drill heads and rigs are operated by Water Development Corporation. This technology is currently available, with process improvements (feedback control and hardware redesign) expected within 2 to 3 yrs.

REGULATORY CONSIDERATIONS

Drilling and subsurface access regulations may vary depending on the waste-site characteristics. Ecological impacts are minimized or eliminated by the

absence of secondary waste streams. Occupational Safety and Health Administration (OSHA) regulations apply for drilling-equipment operation, high noise levels, and potential contaminant exposure.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be applied to water-well, natural-gas-well, geothermal well, and oil-well drilling. It is also useful to industries that may have soil or groundwater contamination problems. Rapid access to the subsurface, without excess soil removal or secondary waste streams, is economically desirable for such industries to determine the scope of the problem and to remediate the contamination. This method of continuous-core removal is useful for other geologic studies and to the mining industry.

BASELINE TECHNOLOGY

This technology is compared to other conventional drilling methods, such as hollow-stem auger and air- and mud-rotary drill rigs that are traditionally used for oil, gas, and river-crossing applications. Field results demonstrate that the daily output of one sonic-drill rig will approximate the daily continuous-core output of three to four hollow-stem auger rigs.

INTELLECTUAL PROPERTY

U.S. patents for ResonantSonic drilling technologies are held by the Water Development Corporation (WDC). Patent numbers are available from the technology developer, WDC.

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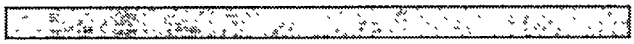


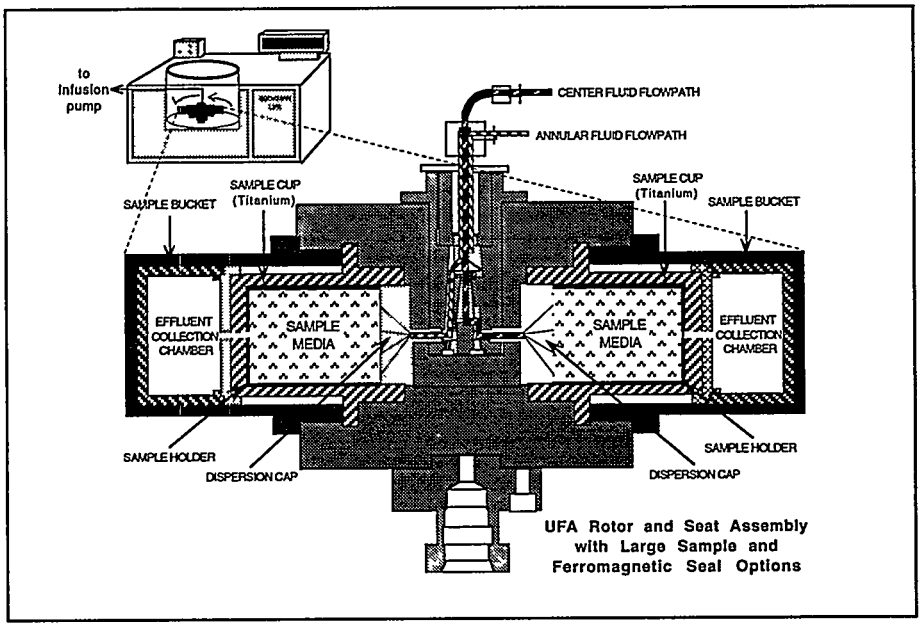
UNSATURATED FLOW APPARATUS CENTRIFUGE

Washington State University
Pacific Northwest Laboratory

DESCRIPTION

The Unsaturated Flow Apparatus (UFA™) is a laboratory instrument that simulates the migration of various compounds (e.g., volatile organic compounds), microbial nutrients, and water in the subsurface environment. Knowledge of the transport properties of soils, sediments, and rocks under unsaturated and saturated conditions, particularly hydraulic conductivity as a function of moisture content, is required for accurate modeling of the transport of contaminants in subsurface materials surrounding hazardous and mixed-waste sites. Traditionally, it has been difficult to obtain transport data on unsaturated and multicomponent systems because of the long experimental durations necessary for achieving hydraulic steady state. The UFA™ is based on open-flow centrifugation and provides a technique in which hydraulic steady-state can be achieved in a matter of hours in most geologic materials (even at very low water content). Therefore, the UFA™ provides the means to experimentally measure transport parameters in a very short time frame under the wide range of conditions found in the field.

The advantage of using centripetal acceleration as the fluid-driving force is that it is a body force similar to gravity and acts simultaneously over the entire system and independently of other driving forces (e.g., matrix suction). The system is the most rapid method for obtaining transport data. The UFA™ can address any flow-transport problem involving any fluid in any porous media under many conditions. The UFA™ improves the predictive capabilities of VOC migration and increases the probability of choosing a successful restoration strategy for site-specific conditions. The technology can also be used for quick screening and can provide data to describe field conditions. As an example, over 500 values of hydraulic conductivity on about 50 samples were measured in less than 6 months using one UFA™ instrument. The data were used to extend the understanding of subsurface interactions under actual field conditions at Hanford Site for characterization, remediation, and predictive modeling. The database could not have been developed without using the UFA™ method.



UFA™ Rotor and Seat Assembly with Large Sample and Ferromagnetic Seal Options

TECHNICAL PERFORMANCE

The UFA™ consists of an ultracentrifuge coupled with a constant, ultra-low-flow-rate pump that provides any liquid to the sample surface through a rotating seal assembly and microdispersal system. The flow rates can be adjusted to as low as 0.001 ml/hr. Sample accelerations up to 20,000 g are attainable at temperatures from -20° C to 150° C. The effluent is collected in a transparent, volumetrically calibrated container at the bottom of the sample assembly that can be observed during centrifugation using a strobe-light assembly. The UFA™ measures transport parameters at water contents as low as a few percent and hydraulic conductivities down to 10^{-10} cm/s in a few days. As an example, a silt sample (from Hanford) accelerated to 2,000 rpm with a flow rate of 3 ml/hr reached hydraulic steady state in two hours at the target volumetric water content of 22.4% and unsaturated conductivity of 2.5×10^{-7} cm/s. For homogeneous samples run in the UFA™, moisture distributions are uniform to within 3%. The rotational speed and flow rate into the sample are chosen to obtain the desired values of flux density, water content, and hydraulic conductivity within the sample.

Several studies were made to compare the UFA™ method with other experimental and estimation methods for determining hydraulic conductivity. All of the UFA™ measurements were conducted in only 3 days. In comparison, direct measurements of the hydraulic conductivity by traditional column-flow experiments under unit-gradient conditions took approximately a year of experimental time. The second method utilized data obtained over 13 years from a field lysimeter. The third method was an estimation derived by using the Campbell relationship to fit laboratory-determined water-retention values to matrix-potential values in order to generate the Maulem relationship. The agreement of the UFA™ data with all three methods is excellent and demonstrates not only the feasibility but also the time saved by using the UFA™ method.

Cost. The present cost of the UFA™ and support equipment is about $100K. The annual operating and maintenance cost is $10K, including the maintenance contract and sample holders. The operating life of the system is up to 30 years.

PROJECTED PERFORMANCE

A new generation UFA™ is being developed. Soil samples will be collected from the Hanford Site using cable-tool drilling/split-spoon sampler technology. The soil or bedrock samples are transferred to a specially designed titanium canister and subjected to as much as 20,000 g. A rotating-seal assembly fitted to the canister allows an ultra-low-flow pump to deliver liquid (carbon tetrachloride in this case) to the sample surface during centripetal acceleration. When steady-state conditions are reached (within a matter of hours), three transport parameters will be evaluated; (1) hydraulic conductivity to measure permeability, (2) diffusion coefficient, and (3) breakthrough retardation. Transport data and a compilation of data for Hanford sediments will also be the final output elements.

Modification may need to be made for application of this technology in radioactive environments.

WASTE APPLICABILITY

The UFA™ can address all flow transport problems involving fluid in any porous medium under almost every condition. This technology is applicable to VOCs, microbial nutrients, water in the subsurface, tank-waste sludges, fluid behavior in ceramics, and other fluid/substrate systems.

STATUS

The UFA™ is now available commercially. The UFA™ was developed and has been deployed in a

number of Pacific Northwest Laboratory programs since 1991. Improvements to the UFA™ are continuing.

REGULATORY CONSIDERATIONS

Environmental regulations are not expected to impact this technology. Proper laboratory procedures will be followed to minimize workers' exposure to contaminants.

POTENTIAL COMMERCIAL APPLICATIONS

The UFA™ supports the development of restoration technologies such as vapor extraction (e.g., estimate vapor-migration rates) or bioremediation (e.g., estimate nutrient-delivery rates) for unsaturated soils. In addition, the UFA™ technology is a predictive tool, that is, a "time machine" that can be used: (1) to validate the predictive models of subsurface contaminant migration, and (2) to screen the performance of various remediation technologies in the field. The UFA™ is being used to investigate tank waste sludges.

The concrete industry has expressed interest in this technology to test reactivity of concrete aggregate to alkaline solutions. Extraction of pristine pore fluid from highly unsaturated materials and highly impermeable materials is possible with the UFA™.

BASELINE TECHNOLOGY

The baseline technology is traditional column experiments or in situ analysis such as lysimeter measurements that require months to years to achieve results. UFA™ data have been shown to be in complete agreement with data generated using traditional column experiments.

INTELLECTUAL PROPERTY

Beckman has the intellectual property rights.

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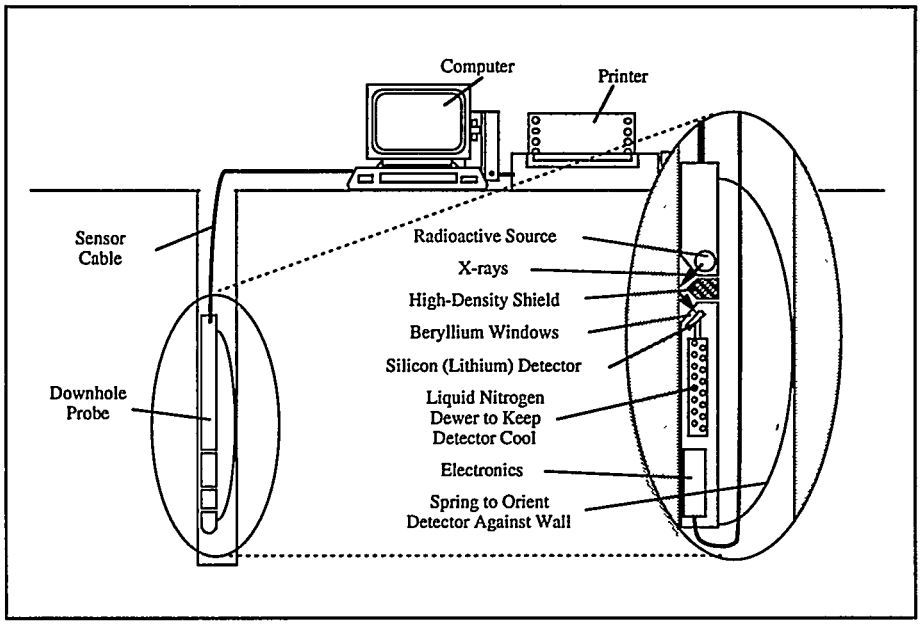
X-RAY FLUORESCENCE SPECTROSCOPY

Pacific Northwest Laboratory

DESCRIPTION

Downhole X-ray fluorescence spectroscopy is a method for detecting and quantifying inorganic (i.e., metal) contaminant concentrations in soils above the water table using a photoelectric process. The X-ray fluorescence (XRF) instrument is a downhole probe consisting of an X-ray source and a photon detector. The instrument probe is placed in a lined borehole. The surrounding soil and the detector are then irradiated with the source X-rays for a specified period of time. The detector receives a combination of Compton backscatter photons, as well as fluorescence photons emitted by atoms in the soil. Real-time assays of soil constituents can be performed when the instrument system is properly calibrated. The system also includes an onboard analog-to-digital converter, a multichannel analyzer, and a computer processor. Calibration of the instrument for a particular element and observation of the number of counts appearing in a specific fluorescence range of the energy spectrum results in a quantitative determination of the concentration of the element in the soil. Multi-element calibration is possible.

Fluorescence occurs when the source X-ray energy is greater than the electron-binding energy of the K or L shell in the target atom. The source photon collides with the target atom and causes an electron vacancy in, for instance, the K shell. This vacancy is filled by a transition of an L electron into the K shell and the emission of either a K_a X-ray photon (especially in heavy elements) or an Auger electron (especially in light elements). The competition between the two processes is described by the fluorescence yield. The probability that a K_a X-ray will be emitted approximates unity in high-atomic-number (Z) elements and approaches zero in low-Z elements. Typically, X-ray fluorescence is useful for elements with a $Z > 20$.



Prototype XRF System

TECHNICAL PERFORMANCE

Several factors affect the minimum detectable concentration of an element. First, the source X-ray energy must be greater than the electron-binding energy in the K or L shell of the target atom. The excitation process is increased when the source and fluorescence energies are closely matched. Second, greater-atomic-number elements (higher-Z elements) have increased probabilities of K_a

(photon) emission compared to Auger electron emission that dominates in lower-Z elements. Third, the detector quantum efficiency depends on the atomic number of the anticipated target atom. Fourth, the energy-band resolution becomes increasingly important to achieve signal discrimination when neighboring elements are present in the soil media (e.g., chromium Z=24, iron Z=26). Finally, attenuation of low-energy X-rays limits the volume of soil that can be probed, but when the element under consideration increases in Z, then a greater volume of soil can be analyzed with increased accuracy. The accuracy is directly related to the minimum-detectable contaminant-concentration level.

A field test of an XRF system was conducted at Sandia National Laboratories (SNL) Chemical Waste Landfill (CWL) by Pacific Northwest Laboratories (PNL) in 1992 and 1993. In 1992, a commercial downhole probe manufactured by Scitec Corporation was employed for measurements of chromium concentration in three boreholes, each 100-ft deep, 9-in. in diameter, and lined with high-density polyethylene material and a nylon cloth outer liner in a landfill. While both copper and chromium were observed, the resolution was not acceptable for waste-characterization applications. In 1993, PNL demonstrated a new prototype downhole XRF probe featuring a liquid-nitrogen-cooled Si(Li) detector and on-board signal processing electronics. In addition, both a radioactive isotope and an X-ray tube were used as sources for excitation X-rays. The probe was demonstrated in the same boreholes as before, and much improved contaminant detection capability was obtained, with chromium detectable at around the 50- to 100- ppm level. However, the detector resolution can still be improved.

Cost. For a commercial Scitec instrument, the cost is estimated to be $50K.

PROJECTED PERFORMANCE

In 1994, an instrument will be developed which will have improved detector resolution and higher count-rate capability. It will have a higher resolution Si(Li) detector and will retain the on-board signal-processing capability. Excitation X-rays can come from either an X-ray tube or an isotopic source. In addition, it will be greatly reduced in size and weight. The outside diameter will be about 1.25 in. with an overall instrument height of about 3 ft. It is designed to operate within a cone penetrometer. It will be capable of analyzing any soil type, but the boreholes must be bare or lined with thin membranes, such as the SEAMIST™ liner.

WASTE APPLICABILITY

The XRF spectroscopy method of detection and quantification of contamination is appropriate for high-Z metals and all other elements where $Z > 20$. The penetration thickness into the soil is limited by X-ray attenuation for low-energy radiation. The low-energy X-rays are likely to be used when the target atom has a low atomic number (lower-Z). However, when higher-Z atoms are to be detected, higher energy X-rays will be used, and the volume of probed/analyzed soil is increased. The applicability of this technology is largely dependent on the desired minimum-detectable concentration, the atomic number of the contaminant, the site characteristics (such as high levels of a natural element with an atomic number close to a contaminant's atomic number), and the resolution of the detecting device.

STATUS

This is a developing technology with respect to low-concentration detection (ppm concentrations) and lower-Z element detection such as chromium (Z=24). The technology has been demonstrated on a field

scale with good success, but some improvements are necessary in terms of size reduction and instrument performance.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and protection of occupational workers from ionizing radiation. In addition, permits may be required for drilling at hazardous waste sites.

POTENTIAL COMMERCIAL APPLICATIONS

This technology could be used to detect metallic contamination near industrial sites. Examples would be Environmental Protection Agency (EPA)-required testing, post-closure monitoring, site investigation, or follow-up soil analysis after structural lead-paint stripping. XRF could also be used in experimental situations to determine concentrations of metals in an aerosol or aerosol filter (radioactive spent-fuel aerosol experiments). In countries that have dated steel-processing facilities (such as Poland), the soil surrounding an industrial plant can be analyzed for metallic contamination, specifically lead. Municipal solid-waste processing and/or disposal facilities can be monitored for undesirable, toxic, or hazardous metallic waste. Other applications may include decontamination/decommissioning and post-closure monitoring for all types of industrial sites (i.e., nuclear, coal, diesel, natural-gas-fired power plants, decommissioned transformers, and others).

BASELINE TECHNOLOGY

The baseline technology for analysis of heavy metals is conventional laboratory analysis such as inductively coupled plasma spectroscopy or atomic absorption. Each requires laboratory sample preparation and data evaluation to detect contaminants in soil. XRF has been used previously in the mining industry to detect soil constituents in concentrations greater than 1 percent. The utilization of XRF in environmental site characterization is a recent application. XRF provides a qualitative indication of heavy-metal content with minimal sample preparation and data evaluation.

INTELLECTUAL PROPERTY

PNL and Scitec have entered into a Cooperative Research and Development Agreement (CRADA) to develop the probe. All intellectual-property rights will be shared among the Department of Energy (DOE), PNL, and Scitec.

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Site Remediation Technology Profiles

Section 5.0

ADSORPTION OF BTEX USING ORGANOZEOLITES

New Mexico State University

DESCRIPTION

Use of organoclays for the adsorption of benzene, toluene, ethyl benzene, and xylene (BTEX) has been extensively investigated over the last ten years. However, use of these materials has limited application in field conditions, where both high water permeability and high chemical retention are desirable. Natural zeolites offer the same cation exchange characteristics found in clays. However, their rigid crystalline structure allows their application in treatment columns in a granular form. This simplified treatment operation can even be used in remote and often unsupervised environments found in the oil and gas industry. Treatment of industrial and hazardous wastes generated in refinery and production operations are considered as major candidates for this technology. However, this technology also addresses treatment of ground and surface waters contaminated by leaking underground storage tanks (LUSTs) and other petrochemical spills. Use of tailored zeolites for the removal of BTEX, cationic, and anionic heavy metals has been investigated in New Mexico State University laboratories over the last three years.

Zeolites are natural minerals that possess high cation-exchange capacities (CECs). The CEC in these minerals can be exploited for environmental applications so that the natural cation on the mineral surface (typically Na^+, K^+, or Ca^{+2}) is exchanged for a hazardous cationic pollutant. For instance, removal of divalent lead, copper, and other cationic heavy metals is possible using this technology.

Organic cations (ammonium compounds) can also be exchanged for the natural cation on clays and zeolites. The surface of the mineral is altered significantly by this process (tailoring) so that the zeolite-organic matrix behaves more closely as an organic adsorbent than as an inorganic silicate mineral. Adsorption of neutral single-ring aromatics is greatly enhanced by this process. Selection of the organic tailoring agent and the mineral type are important factors in the application of this technology.

Small organic compounds (such as tetrametyl ammonium, TMA) form a rigid monolayer around the mineral surface as shown in Figure 1. The intermolecular space created by this tailoring process can be exploited to selectively remove benzene from solution. This process ensures that the adsorbent is not spent by innocuous organics but that it becomes used to remove the targeted pollutant (benzene in this case).

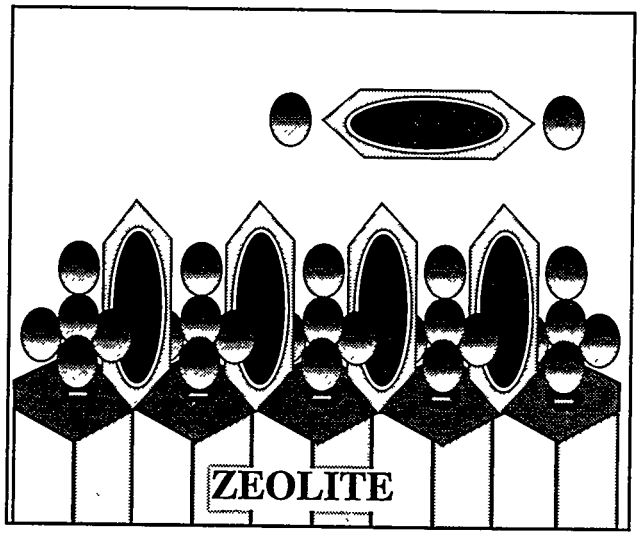

Figure 1. TMA-Zeolite Selective Sorption Mechanism

TECHNICAL PERFORMANCE

The natural adsorption order in a non-selective adsorbent, such as granular activated carbon (GAC), is xylenes > toluene >> benzene as shown by the

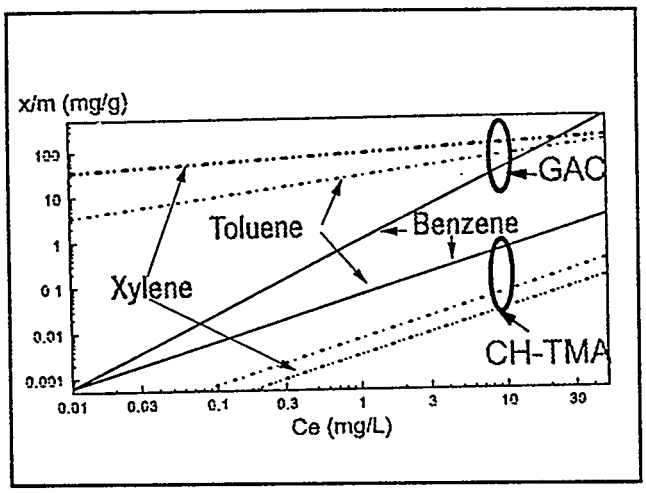

Figure 2. Adsorption Isotherms for GAC and TMA-Zeolite

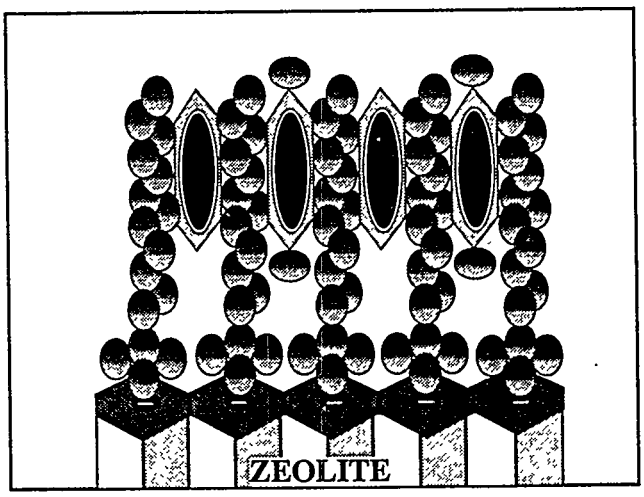

Figure 3. HDTMA-Zeolite Non-Selective BTEX Removal

isotherms labeled GAC in Figure 2. This sorption order represents a major hindrance to the use of non-selective adsorbents since the order of environmental and regulatory concerns demands opposite performance.

TMA-zeolite sorption is a highly selective process that reverses the natural order of adsorption for closely related compounds. Figure 2 shows that the adsorption preference by TMA-zeolite is benzene>> toluene > xylenes (see isotherms labeled CH-TMA). This performance is highly desirable in applications where benzene is present among closely related compounds (such as LUSTs, refinery wastes, groundwaters, industrial-process waters and produced waters). The process optimizes adsorbent use by targeting benzene (the most hazardous single-ring aromatic) leaving behind closely related (and less toxic) compounds, such as toluene and xylenes.

Application of this technology to a variety of wastewaters may require indiscriminate removal of organics from water. Selection of an organic tailoring agent can create an environment favorable for the non-selective removal of soluble organics using the same substrate support. For example, large quaternary amines can coat the mineral with a molecular layer of organic material as shown in Figure 3. In essence, this procedure converts the zeolite into a support medium for an organic-organic extraction. The organic layer induces a non-selective adsorption behavior (similar to the one described for GAC) for the removal of all BTEX.

It is therefore possible, by careful selection of tailoring agent and zeolite substrate, to engineer an organo-zeolite for the removal of single-ring aromatics. Adsorption of benzene (when using a small organic cation) or indiscriminate removal of all BTEX (when using a long-tail amine) from the solution are both quite feasible. Combination of tailoring agents can optimize adsorption of all aromatics without sacrificing removal capacity for benzene.

Use of organoclays for the removal of cations and tailored clays for the adsorption of BTEX has been extensively investigated over the last ten years. However, use of these materials has limited application in field conditions, where both high water permeability and high chemical retention are desirable. Zeolites offer the same cation-exchange characteristics found in clays, but due to their rigid crystalline structure, they can be used in a granular form. This property simplifies waste-treatment operations, even in remote and often unsupervised environments found in oil- and gas-production operations. Tailored zeolites are therefore suitable for column adsorption processes that are relatively easy to operate. A few

manufacturers can provide pelletized clays. However, these materials lack the resistance to abrasion normally found in zeolites. This property makes zeolites particularly attractive for multiple regeneration applications. Additionally, the high cost of pelletized organoclays greatly limits their application to a few selective conditions found in the oil and gas industry.

Regeneration of spent zeolites is also feasible in field conditions. Our results show that temperatures as low as 35°C (95°F) can restore the adsorbent properties of the organo-zeolite within two days. Figure 4 shows that little adsorption capacity is lost by two different TMA-zeolites for up to three regeneration cycles (four adsorption uses). Minor deterioration occurs after the fourth cycle. Actual treatment cost estimates by a Petroleum Environmental Research Forum participant are about $0.22/bbl when using GAC for treatment of a groundwater contaminated by a LUST. Our economic studies show a similar cost after only one regeneration of a TMA-zeolite. This cost is reduced to about $0.08/bbl if the organo-zeolite is regenerated at least five times.

PROJECTED PERFORMANCE

Use of organozeolites is of great interest to the oil and gas industry, where robust and simple-to-operate treatment technologies are required. Preliminary economic analyses indicate that treatment costs for wastewater treatment in offshore oil-production operations could be reduced by over 50 percent. Regeneration of spent zeolites can be accomplished by means of heating by combustion of produced natural gas. Field tests are scheduled through the Petroleum Environmental Research Forum to test the technology using refinery wastewater, produced water, and for groundwater cleanup at a gasoline-spill site.

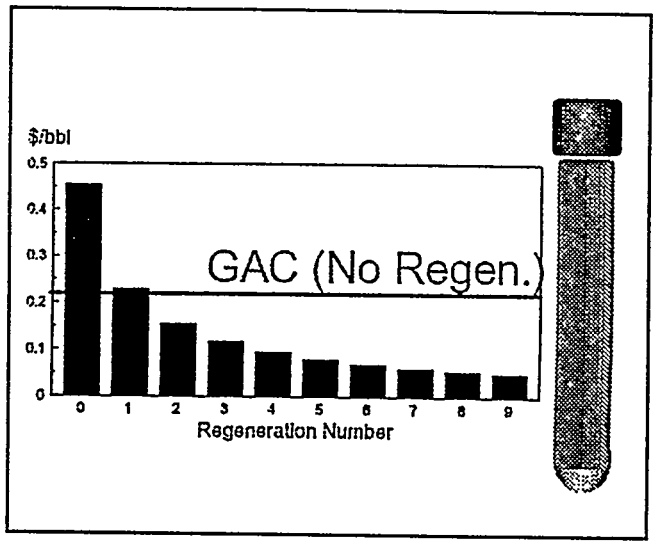

Figure 4. Estimated TEXACO Treatment Costs (CH-TMA)

WASTE APPLICABILITY

Organozeolites are useful for treatment of waters contaminated with BTEX. This technology is particularly attractive for the treatment of complex mixtures of hydrocarbons that require specific removal of benzene to trace concentrations.

STATUS

Testing began in the Fall of 1994.

REGULATORY CONSIDERATIONS

To be evaluated during testing.

POTENTIAL COMMERCIAL APPLICATIONS

Organozeolites can be used to treat waters contaminated with BTEX. These adsorbents can also be used in hazardous and mixed-waste disposal facilities as "getters" in stabilization processes. This technology has potential for the treatment of contaminated waters using chemical barriers. This technology is applicable to industrial and hazardous wastes generated in refinery and production operations.

BASELINE TECHNOLOGY

The baseline technology is adsorption of aromatic compounds into organically modified zeolites.

INTELLECTUAL PROPERTY

Flexible. The PI, WERC administration, university administration, and industrial partners work in conjunction to discuss individual cases.

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None.

ARC MELTER VITRIFICATION

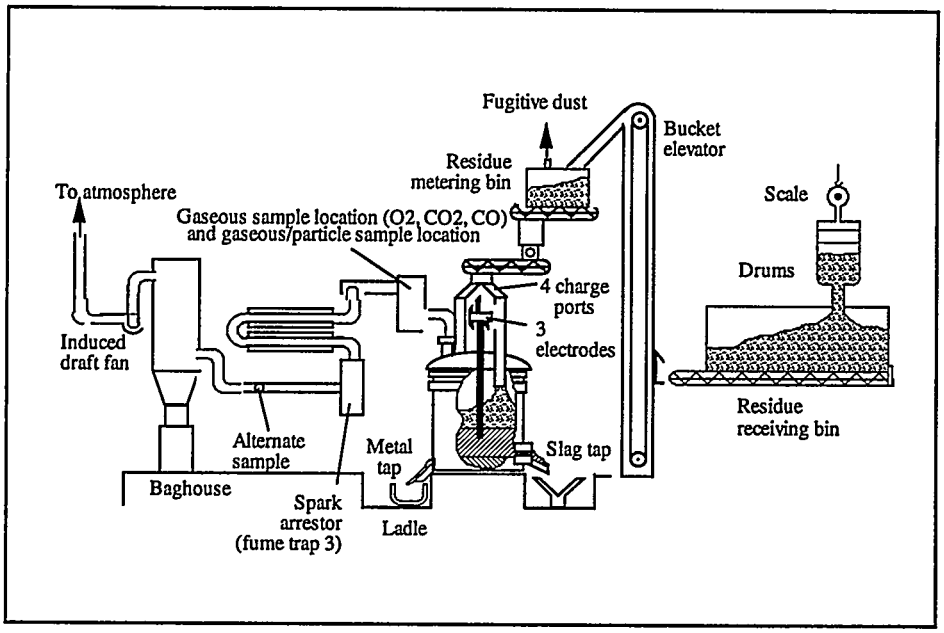
Idaho National Engineering Laboratory

DESCRIPTION

Arc melter vitrification is a high-temperature extractive metallurgy-based technology capable of melting soil and metals, pyrolizing or oxidizing residual organics, melting structural metals from melted slag (silica and metal oxides), and partitioning transuranic (TRU) waste into the slag phase. Depending upon cooling rate and composition, the slag will consist of a glassy phase and several crystalline phases. Suitable composition and heat treatment will partition the TRU into a highly nonleachable, very durable crystalline phase with a probably geological lifetime. High-vapor-pressure metals will probably evaporate from the melted phases and be collected in downstream collectors for further treatment. A process technology to recycle or immobilize the collected high-vapor-pressure metals (HVPM) will need to be developed. Immobilization in a low-temperature final-waste-form material, such as borosilicate glass, is a possibility.

Vitrification can produce a safe and highly durable final waste material for permanent disposal. Waste volumes can be substantially reduced (up to 65%, depending on waste composition). Selected clean metals may be separable for recycling. High-temperature electric-melter technology requires smaller volume off-gas systems and can facilitate processing of a wide range of materials with less presorting, sizing, and separating. The base arc-melter technology has been used for smelting of similar heterogeneous ores for many years, providing a related applications experience base from which to proceed. The glass/ceramic final waste form will likely be suitable for disposal anywhere and may not need to be disposed at a deep geologic repository, such as the Waste Isolation Pilot Plant (WIPP). Further, it would produce a much safer and more compact material to ship.

TECHNICAL PERFORMANCE



Electric Arc Melter

The glass/ceramic (crystalline rock) final waste form product will be the most technically effective waste-form for long-term encapsulation of TRU. Hazardous organics and materials capable of hydrogen generation will be eliminated from the final waste-form material. Buried wastes can be processed essentially as received, along with contaminated soils, with minimal separations, additives, characterization, and pretreatment. However, feed systems will not handle all wastes. Volume of waste

and contaminated soils will be reduced. Selected metals may be separable for reuse.

PROJECTED PERFORMANCE

Arc-furnace applications for pyrometallurgical processing of heterogeneous materials (ores) are a proven industrial-base technology, the operation of which is routinely accepted by the public. Proceeding to design and develop an arc-smelter system for mixed-waste processing from a strong existing technology-experience base should provide a better performing and more publicly acceptable process technology. The cost of developing and implementing a melting process for the encapsulation of TRU will be a small fraction of the total cost of retrieval and processing. Extensive engineering development will be required for the implementation of a reliable, effective process. A pilot facility will require 3 to 5 years to examine and solve such problems as sealing, remote maintenance, process optimization, fume handling, and encapsulation issues.

A well designed melting process will incorporate all the TRUs and selected metals into a durable slag and eliminate organics. All TRU elements are expected to be dissolved and retained in the glass/ceramic material formed upon cooling of the molten slag. Volume will be reduced substantially by vitrification (two to five times, depending upon waste soil mix). Selected clean structural metals (such as iron) may be reduced and tapped. All organics will be pyrolized or combusted, and combustion will be completed in a secondary chamber, possibly in the off-gas system. Fume from the high-temperature melter will require processing by the air-pollution-control system. Depending upon waste composition, fume may contain acid gases, chlorides, heavy metals, and sulfides. Collected residues from the Air Pollution Control System will require further processing for final disposal.

Buried-waste materials and soils are expected to be processable with a minimum of separation, sizing, and precharacterization using a soils-buffering approach to ensure a high-integrity final waste-form material.

Existing arc-melter technology has not been designed for radioactive service; therefore, modifications will be necessary for radiation-contamination control.

Cost. The cost to develop and build a system that will process 5 ton/h is estimated at $50-100M.

WASTE APPLICABILITY

Arc-melter vitrification is applicable to the treatment and immobilization of TRU wastes, toxic metals, hazardous organics in buried wastes, heterogeneous mixed wastes, and soils.

STATUS

Arc-melter technology exists but requires extensive engineering development for alpha-controlled processing and optimization.

The American Society of Mechanical Engineers (ASME) and the U.S. Bureau of Mines (USBOM) had been pursuing the evaluation and demonstration of commercial arc-melter-furnace technology to the vitrification of municipal incinerator-waste ashes. Analysis of this effort in 1992 led to the development of the present technical task plan to evaluate and demonstrate application of this technology to materials typical of buried mixed wastes. A test series on commercial-incinerator waste ash was completed in late 1992 by the USBOM/ASME, showing generally favorable results and identifying some problems to be considered. These results were factored into the test plan for the baseline series of tests for buried-waste-representative materials in April/May 1993. In parallel with this effort on a three-phase AC melter system, Electropyrolisis Inc., in cooperation with

Pacific Northwest Laboratory and Massachusetts Institute of Technology, is evaluating a direct current (DC) arc-melter system of somewhat different proposed configuration. Integration of these projects is in progress.

REGULATORY CONSIDERATIONS

The melter system is part of an overall treatment system. All output materials from the process system will either be clean and suitable for reuse or release to the environment (meeting all environmental standards) or will be in a material form suitable for permanent long-term disposal.

High-temperature processing carries with it inherent hazards requiring thorough safety design and analyses. Alpha-contamination control and hazardous-materials control require further extensive safety considerations typical of any radioactive-materials-processing facility. Remote operation will protect workers. Potential for pressurization transients, e.g., steam explosion or combustibles explosion, requires thorough treatment.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications for the arc-melter-furnace technology include vitrification of municipal-incinerator-waste ashes.

BASELINE TECHNOLOGY

There is no accepted baseline technology for treatment of mixed TRU-contaminated buried wastes. Preliminary systems-design studies for buried wastes identified and compared the most likely treatment options. The highest-ranked process options were those which involved ex situ vitrification in a high-temperature melter. Repackaging of untreated buried waste for disposal storage at WIPP (present baseline plan for stored TRU wastes) is not a probable option. Various arc-melter-furnace configurations are possible. The baseline configuration for arc melters is standard commercially available three-phase graphite-electrode furnace technology. This pilot test system is representative of that baseline electric-arc-furnace configuration. A number of other similar thermal-treatment systems are also under development.

INTELLECTUAL PROPERTY

Patents: None.

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American Society of Mechanical Engineers
Lectromelt
Electropyrolisis, Inc.

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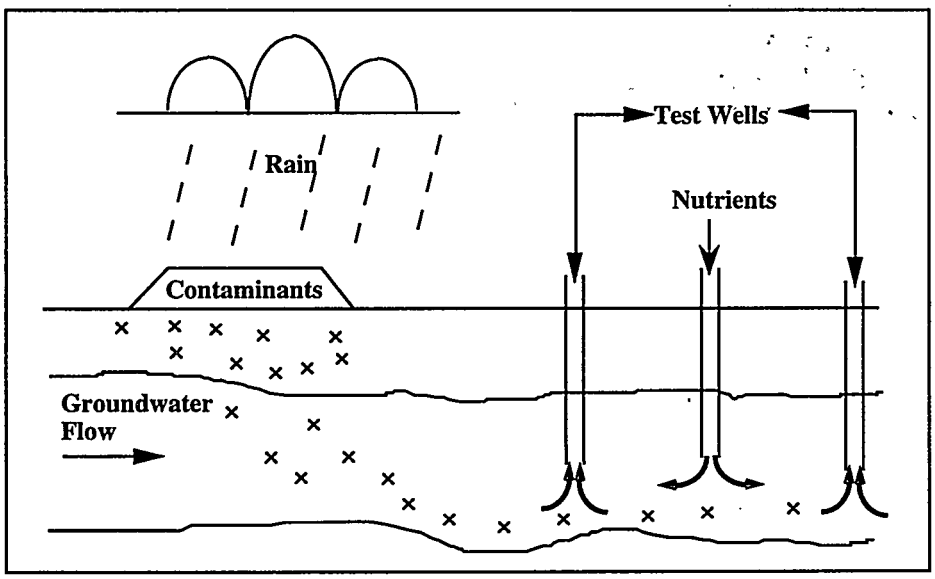
BIO-IMMOBILIZATION OF HEAVY METALS

University of New Mexico

DESCRIPTION

Bio-Immobilization of Heavy Metals (BIHM) is a process that uses bacteria to transform heavy-metal ions into a chemical form that is insoluble and less toxic. The BIHM technology integrates microbiology, waste-water and groundwater treatment, and environmental engineering. The BIHM process can be employed either as an *in situ* treatment for groundwater or as a continuous-flow system that would be appropriate for surface water. BIHM could be employed in conjunction with standard pump-and-treat systems where the final treatment of the contaminated site would be completed by bioremediation activities. In certain conditions, the BIHM process can be applied to groundwaters without previous chemical treatment. Of particular importance is that this system can be used on surface water or deep groundwater contaminated with toxic metals. The adaptability of the BIHM system to a variety of environmental settings indicates a great versatility of this technology. A schematic of the process is shown below.

Bacteria resistant to heavy metals are cultivated either *in situ* or in a reservoir at the site. The bacteria employed are present naturally and have not been genetically engineered. With the interaction of bacteria and toxic cationic or anionic metals, granules or colloids are produced. The biologically produced metallo-colloids are granules of the elemental form of the metal, insoluble heavy-metal sulfides, or metals bound into bacterial cellular matrices, and all have surface properties similar to bacteria. Therefore, flocculation and precipitation procedures that are employed in management of wastewater can be used to collect these metallo-colloids. The insoluble metallo-compounds generated *in situ* resemble ores, and deposition of insoluble metal reduces the concern for toxicities attributed to these metals.



Bio-Immobilization of Heavy Metals Process

TECHNICAL PERFORMANCE

Uranium reduction. This technology provides for a low-cost process that can employ native bacteria for the treatment. For the formation of insoluble U(IV) from soluble U(VI) by biotransformation, inexpensive carbon sources like ethanol or acetate could be added to the groundwater.

In laboratory experiments, it was determined that bacteria present in groundwater containing 1 mM of U(VI) could be stimulated to reduce the level of soluble U(VI) by over 80 percent within a few weeks. Pure cultures of sulfate-reducing and nitrate-respiring bacteria were observed to reduce the level of U(VI) from 1 mM to <0.1 mM in only a few days. The formation of U(IV) from U(VI) by both sulfate-reducing and nitrate-respiring bacteria was verified by Energy Dispersive X-ray Spectroscopy, as well as by X-ray analysis associated with transmission electron microscopy.

Bio-colloid formation with metals. The transformation of selenate or selenite to elemental selenium or the production of insoluble lead from soluble inorganic lead has been examined in laboratory studies. In both of these bacterially catalyzed reactions, 99.9 percent of the toxic metal was removed from solution when supplied at the 1 mM level. This formation of bio-colloids of lead or selenium was accomplished within two days. The bacterially catalyzed reaction with chromate produced cationic chromium which was rapidly bound to the cell walls of bacterial or fungal cells. Rates of this chromium removal by bacterial reduction (coupled to fungal adsorption) are being finalized. While the bacteria can tolerate 10 mM lead, selenium, or chromium salts, it is envisioned that the most appropriate use of this BIHM process would be in final remediation efforts.

