DOE/ER-0501T

SUBSURFACE SCIENCE PROGRAM

Program Overview

June 1991

U.S. Department of Energy
Office of Energy Research
Office of Health and Environmental Research
Washington, DC 20585

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PREFACE

The Office of Health and Environmental Research (OHER) within the Department of Energy's (DOE's) Office of Energy Research conducts long-term fundamental research in the physical, chemical, and biological sciences. OHER's Subsurface Science Program, summarized in this document, supports a university and national laboratory research program that is interdisciplinary, covering such disciplines as geochemistry, microbiology, and hydrology. Departmental needs in environmental restoration, a major issue that DOE will face for several decades, are emphasized. However, the research that is conducted by the Subsurface Science Program also contributes to other energy-related questions, including fossil energy production.

Potential risks to human health and the environment within and outside DOE facilities are the byproduct of more than 40 years of waste generation and disposal at DOE sites. Therefore, DOE has accelerated its efforts in environmental restoration to ensure that its facilities are in compliance with environmental regulations and that long-term environmental risks from existing and inactive facilities are reduced and finally eliminated. Remediation of inactive contaminated waste-disposal sites and the effects of these sites on subsurface environments is the largest and most expensive task facing DOE.

Characterization and cleanup of DOE waste sites are difficult and expensive because the wastes are often unique combinations of radioactive materials, inorganic chemicals (including heavy metals), and organic chemicals. The fundamental scientific information needed for effective cleanup of such complex contaminant mixtures does not exist. Furthermore, because the subsurface environment is inaccessible, delineating the extent of contamination currently relies on costly, closely spaced, disruptive drilling, which may modify natural ground-water flow systems and increase the risk of contamination in new areas. This inaccessibility also limits fundamental understanding of subsurface physical, chemical, and biological variations (heterogeneities) that control the success or failure and the costs of current remediation approaches.

The magnitude, diversity, and unique character of subsurface contamination at DOE sites require significant advances in fundamental knowledge for characterizing the nature and extent of contamination, for remediation, and for evaluating the success of remediation methods. In addition, the costs (estimated to be in the tens of billions of dollars) that DOE faces for remediation or cleanup of inactive waste sites may be significantly reduced with an innovative basic research program that is directed at long-term problems and from which new concepts can emerge.

Some conclusions on the nature of long-term environmental restoration problems and their implications for basic research can be drawn.

- *Dilute and dispersed contaminants in the environment at DOE sites are significant technical and cost challenges for long-term environmental restoration, and such contaminants pose risks, to the public and the environment, that may increase with time.* Low-concentration, potentially toxic mixtures that are dispersed through cubic miles of soils, sediments, and ground waters at DOE facilities pose particular challenges to current technologies. Although the mixtures may be dilute, they can present hazards to ecosystems and human health.

- *Natural variations (heterogeneities) in subsurface systems make characterization, isolation, immobilization, and destruction of contaminants and predictions of risk difficult.* Chemical, physical, and biological processes that control the behavior of contaminants need to be understood. New concepts to reduce costs and complement existing engineered methods need to be developed to reduce the costs of remediation and the risks to health and the environment.
- *Current remediation methods, including engineered technology and scientific methodology, are both primitive and expensive.* Contaminated soils can be cleaned up but at high cost; technologies to process very high-volume contaminant/soil/water mixtures are unavailable or prohibitively expensive. In situ methods are attractive as cost savers.
- *New concepts of environmental restoration (in situ) of radioactive, chemical, and especially mixed-waste sites are likely to emerge from long-term basic research, and the public may benefit as health and environmental risks are reduced.* Technologically, subsurface remediation is in its infancy, and fundamental scientific understanding of many physical, chemical, and biological aspects of the subsurface environment is limited by inaccessibility.

The Subsurface Science Program emphasizes research on subsoils and ground water, i.e., the natural subsurface environments that are most significantly affected by past DOE waste-disposal practices. More specifically, research is being conducted in hydrogeology, in subsurface microbiology, and on the biogeochemistry of chemical mixtures in the subsurface environment. The program is organized into interdisciplinary subprograms, or areas of research emphases, with each subprogram conducting basic research of interest to DOE. For example, fundamental scientific research in several subprograms on microbial distribution, function, and effects is laying a foundation for cost-effective in situ mitigation of contamination at DOE sites. Research on the behavior of organic-radionuclide mixtures in ground water will be used by DOE sites, other Federal agencies, and the international community to assess environmental risks and to establish effective remedial procedures.

This document summarizes the Subsurface Science Program's major research activities. Additional information about the program can be found in the following documents:

- DOE/ER-0432, *Subsurface Science Program, Program Overview and Research Abstracts*—describes the program's detailed research strategy and current research investigations.
- DOE/ER-0419, *Evaluation of Mid-to-Long Term Basic Research for Environmental Restoration*, and DOE/ER-0482T, *Basic Research for Environmental Restoration*—summarize DOE waste problems and technologies and the basic research necessary to address these problems.
- Scientific publications in peer-review journals and proceedings from scientific meetings—contain reports by the program's investigators of their scientific accomplishments.
- Subprogram plans and documents—describe the principal research tasks, provide guidance on the steps required to complete an interdisciplinary research program, and document major DOE scientific meetings, planning seminars, and workshops. (These documents provide a scientific structure for the work of currently funded investigators and guidance to university, national laboratory, and private sector scientists who want to participate in the program in the future.)

Documents are available on written request to the Program Manager, ATTN: Subsurface Science Program (ER-75), U.S. Department of Energy, Washington, DC 20545.

The fundamental research that the Subsurface Science Program supports is focused on high-priority scientific areas (subprograms) on which resources have been concentrated for up to 5 years to better ensure scientific progress. Predicting the outcome of basic research (or guaranteeing results in fixed time frames) is very difficult; nevertheless, goals for each subprogram have been identified in consultation with investigators and the scientific community to serve as guidelines against which research progress can be roughly measured.

Each subprogram is coordinated by one or more senior research scientists (Subprogram Coordinators) who assist the DOE Program Manager in (1) organizing interactive university-national laboratory-private sector teams, (2) organizing scientific workshops that include grantees and external contributors with no program affiliation (e.g., other Federal agency representatives), and (3) facilitating the coordination of a DOE-developed and approved scientific research strategy supported by research and implementation plans. DOE acknowledges the contributions of the following Subprogram Coordinators:

- Co-Contaminant Chemistry Subprogram—Dr. John M. Zachara, Pacific Northwest Laboratory.
- Geochemical Transport Processes/Colloids Subprogram—Dr. John F. McCarthy, Oak Ridge National Laboratory.
- Multiphase Fluid Flow Subprogram—Dr. Avery H. Demond, University of Michigan, and Dr. C.S. Simmons, Pacific Northwest Laboratory.
- Biodegradation/Microbial Physiology Subprogram—Dr. Fred J. Brockman, Pacific Northwest Laboratory.
- Deep Microbiology Subprogram—Dr. David L. Balkwill, Florida State University, and Dr. J.K. Frederickson, Pacific Northwest Laboratory.
- Coupled Processes Subprogram—Dr. Ellyn Murphy, Pacific Northwest Laboratory.
- Multicomponent Predictive Models Subprogram—Dr. Shirley Rawson, Idaho National Environmental Laboratory, and Dr. A.F.B. Tompson, Lawrence Livermore National Laboratory.
- Field-Scale Subprogram—Dr. Frank J. Wobber (acting Coordinator), DOE
- Environmental Science Research Center—Dr. Raymond E. Wildung, Pacific Northwest Laboratory

Proposers are encouraged to review subprogram plans and documents and to contact current investigators before submitting full proposals for external peer review.

Frank J. Wobber, Ph.D.
Program Manager
Subsurface Science Program

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ACRONYMS AND ABBREVIATIONS

CCl_4 carbon tetrachloride

CO_2 carbon dioxide

DNAPL dense nonaqueous phase liquid

DOE Department of Energy

EM Office of Environmental Restoration and Waste Management

ESRC Environmental Science Research Center

FCCSET Federal Coordinating Committee for Science, Engineering, and Technology

FWP field work proposal

FY fiscal year

GEMHEX geological, microbiological, and hydrologic experiments

NAPL nonaqueous phase liquid

NRC Nuclear Regulatory Commission

O_2 molecular oxygen

OBES Office of Basic Energy Sciences

OER Office of Energy Research

OHER Office of Health and Environmental Research

SERF Subsurface Environmental Research Facility

TCE trichloroethylene

USGS U.S. Geological Survey

PROGRAM OVERVIEW

Role and Function of Basic Research: The Department of Energy

The Department of Energy (DOE) is a mission-oriented agency; therefore, basic research within the department is strongly influenced by national energy and environmental policy. Basic research within DOE's Office of Energy Research (OER) is aimed at the advancement of fundamental knowledge and the discovery of new concepts and principles that may or may not have immediate technological applications. Although fortuitous breakthroughs in basic research are sometimes translated rapidly into user applications, most basic research requires a 5- to 20-year time frame for translation into user community benefits.

In contrast to basic research within OER, applied research within DOE is linked to specific departmental programs or technologies and is focused on solving immediate problems, often within strict performance schedules. For example, DOE applied research programs have identified cleanup tasks for contaminated DOE sites that require attention in short (1- to 5-year) and intermediate (5- to 10-year) time frames. The Office of Environmental Restoration and Waste Management (EM) has completed 5-year plans that focus on waste cleanup at DOE sites and has organized integrated demonstrations of potentially useful remediation technologies.

A major portion of OER's basic research that contributes to meeting long-term environmental restoration needs is funded within the Office of Health and Environmental Research (OHER). The Office of Basic Energy Sciences (OBES), particularly its Engineering and Geosciences and Chemical Sciences Divisions, also carries out basic research relevant to environmental restoration.

In addition to its primary goal of sponsoring basic research, OHER's Subsurface Science Program contributes to DOE applied research programs by translating fundamental research in physical, chemical, and biological processes into concepts of potential value to in situ contaminant stabilization and cleanup. Subsurface Science Program basic research is controlled by two primary considerations: (1) creativity and innovation, initially drawn from the scientific community, are introduced into the program through the proposal and peer review process, and (2) priorities among competing research opportunities are established based on long-term needs relating to the DOE mission.

As basic research provides fundamental information and its potential value for meeting DOE needs emerges, DOE's applied research groups and others carry it through to technology development, demonstration, testing, and evaluation. Other users also benefit from Subsurface Science Program technology transfer and collaborative programs. An example of this process for bioremediation is the discovery, through basic research, of diverse communities of microorganisms in deep subsurface systems. These microorganisms are now being screened by the private sector as sources of pharmaceuticals and by DOE's applied research program for use in surface and in situ subsurface cleanup.

Scope of Subsurface Science Program

OHER's Subsurface Science Program is DOE's primary basic research program concerned with subsoils and ground water, the environments that are most significantly affected by DOE's historical waste-disposal practices. These practices have resulted in subsurface contamination by mixtures of organic and inorganic chemicals. (See table 1.) The program's long-term (10- to 30-year) goal is to provide a foundation of fundamental knowledge that will lead to reduction of environmental risks and to cost-effective cleanup strategies. Since the program was initiated in 1984, a substantial amount of research in hydrogeology, subsurface microbiology, and the geochemistry of chemical mixtures has been conducted, leading to improved understanding about the terrestrial transport of solutes and to new insights into microbial distribution and function in the deep subsurface environment. OHER's research on radionuclide behavior in soils and waters has long been used by DOE sites, other Federal agencies, and the international research community to assess environmental risks and to establish effective remedial procedures.