PROJECTED PERFORMANCE

For uranium-mill-tailing sites in arid regions, the bioremediation of contaminated groundwater with the formation of U(IV) would be a desirable event. Treatment of surface streams containing various heavy metals could occur, provided that the design of a collection facility for the bio-colloids would appropriately fit the environment.

WASTE APPLICABILITY

BIHM is applicable to surface waters containing salts of heavy metals including chromate, seleno-oxy anions, and lead. This process may follow conventional chemical treatments to provide final removal of toxic metals from solution. Groundwater contaminated with uranium as U(VI) may be appropriately treated with BIHM to immobilize the reduced-uranium products in the saturated zone.

STATUS

Laboratory-based demonstrations have been conducted for ions of lead, chromium, selenium, and uranium. Application of this process at a uranium-mill-tailings site began in the Fall of 1994.

REGULATORY CONSIDERATIONS

Appropriate permits for treatment of liquid effluents for specific contaminants must be considered, i.e., the Clean Water Act, the Resource Conservation and Recovery Act (RCRA), and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA).

POTENTIAL COMMERCIAL APPLICATIONS

Examples of some commercial applications are streams from abandoned mines, uranium-mill-tailing sites, agricultural waters high in selenium, waste streams from ongoing chemical-processing plants, and contaminated groundwater. The process is ideally suited for contamination attributed to selenate, selenite, lead salts, chromate, and oxidized forms of uranium but can be employed for numerous other toxic metals.

BASELINE TECHNOLOGY

The baseline technology is electron microscopy coupled with energy-dispersive X-ray spectroscopy and metal analysis by atomic absorption or inductive-coupled emission spectroscopy.

INTELLECTUAL PROPERTY

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BIOLOGICAL DESTRUCTION OF TANK WASTE

Idaho National Engineering Laboratory

DESCRIPTION

Biological Destruction of Tank Waste (BDTW; also known as Biodenitrification) is a separation and volume-reduction process for supernatant and sluiced salt-cake waste from underground storage tanks. These wastes are usually composed of various radionuclides and toxic metals in a concentrated nitrate-salt solution. A BDTW system would be located adjacent to storage tanks and applied to the supernatant and sluiced salt-cake effluents. The bacteria act as metal and radionuclide adsorbers and also as denitrification catalysts that reproduce themselves at ambient temperature and pressure. Some degradation of organic contaminants may also occur during the process.

The liquid waste flows into a biosorption/precipitation tank where it is mixed with a recycle stream from the bioreactor to a pH ~ 10. Sodium carbonate and some metals (Al, etc.) form chemical precipitates, while other metals and radionuclides adsorb onto the biomass (biosorption). These solids, together with any suspended solids in the waste, are separated by settling and filtration, washed to remove nitrate, dried, and ashed to produce a low-volume (approximately 80 kg/m^3 of waste), radioactive, biomass/metals waste that is sent for vitrification or other suitable disposal method. The filtrate containing the nitrate, organics, and very low levels of metals flows into the bioreactor, where it is mixed with acetic acid as a carbon source for bacterial growth. The nitrate is reduced to innocuous nitrogen gas that is released to the atmosphere after being HEPA filtered. The effluent from the bioreactor, after filtration, is a concentrated solution in which nitrate has been replaced by bicarbonate. This waste is carefully monitored (subject to regulatory approval) and evaporated to produce a nonhazardous, non-radioactive salt waste. The process uses a mixed culture of natural halophilic denitrifying bacteria, isolated from the Great Salt Lake and Dealth Valley, that are able to grow and reduce nitrate at up to 4 M sodium. The high radioactivity and metals concentration in the biosorption/precipitation tank may kill the bacteria, but this does not matter because dead bacteria biosorb equally well. The removal of metals and radionuclides by biosorption and precipitation protects the growing bacteria in the bioreactor from their effects. Agitation of both tanks is provided by recyclying the N_2 and CO_2 generated by the bacteria. Dissolved-sodium concentration in the bioreactor is limited to ~ 2 M by the solubility of bicarbonate, but precipitate is also present. Control of pH and salinity around the process is accomplished by adjusting the recycle flow rate, the venting of CO_2 from the process, and the volume of wash water employed.

TECHNICAL PERFORMANCE

Design. The field-demonstration bioreactor-tank size is about 100 m^3, which corresponds to a waste-treatment rate of 2 gal/min, sufficient to treat a one million gallon tank in one year. At the 2 gal/min size, the BDTW system is transportable. Power usage is estimated at 20 kW for pumping and agitation.

Laboratory-Scale Testing. In 1992, halophilic bacteria capable of operating at salt concentrations of hundreds of grams per liter were isolated.

In 1993, a mixed culture of these bacteria was grown in 1 l continously stirred tank bioreactors on various simulated bioreactor feeds at salinity up to 4 M sodium, pH up to 8.9, and temperature of 35°C. These reactors operated as selection cultures, allowing the fastest growing strains to dominate.

During 1994, the central idea of combining denitrification with metals/radionuclide removal by biosorption was tested by building a complete large-laboratory-scale unit capable of treating 10 gal/day of simulated waste.

Cost. Accurate start-up costs will not be available until developmental experiments are complete. Operational costs should be minimal because of the nature of biological processing.

PROJECTED PERFORMANCE

The volume and status of the biomass sludge product depends on the metals content in the waste and the effectiveness of biosorption (which is currently under study). In most cases, the biomass product would be a low-level radioactive waste that is ~10% of the feed volume. In some cases, the biomass product would be a high-level waste requiring vitrification. The salt-solution waste will have approximately the same volume as the feed, but the nitrate salts would be replaced by bicarbonate.

WASTE APPLICABILITY

This biological process is applicable to the highly saline supernantants in the underground storage tanks of the Hanford Site, which contain various radionuclides, transuranic and toxic metals, and organic materials in a concentrated sodium-nitrate solution. The salinity of the waste is not a problem (simulant used for development work is 6.6 M sodium), although more concentrated wastes would produce relatively more biomass sludge waste that must be sent to vitirification. Bench-scale treatibility studies are needed for each new tank because some may contain high concentrations of microbial inhibitors that cannot be removed (e.g., flouride), metals that will not biosorb well, or inadequate concentrations of essential microbial nutrients (e.g., Ca, PO_4). Similar supernatants at other tank farms can also be treated, as can liquid solutions resulting from removal of salt cake by "sluicing."

STATUS

The process has been demonstrated in the laboratory. The technology is currently in scale-up design for a field demonstration and is expected to be ready when Hanford tank waste becomes available in 1997. The possibility of using an existing storage tank as the bioreactor is under investigation.

REGULATORY CONSIDERATIONS

No ecological impacts are anticipated. Operation at ambient temperature and pressure enhances worker safety. Full secondary containment is provided to contain leaks. Nitrogen-gas release is through high-efficiency particulate air (HEPA) filters to prevent any radiation release. Concentrated acetic acid brought to the site by tanker trucks is subject to Department of Transportation regulations. The process uses only natural bacteria; no mutant or recombinant strains are used. Consequently, there are no biohazard issues.

POTENTIAL COMMERCIAL APPLICATIONS

This process is versatile and can also treat waste streams from metals-reprocessing facilities in addition to those waste streams from nuclear-fuels-processing and reprocessing facilities. Biosorption is a process that has been commercialized recently for removal of metals from dilute aqueous solutions. It is being used to recover uranium at the Dennisor Mine in Canada at a scale of 90,000 lb/day.

BASELINE TECHNOLOGY

The standard technology consists of ion exchange to remove the radionuclides, followed by calcination and a chromium-separation step. The demonstration of this biological process will increase the number of options available for treating supernatants and salt cakes. It is likely that biological treatment is a cost-effective alternative for volume reduction and denitrification of tank wastes.

INTELLECTUAL PROPERTY

A patent has been applied for under the names of G.F. Andrews and A.J. Tien that would be owned by DOE, Idaho National Engineering Laboratory.

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Industrial/University Partners

None at present.

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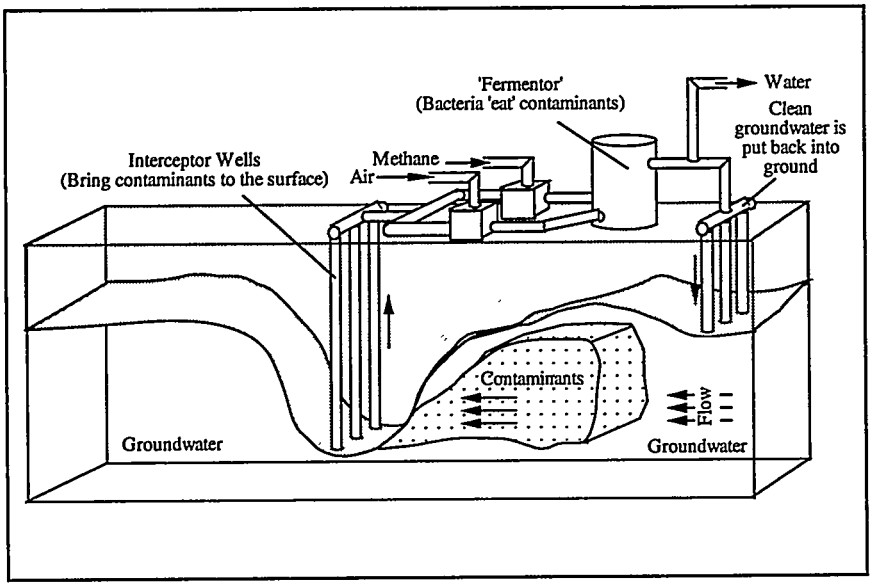
BIOREACTORS FOR BIOREMEDIATION

Westinghouse Savannah River Company

DESCRIPTION

Organic xenobiotic chemical contamination of groundwater has become the most important pollution problem of industrialized nations of the world. More than 15% of community drinking-water supplies in the United States is contaminated with carcinogenic, chlorinated hydrocarbons (Craun, 1986; Patrick et al., 1983). The major organic contaminant of waste sites at DOE facilities is chlorinated solvents. In response to this problem, bioreactors are being developed by The Savannah River Technology Center which utilize methanotrophic microorganisms in an above-ground fermentor (bioreactor). Methanotrophs are microbes which utilize methane as a primary metabolite. This bioreactor technology is based on the concept that methanotrophic bacteria can be immobilized through adsorption in a porous substrate (providing a high surface area) so that contaminated groundwater or waste water can be passed through the porous medium and be consequently purified.



Above-Ground Methanotrophic Bioremediation

Methanotrophs have been demonstrated to degrade more than 256 organic compounds and to also adsorb metals. In particular, methanotrophs have been isolated which effectively degrade the otherwise recalcitrant chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Although this class of microorganism does not degrade TCE or PCE by direct consumption, the TCE and PCE solvents are degraded nonetheless through an ancillary mechanism referred to by some researchers as co-metabolism. The population of microorganisms in the bioreactor is sustained through the injection of low concentrations of methane (≤5% v/v), but the degradation of chlorinated solvents occurs due to a unique primary enzyme named methane monooxygenase type I, or MMO. This powerful oxidizer has been shown to induce the formation of TCE-epoxide from TCE. The resultant compound, TCE-epoxide, is extremely unstable and therefore breaks down to simpler more degradable compounds like formate, etc. All the daughter compounds are either unstable or small and easily metabolized by the microbes in the bioreactor.

In summary, indigenous microorganisms are being stimulated to degrade trichloroethylene (TCE), tetrachloroethylene (PCE), and their daughter products in groundwater by pumping the contaminated water through a large fermentor. The bacteria in the fermentor are attached to a substrate that allows them to adsorb and degrade the contaminants as they pass by. The principal source of carbon and energy for the

bacteria is methane. Thus, methano-trophic organisms dominate in this optimized environment. Methanotrophs have been demonstrated to degrade trichloroethylene completely to carbon dioxide and chloride. The input to the bioreactor is contaminated groundwater, methane/air, and trace amounts of phosphorus and nitrogen as additional nutrients. The subsequent output is decontaminated water with trace amounts of nutrients and bacterial biomass.

Bioreactor destruction of chlorinated hydrocarbons in groundwater will provide a cost-effective and more environmentally acceptable method of groundwater remediation. This has very wide application since chlorinated hydrocarbons are the most common contaminants found in U.S. drinking water. This bioreactor technology provides a method for remediating groundwater not only as part of the remediation of contaminated sites, but also for the cleanup of waste water before discharge, and for destroying chlorinated solvents present in the raw-water sources that are used for community supplies. Concerning waste abatement, this technology has been demonstrated for hydrocarbons other than TCE and PCE, such as toluene, xylene, and benzene.

TECHNICAL PERFORMANCE

Laboratory-Scale Testing. Biodegradation of TCE by methanotrophs (methane-oxidizing bacteria) has been demonstrated in microbiological studies and in methanotrophic laboratory-scale bioreactors. Little et al. (1988) at Oak Ridge National Laboratory (ORNL) isolated a mixed methanotrophic culture from a TCE-contaminated well on the Oak Ridge Reservation. This culture was subsequently used in a prototype lab-scale continuous-flow bioreactor at ORNL (Donaldson et al., 1988). Fliermans et al. (1988) at Savannah River Laboratory isolated consortia and species capable of aerobic degradation of TCE with methane as the primary nutrient from TCE-contaminated soil and groundwater from the Savannah River Site (SRS). These organisms have also been successfully used in laboratory-scale fluidized-bed bioreactors to treat TCE/PCE-contaminated groundwater (Phelps et al., 1990).

Pilot-Scale Studies. In addition to the laboratory bioreactor studies at ORNL, the University of Tennessee, and elsewhere, one pilot-scale bioreactor system has been operated by Battelle Columbus at Tinker Air Force Base, Oklahoma (Wickramanayake et al., 1990). This project was funded by the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida. This pilot-scale study demonstrated that actual TCE-contaminated groundwater can be treated in a trickle-bed bioreactor. The culture used in this test was provided by ORNL. Tyndall AFB is continuing to support development of TCE bioreactor technology at ORNL, the University of Tennessee, and SRS. The bioreactors used at Tinker Air Force Base are being provided by the Air Force for further field tests at Oak Ridge and Savannah River. This process has proven to be very reliable in pilot-scale systems, with unattended operation, 24 hours a day for more than 1 year. This technology is being demonstrated at SRS. Specific results from the recent SRS pilot-scale testing should be available in the near future (FY94-95).

This technology can only achieve ppb clean-up levels if the subsurface source is homogeneous, non-adsorbing matrix (e.g., gravel, sand). At many sites, this technology will be most effective as a containment technology for contaminated groundwater, since it is limited by pumping of the water to the surface. Contaminants adsorbed to the biomass and bioreactor matrix are the only potential process wastes, and these will probably be insignificant.

Costs. The initial capital-equipment investment is $800K and 500 man-hours for site preparation, setup, and assembly. The operations and maintenance costs are dependent on the labor costs for one technician (25% time) and electricity and natural-gas costs. The life-cycle cost is dependent on the frequency of sampling and type of sampling required.

PROJECTED PERFORMANCE

Projected performance data not available.

WASTE APPLICABILITY

This technology is targeted to degrade TCE, PCE, vinyl chloride (VC), dichloroethane (DCE), trichloroethane (TCA), and benzene, toluene, ethyl benzene, xylene (BTEX) as either a component of a pump-and-treat effluent treatment or waste-water treatment technology.

STATUS

This technology is in the pilot-scale testing phase of development. The schedule for scale-up to full-scale groundwater or waste-water remediation bioreactor will be determined after pilot-scale testing results have been analyzed (FY94-95).

REGULATORY CONSIDERATIONS

The basic concepts of this technology are expected to be applicable to other sites having TCE-contaminated soils and water. However, the particular process designs will be site-specific. This remediation technology may not be compatible with some sites if local geologic structures hinder contaminated-water recovery via pumping, which would subsequently hinder attainment of ppb concentrations in the aquifer. In some states, this technology may require a treatment-facility permit and an NPDES discharge permit. Important regulatory drivers are RCRA (40 CFR 264 & 265 Subparts F & G), CERCLA (40 CFR 300 1986 Amendments Section 122), and SDWA (40 CFR 141).

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to industries which have groundwater-contamination problems. Specific industries include the electric utilities, refineries, fuel-storage facilities, and manufacturing industries which use or produce chlorinated solvents.

BASELINE TECHNOLOGY

The comparable baseline technologies include air strippers, soil venting, and pump-and-treat technologies such as carbon adsorption from water and air streams. The principal existing technology for remediation of TCE-contaminated groundwater is pumping followed by air stripping. Unsaturated sediment contamination can only be remediated by vapor extraction. Neither of these are TCE-destruction technologies; in both cases, the TCE is either discharged to the atmosphere or captured on activated carbon for subsequent disposal.

Preliminary economic evaluations have shown that while air stripping without emissions control is the least costly technique, biodegradation will be very competitive with air stripping with emissions control. Cost analysis of methanotrophic bioreactors compared with air stripping combined with carbon adsorption of the air stream and direct carbon adsorption from the water have suggested for several TCE concentrations and flow rates that the methanotrophic system would save 40% to 60% over conventional technologies. We expect that these observations will also be the case for in situ bioremediation of TCE alone or in combination with bioreactors.

The principal uncertainties for this bioremediation technology concern the rate of TCE removal/degradation—how long it will take. The permeability of the soil will influence the recovery of contaminated

the soil will influence the recovery of contaminated water. Similarly, heterogeneities in a stratum may cause some regions to be bypassed. For some sites, this technology may only be used as a containment strategy, not a cleanup strategy.

INTELLECTUAL PROPERTY

There are no specific patents or rights to this technology. Other intellectual property includes "biodegradation of halogenated aliphatic hydrocarbons," and "water purification using microorganism-capable of aerobic degradation of low molecular weight alkanes." The demonstration will also use this process; however, since the assignee for this patent is U.S. EPA, no license is necessary since DOE is also a U.S. government agency.

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Industrial/University Partners

Radian, Gas Research Institute, Michigan Biotechnical Institute, and Envirex. GRI has funded more than $4.8 million over the last 5 years in the Methanotrophic Treatment Program in collaboration with WSRC. GRI is also supplying all of the gas in the current demonstration. Envirex has donated vessels, and MBI has provided scale-up tests for the current demonstration.

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BIOREMEDIATION OF HIGH EXPLOSIVES BY PLANTS

New Mexico State University

DESCRIPTION

Nitroaromatic compounds including 2,4,6-trinitrotoluene (TNT) and dinitrotoluenes are found as soil contaminants at bombing ranges and blast sites, explosives-manufacturing sites, and loading and packing plants. Dinitrotoluenes are also used as intermediates in the manufacture of plastics like polyurethanes and other products derived from diisocyanates. Because of high toxicity and potential carcinogenicity, contamination of soils and waste streams with nitroaromatic compounds is a serious environmental problem, particularly where the contamination of underlying aquifers is a concern.

TECHNICAL PERFORMANCE

Plants can be used to remove nitroaromatics from surface-contaminated soils. Initial studies with plant cells in suspension culture showed that TNT is removed rapidly from the nutrient medium. Concentrations up to 150 ppm were reduced to <1 ppm within 24 hours by growing cultures of *Datura innoxia* (Jimson weed). A more detailed investigation using radiolabeled TNT and gas chromatography/mass spectrometry demonstrated that the TNT is translocated across the cell wall into cultured cells of *Datura* or *Lycopersicon peruvianum*, a wild tomato species. In the cell, TNT is rapidly metabolized by nitro-reduction, deamination, and oxidation of the methyl group, resulting in a variety of biotransformation products leading to aminobenzoic acids.

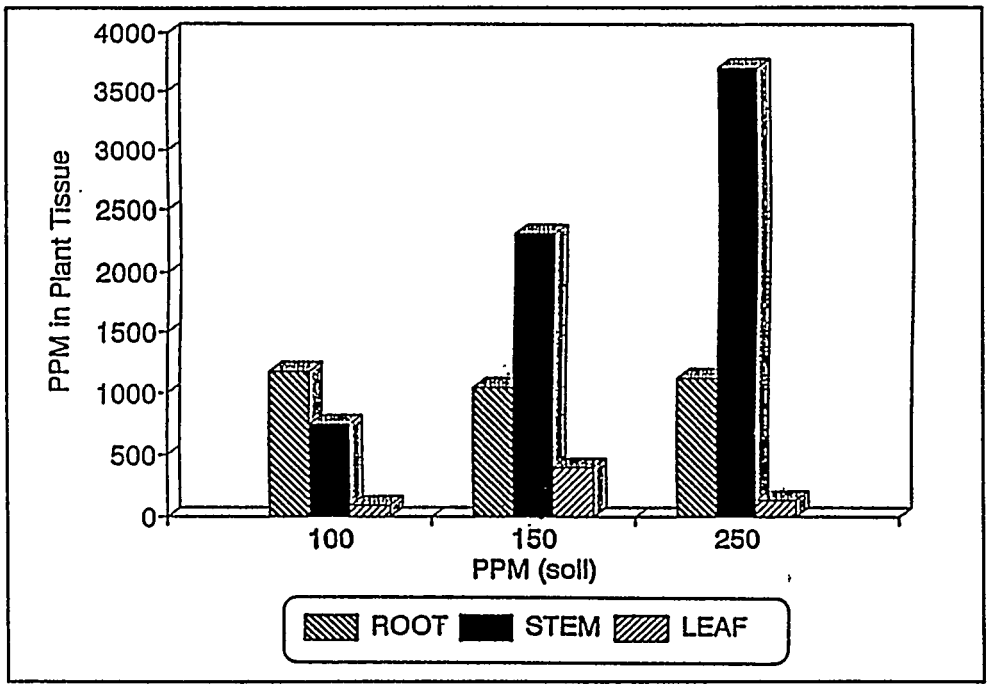

Figure 1. Concentration of TNT and metabolites in plants of Lycopersicon peruvianum grown in soil containing TNT.

After the metabolic fate of TNT had been characterized in plant-cell cultures, the feasibility of soil decontamination by plant uptake was studied under greenhouse conditions. Plants of *D. innoxia* and *L. peruvianum* were grown in soils containing radiolabeled TNT in concentrations ranging from 100 to 1,000 ppm. All plants grew well in sandy soils containing up to 500 ppm TNT. The *Lycopersicon* plants showed signs of slight (750 ppm) to moderate (1,000 ppm) phytotoxicity at the highest concentrations, while the plants

of *D. innoxia* did well even in soil containing 1,000 ppm TNT. During a growth period of two weeks, all plants concentrated radioactive material to levels exceeding the soil concentrations up to 30-fold. At soil concentrations up to 250 ppm, much of the recovered labeled material was found in stems and leaves; at the higher soil concentrations, the roots contained most of the radioactivity. In stems and leaves, all radioactive material consisted of TNT metabolites. Only in the roots of plants grown in soils containing 500 to 1,000 ppm TNT, small amounts of unmetabolized TNT (<1% of radioactivity) were found by HPLC analysis. At the end of the 2-week growth period, the soils were analyzed for residual TNT and metabolites by HPLC and radioactivity counting. Both methods indicated that less than 10 percent of the applied total quantity remained in the soil. It is likely that under the greenhouse conditions of this study with high temperatures and daily irrigation, part of the TNT applied to the soils was volatilized or photodecomposed at the soil surface. Further investigations under field conditions are needed to clarify this aspect of the remediation process.

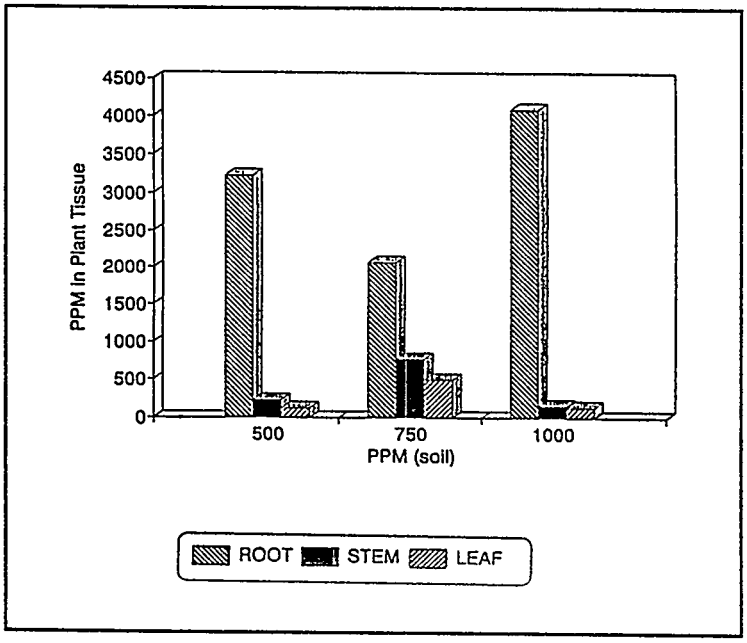

Figure 2. Concentration of TNT and metabolites in Lycopersicon peruvianum grown in soil containing TNT.

PROJECTED PERFORMANCE

The greenhouse studies have shown that higher plants are capable of extracting TNT from soil and breaking it down by biotransformation reactions. For large-area surface-contamination sites such as blasting areas or bombing ranges, the growth of accumulator plants offers a low-cost approach to removal of TNT (and probably other high explosives). As the plants accumulate only TNT metabolites and not TNT itself, there is no explosion hazard associated with this bioremediation method.

WASTE APPLICABILITY

Direct extraction of TNT from soil by accumulator plants such as *Datura* or *Lycopersicon* is applicable to surface-contaminated areas only because of the shallow root zone of these plants. By using deep-rooted plants, the treatable zone could be extended to a depth of several meters, but the slow growth of such plants may mean an unacceptably long time-frame for the bioremediation of some sites. Pump-and-treat systems coupled with irrigation (where necessary) can be used to decontaminate deeper soil layers by using the pumped water to irrigate a field of accumulator plants or sending it through a constructed wetland filter with appropriate plant species. Bioremediation by plants will then be feasible also for industrial-contamination sites, ammunitions loading and packing plants, and disposal sites with deeper subsurface contamination.

STATUS

Laboratory and greenhouse work for two plant species has been completed. Field evaluation is pending. The bioremediation of explosives in surface-contaminated soils by

plants like *Datura* or *Lycopersicon* is ready to be field-tested in the next growing period. Selection of other accumulator plants and the development of pump-and-treat systems using constructed wetland filters will require more laboratory and greenhouse testing.

REGULATORY CONSIDERATIONS

Direct bioremediation of surface-contaminated sites by accumulator plants will produce no off-gas or contaminated run-off water. Pump-and-treat approaches can be set up as closed-loop systems which will not produce any waste water; if under conditions of high water production effluents are generated, permits under the Clean Water Act (NPDES permit or pretreatment standards) have to be considered.

POTENTIAL COMMERCIAL APPLICATIONS

In addition to direct applicability to contaminated sites under the administration of the Departments of Energy and Defense, bioremediation of soils or liquid-waste streams containing nitro-aromatic contaminants would be useful for chemical industry and for plants using nitrotoluenes as intermediates in the manufacture of end products such as polyurethanes.

BASELINE TECHNOLOGY

The baseline technology is bioremediation of nitroaromatic compounds by higher plants.

INTELLECTUAL PROPERTY

Flexible. The PI, WERC Administration, university administration, and industrial partners work in conjunction to discuss individual cases.

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REFERENCES

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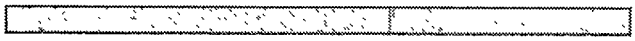

CHELATORS FOR APPLICATION IN RADIOACTIVE ACTINIDE WASTE REMEDIATION

New Mexico State University

DESCRIPTION

The overall goal of this program is to design, develop, and synthesize organic chelators for the selective removal of radioactive and highly toxic actinides ions such as plutonium from process-waste streams and soils. The selective removal of actinides from large amounts of nontoxic metals would significantly reduce the volume of waste requiring long-term storage. Reducing the concentration of the target metal to extremely low levels requires the use of a chelator with a high binding strength for that ion as well as substantial selectivity over other competing ions. The project objectives can be divided into the following major tasks:

- Identification and synthesis of cost-effective chelators for the selective binding of actinides in the presence of a number of other competing metal ions expected to be present in waste streams or soils.
- Development of a series of polymer-supported extraction systems for the selective removal of actinides from wastewater streams.
- Evaluation of the ability of these chelators to remove actinides in a variety of relevant situations.

Also proposed is the development of water-soluble chelating polymers for the separation of actinides from waters using ultrafiltration as the mode of metal-ion separation. Such polymers have the potential to provide rapid-exchange kinetics in comparison to traditional ion-exchange resins due to the homogeneity of the system. These polymers will have a backbone that is hydrophilic and carry ligand moieties previously shown to be effective for binding actinides.

TECHNICAL PERFORMANCE

Efficient separation methods are needed to remove actinides from groundwater and soils to meet increasingly stringent regulatory standards. There is also a need for methods to remove actinides (TRU elements) selectively from other toxic and nontoxic metal ions. New technologies must be applicable under a wide range of conditions ranging from acid-process waste streams to the alkaline supernates present in storage tanks at Hanford and other DOE sites. The removal of TRU elements from solid wastes is also a significant problem.

The chelators being developed must, in addition to high selectivity and binding for the target metal ion, possess chemical stability and desirable solution characteristics. Ideally, the sequestrated actinide can be liberated from its ligand complex under mild conditions in a highly concentrated form. Apart from traditional insoluble polymeric supports, the development of water-soluble chelating polymers is also of relevance for use with ultrafiltration membranes as a mode of metal-ion separation.

PROJECTED PERFORMANCE

A number of tetrahydroxamate chelators have been synthesized in the laboratory which exhibit much promise for the selective binding of actinide ions in solution. These polyhydroxamates were chosen as potential chelating structures based on computer

modeling, solubility properties, and other important features including ease of synthesis. Studies show that some members of this class of chelators are capable of binding plutonium strongly and selectively.

WASTE APPLICABILITY

This technology is applicable to radioactive-waste management at Los Alamos National Laboratories and other DOE facilities.

STATUS

The synthesis of a number of analogs has been completed and their evaluation has been initiated.

Promising structural features of the ligands identified in the study have been incorporated into a variety of polymeric matrices. A number of polymers have been synthesized and are currently under evaluation. Some of these polymers are water-insoluble while others are water-soluble. Preliminary results clearly indicate that this class of polymers has promise for the remediation of actinides in waste waters.

REGULATORY CONSIDERATIONS

The technology is yet to be field tested.

POTENTIAL COMMERCIAL APPLICATIONS

The technology has potential for the cleanup of radioactive toxic waste in a variety of situations.

BASELINE TECHNOLOGY

The baseline technology is the development of novel and cost-effective chelators for application in radioactive actinide waste remediation.

INTELLECTUAL PROPERTY

Flexible. The PI, WERC administration, university administration, and industrial partners work in conjunction to discuss individual cases.

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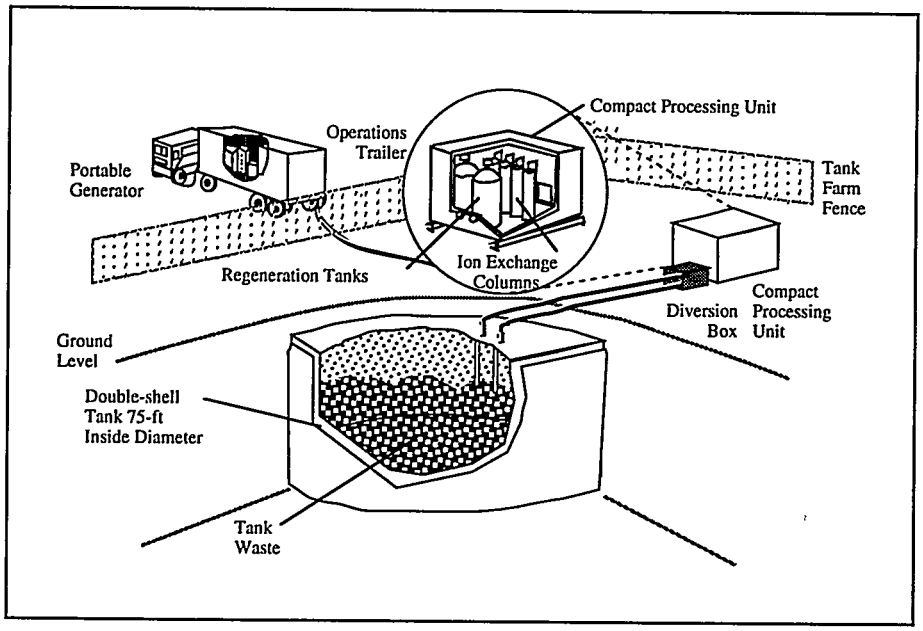
COMPACT PROCESSING UNITS FOR RADIOACTIVE WASTE TREATMENT

Pacific Northwest Laboratory and Savannah River Laboratory

DESCRIPTION

Compact Processing Units (CPUs), or "Modular Waste Treatment Units," are relatively small mobile equipment modules that would be located near the waste-storage tanks or in a conveniently located diversion box in the Hanford waste-transfer system. They perform unit chemical-process operations. The CPUs allow rapid deployment of technologies for the treatment of radioactive wastes in underground storage tanks. The modules would be manufactured offsite by commercial vendors and moved into place using trucks or special transports. The CPU is designed to permit relocation using a construction crane and a transport trailer. The concept of having standardized modules is based on the notion that various radioactive-waste-treatment subsystems could be standardized to match the CPU hardware package, leading to more rapid, cost-effective deployment. The cost benefits are realized even when multiple units are deployed to achieve greater processing rates. The modular design concept will also allow for reuse of CPU components for different unit processes or process deployments. The CPU consists of four major subsystems: the containment system (safety), the process system (e.g., ion exchangers), the control system, and the process-interface subsystem (which includes solid/liquid separations and waste-stream routing).

The ion-exchange CPU will pump undiluted liquid tank waste from an underground storage tank or receive liquid waste from a waste-retrieval system for treatment. The CPU will filter this waste to remove solids. The solids removed will be transferred to a holding tank for further analysis and processing. The filtered tank waste will be adjusted to optimize the waste composition and temperature for maximum efficiency of the ion-exchange process. The waste will then be pumped through three ion-exchange columns in series to remove the cesium from the waste. The waste will be returned to the tank farms after the cesium is removed. The ion-exchange columns will use a new formaldehyde resorcinol ion-exchange resin formulation developed at Savannah River Laboratory. The loaded ion-exchange resin will be regenerated, using nitric acid to remove the cesium. This high-concentration cesium waste will be neutralized and transferred to the tank farms as a waste-feed stream for the vitrification process. The waste stream with the cesium removed will be suitable for disposal as low-level waste.



Compact Processing Unit

TECHNICAL PERFORMANCE

Design Specifications. The CPU is a compact volume approximating a cube with 15-ft sides. The process flow rates are restricted by the size of equipment that can fit into a CPU module. The CPU is designed to process tank waste at up to 19 l/min (5 gpm) with an average rate of 9.5 l/min (2.5 gpm). Staffing of the unit for continuous operation is expected to require 18 operators, 12 engineers, and 6 support personnel.

Feasibility Study. In FY92, Westinghouse Hanford Company (WHC) investigated the practicality of using CPUs as an alternative to a centralized pretreatment facility. This investigation consisted of developing the concept to sufficient detail that a cost estimate for deployment could be made.

Cost. The cost estimate performed by WHC showed that deployment of a group of CPUs as a replacement for the initial pretreatment system could result in a capital cost savings of $300M to $500M. The development cost of this technology, including safety, environmental documentation, and construction of the prototype system, is estimated to be $50M. The annual operating cost of this technology is estimated to be $9.5M/year of operation.

PROJECTED PERFORMANCE

The CPU is designed to treat 1 Mgal of Hanford Double Shell Tank Waste in one year. This would be accomplished at an average process flow rate of 2.5 gpm. The CPU for cesium removal is expected to treat waste streams with concentrations up to 1 Ci/l cesium. It is expected to remove the cesium to levels below the Nuclear Regulatory Commission (NRC) Class A low-level waste standards (1 Ci/m^3). The cesium-removal factor is projected to be 10,000.

WASTE APPLICABILITY

This waste-treatment technology is targeted for radioactive-process liquids, sludges, and slurries. The CPUs are designed to incorporate waste-treatment modules that could potentially have application to all Department of Energy (DOE) radioactive liquid tank wastes. The CPU waste-treatment hardware system is applicable to high-level, low-level, and transuranic chemical separations technologies. The prototype CPU includes a process module of cesium-specific ion-exchange resin columns that are selective to cesium ions.

STATUS

Pacific Northwest Laboratory developed the compact or modular processing unit concept in FY91. WHC performed a detailed feasibility study with further development in FY92. Deployment of the cesium ion-exchange CPU technology is scheduled for the 1996 calendar year. A radioactive waste-treatment demonstration in scheduled for FY97.

REGULATORY CONSIDERATIONS

This process is completely contained and automated, which minimizes worker exposure to hazardous materials and process hazards. No special physical requirements are anticipated for operations personnel. This process will meet or exceed all regulatory requirements imposed by the Environmental Protection Agency and the NRC.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include waste treatment, separation, and volume-reduction operations for reclamation of radioactive-waste liquids, sludges, and slurries stored in underground storage tanks, and processing of effluent pretreatment before appropriate disposal.

BASELINE TECHNOLOGY

The baseline technologies are large, centralized facilities for supernate waste treatment. The advantages of CPUs over the baseline technology are in four areas: cost reduction, schedule improvement, reduction of technical uncertainty, and reduction of process-deployment uncertainty.

INTELLECTUAL PROPERTY

Patents: None.

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REFERENCES

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CRYOGENIC RETRIEVAL OF BURIED WASTE

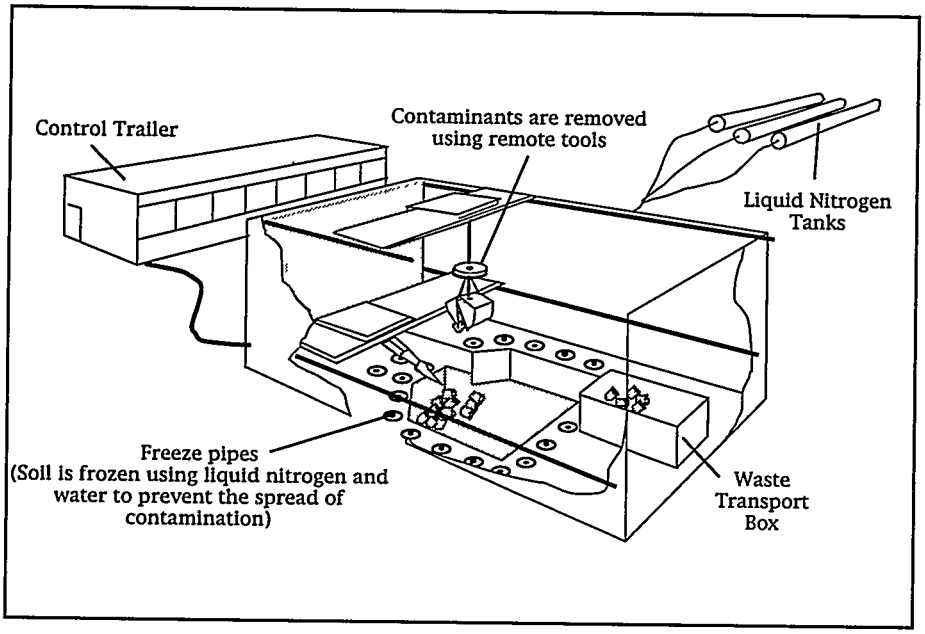
Idaho National Engineering Laboratory
and Pacific Northwest Laboratory

DESCRIPTION

Cryogenic Retrieval (CR) of buried waste is a technology that relies on liquid nitrogen (LN_2) to freeze soil and buried waste in order to immobilize hazardous waste and reduce the spread of contamination while the buried material is retrieved with a series of remotely operated tools. CR is proposed for application to any type of radionuclide or hazardous contaminant that may be contained in transuranic (TRU) buried waste. CR has the potential to be used at any buried-waste site within the Department of Energy (DOE) complex.

To freeze the soil for the CR process, a series of carbon or stainless-steel small-diameter freeze pipes (approximately 10 to 12 ft in length) are driven into an area of soil and buried waste to be frozen and removed. LN_2 is delivered into the pipes and small quantities of water are injected to promote cohesion of the soil and waste particles in the frozen area. While the pit to be excavated is frozen, the perimeters of adjacent pits are also frozen. Once the area to be removed is frozen, an access pit in clean soil is excavated.

The access pit serves to create a dig face from which excavation of the waste can proceed. A gantry with remotely operated tools such as a jackhammer, a hydraulic jack, shears, and a grapple is moved over the frozen area to be retrieved. With the gantry tools in place, the tools are remotely operated, and the frozen soil and waste is broken, chipped, cut, and loaded into transport boxes. The jackhammer chisels and breaks up soil and debris that fall into the access pit. The shears are used to cut and size material, while the grapple picks up the debris and loads it into the transport boxes. The hydraulic jack is used to pry or bend the freeze pipes away from the dig face. During the excavation process, a series of air monitors detects the dispersal of rare-earth tracers. The output of the process is the excavated soil and waste material. The principal benefit of this technology is contaminant mobility reduction, since by freezing the soil both airborne and liquid contaminants are immobilized.



Cryogenic Retrieval

A weather shield (a large portable cover or tent) is used with this technology to minimize waste distribution by air motion and to permit operation in all weather conditions. If the freeze pipes cannot be extracted and reused they would require treatment as another buried waste type. If intact containers exist in the

waste volume, the drilling of injection pipes might rupture the containers, causing an initial spread of contamination. Furthermore, injection of water to help the freeze process may also contribute to some contamination spread if it were to flow out of the retrieval column.

The major technical challenges for this technology are developing a method for placement of freeze pipes in all types of soil and waste; conservation of LN_2; dispersion of water evenly through the soil and waste matrix; reduction of secondary waste created by the freeze pipes; selecting or developing more productive tools for the removal and handling of frozen waste; and improving methods for the measurement of thermal characteristics and for the detection of moisture migration.

TECHNICAL PERFORMANCE

Field Demonstration. A demonstration was conducted at Idaho National Engineering Laboratory (INEL) during the summer of 1992 at a cold test pit (i.e., simulated waste). The technology was shown to function as intended. Refinements will be necessary to develop the technology for full-scale, hot-production use. Eight field personnel were used to conduct the demonstration. A detailed estimate of the energy demands has not been made for full-scale production; however, during the field demonstration, a 400-kW generator was used to service all field power needs, including running up to three tools simultaneously, plus the hydraulic power unit and the control trailer. The estimated cost for large-scale application is $1,250/yd^3 of frozen excavated material.

PROJECTED PERFORMANCE

The production goal for this technology is 80 yds^3/day. It is estimated that 25 to 30 field personnel would be required to set up and operate the Cryogenic Removal equipment in a large-scale application. It is further estimated that an additional 10 to 15 management, safety, engineering, quality, and related technical support personnel would be needed.

WASTE APPLICABILITY

This technology is applicable to the retrieval of TRU buried waste and other types of hazardous buried waste. The technology was developed to mitigate contaminant migration while excavating buried waste.

STATUS

The technology has been demonstrated in a full-scale field demonstration in the summer of 1992. The components of this CR technology exist within current industry and have been integrated for the purpose of developing a new method for exhuming buried waste. Approximately four more years are required to develop this technology to a usable level for full-scale hot production. If this technology is developed by 1998, it will be incorporated into the Record of Decision (ROD) for Buried Waste Pits and Trenches at INEL.

REGULATORY CONSIDERATIONS

Minimal ecological impacts are anticipated from use of the proposed technology. LN_2 is not a hazard to the environment. However, while working with LN_2, caution must be used to prevent human contact. Good ventilation is required to ensure adequate oxygen concentration. There are no unusual physical requirements for worker safety because the concept relies on remote operation of tools to extract the buried waste.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include retrieval of buried wastes that are extremely hazardous and/or radioactive.

BASELINE TECHNOLOGY

A baseline technology has not been established for the retrieval of TRU buried waste. However, a reasonable comparison might be excavation without cryogenic pretreatment to minimize contaminant dispersal during removal with or without remote operation.

INTELLECTUAL PROPERTY

A patent has not been filed for CR.

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REFERENCES

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DECISION SUPPORT SYSTEM TO SELECT MIGRATION BARRIER COVER SYSTEMS

Los Alamos National Laboratory

DESCRIPTION

A Decision Support System (DSS) is being developed to integrate the knowledge of experts from scientific, engineering, and management disciplines to help in selecting the "best capping practice" for a landfill site. Containment technologies, including surface caps, reduce the potential for contaminant migration from the landfill by an alteration of the surface and/or subsurface soils. The process of selecting containment cover technologies for mixed-waste landfills requires consideration of many complex and interrelated technical, regulatory, and economic issues. The DSS uses an EPA-recommended hydrologic model and a recent soil-erosion model along with decision software (a knowledge-based expert system) to give an objective remedial action decision for radioactive, hazardous, or mixed-waste landfills. Possible options for remedial-action range from no action (or monitoring only) to physically removing the waste.

The DSS provides a scientific method for choosing between several engineered-landfill cover designs. The EPA-recommended landfill cover is the RCRA Cap. However, in certain geologic and climate situations, there may be other capping technologies which are equally suited and possibly less expensive than this baseline technology. The DSS software provides modeling and decision capability to choose among appropriate technologies considering regulatory problems, long-term performance, cost, and risk. The long-term performance of multifarious remedial options is determined by the intrinsic hydrogeologic and soil-erosion models. The decision component of the software subsequently calculates several dimensionless decision variables. The remedial alternatives are ranked according to a composite score based on a weighted combination of several decision variables. The actual default decision variables and additional variables used are given in Table 1.

Table 1. Decision Variables Considered by DSS

Default Decision Variables	Input Source
Surface Runoff	HELP
Lateral Drainage	HELP
Evapotranspiration	HELP
Deep Percolation	HELP
Erosion	CREAMS
Materials Cost	User Supplied
Construction Cost	User Supplied
Additional Decision Variables (optional)	
Remediation Cost	User Supplied
Maintenance Cost	User Supplied
Risk	User Supplied
LANL lateral drainage[1]	User Supplied
SNL lateral drainage[2]	User Supplied

1. Los Alamos capillary barrier; 2. Sandia dry barrier.

The objective of this DSS software is to provide risk managers with a defensible, objective way to select capping alternatives for remediating radioactive and mixed-waste landfills. This goal is being achieved through a joint project between Los Alamos National Laboratory (LANL) and the U.S. Department of Agriculture, Agricultural Research Service. The DSS is being developed as a multi-objective decision-making software system, with embedded simulation models, to design and/or evaluate engineered surface barriers for mixed-waste landfills. The embedded simulation models include HELP (Hydrologic Evaluation of Landfill Performance), which is the EPA-recommended model for hydrologic performance evaluation, and CREAM (Chemicals, Run-

off, and Erosion from Agricultural Management Systems), which is useful for modeling erosion and runoff. The data collected from the migration barrier covers will be used to evaluate the DSS.

The DSS software ensures that the risk manager uses the best scientific information on barrier design and performance along with other criteria to select the best remediation practice within the constraints of technical performance, regulatory requirements, and cost. The use of the program to design and evaluate barrier-cover remediation technology will reduce the likelihood of selecting a barrier-cover technology that does not meet performance objectives and the attendant costs of fixing mistakes. Candidate remediation technologies can be evaluated with the DSS beforehand to identify technical and regulatory problems inherent in the technologies. It can also be used to evaluate projected long-term performance and the practicality of the designs from a construction and economic viewpoint. The general structure and methodology of the DSS is shown in Figure 1.

Since the software is UNIX-workstation-based, it is compatible with many types of computer systems. A PC-based prototype DSS software package, running under Windows 3.1, is being developed. It will be a user-friendly coupling of symbolic processing and numerical near-surface hydrologic modeling. The embedded Knowledge Based System (KBS) will integrate confidence limits and exceedence probabilities from stochastic conjectural analyses of hydrologic variables in space and time and the symbolic objects that influence landfill technology. The integration will result in a DSS that should improve long-range predictability of migration-barrier performance by incorporating complex environmental processes, along with the management issues, into the decision-making process.

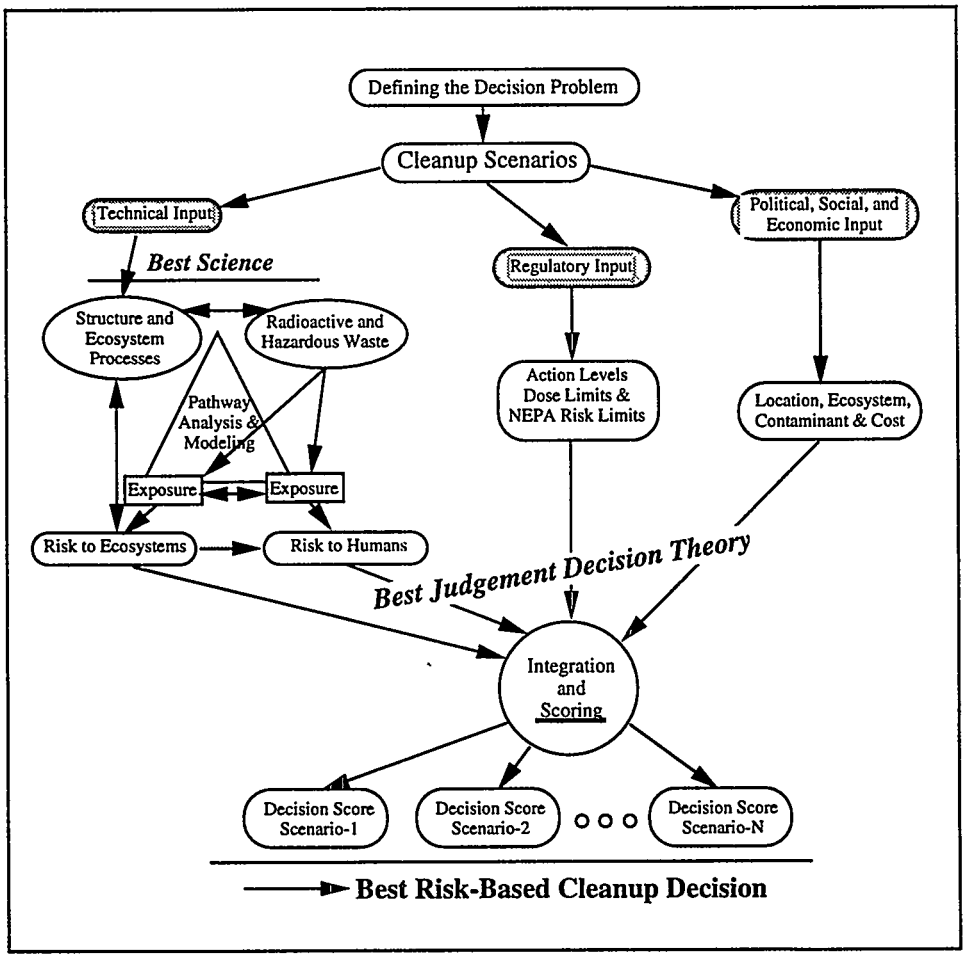

Figure 1. Decision process in managing risks to humans and ecosystems.

The DSS will use dimensionless scoring or utility functions parameterized from the quantitative KBS output and expert judgment to convert the range of the decision variables to a unitless common range. This process allows one to combine the decision variables and rank the alternative designs. A major task is to integrate a new decision-making methodology into the existing DSS to eliminate much of the subjectivity in existing multi-objective methods. Since the DSS requires data to initialize and parameterize the embedded simulation models and the

consensus of technical experts in developing the heuristic and scoring function information, there is some inherent subjectivity in the program.

TECHNICAL PERFORMANCE

Field Demonstration. The DSS has been tested at Hill Air Force Base (AFB) in Utah and was found to perform remarkably well. The program is extremely fast and can parameterize and score a site in five minutes. The default input parameters for the hydraulic conductivity (HC) model are given in Table 2, and the observed results of four decision variables are presented in Table 3.

Table 2. Default Input Parameters for the HC Model.

Parameter	Source
Curve number	Soil Texture
Vegetation type	Vegetation zone
Initial soil water content	Climate
Leakage fractions for liners	Liner type
Porosity	Soil texture
Saturated HC	Soil texture
1/3 bar soil water	Soil texture
15 bar soil water	Soil texture
Bare soil evaporative depth	Soil texture
Cover erosion factor	Soil, vegetation
Conservation erosion factor	Soil surface characteristic
Manning's n parameter	Soil, vegetation
Rooting depth	Vegetation

Costs. Software costs have not been estimated. Startup costs include computer hardware and a person to utilize the program. The maintenance cost will be minimal (less than $1,000/yr to maintain and update the software as improvements are made). A comparison of remedial alternatives for landfills at Los Alamos is presented in Table 4.

Table 3. Observed Results from Hill AFB: Average annual values and range for four decision variables.

Cap Design		Runoff[1] (cm)	Sed. yield (Kg/ha)	ET (cm)	Percolation[2] (cm)
Control Cap	min:	0.04	0.00	17.53	2.60
	ave:	1.40	118.70	27.37	14.74
	max:	3.98	390.31	35.66	29.43
EPA RCRA	min:	3.63	0.00	23.34	0.00
	ave:	12.05	76.70	28.80	0.13
	max:	20.90	187.82	35.33	0.51
Los Alamos 1	min:	0.34	0.00	18.00	0.34
	ave:	5.18	4.50	24.25	6.82
	max:	8.21	19.98	28.00	13.15
Los Alamos 2	min:	1.39	0.00	22.92	1.25
	ave:	3.50	4.80	33.99	7.28
	max:	4.28	18.81	44.58	17.45

1. percolation out of trench cap and into waste-storage layer
2. includes lateral flow where applicable

Table 4. Estimated 1992 costs of remediation alternatives for landfills at Los Alamos, NM.

Alternative	Cost ($M/ha)[1]
Excavate	80
RCRA cap	4.9
Soil/capillary barrier cover	3.7
Bio-engineered soil/veg. cover	0.24
Surface management w/erosion control	0.12

1. hectare (ha) = 10,000 m^2 (2.471 acres).

PROJECTED PERFORMANCE

The DSS technology will be adapted and tested for remediation of waste-disposal sites with migration-barrier-cover technology using the designs and database from the existing cover-barrier field

demonstration at Hill AFB. The multi-objective decision-making capability, incorporating a KBS (or expert system) with embedded simulation models and using Hill AFB monitoring data, will be demonstrated.

WASTE APPLICABILITY

Since this technology is specifically used for aiding environmental restoration personnel in the selection of the best capping method for a given waste site, the technology is waste-independent. This technology is applicable to landfill remedial-action decisions. The landfill could have radioactive, hazardous, or mixed wastes.

STATUS

A UNIX workstation-based DSS software package will be available in FY94. A PC-based prototype DSS software package, running under Windows 3.1, is under development. On completion of the technology, software and documentation will be made available to user groups.

REGULATORY CONSIDERATIONS

Currently, the EPA recommends the Resource Conservation and Recovery Act (RCRA) cap, but does not exclude the use of alternative designs if equivalency can be shown. There currently is no objective way to develop and evaluate alternative designs. EPA guidance to permit applicants (EPA-530-SW-84-004) recommends that an analysis of the final cover design be presented in the closure plan. The analysis of the final cover design should describe how the design addresses six performance criteria: 1) minimizes liquid migration, 2) promotes drainage while controlling erosion, 3) minimizes maintenance, 4) has a permeability equal to or less than the permeability of natural subsoil, 5) accounts for freeze/thaw effects, and 6) accommodates settling and subsidence so that the cover's integrity is maintained. From a technical point of view, the DSS is particularly valuable in supporting a selected design that meets performance criteria. The DSS will include intrinsic software such as HELP (which is the only model currently sanctioned by the EPA for design and evaluation of landfill covers). With the addition of CREAMS erosion component and the decision software, the DSS will be a powerful tool for other agencies that are concerned with the design and evaluation of landfills.

POTENTIAL COMMERCIAL APPLICATIONS

Since the objective of the DSS technology is to provide risk managers with a defensible, objective way to select the best capping method for a given waste site, all environmental-restoration personnel considering the use of capping technologies could potentially be customers.

BASELINE TECHNOLOGY

The alternative to a formal decision-support system is to attempt to integrate the large and diverse sources of information in an ad hoc manner, with the attendant risks of omitting key information needed to make a quality decision. Many examples of selecting cover-remediation strategies that exacerbated, rather than resolved, contaminant-migration problems at a waste site exist. There is currently no objective way to select landfill-capping designs. Current practice is to use EPA guidance for the RCRA cap regardless of the level of risk associated with the site. This results in the use of a costly capping design that often greatly exceeds requirements based on real risks and that has very little field-performance data.

INTELLECTUAL PROPERTY

Patents: None.

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DRY BARRIERS FOR CONTAINMENT AND REMEDIATION AT WASTE SITES

Sandia National Laboratories, University of New Mexico,
and Daniel B. Stephens & Associates

DESCRIPTION

A "dry barrier" may be formed by circulating dry air through a soil layer above or below a waste-disposal site which reduces the soil-moisture content to very low values. Drying a horizontal soil layer creates a barrier to vertical water movement in three ways. First, the drying removes water from the system, intercepting water infiltrating down from the surface. Second, drying a soil layer increases its water-storage capacity so the soil will tend to retain rather than transmit water. Third, as a soil layer dries, moisture is removed from progressively smaller and smaller interstitial pores, and the hydraulic conductivity of the formation for liquid flow decreases. For example, the hydraulic conductivity of a typical sand may decrease three orders of magnitude as its moisture content is reduced from 20 to 10 percent. The more coarse a soil layer is, the greater the reduction in its hydraulic conductivity as it dries; therefore, an ideal application would consist of a stratigraphic section with sand or gravel materials interbedded with finer-grained silts or clays. This is the fundamental concept behind the development of capillary barriers, the principal difference being the circulation of dry air through the barrier to remove moisture. Because a dry barrier functions by increasing the soil tension, it has also been called a tensiometric barrier. A schematic diagram of a dry barrier for containment of a contaminant plume is shown in Figure 1.

In a field application, it is likely that dry air would be circulated through the formation through a combination of air-injection and extraction wells. In a cover application, the barrier would be used to augment performance of a conventional impermeable zone, and air circulation would be achieved using perforated pipe placed during construction of the cover. In a subsurface application, the injection and extraction wells would be placed using either horizontal-drilling technology (shown) or systems of vertical wells.

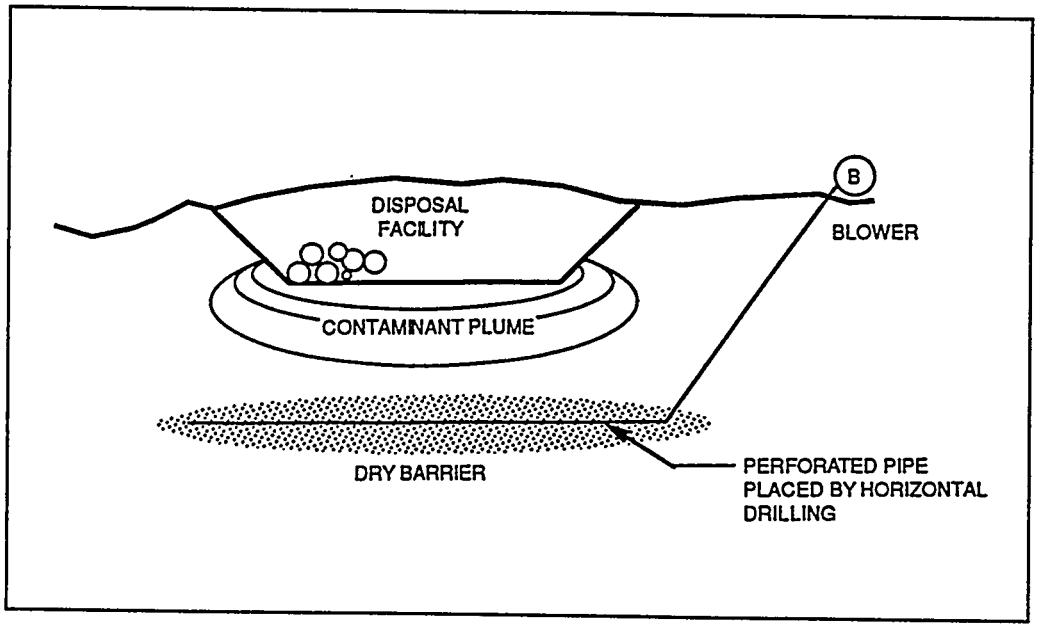

Figure 1. Schematic of a Dry Barrier for a Contaminant Plume

In addition to providing containment beneath a waste-source term, air circulated to create the dry barrier would enhance subsurface remediation processes. First, air circulation would provide removal of

volatile constituents (i.e., VOCs) analogous to the familiar vacuum-extraction process. Second, at many sites contaminated with high concentrations of organic compounds (such as leaking underground gasoline storage tanks), biodegradation of the pollutants is limited by the lack of oxygen for aerobic microbial metabolism. Air circulation through the subsurface environment would increase the oxygen content of subsurface soils and thus would enhance microbial degradation processes.

TECHNICAL PERFORMANCE

The technical viability of a dry barrier depends principally upon two factors: 1) the ability to circulate air through a porous medium, either a cover or the soil beneath a contaminated site; and, 2) atmospheric conditions which provide sufficiently dry air to enable removal of soil moisture through evaporation. At normal flow rates, air flow through porous media is governed by Darcy's Law and, due to its low viscosity, is able to flow through all but the tightest soils. The principal atmospheric condition of interest is the specific humidity of the air which is the ratio of the mass of water vapor (m_v) to the mass of moist air (m_a) in the mixture:

$$W = m_v / m_a$$

The actual specific humidity (W_{act}) of air can be calculated from measured relative humidity and temperature. The maximum specific humidity (W_{max}) depends on the vapor pressure of water and is therefore a function of air temperature and atmospheric pressure. The difference between the W_{act} and W_{max} represents the drying potential of the air (W_{DP}).

$$W_{DP} = W_{max} - W_{act}$$

The soil associated with a dry barrier will have a large thermal mass that will affect the subsurface air temperature, and therefore its drying potential. As a first

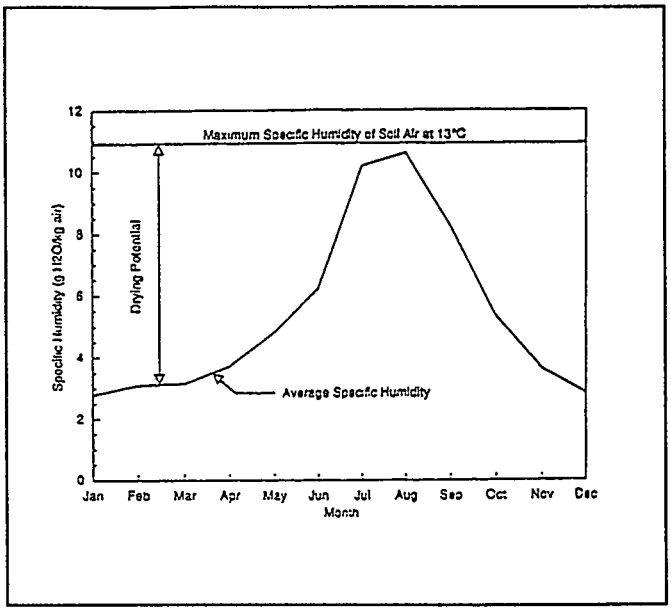

Figure 2. Drying Power of Albuquerque, NM Air Adjusted to 13°C to Reflect Subsurface Drying of Soils.

approximation, a constant soil temperature of 13°C is used which is the temperature of soils near Albuquerque, New Mexico. Figure 2 is a plot of the drying power of Albuquerque air adjusted to 13°C to reflect subsurface drying of soils. The drying potential of the air is the vertical difference between the lines representing atmospheric specific humidity and the maximum specific humidity. It is interesting to note that even though winter months have the highest atmospheric relative humidity, the air can hold very little moisture due to the low ambient air temperature so that when the temperature is adjusted to the 13°C of the subsurface environment, the drying potential is very large.

PROJECTED PERFORMANCE

Feasibility analyses have been conducted for application of dry barriers both in landfill cover systems and in subsurface barrier systems. These analyses developed preliminary designs for dry barriers and estimated capital and operating costs for both applications. Due to the dependence on dry air, it appears that the dry-barrier concept is most suitable for arid

regions of the country. Therefore, the focus of the studies was on systems located in New Mexico and Utah. Similar atmospheric conditions are present at major DOE facilities in Idaho and Washington.

The design of a dry barrier system is predicated upon removal of all of the moisture migrating through the barrier region. In a cover application, this moisture flux would occur during conditions of highest monthly precipitation. In Albuquerque, NM, this design criterion is 1.3 cm/month. In a deeper subsurface application, the design moisture flux will be the annual average infiltration rate which is about 2.3 cm/year. The drying potential of the air can then be used to determine the required air flow rate through the soil to remove this amount of moisture.

Preliminary designs were prepared for dry barriers of 1 ha (10,000 m^2) located in Albuquerque, NM. The capital costs for a landfill cover system were $65,000, and projected annual operating costs were approximately $130,000. The high operating costs reflect the power requirements for a blower large enough to remove infiltrating moisture under worst-case conditions. In practice, it is likely that the power requirements could be substantially reduced by using variable-speed motors operated at low power during most of the year. The capital costs for a 1 ha subsurface barrier design are dominated by the cost of the horizontal-drilling process. Unit drilling costs ranged between $108/ft and $218/ft. Using one injection and one vacuum well results in drilling costs from $130,000 to $262,000. Equipment costs were estimated at $26,000. Annual operating costs were projected to be $10,000/year.

An improvement to the dry-barrier concept for application to landfill covers can be made by using a coarse-layer material which has internal pores. Materials with high internal porosity include non-welded tuffs, scorias, and some sandstones. For example, the primary porosity of scoria is about 30 percent, while the secondary porosity (i.e., interstitial porosity between grains of media) of loosely packed coarse gravel may approach 40 percent. In this design, water which moves from the fine layer into the coarse layer is principally held in place by the primary storage associated with the internal pores. Air flow through the system will be principally determined by the secondary porosity. The dry barrier can then remove water over a greater time than if the water were held only in the interstitial pores. This makes it possible to use smaller blowers with correspondingly lower capital and operating costs. Two criteria are of special interest in identifying material for a landfill cover: 1) the material should be coarse, nominally of one-inch diameter, with less than 5 percent fines (i.e., material with diameter of less than 1 mm); and 2) the primary porosity should be greater than 20 percent and should be well connected.

One of the objectives of current research is to determine the feasibility of using passive atmospheric conditions to provide air circulation through the dry barrier which would significantly reduce the operating costs. Examples being considered include use of wind turbines and pumping by atmospheric pressure changes.

WASTE APPLICABILITY

Dry barriers are applicable to any site where vertical migration of water or other volatile liquid may present a containment problem. In addition, air circulated in a subsurface environment to create a dry barrier will also assist in remediating unsaturated soils contaminated with volatile constituents such as petroleum fuels or volatile solvents.

STATUS

A testing program for the dry-barrier concept for landfill covers is in progress at Sandia National Laboratories (SNL). Two tests are underway using a large tank through which air can be circulated, and another test is being conducted with a 20m X 2m cover. Funding is being sought for a "cold test" of the subsurface dry-barrier application for 1995.

REGULATORY CONSIDERATIONS

Appropriate permits for management of off-gases subject to regulations under the Clean Air Act must be obtained if VOCs are present. However, since subsurface dry barriers are principally a containment system, it is not anticipated that any other permits will be required.

Landfill covers will require regulatory approval prior to closure; therefore, it will need to be demonstrated to be comparable to a RCRA cover.

POTENTIAL COMMERCIAL APPLICATIONS

Dry barriers as landfill covers offer an alternative to conventional cover technologies for landfills. Of particular merit is the ability of a dry barrier to recover from a failure such as might occur during a particularly heavy precipitation event. Conventional covers using capillary barriers are much less forgiving in this respect.

Establishment of a dry barrier beneath a contaminant plume in a subsurface setting offers a method of containment that is difficult to achieve with any other technology. Potential applications may be as a barrier beneath a leaking landfill or as part of a containment and remediation system beneath a leaking underground storage tank. Recognizing the need for continuing power costs, it is suggested that the dry-barrier concept may have its most immediate application as a temporary containment system which will function until a permanent remediation strategy can be developed and implemented.

BASELINE TECHNOLOGY

The baseline technology for landfill covers is the RCRA multi-layer cover. One version of this cover design includes provision of a capillary barrier. There is no established technology for containing pollutants migrating through a deep vadose zone for comparison to the subsurface dry-barrier concept.

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DYNAMIC UNDERGROUND STRIPPING OF VOCS

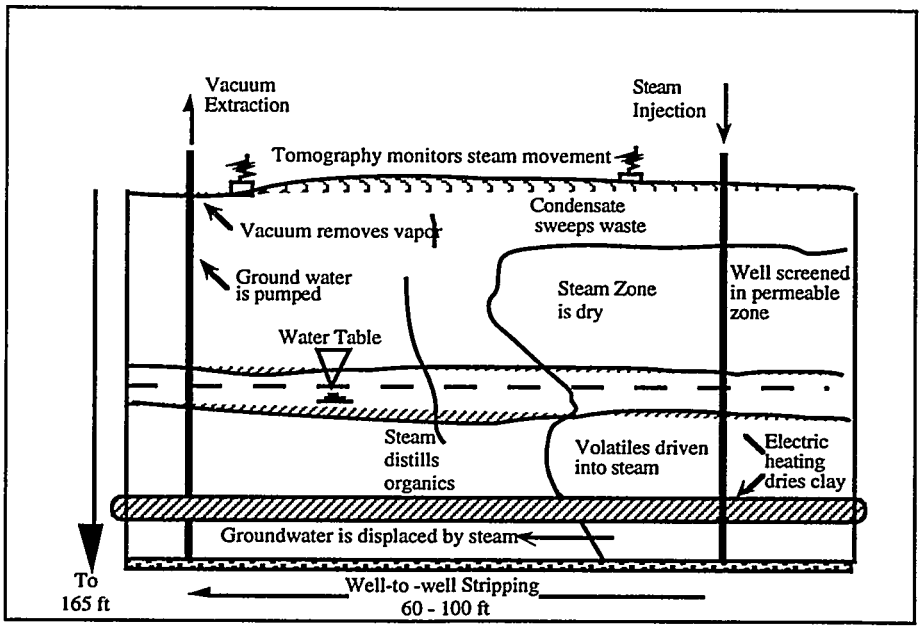
Lawrence Livermore National Laboratory

DESCRIPTION

Dynamic Underground Stripping (DUS) is an innovative method for rapid cleanup of localized, underground toxic-chemical spills. DUS integrates the technologies of steam injection, vacuum extraction, direct electric heating, and tomographic geophysical imaging for the remediation of saturated and unsaturated soil zones. Fluid-injection wells surround the concentrated contaminant plume. Groundwater and soil-vapor extraction wells are centrally located in the contaminant region. High-pressure steam at about 50-60 psi is injected into soil surrounding a contaminant plume. The resulting dynamic steam-condensate pressure front drives groundwater with aqueous-phase and separate-phase contaminants, such as nonaqueous phase liquids (NAPLs), toward the extraction well. The dynamic underground steam cloud heats and strips soil of organic contamination by volatilization. The resulting soil behind the moving steam front is dry with a significantly reduced toxic-chemical contaminant concentration. A schematic of the process is shown below.

To enhance DUS, electrical current is applied to dense soil zones where steam does not easily penetrate. Steam injection is a cost-effective in situ heating method, and when combined with joule heating of dense formations, the entire subsurface can be remediated by this dynamic process, including clay and silt layers. Electrical resistance heating of intermittent or interspersed, low-steam permeable zones will increase volatilization and contaminant mobility in these regions, driving chemical contamination into steam-stripped, highly permeable soil regions. Vacuum extraction and groundwater pumping are continuous. Electrical heating may be followed by one or more additional steam-injection phases for contaminant removal and to keep permeable zones "hot."

Applicable geophysical techniques for process monitoring and engineering analysis include temperature-measurement techniques, electrical-resistance tomography, seismic tomography (cross-borehole), induction tomography, and passive seismic monitoring, in addition to conventional geophysical well logging.



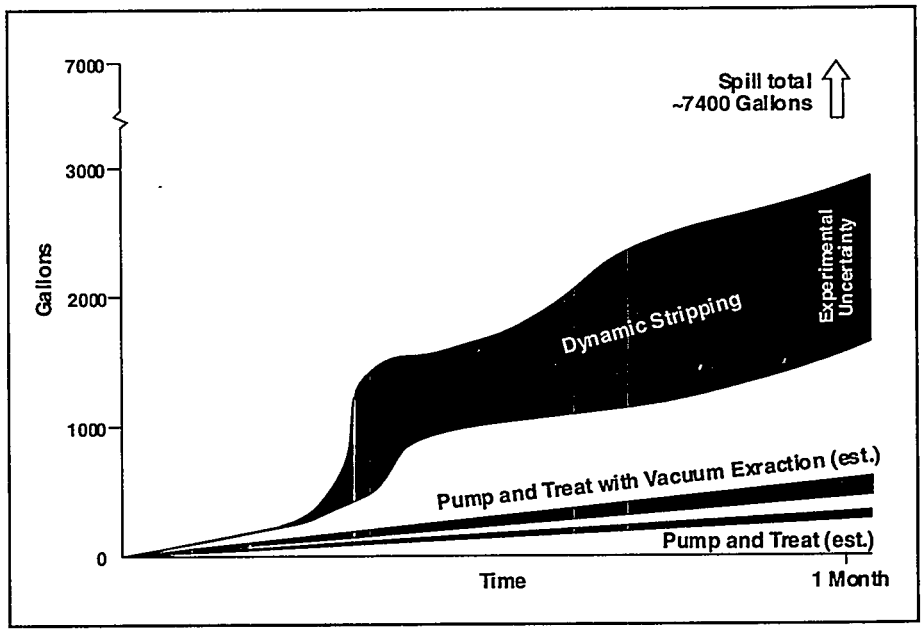
The DUS Process

TECHNICAL PERFORMANCE

Clean Site Engineering Test. This test was completed in 1991 at the Sandia National

Laboratories, Livermore Site. Approximately 10,000 yd^3 of soil were heated to the steam temperature (~100° C). A 10-million-BTU, portable, propane-gas-fired boiler was used to heat water. Saturated steam at 50 psi was injected at a rate of 8.5 gpm (as water) to a depth of 135 to 155 ft. Vapor and groundwater were extracted from a well 65 ft away. It took approximately 150 h for the initially injected steam to reach the extraction well. Electrical heating at the Clean Site emphasized electrode design and verification of heating-rate predictive models. A six-electrode pattern was used, passing a 480-V current at up to 1,000 A per electrode.

LLNL Gasoline Spill Remediation. Approximately 17,000 gal of gasoline were spilled at the LLNL gas pad, with an estimated 5,000 gal existing in free phase from below the water table. The first pass was completed in March 1993, and these results are given below. During 34 days of operation, 8.6 million kg of steam were injected into the ground. Steam that was injected below the water table broke through in 10 days. Large quantities of gasoline were removed, mostly in the vapor state. Fourteen hundred and fifty gallons of gasoline were removed and recycled; between 250 and 1,200 gal were destroyed in the treatment system. The gasoline removal rate reached the 100 gal/day limit of the treatment system. The initial removal rate of the DUS system is 25 to 40 times greater than pump-and-treat alone and 7 to 13 times faster than pump-and-treat with vapor extraction. Clay layers were heated to a maximum of 70° C. The initial test heated over 85,000 yd^3 (65,000 m^3) of soil by both steam injection and electrical heating. The estimated remediation costs are approximately $40 to $70/$yd^3$; the energy cost is $2/$yd^3$ (steam heating) and $5/$yd^3$ (electric heating). The superior performance over the baseline method is shown in the figure below.



Performance by Cumulative Gasoline Removed

PROJECTED PERFORMANCE

For arid-zone spills with an NAPL core, DUS can reduce operating costs for removal by approximately 50%, principally through the shortening of operational time by the removal of free-phase contaminants. Well-to-well stripping would occur for 1 to 3 months for interwell distances of 60 to 100 ft. The application of dynamic steam stripping is being studied for future application to mixed wastes. A pilot test of a mixed waste application may be performed in the future at the Rocky Flats Site.

Estimated cost savings. Potential cost savings using DUS over pump-and-treat for 19 DOE sites are estimated as follows:

- Estimated cost to pump-and-treat LLNL site (30-60 years) $20-$60M
- Cost to remediate LLNL site using DUS (6 months) $6-$8M

- Cost savings using DUS at LLNL site $12M minimum

- Estimated potential savings for DOE Complex (19 site) for applicable spills 60-85%, $200-$900M

Assumptions/Basis for estimate.

- Estimates based on 100,000 yd^3 gasoline plume at LLNL

- Minimum cost savings based on 30-year pump-and-treat (experience at other sites indicates 60 years or more may actually be required)

- DUS costs based on actual LLNL demonstration cost, reduced by nonrecurring costs

National Projections. If the projections for 19 DOE sites are extended to 3,200 national sites, the estimated savings are as follows:

Total savings on 30 year pump-and-treat is $37B. Total savings based on 60 year pump-and-treat is $160B.

WASTE APPLICABILITY

Dynamic stripping is applicable to free-phase organic plumes below 20-ft depths (beyond excavation). It is amenable to all types of liquid contamination including NAPLs and dense nonaqueous phase liquids (DNAPLs), and potentially to mixed wastes.

STATUS

The DUS method was demonstrated in March 1993; however, process optimization is continuing, based on experience gained from the first-pass remediation at the LLNL gasoline-spill site. Continuing process operations will begin in May 1993.

REGULATORY CONSIDERATIONS

Appropriate permits for treatment of off-gases and liquid effluents for specific contaminants must be considered (i.e., the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act (RCRA), and Comprehensive Environmental Response Compensation and Liability Act (CERCLA)).

In 1988, LLNL received permission from the Environmental Protection Agency (EPA), the Department of Health Services, and the Regional Water Quality Control Board for conducting a full-scale pilot study at the gasoline-spill site. Requirements include Occupational Safety and Health Administration (OSHA) worker safety regulations for boiler/steam injection operations and for in situ electrical-heating operations. The Environmental Restoration Program requires National Pollutant Discharge Elimination System (NPDES), Section 402 of the Federal Water Pollution Control Act, Clean Water Act, water-discharge permits, and thermal-oxidizer discharge permits.

POTENTIAL COMMERCIAL APPLICATIONS

Dynamic steam stripping has application for rapid remediation of deep, concentrated, organic-contaminant plumes. Examples of some commercial applications are power plants, fuel pipe lines, chemical plants, refineries, and other fuel, chemical, or solvent storage and dispensing operations. The Electric Resistance Tomography (ERT) monitoring technology is able to detect surface leaks, as well as soil moisture and temperature.

This technology is potentially applicable to 3,200 national sites for remediation of volatile organic compound leaks into soil and groundwater.

BASELINE TECHNOLOGY

The baseline technology is vacuum extraction with pump and ex situ treatment of groundwater.

INTELLECTUAL PROPERTY

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ELECTROKINETIC REMEDIATION OF HEAVY METALS AND RADIONUCLIDES

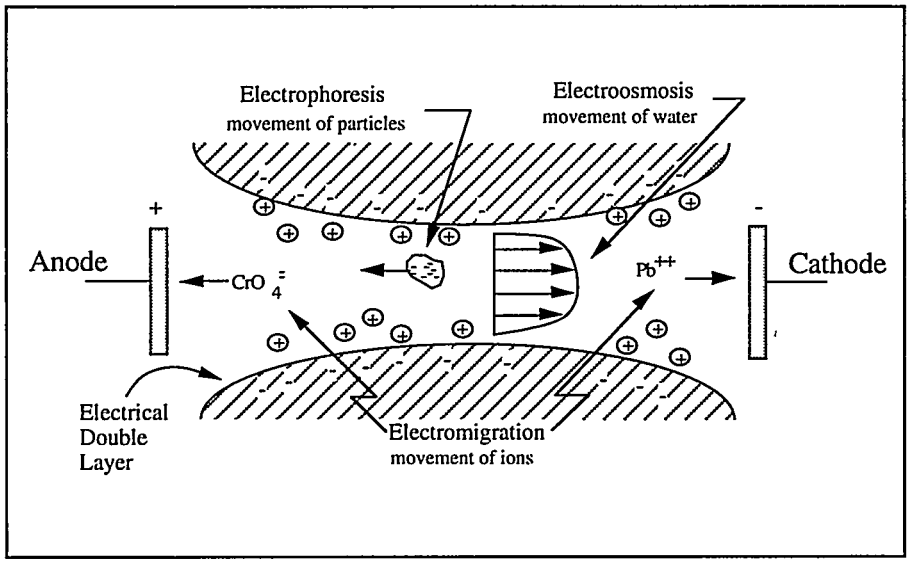
Sandia National Laboratories

DESCRIPTION

Electrokinetic Remediation (EKR) is a developing technology for in situ removal of heavy metals and radionuclides. The application of direct current in a porous medium leads to two transport phenomena; ionic species in the soil-water solution will migrate to the oppositely charged electrode (electromigration), and accompanying this migration, a bulk flow of soil-water is induced, usually toward the cathode (electroosmosis). The combination of these two transport phenomena leads to a movement of contaminant ions towards one or the other electrode, illustrated by the figure below. The direction and rate of movement of an ionic species will depend on its charge, both in magnitude and polarity, as well as the magnitude of the electroosmosis-induced flow velocity. Non-ionic species will be transported along with the electroosmosis-induced water flow.

The electrokinetic transport phenomena pertinent to in situ remediation include electroosmosis (movement of water in response to an electric field), electrophoresis (movement of a charged particle or colloid in an electric field), and electromigration (movement of solute ions in the electric field).

Electrokinetic remediation is accomplished by implanting electrodes in the soil whereby a relatively small direct electrical current is supplied between the electrodes. Ions in solution will migrate toward an electrode by electromigration. Experimental results indicate significant dependence of the electromigration rates on the soil pore water current density. The process efficiency is not as dependent on the fluid permeability of soil as it is on the pore water electrical conductivity and the path length through the soil, both of which are functions of the soil-moisture content. Removal of contaminants at the electrode may be accomplished by several means, among which are: electroplating at the electrode; precipitation or co-precipitation at the electrode; pumping of water near the electrode; or complexing with ion-exchange resins. An alternate method suggested is adsorption into the electrode because some ionic species will change valence near the electrode (depending on the soil pH), making them more likely to adsorb.