The Subsurface Science Program is focused on achieving long-term scientific advances that will assist DOE in the following key areas:

- Providing the scientific basis for new and innovative in situ remediation technologies based on a concept of decontamination through manipulation of natural systems, particularly in the deep subsurface, where pumping and surface treatment is not economical and/or feasible. These technologies may range from the physical limitation of contaminant transport (such as in pore clogging by aggregation of colloids or by microbial growth) to the geochemical and microbial processes (such as microbial degradation of organic-radionuclide complexes) that limit chemical mobility or alter chemical form.
- Understanding the multiple mechanisms and process interactions that occur in the subsurface, such as the synergistic or antagonistic relationships between contaminant sorption and microbial degradation, to reduce environmental risks and better ensure successful, cost-effective biological and chemical remediation.

***Table 1.** Examples of Contamination at Inactive DOE Waste Sites.*

Examples of Waste Generated	Potential Sources of Environmental Release	Example Contaminants*	
		Ground Water	Soil
Radionuclides (high- and low-level, including transuranic elements)	Burial grounds Underground storage tanks Cribs, trenches, and pits	Radionuclides (tritium, radium, iodine-129, and cobalt-60)	Radionuclides (strontium-90, cesium-137, cobalt-60, and plutonium-239)
Inorganic Chemicals (acids, bases, and salts, including the metals lead, chromium, and copper)	Ponds and lagoons Spills	Nitrates, chlorides, uranium, chromium, mercury, and lead	Uranium, mercury, chromium, and lead
Organic Chemicals (solvents, polychlorinated biphenyls, and waste oils)	Drains and pipelines Sanitary landfills Discharges diverted to soil or aquifer	Chlorinated hydrocarbons, solvents, and fuel hydrocarbons	Fuel hydrocarbons, solvents, hydraulic oils, and volatile hydrocarbons

**Contaminants commonly occur as complex organic-radionuclide, organic-metal, and organic chemical mixtures.*

- Determining the influence of chemical and coupled chemical-microbial processes on co-contaminant mobility (such as the competitive effects of mixtures of chemicals for available sorption sites in ground-water systems and the influence of combined microbial and chemical processes on the stability and mobility of organically complexed radionuclides) to reduce environmental risks.
- Developing numerical models that incorporate fundamental knowledge of contaminant behavior in the context of subsurface heterogeneity and scale, particularly for chemical mixtures and immiscible fluids, to improve cleanup effectiveness and to predict environmental risks.

Technology and research information transfer is important to ensuring that investments in basic research are maximized to benefit DOE, the private sector, and others. Representatives in DOE Operations Offices and at DOE sites often assist the Subsurface Science Program with technology and information transfer. Within the program, this function is also performed by the Environmental Science Research Center (ESRC) at Pacific Northwest Laboratory. ESRC explores and refines new fundamental concepts that have potential for in situ remediation of subsurface contamination. ESRC also links the Subsurface Science Program with the university community through grants to graduate and postdoctoral students who are assigned research tasks in support of subprograms.

The national scientific community has assisted DOE in defining long-term research needs in environmental restoration. A basic research plan (DOE/ER-0428T) describes potential departmental scientific research needs and provides guidance to universities, national laboratories, and others on the research areas that are likely to be relevant to DOE.

Program Research Goals

The Subsurface Science Program sponsors long-term basic research on (1) the fundamental physical, chemical, and biological mechanisms that control the reactivity, mobilization, stability, and transport of chemical mixtures in subsoils and ground water; (2) hydrogeology, including the hydraulic, microbiological, and geochemical properties of the subsurface that affect contaminant mobility and stability and the numerical (predictive) modeling of coupled hydraulic-geochemical-microbial processes; and (3) the microbiology of deep sediments and ground water. The program has the following general goals:

- To develop a mechanistic understanding of subsurface (subsoil/ground-water) processes and properties, including contaminant interactions.
- To evaluate the long-term effects of contaminants and remedial action on natural subsurface systems, with emphasis on microbial ecosystems.
- To improve prediction of contaminant mobilization, stabilization, and transport, with emphasis on complex chemical mixtures.
- To develop new and more effective methods for in situ physical, chemical, and microbiological sampling, characterization, and monitoring, with emphasis on field methods.
- To identify innovative in situ remediation concepts, with emphasis on environmental manipulation (exploitation of natural subsurface properties and processes).
- To facilitate the transfer of new technology and scientific information to DOE sites; DOE's applied research, development, demonstration, test, and evaluation program; and industry.

Research Mechanisms

The Subsurface Science Program emphasizes interdisciplinary and multi-institutional research with the long-term objective of providing the scientific basis for in situ remediation of contaminated subsurface systems. New concepts for remediation that emerge from basic research on hydraulic, geochemical, and microbial processes are investigated by controlled experiments (1) at the molecular and pore scale in the laboratory, (2) using intermediate-scale flow cells and block simulators, and (3) at natural field sites on and off DOE lands. Subsurface Environmental Research Facilities (SERFs) are established at national laboratories and universities to assist investigators in conducting interdisciplinary experiments in contaminant transport and subsurface processes.

Research is conducted by interdisciplinary, multi-institutional research teams, as part of each subprogram. Goals described in this document for each subprogram provide guidance to these research teams. The goals, are expressed as projected milestones by fiscal year (FY). These milestones are difficult to predict with certainty (given the inherent uncertainties in the conduct of long-term basic research), but they serve as rough measures of progress. The goals emphasize the potential contributions of the Subsurface Science Program to the solution of DOE's environmental restoration problems; however, achievement of these goals is likely to have broader national scientific benefits.

Research Organization: Subprograms

The program is organized into subprograms in which high-priority, interdisciplinary basic research is conducted by a consortia of national laboratories and universities. Each subprogram is guided by 5-year research plans, and each has a specific research motivation, as follows:

- Co-Contaminant Chemistry Subprogram—the geochemical processes that control the reactivity, stability, and mobility of complex chemical mixtures.
- Geochemical Transport Processes/Colloids Subprogram—the genesis and role of mobile organic and inorganic particles in chemical stability and mobility.
- Multiphase Fluid Flow Subprogram—prediction of the stability and transport of immiscible fluid phases.
- Biodegradation/Microbial Physiology Subprogram—the microbiological mechanisms that control chemical stability and mobility.
- Deep Microbiology Subprogram—the microbial ecology of deep sediments and aquifers.
- Coupled Processes Subprogram—complex synergistic and antagonistic interactions among physical, chemical, and microbiological processes.
- Multicomponent Predictive Models Subprogram—strengthening of numerical predictions of coupled physical, chemical, and biological processes.
- Field Scale Subprogram—the influence of heterogeneity and scale on physical, chemical, and biological processes.

In addition to these subprograms, the Subsurface Science Program sponsors ESRC, which also conducts fundamental research in addition to its activities in university outreach, intermediate- and field-scale research facilities, and technology transfer to DOE sites.

All subprograms have information-transfer goals to ensure that new concepts that emerge from basic research investigations are made available to DOE sites, industry, and others. Approximately 2,000 plans and supporting program documents are distributed annually to DOE sites, academia, the private sector, and others. Specific technology transfer tasks within the subprograms are also delegated to DOE national laboratories, e.g., the transfer of DOE's Subsurface Microbial Culture Collection to industry at the Savannah River Laboratory.

Setting Scientific Research Priorities

Basic research within DOE is mission sensitive; therefore, consideration of long-term DOE needs is an important and necessary part of the scientific priority-setting process within the Subsurface Science Program. A formalized priority-planning process has operated since the Subsurface Science Program was established in the mid-1980's. Scientific results from each step are documented in writing. The process is as follows:

- Scientific documents that reflect new scientific advances, analysis by the Program Manager, and anticipated mission needs are merged into a preliminary scientific subprogram summary, a candidate for focused research support. The product of this step is an interdisciplinary draft scientific plan with proposed goals and priorities, candidate research opportunities, and expected future directions.
- Scientific workshops are sponsored to critique the draft subprogram summary. The workshops draw on a diversity of multidisciplinary senior scientific skills. Invited participants represent those with research interests in the scientific goals, disinterested scientists, and those with opposing scientific viewpoints. Federal and State scientific agencies are represented. Priorities are refined and reports are prepared. The products of the workshops are DOE-prepared scientific subprogram plans with research priorities, which are tools to guide multi-institutional, interdisciplinary research.
- These subprogram plans and supporting working papers are distributed widely to assist the scientific community, a source of new proposals, in determining DOE research interests and to serve as information sources to DOE offices, other agencies, and industry. Research announcements are distributed through the Federal Register or other mechanisms. The subprogram plans also assist DOE in coordination among projects.

This Subsurface Science Program priority-setting process also contributes to DOE national research plans, e.g., DOE's *Basic Research Plan for Environmental Restoration* (DOE/ER-0432T, December 1990).

Internal and External Coordination

Basic research that may lead to new environmental restoration concepts is coordinated with DOE's applied environmental restoration research programs. The primary goal is to transfer scientific concepts rapidly so that the effectiveness of environmental restoration is increased and the technological challenges associated with the use of new or existing technologies are addressed. In meeting this goal, Subsurface Science Program investigators conceptualize and conduct experiments jointly with other groups to determine the feasibility of new approaches that might increase the effectiveness of restoration and decrease DOE's environmental restoration costs.

The program coordinates the transfer of new scientific information and new environmental restoration concepts to DOE sites through workshops and on-site briefings. Also, a particularly effective means of coordination has been field research projects in which universities, national laboratories, and industry collaborate.

Various formal and informal mechanisms for interagency cooperation and coordination in basic research already exist. For example, the U.S. Geological Survey (USGS) conducts long-term research on volatilization and immiscible fluid flow that could complement DOE's research and lead to improved methods of controlling trichloroethylene (TCE) or carbon tetrachloride (CCl_4) contamination. USGS is also a leader in developing and applying new techniques for ground-water sampling and geophysical technologies. The Subsurface Science Program coordinates with the USGS's Water Resources Program and other agencies to minimize duplication of effort in university research. The Subsurface Science Program also coordinates with the Nuclear Regulatory Commission (NRC) in a variety of areas including organically complexed radionuclides, field research, and microbial processes.

The National Academy of Sciences often provides a common ground for interagency information exchange related to the physical, chemical, and biological sciences. For example, important research and priorities in the hydrologic sciences are identified in the report of the Committee on Opportunities in the Hydrologic Sciences, Water Sciences Board. The Subsurface Science Program also participates actively in the Federal Coordinating Council for Science, Engineering, and Technology (FCCSET) with representatives serving on its Committee on Earth and Environmental Sciences' Subcommittee on Water Resources Research. In addition, since 1984, numerous workshops with participants representing Federal agencies, State groups, and international agencies have been conducted to evaluate DOE's proposed future research directions.

Opportunities for Program Participation

Research grants are awarded based on competitive 3-year basic research proposals from any source. Field work proposals (FWPs) from national laboratories are treated as preliminary proposals. Full proposals, which are due on November 1 annually, are subject to review by an interdisciplinary panel in February of the following year. Full proposals (from all sources) that respond to program needs are subject to external peer review.

CO-CONTAMINANT CHEMISTRY SUBPROGRAM

Scope

Geochemical processes play a pivotal role in controlling the concentration and chemical form of contaminants in subsoil pore waters and ground waters and greatly influence subsurface transport velocities and remediation efficiencies. Research in this subprogram is addressing the aqueous-solid phase geochemical reactions of contaminant mixtures, or co-contaminants, because current scientific understanding is insufficient for forecasting contaminant behavior under the diverse subsurface conditions. The behavior of organic-radionuclide mixtures is emphasized because these mixtures are especially problematic scientifically and are unique to DOE sites. The subprogram includes research on aqueous complexation, absorption/desorption, precipitation/dissolution, valence transformation, and abiotic transformation reactions and on the manifestation of these geochemical reactions at solid phase interfaces from the molecular scale to the field scale. An improved understanding of these reactions as they relate to complex contaminant mixtures will improve predictions of environmental concentrations and risk assessment and will establish a firm scientific basis for new remediation methods.