Electrokinetic Phenomena

The direction and quantity of contaminant movement is influenced by contaminant concentration (anions versus cations), soil type and structure, inter-facial chemistry, and current density in the soil pore water. For the process to work, the soil-moisture content must be above a minimum value. This minimum moisture content required for electromigration is related to,

and can be estimated from, the residual moisture content of a soil, also called "immobile water." Preliminary results indicate that the optimum soil moisture content for electromigration is less than saturation due to competing effects of tortuosity and pore water content.

TECHNICAL PERFORMANCE

EKR is being studied at Sandia National Laboratories (SNL) by means of laboratory bench-top experiments. Separate experiments were performed using an anionic dye (FD&C Red No. 40) and chromate. The electrokinetic behavior of the dye was found to be similar to that of the chromate. The dye is used as a surrogate for the hazardous chromate ion. The initial goals of the benchtop study were to determine the effects of moisture content and soil grain size on the electromigration rate.

Experimental results indicate that the minimum moisture content for which electromigration can take place was 3.5 wt% for the prepared medium-grit sand (50-100 mesh) test bed. Optimum moisture content was determined to be between 14 and 18%.

PROJECTED PERFORMANCE

The EKR technology is a developing technology. Projected performance will be determined after a predictive model for migration rates is developed. The migration rate is a function of moisture content, sand-grain size, ionic mobility, pore water current density, contaminant concentration, and total ionic concentration. Others have projected the total remediation cost to be in the range of \$50 - \$150/yd^3. The cost of EKR is dependent on specific chemical and hydraulic properties present at the site.

WASTE APPLICABILITY

This remediation technology is applicable to heavy metals and radionuclides which are mobile as ions in the aqueous phase. EKR has the potential to be used with other groundwater remediation technologies such as dynamic steam stripping to remove both organic and metallic contamination in one hybrid process.

STATUS

This is a developing technology. Laboratory bench-scale tests have been conducted, and the results will be used to develop a predictive model of the migration rates. A pilot-scale test is being conducted in FY94, first in a sand-box with chromate and then on clean soil. A field test at the chromic acid pit at SNL will be conducted in FY95. A system to remove contaminants collected at the electrodes is currently under development.

REGULATORY CONSIDERATIONS

For use of EKR in unsaturated soils, the addition of water is a concern because of the potential of hydraulically washing contaminants out of the range of capture. SNL's unsaturated soil extraction electrode system is designed to minimize this problem, and its in situ performance will be demonstrated in a FY94 field test.

POTENTIAL COMMERCIAL APPLICATIONS

EKR has many applications for remediation of industrial-process ground contamination. There are many commercial sites where toxic metallic con-

tamination may be mixed with other chemical contamination in unsaturated or saturated soils.

One example of an important application is near dated steel processing plants, such as in Poland where lead contamination in soil and groundwater is a significant problem. In addition, there are locations in the U.S. where soil has been contaminated after paint-stripping operations on comparatively old structures where the paint contained high concentrations of lead. EKR has been used by both the former Soviet Union and India in applications in unsaturated soils for mining exploration.

BASELINE TECHNOLOGY

The conventional technology to remediate heavy-metal-contaminated soils is excavation and solidification. There have been some field-scale attempts to use EKR methods to remove heavy metals from saturated soils in the Netherlands. A field-scale trial funded by the Environmental Protection Agency for removal of chromium contamination from soils has met with partial success, but the success was limited by inadequate site characterization.

INTELLECTUAL PROPERTY

A patent application for SNL's unsaturated soil electrode system is being prepared.

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ENCAPSULATION OF HAZARDOUS WASTES

New Mexico State University

DESCRIPTION

Studies in the 1980s found uses for fly ash in commercial construction as a filler. Its natural pozzolanic activity allows the fly ash to form a chemically bonded matrix when water is added. The strength of the matrix can be increased using additives such as ordinary Portland cement or lime. Recently, a variation on the process was developed that utilized low-pressure compaction of a homogeneous mixture of waste, fly ash, and water to form the encapsulating solid. The initial operating space for the process depended on the waste type used, but for an aqueous solution of nitric salts, it was between 12.5 wt% and 17.5 wt% waste.

This research uses statistical procedures to examine the effects of additives on the waste-fly ash encapsulation process. Obviously, maximizing the waste content in the monolith is desired. The effects of lime and bentonite on the process are studied. The four components were modeled as a three-dimensional tetrahedron simplex space. At the present time, the work has determined the manufacturability of the monoliths while maximizing the waste content.

To create a monolith, initially the dry components were blended together and then the liquid added. However, the process has been modified to add the lime as the final ingredient, allowing the fly ash and/or bentonite to act as a heat sink for the exothermic reaction converting quicklime (CaO) to hydrated lime ($Ca(OH)_2$). The liquid waste is added slowly until balls (5 to 10 mm) are formed from the dry materials. In most cases, this fairly dry mixture can be compressed into a monolith. Additional waste can be added until the ball size exceeds 15 mm or becomes shiny (wet surface). The compression feature of the process is accomplished using a hydraulic press. The piston cylinder is approximately 25 mm (1.0 in) in diameter, and a gauge pressure of 14.0 MPa (2,000 psi) is possible. The piston connects to a rectangular press of 7 cm by 12.5 cm; the equivalent maximum pressure is 2.4 MPa (350 psi).

The mixture is compressed to the maximum pressure for approximately one second then released. If the monolith is properly formed, the brick can be removed without much difficulty. Some monoliths with a clayey consistency need to remain on the piston for several minutes to decrease the likelihood that the monolith will fracture and stick to the piston head. If the mixture is too liquid to form a monolith, the material is squeezed out of the press around the piston. When this occurs, the hydraulic gauge pressure does not typically reach 14.0 MPa. The brick is cured for a minimum of 24 hours prior to any testing.

Since monoliths of pure components cannot be manufactured (much less pass the extraction test), a region of interest inside the simplex space is defined by manufacturability, indicating that the mixture does not squeeze out of the mold (wet) or does not fall apart when removed from the press (dry). Experiments were performed to create monoliths of maximum and minimum waste content along a line of constant fly ash to filler ratio. In the event that no monolith could be formed along typical fly ash-to-filler ratio lines, a constant waste-to-fly ash ratio greater than the maximum waste content for brick production was selected. Lime, for example, was added until a maximum or minimum waste content was achieved. Other variations from the brick-making process included using a drier-than-normal mixture when bentonite was used as a filler. Bentonite-based mixtures tended to squeeze out of the press even when appearing dry. This is probably a function of bentonite particle size and/or morphology.

It is interesting to note that the quicklime addition does not immediately dry the mixture. Instead, the mixture must be blended for an additional one to two minutes. The mixture heats up and evolves steam and ammonia. When the 15 mm balls begin to have a dry exterior, the mixture is compressed. Eventually, any mixture will dry; however, since the exothermic hydration of the quicklime is proceeding rapidly during the mixing process, steam evolution was assumed a part of the reaction and not ambient drying, which disqualified other formulations.

TECHNICAL PERFORMANCE

The original applications of this technology examined encapsulation of a lead-contaminated slurry and an aqueous solution of nitric salts simulating a waste stream from a metals-processing operation. In both cases, only the waste, fly ash, and an inert filler (if needed) were used in the formulations.

The first encapsulation study used a slurry that was a by-product of a soil-washing operation. It contained 70 percent moisture with a total lead content of 15,600 mg/kg. The TCLP lead of the slurry was measured to be 206,000 Fg/L. Samples with up to 20 wt% waste were made, and the TCLP results on all samples were below the detection limit of 35 Fg/L.

The second encapsulation study used a waste stream that contained chromium, cadmium, and lead in an aqueous solution of nitrate salts. This waste was encapsulated with 15.5 wt% to 17.5 wt% waste in fly ash, resulting in a heavy-metal concentration of 15,000-20,000 ppm in the monolith. Again, the results of the TCLP test on all the samples were below the EPA threshold limits.

To examine interactions of the four components and expand the maximum waste content, the process was modified using combinations of waste, fly ash, lime and bentonite. First, the fly ash and bentonite were blended 50/50. This blend was added to the waste along constant ratio lines (32%, 40%, and 50% waste). The lime was added to produce a maximum (wet) and minimum (dry) waste content. A maximum waste content of 35 percent was achieved.

The region of maximum waste content was explored further by selecting test points which contained final waste composition of 40 percent. A large region of manufacturability was noted at 40 percent waste, and, therefore, this procedure was repeated at 45 percent waste. Only one formulation (45% waste, 11% fly ash, 28% lime, and 17% bentonite) formed a suitable monolith.

Having identified the appropriate operating space, preparations to conduct TCLP tests on formulation within the space are underway. The high waste concentration formulations may be less capable of passing the TCLP test since the high $Ca(OH)_2$ concentrations in the matrix may result in a porous matrix when subjected to the leaching acid in the TCLP test. Thus, there may be formulations that can be used to make a monolith but will not pass the TCLP test. This has not been observed before.

PROJECTED PERFORMANCE

Prior work has indicated that this technology is capable of encapsulating a variety of waste forms and passing TCLP test requirements for chromium, lead, and cadmium contaminants. The current work is improving the economics of the process by increasing the waste content in the monolith. It must be determined how high a waste content can be accommodated.

WASTE APPLICABILITY

Work to date indicates that this technology is suitable for the encapsulation of liquid, slurry, and solid waste contaminated with metals and other inorganic com-

pounds. It has not been tested on organic-contaminated, radioactive, or mixed wastes.

STATUS

This technology is in the development phase and has not yet been demonstrated on a commercial scale.

REGULATORY CONSIDERATIONS

This technology does involve the use of hazardous materials, and the necessary precautions must be followed. However, the product is benign and should not present a hazard to workers or the environment.

POTENTIAL COMMERCIAL APPLICATIONS

The potential commercial applications of this technology include the solidification/stabilization of hazardous liquids, slurries, and solids. The most promising appears to be the encapsulation of inorganic contaminants; however, a study of organic contaminants has not been conducted.

BASELINE TECHNOLOGY

The baseline technology is the pozzolanic chemistry of c-grade fly ash in conjunction with quicklime in the presence of water to form a matrix capable of encapsulating the waste material.

INTELLECTUAL PROPERTY

An initial patent has been awarded on this technology. A subsequent improvement patent is being applied for.

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REFERENCES

None.

ENGINEERED SYSTEM FOR IN SITU BIOREMEDIATION OF GROUNDWATER

Pacific Northwest Laboratory

DESCRIPTION

In situ bioremediation, as applied in this project, is based on the principal of supplying nutrients to indigenous microorganisms to stimulate their metabolic activity and subsequent degradation of contaminants. A field demonstration at the U.S. Department of Energy's (DOE) Hanford Site will implement in situ bioremediation of carbon tetrachloride and nitrate. This demonstration is sponsored by the U.S. DOE, Office of Technology Development.

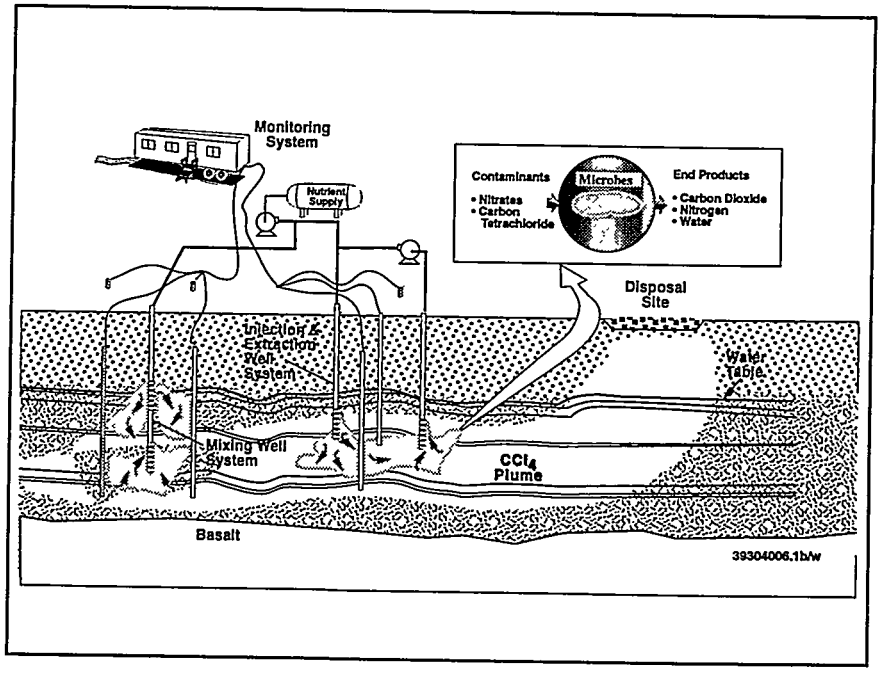
There are three overall objectives for the field demonstration project:

1. In Situ Contaminant Destruction
2. Improved Volumetric Treatment
3. In Situ Design Tool

The first objective is focused on demonstrating in situ biological destruction of CCl_4 and nitrate in the Hanford groundwater with sufficient control such that byproducts are either non-hazardous, or, for potential byproducts such as chloroform and nitrite, are below the regulatory drinking-water limit. Demonstrating improved volumetric treatment involves utilizing nutrient addition and operating strategies that minimize the effects of biofouling and provide maximum distribution of nutrients and microbial activity around the injection well.

The third objective is to develop and demonstrate a design tool for designing, deploying, operating, and monitoring in situ bioremediation processes for chlorinated hydrocarbons.

Because of the difficult technical issues and the ambitious goals associated with the demonstration, a rigorous approach to the problem was implemented. For this approach, a computer model was used to simulate the important interactions of the process. Site characterization provided parameters for the flow and transport expressions in the process model. Kinetic expressions for the microbial reactions were developed in laboratory experiments for use as the reaction component of the process model. Because the process operates in situ, flow-cell experiments in porous media were used to examine relevant bacterial transport rates and to confirm the process model. Laboratory experiments and model refinement were iterated until an acceptable description of the process was obtained. The final process model is both a



In Situ Biological Treatment

process simulator and a design tool that was employed for field design and optimization of operating strategies.

TECHNICAL PERFORMANCE

In the bioremediation process for the field demonstration, acetate is utilized as a carbon and energy source by indigenous bacteria that employ nitrate as a terminal electron acceptor. While the primary cellular metabolism is directed at acetate utilization through denitrification, carbon tetrachloride is concurrently dechlorinated. This dechlorination results primarily in the formation of carbon dioxide and chloride ions, while biomass, water, carbon dioxide, and nitrogen gas are produced from acetate utilization and denitrification. Under some conditions of cellular activity, chloroform is produced as a byproduct. Chloroform production can be controlled in the laboratory, and implementing byproduct control in situ is an objective of this demonstration.

In the field, in situ bioremediation requires groundwater recirculation and distribution of nutrients to the aquifer. A biologically active zone is created around the injection well where nutrient utilization and contaminant destruction occurs. The size of this zone is dependent on the ratio of reaction rates to transport rates. In this field demonstration, the extent of this zone will be controlled by using nutrient pulses designed to move the active zone away from the injection well and provide a relatively large uniform biomass distribution. This is necessary to avoid plugging of the aquifer due to extensive biomass buildup near the well. Techniques other than nutrient pulses may be necessary to produce very large (10s of meters) active zones for true "volumetric treatment." Identifying potential techniques for inducing volumetric treatment is part of the scope of the technology development effort and will be important to future full-scale applications of in situ bioremediation for co-metabolically degraded contaminants.

Cost. In situ bioremediation was compared to ex situ bioremediation and ex situ air stripping/activated carbon (AS/AC) in a cost/benefit analysis (Skeen, et al., 1993). Because ex situ AS/AC and bioremediation both rely on extracting contaminant from the aquifer, the duration of remediation for these technologies is twice as long as the duration for in situ bioremediation. In situ bioremediation present-value costs ($250/m^3) were found to be less than half of the cost for ex situ bioremediation ($690/m^3). This difference is due primarily to the much shorter treatment time associated with in situ treatment. The present-value cost for in situ bioremediation was comparable to ex situ AS/AC ($260/m^3) because operating costs are much lower for AS/AC. However, in situ bioremediation has the added advantage over AS/AC of destroying the contaminant in place. Thus, AS/AC has risks associated with transport and handling of hazardous secondary waste that are not present with in situ bioremediation. As well, AS/AC is only applicable to the volatile contaminants in the groundwater, and further processing may be necessary before discharge of the extracted groundwater. In situ bioremediation can destroy some non-volatile co-contaminants such as nitrate, and, since groundwater does not need to be discharged on the surface, treatment requirements may be less stringent.

PROJECTED PERFORMANCE

Destruction of contaminants to their regulatory drinking-water standard concentrations is possible with in situ bioremediation. Carbon tetrachloride concentrations of 2 ppm have been reduced to less than 5 ppb in laboratory tests using Hanford groundwater and indigenous microorganisms. In situ bioremediation is particularly effective compared to pump-and-treat technologies for remediating contaminants sorbed to aquifer solids.

WASTE APPLICABILITY

The field demonstration is focused on remediation of carbon tetrachloride and nitrate. However, the in situ bioremediation technology and design methodology being developed is applicable, in particular, to co-metabolically degraded contaminants such as chlorinated solvents and, in general, to most biodegradable contaminants.

STATUS

A field demonstration for bioremediation of carbon tetrachloride and nitrate in Hanford groundwater is planned to start in October 1994. The duration of the field test will be 1 year. A field demonstration of in situ bioremediation for TCE was performed at the U.S. DOE Savannah River Site. However, implementing in situ bioremediation for TCE at the Savannah River Site was significantly different than the in situ bioremediation process to be implemented in the Hanford Site demonstration. In addition, a research effort is determining the process requirements for in situ bioremediation of mixtures of chlorinated solvents such as mixtures of TCE (an aerobically-degraded contaminant) and PCE or carbon tetrachloride (anaerobically-degraded contaminants).

REGULATORY CONSIDERATIONS

Approval for injecting appropriate substrates and electron acceptor into the groundwater must be obtained to implement in situ bioremediation. Typically, benign compounds are used for injection and are not a regulatory issue. The technique for recirculating the groundwater may be of regulatory concern. Additional concerns about the long-term effect of the process on the aquifer must be addressed. These concerns are primarily related to the large numbers of bacteria that grow in the aquifer during the process and their potential effect on water quality as they decompose. Adequately monitoring the success of the remediation is also an important issue for all in situ processes.

POTENTIAL COMMERCIAL APPLICATIONS

The remediation technology is applicable to in situ destruction of chlorinated solvents. Remediation of chlorinated solvents is a significant need for many contaminated sites, but other technologies are not sufficient for many of these applications. The in situ bioremediation design tools and methodology being developed are applicable to a wide range of remediation applications.

BASELINE TECHNOLOGY

The comparative baseline for remediation of chlorinated solvents in groundwater is pump-and-treat technology. This may consist of several different remediation techniques on the surface such as activated carbon, air stripping, or oxidation processes, but all rely on extraction of small amounts of contaminants in large volumes of water.

INTELLECTUAL PROPERTY

No single patent exists for the technology. Elements of the technology are the intellectual property of various organizations. Stanford University has applied for a patent on the mixing-well designs. Rice University has the rights to the design simulation software. Treatability study equipment was developed by Pacific Northwest Laboratory, and an invention disclosure has been filed. Specific enhancements to the technology have also been described in invention disclosures.

Other Owners: Owners of various patents that apply to this technology include Stanford University, Rice University, and possibly IEG, owners of the German UVB technology for vacuum stripping of VOCs in groundwater.

Patent Number: The patent numbers are not known.

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HIGH-ENERGY CORONA

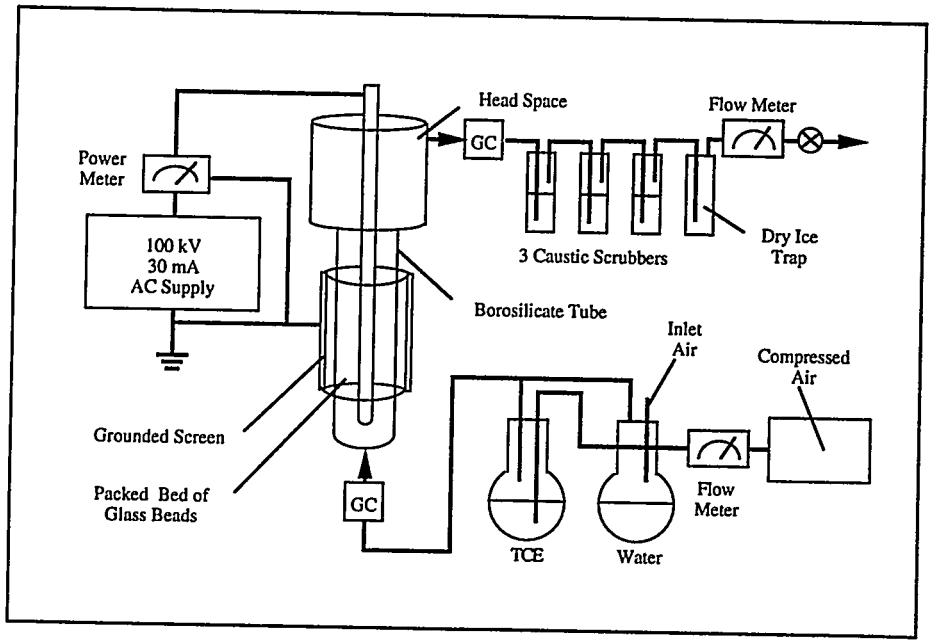
Pacific Northwest Laboratory

DESCRIPTION

Most Department of Energy (DOE) sites have been contaminated with volatile organic compounds (VOCs). Techniques for retrieving these VOCs from soils are being developed and demonstrated at various sites. These techniques generally remove VOCs as vapors (off-gas) from contaminated soil. These vapors must, in most cases, be treated prior to release to the environment. The High Energy Corona (HEC) technology is one of many approaches toward decontaminating soil off-gases prior to atmospheric release. The objective of the HEC technology is to provide a stand-alone, field-portable means of treating soil off-gases produced during soil treatment operations. Contaminants that can be treated include most or all volatile and semivolatile organic compounds. The potential also exists for treating inorganic compounds, such as oxides of nitrogen and oxides of sulfur.

The HEC process uses high-voltage electricity to destroy VOCs at room temperature. As shown in the figure below, the equipment consists of the following: an HEC reactor in which the VOCs are destroyed; inlet and outlet piping containing process instrumentation to measure humidity, temperature, pressure, contaminant concentration, and mass flow rate; means for controlling inlet flowrates and inlet humidity; and a secondary scrubber.

The HEC reactor is a glass tube filled with glass beads through which the prefiltered contaminated off-gas is passed. Each reactor is 2-in. in diameter, 4 ft long, and weighs less than 20 lb. A high-voltage electrode is placed along the centerline of the reactor, and a grounded metal screen is attached to the outer glass surface of the reactor. A high-voltage power supply is connected across the electrodes to provide 0 to 50 mA of 60-Hz electricity at 30 kV. The electrode current and power depend upon the type and concentration of contaminant.



Low-Temperature Plasma Reactor

The technology is packaged in a self-contained mobile office that includes gas-handling equipment and on-line analytical capabilities. Site power is not absolutely required. Installation consists of connecting inlet and outlet hoses to the HEC process trailer. Training in the use of the equipment can usually be accomplished well within one hour. Failure control is provided by a combination of automated and manually activated means, addressing electri-

cal failure, loss of flow, and loss of VOC containment caused by breakage of the glass reactor vessel. The HEC process can be operated with little, if any, maintenance required. Neither catastrophic failure nor any diminishing in levels of performance have been observed through months of periodic operation in the laboratory. The on-line gas chromatograph and process instruments do require periodic recalibration to ensure data quality.

TECHNICAL PERFORMANCE

The HEC technology appears to destroy more than 99.9% trichloroethylene (TCE). The technology destroys tetrachloroethylene (PCE) to a level of 90 to 95%. In preliminary tests with heptane, destruction levels appear to be extremely high, but have not been quantified. When chlorinated VOCs are treated, water containing either sodium hydroxide or baking soda is recirculated in a scrubber to remove acid gases from the reactor effluent (hydrochloric acid and bleach). It should also be noted that further contaminant destruction appears likely in this wet scrubber. This is presumably because of strong gaseous oxidants that exit the HEC reactor. Typical outlet properties would be nondetectable concentrations of TCE, ozone, hydrochloric acid, phosgene, and chlorine, with up to 1 ppmv NOx (below regulatory limits). Air exits the HEC process at temperatures of 100° C or lower (or slightly above ambient temperature if a wet scrubber is used). A scrub solution (containing less than 10-wt% table salt in water) is produced when chlorinated VOCs are treated.

One reactor processes up to 5 scfm of soil off gas. The HEC field-scale process that will be demonstrated early in 1993 at Savannah River uses 21 HEC reactors in parallel to treat up to 105 scfm of contaminated soil off-gas. A typical application will involve an inlet stream containing 1,800 ppmv of TCE in humid air at 10 to 20° C. Power input is typically 50 to 150 W/scfm being processed. For dry inlet streams, deionized water is added as steam to produce an inlet humidity (hr) of 60 to 80%. Less than 20 ml/min of water is required to humidify a bone-dry stream at a flow of 105 scfm. For water-saturated inlet streams, the stream is preheated (using electric heaters) to lower the inlet humidity (hr) from 100 to 80%. In many cases, the vapor-extraction blower associated with retrieving the VOCs from soil will sufficiently preheat the soil off gas to 80% hr or lower so that no further preheating is required.

Cost. Initial outlay for a 105 scfm process, the prototype field treatment system, is $50K. As with any other technology, large-scale production and customization would significantly reduce costs, perhaps to as little as $20K. Labor requirements are projected as ~0.25 fulltime equivalent (FTE). Energy requirements are $27/day, or roughly $0.35/lb of contaminant. Total cost is roughly $10.00/lb contaminant, including a 25% contingency to account for any unknown additional costs. Although maintenance costs are minimal, the total cost figure assumes 8% downtime and a capital payback period of 6 months.

PROJECTED PERFORMANCE

Continued research & development (R&D) is planned to accomplish the following: fully characterize the reactor emissions to complete mass balances; adapt the HEC process to complete real-time control; better understand the physical and chemical phenomena that make the HEC process work; develop larger reactors; and optimize the hardware and packaging associated with the technology for specific, as well as modular or generic, treatment applications.

WASTE APPLICABILITY

This technique is specifically useful for destroying organics and chlorinated solvents such as TCE, PCE, carbon tetrachloride, chloroform, diesel fuel, and gasoline. Both gas- and liquid-phase contaminants are treatable.

STATUS

Discussions with manufacturers/licensees have been initiated with the belief that HEC is now ready for commercial availability. The 105-scfm field prototype is available now for commercial testing and evaluation. Pacific Northwest Laboratory (PNL) is continuing R&D to improve and scale the technology. Scaleup to 50 scfm per reactor seems feasible for extremely large applications.

REGULATORY CONSIDERATIONS

Compliance with the Occupational Safety and Health Administration regulations is required for hazardous-waste operations and protection of occupational workers from high-voltage electricity.

POTENTIAL COMMERCIAL APPLICATIONS

Since this technology is applicable to treating process off-gases and liquid contaminants in government or industrial settings, the potential commercial applications are very broad. Any remediation or manufacturing process that produces off-gases and/or liquid contaminants that contain organic compounds could possibly be treated with this technology.

BASELINE TECHNOLOGY

The most ubiquitous baseline technology is carbon sorption, in which off-gas contaminants are absorbed onto containerized activated carbon. Once "spent," the carbon is shipped off-site and incinerated, which partially reactivates the carbon for reuse. In many or most cases, the spent carbon must be treated as Mixed Waste because of radon contamination, even if the soil being cleaned has not been contaminated with radioactive wastes. This further increases the cost of baseline carbon sorption use. Some other baseline technologies involve thermal treatment, such as incineration and high-temperature catalysis. Ionizing radiation sources, such as X-rays and electron beams, are also used.

INTELLECTUAL PROPERTY

Pacific Northwest Laboratory has applied for a patent.

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None at present.

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HYDRAULIC IMPACT END EFFECTOR

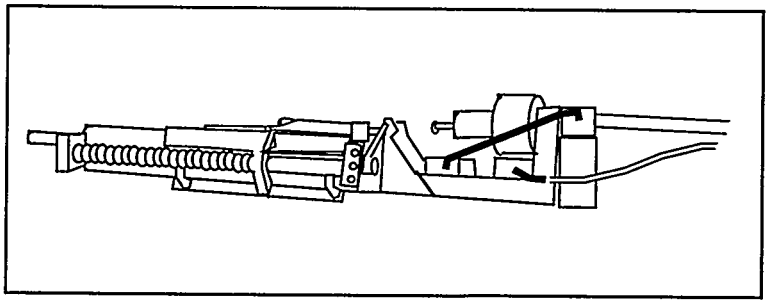
Lawrence Livermore National Laboratory

DESCRIPTION

The Hydraulic Impact End Effector (HIEF) is a remote tool attached to the end of a robotic manipulator arm. HIEF is used to break up monolithic or large pieces of hard cake into smaller fragments. (Hard cake is a solid waste form, typically sodium nitrate or sodium nitrite salts, that has been precipitated out of radioactively contaminated process sludges and stored in underground storage tanks.) After the HIEF tool breaks up monoliths and large waste boulders, the product can be easily handled by other effectors for further size reduction or for pneumatic conveyance out of the waste tank. The HIEF tool has also been called a water cannon or rubblizer. Using brief blasts of ultra-high-pressure (UHP) water, the water cannon has been shown to be effective in breaking up large monoliths. The HIEF is a beneficial means to dislodge hard waste adhering to various vertical structures within an underground storage tank. Presently, there is no other technology proposed that can break up the monoliths around the risers in a tank as effectively as the HIEF. Another possible means is the water-jet technology, but positioning of the device is much more complex and unforgiving.

The HIEF provides a means for continuous high-pressure pulse generation capable of fracturing hard salt cake. The system consists of the end effector tool, the UHP power unit, and the control console. The system uses the energy stored in a volume of water compressed to 40,000 psi to generate a powerful hydraulic shock to fragment monoliths of hard salt cake. The current tool uses water as the working fluid, but evaluation of alternate fluids is in progress. The use of an alternative fluid that vaporizes at ambient temperature would be very beneficial. The control console monitors the pressurization and controls the discharge through the control valve assembly. Fragmentation with the hydraulic impact end effector is comparable to that achieved by explosive charges without the hazards of "fly" rock or toxic fumes. The HIEF system has been designed for either automatic or manual operation. In the manual mode, the operator charges and discharges the tool at his discretion. In the automatic mode, the time intervals for charging and discharging are selected by the operator, and the tool then operates at these settings until shut off. Aiming of the tool is as simple as shooting a rifle. No close tolerances are required.

TECHNICAL PERFORMANCE



Impact End Effector

The HIEF discharges 200 ml volume of water compressed to 40 kpsi. The end effector can be fired repeatedly with 5 s between blasts. The UHP power unit is located 100 ft from the end effector and requires 480-VAC electrical power, 7-gpm cooling water, and 90-psi compressed air. The UHP hose has been designed to have a minimum fatigue life of 30,000 cycles. The flexible high-pressure hose is surrounded by a safety shield and has a typical

burst pressure of 105 kpsi and a minimum blast pressure of 95 kpsi.

Laboratory Testing. The hydraulic impact end effector was successfully demonstrated in FY92 as a tool capable of fracturing hard salt cake. The hydraulic end effector was effective on a number of different strength simulated hard salt-cake compositions. Depending upon the brittleness, cohesiveness, and density of the target, varying degrees of fragmentation result from complete fragmentation with one blast to penetration through the sample. HIEF was very effective in removing salt cake encrusted around pump shafts and pipes. The rubblizer will not damage the steel tank liners, although the hydraulic impact end effector may be limited in use to those tanks known to be structurally intact. Test results have shown that the end effector can be discharged directly into a solid-steel, unsupported plate without noticeable deformation of the plate.

Cost. The cost of the end effector is approximately $90K, including design, and the cost of the UHP power source is $50K.

PROJECTED PERFORMANCE

Currently, the control valve assembly is located at the rear of the effector. In the near term, the control valves will be distanced 75 to 100 ft from the end effector. The rubblizer is expected to break up waste at rate of 12 gpm. Fragments should not exceed a maximum dimension of 14 in. High-pressure, liquid carbon dioxide is being considered as an alternative fluid.

WASTE APPLICABILITY

HIEF is applicable to monoliths and large boulders of the sodium nitrate and the sodium nitrite hard-cake form of plutonium-processing waste byproduct. The system is designed for applicability to waste stored in underground storage tanks (0.5 to 1 Mgal in size) that may have limited access ports. Hydraulic impact methods have been used to break up natural geologic boulders and rocks in mining applications.

STATUS

The HIEF unit is a modified off-the-shelf commercial unit that has been modified to match the manipulator arm interface. The prototype has been demonstrated on simulated hard cake in 1992. The system with remote maintenance features and alternate fluid usage should be completed in FY95.

REGULATORY CONSIDERATIONS

The HIEF unit was initially developed for use at the Three Mile Island Nuclear Power Plant. The design met all water-jet and decontamination regulations, as well as Environmental Protection Agency (EPA) and Occupational Safety & Health Administration (OSHA) requirements. The HIEF is being designed for deployment by the long-reach manipulator arm in the single-shell tanks at Hanford. This technology complies with all regulations governing tank-farm technologies at Hanford.

POTENTIAL COMMERCIAL APPLICATIONS

A hydraulic impact end effector unit is commercially available for use in rock fragmentation to provide powderless gun propulsion shock processing of advanced materials, or for use as a versatile underwater sound source for geophysical applications.

BASELINE TECHNOLOGY

There is currently no baseline technology to break up monoliths around risers in underground storage tanks. The water-jet scarifier is the only reasonable competition to this technology.

INTELLECTUAL PROPERTY

The patent is owned by QUEST Integrated, Inc.

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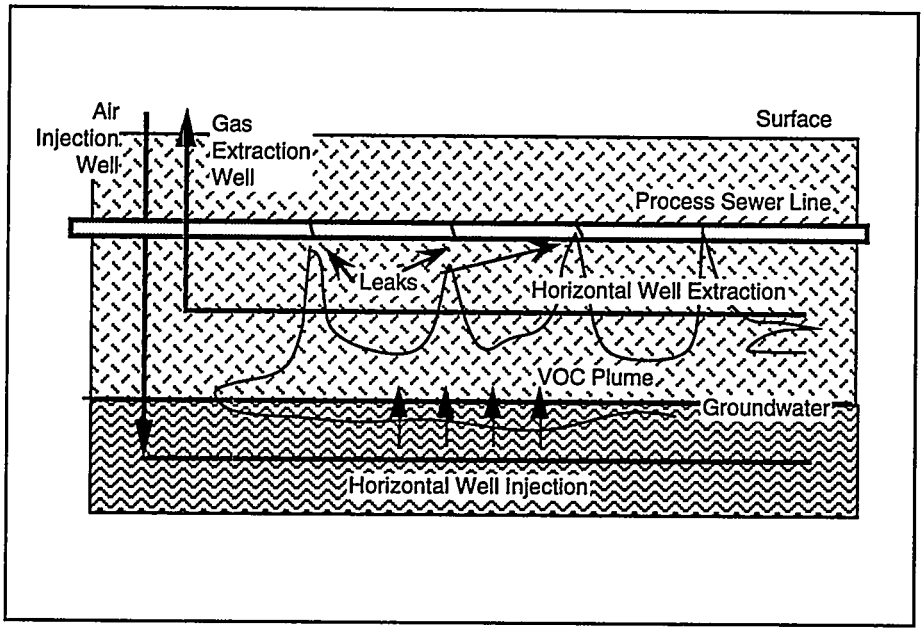
IN SITU AIR STRIPPING OF VOCS USING HORIZONTAL WELLS

Westinghouse Savannah River Company

DESCRIPTION

In situ air stripping (ISAS) is a mass-transfer process that utilizes horizontal-injection and vacuum-extraction wells to remediate sites contaminated with volatile organic compounds (VOCs) within the vadose zone and soil/groundwater in the saturated zone. Air is injected into the saturated zone via horizontal injection wells placed below the water table. As the air passes through the contaminant plume, it volatilizes the chemical constituents. The amount of volatilization and movement of the solute mass into the air stream is a function of the contaminant concentration, temperature, pressure, and Henry's Law constant of the particular solute. Vapors are collected by upper horizontal gas-extraction wells. The extracted air stream is then processed to remove or destroy the liquid and vapor toxic chemicals.



Schematic Diagram of Horizontal Well In Situ Air Stripping

ISAS performs best in homogeneous soil conditions, while heterogeneities such as formations, fractures, clay layers, and partial clay lenses hinder performance. Clay layers often have high contaminant concentrations, while stratigraphy can cause preferential flow paths and limit the process' efficiency. ISAS has been shown to be effective when some interbedded thin and/or discontinuous clays are present.

TECHNICAL PERFORMANCE

A field demonstration of ISAS was conducted during FY90 at the Savannah River Site (SRS). The site featured a pre-existing line source of soil- and groundwater-based contamination. The soil geology consisted of interbedded soils, silts, and clays, with sands predominating. Vertical-well groundwater and sediment sampling was used to collect multiple samples at various depths. Biomolecular probes were used for laboratory characterization of soil microorganisms. The soil and groundwater at the site have naturally occurring organisms that degrade toxic organic chemicals. Biological monitoring has shown that some contaminant-degrading organisms have flourished at the site during air injection. Geophysical tomography was used to map water-saturation distribu-

tions in the subsurface; three different geophysical techniques were employed using cross-borehole techniques.

During field testing, two horizontal wells were used, including a 300-ft injection well (165 ft deep, 35 ft below the water table) and a 175-ft long extraction well (75 ft deep). Air was extracted from the upper well at a rate of 55 to 600 scfm for a period of 139 days. Air injection began on day 16 at a rate of 65 scfm. On day 28, the air-injection rate was increased to 170 scfm, and on day 69, it was increased again to 270 scfm. Injection stopped on day 113. A total of 16,000 lb of VOC contamination (trichloroethylene, tetrachloroethylene, and others) was removed through the extraction well.

Soil core samples revealed that an even larger quantity of contamination was destroyed by aerobically activated microorganisms in the soil than was extracted by ISAS. The extraction rate of contaminant removed from the subsurface without air injection (Soil Vapor Extraction or SVE alone) was about 109 lb/day, and the extraction rate increased to approximately 130 lb/day when air was injected through the lower well.

The total cost of VOC removal for the ISAS field experiment at SRS was $15.59/lb. In comparison, an equivalent base technology extraction system, consisting of four vertical vacuum extraction/injection wells and one pump-and-treat well and processing system, costs approximately $27.07/lb of VOC removed. Although the capital costs are higher for the ISAS system, the higher rate of VOC removal makes it comparatively more cost effective.

PROJECTED PERFORMANCE

ISAS performance with different geometries and/or heating and/or bioremediation nutrient injection is likely to be improved over earlier testing. Future developments will include other geometries, multiple wells, combinations of horizontal wells and vertical wells (giving hydraulic control), and orientation of horizontal injection wells perpendicular to the direction of groundwater flow. The fundamental problems for ISAS are the physical limits of volatilization and requirements of the mass-transfer processes. Remaining issues are how to remove the contaminant effectively from the clays and the exponential tail recovery curves. Using heating, steam injection, and alcohol flooding are possible options to increase volatilization in the clay zones and tight soil pores.

WASTE APPLICABILITY

Geologic Setting. For ISAS to be effective, the geologic setting should have a moderate-to-high saturated soil permeability, homogeneous saturated zone, and sufficient saturated thickness. The vadose zone should have high permeability and homogeneity; coarse-grained soil is most effective. Clay layers have a low permeability, so they are the most difficult to remediate with air stripping.

Contaminant Requirements. Air stripping involves transport among soil, groundwater, and sparged air, so contaminants must be mobile for all phases. Contaminants must have a Henry's Law constant >0.01, vapor pressure >0.1 mm Hg, and soil/water partition coefficient <1,000 to be physically removable by air stripping. Most light hydrocarbons and chlorinated solvents satisfy these conditions.

Plume Geometry. Horizontal wells provide better contact with linearly shaped contaminant plumes. Thin plumes are probably more amenable to the air-stripping process. The plume depth affects the cost effectiveness of ISAS.

STATUS

A field demonstration was performed in FY90. A full-scale demonstration, including 4% methane enhancement as a bioremediation nutrient in the injection well, was conducted during FY92, with results to be available in FY93. Better under-ground transport modeling and bioremediation modeling are needed.

REGULATORY CONSIDERATIONS

A state Underground Injection Control (UIC) permit is required because of the active injection of air into the subsurface. ISAS application requires an air permit for discharge of processed off-gases at the surface. This is required to meet Clean Air Act Regulations. The demonstration work at SRS falls under the Resource Conservation and Recovery Act (RCRA) groundwater corrective-action permit.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include remediation of leaking underground process lines (especially those where chlorinated solvents or other VOC wastes are present), and remediation of VOC contamination (or semi-volatile organic chemical contamination) where the contaminant plume has a linear geometry in the soil or where the contamination covers a large area. In remedial action applications where there is a very large volume of soil contamination spread out over a large area at great depths, both vertical and horizontal wells could be properly used to remediate the contamination zone.

BASELINE TECHNOLOGY

ISAS is an improvement over the vertical-well SVE technology or the vertical-well air-sparging technology. Broad application of ISAS is possible because of the placement of the lower injection well below the water line, which can remediate both groundwater and soil in the saturated zone. Consequently, ISAS is also an improvement or alternative to a vertical-well pump-and-treat process of groundwater remediation.