This research is addressing the following questions:

- What surface chemical reactions occur between metals/radionuclides and codisposed organic chemicals at the mineral-water interface, and how do these interactions affect contaminant mobility?
- What is the role of natural organic matter in controlling metal or radionuclide stability, mobilization, and transport in subsoils and ground water with low carbon content?
- Does aqueous complexation of a metal cation by an organic ligand invariably lead to enhanced subsurface mobility? How do complexed metal or radionuclide ions sorb to mineral surfaces? What geochemical conditions enhance or suppress their reaction at the mineral-water interface?
- To what extent does the coupling of geochemical and microbiological processes control the overall subsurface mobility of (1) metals and radionuclides and (2) complexes of these components with organic ligands?

Goals

The overall goal of the Co-Contaminant Chemistry Subprogram is to develop a fundamental understanding of the geochemical reactions that control subsurface concentrations and fluxes and that can be used to forecast chemical stability or migration and to improve the effectiveness of environmental restoration technologies. New fundamental understanding of the interfacial processes that control ground-water chemistry and chemical evolution will also emerge from this research.

The specific subprogram research goals (which are supported by subprogram documents on model subsoils and chemical mixtures) are summarized below:

- Complete a preliminary analysis of the geochemical behavior of different types of organic chemical-radionuclide mixtures to direct future research (FY 1991); define model mixtures based on complex chemical mixtures at DOE sites (FY 1992).
- Refine technologies for measuring the speciation for inorganic and organic solutes and surface species, emphasizing uranium, plutonium, and cobalt (FY 1991-1992).
- Cooperatively with ESRC, initiate selection of a field research site (FY 1991), complete the research plan, and begin field-site characterization and measurements (FY 1992-1993).
- Identify the chemical nature (e.g., structure and bonding) of metal/radionuclide-organic ligand complexes on important subsurface mineral surfaces through direct spectroscopic interrogation (FY 1992-1993).
- Develop an improved surface-complexation modeling capability to describe sorption reactions of radionuclide complexes and mixed chemical contaminants on subsurface materials (FY 1993).
- Cooperatively with the Coupled Processes Subprogram, complete experiments on the mobility of organic-organic and organic-inorganic mixtures at the intermediate scale (FY 1993-1994).
- Provide mechanistic aqueous and surface-complexation data for organic chemical-radionuclide mixtures on subsurface materials for use with improved modeling capability (FY 1994).

Scientific Opportunities

Geochemical processes and reactions in the subsurface environment (in concert with biochemical processes) control both the chemical identity and association of contaminants and their distributions between solid and liquid phases. As a result, geochemistry determines contaminant concentrations in soil or ground water and therefore controls contaminant migration velocities and the time required to remove bound chemical contaminants from soil and aquifer solids. Geochemical reactions also exert a strong influence on the efficiency of bioremediation activities because chemicals that are bound or sorbed to the solid phase may be inaccessible to microbial degradation.

Accurate predictions of the concentrations and migration velocities of contaminants within subsoils or aquifers are currently restricted because geochemical processes associated with heterogeneous mineral material are too poorly understood. Scientific understanding of interfacial reactions, mixed solid-precipitation/dissolution reactions, and organic-inorganic aqueous and solid-phase reactions is especially limited. This lack of understanding prevents accurate prediction of contaminant geochemical behavior. Complex chemical mixtures add scientific complications in that synergistic or antagonistic reactions among contaminant species may significantly affect migration velocities. The nature, magnitude, and rates of such interactions are mostly unknown. Data bases, models, and information relevant to unique contaminant mixtures, such as organic-radionuclide mixtures found at DOE sites, are very limited.

In subsurface environments, geochemical and microbiological processes are often coupled; i.e., the progress or direction of one of these processes affects the other. An example of such coupling is the microbiological use of sulfate as a terminal electron acceptor, which leads to its reduction to sulfide. This microbially mediated change in the valence state of sulfur has profound effects on all geochemical reactions in the system. The implications of such process coupling are very poorly known and have received very little research attention within the context of contaminant geochemistry; scientific publications in this area are very limited. Lack of understanding of the effects of process coupling is one of several major reasons why predictions of mixed contaminant dynamics in the subsurface cannot be made. However, interdisciplinary research on subsurface microbiology that is being conducted in two subprograms (Biodegradation/Microbial Physiology and Deep Microbiology) provides unique opportunities for investigation of coupled geochemical-microbiological processes. Recognizing this opportunity, geochemists and microbiologists have initiated collaborative research on the influence of sorption and desorption on microbiologic degradation and transformation rates of (1) organic contaminants and (2) metals and radionuclides complexed by organic ligands.

Major research opportunities exist in the following areas:

- Interfacial processes, such as sorption and surface-catalyzed transformation on subsurface materials, with or without microbially mediated changes.
- Organic-inorganic contaminant interactions in solutions and on surfaces.
- Speciation measurements in ground water and on aquifer surfaces using spectroscopic techniques.
- Solid-solution behavior of radionuclides with major-ion solids.
- Modeling of multicomponent interfacial reactions on heterogeneous materials.
- Behavior of mixed inorganic and organic contaminants at the field scale.

Relevance and Benefits

A comprehensive understanding of the subsurface geochemical processes controlling contaminant dynamics is essential for environmental risk assessment and improved cleanup effectiveness. This research will provide basic mechanistic knowledge for improved predictions of the geochemical behavior of chemical mixtures under a variety of subsurface geochemical conditions at DOE sites. This scientific knowledge will improve predictions of the subsurface concentrations, distributions, and transport velocities of single contaminants and mixtures in the subsurface. The information and tools developed will be used to assess and minimize environmental and health risks and to prioritize sites for cleanup. Additionally, this research will establish a scientific basis for (1) selecting better restoration techniques given knowledge of contaminant types and subsurface chemistry, (2) evaluating the effectiveness of proposed site-remediation activities (e.g., well placement and ground-water extraction rates), and (3) estimating the time required for contaminants to be removed from subsurface sediments and ground water.

Basic research on subsurface geochemistry will also lead to in situ strategies to improve the effectiveness of current restoration technologies; information on contaminant dynamics can be used to identify ways of manipulating subsurface system chemistry to increase rates of desorption or dissolution of solid-associated contaminants, thereby facilitating pump-and-treat methods. Other manipulation strategies may immobilize or significantly retard the migration of mobile species, making treatment by excavation or vitrification more feasible. Methods may also be found to modify ground-water chemistry so that abiotic degradation of organic mixtures is hastened, biologic activity or toxicity is altered, and contaminant mixtures are stabilized.

GEOCHEMICAL TRANSPORT PROCESSES/ COLLOIDS SUBPROGRAM

Scope

Attempts to eliminate and remediate contaminant migration can succeed only if scientists can account for the major pathways and mechanisms of transport. This subprogram emphasizes research on the poorly understood role of submicron-size particles, or colloids, in mobilizing or stabilizing contaminants and in facilitating remediation. Models of contaminant transport processes typically treat ground water as a two-phase system with contaminants partitioning between immobile solid constituents and the mobile aqueous phase. However, solid-phase components in the colloidal size range are now known to be mobile in the subsurface, although the processes that control their genesis and mobility are poorly understood. Association of contaminants with mobile colloids may enhance the transport of strongly sorbing contaminants. Current approaches to monitoring and predicting solute transport generally neglect colloid-related mechanisms because little, if any, information is available on the abundance and distribution of colloids in ground water, the hydrogeochemical conditions controlling their formation, their affinity to bind contaminants, or their mobility in subsurface systems. Accurate assessment of current contaminant problems, engineering of containment strategies, and cost-effective remediation approaches are all dependent on a fundamental understanding of transport processes.

This research is addressing the following questions:

- Why are colloids present in ground water? Can the presence of stable colloids be predicted based on the mineralogy and hydrochemistry of the vadose and saturated zones? What is the composition, physicochemical nature, and abundance of colloids in the subsurface?
- Are colloids mobile in the subsurface? What chemical and hydrologic factors control their stabilization, transport, and deposition? Can this mobility be predicted?
- What is the capacity of ground-water colloids to sorb and transport contaminants? What mechanisms control the precipitation or deposition of chemical and radioactive contaminants sorbed to colloids?
- Can improved understanding of colloid biogeochemistry lead to remediation strategies based on manipulation of colloid mobilization or deposition?

Goals

The overall goal of the Geochemical Transport Processes/Colloids Subprogram is to establish a fundamental understanding of the physical, chemical, and hydrologic factors that control the formation, stability, and transport of colloids and colloid-associated contaminants in subsoils and ground water. A high priority has been placed on understanding the role of mobile particles on contaminant migration, especially processes controlling the genesis, stabilization, and transport of ground-water colloids under natural hydrogeochemical conditions. The interaction of mixed-waste contaminants with organic and inorganic colloids and the role of colloids in the transport of contaminant mixtures are high priorities; such fundamental understanding of mobile colloids can lead to improved contaminant transport models. This understanding will also assist in the evaluation of innovative environmental restoration strategies based on in situ manipulation of colloids. Field experiments are needed to explore colloid genesis and behavior and to determine the feasibility of remediation strategies based on geochemical manipulation of colloid behavior.

The specific subprogram research goals (which are developed in additional detail in a 5-year plan and in supporting workshop reports) are summarized below:

- Provide a framework for development of a network of field research sites across a range of conditions where colloids may occur. Initiate mechanistic laboratory, intermediate-scale, and field-scale research to identify hydrogeochemical processes that control colloid behavior (FY 1991-1992).
- Conduct an international workshop to define concepts and identify innovative strategies to manipulate colloid mobility or deposition for environmental restoration (FY 1991).
- Develop laboratory data to test and improve mathematical models that describe partitioning and transport of organic, inorganic, and radioactive contaminants in a ternary system (water, colloids, and aquifer material) (FY 1992).
- Initiate field- and intermediate-scale experiments to evaluate the effect of chemical and physical heterogeneity on colloid mobility in the vadose and saturated zones (FY 1993).
- Initiate field testing of concepts for manipulating geochemical regimes to reduce/enhance colloid mobility so that knowledge of basic principles that control colloid behavior can be used to formulate innovative in situ approaches for limiting migration or promoting recovery of subsurface contaminants (FY 1993-1994).
- Improve fundamental understanding of the formation, stability, and mobility of groundwater colloids, with an emphasis on geochemical conditions and processes encountered in natural subsurface environments (FY 1995).
- Cooperatively with the Co-Contaminant Chemistry Subprogram, describe contaminant-colloid-aquifer interactions so that partitioning and transport of contaminants in a ternary system can be modeled, including the colloid phase in contaminant partitioning (FY 1996).

Scientific Opportunities

The significance of colloids in transporting contaminants at DOE sites was identified early in 1984 as part of the planning process for DOE's Subsurface Science Program, and two international meetings on this subject were subsequently organized by DOE/OHER. This series of "Manteo Meetings" on ground-water colloids has included representatives of Federal and international research agencies and has facilitated the coordination of subprogram research with international research efforts.

Current approaches to monitoring and predicting solute transport generally neglect colloid-facilitated transport mechanisms because little or no information is available on the abundance and distribution of colloids in ground water, their affinity to bind contaminants, or their mobility in subsurface systems. Based on existing data, mobile colloids appear to be an important mechanism of contaminant transport through the vadose zone and within the saturated zone. However, this information is largely anecdotal and is inadequate either to evaluate the general significance of colloid mobility or to develop a capability to include colloid-facilitated transport in computer models that predict contaminant migration in the subsurface. The Geochemical Transport Processes/Colloids Subprogram will address these issues by providing information on the occurrence and nature of subsurface colloids and fundamental understanding of the interactions of colloids with contaminants and with immobile phases of subsurface systems.

Major research opportunities exist in the following areas:

- Identifying the physicochemical nature and abundance of colloids under a range of subsurface conditions.
- Elucidating the basic chemical, mineralogic, and hydrologic processes controlling colloid formation and deposition.
- Determining the fundamental chemical and hydrologic controls on colloid mobility and improving relevant theory.
- Applying improved understanding of contaminant-colloid and colloid-aquifer interactions to the development and validation of contaminant transport models of ternary systems that include both mobile (colloidal) and immobile solid phases.
- Evaluating the feasibility of new and innovative concepts to manipulate colloids in situ.

Relevance and Benefits

Accurate assessment of environmental risk and cost-effective remediation approaches can benefit from a fundamental understanding of geochemical transport properties. For example, research supported by DOE has revealed that transuranic elements have migrated much further at several DOE sites than had been predicted using state-of-the-art numerical models. Metals and radionuclides associated with organic or inorganic colloids have been observed migrating from disposal trenches at the Oak Ridge National Laboratory, from mixed-waste sludges at Los Alamos, from a nuclear detonation cavity at the Nevada Test Site, and in contaminant plumes at the Chalk River Nuclear Laboratory in Canada. New insights into the hydrogeochemical processes that control colloid formation, deposition, and transport can lead to new cost-effective strategies to use the environment itself to assist in environmental restoration. Research at a network of field sites, once integrated, will lead to predictions on the specific hydrogeochemical conditions that control the formation and mobilization of colloids and the environmental risks that may be a result of colloid-facilitated transport. New information on the interaction of natural colloids with single contaminants and co-contaminants and on the role of mobile colloids on contaminant transport is needed for improved predictive models. Integrated laboratory and field studies that are directed to increasing fundamental understanding of colloid behavior and of the factors governing colloid formation and mobilization may also provide a basis for colloid manipulation that will facilitate environmental restoration at DOE sites.

MULTIPHASE FLUID FLOW SUBPROGRAM

Scope

The subsurface of many DOE sites is contaminated by organic liquids, such as fuels and chlorinated hydrocarbon solvents, that may include other dissolved contaminants such as radionuclides. Whether these liquids are retained or move in subsoils or ground water depends on their physical and chemical properties; they are generally immiscible with water and migrate as separate, nonaqueous phase liquids (NAPLs) in ways that are difficult to predict. These liquids are also potential long-term sources of subsurface contamination as they slowly dissolve in ground water. Their finite solubility in water requires an understanding of the mechanisms that control their dissolution, biodegradation, and transport in ground water. This subprogram focuses on developing an improved fundamental understanding of how water and organic liquids interact and of the physical and chemical conditions under which they are retained in porous media or transported as separate phases. Experimental approaches that clarify the theory underlying the mobility of immisicible organic liquids are emphasized. The subprogram assists in experimentally verifying hypotheses on liquid partitioning at the pore and multipore levels, extending these observations to heterogeneous systems, refining theory as required, and devising predictive tools based on confirmed principles.

This research is addressing the following questions:

- What physicochemical phenomena influence the retention and mobility of organic liquids in subsurface porous media?
- What mechanisms control their transfer between gaseous and aqueous phases?
- What mechanisms govern the behavior of these organic contaminants in the unsaturated zone and in ground water?
- How do interfacial tensions between water and organic fluids influence pressure differences between fluids; what is the relationship of these pressures to the retention of fluids in small pores or capillaries?
- What are the effects of pore-size distribution, interconnection, and orientation on flow at the macroscopic scale where a continuum of these effects is manifested?

Goals

The overall goal of the Multiphase Fluid Flow Subprogram is to develop a better fundamental understanding of how immiscible organic liquids behave in the subsurface as a basis for improved predictions of flow and transport in unsaturated and saturated systems. This overall research effort provides the basis for a constitutive theory that links observations at the pore level to the macroscopic scale encompassing many pores. This information is verified in three dimensions by evaluating the influence of heterogeneities such as layering and by scaling relationships up from the laboratory to the intermediate and field scales.

The specific research goals (which are supported by various workshop reports and research plans) are summarized below:

- Establish the relationship between interfacial chemical properties and retention behavior for water and organic liquids in aquifer porous materials (FY 1992).
- Transfer subprogram experience in predicting subsurface multiphase fluid movement to assist in a DOE-integrated demonstration of the cleanup of hazardous organic liquids at one DOE site (FY 1994).
- Complete intermediate-scale experiments to identify effects of heterogeneity on immiscible fluid flow in porous media using experimental flow cells (FY 1995).
- Incorporate understanding of pore-scale processes and transport porous media into improved predictive models to assist those involved in the restoration of sites contaminated by organic liquids (FY 1995).

Scientific Opportunities

The ability of existing multiphase flow and transport models to predict the location and extent of NAPL or dense nonaqueous phase liquid (DNAPL) contamination in the subsurface environment has not been confirmed. Moreover, models used in the petroleum industry are not directly applicable to contamination problems occurring at DOE sites, especially in vadose zones. Few experiments have been conducted and compared with model simulations for liquid and vapor movement of a volatile organic liquid such as TCE within the vadose zone. Current multiphase flow models cannot predict three-dimensional fluid movement in heterogeneous subsurface media. Thus, experiments are needed to study the actual behavior of organic liquids and to refine multiphase models.

Immiscible organic liquids that enter the subsurface may exhibit either continuous or fragmented (fingering and channeling) flow behavior, depending on their density and chemical interfacial properties with water and the characteristics of the porous medium within which they move. Progress has been made on understanding constitutive relations (model parameters governing retention and fluid conduction) for granular porous media when flow is continuous. But when flow is fragmented, the models' ability to describe that behavior is unknown. Thus, the predictability of flow for organic liquids such as TCE or CCl_4 is uncertain.

Assessing NAPL contamination in a vadose zone is difficult because no standard techniques or instruments exist for measuring liquid concentration. Instruments that measure vapor-phase concentrations do not determine the amount of trapped organic liquid that may cause continued ground-water contamination. Measurements must be used with models to assess the contamination before appropriate remediation strategies can be planned. Thus, improved fundamental understanding of NAPL behavior should provide the basis for identification of the nature and scale of measurements required for models that integrate key factors to predict subsurface migration and contamination by NAPLs.

To predict soluble transport of organic chemical components, their dissolution rates must be modeled accurately. However, the theory for interphase mass transfer is not fully developed, nor is the vapor-phase flow of volatile organics adequately understood. Thus, research is needed to determine the appropriate mass transfer coefficients for NAPLs in the subsurface media that exhibit the range of properties characteristic of DOE sites.

It is not known whether multiphase flow processes can be accurately simulated for the heterogeneous subsurface. Field-scale manifestations of processes are quite different from those observed at pore scale. Subsurface heterogeneity does not allow the direct extrapolation of laboratory-scale parameters to field-scale conditions. Thus, parameters that are required for field-sale modeling may differ from those determined in the laboratory. Better mathematical formulations are needed to incorporate experimentally determined parameters that describe flow and transport and to scale these observations to the field.

Major research opportunities exist in the following areas:

- Field research at sites with NAPL and DNAPL contamination to confirm and scale observations in the laboratories.
- Mathematical approaches for addressing the problems of scaling caused by subsurface heterogeneity.
- Efficient multiphase flow and transport codes to implement the theory for integration of processes in three dimensions; models, both conceptual and mathematical, to predict the movement of organic liquids and their distribution in different phases in the subsurface.
- Organic vapor flow in the vadose zone, especially with dense liquids such as TCE.
- Constitutive theory for nonisothermal influences on multiphase flow behavior.
- Field instruments to measure NAPL fluid content in subsurface media and other parameters essential to prediction of behavior; new concepts and methods for determining the types and quantities of organic liquids in the subsurface environment.

Relevance and Benefits

Dating back to the 1950's, some DOE sites have experienced spills and leakage of hydrocarbon products and organic chemical solvents that enter the subsurface environment and become potential sources of ground-water contamination. Adequate predictions of the mobility of these liquids require a better theoretical and experimental understanding of multiphase flow and transport behavior. New insights are needed, especially into the subsurface behavior of DNAPLs such as CCl_4 and TCE. Knowledge of multiphase flow behavior of NAPLs and DNAPLs in the subsurface is limited to theory based on physical principles, which have yet to be confirmed for the vadose zone or for naturally heterogeneous aquifers.

Although high concentrations of dissolved petroleum products and halogenated hydrocarbon solvents have been found in ground water beneath some DOE sites, it is usually not known whether immiscible organic liquids now exist as free-form NAPLs or DNAPLs in the subsurface at these sites. Existing ground-water monitoring programs at DOE sites are poorly equipped to determine the presence of NAPLs and DNAPLs in the vadose zone. New concepts for explaining their behavior and specialized measurement and predictive techniques are required to determine if NAPLs or DNAPLs are trapped in the unsaturated or saturated zones and will be long-term, continuing sources of ground-water contamination. New strategies for remediating residual organic liquid contaminants trapped by capillary effects in the subsurface environment may emerge from the research.

BIODEGRADATION/MICROBIAL PHYSIOLOGY SUBPROGRAM

Scope

Microbiologically mediated processes control the concentration, toxicity, and chemical form of contaminants in the subsurface. Bioremediation, which includes the use of microorganisms to transform and/or immobilize environmental contaminants, has been identified by DOE as a tool that has considerable potential for environmental restoration of DOE sites and other hazardous-waste sites nationwide. Bioremediation is the focus of an emerging industry founded on empirical results and rarely on a basic scientific understanding of microbial ecology. Research within this subprogram will focus on developing information on the mechanisms that are fundamental to successful bioremediation of contaminated subsurface environments. Research on metabolic pathways, mechanisms of microbiological growth and transport, and the genetics of microbial strains is conducted at scales ranging from the molecular (genetic and enzymatic processes) to the field using iterative laboratory and field experimentation.

Although this subprogram collaborates with the Deep Microbiology Subprogram, the two subprograms differ in their experimental approach, the time frame within which they are likely to be relevant to DOE remediation needs, and their focus. The Biodegradation/Microbial Physiology Subprogram focuses on developing fundamental information for in situ bioremediation, with the goal of refining an emerging technology. The Deep Microbiology Subprogram focuses on the ecology and functions of subsurface microorganisms in deep sediments and aquifers where bioremediation (or other cleanup) technology has yet to be demonstrated.

The research conducted by the Biodegration/Microbial Physiology Subprogram is addressing the following questions:

- What microbial aerobic and anaerobic metabolic pathways lead to degradation or alteration of the constituents present in organic/organic and organic/radionuclide-metal contaminant mixtures?
- What hydrophysical, chemical, and biological mechanisms limit the growth, activity, and transport of bacteria in porous media?
- What catabolic and resistance genes and promoter sequences are candidates for improving microbial strains for contaminated site restoration?

Goals

The overall goal of the Biodegradation/Microbial Physiology Subprogram is to develop a fundamental understanding of the biochemistry and genetic regulation of aerobic and anaerobic microbial metabolism of contaminant mixtures; biological, chemical, and hydrophysical factors limiting metabolism, cometabolism, and other biotransformations; and bacterial transport and function in porous media. New fundamental understanding of microbially related mechanisms will lead to improved predictions of the fate and transport of contaminants in the subsurface and to improved concepts for in situ biodegradation and stabilization of dispersed inorganic contaminants.

The specific research goals of the subprogram are summarized below:

- Evaluate the DOE Subsurface Microbial Culture Collection for bacteria with phenotypic and genotypic features that are useful for remediation/stabilization of DOE wastes (FY 1992-1993).
- Improve the mechanistic understanding of the microbial metabolism of organic-radionuclide mixtures and its impacts on radionuclide mobility (FY 1991-1995).
- In cooperation with the Deep Microbiology Subprogram, initiate sampling of stressed environments (e.g., high-temperature environments, deep pristine and contaminated ground-water systems, and natural deposits of radionuclides) to isolate and characterize microorganisms for use at remediation sites and for genetic engineering (FY 1992-1994).
- In cooperation with DOE's applied research program, construct strains to enhance degradation of organic chemicals or resistance to metals and radionuclides (FY 1993-1996).
- Develop and evaluate in situ bioremediation concepts for chemical contaminant mixtures using laboratory and intermediate-scale experimental systems containing heterogeneous media (FY 1993-1996).
- Evaluate the ability of microorganisms to limit the transport of radionuclides and metals in porous media by means of bioaccumulation/biosorption. This evaluation may lead to new concepts for in situ containment of contaminants (FY 1993-1995).
- In cooperation with the Coupled Processes Subprogram, develop and test concepts and predictive models for delivering microorganisms, nutrients, electron acceptors, and electron donors to the subsurface environment to stimulate in situ growth and metabolism (FY 1991-1995).
- Evaluate in situ biological processes such as transport of microorganisms, stimulation of growth and metabolism, and bioclogging at a DOE field site (FY 1994).
- In cooperation with ESRC, evaluate and refine approaches for in situ biological degradation of organic components (and stabilization of inorganic components) of co-contaminants at a DOE field site (FY 1992-1996).