INTELLECTUAL PROPERTY

U.S. patent 4660639, "Removal of Volatile Contaminants from the Vadose Zone of Contaminated Ground," was issued on April 28, 1987. The vapor extraction from the upper horizontal well is covered by this patent, and Westinghouse Savannah River Company has paid a one-time license with the assignee, the UpJohn Company, for the use of this process with horizontal wells. U.S. patent 4832122, "In-Situ Remediation System and Method for Contaminated Groundwater," was issued May 23, 1989. This patent is assigned to the Westinghouse Savannah River Company and the Department of Energy (DOE).

Thirteen license applications have been issued, and one full-scale system has been implemented at a commercial remediation site.

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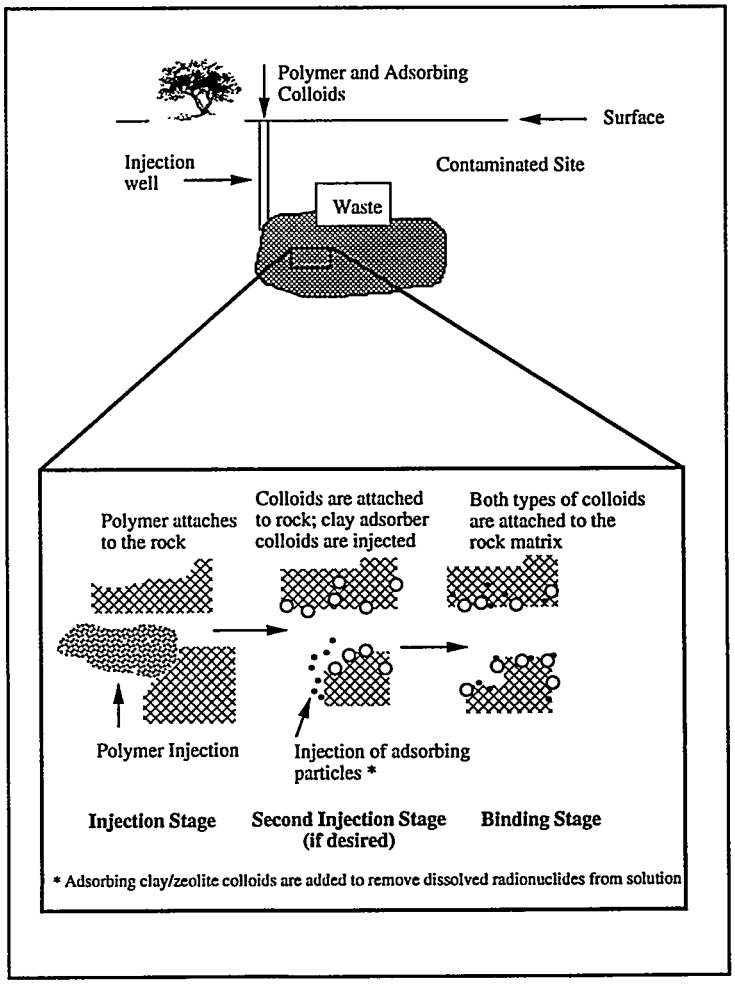
IN SITU GROUNDWATER REMEDIATION USING COLLOID TECHNOLOGY

University of New Mexico
New Mexico State University

DESCRIPTION

Facilitated migration of radionuclides in groundwater is a problem observed at numerous DOE facilities. The mechanisms for facilitated transport are not well understood. Researchers suggest that radiocolloids may be a potential factor. Radioactive colloids in groundwater are fine particles of soil or macro organic molecules that contain radionuclides. At Los Alamos National Laboratory's (LANL) Mortandad Canyon site, researchers have shown that plutonium-contaminated colloidal particles are present in well-water samples, and they suggest that these radioactive colloids are responsible for the facilitated transport of actinide waste material in the Canyon's perched aquifer. Similar findings of facilitated plutonium transport by colloids have been reported at several other DOE facilities(e.g., Idaho National Engineering Laboratory, Nevada Test Site, and Maxey Flats). On an international scale, a review of reported field observations, laboratory column studies, and carefully collected field samples provide compelling evidence that colloidal particles enhance both radioactive and toxic waste migration. Since the migration of radioactive waste by groundwater colloids is poorly understood, a team of researchers from the University of New Mexico (UNM) and New Mexico State University (NMSU) has investigated the problem. The objective of this three-year study was to understand and predict colloid-contaminant migration through fundamental mathematical models, water sampling, and laboratory experiments. Using this information, the team was to develop an effective and scientifically based colloid immobilization strategy. This strategy for in situ immobilization of colloids is illustrated in the figure below.

To date, a state-of-the-art radiocolloid characterization laboratory has been established, and colloids contained in water samples from three Mortandad Canyon wells have been characterized. A team of researchers at NMSU has completed numerical simulations of the groundwater and contaminant transport for Mortandad Canyon. These findings strongly



Colloidal Waste Immobilization Process

suggest facilitated transport of plutonium at Mortandad Canyon by colloid transport (though it is not possible with field sites to guarantee the exact transport mechanism at this time).

Laboratory studies were performed to develop an in situ colloid immobilization process. The experimental results showed that natural inorganic colloids from the Mortandad Canyon site are electrostatically stabilized in groundwater and were likely produced from the surrounding rock matrix since the colloids and rock exhibited similar composition. As part of the laboratory studies, column experiments were performed to simulate actual field conditions, to investigate colloid transport in porous media, and to test the proposed polyelectrolyte colloid remediation concept. Tests were performed under simulated conditions using both silica colloids and Mortandad colloid/water samples flowing through quartz sand packed columns. The experiments were very successful showing that colloids could be readily captured and removed from flowing groundwater using a standard cationic polyelectrolyte (polydiallyldimethyl ammonium chloride, CATFLOC) coating on the column packing.

TECHNICAL PERFORMANCE

Results from this study provided fundamental understanding about the nature of the radiocolloids at Mortandad Canyon but did not fully determine the role of colloids in transporting actinides in the perched aquifer at Mortandad Canyon. The study verified and quantified the presence of groundwater plutonium-containing colloids at the Mortandad Canyon site. Numerical calculations showed that plutonium was migrating in a facilitated manner. Our studies have confirmed the presence of plutonium on the groundwater colloids at LANL's Mortandad Canyon site and in concentrations about 100 times greater than for surrounding soils. The chemical composition of the colloids matched the soil's composition, i.e., feldspar, quartz, and clay. The Mortandad colloids are electrostatically stabilized in the groundwater, and their measured zeta potential is -19 mV. In laboratory column experiments with a simulated soil packing of crushed quartz, Mortandad colloids passed readily through the 0.8 cm x 20 cm packed columns. The polyelectrolyte (polydiallyldimethyl ammonium chloride — CATFLOC) was demonstrated to be effective in retarding Mortandad colloid transport in quartz packed columns. However, we were successful in fully retarding colloid migration when using columns packed with core sample material. This unconsolidated non-welded tuff continued to release abundant quantities of colloids even after many washings with de-ionized water and treatment of the core packing with CATFLOC. Microscope (ESEM) photographs of the core material verified the presence and abundance of free colloidal-size grains.

PROJECTED PERFORMANCE

The technology of in situ colloid remediation of groundwater is in the early stages of development. The technology is currently being extended to the in situ bioremediation of uranium mine tailings groundwater sites.

WASTE APPLICABILITY

The new technology will be applicable to in situ remediation of groundwater conatminated with radionuclides, heavy metals, and pesticides absorbed on clay or silica.

STATUS

The concept has been laboratory tested and is awaiting opportunities for field demonstration.

REGULATORY CONSIDERATIONS

This technology does not involve hazardous chemicals or physical hazards to workers. It is environmentally safe.

POTENTIAL COMMERCIAL APPLICATIONS

This new technology will be applicable to certain contaminated groundwater sites within the DOE complex and may be applicable to other sites as well.

BASELINE TECHNOLOGY

The baseline technology is in situ vitrification for plume containment.

INTELLECTUAL PROPERTY

Flexible. The PI, WERC Administration, university administration, and industrial partners work in conjunction to discuss individual cases.

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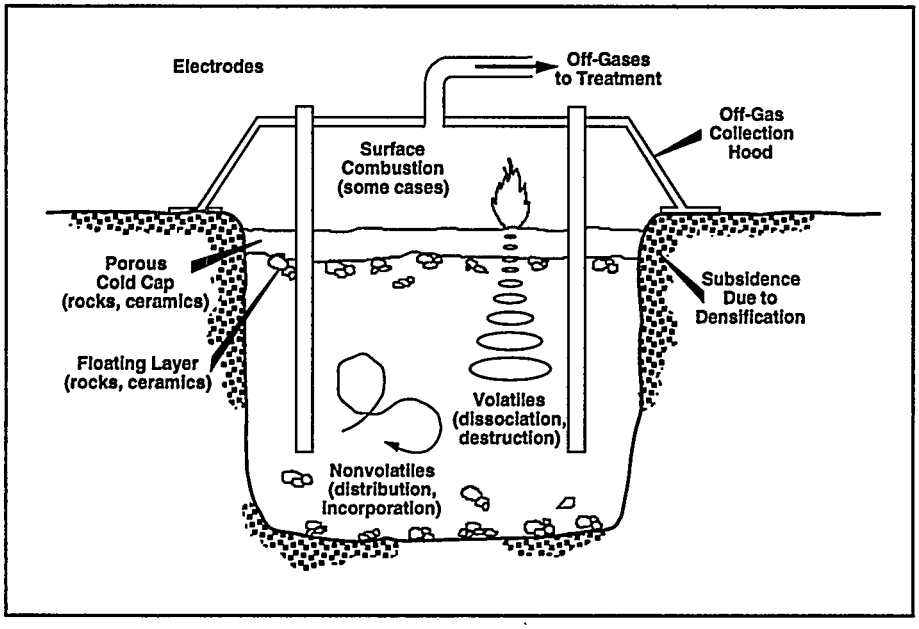
IN SITU VITRIFICATION OF CONTAMINATED SOILS

Pacific Northwest Laboratory

DESCRIPTION

In Situ Vitrification (ISV) is a patented thermal-treatment process for the in-place destruction and immobilization of contamination in soil. Temperatures of about 1,600 °C are achieved using a square array of four graphite electrodes. To initiate the process, a path of conducting material (graphite) is placed on the surface of the soil so that current can flow in the soil beyond the boiling temperature of water (dry soil is not conductive after the conduction path in soil pore water is boiled off) to the melting point of the soil. The joule heating of the starter path achieves temperatures high enough to melt the soil (value is dependent on the soil's alkali metal-oxide content), at which point the soil becomes conductive. The molten soil zone grows downward and outward. New designs incorporate a moving-electrode mechanism to achieve a greater process depth. A vacuum pressurized hood is placed over the vitrification zone to contain and process any contaminants emanating from the soil during vitrification. The vitrification product is a chemically stable, leach-resistant, glass and crystalline material similar to obsidian or basalt rock. The process destroys and/or removes organic materials. Radionuclides and heavy metals are retained within the molten soil.



Disposition of Materials During ISV Processing

TECHNICAL PERFORMANCE

Soil Type. ISV is applicable to contaminated soils and sludge, including rocks, sand, silt, or clay. Vapor-pressure buildup above the static pressure head of the molten soil is a problem when vitrifying "silty or nonswelling clays" that have low permeabilities ($<10^{-3}$ cm/s) even after drying.

Soil Moisture Content. ISV is applicable regardless of moisture content. Soils and sludges that had moisture contents of 4 to 50 wt% were successfully vitrified. Groundwater diversion during processing may be necessary in permeable aquifers.

Soil Composition. It is necessary to have glass-forming materials in the soil to process without modification. A minimal alkali content (sodium and potassium oxides) of 1.4 wt% is necessary. The composition of most soils is well within the range of processability.

Depth. Process depths up to 19 ft have been achieved in relatively homogeneous soils. The achievable depth is limited under certain heterogeneous conditions.

Radionuclides. ISV is extremely effective in immobilizing radionuclides, including transuranics and fission products. Criticality limits are conservatively placed at 30-kg plutonium/setting. Typically, there is no volatilization of ^{90}Sr, ^{241}Am, or $^{239,240}Pu$, and measurements indicate greater than 99.993% retention of these isotopes. Rare-earth tracers (Ce, La, and Nd) were used as surrogates for transuranic isotopes in an Oak Ridge National Laboratory (ORNL) field test with greater than 99.9995 wt% retention in the melt. Cesium is more volatile than most radionuclides and has been measured with volatilization of 0.029% up to 2.4 wt% of ^{137}Cs, in some cases.

Hazardous Inorganic Chemicals. ISV is extremely effective for immobilizing heavy metals and other hazardous inorganics from 70 to 99.99 wt% retention in the vitrified block. Chromium and lead retention at the Hanford Site field test was greater than 99.99 wt%. Nitrates are decomposed, and mercury is removed and collected by the off-gas system.

Hazardous Organic Chemicals. High process temperatures destroy organics by pyrolysis. Concentrations up to 7 wt% in the soil can be processed. The small percentage that is not destroyed, 0.01 to 1 wt%, is removed and collected by the off-gas system. ISV is not applicable to reactive or explosive materials. Limited empirical data suggest that VOCs can be effectively treated; however, treatability studies on a site-specific basis are recommended.

Scrap Metals. Up to 25 wt% has been processed, forming a molten pool at the bottom of the melt. However, electrical short-circuiting problems can be avoided by electrode retraction.

Debris and Rubble. Inclusions of high concentrations of concrete rubble, rock, and other debris (up to 50 wt%) can generally be processed by ISV. Monolithic structures that trap moisture should be avoided.

Combustibles. Based on heat-removal capabilities of existing equipment, combustible inclusions of up to 7 wt% can be processed.

Sealed Containers. Sealed containers and other confined spaces are not processable by ISV due to the potential for sudden pressure release through the melt into the off-gas hood. Similar concerns exist with pocketed liquids and void spaces which should be carefully evaluated.

Power and Energy Requirements. These requirements will vary with soil geologies and conditions. Maximum current delivery to the melt for the 3,750 kVA large-scale ISV system is 4,000 A on each phase. Energy requirements can be conservatively estimated at 1 KWh per kg of soil melted.

Cost Data. Geosafe Corporation offers the following general cost estimates; actual values must be determined on a site-specific basis: Treatability tests of all types $25K + analytical, PCBs and dioxins $30K + analytical, Remedial Design - varies with design firm; Equipment Mobilization and Demobilization - $200K to 300K combined; Vitrification Operation varies with electricity costs, quantity of water, and depth of process. Hazardous Waste - $350 to $450/ton; Radioactive Waste $400 to $550/ton.

PROJECTED PERFORMANCE

Improved performance includes application to buried waste and underground storage tanks, application to nonalkali soils, increasing the process depth to 30 ft (~9 m), control melt shape, VOC transport modeling, and VOC migration control.

WASTE APPLICABILITY

ISV is applicable to soils containing radionuclides, transuranics, fission products, organic chemicals, metals and inorganic chemicals, and mixed waste. Amenability and achievable depth may be limited by the presence of rock or gravel layers where heat transfer is less efficient.

STATUS

Field-scale demonstrations of contaminated soils have been performed at the Hanford and Oak Ridge Sites. Large-scale demonstrations have been completed at the Hanford Site. Demonstration in acidic soil is planned for the Savannah River Site. The technology is being evaluated for future application to buried wastes and underground storage tanks. Commercial operations for full-scale hazardous-waste-site remediation began during the summer of 1993.

REGULATORY CONSIDERATIONS

Regulatory issues include determination of Comprehensive Environmental Response Compensation and Liability Act (CERCLA)/Superfund Amendments and Reauthorization Act (SARA) and Resource Conservation and Recovery Act (RCRA) requirements, as well as state and local requirements.

POTENTIAL COMMERCIAL APPLICATIONS

Geosafe Corporation is offering the technology for commercial applications.

BASELINE TECHNOLOGY

ISV is a new technology to replace retrieve-and-treat technologies. ISV replaces the excavation of soil and above-ground treatment for decreasing toxicity and mobility of hazardous constituents. Other alternatives include grouting and chemical fixation.

INTELLECTUAL PROPERTY

The ISV process was invented by Battelle, Pacific Northwest Laboratory (PNL) for the U.S. Department of Energy (DOE) in 1980. The patent is assigned to DOE, is licensed to Battelle, and is sublicensed to Geosafe Corp. for world-wide rights. Patent No. 4,376,598 was issued March 15, 1983.

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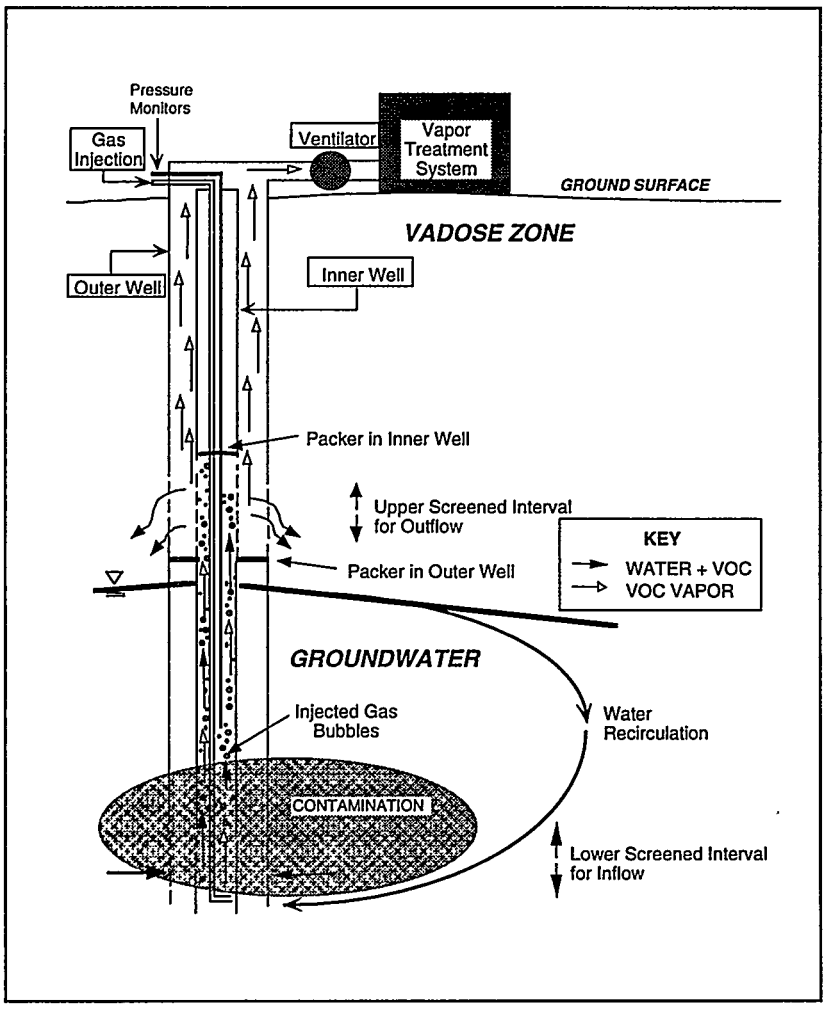
IN-WELL VAPOR STRIPPING

Stanford University

DESCRIPTION

During the last decade, over 1,200 hazardous waste sites in the U. S. have been placed on the National Priorities List of the Environmental Protection Agency (EPA) for remedial investigation and cleanup. The U. S. EPA estimates that there are more than 2 million underground tanks in the United States and that 20% of them leak and contaminate groundwater. Such tanks leak benzene, toluene, and their derivatives which become dissolved in groundwater. Another important group are the Volatile Organic Compounds (VOCs), notably trichloroethylene (TCE) and its degradation products. However, current remediation methods are often very expensive, and alternative concepts and techniques are needed. In-Well Vapor Stripping (IVS) is an effective and efficient process of removing VOCs from the groundwater. The IVS method involves a combination of the technique of air-lift pumping with a form of vapor stripping.



In-Well Vapor Stripping System

The IVS system creates a groundwater recirculation and VOC reduction zone by utilizing a well-within-well design that is screened at two intervals. A lower screened interval is located at depth beneath the water table and allows contaminated groundwater to enter the well. An upper screened interval is located above the water table and allows water depleted in VOCs to be returned to the aquifer. An eductor pipe is installed inside the well casing creating a well-within-a-well. Inside the inner well, an air line is introduced into which air is injected. The air is released beneath the water table, creating bubbles that rise. Due to the density difference between the water column outside the well and the water-bubble mixture within the inner well, a lift is created. Water and air rise within the inner well, forcing additional water to flow from the aquifer into the well through the lower screened interval. The water-and-bubble mixture flows upward in the annular space around the air line.

A simple separator plate is located within the inner well at an elevation above the water table. As the water-bubble mixture hits this separator plate, the water is forced laterally into the outer well and exits into the unsaturated zone through the upper screened interval. From there, the water freely infiltrates back to the water table. The air bubbles are released into the outer well and are extracted to the ground surface under a vacuum. Because the water enters the well at the lower screened interval and returns to the water table, a groundwater circulation cell is developed in the vicinity of the well. The radius of this circulation cell can be hundreds of feet or more depending on the pumping rate, the depth of the lower screened interval, and the aquifer properties.

Simultaneously, an air-stripping "chamber" is created within the eductor pipe. During the period in which the air bubbles flow through the water in the inner well, VOCs are transferred from the water to the gas phase due to the concentration gradient. The air bubbles, including the VOC vapor, are collected using vapor-extraction techniques at the top of the well. The organic-rich vapor is treated using existing methods such as sorption onto activated carbon or incineration.

As this process continues, water circulates from the aquifer to the well and then back to the water table. The concentration of VOCs is reduced, and after a sufficient number of circulation cycles, it will reach the permitted standards.

TECHNICAL PERFORMANCE

Monitoring-well installation and baseline studies will be conducted during the summer of 1994 to gather data to enable updating of the design features for the test well and updates of the injection requirements. Operation for the initial 90-day demonstration commenced in the early fall of 1994 at the 200 West Area at the Hanford Site. Results from the demonstration will guide sensitivity studies for the following two-year period.

Costs. Specific costs have not been determined. The primary cost components are the well installation, the compressor and packer, monitoring, and the GAC system. Because all VOC removal is accomplished in situ, the primary cost savings component over a pump-and-treat system is that there is no need for a vapor stripping tower and a separate reinjection well.

PROJECTED PERFORMANCE

The IVS process is expected to be an efficient and effective method of removing VOCs from the groundwater. Once the tests are completed, statistics will be available and work on improving performance can begin.

WASTE APPLICABILITY

This technology is applicable for extracting VOCs (such as carbon tetrachloride, chloroform, and trichloroethylene) from the aquifer and the vadose zone.

STATUS

Demonstration is currently in progress. This technology should be available in 1995.

REGULATORY CONSIDERATIONS

Drilling and subsurface-access regulations may vary depending on the waste-site characteristics. Precautions must be taken to prevent spills during transportation of the activated charcoal used to remove the VOCs. All local, state, and federal regulations must be satisfied.

POTENTIAL COMMERCIAL APPLICATIONS

This technology can be applied to any VOC contamination that is beyond the stage of soil removal (greater than twenty-feet deep). This includes any industry that may have soil and groundwater VOC-contamination problems.

BASELINE TECHNOLOGY

This technology, when compared to conventional VOC-removal schemes (which involve pumping out many gallons of water and treatment above ground), is much more effective and efficient.

INTELLECTUAL PROPERTY

U.S. patents for the IVS technology are held by Stanford University.

Patent number: 5,180,503 (January 19, 1993)

Licensing of this technology has been transferred from Stanford to NoVOCs, Inc.

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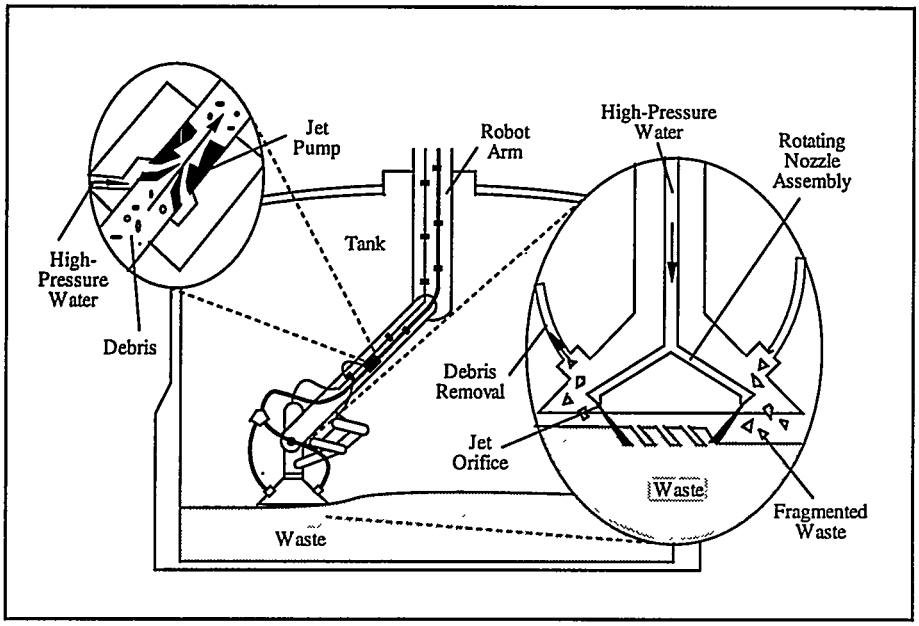
MEDIUM PRESSURE WATERJET DISLODGING AND CONVEYANCE END EFFECTOR USING CONFINED SLUICING

Pacific Northwest Laboratory

DESCRIPTION

The Confined Sluicing End Effector (CSEF) is a remotely operated tool attached to the end of a robotic manipulator arm. Confined sluicing is applicable for dislodging, mobilizing, and removing all waste forms (hard cake, sludge, and bulk supernate) stored in the Hanford Underground Storage Tanks (USTs). The confined-sluicing device is attached as an end effector to an articulated arm that enters the tank through an existing access riser. The CSEF is lowered into a tank containing hazardous waste and is used to cut, dislodge, and remove waste material. It is also used to clean and decontaminate the walls of the tank and any residual hardware that remains in the tank. Confined sluicing uses high-pressure (10,000 psi or 70 MPa) waterjets to cut the material in the tank into small pieces, and then sucks the material out using a high-pressure (around 7,000 psi or 50 MPa) jet pump. The cutting operations take place in a confining shroud, which leads to an aspirating, high-pressure jet pump. Water expelled by the jets and all debris excavated by the process are caught and pumped out of the tank before they can flow into the main body of the tank. Therefore, the injected water and fragmented debris are removed without significant water loss to the tank, and the excavations of mixed waste are carried out of the tank as an aqueous slurry. Conveyance of the waste in a slurry pipeline facilitates feed to downstream waste processors and separators. Although waste processing is external to this waste-removal system, the slurry water is captured and separated and then recycled back to the waterjet feed tank, forming an approximate closed loop. Some make-up water may be necessary. Recycling the water results in waste minimization because the volume of waste water generated by the sluicing process is minimized. At the end of the entire tank farm remediation program, the waste water would be treated and reclaimed or suitably disposed.



Waterjet Cutter

TECHNICAL PERFORMANCE

Design Specifications. The waterjet operates at 10 kpsi, and the jet pump for the pneumatic conveyor develops a 7 kpsi pressure head. The CSEF system is designed to remove all excavated tank waste at a steady flow of 30 gpm or higher. Confined sluicing will break the waste down into a slurry of small

particles that are easily processed. It is anticipated that the water-to-solid ratio will be between 2:1 and 4:1. The system will probably require less than 500 hp, but exact requirements are yet to be defined.

Feasibility Study. A feasibility study was conducted in 1992. Feasibility studies have shown that targeted waste-removal flow rates of 30 gpm are achievable.

Cost. The cost of this item has not been estimated because of the ongoing refinement of the technology.

PROJECTED PERFORMANCE

It is projected that CSEF will be able to excavate and remove all types of tank waste, including hard cake, sludge, and bulk supernate. The projected removal rate is 30 gpm with a water-to-solid ratio of 2:1 to 4:1. It is projected that the water expelled by the waterjets and retrieved by the pneumatic conveyor will be "close-looped" and recirculated throughout the entire tank farm reclamation process.

WASTE APPLICABILITY

Confined sluicing provides a means to empty and decontaminate the USTs currently used to store radioactive waste. The CSEF is designed for in situ application in the Hanford USTs. The confined-sluicing method is applicable for excavation, mobilization, and removal of all the hazardous radioactive material stored in the Hanford USTs, including hard salt cake, sludge, and bulk supernate.

STATUS

Preliminary feasibility studies were conducted in FY92. It is anticipated that this system will be fielded in FY97. Much of the equipment and support systems are commercially available now. However, much of the specific design of the waterjet head required for this application must be developed and validated.

REGULATORY CONSIDERATIONS

No significant environmental impacts are anticipated by the use of this technology. The "closed loop" processing of the waterjet feed water may make this technology more acceptable than other alternatives.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is potentially applicable to radioactive or hazardous excavations in remote settings (such as an underground storage tank). The waterjet cutting technology has applications in advanced manufacturing, material research, and in the mining industry.

BASELINE TECHNOLOGY

There is presently no baseline technology that can break up and remove all types of tank waste. One possible alternative to confined sluicing is flooding of the tanks with water and continuously pumping the water out; such a method is referred to as general sluicing. General sluicing requires large quantities of water, cannot be used in leaking tanks, and cannot deal with hard, insoluble materials.

INTELLECTUAL PROPERTY

Patents: None.

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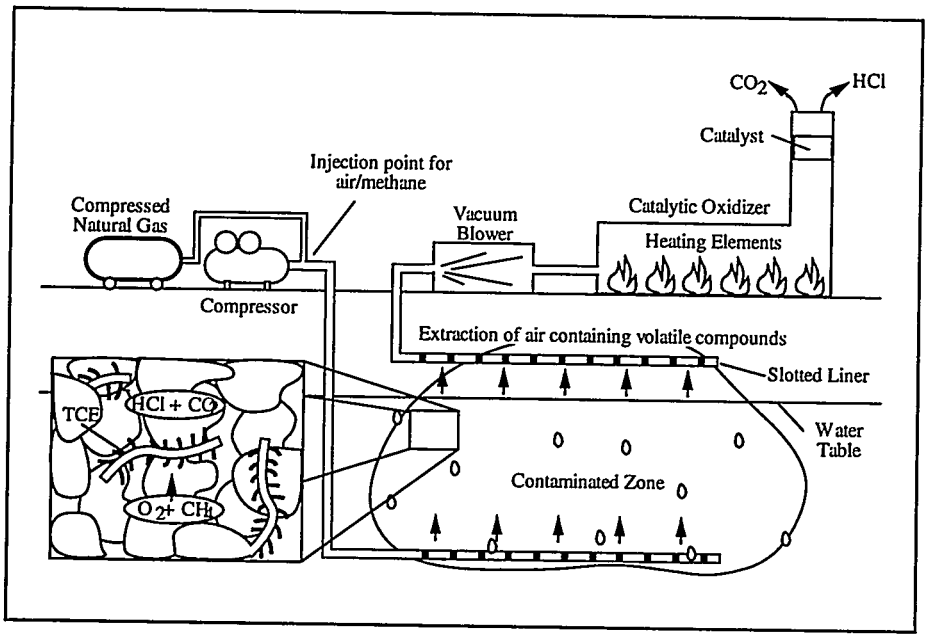
METHANE ENHANCED BIOREMEDIATION FOR THE DESTRUCTION OF TRICHLOROETHYLENE USING HORIZONTAL WELLS

Westinghouse Savannah River Company

DESCRIPTION

Methane Enhanced Bioremediation (MEBR) using horizontal wells is an in situ method to stimulate cometabolic destruction of halogenated aliphatic chemical contamination in the sub-surface, such as trichloroethylene (TCE) and tetrachloroethylene (PCE). This destruction is achieved by enzyme-catalyzed reactions brought on by the methane monooxygenase enzyme (MMO) of indigenous methane-utilizing bacteria (methanotrophs). The process has the capacity to degrade the contaminants into carbon dioxide, water, and soluble chlorine.

Horizontal wells provide better contact for nutrient delivery and more efficient aerobic stimulation of the subsurface microflora. A methane-and-air mixture (<5 vol %) is injected through a horizontal well into an aquifer below the contaminant plume to stimulate microbe biomass growth above the well. One strategy to optimize growth and degradation is pulsing of the methane/air mixture and another is injection of nitrogen- and phosphorous-rich nutrients with concomitant methane treatments. The gaseous nutrients will flow upward through the contamination plume to an upper-duty vacuum-extraction well. The upper parallel, horizontal, vapor-extraction well is located in the vadose zone above the linear contamination plume. A thermal catalytic oxidation (CatOx) system, operated at 825 °C, is used to treat extracted soil vapors. The figure below is a general schematic of the process.



Nutrient Enhanced Bioremediation System

TECHNICAL PERFORMANCE

Pilot-Scale Demonstration. Performed at the Savannah River Site, M area, abandoned seepage basin and process sewer line employed for disposal of solvents used to degrease nuclear fuel target elements. Contamination is mostly TCE and PCE with concentrations of 10,000 ppb in soil and 1,000 ppb in groundwater. Extensive soil and groundwater monitoring has demonstrated that methanotroph densities increased 5 orders of magnitude and TCE/PCE concentrations declined to less than 2 ppb; the current drinking water standard is 5 ppb.

Capital investment costs are $150K and 200 man hr for site preparation, setup, and assembly. The operation is low

maintenance, requiring only one technician at 25% time (10 hr/wk); other operational costs are for electricity, natural gas, and equipment maintenance. In 429 days of operation, 12,096 lbs of VOC were extracted and treated with the CatOx system; less than 726 lbs were emitted, and the remaining amount was destroyed by the CatOx system. Biodegradation was indicated by increased concentrations of carbon dioxide in the extracted vapors and increased concentrations of soluble chlorine in groundwater monitoring wells.

There were four consecutive stages to the demonstration, not including the baseline tests that are vacuum extraction-only (240 scfm) and vacuum extraction coupled with 100% air injection at 84% of the extraction flow rate (202 scfm).

The first stage, lasting 3 months, was with 1% (vol) methane added to the injected air flow. Helium conservative tracer tests indicate that more than 50% of the 1,392,774 scf of injected methane was consumed by the indigenous microbes, contributing to biomass growth and contaminant degradation. Initially, biomass grew at an approximate average rate of an order of magnitude every 2 wks. Growth slowed after two months because of the reduction of naturally occurring nitrates and other nutrients. Technical-grade methane was also found to be growth-inhibiting because it contains small amounts of acetylene, which is poisonous to methanotrophs.

The second injection campaign was 4% methane added to the injected air stream. Populations of methanotroph bacteria increased while TCE/PCE concentrations decreased. The third stage used pulsing of the injected methane at a rate of 8 hr every 2 days to minimize nutrient competition and optimize growth. However, it was realized that more rapid pulsing produced a more optimum growth rate. Ultimately, the growth and degradation efficiency of the methanotroph bacteria is limited by the paucity of other essential nutrients. The final stage of the demonstration included pulsing of methane with continuous injection of a confluence of air, nitrous oxide at 0.007%, and tri-ethyl phosphate at 0.07%. Rates of mineralization and physiological activity increased dramatically, although nutrient injection had only minor effects on the total biomass. It was concluded that there must be a further deficiency in some other necessary nutrient.

PROJECTED PERFORMANCE

The knowledge gained will enable future applications to have a high-quality nutrient-injection schedule, approaching an optimum. The results expected are rapid biomass growth, metabolism, contaminant mineralization, and site restoration.

WASTE APPLICABILITY

This technique is specifically useful for destruction of halogenated aliphatic compounds and chlorinated solvents (TCE, PCE etc.); furthermore, the non-specific MMO enzyme has been demonstrated to degrade more than 250 different compounds. It is applicable where the subsurface does not contain significant amounts of copper or azide compounds that either poison the methanotrophs or limit their growth.

STATUS

This is an emerging technology, but it is available for application now. The knowledge base gained will be applied to future designs for full-scale demonstrations and applications at the Savannah River Site (SRS) and other sites.

REGULATORY CONSIDERATIONS

Resource Conservation and Recovery Act (RCRA) permits and compliance with the Clean Air Act and Clean Water Act for injection control may be required. Comprehensive Environmental Response Compensation and Liability Act (CERCLA), as amended by the Superfund Amendments and Reauthorization Act (SARA), provides the mandate for implementing the demonstration tests to remediate the contamination of soils and aquifers at the SRS.

POTENTIAL COMMERCIAL APPLICATIONS

The use of horizontal wells for microbial stimulation makes restoration of soils and aquifers in otherwise inaccessible areas (e.g., under structures) possible. It is applicable for remediation of organic chemical spills, chemical-process sewer leaks, and storage-tank leaks. The enhanced bioremediation technology is useful for timely remediation of contaminant plumes that are attributable to the transportation fuel industry, chemical industry, uranium purification, and other activities that may produce, utilize, store, or dispose of chlorinated solvents.

BASELINE TECHNOLOGY

The baseline technology is vacuum extraction alone with effluent treatment or in situ air stripping with effluent treatment but without biomass or nutrient injection. In contrast, the MEBR technology is based on biological destruction of contaminants in situ. Nutrient injection for enhanced bioremediation has the potential to enhance the performance of in situ air stripping, as well as offering stand-alone remediation. The use of horizontal wells gives an increased surface area and contact efficiency for better delivery and distribution of nutrients, for easier recovery of soil-gas and water, and for minimization of formation clogging and plugging phenomena. This technology is capable of decreasing contaminant concentrations to drinking water standards (5 ppm) in heterogeneous environments. Few pump-and-treat technologies are comparable.

INTELLECTUAL PROPERTY

The Department of Energy (DOE) applied for a patent for methane and gaseous nutrient injection through horizontal wells. Patent US 4713343 was issued December 15, 1987, for biodegradation of halogenated aliphatic hydro-carbons and for water purification using micro-organisms capable of aerobic degradation of low-molecular-weight alkanes; the assignee is U.S. EPA. Patent US 4832122 was issued May 23, 1989, for In Situ Remediation System and Methodology for Contaminated Groundwater; the assignee is U.S. DOE.

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MIGRATION BARRIER COVERS

Los Alamos National Laboratory

DESCRIPTION

The subject technologies focus on remedial options for landfills which can be rapidly implemented such as engineered landfill capping (near-surface barriers), other subsurface barriers, contained bio-treatment, and post-closure monitoring technologies. The scope of this technology profile includes impermeable and permeable capping technologies, gel-barrier materials, enhancement of natural biologic communities, chemical-tracer approaches, and remote monitoring of the hydrologic systems. Two different potential applications of barriers are being evaluated. The first is the use of impermeable barriers for chemical containment for future remedial action including in-trench leaching or in situ bioremediation. The second is the integration of permeable reactive barriers and petroleum-reservoir gel/foam/polymer technology with grout or clay slurry walls to direct horizontal surface and subsurface water flows around a contaminated area.

Barrier and post-closure monitoring tests are being conducted in field-scale demonstration plots and are being designed for actual contaminated sites. The range of materials available for augmenting existing barrier practice is broad. The initial focus has been the design and demonstration of capping technologies which modify the water balance of a landfill to minimize or eliminate percolation which leads to leaching and cap erosion which could lead to waste exposure and migration. The most recent demonstration results are presented for landfill-capping technologies and techniques for remote monitoring of soil moisture. The landfill capping demonstration evaluated hydrologic performance of a conventional soil cap, a modified EPA-RCRA cap, a Los Alamos (LA) capillary barrier, and an LA capillary barrier with an enhanced vegetation cover. This demonstration was benefited by a concomitant remote monitoring evaluation which compared neutron-probe and time-domain reflectometry techniques for soil-moisture analysis.

The remediation technology area for which capping is a part is referred to as "containment" (Figure 1) and involves leaving all or some of the contaminant source in place and controlling the processes that cause the waste to migrate using appropriate barrier technology. These barriers take advantage of the fact that there are strong interactions among the various components of the water balance of a site. The fate of meteoric water falling on the surface of a landfill is referred to as the water balance (Eq. 1).

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial t}(P - Q - ET - L) \qquad (1)$$

The term on the left-hand side is the rate of change of soil moisture, P is a precipitation term, Q is the runoff term, ET is the evapotranspiration term, L is the percolation below the root zone, and t is the time variable. The reduction or elimination of the runoff term (Q), increases infiltration of water into the soil, resulting in increased moisture storage followed by an increase in ET and/or percolation. Likewise, reducing percolation necessitates that more of the precipitation be partitioned among soil-moisture storage, ET, runoff, or that it is diverted laterally using an appropriate barrier technology (e.g., LA capillary barrier). The coupled nature of the process comprising the water balance can be used to an advantage in designing landfill caps that minimize or eliminate process in Eq. 1 which contribute to contaminant migration (i.e., percolation) while enhancing other

eliminate process in Eq. 1 which contributes to contaminant migration (i.e., percolation) while enhancing other terms (i.e., ET).