Scientific Opportunities

The subsurface contaminants at DOE sites are complex mixtures of organic and inorganic chemicals, including short- and long-lived radionuclides, that represent unusual scientific challenges. First, relatively little scientific information exists concerning the basic biochemical mechanisms involved in the aerobic, anaerobic, and microaerophilic microbiological transformation of contaminant mixtures. Also, toxic mixtures of organic and inorganic contaminants may be limiting in situ bioremediation. The toxicity of organics, radionuclides, and metals to microbial activity is likely to be an acute problem at DOE sites. As a result, introduction of resistant microbial strains may be necessary to degrade organic, and stabilize inorganic, contaminants. Successful introduction of microorganisms to the subsurface will require an understanding of biological, chemical, and hydrophysical factors, including transport of microorganisms. The use of molecular biological techniques to improve microbial strains for subsurface biodegradation of organic contaminants and transformation of inorganic contaminants offers considerable promise for bioremediation. However, the molecular biology of indigenous subsurface microorganisms must be better understood and novel approaches and genes must be identified before improved remediative strains can be developed. The Biodegradation/Microbial Physiology Subprogram focuses on developing the scientific information necessary to overcome such biological and physicochemical limitations to in situ subsurface bioremediation in the long term.

Major research opportunities exist in the following areas:

- Understanding of aerobic and anaerobic microbial metabolism of contaminant mixtures such as organic-radionuclide complexes.
- Novel approaches for stimulating and maintaining microbial viability and activity in the unsaturated and saturated zones of the subsurface.
- Identification, characterization, cloning, and expression of microbial genes useful for bioremediation, such as catabolic and resistance genes.
- Understanding of the interactions between microbial processes and geochemical and hydrologic processes, including biodegradation-sorption relationships, that influence contaminant fate.
- Laboratory and field research that can lead to new concepts of bioremediation, including in situ stimulation of microbial metabolism, transport of bacteria, and bioclogging processes.
- Understanding of the microbial processes that control the degradation of organic chemicals in organic-radionuclide mixtures and the effects of such degradation on radionuclide mobility.
- Identification of microorganisms with genes that code for specialized functions that are potentially useful for biodegrading/stabilizing complex chemical mixtures.

Relevance and Benefits

The use of microorganisms for modifying or stabilizing contaminants at DOE sites offers considerable promise for site restoration. However, in situ microbiological processes in subsurface environments must be better understood before advances in bioremediation technology can be achieved. Little fundamental information is available regarding deep subsurface microbial ecology, and even less information is available on microbial transformation of the complex contaminant mixtures that are common at DOE sites. The factors often identified as potential limitations of successful in situ remediation include (1) a lack of indigenous microorganisms that can degrade or transform the target contaminant(s); (2) the recalcitrant nature of certain contaminants, which inhibits the rate of degradation by microbes; (3) inhibition of microbial activity by contaminant toxicity; (4) ineffective delivery of electron donors, electron acceptors, or other nutrients to stimulate the growth and metabolism of indigenous microorganisms and ineffective delivery of microorganisms themselves (e.g., genetically engineered microorganisms); and (5) physicochemical inaccessibility of contaminants to microorganisms (e.g., contaminants sorbed to inorganic/organic solids).

The biodegradation or stabilization of contaminants and the transport processes that control the delivery of nutrients and microorganisms in the subsurface must be better understood to predict environmental and human health risks and to develop bioremediation concepts in the long term. Understanding transport processes is important because economical bioremediation of DOE sites will require the addition of nutrients and/or microorganisms. Microorganisms that can survive and function under harsh (e.g., alkaline, radioactive, metallic, or otherwise toxic) environmental conditions will be needed for in situ treatment of DOE wastes. Therefore, microorganisms obtained from environments with such harsh conditions (e.g., radioactive mineral deposits, deep carbonate aquifers, and contaminated DOE sites) will be isolated and characterized. The probability is high that these microorganisms will possess genes that code for useful functions or traits, and such microorganisms can be used in developing concepts and microbial strains for bioremediation.

Benefits specific to DOE site remediation include the following: new concepts for in situ remediation/ stabilization of DOE-waste-derived chemical mixtures in subsurface environments; new general concepts and models for in situ stimulation of microbial activity and transport of microorganisms and solutes through porous media; improved predictions of the fate and transport of DOE-specific contaminants; identification of biological transformation products, which may pose less or greater environmental risk than their parent chemical mixtures; selection of biologically treatable contaminants and sites; and potential cost reductions for site cleanup.

DEEP MICROBIOLOGY SUBPROGRAM

Scope

The Deep Microbiology Subprogram supports fundamental research to determine the presence, abundance, diversity, metabolic capabilities, and genetic/phylogenetic traits of microorganisms in saturated and unsaturated subsurface environments. The subprogram also conducts research to determine how chemical and physical environmental factors affect subsurface microbial communities and microbial metabolism as it, in turn, affects degradation or stabilization of contaminants. Long-term basic research in deep microbiology can be expected to provide (1) significant new information on subsurface microbial ecology and heterogeneity, (2) new methodologies, e.g., methods for rapid characterization of microbes and for aseptic sampling of subsurface materials, and (3) new concepts that can be used in developing new technologies for in situ bioremediation of contaminated subsurface systems. Developing new bioremediation methods that use deep subsurface microbes will require detailed knowledge about these organisms and how they interact with their environment.

This research is addressing the following questions:

- Are microorganisms present in deep subsurface environments? If so, are they metabolically active or in a dormant or inactive physiological state? Do the microbial populations that are present represent diverse functional groups and species or are they dominated by relatively few individuals?
- What are the relationships between the population size, diversity, and activities of subsurface microbial communities and the physical and chemical properties of their surrounding environment? Can such relationships be generalized across different subsurface environments so that they can be used to predict the presence, abundance, and activities of subsurface microorganisms based on known or measurable geological, geochemical, or hydrophysical properties?
- Are deep subsurface microorganisms phylogenetically distinct from surface microorganisms? Do they have novel metabolic functions that may have potential applications for bioremediation?
- Do subsurface microbial communities vary with different geological parent material, or do they vary in composition and activity on a finer (e.g., centimeters or less) scale? Are subsurface microbial communities more diverse and their associated metabolic activities higher in strata that are relatively permeable to water, at interfaces between different geological strata, and/or in strata of varying hydraulic conductivity?
- What is the origin of deep subsurface microbial communities? Do these communities represent descendants of organisms associated with the original surficial deposits, and how does their phylogeny compare with ancient genera of surface bacteria (e.g., archaebacteria)? Alternatively, have these communities been transported to their present location more recently and, if so, when?

Goals

The overall goal of the Deep Microbiology Subprogram is to conduct basic research leading to an improved understanding of subsurface microorganisms and their ecology. Of particular interest will be information relevant to the use of subsurface microorganisms for in situ bioremediation (degradation and/or stabilization) of contaminants at DOE sites.

The specific subprogram research goals are summarized below:

- Develop an information base on spatial and vertical presence, abundance, diversity, and metabolic traits of subsurface microorganisms at one research site (FY 1990).
- Transfer the Subsurface Microbial Culture Collection to pharmaceutical industries (FY 1990) and bioremediation industries (FY 1992); increase university access to the collection (FY 1991).
- Develop and refine sampling protocols and sample-handling methodologies for obtaining uncompromised subsurface samples for microbiological, hydrogeologic, and chemical analyses (FY 1990).
- Make novel aseptic sampling protocols and sampling-handling methodologies available to DOE sites and private industry (FY 1991-1992).
- Develop a comparative knowledge base on microbial presence, abundance, diversity, metabolic capabilities, and genetic traits in geochemically and hydrologically diverse subsurface systems (FY 1992-1994).
- Develop a knowledge base on sediment/ground-water/microbial interactions to assist in the prediction of microbial bioremediation capabilities based on physical and chemical data (FY 1993-1995).
- Begin research to refine concepts for bioremediation of a deep hydrogeologic system at a field research site (FY 1995).

Scientific Opportunities

The subsurface environment was virtually ignored by microbial ecologists for many years because subsurface microbial populations were generally believed to be much smaller and less diverse than those in surface soils and other surface environments. Although studies describing the presence of microbes in the subsurface (sometimes at considerable depths) were reported sporadically between 1915 and 1980, none of these studies included a thorough analysis of aseptically obtained subsurface materials. Interest in subsurface microbiology was rekindled in the early 1980's, however, when ground-water contamination emerged as a major environmental issue and when new sampling methods and new methods for isolating microbes from low-nutrient environments made it possible to show conclusively that subsurface environments (specifically, shallow aquifers less than 100 feet below land surface) actually contain surprisingly large microbial populations. Although this finding suggested that deeper systems might also contain substantial numbers of microorganisms, the deeper systems had yet to be studied in detail when planning for the Deep Microbiology Subprogram began in 1984.

The Deep Microbiology Subprogram addresses the current lack of information on subsurface microorganisms, their activities, and their ecology. Microorganisms in relatively deep environments (those more than 100 feet below land surface) have been given highest priority, although surface and near-surface organisms are included for comparison. Because almost nothing was known when the program began, obtaining fundamental data on deep subsurface microbiology and microbial ecology was necessary before issues more directly related to the bioremediation of contaminants could be addressed.

Major research opportunities exist in the following areas:

- Spatial distributions of microorganisms in subsurface environments.
- Determination of the phylogenetic relationships among subsurface bacteria.
- Determination of the genesis of deep microorganisms.

- Interactions between microorganisms and deep subsurface sediments and lithologies (geomicrobiology).
- Geological, geochemical, and hydrologic factors controlling the distributions and activities of deep subsurface microorganisms.
- Diversity and metabolic properties of deep subsurface microorganisms.
- Capacity of aerobic and anaerobic subsurface bacteria for degrading organic contaminants and transforming organic radionuclide complexes.
- Impact of organic-radionuclide-metal contaminants on the composition and activities of subsurface microorganisms.
- Functions and activities of microorganisms in deep vadose-zone sediments and lithologies.
- Factors limiting in situ growth, survival, and metabolic activity.

Relevance and Benefits

Detailed information on subsurface microorganisms and their ecology is needed to (1) assess the potential for in situ bioremediation of subsurface contaminants at DOE sites and (2) develop approaches for stimulating the subsurface microbiota at these sites for bioremediation. Technology to clean up deep sediments and aquifers cost effectively is unavailable. The restoration of subsurface environments with mixed hazardous wastes will be very expensive if carried out with current methods. Treatment of contamination in situ appears to be more practical than traditional approaches (such as pump-and-treat methods) because the contaminants are typically located far (sometimes hundreds of feet) below the land surface. As a result, cost-effective techniques for the in situ removal and/or stabilization of subsurface contaminants are clearly needed.

Bioremediation—the use of living organisms (usually microorganisms) to degrade or stabilize environmental contaminants—is a potentially powerful method for the in situ treatment of subsurface contaminants. Microorganisms have been shown to effectively degrade a variety of toxic substances in near surface soils and sediments (depths to 100 feet). DOE has recently found that substantial numbers of microorganisms inhabit even deeper environments, and some of the newly discovered microorganisms are physiologically capable of degrading recalcitrant organic chemicals. Although the deep subsurface microbes have been characterized preliminarily, little or no specific information is available on how they might be used for bioremediation.

Long-term basic research within this subprogram will include characterization of subsurface microbial communities (in terms of presence, abundance, diversity, metabolic capabilities, and phylogeny) and will examine the ways in which subsurface microorganisms interact with and are affected by their environment. Such research can assist in subsurface restoration by providing information useful in the development of new in situ bioremediation methods. In turn, new bioremediation methods can help DOE meet its long-term site restoration needs.

The Deep Microbiology Subprogram's fundamental research activities are also likely to have benefits unrelated to bioremediation of subsurface contaminants, such as a substantially increased basic understanding of subsurface microbial ecology. New methods for obtaining subsurface samples and new molecular biological techniques for rapid characterization of microorganisms will also have general applications. Additional benefits (e.g., an important new antibiotic) may result from the transfer of the Subsurface Microbial Culture Collection to the pharmaceutical industry and other parts of the private sector.

COUPLED PROCESSES SUBPROGRAM

Scope

Simultaneous chemical, microbiological, and hydrologic processes affect the fate of contaminants in the subsurface environment. Furthermore, these interacting processes at the pore scale can greatly influence contaminant migration and the effectiveness of remediation methodologies at the field scale. For example, sorption may render contaminants inaccessible to microbes and thereby reduce the rate of biodegradation. Microbial activity/growth may alter the sorbent properties of subsurface materials and the affinity of contaminants for these materials or may reduce hydraulic conductivity, thereby changing contaminant aqueous concentrations and transport velocities. Research is needed to quantify the mechanisms of important process interactions and to find mathematical means for describing these phenomena for predictive purposes. Moreover, because the subsurface is spatially heterogeneous with respect to chemical, microbial, and physical properties, the manifestation of these interacting processes at the field scale must be understood. This subprogram conducts interdisciplinary research focused on the interactions of sorption and degradation processes during the transport of organic/organic and organic/radionuclide mixtures through porous media. The subprogram emphasizes experiments at the intermediate scale, in which process interactions and heterogeneity can be examined systematically under controlled conditions, to better understand how the phenomena occur in the field.

This research is addressing the following questions:

- How does sorption/desorption of other forms of multicomponent chemical equilibria affect contaminant biodegradation in dynamic flow systems?
- How do attached microorganisms or organic coatings of microbial origin affect the sorption capacity and permeability of surface sediments? How do these alterations affect the reactive transport of mixtures of organic and radionuclide contaminants?
- How does microbial activity alter the spatial variability of inorganic chemistry and dissolved gases in ground water? How do these changes affect chemical speciation, mineral weathering, and transport of reactive contaminants? How do chemical microenvironments influence microbial diversity, distribution, and evolution in dynamic flow systems?
- Do the nature and reactivity of natural organic matter influence the availability of electron donors and acceptors that facilitate biological processes? Does the coupled interaction or dependence of aerobic and anaerobic microorganisms promote biodegradation of contaminants during transport?
- How do microbial distribution and transport, as affected by sediment properties, contaminant plume composition, and groundwater flux, influence contaminant biodegradation?
- Are microbial growth and activity significantly different in adjacent porous media layers and at the layer interface? What processes at the interface affect contaminant sorption, degradation, and transport?
- How can the understanding of process mechanisms and interactions gained through laboratory experimentation be scaled up for use in the field, where spatial heterogeneity is complex and measurements are limited?

Goals

The overall goal of the Coupled Processes Subprogram is to develop a fundamental understanding of the interactions between sorption, degradation, and microbial growth that occur during water flow and contaminant transport through spatially heterogeneous porous media. Emphasis is placed on experimentation in multidimensional flow cells of sufficient size where coupled physical, chemical, and microbiological phenomena are manifested and can be examined in heterogeneous porous media under controlled conditions (i.e., intermediate in size between pore-scale and field-scale investigations). Such intermediate-scale experiments provide the critical step in scaling up laboratory understanding of subsurface processes to the field. Emphasis is on contaminant mixtures of concern to DOE: initially, organic/organic and organic/radionuclide solute mixtures and, over the longer term, contaminants associated either with immiscible organic liquid phases or with mobile colloids. The research goals of the subprogram evolved from the results of three DOE/OHER-sponsored workshops held between 1987 and 1990 that identified the need for intermediate-scale experimentation, defined the nature of experimentation required, established research priorities, and evaluated the results of initial approaches.

Specific subprogram goals are summarized below:

- Evaluate the following advanced methods/instruments for measuring coupled process interactions at the intermediate scale: seismic imaging for hydrophysical properties, in collaboration with the Field Scale Subprogram (FY 1991); fiber-optrode sensors for contaminant concentrations, in collaboration with the Biodegradation/Microbial Physiology Subprogram (FY 1992); and fluorescent compound probes for microbial biomass/activity, in collaboration with the Deep Microbiology Subprogram (FY 1993).
- Determine the role of spatial heterogeneity in redox potential in radionuclide transport, in collaboration with Co-Contaminant Chemistry Subprogram (FY 1992-1994).
- Determine the effect of redox manipulation on geochemical and microbial processes during fluid flow, in collaboration with ESRC (FY 1992-1994).
- Define sorption/degradation interactions during the transport of organic/organic and organic/radionuclide mixtures in layered porous media, in collaboration with the Co-Contaminant Chemistry Subprogram (FY 1992-1994).
- Conduct experiments on contaminant sorption and biodegradation during transport using whole cores obtained during field-site drilling (termed GEMHEX experiments), in collaboration with the Deep Microbiology Subprogram (FY 1991-1993).
- Examine the effect of the coupling of microbial growth and hydraulic permeability on contaminant transport in multidimensional flow systems, in collaboration with the Biodegradation/Microbial Physiology Subprogram (FY 1993-1994).
- Test hypotheses on spatial distributions and movement of microbes across sediment layer interfaces, in collaboration with the Deep Microbiology Subprogram (FY 1993-1995).
- Define complex interactions that control the transport of microorganisms, nutrients, electron acceptors, and electron donors in multidimensional, radial flow systems to stimulate in situ growth and metabolism, in collaboration with the Biodegradation/Microbial Physiology Subprogram (FY 1991-1995).
- Transfer application models that have been simplified (based on mechanistic understanding gained through intermediate-scale experimentation) to use limited measurements available in the field (FY 1992-1996).

Scientific Opportunities

A strong need exists for understanding the mechanisms of interactions that take place when multiple processes occur simultaneously in subsurface systems. Conceptualizations of the role of interactive chemistry and microbiology in transport theory have yet to be validated through experimentation. Furthermore, most mechanistic laboratory research and associated theory for sorption and biodegradation focus on systems with a single contaminant solute rather than dealing with chemical mixtures, which are characteristic of DOE site contamination. Thus, the need to explain the behavior of contaminant mixtures and the interaction of processes that influence that behavior constitutes one of the greatest scientific challenges to predicting contaminant transport in the subsurface.

Several recent field studies have resulted in observations that cannot be explained on the basis of field and small-scale laboratory measurements alone. The inability to explain these observations is the result, in part, of a lack of understanding on how to scale knowledge gained from small-scale laboratory experiments (and associated modeling theory) to the field, where multiple processes occur simultaneously and spatial heterogeneity is often complex.

Intermediate-scale experiments are a critical rung in the ladder of scaling laboratory observations to the field because of the new insights they provide. For example, batch studies of biodegradation provide critical information regarding degradation pathways and rates. Column studies provide additional information on how degradation rates may be enhanced during water flow because toxic byproducts of biodegradation are removed. However, these studies together still cannot provide information regarding additional important phenomena that are caused by macroscopic-scale porous media heterogeneity. For example, recent intermediate-scale research has shown that microbial distribution, growth, and activity across sediment layer interfaces can be significantly different from the distribution, growth, and activity within the layers. The differences can have a major influence on overall contaminant transport and transformation.

Intermediate-scale experimentation provides the opportunity to test hypotheses related to the manifestation of processes and process interactions in systems with spatial heterogeneities in physical, chemical, and microbiological properties. Because systems used in intermediate-scale experimentation allow the use of field-relevant flow rates and residence times, they will be particularly suited for the evaluation of new ways to manipulate and measure physical, chemical, and microbiological processes and their interactions under controlled conditions.

A key issue in scaling up to the field is the formulation of reactive transport models that account for important processes and process interaction mechanisms using parameters that can feasibly be measured in the field. Intermediate-scale experimentation can help fill the gap in modeling theory because mechanistic experimental data can be reanalyzed within the context of simplified or spatially averaged models so that improved methods for calculating parameters for more field-applicable models can be developed.

Major research opportunities exist in the following areas:

- Mechanistic understanding of interactive sorption, biodegradation, microbial growth, and solute transport processes in porous media.
- Solute competition effects (during sorption and biodegradation) in organic/organic and organic/radionuclide mixtures, including competitive effects of biotransformation products.
- Microbial distribution and function across layer interfaces and mechanistic descriptions of how spatial heterogeneities in sediments affect contaminant biodegradation during transport.
- Methods for scaling up process-level information to the field and incorporation of these methods into simplified or spatially averaged transport models.

Relevance and Benefits

Understanding and accurately predicting the role of process interactions on subsurface contaminant behavior in the field is essential to DOE environmental restoration. Research in this subprogram will lead to improved predictions of contaminant distribution, concentration, transformation rate, and transport velocity in the field. Controlled laboratory experimentation will allow development of quantitative mathematical descriptions (governing equations and analytical or numerical solutions) of process interactions and of the alteration of subsurface behavior by interactions between contaminants within a mixture. New concepts will be developed to address spatial heterogeneity in the field, which exerts a profound influence on overall contaminant transport and transformation behavior. For example, recent field research has shown that the source of simple organic compounds needed by microbes for degradation in aquifers may be fermentation by other microbes in adjacent low-permeability layers followed by diffusive interlayer transfer. Intermediate-scale experimentation in layered flow cells has already helped quantify microbiological and physical phenomena involved in these important field processes. Recent field experiments on reactive solute transport have also shown apparent scale effects in field estimates of sorptive retardation coefficients. The results of studies in porous media with controlled heterogeneity are advancing the theory needed to predict these scale effects from mechanistic understanding of how the heterogeneities affect the manifestation of sorption and degradation during transport. In addition, during intermediate-scale experimentation, opportunities are available to develop and test advanced methods/instrumentation for measuring parameters critical to quantifying the effects of these processes in the field.

This research will assist in providing a scientific basis for new remediation concepts that involve manipulating process interactions, i.e., methods in which one process is manipulated to cause a change in another process. The research will also improve the design of current remediation methods. For example, attempts to remediate contaminated field sites through injection of microbes and chemical compounds intended to stimulate microbial growth and degradation have resulted in aquifer plugging due to excess microbial growth. The interactions that cause this excess growth are not fully understood. Identifying and quantifying these interactions ensures that the probability of these secondary effects of manipulation can be minimized.

MULTICOMPONENT PREDICTIVE MODELS SUBPROGRAM

Scope

Predictive hydrologic models may be used in many practical and theoretical endeavors. Traditionally, they have been associated with practical engineering applications encountered in hazardous waste problems where they can be used to (1) characterize groundwater flow, contaminant migration, and contaminant transformation in soils beneath waste sites under natural or stressed conditions; (2) design, analyze, or optimize the performance of restoration projects; or (3) assess associated health risks, aid in making regulatory decisions, or demonstrate compliance with environmental laws. Recently, models have also been applied in a fundamental role to visualize, examine, or quantify complex, interacting processes that might otherwise be immeasurable in the field or the laboratory. Models may also serve as alternative environments in which detailed physical or chemical experiments may be conducted. The scope of research in this subprogram is focused in this latter direction. In this perspective, large-scale, sophisticated computer simulations can be used to improve our understanding of complicated phenomena that occur in (pseudo) realistic systems, to develop newer measures of uncertainty or reliability in practical or simple modeling efforts, or to provide a systematic, process-oriented approach for design and interpretation of intermediate-scale or field experiments.