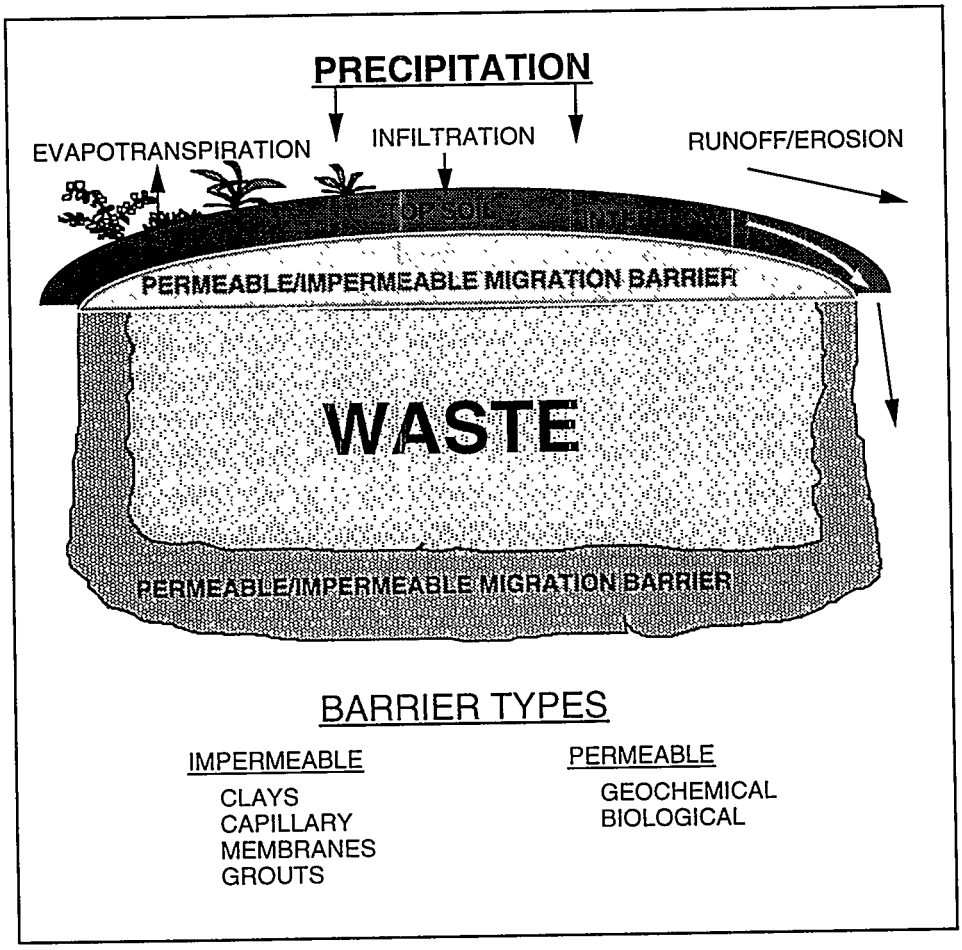

Figure 1. Overview of Migration Control Barriers and the Water Balance Concept.

Permeable, Reactive Barriers. These barriers allow the passage of water while prohibiting the movement of contaminants by employing such agents as chelators (ligands selected for their specificity for a given metal), sorbents, microbes, and others. In Department of Energy (DOE) sites where multiple contaminants are ubiquitous, multicomponent barriers need to be evaluated. Field-scale experiments were constructed using natural sand with the permeable barriers consisting of zeolite + silica gel + sand, bentonite + Al crosslink polyacrylimide + sand, and peat + Al crosslink polyacrylimide + sand. The reactive barriers could be designed: (1) to remain in place as permanent or semi-permanent installations; (2) to be removed and replaced periodically, thus serving as a component of the remediation process; and/or (3) to be used as part of the post-closure monitoring system in which the appearance of a contaminant in the barrier would then serve to warn of impending contaminant migration.

In-Place Bioreactors. This technical approach uses the capabilities of native bacteria for degrading hazardous organic compounds in a cost-effective, publicly acceptable manner. The capability can be managed to provide prolonged treatment, as well as treatment of relatively short duration. In addition to full-scale site remediation, biodegradation has significant near-term potential as an effective containment strategy. Thus, evaluation of approaches to managing biologic communities on the margins of a site, in combination with other barrier approaches, will provide significant information for both limitation of contaminant transport and full-site cleanup.

Post-closure monitoring. The field experiments have focused on evaluation of water saturation and chemical transport. Comparison of established neutron-probe measurements of water saturation in arid soils with developments in Time Domain Reflectometry probe systems is being used to evaluate opportunities for automated and more detailed characterization. Chemical transport is being evaluated through the

use of contaminant and chemical-tracer materials. Application of tagged tracers allows evaluation of both barrier-system effectiveness and potential contaminant-transport pathways or imminent arrival. Tracers for the permeable-barrier experiments included low concentrations of common anions (e.g., bromide), soluble organic acids, semi-volatile organic acids, fluorescein, chromium, and EDTA. The tracer/pseudo-contaminant for the bio-barrier experiments focused on toluene, labeled with carbon-13, to allow specific characterization of transport and biodegredation processes as a function of plant cover and fertilization.

TECHNICAL PERFORMANCE

The permeable barriers are being designed to operate unattended with minimal maintenance for long periods of time (i.e., years). However, periodic inspections will be required because these enhanced barriers might fail because of cracking. Since the barriers are passive, no power is required for their operation. Demonstration results are not currently available for the advanced Permeable/Reactive Barriers nor are results available for the Contained In-Place Bioreactors.

Impermeable/semi-permeable landfill covers were installed and monitored for 45 months (Jan. 1, 1990 to Sept. 20, 1993) at Hill Air Force Base and results became available in 1994. Four field-scale landfill-cap designs were installed in modular swimming pools at a finished dimension of 5 x10m. One cap was a conventional soil cap which consisted of 90 cm of local Hill AFB soil over 30 cm of a gravel drainage layer to promote rapid collection of leachate. The top-soil in this and the other plots was a sandy loam compacted to a density of 1.86 g/cc or 97% of the optimum based on Proctor tests and in situ gamma density measurements. The hydraulic conductivity of this soil was 2.8×10^{-4} cm/s$\pm 0.3 \times 10^{-4}$ (measured in the laboratory). Complete saturation of the top-soil occurred at 30% volumetric water content.

The EPA-recommended RCRA cap was also demonstrated in a modified configuration. EPA recommends installing a Flexible Membrane Layer (FML) between the sand drainage layer and the compacted clay layer (Fig. 2) which is likely to fail after an unspecified period of time. Therefore, the RCRA cover was studied in a configuration after the FML would have failed. The modified RCRA cap consisted of 120 cm top soil over 30 cm of a sand drainage layer over 60 cm of compacted clay loam

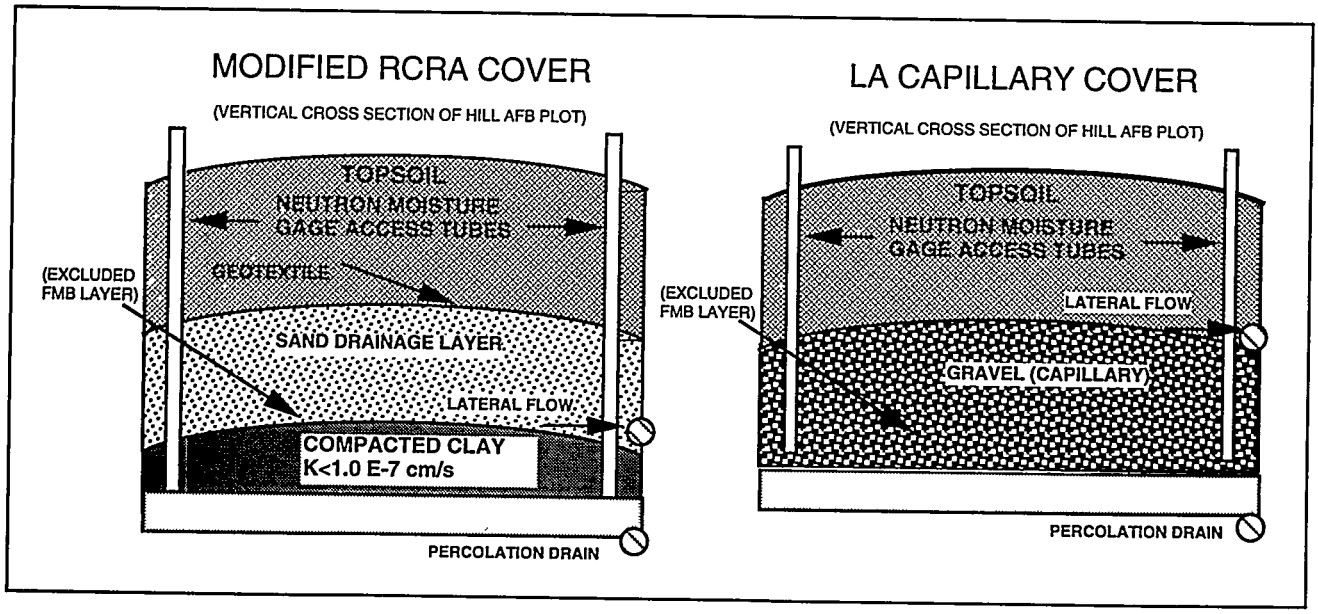

Figure 2. Comparison of EPA-RCRA Cap and the Los Alamos Capillary Cap.

emended with bentonite. The clay layer was compacted to 1.76 g/cc (96% of optimum) with a saturated hydraulic conductivity of 3.4 x 10^{-6} cm/s. Complete saturation of the clay occurred at 50% volumetric water content.

Los Alamos Capillary Barriers which contain erosion-control measures were demonstrated in two configurations. One LA Capillary cover had enhanced vegetation cover for improved evapotranspiration (ET) and the other had standard vegetation cover equivalent to the other plots. The LA Caps consisted of 150 cm topsoil over 30 cm of ~1 cm diameter washed gravel to serve as a capillary break. A geotextile fabric, highly permeable to water, was placed between the soil and gravel layers to retard the rate of soil penetration downward into the gravel capillary break. A final 30 cm of gravel at the bottom of the profile served as a drainage layer for any leachate produced from the cap profiles. Both of these latter designs also included a thin gravel cover on the soil surface that past studies have shown to be very effective in controlling erosion. The gravel cover had the added benefit (though non-intuitive) of increasing biomass by increasing infiltration, and thus, availability of water in the soil. All plots had 4% slope on the cap surface and on all subsurface barriers. Table 1 gives water-balance estimates based on neutron-probe moisture logging for the Hill AFB Cover Demonstration.

The 45 month demonstration results show that the RCRA cap was the most effective in preventing soil-water movement completely through the cap (Figures 3 and 4). Break-through occurred 27 months after the demonstration began. The ability to control percolation was strongly related to the cap design with very good protection being provided by the clay barrier in the RCRA design.

The clay barrier was approaching saturation near the end of the study; therefore, evaluation of the long-term performance of the clay barrier in diverting soil water laterally or in preventing leachate production will require additional monitoring. Since the RCRA cap had greater interflow and more soil-moisture storage in the clay layer, the cumulative leachate was much less than the conventional soil cap. The LA Caps had average performance on limiting leachate but had excellent performance in limiting erosion (Figures 5 and 6). Erosion is a key contributor to contaminant migration when exposure occurs and

Table 1. Water Balance Estimates, Hill AFB Cover Demonstration (Jan90-Sep93)

	--Plot Design--			
Parameter	LA-1 (Grass)	LA-2 (Grass & Shrub)	RCRA	Control
Precipitation (cm)	173	173	173	173
Initial (CY90) Soil Water Storage (cm)	32	31	35	20
Net Change in Soil Water Storage (CY90-10/93)	-17 (-10%)	-15 (9%)	+11 (6%)	-11 (-6%)
Leachate (cm)	27 (16%)	28 (16%)	0.5 (0.3%)*	59 (34%)
Interflow (cm)	20(11%)	12 (7%)	43 (25%)	0 (0%)
Runoff (cm)	1.4 (0.8%)	2.2 (1.3%)	5.5 (3.2%)	5.8 (3.4%)
ET (cm)	142 (82%)	146 (84%)	113 (65%)	119 (69%)
Sediment (g)	102	95	1,534	2,374

* Breakthrough began March 20, 1992 (27 months elapsed time)

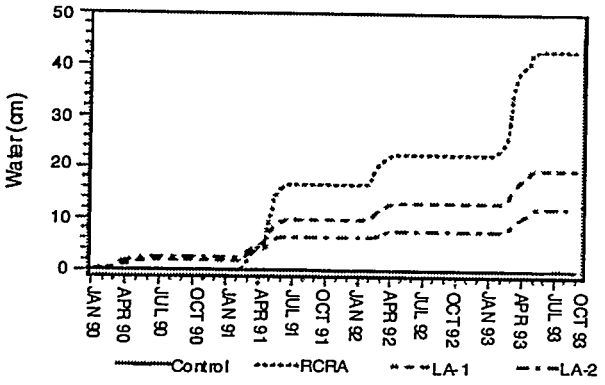

Figure 3. Cumulative barrier lateral flow as a function of time for all cap designs at Hill AFB.

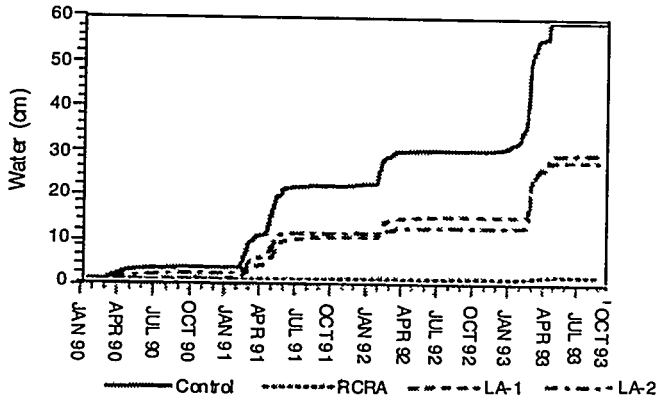

Figure 4. Cumulative leachate flow as a function of time for all cap designs at Hill AFB.

has the potential for catastrophic migration. In all plots, however, the erosion rates were less than the EPA limit of 4.4 Tonnes/hectare-yr.

It is important to note that although capping technologies will be useful in remediating radioactive, hazardous, and municipal-waste landfills, there is no one cap that will work universally across all sites. Many questions about the performance characteristics of capillary and clay barriers advise caution in their use for landfill remediation. For example, little is known about how to optimize barrier design to enhance lateral flow, the limits on the slope length in diverting flow, the influence of type, seasonality and amount of precipitation, and the effects of biological intrusion through the capillary break on barrier performance. An issue seldom addressed relative to clay or capillary barriers is the provision for disposing the lateral-flow water generated by the barriers in a way which prevents the water from reentering the waste environment.

Cost. The field tests at Los Alamos National Laboratory (LANL) which were completed in early 1994 had a start-up cost of $1.2M and an operations/maintenance cost of $670K in FY93. The operating and maintenance costs realized in the experimental demonstration may or may not be reflective of the costs of a full-scale installation, as the covers are intended to be low maintenance with automated monitoring. Life-cycle costs for operational systems have not been estimated, but are expected to be 5 to 10 times less than excavation. Table 2 gives representative costs taken from the literature for excavation compared to various capping remedial options.

PROJECTED PERFORMANCE

Quantified performance data have not been estimated for production systems. However, significant improvements are anticipated in both operational costs and acceptance by public and regulatory communities.

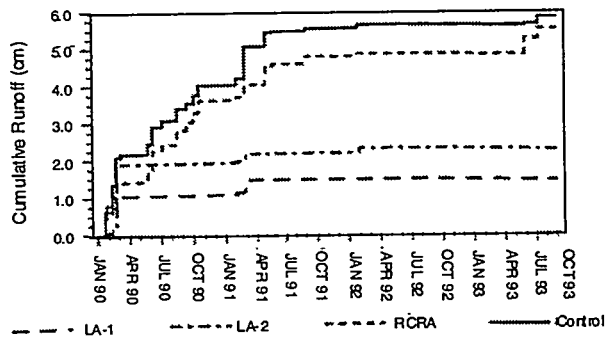

Figure 5. Cumulative runoff from the Landfill Capping Demonstration plots as a function of time for all cap designs at Hill AFB.

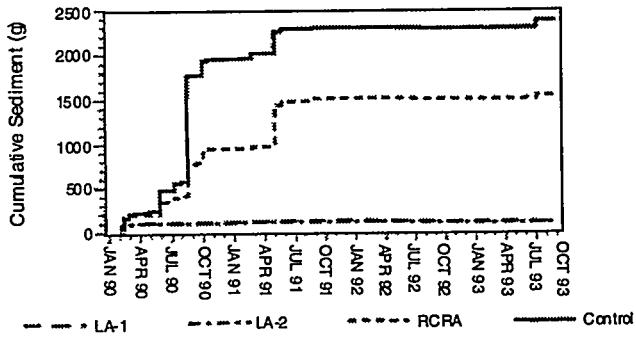

Figure 6. Cumulative sediment from the Landfill Capping Demonstration plots as a function of time for all cap designs at Hill AFB.

Table 2. Cost Comparison: Estimated 1992 costs of landfill remedial alternatives at Los Alamos, NM.

Alternative	Cost ($M/ha)[1]
Excavate	80
RCRA cap	4.9
Soil/capillary barrier cover	3.7
Bio-engineered soil/veg. cover	0.24
Surface management w/erosion control	0.12

1. hectare (ha) = 10,000 m^2 (2.471 acres).

WASTE APPLICABILITY

These barrier technologies are primarily intended for in situ treatment/containment of soluble metals and organics in arid soils. Potential landfill applications include radioactive, hazardous and mixed-waste landfill applications where the level of containment is compatible with determined risk. A decision Support System is being developed which considers hydrologic, erosion, remediation cost, and risk factors to determine suitability and assist in containment design. According to this subject technology, the contaminants will either be contained within the landfill volume, biologically degraded, or retained in a concentrated form by the barrier material. The barrier could provide permanent containment for the relatively benign residues or provide a decreased volume of the more toxic contaminants for subsequent treatment.

STATUS

Evaluation of the currently installed (CY89) landfill cover systems was completed early in CY94. The first reactive barrier and monitoring systems were installed in 1992. The tracer tests, which would include the effects of seasonal changes in the environment, were scheduled for completion in 1993. Approximately two additional years would be required to test and evaluate each additional barrier system.

REGULATORY CONSIDERATIONS

Closure and post-closure monitoring will be required under Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Superfund Amendments Reauthorization Act (SARA), and Department of Energy (DOE) Order 5820.2A. For hazardous chemical sites, the required post-closure monitoring period is 30 yrs. For radioactive sites that have been closed, DOE Order 5820.2A requires monitoring and maintenance of the site for 100 yrs. According to EPA closure regulations, cap erosion must be less than 4.4 metric tons/hectare-yr. (EPA/530-SW-89-047, July 1989).

POTENTIAL COMMERCIAL APPLICATIONS

The landfill cover systems presented in the technical performance section have important potential application for municipal- and industrial-waste landfills. The components of the barrier and monitoring systems that are currently being field tested have all been obtained from commercial vendors. Thus, these technologies can lend to full commercialization. Furthermore, chemical and petroleum companies are now actively applying the proposed types of permeable barrier and bio-technological technologies in enhanced oil-recovery operations.

BASELINE TECHNOLOGY

The conventional landfill cover system is a regional soil cover. On the other hand, the baseline technology for hazardous- or radioactive-waste landfills must be defined as the RCRA cap since it is the EPA standard cover system. If a landfill cover can be shown to perform equivalent to the RCRA cap, it would be accepted as a closure option. Baseline materials currently being used by the DOE for barrier emplacement include grouts, clay slurries, and cements for pure hydrologic barriers. Landfill caps are baselined for the biotreatment systems, and the neutron probe is baselined for soil-moisture and post-closure monitoring. By design, landfill barriers and cover systems restrict water transport through the contained area but may often require active biological treatment and/or reactive systems to maintain a stability.

INTELLECTUAL PROPERTY

Patent Ownership: To be determined.

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PLASMA HEARTH PROCESS

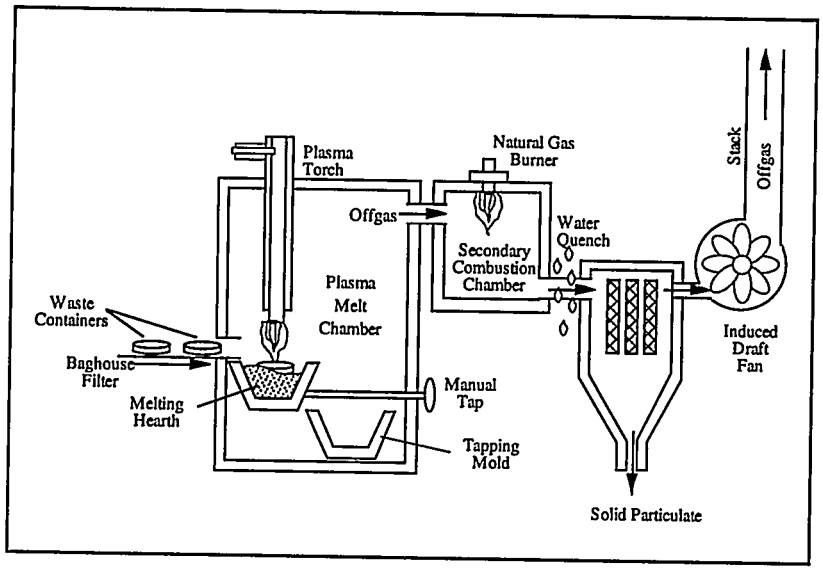
Science Applications International Corporation

DESCRIPTION

The Plasma Hearth Process (PHP) is an ex situ, vitrification process that can convert nearly all forms of mixed waste into a stabilized, leach-resistant form. The objective of the PHP project is to develop, test, and field-demonstrate a technology that will convert full drums of waste materials directly to an enhanced waste form in a one-step process with little or no need for pretreatment or characterization. The system can be used to treat both the uncharacterized, heterogeneous waste streams resulting from buried-waste-site remediation as well as entire drums of stored waste that might otherwise require extensive pretreatment with existing technologies.

The Plasma Hearth Process uses a transferred arc-plasma torch to convert full drums of unprocessed waste material into a vitreous final form in a specially designed refractory hearth. The PHP design was based on concepts developed for vacuum metallurgy, and the result is a highly sealed system. The waste materials are fed into the plasma chamber, where any volatile materials vaporize. These materials are sent to the secondary combustion chamber, where they react at high temperatures to form innocuous products. Solids are retained in the plasma chamber, where they are incorporated into a molten bath. The material in the molten bath forms separable metallic and vitreous phases. Transuranic components have the tendency to incorporate into the vitreous slag rather than the metallic phase, which is beneficial. When cooled and solidified, the vitrified material forms an extremely durable, leach-resistant slag.

Components of PHP include the primary plasma chamber, waste-material feed system, plasma torch, power supply, hydraulic equipment, refractory hearth, secondary combustion chamber with a natural gas burner, off-gas cleaning equipment, off-gas monitoring equipment, a control system, and an operator interface. During operation, the PHP requires plasma-torch gas, electricity to run the torch, fuel for the secondary burner, air, water, and waste-feed materials. The outputs from the system are heat, solidified metal, vitrified slag, salts from the off-gas system, and clean off-gas. The system will process hazardous, transuranic, and mixed wastes without extensive pretreatment and characterization. The ability to process a heterogeneous waste stream without pretreatment or characterization is important because both activities are extremely expensive and time-consuming and require hands-on involvement by workers. The current development activities are for the material-feed systems, product-removal and handling systems, off-gas system



Fixed Hearth DC Plasma Process

design, and control-system design to handle unknown heterogeneous feeds.

TECHNICAL PERFORMANCE

PHP is designed to vitrify 250-1,000 kg/h of contaminated soil and waste material. The plasma chamber achieves a molten-bath temperature of approximately 1,650 °C. The secondary combustion chamber for destruction of volatilized organic components is designed to maintain reaction temperatures between 1,000 and 1,200 °C to ensure EPA-required destruction efficiencies are maintained. The PHP operates under a vacuum.

Pilot-Scale Testing. Test indicators have shown an extremely high destruction efficiency for organics (99.99%). Residuals from PHP testing have been analyzed using EPA's Toxicity Characteristic Leaching Procedure (TCLP) and DOE's Product Consistency Test (PCT) leachability protocols. All PHP residuals analyzed to date have exceeded the Resource Conservation and Recovery Act (RCRA) land-disposal restrictions and have shown the slag to be extremely durable.

Cost. Complete procurement, development, construction, testing, and evaluation for a full-scale (1,000 kg/h) system is expected to cost about $5M. The largest development cost is expected to be associated with Environmental Protection Agency (EPA) quality trial-burn testing and radioactive demonstration testing.

PROJECTED PERFORMANCE

Initiating and maintaining the plasma-arc column for the full-scale PHP system is expected to require nominally 1.5 MW of power. It is anticipated that PHP will operate reliably and with minimal down time. The full-scale melter system is expected to process soil and waste material at a rate of 1,000 kg/h.

WASTE APPLICABILITY

The PHP can process virtually all types of solid and liquid waste, including such diverse materials as paper, plastic, wood, soil, concrete, steel, aluminum, and copper. However, it would not be economical to process large volumes of low-heating-value liquid wastes such as waste water. The PHP is not designed for the processing of gaseous wastes.

STATUS

The final system has not been established. Design, construction, and testing of a full-scale, continuous-operation, prototype system was underway in FY94. Radioactive development testing and evaluation (DT&E) of a bench-scale PHP system is scheduled to begin in FY94 and to be completed in FY97. Design and construction of the production system is scheduled to begin in FY95 and to be demonstrated on a DOE site in FY98.

REGULATORY CONSIDERATIONS

Pilot-scale analysis has shown the residual slag to be highly durable and leach-resistant according to TCLP and PCT. The implementation of PHP is expected to have negligible environmental impact. Best Available Control Technology (BACT) guidelines will be employed to control stack emissions. The PHP is being designed to process transuranic-contaminated materials; therefore, under the regulations governing radioactive processes, no fugitive emissions will be

allowed. Residuals from PHP testing have all met the RCRA Land Disposal Restrictions (LDRs).

POTENTIAL COMMERCIAL APPLICATIONS

The PHP system is potentially applicable to industrial process wastes and buried radioactive wastes. It could be used as a component system along with criticality considerations to decommission spent nuclear-fuel rods. Commercial hazardous, municipal, and hospital waste treatment by the PHP is an alternative.

BASELINE TECHNOLOGY

The baseline technology is vitrification of waste materials after extensive treatment and characterization. PHP will process entire unopened drums of stored waste material and the heterogeneous waste materials resulting from buried-waste-site remediation. The system will process hazardous, radioactive, transuranic, and mixed wastes with minimal pretreatment or characterization.

INTELLECTUAL PROPERTY

Patent: None.

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Industrial Partners

SAIC has teamed with Argonne National Laboratory-West at the Idaho National Engineering Laboratory (INEL) to demonstrate the application of the PHP technology to treat large volumes of mixed wastes at the INEL containing alpha-emitting radioactive species.

The PHP uses a Retech, Inc. plasma torch in a large process chamber to destroy organic materials and melt non-organic materials into separate, stable metal and slag phases for disposal.

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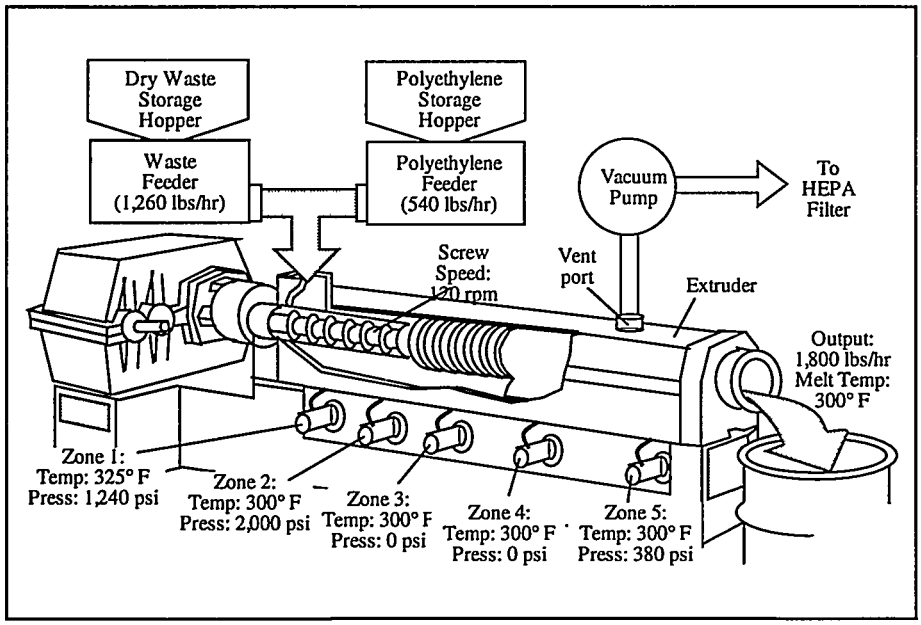
POLYETHYLENE ENCAPSULATION OF RADIONUCLIDES AND HEAVY METALS

Brookhaven National Laboratory

DESCRIPTION

Polyethylene Encapsulation of Radionuclides and Heavy Metals (PERM) is a waste-treatment and stabilization technology for low-level mixed waste. Specific targeted contaminants include radionuclides (e.g., cesium, strontium, cobalt), and toxic metals (e.g., chromium, lead, cadmium). A polyethylene encapsulation process was developed several years ago at Brookhaven National Laboratory (BNL) for solidification of low-level radioactive waste (LLW) such as evaporator concentrate salts and ion-exchange resins. Recently, it has been successfully applied for treatment of hazardous and mixed-waste streams such as sodium-nitrate salts and sludges. Polyethylene, which has a processing temperature of about 150°C, is an inert thermoplastic; as such, it is not susceptible to chemical interactions between the waste and binder matrix, which could adversely impact solidification. In general, polyethylene encapsulation can be accomplished with greater efficiency (more waste encapsulated per volume of product) and with better waste-form performance than is possible using conventional cement-based grout encapsulation technologies.

The PERM process begins by optimizing the polymer matrix for the given waste stream by adjusting property parameters such as the density, molecular weight, and melt index. Aqueous salts, sludges and salt cake are pretreated to remove residual moisture efficiently and prepare the waste for polyethylene processing by extrusion. The dehydrated wastes and polyethylene binder are then precisely metered at predetermined ratios by a loss-in-weight/volumetric feed system. The process extrudes a molten, homogeneous mixture of waste and polyethylene binder into a suitable mold (e.g., large metal drum or cube), where it cools to form a monolithic solid-waste form. It can then be removed from the mold for transport and disposal or disposed using the mold as a storage/disposal container. The PERM system can be operated in continuous or batch mode.



Polyethylene Encapsulation System

PERM has an integrated system control, including computerized feed control with an output feedback loop that reduces the demand on the operator's attention. Key process parameters are monitored constantly, including feed rates for waste and binder, extruder-zone temperatures and pressures, final-melt temperature and pressure, extruder screw rotational speed, motor load, and output mass flow

rate. A Transient Infrared Spectrometer (TIRS) system developed by Ames Laboratory will be used to provide real-time monitoring and confirmation of waste loading. All controls can be operated remotely to minimize operator exposure. Key process systems are connected to an audible alarm and can trigger automatic, efficient, and orderly shutdown of the system under failure conditions.

TECHNICAL PERFORMANCE

Production-Scale Feasibility Study. Scale-up from bench-scale tests has demonstrated the feasibility to process waste at approximately 2,000 lb/hr. The scale-up feasibility tests have successfully demonstrated the potential to encapsulate at least 60 wt% nitrate salt in polyethylene. A production-scale system would fit on a pad about 3 m x 6 m and would be about 4 m high. Polyethylene waste forms have been demonstrated to exceed Nuclear Regulatory Commission, Environmental Protection Agency, and Department of Transportation waste-form criteria. Waste forms containing up to several thousand parts per million of toxic-metal contaminants have passed the EPA's Toxicity Characteristic Leaching Procedure (TCLP).

Cost. The extrusion processing system would cost $250K, and the integrated treatment system (including pretreatment) would cost $1,000K. Operation costs are associated with energy costs for the required thermal input, the salaries for the operator technicians and engineers, and the polymer binder feed material costs.

PROJECTED PERFORMANCE

PERM is projected to achieve production-scale waste processing rates between 1 to 3 metric tons/hour with 60 wt% nitrate-salt loading in the polymer matrix. The use of recycled polyethylene is being considered for material cost savings and petroleum resource conservation.

WASTE APPLICABILITY

PERM is applicable for stabilization of low-level radioactive and heavy-metal waste components that may be in media such as aqueous salt concentrates, salt cake, sludge, fly ash, and ion-exchange resins. Some specific contaminants this technology is designed to encapsulate and stabilize are radioisotopes of cesium, strontium, cobalt, and toxic heavy metals, including chromium, lead, and cadmium.

STATUS

The process should be ready for implementation by FY95. Following "cold" pilot testing at BNL and "hot" testing at a DOE facility, the PERM process will be ready for implementation. Full-scale implementation is anticipated by the end of FY95. Installation, start-up, and testing of the prototype facility can be accomplished by FY94.

REGULATORY CONSIDERATIONS

No ecological impacts are anticipated because no gaseous or liquid effluents will be released as a result of this process. Extensive waste-form performance testing has been completed, including compressive strength, water immersion, thermal cycling, radioactive and hazardous constituent leachability, radiation stability, and biodegradation. In each case, waste-form performance exceeded regulatory criteria by a wide margin.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include waste stabilization in the nuclear power industry and other commercial nuclear-waste generation sites. Devel-

opers are working with several U.S. companies interested in commercializing this technology.

BASELINE TECHNOLOGY

Cementation by grout is the current baseline treatment technology for low-level waste. Vitrification into a glass form is the baseline for stabilization of high-level, concentrated waste streams. Although glass processing is an excellent waste-stabilization option, it is not compatible with some waste constituents and requires sophisticated off-gas capture and secondary-waste treatment. For low-level waste, a PERM provides 5 times greater volume reduction, while reducing contaminant mobility by more than 100 times compared with baseline grout formulations. Microencapsulation of individual contaminant particles results in leachabilities measured 100 to 1,000 times lower than the equivalent grout waste form.

INTELLECTUAL PROPERTY

A patent application is being prepared for submission.

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REFERENCES

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POLYMER GEL AS A BARRIER FOR GROUND SPILL CONTAMINANTS

University of New Mexico

DESCRIPTION

Three basic approaches can be used to control contaminants in soil. These are removal, chemical or biological modification, and retention.

Removal is most desirable as far as the site is concerned, but is always costly, and in many cases almost impossible. Further, unless the removed material is treated chemically or biologically to remove the contaminants, this merely moves the problem elsewhere. Chemical and/or biological modification of the contaminant *in situ* is attractive, but is critically dependent on the nature of the contaminants and the chemistry of the site. Currently, it is only applicable to small and well characterized shallow sites with certain specific contaminants and is not technologically well developed. Retention or plume steering is a temporary measure, certainly on geological time scales, and often on human time scales too. It basically relies on engineering a barrier to contaminant transport and diffusion. But if no horizontal shallow impermeable stratum exists, attempts to engineer horizontal barriers by grouting techniques have generally proven to be ineffective or prohibitively expensive.

There are four major classes of retention barriers: cement-based, lime-based, thermoplastic, and organic polymer.

Cement-based barriers are the most common, despite the high costs of pumping to inject cements into the ground. The advantages of cement-class barriers are that the materials set hard and are water resistant. But transport of some kinds of metals can be enhanced by a cement barrier, as can dissolution products of humic acid complexes. The setting of cements can be retarded by organic solvents and oils, sulfates, and halides. Lime-based barriers are very similar in behavior to cement-class. Also, the pozzolanic materials behave in similar fashion. Thermoplastic barriers require heat for injection, thus being limited by cost for pump power and heating. Further, organics can be vaporized from the heating source and pollute the air. Also oxidizers, sulfates, or halides from the contaminant source can undergo undesirable reactions with these thermoplastic materials.

The technique proposed herein is the polymer-gel barrier which has many distinct advantages over more conventional slurry-wall techniques. The fluid gels *in situ* in controlled fashion, forming a strongly cross-linked gel that is highly impermeable to many chemicals. The wall-forming fluid that will be injected via drill holes has a viscosity and density close to that of water; hence, pump power is greatly reduced. The low viscosity and controllable gelation of the proposed barrier material will allow the use of larger numbers of deeper drill holes than has been used to date, and the polymer will penetrate much further into soils and fractured rock while ungelled. Hence, the engineering of particular barriers with specific shapes and other characteristics will be far easier than with conventional costly and limited techniques.

TECHNICAL PERFORMANCE

This technique should either completely immobilize or at least significantly retard the migration of contaminants in the soil. Stopping or slowing the migration of contaminants will allow remediation of the source of the contamination or at least provide more time for the required remediation technology to be developed and applied. The polymers to be employed have already been developed and applied for

different applications. The barrier will be formed by injection into the ground of ungelled polymers which will then be gelled in controlled fashion *in situ.* The importance and innovation of the technique lie in the use of "ungelled" polymer which will reduce pumping cost.

Cost. Cost estimates are not yet available because this technology is still under development, but it is obvious that the cost of pumping a water-like material will be significantly less than for gel-like materials which are far more viscous than water.

PROJECTED PERFORMANCE

Because the transport of a contaminant involves two mechanisms, convection and diffusion, the ideal polymer-gel barrier (combined with soil) should be resistant to water (i.e., permeability less than 10^{-7} cm/s, a criterion for evaluation). The diffusivity of contaminants through the gel barriers should also be much less than that in saturated soil. On the other hand, the polymer should have controllable gelation time (two hours or more) and have a specific viscosity near that of water before injection, and the gel barrier should have high stability under long-term condition. The results of this work will provide the technology to at least significantly retard or even prevent migration of contaminants in soil while the site is remediated, or even while the required remediation technology is being developed.

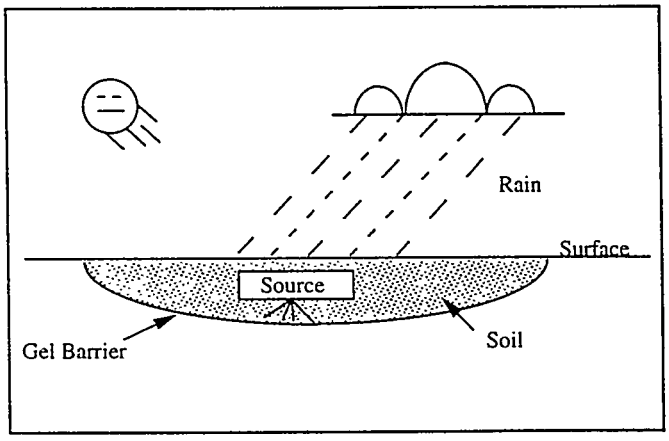

Figure 1. Gel Barrier for In Situ Use.

Figure 1 shows the use of a gel as a barrier to the transport of nuclear wastes because of corrosion of a waste tank.

The first objective of the polymer barrier development is to identify a few potential polymers out of the hundreds possible based on established criteria. Five different polymers have been identified to form good gels. Tests have been performed to evaluate the effect of pH, concentration of cross-linking agent and concentration of polymer on the gelation time, the gel strength, and the amount of gel formed. Several cross-linking agents were also studied to optimize the gel. Figure 2 shows the effect of pH on the

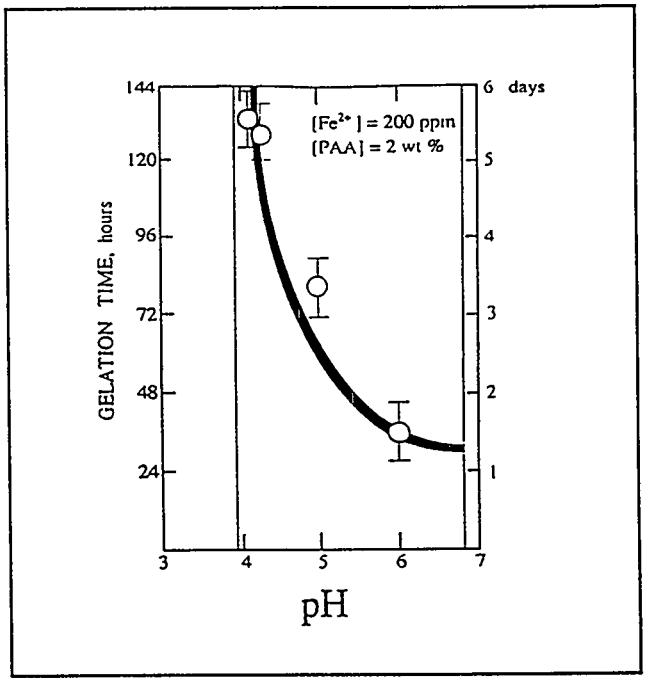

Figure 2. The Effect of pH on Gelation Time.

gelation time for PAA gel. Also, some rheological properties of the barrier material such as swelling due to moisture adsorption, viscosity, density, etc. have been evaluated in order to perform stability analyses.

The next step is the characterization and development of a few selected polymer barriers. Permeability of the gel barrier (combined with soil) and the diffusivities of contaminants in the barriers will be tested. It has been found that the diffusivities of

several metal ions in the gels are much lower than those in water. The end result will be one or more barrier polymers tailored to the particular contaminants and soils under consideration.

The third step is to apply the developed barrier polymer to a particular and well characterized site.

WASTE APPLICABILITY

The main role of the gel barrier is permeability reduction; hence, the barrier can be applied to retard the migration of different types of contaminants that will not react with the gel in the soil. Leakage of radioactive material to the water table can be reduced until remediation has taken place.

STATUS

This technology is being studied and developed.