Key research priorities in this subprogram include (1) the development of computationally efficient, chemical transport models that incorporate diverse chemical or biological phenomena (specific adsorption, ion exchange, dissolution/precipitation, or microbial transformation and degradation) associated with complex organic-radionuclide mixtures; (2) experimental use of such models in spatially variable systems to discern the effects of physical, chemical, or biological heterogeneities on contaminant migration patterns (e.g., to determine the more dominant processes that influence migration or to study homogenized or effective behavior in field systems); and (3) development of specific methodologies for quantifying and reducing uncertainties associated with variable physical scale, measurement error, and minimal data sets. In many of these applications, implementation of the models on parallel or other large-scale computational equipment is required because of problems of size, complexity, or overall computational cost efficiency. This research also contributes to artificial intelligence-based expert systems that can be used by environmental engineers and site managers to design and apply cost-effective contaminant containment and restoration technologies.

Research in this subprogram is addressing the following questions:

- How may computational models be used to investigate complex processes or to quantify effective and scale-dependent behavior associated with the migration and transformation of reactive organic/radionuclide mixtures in heterogeneous subsurface environments?

- What computational approaches may be taken to integrate geochemical and microbiological processes (specific adsorption, ion exchange, dissolution/precipitation, or microbial transformation and degradation) into numerical models that describe hydrologic flow and transport in heterogeneous porous media?
- What types of physical, chemical, and biological processes most strongly influence migration behavior? What particular mechanisms or processes will be relevant for the description of effective or scale-dependent behavior? Can the bulk of effective behavior be simply and quantitatively described for practical use in field problems?
- What approaches should be used to quantify or describe uncertainty (arising from variable physical scale, measurement error, and minimal data sets) in predictive models? What kinds of methods may be used to assess the reliability of model predictions?
- How will analyses and descriptions of effective or dominant behavior, reliability, or uncertainty (as determined through simulations using idealized representations of heterogeneity or chemical phenomena) compare with actual behavior in real systems?

Goals

The principal research goal of this subprogram is to improve the ability to predict contaminant migration and transformation of complex chemical mixtures within naturally heterogeneous subsurface systems, as based on a stronger understanding of the dominant physical, chemical, and biological processes. The goal is expected to be accomplished through a combination of efforts devoted to (1) implementation of more realistic descriptions of chemical and biological transformation processes within transport models, (2) large-scale computational experimentation to quantify the effects of process coupling, (3) development of methodologies to quantify various types of uncertainty, and (4) ongoing comparison with laboratory and field experiments. Ultimately, understanding of process coupling will be necessary for its incorporation in knowledge-based expert systems.

The specific subprogram research goals are summarized below:

- Conduct a workshop to refine research priorities (FY 1990); begin cooperative research with OER Scientific Computing staff (FY 1991).
- Complete initial research on geochemical expert systems modules (FY 1991).
- Modify contaminant transport models to incorporate refined geochemical modules (for dissolution/precipitation, ion exchange, and specific adsorption) that draw on process-level understanding developed in other subprograms (FY 1992).
- Evaluate the effects of process coupling through modeling and experimental design related to the ESRC manipulative field site (FY 1992-1995).
- Modify contaminant transport models to account for the abundance, migration, and growth of distinct bacterial populations and their interaction (through metabolic processes) with dissolved chemical contaminants (FY 1994).
- Improve transport codes to include geochemical and microbial controls on mixed organic-radionuclide contaminant mobility (FY 1994).
- Conduct computational experiments on the effects of variable physical scale, measurement error, and minimal data sets on contaminant migration patterns (FY 1995).

Scientific Opportunities

The scientific community now recognizes that the direction and rate of contaminant migration, dilution, or transformation can be strongly influenced by local material variabilities of the subsurface medium. Contamination problems in natural, heterogeneous environments are three dimensional and exhibit complex chemical behavior. Accurate and reliable prediction of effective transport behavior in heterogeneous systems remains elusive, largely because of uncertainties regarding the type and nature of chemical or biological reactions, the impracticality of measuring material properties at a sufficient degree of resolution, various computational complexities that arise from three-dimensional behavior, or the lack of any reliable and simple description of large-scale migration behavior in heterogeneous systems.

Nevertheless, models based upon assumptions of homogeneity, conservative (or nonreactive) chemical behavior, or over simplified lumping of chemical reactivity into one or more retardation factors continue to be widely used. Although such idealizations may be useful and necessary to make problems tractable, they frequently misrepresent or neglect important physical or chemical phenomena, regardless of how much is known about the mechanisms involved. Complex interactions associated with diverse chemical behavior, spatially variable aquifer properties, or microbial activity are effectively ignored in such models. As a result, existing models may become less reliable in simulating the spatial and temporal evolution of reactive contaminant plumes in naturally complex media, thereby diminishing their effectiveness as planning and evaluation tools for environmental restoration. In contrast, experimental simulations of behavior in idealized natural environments allow visualization of the combined effects of coupled phenomena and assessment of the relative importance of each process in the overall migration of a contaminant, and these simulations may ultimately allow identification and description of the more dominant kinds of processes at actual sites.

This mismatch between the capabilities of existing contaminant transport models and DOE's technological needs for dealing with the transport of mixed organic-radionuclide wastes in natural subsurface systems provides numerous scientific opportunities. Research efforts in this subprogram are directed at incorporating geochemical and microbiological mechanisms and heterogeneities into highly resolved contaminant transport models and at assessing the effects of uncertainty in modeling real sites, given the inherent variability in chemical, biological, and physical scales, measurement error, and minimal data sets.

Major research opportunities exist in the following areas:

- Implementation of realistic chemical and biological transformation processes within large-scale models of chemical migration in subsurface systems.
- Use of large-scale computational experimentation as a method to investigate and quantify the impact of complex chemical, biological, and physical processes on contaminant migration in heterogeneous porous media.
- Comparison and integration of observed field or laboratory behavior with computational descriptions of contaminant migration in idealized, heterogeneous systems.
- Methodologies for evaluating the sensitivity or reliability of predictive models through assessment of the effects of variable scale and parameter uncertainty.

Relevance and Benefits

The following issues are crucial to DOE's environmental restoration/contaminant efforts: (1) the potential for offsite migration of mixed contaminants from wastes, (2) the specific action(s) that should be taken to minimize the migration of contaminants at DOE sites, (3) the basis on which the health risks associated with various sites should be ranked, (4) the method of environmental restoration that will work best and how long it will take, (5) the least expensive method for restoration at a specific site, and (6) the steps to be taken to ensure that a particular method of environmental restoration will achieve a specified set of cleanup criteria.

In environmental engineering and regulatory contexts, methods for addressing these issues commonly include application of quantitative models. Such models can be used in assessing the potential for contaminant transport from DOE sites and the risk of ground-water contamination; they can also be used in ranking the risks of contamination from various sites and in prioritizing restoration activities. In the long term, quantitative models of coupled chemical, physical, and microbiological processes will help in the development of innovative, cost-effective methods of environmental restoration. An example of an innovative restoration concept is the manipulation of the subsurface system to facilitate biodegradation of organic wastes without plugging the aquifer or generating undesirable byproducts in the system.

When used in a framework of experimental computation, models can provide a method of visualizing and quantifying complex processes that cannot be measured directly in field conditions. They also offer several new perspectives for problem analysis, such as identification of critical processes that affect bulk migration behavior; enhanced understanding of unanticipated process interactions; justification for simplified models used in engineering; and improved practical intuition for interpreting field data, designing field experiments, or implementing remediation strategies.

In general, the use of comprehensive computer models to study hydrologic, geochemical, and microbial interactions of interest at DOE sites requires expertise in a variety of fields, including hydrology, geochemistry, chemistry, and computing, and usually requires a team of highly skilled individuals. Although the need for such trained staff can be met in research laboratories and academic settings, assembling similar large teams at numerous waste sites may be difficult. The knowledge gained through reactive chemical transport model development and computational experiments on the effects of process coupling on subsurface contaminant migration patterns can be made available for incorporation in expert systems, which in turn simplify environmental decisionmaking by waste-site managers.

FIELD SCALE SUBPROGRAM

Scope

Field experimental sites are critical to long-term basic research, and they provide the integrative framework for all research that is conducted at the molecular and intermediate scales. Because DOE site-contamination problems are field problems, field research is necessarily an important research priority, but it is costly. Furthermore, fundamental scientific advances are needed to determine hydraulic conductivity, understand the role of natural heterogeneity on contaminant transport, and scale up from the laboratory to the field.

Field research is usually conducted within the boundaries of DOE installations and in cooperation with various DOE groups and other Federal agencies. Sites both on and off DOE lands are used to analyze how individual or coupled chemical, microbial, and hydraulic mechanisms are influenced by natural subsurface heterogeneities. Scaling up is coordinated with intermediate-scale research (and facilities) within the Subsurface Science Program.

An iterative approach (field observations that contribute to laboratory experiments and vice versa) has been adopted. Field research conducted within this subprogram also assists in the development of concepts or hypotheses that, in turn, may shape the design of laboratory experiments. Field experiments to investigate coupled processes are already being planned, and research is under way at other sites. For example, two watersheds at the Oak Ridge National Laboratory have been instrumented, an in-ground subsurface facility is being used for studying shallow subsoil transport properties, and a manipulative field research experiment involving organic-radionuclide complexes is being planned.

All of the Subsurface Science Program's field research is organized and managed within this subprogram. However, once sites are operational and research is in progress, the sites are fully integrated into other subprograms. An example is the successful implementation of drilling and aseptic sampling for the study of deep microbial communities, which began within the Field Scale Subprogram and was transferred to the Deep Microbiology Subprogram in 1988.

After basic research is completed, many field sites will be useful as outdoor laboratories for exploring new remediation concepts of interest to DOE's applied programs. Scientific data derived from experiments at these sites will be transferred to DOE offices who have responsibility for testing, cost evaluation, and demonstration of engineering feasibility.

The research conducted within the Field Scale Subprogram is addressing the following questions:

- How does natural physical, chemical, and microbiological heterogeneity at the field scale influence reactive chemical transport, transformation, and stability, both spatially and temporally? To what extent can new geophysical, mathematical, and chemical tracer technology contribute to understanding such natural heterogeneity?
- How do physical, chemical, and microbiological processes change from the molecular (and microscopic) to the intermediate and field scales? How do they influence chemical transport or stability?

- What physical and statistical refinements in the theory of scaling up are needed, and what field experimentation is needed to test these new concepts? How should intermediate and field research be linked?
- What new quantitative field data bases that reflect natural chemical, physical, and microbiological heterogeneity in the subsurface are needed for research?

Goals

The overall goals of the Field Scale Subprogram are (1) an improved understanding of natural heterogeneity as a basis for interpreting reactive mixed-chemical transport and stability and (2) a refined theory of scaling up from the laboratory through the intermediate scale to the field scale, i.e., to a scale that is relevant to long-term DOE cleanup problems and remediation. Plans include two field research sites (one in relatively homogeneous porous media and one in the unsaturated zone extending through the capillary fringe), probably as an extension of companion intermediate-scale research. Other field sites will examine (1) chemical-microbiological processes that control complex chemical mixtures and (2) mechanisms, such as bacterial transport, that contribute to long-term remediation success or failure. Understanding of these mechanisms will provide new, fundamental understanding of the genesis of deep microbial communities. Priority will be given to questions regarding the stabilization or immobilization (containment) of mixed organic and inorganic chemicals in the long term; new remediation concepts are needed to reduce environmental restoration costs and the continuing damage that results from uncontained releases. New monitoring and sampling strategies may have to be devised to improve spatial and temporal characterization of contaminant composition and to measure (e.g.) natural physical and microbiological heterogeneities.

The specific subprogram research goals are summarized below:

- Develop a network of field research sites for colloid research (FY 1988); complete field experiments on inorganic colloids in Delaware and New Jersey (FY 1989) and on organic colloids at Georgetown, South Carolina (FY 1991).
- Develop a network of deep microbiology research sites nationwide to compare the presence, abundance, and diversity of microbial communities under different hydrogeologic conditions (FY 1990); add new sites as needed to test hypotheses on community genesis and survival (FY 1993-1996).
- Complete initial planning for a field site relevant to stabilization of organic-radionuclide complexes (FY 1990) for transfer to ESRC; complete field experiments to refine concepts for environmental manipulation of geochemical processes in an aquifer (FY 1995), leading to a conceptual proof of principle that may contribute to geochemical manipulation to remediate a shallow ground-water system (FY 1996).
- Plan for an experimental field site at a location to be determined to explore the fundamental hydrologic, chemical, and biological mechanisms that control bioremediation (FY 1991-1993).
- Accelerate research to improve understanding of the theory of scaling up physical, microbiological, and chemical processes with linkage to controlled, intermediate-scale experiments (FY 1993).
- Identify and characterize a DOE field site to refine new concepts related to colloids, with emphasis on manipulating inorganic colloids in situ to stabilize contaminants (FY 1994); transfer the site to the Geochemical Transport Processes/Colloids Subprogram.
- In coordination with the Coupled Processes Subprogram, begin field experiments that will contribute to fundamental understanding of coupled chemical, microbiological, and hydraulic processes (FY 1995).
- Evaluate new and advanced geostatistical and field geophysical methods to assess hydraulic conductivity in porous media and begin to integrate new technology into field programs (FY 1990-1995).

- Refine and apply new and innovative field tracers, specifically new chemical and microbial tracers (FY 1989-1995).

Scientific Opportunities

Natural heterogeneity in subsurface chemical, microbiological, and hydraulic properties makes characterizing and predicting the movement and stability of chemical mixtures difficult. The spatial variability of contaminants within the vadose and saturated zones is influenced by (e.g.) natural variations in ground-water chemistry and the variability of in situ microbial biomass in subsoils, sediments, and lithologies. Research addressing such variability is limited; available literature is very limited. Yet such heterogeneity directly controls chemical mobility and confounds the restoration of contaminated sites. This natural heterogeneity, although a function of a depositional environment that may be thousands to tens of millions of years old, today controls hydraulic conductivity, microbial distribution, and aquifer chemistry.

Developing integrated hydraulic, microbial, and geochemical data sets is essential to scientific understanding of the interactions among subsurface processes and to making improved mathematical predictions about chemical transport or stability. Advanced technology is badly needed for collecting uncompromised in situ samples and for analyzing subsurface geohydrologic properties (including heterogeneity) with a minimal number of boreholes.

Major research opportunities exist in the following areas:

- Evaluating the effects of natural chemical, microbiological, and physical heterogeneity on reactive chemical transport using advanced sampling and geostatistical methods; quantifying natural chemical and microbial heterogeneity, which is poorly understood compared to physical heterogeneity.
- Refining the theory of scaling up from the laboratory to the field and evaluating the relationship between the scale of measurement and scaling up.
- Developing new approaches to mapping, analyzing, and understanding how geological, hydraulic (physical), hydrochemical, and microbiological heterogeneity affects subsurface processes and chemical migration.

Relevance and Benefits

Concepts for characterizing, modeling, or manipulating subsurface environments are essential and fundamental to remediation at DOE sites. New concepts that emerge from basic research in the laboratory must ultimately be tested by field experimentation.

Technology transfer is an essential element of the Field Scale Subprogram. As field experiments proceed, new scientific concepts will be transferred through onsite participation, briefings, and workshops. This process will meet an important DOE goal to begin transferring scientific concepts that have value for remediation as soon as possible. Between 1986 and 1989, the Subsurface Science Program drew on multi-institutional field research teams in the Deep Microbiology Subprogram to facilitate information transfer to DOE sites. This approach proved successful for transferring knowledge about deep microbiology to DOE sites several years sooner than could have been done through traditional scientific publication. Since that time, principal responsibility for technology transfer has been assigned to ESRC.

ENVIRONMENTAL SCIENCE RESEARCH CENTER

Scope

DOE faces an unprecedented problem in restoring subsurface environments contaminated with unique, dispersed mixtures of radionuclides and other chemicals. The large volume of waste, its mixed-contaminant composition and inaccessibility, and the geohydrologic complexity of many of these sites limit options for treatment. Manipulation of natural phenomena operating in situ may offer real potential for immobilizing contaminants, converting them to innocuous forms, or mobilizing them for pumping and treatment on the surface. However, before these processes can become part of an engineering solution, complementary basic research is needed to provide an understanding of the chemical, microbiological, and physical processes operating in the subsurface, their interaction at different scales in the environment, and ways to manipulate them to achieve remediation without long-term impact on the natural system. This information will serve as a basis for estimating the need for remediation and for emerging new remediation concepts. If these concepts are to be used effectively, mechanisms must also be developed for transferring them to applied research, demonstration, and application and into technology.

The role of ESRC in the Subsurface Science Program is to conduct basic research leading to the development and first-principle evaluation of emerging new concepts for use of natural processes in restoring contaminated subsurface environments. User facilities (intermediate- and field-scale) are being developed within ESRC to resolve key scientific issues critical to support of this mission. These issues include the effects of manipulation on natural processes operating simultaneously and interactively and the scaling of these observations to provide an understanding of response and recovery at the system level in the field.

Research performed within ESRC is addressing the following questions:

- Can specific chemical, microbial, and physical phenomena be used to modify the form and/or mobility of subsurface contaminants?
- Can natural processes operating together and at different scales be adequately described to predict system-level response to manipulation?
- Do natural subsurface processes and their interactions have potential for complementing engineering solutions for restoration of mixed contaminants at DOE sites?
- Given the unique diversity of DOE efforts in restoration, can the necessary expertise in basic research at the national laboratories and universities be effectively integrated to offer meaningful new concepts for addressing long-term problems of in situ restoration critical to DOE's mission?

Goals

The overall goals of ESRC are to develop new scientific knowledge and concepts for the use of natural processes in restoring contaminated subsurface

environments and to ensure that this information is available for timely resolution of long-term problems faced by DOE. These goals are implemented through a basic research program that includes laboratory studies of basic mechanisms and field- and intermediate-scale experimentation to determine (1) how key natural phenomena, operating together, control contaminant behavior and (2) if concepts for remediation of complex, heterogeneous subsurface systems are feasible. Advanced statistical and modeling concepts are developed to use new knowledge of subsurface processes in predicting the effects of subsurface manipulation. An outreach program ensures that the university community and DOE sites participate fully in the development and application of knowledge and concepts for environmental restoration.

Specific ESRC research goals are summarized below:

- Selectively augment fundamental research on natural subsurface systems to accelerate the development of new restoration concepts based on manipulation of natural subsurface processes and properties (FY 1990-1995).
- Expand cooperative research with universities through postdoctoral support (FY 1990) and research grants (FY 1991-1995).
- Conduct intermediate-scale experiments in highly instrumented cells to determine how processes interact to affect (1) biostabilization/biodegradation of organic-radionuclide complexes (FY 1992-1994), (2) partitioning and removal of immiscible fluids from ground water (FY 1993-1994), and (3) the ability to scale this knowledge to the field.
- Conduct exploratory research to determine how advanced geostatistical and modeling concepts can be used to evaluate new remediation strategies based on subsurface manipulation (FY 1991-1993).
- Initiate planning (FY 1991) and begin development of a national experimental field site to examine the role of coupled chemical and microbial phenomena in mixed-chemical behavior and the system-level response to subtle manipulation (FY 1993).
- Test promising remedial concepts by manipulating natural phenomena at intermediate (FY 1993) and field scales (FY 1995) and develop new concepts for scaling laboratory and intermediate-scale observations to the field (FY 1993).
- Transfer feasible remediation concepts to applied research programs and industry (FY 1994-1997) in cooperation with DOE EM programs and Operations Offices.

Scientific Opportunities

DOE faces unique scientific problems in addressing the subsurface interactions and behavior of radionuclides and other inorganic and organic contaminants. These problems include the magnitude of subsurface contamination, the broad range of geohydrologic conditions under which contamination exists, and the interactions of codisposed contaminants. The ESRC role will be to assist the Subsurface Science Program in directing fundamental knowledge of the subsurface system to remediation of site problems. This role entails the development of new scientific concepts for using natural processes in in situ remediation and of new approaches for taking these concepts to the proof-of-feasibility stage. These new approaches include ways to address the coupled effects of complex interrelated chemical, microbial, and hydrologic processes and methods of scaling up from the molecular to the field scale.

The magnitude of the DOE problem and the speed with which resources are being allocated for applied research, demonstration, and application offer unprecedented challenges to ensure that fundamental research is applicable to evolving needs and that results can be communicated and transferred appropriately. Major opportunities exist in the following areas:

- Developing an understanding of multisolute and kinetic phenomena that control contaminant association with mineral surfaces.
- Identifying specialized biochemical pathways and novel enzyme systems for transformation of mixed contaminants.

- Using microbial systems for long-term solubilization and partitioning of radionuclides and metals.
- Manipulating coupled chemical and microbial processes to achieve multiple remediation goals (e.g., desorption, degradation, and physical partitioning).
- Developing new concepts for iterative use of laboratory-, intermediate-, and field-scale experimentation to provide an understanding of the response and recovery of natural subsurface systems.
- Using modeling and statistics to acquire and apply fundamental knowledge at the field scale.
- Creating new linkages and avenues for movement of emerging concepts from the science arena to other DOE groups engaged in integrated demonstration of technology.

Relevance and Benefits

DOE has a strong commitment to minimizing the effects of radioactive- and mixed-waste disposal at sites currently under its control and to developing more effective waste-management practices for the future. Many long-term regulatory milestones for restoring subsurface environments at DOE sites are based on the assumption that sophisticated restoration methods will be developed in a timely fashion.

The Subsurface Science Program is developing a unique reservoir of knowledge that can make major contributions to meeting DOE commitments. ESRC will draw on this knowledge and will begin to move new concepts for using natural systems toward their application in remediation efforts. This process will ensure that the technologist engaged in environmental restoration has a continuous supply of feasible concepts for applied research and development. Applied research and technology development at DOE sites is conducted and coordinated through the DOE EM office. Technology is applied through operating contractors and the Operations Offices at DOE sites. The effective transfer of new knowledge and concepts derived from basic research conducted within OER to this user community will be a key factor influencing DOE's ability to address long-term restoration problems.

Clearly, full and effective communication will be required to make maximum use of DOE resources in development, testing, and application of new concepts for environmental restoration. Therefore, the Subsurface Science Program conducts biannual meetings, where basic research is presented to a general audience and roundtable discussions and forums are dedicated to technology transfer. As a result, parts of the Subsurface Microbial Culture Collection have been transferred directly to the pharmaceutical industry for evaluation, and a new, inexpensive sensor for measuring immiscible solvents in ground water is being used at DOE sites. However, these interactions need to be expanded systematically, and ESRC, under the auspices of the Subsurface Science Program, is helping DOE refine research needs and priorities, coordinate scientific information, and transfer information to user groups. Selected topics, such as manipulation of natural chemical, microbial, hydrologic, and coupled processes for in situ remediation, are being examined in joint workshops attended by representatives of OER, EM, universities, and industry. These workshops bring the user and scientific communities together to discuss the successes and failures of in situ remediation, to define research needed to improve the probability of success and reduce possible deleterious effects on subsurface systems, and to transfer existing knowledge for direct application. Intermediate- and field-scale experimental facilities are being used in joint experimentation to assess the scientific feasibility of new concepts. The Subsurface Science Program is also developing mechanisms for coordination with EM at the program and site levels. These mechanisms should help ensure that EM will have the full benefit of the knowledge and concepts that evolve from OER basic research in its design of integrated demonstrations of in situ remediation technology at the DOE sites.

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