REGULATORY CONSIDERATIONS

The gel barrier does not involve any chemical or physical hazards to workers, is inherently safe, and poses no risk to the environment. It may also be possible to remove the gel barrier when an appropriate remediation technology is developed.

POTENTIAL COMMERCIAL APPLICATIONS

This technology will be tested at Sandia National Laboratories (SNL) using a large-scale ground-contaminant test site. Factors such as stability and permeability which have been described in this work will be measured in cooperation with SNL. This is commercial-scale testing of this technology. The data from these tests will enable modification of the gel to meet the required criteria.

BASELINE TECHNOLOGY

The baseline technology is gel-and-soil technology.

INTELLECTUAL PROPERTY

Flexible. The PI, WERC Administration, university administration, and industrial partners work in conjunction to discuss individual cases.

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REMEDIATION OF METALS CONTAMINATED SOILS USING LIGAND-BASED EXTRACTION TECHNOLOGY

New Mexico State University

DESCRIPTION

The treatment uses a combination of density classification and extraction to treat the contaminated soil. Density classification is used to separate lead particulate from the soil. Extraction is then used to remove the remaining lead from the soil. The Pb:EDTA complex is then flushed out of the soil, the complex is broken, and the Pb is precipitated as a hydroxide. Based on the experience with the small-scale pad work, it is anticipated that this technology should produce lead concentrations in the soil below background values (10-15 mg Pb/Kg of soil). The soil should easily pass the TCLP test.

This technology involves the application of an aqueous-based ligand system to the soil. The ligand, or chelator, dissolves the metal and removes it from the soil. The metal is then removed from the ligand, and the ligand is recycled back to the soil in a closed loop. This technology is in various stages of development for a number of metal contaminants, including lead, mercury, uranium, and chromium.

There are two common soil-leaching technologies: soil washing and heap leaching. Both of the technologies have strong and weak points. The "soil washing" treatment technology can typically achieve short treatment times, and it provides excellent process control. It is also common for this technology to require high liquid-to-solid ratios, 3 to 1 to as high as 100 to 1. This requires the treatment of a large secondary waste stream and increases the difficulty of treating the waste stream. The combination of secondary waste-stream treatment costs, solid/liquid separation costs, and the high energy (for agitation) often makes "soil washing" uneconomical.

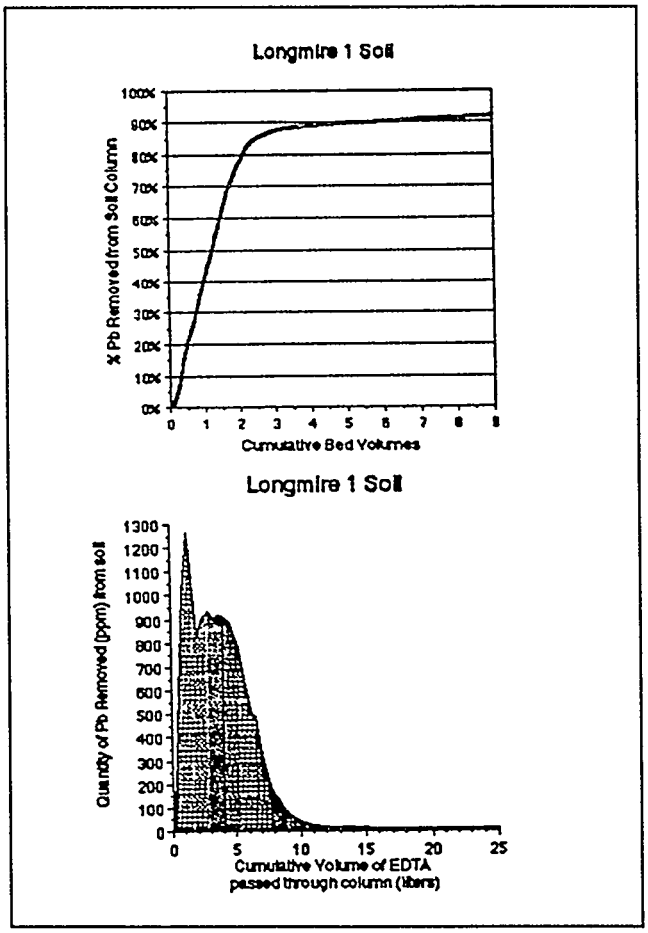
Heap leaching is a process adapted from the mining industry. The gold and silver mining industries use sodium cyanide (NaCN) at high pH (10.5 to avoid CN^- off gassing), while the copper industry uses sulfuric acid (H_2SO_4). The processes are equilibrium-driven and have shown high removal efficiencies (90 -100 percent), but do require some time to complete. The process is as follows: (1) the matrix (soil or crushed ore) is piled upon an impermeable leach pad with specified drainage characteristics; (2) the extractant is introduced at the top of the heap and allowed to percolate down through the heap under the force of gravity; (3) the solubilized metal solution is then separated so that the metal can be concentrated (for resale or disposal) and the solvent can be reused. The term 'heap' may inspire negative connotations with the main concerns being fugitive dust and treatment uniformity. It is possible to design the heap as a closed system to control fugitive dust. Treatment uniformity is addressed in the section that follows.

TECHNICAL PERFORMANCE

Technical performance data available through the authors are small-scale batch data (5 g of soil), large-scale column data (3 to 10 Kg of soil), and pilot-scale data (500 to 1,000 Kg of soil). The batch-scale data were used to select the solutions used in the other tests. The column-scale data were used to evaluate extraction solution/soil interactions. The column, as used in this study, mimics the inside of a soil heap. The complexation reaction between Pb and EDTA is greater than zero order (i.e., concentration dependent); thus, reaction efficiency is optimized in a "flow through" column reactor. A large amount of column-scale data is available. Typical data are presented in the following paragraph and plots.

A solution of 0.01M di-K EDTA was applied at a rate of approximately 250 ml/hour to a 7.5 cm diameter column. Once the column was completely wetted, hydraulic loading rates as high as 400 ml/hr were used. The flow rate averaged around 325 ml/hour. Because the removal of the lead from the soil is concentration-dependent, the highest quantities are removed in the first one-third of the run. For this column, 50 percent lead removal was achieved within 1.25 bed volumes (approximately 2.5 pore volumes) and 80 percent at 2.1 bed volumes. The last 20 percent of removal is characteristically asymptotic. As the lead concentration in the soil drops, so does the driving force for chelation. This column was shut off at 92.26 percent removal achieved in 9.18 bed volumes, resulting in 0.5 grams of Pb left in the soil column.

In addition to the column tests, a number of pilot-scale tests have been performed with both Pb and Cr(VI). According to the soil-mass balances, all of the pilot-scale tests on lead contaminated soils have removed more than 95 percent of the lead. The liquid-mass balances show better than 89 percent removal for all tests. The process removal efficiencies for all of the tests conducted with both hexavalent chromium- and lead-contaminated soils are shown in Table 1. These data are all for 1/2 cubic meter soil volumes (760 Kg soil/test) treated in the conical heap and enclosed box configurations.



Typical Column Scale Data

Table 1. Summary of Data for the Field-scale Tests.

Test: (All tests contaminated to 500 mg/kg)	Percent Removed by Soil Mass Balance	Percent Removed by Leachate Mass Balance	Overall Bed Volumes Used	Final TCLP (mg/l) *(Pass if value <5 mg/l)*
Pajarito Soil, Cr VI, Box	99.0	106.0	2.36	0.1
Pajarito Soil, Cr VI, Pile	99.1	93.6	2.61	0.02
Harkey Soil, Cr VI, Box	71.2	86.1	1.51	0.28
Pajarito Soil, Pb II, Pile	95.8	89.1	6.05	0.07
Pajarito Soil, Pb II, Box, *Rep. 1*	97.8	93.0	2.88	0.18
Pajarito Soil, Pb II, Box, *Rep. 2*	98.1	90.1	4.03	1.14

Based on these data, it is anticipated that acceptable soil-cleanup levels can be reached. There are also data available from these tests which indicate the uniformity of treatment is extremely good. The box reactor was cored at a number of points, and soil samples were taken from the top, middle, and bottom of each core. These soils data showed very good uniformity, with residual concentrations of lead in the soil ranging from 13-17 mg/Kg. These values are below general background levels for soils from this region.

If one is to recycle the extraction solution (EDTA), it will be necessary to separate the Pb from the EDTA and then put the EDTA back into service. The authors have been successful in separating the Pb from the EDTA by simply raising the pH to 12. At this pH, the Pb is released and precipitates as a hydroxide. Residual total lead levels as low as 200 mg/l have been achieved. Considering the initial Pb concentration is 1,000 to 6,000 mg/l, this residual is

adequate for reuse of the extraction solution. A higher pH with ion-exchange polishing or sulfide precipitation may be required for final polishing of the extraction solution before disposal.

- EDTA is the extraction solution of choice.
- It appears that all of the Pb can be readily extracted from soil.
- The extraction solution can be easily reused with a simple pH adjustment and solid/ liquid separation of the precipitate.

PROJECTED PERFORMANCE

Based on the experience with the small-scale pad work, it is anticipated that this technology should produce lead concentrations in the soil below background values (10-15 mg Pb/Kg of soil). The soil should easily pass the TCLP test. The total residence time in a heap may range from 1 to 3 weeks. With appropriately designed heaps, it is possible to treat large volumes of soil. If it is desirable to treat small volumes of soil (drum scale), it is likely the time scales for treatment will be reduced to 4 to 8 hours per drum.

WASTE APPLICABILITY

The technology is applicable to most metal-contaminated soils. Of special interest are soils with high concentrations of metals near the surface. It is not uncommon to have the top 6 inches of soil contaminated over a fairly large area. This would be an ideal application for this technology. This does not mean it is not also applicable on a small scale. The authors have proposed a completely sealed, 55 gallon drum-scale unit with the advantages of both vat leaching and heap leaching. This unit is of particular interest at DOE and DOD facilities where waste is often stored in 55 gallon drums.

The authors believe the applicability goes far beyond soils contaminated with Pb. They are currently working on a system for removal of Hg from contaminated soil. It is anticipated that the mercury system will remove 90 to 95 percent of the mercury in the metallic state using a gravity-separation technique. The remaining Hg will be removed using hydrometalurgy.

STATUS

Investigators with New Mexico State University (NMSU) and the Waste-mangement Education & Research Consortium (WERC) have applied the technology at a pilot scale with success as demonstrated in the Technical Performance section. In addition, there have been two full-scale applications that the authors are aware of, one performed by a consulting firm in Colorado, and one by the U.S. Bureau of Mines in conjunction with the Naval Civil Engineering Laboratory. It is believed that all aspects of this technology, except one, are currently available off the shelf for removal of lead from soil. One aspect that is poorly understood is agglomeration of soils when using EDTA. Standard agglomeration techniques raise system pH to levels where EDTA does not bind Pb. The authors used manipulation of the carbonate buffer system to overcome this problem on a small scale, but large-scale data are non-existent.

The system is currently being lab tested for Hg-contaminated soils. The gravity-separation step is off-the-shelf technology, and the extraction solution is in laboratory-scale testing.

REGULATORY CONSIDERATIONS

Appropriate permits for on-site treatment of hazardous waste, eventual discharge of the extraction liquid, and for transportation and disposal of the final

residuals must be considered. The legislation of concern will be the Clean Air Act (fugitive-dust issues), Clean Water Act (possible surface-water or sewer discharge [City's NPDES Permit] of spent extraction solution), Resource Conservation and Recovery Act (RCRA), and Comprehensive Environmental Response Compensation and Liability Act (CERCLA).

There are potential OSHA concerns with regard to worker protection in the presence of airborne Pb contaminant.

POTENTIAL COMMERCIAL APPLICATION

This is a public-domain technology in the sense that it has been widely used in the mining industry for 20 years. It is applicable to all soils contaminated with metals if the appropriate extraction agent can be identified. There are a wide number of applications for the Pb removal for soil, including historic auto salvage yards, battery-cracking facilities, and firing ranges.

BASELINE TECHNOLOGY

The baseline technologies are heap leaching and vat leaching (which are hydrometalurgical mineral extraction technologies from the mining industry). Both are on-site, ex situ technologies.

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REMOTE EXCAVATION SYSTEM

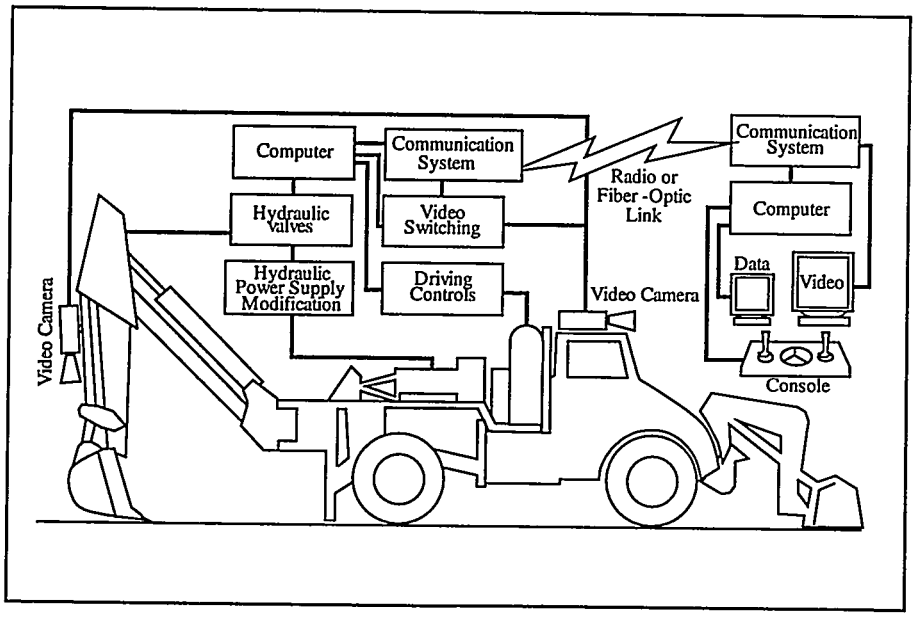
Oak Ridge National Laboratory

DESCRIPTION

The Remote Excavation System (RES) is a military tractor, the Small Emplacement Excavator (SEE), which has been modified for telerobotic operation by the Oak Ridge National Laboratory (ORNL). The primary applications for this remote excavation technology are buried-waste retrieval for the Department of Energy (DOE) and unexploded ordnance retrieval for the U.S. Army. The hazards of buried-waste retrieval are significant if performed by conventional manned operations. The potential hazards include exposure to radiation, pyrophorics (capable of spontaneous ignition when exposed to air), toxic chemicals, and explosives. Consequently, it is highly desirable to excavate and retrieve these wastes by using remotely operated equipment. The RES could be used to excavate and remove buried waste and contaminated soil for ex situ treatment.

The SEE is a multiuse vehicle developed for the U.S. Army that has been configured with a backhoe and a front-end loader. The backhoe is an adaptation of the Case 580E commercial backhoe, and the vehicle is a modified Mercedes Benz Unimog truck. The SEE is not necessarily the excavator of choice for large-scale waste-retrieval campaigns; however, the controls technology developed for the RES/SEE is readily transferable to other mechanical systems.

The ORNL alterations to the vehicle center around modifying the hydraulic systems for computer control. High-performance proportional valves were used to greatly improve the dexterity over the existing manual valves. Hydraulic pressure sensors provide limited indications of force and torque exerted by the backhoe. The backhoe and front-end loader have been outfitted with position encoders for use in robotic operations. Remote viewing is provided by two color television cameras with pan-and-tilt mechanisms mounted on the truck body and a camera mounted on the backhoe boom. A pair of stabilizers can also be adjusted remotely to lift the rear tires off the ground during backhoe operation. The vehicle drive system has been modified for remote driving. A hydraulic motor system is used for steering while pneumatic actuators are used to operate the clutch, gear shift, and power-take off unit (PTO). The PTO must be engaged to enable backhoe operation. The control system includes a highly intuitive hand controller and a graphical user interface for data display and display of joint position.



Remote Excavation System

The computer system for RES is composed of a SUN workstation host (for the base station) networked to VME-based Motorola 68040 target computer (on-board the excavator truck) running the VxWorks operating system. The communications system between the vehicle and base station consists of two microwave video channels and an Ethernet data radio. Current microwave systems perform well, but are susceptible to multipath distortion and are poor in over-the-hill performance. Digital radios are being considered as a possibility for digitizing and compressing video to deliver over a digital link. Technology is advancing in this area, and it is anticipated that digital video transmission will soon become practical at a lower cost. For military applications where secure communications are required, a fiber-optic communications link has been implemented.

TECHNICAL PERFORMANCE

A 110/220 V, 25 kW power supply is required to run the control station. The SEE operates on diesel fuel. The 110 hp, 6-cylinder engine consumes approximately 30 gal of fuel/day. Monthly oil changes are anticipated as part of a regular maintenance program. The front-end loader has a 75 ft^3 capacity, a lift height of 8 ft 2 in, lift capacity of 3,000 lbs, and a breakout force of 6,000 lbs. The backhoe has a bucket capacity of 7 ft^3, loading height of 11 ft, digging depth of 14 ft, digging radius of 17 ft 8 in., a swing arc of 180°, and a digging force of 10,000 lbs.

Field Demonstration. A field demonstration was completed in July 1993 at an Idaho National Engineering Laboratory cold-test site that included remote controlled excavation and remote driving. Information on the waste-retrieval rate, system reliability, human-factors analysis, and operating cost for the RES was determined during the demonstration. A Technology Assessment Report was issued in September 1993.

Cost. The estimated cost to duplicate the RES is $400K. Use of a common piece of construction equipment rather than the SEE military tractor could reduce the cost by about $100K.

PROJECTED PERFORMANCE

The primary objective of the demonstration was to evaluate the feasibility of remote excavation. The supporting objectives were to determine digging precision and accuracy, the system reliability, the usability, the factors that affect the system performance, and to develop knowledge based on remote excavation to assist in future improvements.

WASTE APPLICABILITY

This technology is applicable to any buried waste, excavation, or material-handling task.

STATUS

The prototype has been completed and demonstrated in the summer of 1993. The SEE currently has remote digging and driving capabilities. The Technology Evaluation Report was completed in September 1993. In 1994, a grappling end-effector was being developed for the RES. A field demonstration was scheduled for August 1994 at the ORNL Hill Cut Test Facility.

REGULATORY CONSIDERATIONS

The equipment should be acceptable to regulators because it is teleoperated and removes the operator from hazardous environments. Operation of the

vehicle and excavator pose no hazard to personnel as long as prescribed safety procedures are followed. On-board sensors are available to monitor the safety status of the system and to prevent accidents. Decontamination of equipment may be required if the excavator becomes contaminated during operation in a hazardous environment. The use of this technology results in disturbance of buried wastes, as does manual excavation, that may result in the spread of contamination.

POTENTIAL COMMERCIAL APPLICATIONS

The RES could be used for excavation around buried-waste or decommissioning sites, for soil excavation, and for handling of bulk hazardous materials. The control technology being developed is adaptable to other excavation and construction equipment.

BASELINE TECHNOLOGY

The primary alternative to the use of telerobotics in excavation is to perform the operations using conventional excavation techniques and equipment, though the operator may be in a protective cab or bubble suit. Teleoperated equipment allows the worker to be removed from the potentially hazardous environments, increasing operator safety. Automated operator-assist functions increase productivity.

INTELLECTUAL PROPERTY

Patent ownership is assigned to DOE and the Department of Defense.

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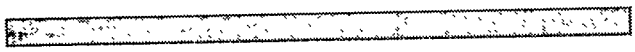

RESORCINOL-FORMALDEHYDE ION EXCHANGE RESIN FOR CESIUM REMOVAL

Westinghouse Savannah River Company

DESCRIPTION

The Resorcinol-Formaldehyde Ion Exchange (ReFIX) resin is applicable to high-level waste streams containing cesium-supernate salt solutions. Radioactive cesium is a fission product found in waste produced by reprocessing fuels from nuclear-power reactors. The highest concentrations of this isotope are found in alkaline high-activity wastes, a mixture primarily of sodium nitrate and sodium hydroxide that is called the supernate. This technology is a selective ion-exchange resin (specific sorption of cesium ions) that has 10 times the capacity of the baseline Duolite™ CS-100 phenol-formaldehyde resin. Columns of ReFIX resins will be packaged in a standardized module to fit the Compact Processing Unit (CPU) waste-processing module specifications. One specific benefit of ReFIX resin is that it is essentially unaffected by changes in temperature. However, high concentrations of competing sodium and potassium ions reduce the cesium sorption capacity and diffusion efficiency of the ReFIX resin.

High-level supernate from a Hanford waste tank will be processed through an appropriate number of ion-exchange columns in a CPU-processing module (see the catalogue entry for CPU). Cesium will be removed by sorption onto the ReFIX resin in the processing columns. When a column becomes saturated, it will be temporarily removed from service so that the cesium can be eluted from the resin with acid (most likely nitric acid) in a concentrated stream that can be sent for vitrification. Once eluted, the newly regenerated column will be placed in service when another column is removed for elution. The treated streams from these columns may have to be processed with another series of columns containing resin specific for strontium removal before the stream can be incorporated in cement for final storage. Spent resin can be subjected to rigorous elution before disposal to lower its radionuclide content. Carefully eluted resin can then be stored or disposed of by incineration or chemical destruction before incorporation into cement.

TECHNICAL PERFORMANCE

Design Specifications. The column volume is approximately 5,000 gallons. The ReFIX resin supports a cesium capacity of approximately 200 column volumes of throughput.

Laboratory Testing. Laboratory-scale test results with Savannah River Site simulant were published in 1990. Elution of the filled resin columns with 20 column volumes of 0.1 M nitric acid removes 99% of the sorbed cesium. After six feed-elute cycles have been completed, approximately 20% of the resin capacity is lost, requiring either partial reconstitution or replacement of the column resin. This resin appears to be useful for a large variety of concentrations of feed streams over a wide range of temperatures. Preliminary results have shown that the diffusion kinetics of Cs^+ to the sorbing medium are quite slow (from Hanford 101-AW), and high concentrations of potassium cations may reduce the throughput. Recent analysis suggests that ReFIX resin may have a short shelf life. The tests with Hanford 101-AW simulant were published in 1994.

Cost. The cost of ReFIX resin is estimated at $1,000/ft^3.

PROJECTED PERFORMANCE

If operated properly with columns in series, the resin is capable of removing 137 Cs to any level desired. The ReFIX waste-treatment module for the CPU system is expected to treat the liquid waste at an average flow rate of 2.5 gpm. The ReFIX resin is expected to have a shelf life for optimum performance of one year, at which point the cesium capacity and diffusion efficiency would have decreased by a factor of 10 or more. Failure of the resin can be averted by setting tight specifications on receipt of the resin and distribution coefficient tests (diffusion efficiency) before use.

WASTE APPLICABILITY

This technology is applicable for cesium removal in high-level liquid-waste streams, such as the Hanford Underground Storage Tank supernate salt solutions.

STATUS

A prototype is being developed for demonstration at the Hanford Site in FY97. A module of ReFIX resin columns will be demonstrated and optimized with waste from Hanford tank number 241-101-AW. The ion-exchange process equipment could use any resin, should a better material be developed at a later date.

REGULATORY CONSIDERATIONS

No ecological impacts are anticipated from the use of this technology. The only safety consideration is radiolytic products, especially benzene derivatives, that may be produced when the resin is placed in a radioactive environment. However, preliminary radiolysis studies indicate that no volatile organic compounds (i.e., benzene derivatives) are formed, but a small amount of hydrogen gas is formed in the presence of organic materials. The hydrogen concentration in the ventilation system is expected to be below the lower explosive mixture.

POTENTIAL COMMERCIAL APPLICATIONS

The ReFIX polymer matrix resin could have applications in the nuclear-power industry with cesium removal from both active coolant water and spent-fuel storage-tank water. In addition, potential applications include decontamination and decommissioning operations and domestic (U.S. Department of Energy) or foreign spent-fuel reprocessing effluents.

BASELINE TECHNOLOGY

The baseline technology is ion-exchange using Duolite™ CS-100 phenol-formaldehyde resin, which has approximately one-tenth the capacity of the resorcinol-formaldehyde resin.

INTELLECTUAL PROPERTY

Westinghouse Savannah River Company applied for a patent in the names of R.M. Wallace (now deceased) and Jane P. Bibler. The DOE would also be a patent owner. The patent is pending.

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SELECTIVE EXTRACTION/LEACHING OF URANIUM FROM SOIL

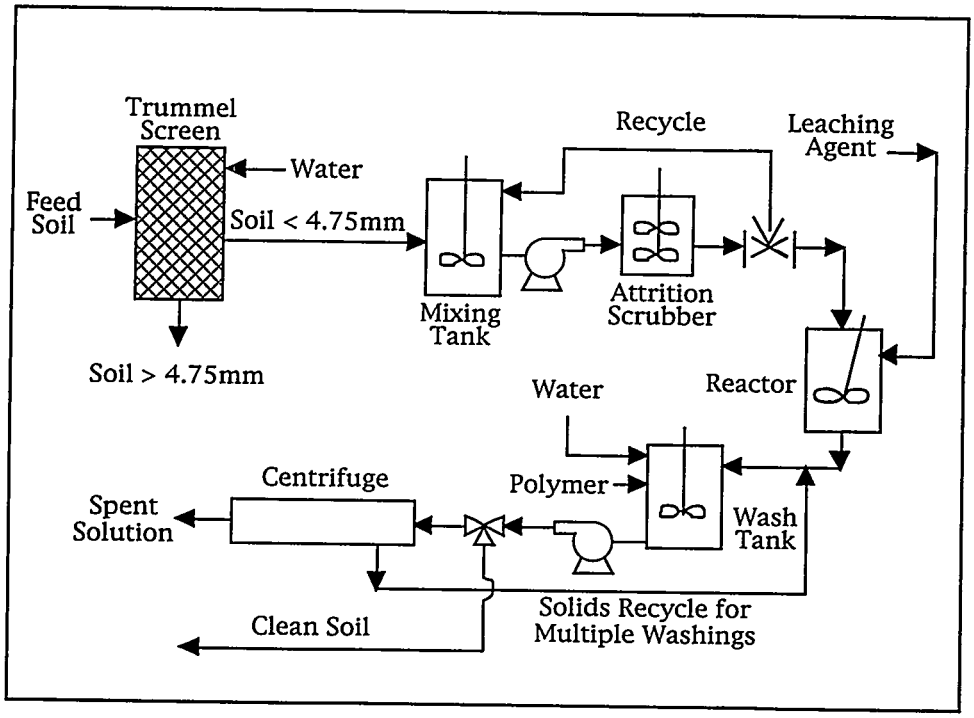
Oak Ridge National Laboratory

DESCRIPTION

Oak Ridge National Laboratory is conducting bench-scale investigations of selective leaching of uranium from soils from the Fernald Environmental Management Project (FEMP) site in Ohio. Physical and chemical processes were used in combination with extractants to increase the rate of uranium release from soils.

Selective Extraction/Leaching of Uranium from Soil provides an efficient means of removing uranium from contaminated soil without appreciably affecting the soil properties. This technology improves on current soil-decontamination techniques in that the native soil can be reclaimed rather than disposed of at a low-level-waste burial ground.

One approach to decontaminating soil is to use a carbonate to leach the uranium out of the soil. The first step of this process is to get uranium into its hexavalent state (uranium (VI)). The reason is that uranium forms a stable, water-soluble, anionic complex with the carbonate radical if uranium (VI) is used. In order to get uranium (VI), an oxidant must be added to the uranium (IV). The oxidant (typically potassium permanganate (KM_nO_4)) is added to the soil to oxidize any uranium that may be in the tetravalent state (uranium (IV)) to uranium (VI) in the hexavalent state. Finally, a complex which contains the carbonate radical in solution (typically sodium carbonate or bicarbonate) is added to the mixture and forms the complex with uranium (VI) which can be removed in a centrifuge or by other means.



Selective Extraction/Leaching

A process called attrition scrubbing is used to speed up the process of removal of contaminants from the soil by increasing the exposed surface area. Attrition scrubbing is a physical process that abrades particles through collision in a closed chamber at high solids loadings (typically 50% to 70% solids). Particle abrasion is accomplished by a set of propeller blades pitched in opposite directions. The abrasive action reduces the size of the scrubbed particles (increasing the total surface area) and exposes fresh surfaces on the abraded par-

ticles. The overall effect of this process is to increase the extractability of the target contaminant.

The soil that remains, if enough uranium is removed, can be reclaimed and returned to the site. The leached uranium can be separated from the carbonate and either recycled or disposed.

TECHNICAL PERFORMANCE

Initial Tests At Oak Ridge National Laboratory (ORNL). Testing of soil washing/leaching utilizing attrition scrubbing was completed at ORNL in February 1993. Three soils and a sediment sampled from a storm-sewer sediment trap at the Oak Ridge Y-12 Plant were used in this study. Two of the soils were from FEMP. The FEMP soils were sampled and mixed by FEMP personnel. One of the samples was taken from near the Waste Incinerator of particulate contamination resulting from incinerator-stack emissions. The other sample from FEMP was taken from a storage-pad area where contamination resulted from spills of spent process solvents. The remaining soil sample was a Y-12 landfarm sample. The uranium concentrations in the Fernald soils ranged from 450 to 550 μg U/g of soil, while the samples from the Y-12 plant ranged from 150 to 200 μg U/g of soil (air-dried basis).

Carbonate extractions generally removed from 70% to 90% of the uranium from the Fernald storage-pad soil. Uranium was slightly more difficult to extract, from carbonate extractions, from the Fernald incinerator and Y-12 landfarm soils (extraction efficiencies ranged from ≈40% to 75%). Very small amounts of uranium could be extracted (<8%) from the storm-sewer sediment using sodium-carbonate extractions. Increasing the temperature from 22°C to 40°C for the sodium-carbonate extractions of the Fernald waste-incinerator soil increased the fraction of uranium leached from approximately 40% to 80%. However, the increased extraction temperature did not appear to increase extraction effectiveness for the soil from the Fernald storage-pad area. Extraction with carbonate at high solution-to-soil ratios was as effective at low solution-to-soil ratios, indicating attrition by the paddle mixer was not significantly different than that provided in a rotary extractor. Also, pretreatments such as milling or pulverizing the soil sample did not appear to increase the extraction efficiency when carbonate extractions were carried out at elevated temperatures (60°C) or long extraction times (23h). Adding $KMnO_4$ in the carbonate extraction appeared to increase the extraction efficiency from the Fernald incinerator soil but not from the storage-pad soil. Also, additions of $KMnO_4$ to the carbonate extractions appeared to be more effective in removing uranium from the silt and sand size fractions (>2μm) of soil than from the clay size fractions (<2μm).

Results of the initial tests indicate that significant quantities of uranium can be extracted from the Fernald and Y-12 soils without seriously degrading the soil's physiochemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or to dispose of. Meeting the proposed screening level (52 μg U/g of soil) will be much easier with the storage-pad soil than the incinerator soil. For example, these levels were routinely observed in the extractions of the storage-pad soil using carbonate (2h at 40°C). Uranium in the incinerator soil is contaminated in the very top surface of the soil and has mineralogical characteristics of a low-temperature ash. The total volume of contaminated soil at the incinerator site is very low (<40 yd^3), and much of it has already been removed as part of a removal action.

Cost. Costs are not available at this time.

PROJECTED PERFORMANCE

Future research is expected to be directed at speeding up the rates at which uranium is leached from the soils. Residence times in conventional soil-washing operations (based on physical-separation processes) are characteristically <5 min. A soil washing/leach-

ing operation (based on chemical-leaching processes) will require longer residence times; however, long residence times, such as hours, will require unacceptably large reaction vessels or very slow load factor (in terms of yd^3/hr, etc.). Work in FY 94 is focused on the establishment of acceptable engineering residence times for a soil washing/leaching operation at Fernald, and the leaching-research aspect of the project will be used in combination with elevated temperatures and a variety of leaching media (based on carbonate and citric acid).

Although research has centered on the use of sodium carbonate/bicarbonate as extraction media, the use of ammonium carbonate has certain advantages that will be examined.

WASTE APPLICABILITY

This technology is applicable to soil and sediment contaminated with uranium.

STATUS

Research is ongoing, with the possibility of a full-time facility being implemented in <3 years.

REGULATORY CONSIDERATIONS

Most sites will be regulated via the CERCLA process. In addition, all SARA/OSHA regulations must be met.

POTENTIAL COMMERCIAL APPLICATIONS

Although federal and state governments are the principal customers, this technology is potentially applicable to industries having toxic-metal (chromium, etc.) or radioactive contamination in soils (or groundwater and sludges). Possible industries include steel-production facilities, nuclear-medicine facilities and support industries, nuclear-fuel manufacturers, and chemical industries.

BASELINE TECHNOLOGY

The baseline technology is excavation and disposal, which is expensive and eliminates the possibility of reclamation.

INTELLECTUAL PROPERTY

Patents: DOE/ORNL for those processes developed at ORNL.

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Industrial/University Partners

None at present.

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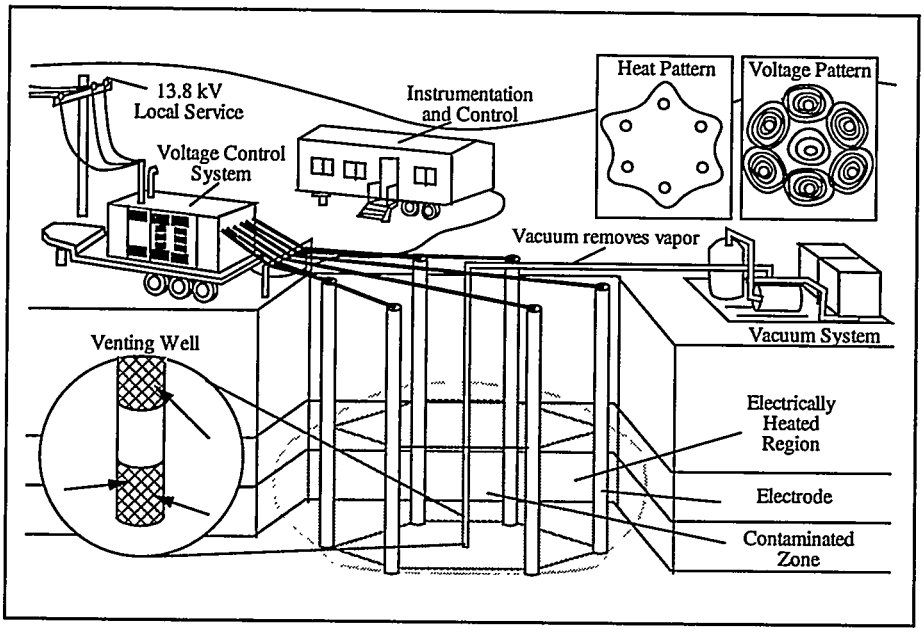
SIX-PHASE SOIL HEATING

Pacific Northwest Laboratory

DESCRIPTION

Six-Phase Soil Heating (SPSH) is an emerging technology for thermally enhancing the removal of volatile and semi-volatile organic compounds from soils via conventional soil-vapor extraction (SVE). By increasing the temperature of the soil and contaminant, the contaminant's vapor pressure is increased, increasing its removal rate. In addition, soils are heated to the soil moisture's boiling point to create an in situ source of steam that then strips out the less volatile organic compounds that venting alone does not remove. Removal of soil moisture (as steam) also tends to increase the flow permeability of soils, which can further increase the rate of contaminant removal by simultaneous venting.

The six-phase soil-heating technique is based on the ability to split conventional three-phase electricity into six separate electrical phases. Each phase is connected to six separate electrodes placed in a circle. Because each electrode is at a separate phase, each one conducts to all the others. Voltage gradients in the six-phase array are relatively uniform, thus facilitating very uniform heating throughout the volume bounded by the six electrodes. A seventh, electrically neutral pipe is inserted in the center of the hexagon and connected to a vacuum blower in order to vent the soil.



Six-Phase Soil Heating

TECHNICAL PERFORMANCE

Effectiveness and efficiency depend largely on uniformity of heating, the site's stratigraphy, and the soil's permeability. Other soil-heating methods, such as steam or hot-air injection, require permeable, unsaturated soil to be effective and therefore do not work in clays or silts. Since electrical soil heating heats the soil internally by passing current through the indigenous soil moisture, clays and silts are heated as effectively as sands. Treatment of a broad range of sites with complex stratigraphy is possible with SPSH.

Field Demonstration. A field demonstration of SPSH at a contaminated site was performed in November 1993 at DOE's Savannah River Site. The site consisted of a 10-ft thick clay layer, 35 ft below the surface, contaminated with perchloroethylene (PCE) and trichloroethylene (TCE). The goal of the demonstration was to determine the ability of SPSH to enhance the removal of volatile contaminants from

low-permeability clay soils. The soil electrodes were inserted to a total depth of 45-ft and were set out in a 30-ft diameter hexagonal array.

Power was applied to the soil for approximately 25 days at an average level of 200 kW. Over a period of approximately 7 days, soil temperatures uniformly increased to 100° C and remained there for approximately 18 days while data were collected on moisture-removal rates, soil temperatures, pressures within the soil, and off-gas contaminant concentrations. During this period, a total of 17,000 gallons of moisture was removed from the soil pattern at a peak rate of approximately 1,500 gpd. Pre- and post-test soil samples were taken at various locations within the soil to determine the overall increase in remediation rate. In the clay zone within the electrode array (which was heated to 100° C), about 0.1% of the initial PCE/TCE remained after heating, corresponding to a 99.9% removal of the contaminants. About 5% of the initial PCE/TCE contamination remained in the clay zone outside of the electrode array where the temperature rose to only 60°C. This demonstrates that six-phase heating accelerated the removal of the PCE/TCE from the clay.

Laboratory Tests. Pacific Northwest Laboratory (PNL) has developed extensive laboratory capabilities for treatability testing of SPSH for any soil/contaminant combination. Laboratory capabilities include soil column, bench-scale, and pilot-scale tests to evaluate the uniformity of heating and drying, the effectiveness of contaminant removal, and the performance of engineering systems to control the process.

Cost. Treatment costs are dependent on soil type and moisture content and range between \$30 to \$60/yd^3 of soil. This is four to ten times less expensive than traditional thermal-treatment technologies like incineration and above-surface thermal volatilization. As an in situ technique, SPSH avoids additional costs for excavation and soil handling, as well as cost for disposing the treated soil. The six-phase system delivers significantly more power to the bulk soil and less at the electrodes than other resistive-heating techniques. This gives more uniform heating and requires fewer electrodes compared to the volume of soil being heated. The system also uses conventional utility power transformers at a low capital cost estimated between \$200-\$300K. This is one-fifth to one-tenth of the capital cost of higher frequency soil-heating systems (e.g., radio-frequency or microwave heating). The SPSH equipment can be disposed of as sanitary waste at the end of its useful life, which is estimated at 5 years.

PROJECTED PERFORMANCE

An in situ destruction system will be developed to buildup on the on-going in situ heating and off-gas destruction tasks and will focus on effective production of high-energy corona in the subsurface to destroy organics, particularly carbon tetrachloride.

WASTE APPLICABILITY

Target contaminants are volatile organic compounds (VOCs) in soils. SPSH is being developed for maximum applicability to complex stratigraphies, impermeable soils such as clays and silts, and semivolatile contaminants.

STATUS

The Six-Phase Soil Heating technique has been demonstrated both in a sandy, arid soil and in a clay, humid soil. A finite-element code has been adapted to calculate spatial and temporal variations in soil temperature, pressure, moisture content, and electrical properties during combined SPSH and soil venting.

REGULATORY CONSIDERATIONS

The 1990 Clean Air Act Amendments must be considered for VOC emissions. Application of the technology is covered under Resource Compliance and Recovery Act (RCRA) Part A Interim Status and a National Environmental Protection Act (NEPA) categorical exclusion.

POTENTIAL COMMERCIAL APPLICATIONS

This technology has wide-spread commercial applications, such as in cleanup of gasoline spills, etc. A relationship is presently being developed with an industrial firm that is expected to culminate in a licensing agreement with PNL for use of SPSH at a large number of their sites.

BASELINE TECHNOLOGY

The baseline technology is soil-vapor extraction.

INTELLECTUAL PROPERTY

On November 14, 1991, a patent was obtained for electrical soil heating (US 4,957,393). A second patent has been allowed and will be issued shortly. A third patent application has been submitted. Applications for foreign rights have also been completed.

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REFERENCES

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SUBSURFACE BARRIER EMPLACEMENT DEVELOPMENT

Sandia National Laboratories

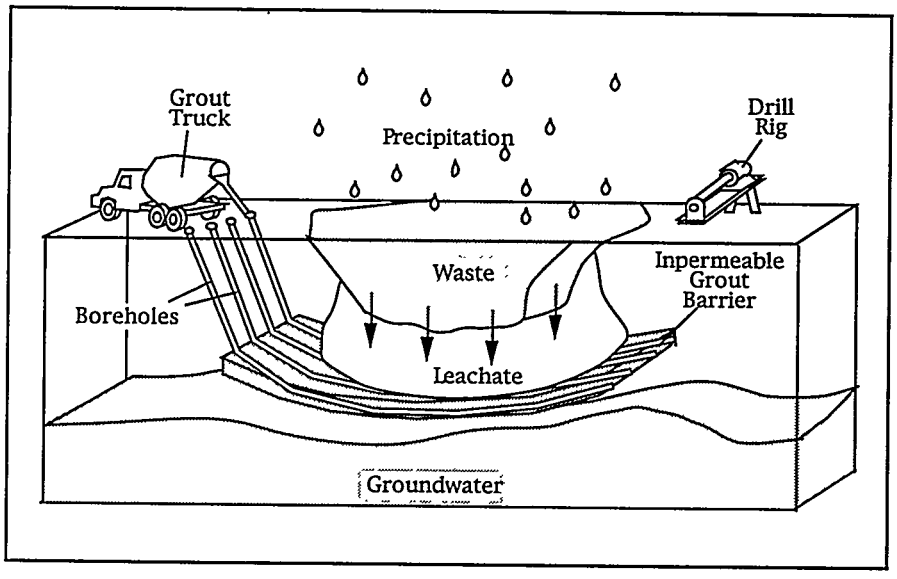
DESCRIPTION

In the past, wastes were buried or dumped in unlined pits with the idea that surrounding soil would act as a natural barrier between the waste and the groundwater. It is now known that some of these waste forms are breaking through to the groundwater. Today, additional precautions such as surface caps and subsurface barriers are an integral part of every waste-disposal site design, but the question still remains: what can be done with existing waste sites? In response to this problem, Sandia National Laboratories (SNL) is currently developing mitigation measures that can be employed in three years or less.

The Subsurface Barrier Emplacement development program is directed at developing a systematic program for installing an impermeable barrier beneath waste sites. The development requires the integration of several subsystems including subsurface access (drilling), barrier-material selection, barrier injection, barrier-continuity verification, and post-construction monitoring. The installation of the horizontal-barrier lenses must not disturb the waste above. Two emplacement techniques are currently being evaluated, permeation grouting and jet grouting. Permeation grouting injects a low-viscosity grout into the soil at low pressures which fills the voids without significantly changing the soil's structure or volume. Jet grouting, in contrast, injects grout at a high pressure and velocity, which completely destroys the soil's structure while forming the subsurface barrier. The grout and the soil are intimately mixed forming a homogeneous mass.

Initially, feasibility of each technique was evaluated, followed by evaluation of design parameters such as borehole separation, depth limitations, etc. Accomplishments to date include a completed field-scale permeation-grouting experiment. Field testing consisted of grouting in vertical and horizontal boreholes using four different barrier materials. The barrier materials used were two ultra-fine cements, a mineral wax/bentonite mixture, and a sodium silicate. Numerous non-intrusive geophysical techniques were used to identify where the grout flowed. Geophysical techniques used included: cross-hole seismic tomography, ground-penetrating radar, electromagnetic induction, neutron probe, and downhole-temperature logs. Finally, the cementitious grout site was excavated to expose the grout. Observations were compared with crosshole tomography data when the analysis was complete.

The installation of vertical subsurface barriers is standard practice in civil and mining



Subsurface Barrier Application

engineering, but methods for constructing horizontal barriers in situ have not been developed. The benefits of this emplacement program are:

- Directionally drilled boreholes provide access without disturbing the waste above;
- Interim containment allows time for the development of remediation options;
- In the interim, the volume of waste remains fixed;
- Barriers may enhance the effectiveness of in situ remediation actions; and
- Barrier systems may provide permanent waste containment.

TECHNICAL PERFORMANCE

Field-Scale Experiments. The Subsurface Barrier Emplacement demonstration site is located in the southeast corner of Technical Area III, Sandia National Laboratories, Albuquerque, NM. The area typically has a dry, semi-arid climate. The field-test site is composed of alternating layers of unsaturated soils which were deposited during flooding episodes. Four vertical sample borings to a depth of 30 ft. indicate that the soil consists primarily of unconsolidated, unsaturated, silty-sand, with intermittent cobble layers. The vertical boreholes in the vicinity of the Mixed Waste and Chemical Waste Landfills reveal the heterogeneity (horizontal and vertical) of the near-surface deposits. The site is approximately 480 ft above regional groundwater.

Two horizontal boreholes were directionally drilled and cased with tube-á-manchette (sleeve) pipe. This sleeve-pipe design allows a temporary, brittle, annular grout to be installed and selectively fractured to allow the permeation grout to flow radially outward at selected intervals. The permeation grout is injected at a pressure less than or equal to 50 psi after the temporary grout is fractured. The injection pressure is less than the fracture strength of the local geology. After grout injection and post-construction non-intrusive testing (e.g., seismic tomography, neutron logging, etc.), the overburden was excavated and core samples were taken and compared to the results of non-intrusive testing. In general, the radius of penetration for permeation grouts is primarily a function of the formation characteristics (e.g., hydraulic conductivity, porosity, etc.), grout viscosity, and injection pressure. Due to the anisotropic nature of site formations and the unpredictable nature of grout set times, determination of the penetration radius should be empirically derived. During this experiment, the grout viscosity and injection pressure were held relatively constant; therefore, the variation in the soil matrix properties was the primary contributor to the non-uniform grout flow. Excavation also revealed variation radially in the soil within the targeted strata. The grout permeated the soil matrix in the coarse sand/gravel, but simply displaced the soil in the more fine sand/silty soil. Table 1 gives an approximate relationship between hydraulic conductivity and groutability of a stratum. Table 2 gives estimates of permeation radius in various soils.

Costs. It is intended that this demonstration will define the expected costs for emplacement. Most likely it will cost around $500K initially to install and evaluate a subsurface barrier in a landfill similar to those at SNL.

PROJECTED PERFORMANCE

Future work will demonstrate the feasibility of high-pressure jet grouting. The rate of injection for jet grouting is expected to be approximately 20-50 cm/min up to a one-half meter diameter. Future work will include grouting multiple boreholes in a place close enough for the grout to permeate the entire space between and around neighboring boreholes in order to form a continuous grout layer. Important verification methods will also be tested. For example, the barrier integrity would be evaluated by

Table 1. Approximate Relationship between Hydraulic Conductivity and Groutability. (Karol, 1990)

Hydraulic Conductivity (cm/sec)	**Groutability (Ability of the Soil to Receive Grout)**
$\leq 10^{-6}$	Ungroutable
10^{-5} to 10^{-6}	Groutable with difficulty by grouts with viscosity < 5 mPa • s and ungroutable with grouts having a viscosity > 5 mPa • s
10^{-3} to 10^{-5}	Groutable with low-viscosity grouts but difficult with grouts with a viscosity greater than 10 mPa • s
10^{-1} to 10^{-3}	Groutable with all commonly used chemical grouts
$\geq 10^{-1}$	Requires suspension grouts or chemical grouts containing a filler material

Table 2. Permeation Estimates in Various Soils (Naudts, 1992)

Type of Soil	Permeation Radius (meters)
Gravel	4-6
Coarse Sand	6-10
Medium Sand	4-6
Fine Sand	2-4
Silty Sand	1-2

testing the transmissibility to fluid flow across its entire surface. Applicable verification technologies include emerging 3-D seismic tomographic imaging which has the potential for resolving the correct spatial position of a shallow grout lens. However, this technology may not provide sufficient resolution to identify flaws such as a 1 ft^2 hole in the grout lens.

WASTE APPLICABILITY

This subsurface barrier-emplacement technology is intended to be a near-term (3 yrs. or less) corrective or mitigating measure for unlined chemical-waste pits and buried-waste landfills.

STATUS

This technology has been demonstrated in a field-scale capacity for low-pressure permeation grouting. High-pressure jet grouting has not been demonstrated, but should be demonstrated in the near future (i.e., FY94-95). In general, more development and demonstration is needed, but the technology may be available for transfer in FY96 or 97.

Table 3. Cement Grout Particle Size and Viscosity

Borehole	Average Particle Size of 90% of Particles	Average Viscosity (mPa - s)
1 (WIPP - microfine cementatious grout)	8.5μm or less	45
2 (BNL - ultrafine bentonite/cementatious grout)	9μm or less	16

REGULATORY CONSIDERATIONS

This technology will aid in the achievement of regulatory cleanup milestones. This technology will use chemically compatible grouts which are compatible with the local ecology. Although there are not specific regulations for barriers placed beneath existing waste sites, the standard for new installation of waste impoundment liners (40 CFR Part 264 Subpart N) will likely apply.

POTENTIAL COMMERCIAL APPLICATIONS

This technology has been used in similar forms in the civil construction and mining industries. The additional development made to adapt the concepts to horizontal barriers and environmental applications may well be applicable to these industries. The micro-fine cement demonstrated in borehole 1 (see Table 3) was developed to seal micro-cracks at the WIPP site; therefore, there may be structural applications resembling the WIPP application.

BASELINE TECHNOLOGY

There is no baseline technology for emplacement of horizontal grout lenses.

INTELLECTUAL PROPERTY

There are no patents pending at this time.

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Industrial/University Partners

There are no industrial partners sharing in development costs at this time.

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THERMAL ENHANCED VAPOR EXTRACTION SYSTEM

Sandia National Laboratories

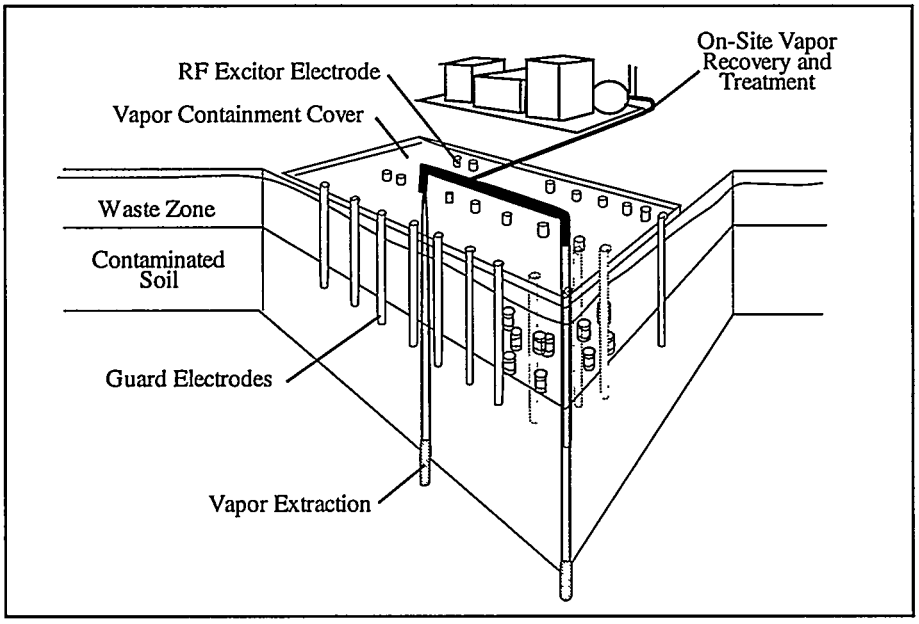
DESCRIPTION

The Thermal Enhanced Vapor Extraction System (TEVES) combines conventional vacuum vapor extraction with both powerline frequency (PLF) soil heating and radiofrequency (RF) soil heating to accelerate the removal of contaminants typically found in hazardous waste landfills.

TEVES will demonstrate and evaluate the effects of temperature on the waste-soil system. The principle effects of temperature on the waste-soil system are increased mass-removal rates, especially for lower volatility constituents.

The two types of heating will be demonstrated in series. The first type of heating is powerline frequency heating that is characterized by resistive heat generation by 60Hz alternating current carried by the soil water between two electrodes. As the soil is heated and as vacuum extraction removes contaminants and soil water, electrical conduction between the electrodes diminishes and uniform heating declines. Soil heating by powerline frequency heating is limited to 100 °C. The second type of heating, known as radiofrequency heating, is then initiated to heat the soil past 100 °C. Radiofrequency (RF) heating uses radiowaves to provide dielectric soil heating. In contrast to electric-resistance soil heating, RF heating does not require the current-conduction path of soil water.

Testing will be performed in six phases at the Sandia National Laboratories (SNL) Chemical Waste Landfill (CWL) as follows: Phase I - Site Investigation; Phase II - Off-Gas Treatment System Design; Phase III - Vacuum Venting and In Situ Heating System Design; Phase IV - Vacuum Venting and Off-Gas Treatment Systems Operation; Phase V- Powerline Frequency Heating and Venting Operation; and Phase VI - Radio-Frequency Heating and Venting Operation.



Artist's Rendition of the TEVES System

TECHNICAL PERFORMANCE

Temperature Effects on Vapor Pressure. The vapor pressure of most organic chemicals increases strongly with temperature. The relationship between vapor pressure and temperature is exponential.

Effects of Heat on Vapor Extraction. The following figure shows the effects over time of soil heating on the soil contaminant mass remaining during vacuum extraction for

a mixture of volatile and semivolatile organics present at the CWL. The slope is more precipitous for the higher soil temperatures, indicating higher removal rates.

Powerline Frequency Heating and Venting Operation. This process utilizes 60 Hz PLF heating up to a maximum of 100 °C. Hardware includes a transformer, electrical-control equipment, cables, vapor-extraction wells, and off-gas treatment system. System operation is anticipated to occur for 14 to 35 days. Parameters to be evaluated are mass-removal rate and distribution of contaminant species.

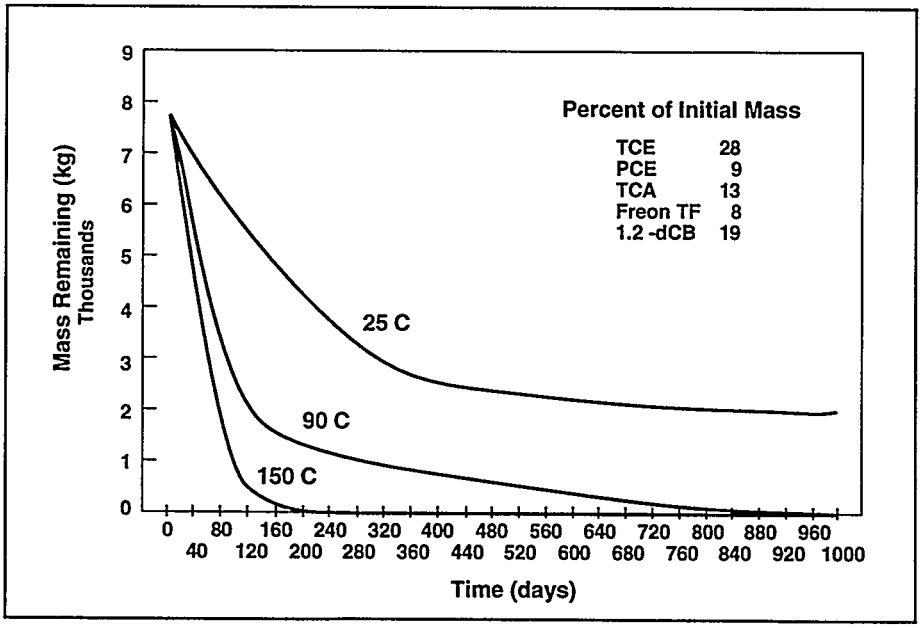
Radiofrequency Heating and Venting Operation. This process utilizes 2 to 20 MHz of radiofrequency energy and can heat up to a maximum of 250 °C. Additional hardware includes a radiofrequency generator, matching network, electrical control equipment, and cables. System operation is anticipated to be 10 to 30 days. Parameters to be evaluated are increase in mass-removal rate and change in distribution of contaminant species (additional lower volatility species are expected to be removed).

Treatment Limitations. 1,000 to 3,000 yd^3/treatment. Large quantities of buried metal objects influence the efficacy of resistive and dielectric heating.

Cost. Costs of electricity for the soil heating are a small part of the remediation effort. For example, the CWL demonstration requires 85,000 kWh energy at a nominal cost of $7,000 (at $0.10/kWh). Of the total energy required, 61% is required to heat the subsurface volume to 90 °C (and evaporate soil water from 7% to 2% moisture) using PLF heating; whereas 39% of the total electrical energy is required for RF heating to raise the temperature from 90 to 150 °C. RF heating is less efficient because 6 Hz of electrical energy must be converted to RF energy. RF generator efficiencies range from 40 to 60%.

PROJECTED PERFORMANCE

Soil cleanup of 95+% is possible depending on the contaminant profile. Phase III of the TEVES demonstration will utilize the extent of contamination and air permeability measurements from Phase I to estimate the expected mass-removal rates with increased temperatures (see the Table that follows).



Effects of Soil Heat on Mass Removal by Vacuum Extraction

WASTE APPLICABILITY

Volatile organic compounds (VOCs), semi-VOCs, and VOC-oil mixtures. Organic chemicals having a vapor pressure less than 0.002 atm at 20 °C that are difficult to remove with ambient-temperature vacuum extraction.

Component Mass Removal Rates for TEVES Demonstration			
Component	Removal Rate (lbs/hr)		
	25 °C	90 °C	150 °C
Trichloroethylene (TCE)	0.28	0.97	0.97
1, 1, 1 -Trichloroethane (TCA)	0.12	0.33	0.33
Tetrachloroethylene	0.11	1.76	3.76
Freon 113	0.14	0.15	0.15

STATUS

Thermal enhancement is a near-term technology. There have been previous field tests at Volk ANG Base, Rocky Mountain Arsenal, and Kelly AFB. Phases I-III have been completed. Phases IV-VI are expected to be initiated in the fall of 1993, pending approval of the Resource Conservation and Recovery Act (RCRA) Research Development and Demonstration (RD&D) permit. Final data analysis, applications analysis, and presentation of results are scheduled for FY94.

REGULATORY CONSIDERATIONS

The primary regulatory issues/requirements are for the RF spectrum to be approved by the Federal Communication Commission (FCC) and the Department of Energy (DOE)/NTIA and for the off-gas treatment system to meet the Clean Air Act requirements. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA)/ RCRA waste-treatment permits are also needed.

POTENTIAL COMMERCIAL APPLICATIONS

RF heating can be used near the surface, but PLF heating can be used at almost any depth and has been applied to oil-field stimulation projects at great depths (several thousands of feet). TEVES can be used for remediation of industrial-waste facilities with organic chemical contamination or other landfills with organic chemical contamination, industrial-process sewage leaks, storage-tank leaks, etc.

BASELINE TECHNOLOGY

TEVES is an improvement over the ambient-temperature vacuum vapor extraction technology. Ambient-temperature vacuum vapor extraction has been successful in pilot-scale demonstrations for compounds with high vapor pressures (above 0.001 atm at 20 °C, such as trichloroethylene, jet fuel, and gasoline). Thermal augmentation of vacuum vapor extraction will promote volatilization of a wider spectrum of soil contaminants and increase contaminant mobility.

INTELLECTUAL PROPERTY

Patent Ownership: Bridges, J.B., Park Ridge, IL; Harsh Dev, Chicago, IL; Richard H. Snow, Bartlesville, OK; Allen Taflove, Willamette, IL. Assignee: IIT Research Institute.

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TUNABLE HYBRID PLASMA REACTOR

Massachusetts Institute of Technology

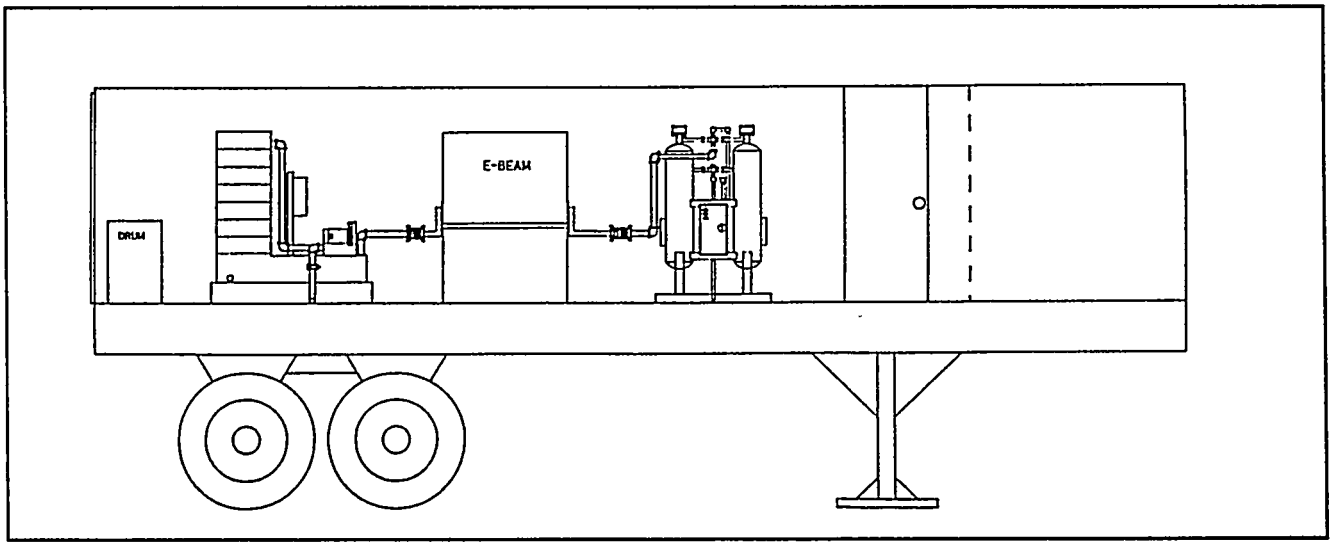
DESCRIPTION

Researchers at the Massachusetts Institute of Technology (MIT) are investigating plasma chemical processes relevant to the development of a versatile mobile electron-beam driven plasma reactor for efficient on-site decomposition of carbon tetrachloride (CCl_4) and other volatile organic compounds (VOCs). The reactor uses a moderate-energy electron beam (100-300 keV) that is injected into atmospheric air containing the organic contaminants. The organics are destroyed or oxidized to non-toxic chemicals through their interaction with the electrons and plasma generated from the electron beam. Since a plasma is generated, use of either alternating current (AC) or direct current (DC) electric fields allows a further increase in the electron and gas temperatures to optimize the treatment process. The high degree of tunability of the reactor gave rise to the name tunable hybrid plasma (THP) reactor. The capability for varying electron density and electron temperature in a highly controllable way and the provisions for the introduction of auxiliary gases to the THP reactor are expected to result in efficient decomposition of VOCs over a wide range of conditions. The objective is a versatile, low cost, on-site treatment system with minimal environmental impact.

A drawing of the field-test unit is shown in the figure. The system consists of an air dryer to remove water vapor from the process stream (to the right of the electron beam), the electron beam and reaction chamber, and a scrubber using an aqueous solution of NaOH to convert the acid gases produced by the electron beam to salt. The trailer will be located at the Hanford site for preliminary trials; it will be moved to other U.S. Department of Energy sites to establish remediation criteria for other halogenated hydrocarbons.

TECHNICAL PERFORMANCE

Preliminary data show that the THP reactor can provide a high degree of decomposition of CCl_4 at low gas temperatures with only modest power requirements. As an example, for 90% destruction of



Field Test Unit

CCl_4 at an intake concentration of 26 ppm, the adiabatic temperature rise is on the order of 15 °K in the laboratory test reactor. For an intake concentration of 352 ppm, 99% decomposition was obtained with an adiabatic temperature rise of about 140 °K. These temperature increases are significantly lower than obtained with typical incineration, which is around 1800 °K. A field-test system has been assembled and tested at MIT. It has been used to demonstrate the reduction in CCl_4 concentration from 760 ppm to 0.6 ppm with a 99.97% removal efficiency. The THP reactor, being a low-temperature process, may provide more control over the generation of decomposition products than high-temperature thermal-treatment processes.

For the case where CCl_4 is the main contaminant, dissociative electron attachment initiates the breakup of the CCl_4. The reaction products (Cl_2, HCl, CO_2) are passed through a conventional scrubber. All of these gaseous products either dissolve in an aqueous solution (Cl_2, HCl) or are passed through the scrubber and released to the atmosphere (CO_2). The scrubber can contain an aqueous solution with or without a caustic such as NaOH. The caustic solution is preferred since it produces NaCl and CO_2 gas, which can easy be disposed.

Trichloroethene (TCE) has been tested with the laboratory THP reactor. The destruction of TCE requires less than 10% of the energy required to destroy CCl_4. The byproducts can be dissolved in an aqueous solution containing NaOH, producing a non-toxic sodium salt. The air stream need not have a low vapor pressure of water, negating the necessity of the dryer required for CCl_4.

Cost. Only projected cost information is available. For a full-scale THP reactor system (175 kW electron beam that deposits 100 kW into the gas), the unit cost is about $1 million. This cost includes the electron beam and support equipment. The system is projected to treat about 10 pounds of CCl_4 per hour and operate 90% of the time. Hence, the system should be able to treat about 78,800 pounds of CCl_4 per year. For a practical field device, the objective is to treat one pound of CCl_4 for about $4.

The costs for destroying TCE are much lower. The same system described above can destroy nearly ten times as much TCE, resulting in a cost per pound of TCE destroyed of less than 40 cents.

PROJECTED PERFORMANCE

This technology employs modest-voltage electron beams (up to 300 keV) which lead to duct cross sections with dimensions of the order of 10-30 cm. This allows the construction of systems which can be compact, portable, self-shielded, and capable of high operational availability based upon a well established commercial electron-beam technology.

Different-size devices have or will have different throughputs. The throughputs for the laboratory unit, field test unit, demonstration unit, and full-scale (practical) field unit are projected to range from 0.1-1, 1-20, 20-200, and 200-1,000 ft^3/min, respectively.

WASTE APPLICABILITY

The THP technology is best suited for treatment of gaseous streams with small concentrations of VOCs, especially chlorinated compounds. The process is very efficient in removing contaminant concentrations lower than approximately 1,000 ppm.

STATUS

The moderate-energy electron-beam technology, which is being incorporated into the THP reactor systems, is a well established commercial technology with modest shielding requirements and high

reliability. Laboratory-scale units have been tested in treating carbon tetrachloride, dichloromethane, and trichloroethylene, with initial results showing the technology is competitive with current technologies. A field unit is currently being constructed that will include a pre-processor for the system and dryers, a post-processor for monitoring the system and scrubber, and an automated control system. The field unit will be demonstrated at a site in Washington State in 1994.

REGULATORY CONSIDERATIONS

Air with carbon dioxide and water will be exhausted from the device. Small amounts of oxides of nitrogen (NOx) may be present but are expected to fall below regulatory limits. Compliance with the Occupational Safety and Health Act is required for hazardous-waste operations, handling of heavy equipment, and protection of occupational workers from electrical power.

POTENTIAL COMMERCIAL APPLICATIONS

Potential commercial applications include industries with gaseous or liquid effluents or emissions from remediation sites (e.g., semiconductor fabrication plants).

BASELINE TECHNOLOGY

The baseline treatment technology for gaseous effluents is granulated activated-charcoal adsorption with off-site regeneration and disposal. The advantages of the THP technology include: (1) on-site treatment of toxic substances in gas streams with high destruction and removal efficiency; (2) capability of eliminating contaminants from high-volume waste gas streams with end products of small volumes of solid precipitates and toxic gases; (3) relatively low cost; (4) minimum pre- and post-treatment requirements; (5) ability to treat gases from solid-waste treatment systems resulting in non-toxic emissions and small volumes of solid non-toxic residues; and (6) versatile operation that can be used to process a wide range of substances and concentrations.

INTELLECTUAL PROPERTY

Patents have been filed.

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Pacific Northwest Laboratory is providing service in kind.

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VOC OFF-GAS MEMBRANE SEPARATION

Westinghouse Hanford Company

DESCRIPTION

Vacuum extraction will remove the volatile organics from the contaminated soil. A high-pressure system has been designed to treat feed streams that contain dilute concentrations of volatile organic compounds (VOCs). The organic vapor/air-separation technology involves the preferential transport of organic vapors through a semi-permeable gas-separation membrane (diffusion process analogous to putting oil on a piece of waxed paper). In this system, the feedstream is compressed and sent to a condenser where the liquid solvent is recovered. The condenser bleed stream, which contains approximately 5,000 ppm of the VOC, is then sent to the membrane module. The membrane module comprises spiral-wound modules of thin-film membranes separated by plastic-mesh spacers. The membrane and the spacers are wound spirally around a central collection pipe. In the membrane module, the stream is further concentrated to 3% VOC. The concentrated stream is then returned to the compressor for further recovery in the condenser.

TECHNICAL PERFORMANCE

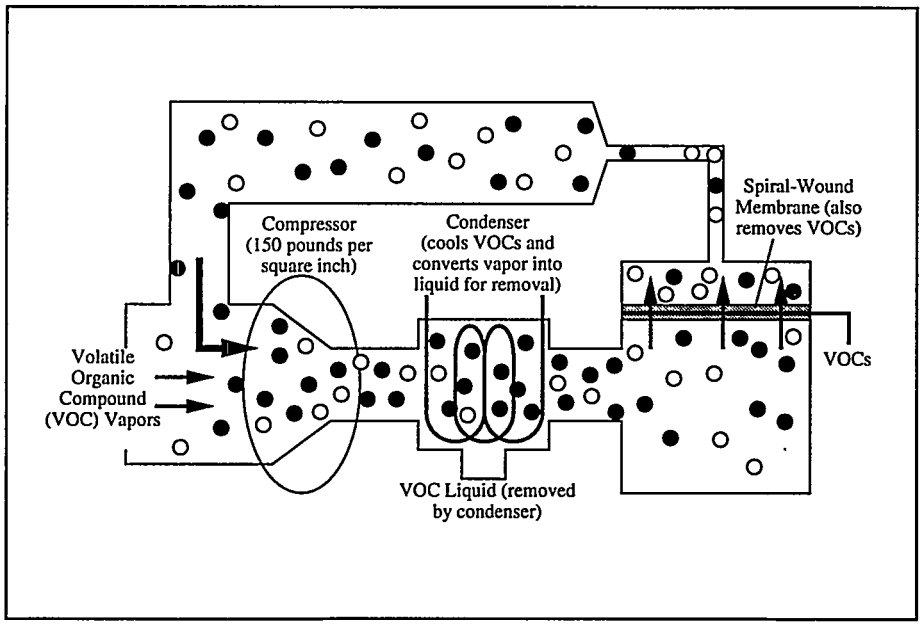
Cost. Capital Equipment (1,000 cfm) is $850K; Operations and Maintenance is $494K/yr (membrane replacement every 3 yrs). This equates to a cost of $2.80/lb of VOC removed (including disposal costs).

No fouling of the membrane has occurred during the 6-month pilot operation. Radon will not affect the functionality of the membrane separation unit.

PROJECTED PERFORMANCE

Based upon a VOC effluent concentration of 1,000 ppm, there is a 95% removal efficiency. The remaining 5% is polished using granulated activated carbon (GAC).

The system is ready for full-scale deployment.



High-Pressure Gas Membrane Separation

WASTE APPLICABILITY

The targeted contaminants are VOCs, carbon tetrachloride, and chloroform in gas streams.

STATUS

The field-ready system was placed at a contaminated site at Hanford and operated for a period of 6 months. The system operated as designed. This technology is off-the-shelf and ready for deployment. It is being used for a number of industrial applications.

REGULATORY CONSIDERATIONS

The 1990 Clean Air Act Amendments must be considered when treating VOCs.

POTENTIAL COMMERCIAL APPLICATIONS

This technology is applicable to the treatment of any waste stream emitting VOCs and presents a cost-effective alternative to treatment by GAC adsorption currently used by industry.

BASELINE TECHNOLOGY

The baseline technology for treatment of VOCs is GAC adsorption. GAC adsorption generates a secondary waste that requires disposal or regeneration on a regular basis. The membrane system would minimize the secondary waste stream while providing a recyclable product.

INTELLECTUAL PROPERTY

Membrane Technology and Research, Inc. owns several patents.

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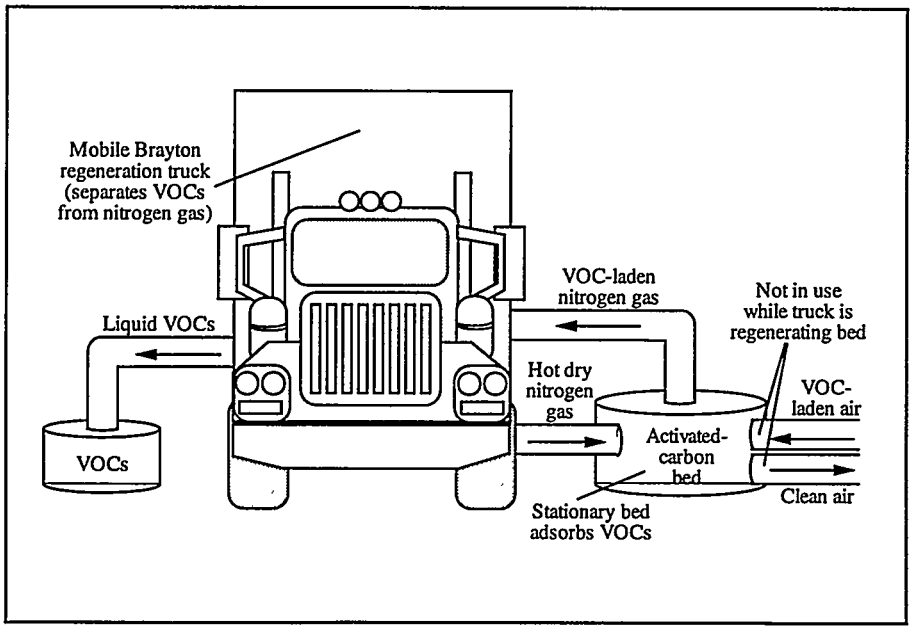
VOC RECOVERY AND RECYCLE

Idaho National Engineering Laboratory

DESCRIPTION

Many DOE sites have soil and/or groundwater that is contaminated with organic compounds. These sites will have to undergo remediation in the near future. One method is vapor vacuum extraction, but air-quality regulations will prevent the organics from being simply vented to the atmosphere. Therefore, some method of recovery or destruction will be required. A Brayton-cycle heat pump (BCHP) can condense volatile organic compounds (VOCs) from an air stream, which offers the potential for both recovery and either on-site or off-site recycle of a wide range of VOCs. The VOC-laden air stream can come from either vapor vacuum extraction of soil or air stripping of contaminated groundwater.

The technology consists of activated-carbon adsorbers located at each extraction well, plus a truck-mounted Brayton-cycle heat pump to regenerate the adsorbers on a periodic basis. The VOC-laden air from the well is passed through the carbon bed, adsorbing the VOCs. When the bed becomes saturated, hot nitrogen from the regenerator is used to desorb the VOCs from the bed. The nitrogen passes through a chiller, is compressed, and is then cooled in a recuperator, where 50% to 80% of the organics are recovered. The partially depleted nitrogen stream is then expanded through a turbine, lowering the temperature to as low as -150°F and condensing the remaining organics. The now-clean nitrogen passes through the recuperator to cool the VOC-laden nitrogen before returning to the carbon bed. A pilot-plant system will be demonstrated on a single extraction well. The input will be 250 scfm of vapor from the extraction well. The only outputs will be the clean off-gas from the well and a small amount of recovered organics.



Decoupled Brayton-Cycle Solvent-Recovery Heat Pump for Small Emitters

TECHNICAL PERFORMANCE

General. In terms of performance, the BCHP would have no effect on the remaining contamination in the ground; this is an off-gas treatment/recovery/recycle technology. The process waste for the Savannah River Site (SRS) demonstration will be a small amount (less than one drum) of mixed liquid trichloroethylene/tetrachloroethylene (TCE/PCE), recovered during the demonstration. Liquid TCE/PCE recovered during the pilot-plant demonstration will require disposal according to

existing SRS regulations for organic waste. A full-scale system would require an off-site solvent recycler to pick up the recovered solvent on a periodic basis. The pilot plant is mounted on a lowboy trailer. The full-scale regenerator is mounted on a 40 ft. trailer (40-ft long x 8-ft wide x 13.5-ft high). The pilot plant requires one technician for setup. However, the operation is computer-controlled. A full-scale decoupled system would require two operators to run the regenerator. Adsorbers at each site would require no additional labor.

Pilot-Plant Test Results. A pilot-scale study was conducted at the SRS over a two-week period in April 1993. Initial operation at 100 scfm showed that the solvent concentration from the well was higher than anticipated (7,000 ppm rather than 100 to 200 ppm). At this high concentration, breakthrough in the carbon beds occurred very rapidly, making the tests less representative of a full-scale system. Therefore, a 75 scfm slipstream was taken from the extraction well for use in the tests. This resulted in an adsorption cycle time of about 12 hours. With an inlet concentration of about 7,000 ppm, the outlet concentration was 100 to 200 ppm. The system removed more than 97% of TCE/PCE from the vapor-extraction stream and recovered solvent as a liquid for recycling or sale off-site. Single desorption of one carbon bed required approximately 6 hours. The total time for the pilot-scale application was determined by the rate of vapor extraction and the concentration of the contaminants. The pilot-plant system required 50 kW of 480 V power. The full-scale system would require 200 kW of 480 V power. The system is suitable for a variety of VOC types, volumes, and concentrations. The system is compatible with most VOC-laden air streams and has the appropriate interlocks in case of any malfunction.

Regeneration required about four hours. The time would have been shorter; however, the nitrogen flow from the vaporizer was low. The system was operated for a total of five regeneration cycles, with an average of 93 lbs of solvent recovered per regeneration. There were 200 lbs of carbon in each adsorber, resulting in a working capacity of 47%. The total solvent recovered was approximately 465 lbs.

Cost. The pilot plant required less than $2K for startup, including nitrogen supply. Full-scale system capital cost would be approximately $1,500K for 10 adsorbers, plus installation and electrical connections. Adsorbers would either be purchased or leased by SRS during the soil remediation. Ten wells would be treated at a time, after which the adsorbers would be removed to other wells. The pilot-plant demonstration will cost $7.5K. The full-scale system would cost $4K/mo per well, assuming two regenerations per day, five days a week. The operations cost assumes a service company would own the regenerator and would charge a fee (of about $1.4K) for each regeneration.

PROJECTED PERFORMANCE

Based on successful operation of the pilot plant, a decoupled carbon-adsorption/Brayton-cycle regeneration system has been designed for the SRS. Two adsorbers, each containing 3,000 lbs of carbon, would be located at each well. The beds will be operated in series, as demonstrated in the pilot plant, to provide a greater working capacity in the bed. Assuming a flow rate from a typical well of 500 scfm, the adsorption time for each bed would depend on the solvent concentration from the well. Adsorption times are given in Table 1 for three concentrations. The highest concentration (7,000 ppm) was taken from pilot plant data but is likely to be very atypical. Concentrations between 50 and 300 ppm are more likely.

Table 1. Adsorption Times for Given Concentrations.

Concentration (ppm)	Adsorption time (days)
7,000	3
300	10
50	30

Each well will contain a sacrificial guard bed to remove high-boiling components and other contaminants from the extraction-well air stream, which could reduce the working capacity of the carbon adsorbers.

At breakthrough, the saturated adsorber would be transported to the regenerator (with the same general configuration as the pilot plant). The regeneration nitrogen flow rate would be 1,500 scfm, which is sufficient to regenerate two adsorbers in parallel in a total time of six hours. The trailer and skid-mounted regenerator will contain a chiller, an air compressor, and a motor control center. External needs include 200kW of 480 V power and nitrogen.

Costs. Capital costs for the full-scale decoupled Brayton-cycle Savannah River heat pump are: Adsorbers (20 total) - $700K; Regenerator - $850K. Operating costs would depend on the value of the recovered solvent and whether the system is vendor-owned/leased. At one lb/h per well, the total solvent recovered would be approximately 90,000 lb/y.

If vendor-owned, there would be a fee of $1,800 per regeneration or about $470K/y. If the system were purchased, the primary operating costs relate to labor and electricity. Assuming the solvent concentration is in the range of 50 to 300 ppm rather than 7,000 ppm, the regenerator would need to be operated for one shift per day, five days per week. It would require one full-time operator for the regenerator, plus one full-time helper to drive the truck for the adsorbers and to help set up for each regeneration. Fully burdened labor would then be approximately $125K/y. At $0.04/kWh, this would result in approximately $12.5K/y.

WASTE APPLICABILITY

This technology is applicable to ex situ (above-ground) recovery of VOCs from carbon-adsorption canister regeneration. The targeted contaminants include TCE, PCE, and trichloroethane (TCA). This technology is also applicable for the regeneration of carbon adsorbers in other applications.

STATUS

Based on successful operation of the pilot plant, a decoupled carbon-adsorption/Brayton-cycle regeneration system has been designed for the SRS. The technology is commercially available now. The technology is currently being used successfully in several locations, including one in Greenville, SC.

REGULATORY CONSIDERATIONS

The BCHP technology has been shown to meet emission regulations in other areas of the country and is expected to meet future regulations as they are implemented. The system will achieve 95% recovery and is available to meet near-term regulatory milestones.

POTENTIAL COMMERCIAL APPLICATIONS

Potential applications include regeneration of carbon filters and adsorbers used in the chemical industry and other industries. The technology has principal applications where VOC vapors are removed from an air stream (e.g., using carbon adsorption for vacuum soil-vapor extraction off-gas treatment). Other applications might be in the regeneration of carbon adsorption filters in other chemical-process off-gas treatment applications.

BASELINE TECHNOLOGY

The baseline technology is activated-carbon canisters with off-site disposal. The BCHP offers a less expensive alternative to activated-carbon canisters. Also, it is becoming increasingly difficult to dispose of carbon canisters that have been loaded with chlorinated organics. The BCHP suffers no limitations compared with the carbon canisters. Few technical challenges exist. The basic technology has been demonstrated on several processes in industry, though the decoupled concept is still in the demonstration phase.

INTELLECTUAL PROPERTY

Patents are owned by the 3M company and NUCON International, Inc. The patent numbers are: 4,295,282; 4,480,393; and 4,539,816. NUCON has an exclusive license to market the BCHP technology for solvent recovery.

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